

ABSTRACT

DATLA, VASANTHA MADHURI. Surface Modification of Fibers and Nonwovens with Melt Additives. (Under the direction of Dr. Behnam Pourdeyhimi and Dr. Eunkyong Shim).

Polypropylene (PP) fibers, widely utilized in woven and nonwoven industry, have highly inert and hydrophobic surfaces. Therefore a modification aimed at the creation of a more polar surface is an important issue in the application areas where wettability and adhesion properties are required. One way to impart surface hydrophilicity into polypropylene is blending of the melt additives prior to or during the fiber spinning process. It is reported that some oligomeric melt additives spun with host polymer migrate to surface and generate surface reactivity at low concentration without altering bulk properties.

The principal objective of the study is to explore effective ways of imparting hydrophilicity to polypropylene fibers and nonwovens with the melt additives based on an understanding of hydrophilic surface formation on polypropylene and key parameters related to the process. It involves study of possible interactions between polypropylene polymer and the melt additive leading to a hydrophilic surface by melt additive surface migration. For this purpose, different classes of nonionic melt additives were melt extruded with a twin-screw extruder using a melt additive concentration of 2% to investigate how hydrophilic surfaces are created. The mechanism of hydrophilic surface creation by melt additives was explored using X-ray photoelectron spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), Atomic Force Microscopy (AFM) and dynamic contact angle analyses. XPS analysis revealed migration and surface enrichment of melt additives by increase in the surface amount of polar oxygen groups leading to a more hydrophilic surface. Melt additives with different chemistries were studied for their surface modifying effectiveness. It is found that both size and characteristics of hydrophilic and hydrophobic groups in melt additives as well as their relative size; represented by HLB (Hydrophilic-Lipophilic Balance) value, affect the rate and the degree of surface additive segregation.

The surface energy and the polar contribution of the polypropylene film increased due to the migration of low-molecular-mass components (additives) to the surface resulting in increase in surface wettability. Low molecular weight oxidized materials were observed in the form of a globular morphology on the surface of the film. Additionally thermal analysis of melt blended PP films using DSC revealed phase-separated nature. We also found that resulting surface characteristics are very dynamic, so melt additive containing polymer surfaces response to water or heat application effected surface properties and composition. Some melt additive containing PP films response to water enhanced surface migration and wettability leading to a durable hydrophilic PP surface.

Analyses of melt additive concentration effects established that the minimum additive concentration to cause surface chemical changes is about 1 wt%. Finally evaluation of surface properties of spunbond PP nonwoven fabrics with the melt additives indicated that the structural and geometrical differences between the films and fabrics clearly affected the polymer surface characteristics and migration on surface wettability. It is shown that hydroentangling and heat calendaring, which are typical spunbond nonwoven bonding processes, resulted in changes in the fiber surfaces. Heat calendaring hastened the blooming of the melt additive by facilitating surface migration leading to enhanced wettability over time and found that 130°C is an optimum temperature to bring the desired surface hydrophilicity (complete wettability) in PP films or fabrics with 2-wt% of ethoxylated alcohol melt additives.

Surface Modification of Fibers and Nonwovens With Melt Additives

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DEDICATION

To my parents, Hari Kumari and Sivarama Raju Datla, my sisters Vijaya and Chaitanya Datla, and my grandmother.

BIOGRAPHY

Vasantha Madhuri Datla was born on June 15, 1976 in Vijayawada, Andhra Pradesh, India. She received her Bachelor's degree in Textile Technology from Osmania University, Hyderabad, India. In pursuit of further studies, she joined North Carolina State University in August 1999 and completed the Master of Science program in Textile Technology in May 2002. In Spring 2004, she was admitted into the PhD program in Fiber and Polymer Science and held a research assistantship with the Nonwovens Cooperative Research Center (currently 'The Nonwovens Institute') in the College of Textiles at NCSU. After graduation she will begin working for Pall Corporation in Timonium, Maryland from January 2008 as a Research & Developer.

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1. INTRODUCTION

Surface structure and behavior of fibers are of utmost importance for the properties of fibers and textiles in processing and use, since friction, abrasion, wetting, adhesion, adsorption, and penetration phenomena are involved. Surface chemistry modification, either applied to the fiber as a finish, or later on the formed fabric, is perhaps the most efficient route to add value to the nonwoven fabric and solve specific end-use problems.

Polypropylene fiber is a very important fiber in nonwoven processing, and dominates in many nonwoven markets, particularly absorbent product coverstock markets. It is the preferred fiber for most calender bonding processes and is used extensively in through-air bonding as well. Today's production of nonwovens is very dependent upon polypropylene fibers to ensure [1]:

- Lightweight materials typically used in disposable nonwoven types, and
- Durable, resistant and strong materials for durable nonwoven applications.

Of the world's total nonwoven production, polypropylene is the most common nonwoven fiber, accounting for approx. 62% of all fibers [1]. Unfortunately it is also the most difficult fiber to treat with a topical finish because of its hydrophobic nature and attaining a hydrophilic surface is crucial in some applications, including hygiene, medical, absorbents, wipes, filters, and battery separators.

There is a technologically driven demand for the development of durable and permanent hydrophilic polypropylene fibers. As mentioned earlier, the process of melt blending the additive with the polymer has been utilized to improve the surface properties of fibers in many applications. Despite the method's appeal, there has been surprisingly little fundamental research conducted to establish principles for additive selection and for optimizing processing conditions to enhance the transport of surface functionalizing additives in polymeric hosts [2].

In order to perform as a melt additive, which is able to modify surface properties, a chemical should have adequate thermal stability to survive the extrusion process, be mobile enough to migrate to the surface, and have the right structure to generate the desired surface properties. In addition, such polymer melt additives should show high efficiency at low concentrations in order to minimize or prevent possible negative effects on polymer processing and mechanical properties of the final fiber or web and to be cost efficient [3].

The main objectives of this study are to understand the hydrophilic surface formation on polypropylene with the melt additives and explore effective ways to impart hydrophilicity to polypropylene fibers and nonwovens based on an understanding of key parameters related to the process. Determining the basic mechanism and principles that govern the hydrophilic surface formation with these melt additives will help extend the technology to a more practical use by achieving specific balanced combinations of properties, processability, and cost.

Creation of the hydrophilic polypropylene nonwovens is a multi-step process involving compounding, fiber spinning, bonding, exposure to the environments, and finally contact with the liquid. Surface hydrophilicity will be governed by various material parameters, processing parameters, fiber structure, and environmental factors. List of related parameters are shown in Figure 1.1.

The initial part of the study was focused on the effect of various melt additive parameters/molecular characteristics on the hydrophilic surface modification of polypropylene. We believe PP-additive interactions and additive characteristics are the most fundamental and essential aspects of hydrophilic surface creation, so different chemical structures of melt additives may be most significant and designable aspects of the process. Accordingly the chemical structure of the melt additive was changed systematically and its effect investigated and results are described in Chapter 4.1-4.9. Additives with different chemical classes were also used, and modification of the additives was also made within the

chemical class. Hydrophilic surface formation with melt additives on fiber morphology and its impact on surface wettability in nonwoven fabrics was explored and the results are discussed in Chapter 4.10.

Chapter 2 explains various aspects of the surface modification process with additives, including basics of the surface segregation and migration phenomena and the several factors, such as additive structure, size and composition, and polymer fine structure that affect the migration efficiency. Chapter 3 details the materials and the experimental methods used to fulfill the objectives discussed above. The results and discussion of the experimental data are presented in chapter 4, followed by detailed conclusions of the study in chapter 5.

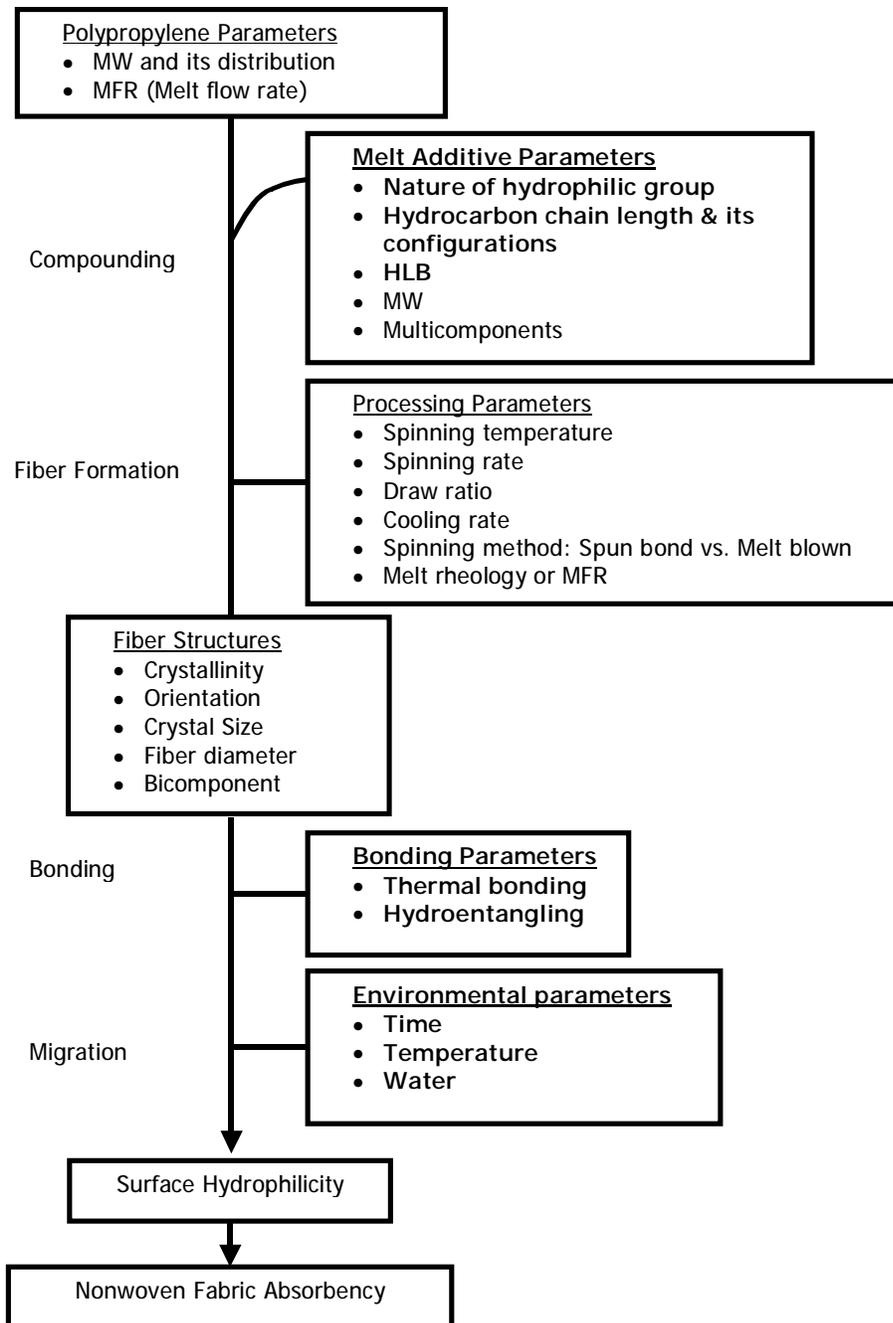


Figure 1.1: Possible parameters in hydrophilic modification of the polypropylene fiber and nonwovens with melt additives

2. BACKGROUND

The purpose of this chapter is to present a brief overview of the current state of knowledge in the surface modification of fibers using melt additives and their applications, starting with the fundamental aspects of surface modification techniques and the additives used in polymers.

2.1. POLYPROPYLENE SURFACE PROPERTIES AND MODIFICATION METHODS

2.1.1. Polypropylene

Polypropylene (PP), a thermoplastic polymer was discovered in the early 1950^s by Giulio Natta. Polypropylene is prepared by polymerizing propylene (Figure 2.1), a gaseous byproduct of petroleum refining, in the presence of a catalyst under carefully controlled heat and pressure [4]. Propylene is an unsaturated hydrocarbon, containing only carbon and hydrogen atoms.

Depending on the catalyst and the polymerization method used, the molecular configuration can be altered to produce three types of polypropylene: atactic, isotactic, and syndiotactic configurations. Only the isotactic and syndiotactic form are used in fiber production because it allows the chains to pack closely to form crystals. The Ziegler-Natta catalysts developed in the 1950s made the isotactic formation possible. While polypropylene fibers were first manufactured in Italy in 1957 and U.S. production began in 1962, these fibers did not truly thrive until the 1970-80s, when antioxidants and thermal and ultraviolet stabilizers overcame the polymer's susceptibility to oxidation and radiation induced degradation [5].

Polypropylene is a versatile thermoplastic material, compatible with many processing techniques and used in many different commercial applications [6]. The moderate cost and following favorable properties of polypropylene contribute to its strong growth rate [7, 8].

- i. It is one of the lightest of all thermoplastics, with a density of 0.9 g/cc.
- ii. Due to the high strength-to-weight ratio, it is more rigid than other polyolefin polymers.
- iii. It has better heat resistance than other low-cost thermoplastics.
- iv. Its excellent chemical resistance includes resistance to most organic solvents, except for strong oxidizing agents.
- v. Its good fatigue resistance makes it widely used in living hinge applications.
- vi. It is usually not susceptible to environmental stress cracking [7, 9].

Gradually, polypropylene fibers have substituted other fibers in a variety of applications and are today the mostly used nonwoven fiber [10]. In textile applications, the typical melt flow rates range between 1.5-2.5 g/min, corresponding to moderate molecular weights, are used. High molecular weights in the range of 0.3-0.5 g/min are used in more technical applications. The polydispersity (PDI) ranges from 2-12 or greater. A PDI of 3 is considered ideal for high speed spinning [11].

For many applications the surface properties of the finished products (e.g. film, fiber, and fabric) are most important in controlling the performance of the nonwoven products. Many essential properties including hydrophilicity, friction, antistatic, softness, dyeability, barrier properties, oil and water repellency and others are directly related to surface properties - surface chemical composition (related to surface energy) and surface morphology (Geometrical shapes, surface roughness, crystallinity, and surface area). In textile related applications, gloss, water repellency, dye reception, abrasion and stain resistance of the fibers are of critical importance. For film, and other industrial applications, adhesion, printability, surface release, and lubricity and coefficient of friction mainly determine the end use and the

performance [12]. One of the most important surface characteristics is wettability or hydrophilicity of the surface, which affects liquid transport properties, absorbency, hand, and comfort of the product.

Polypropylene fibers with its low cost, desirable mechanical, physical and thermal properties and growing commercial application is widely used to make both woven and non-woven fabrics, such as carded webs, spun bond, melt blown, or composites thereof for use in various applications, including hygiene, medical, absorbents, wipes, filters, and battery separators. Some of these applications require a hydrophilic surface. However, polypropylene (PP) fibers are highly hydrophobic in nature, and require the addition of finishes that may lead at best to a temporary hydrophilicity. Permanently hydrophilic PP fibers are highly desirable and sought after. The development of a low-cost reliable method for creating permanently hydrophilic PP fiber is long overdue [13].

Therefore, a surface modification technique aimed at the creation of a more polar surface is an important issue considering, for example, wettability, adhesion, barrier properties or dyeability. The frequently used surface treatments for PP include: topical finish, plasma, corona and flame treatments and an overview of these techniques is discussed in the following sections. But we believe that hydrophilic melt additives may be employed to provide a durable, reliable, cost effective method to achieve hydrophilic surface [14].

2.1.2. Applications of Hydrophilic PP

Modification of polypropylene using hydrophilic polymer melt additives can offer a wide variety of applications in the fiber and nonwoven areas, and also in film and molded articles. Examples of such application areas include [3]:

- Diaper coverstock
- Industrial sorbents and wipes
- Battery separators

- Filtration media
- Carpet backings (improved wettability by adhesives)
- Hydrophilic staple fibers (reinforcement fibers in construction materials)
- Wettable porous films and substrates (improved coatability)

2.1.3. Other Surface Modification Methods Used to Impart Hydrophilicity

Several methods have been reported in the literature for the hydrophilization of polypropylene. The basis of hydrophilization is to maximize hydration and hydrogen bonding interactions. This demands an increase of the amount of surface polar groups [13].

The frequently used surface treatments for polypropylene include: topical finish, plasma, corona and flame treatments. Among them, the most common method of surface modification is the use of topical treatments of hydrophilic finishes. However, this method has several disadvantages. During the topical treatment process, finishes tend to coalesce into large droplets brought about by the surface tension that dominates annular film instability leading to non-uniform finish distribution on the fibers. Since finishes are held on the fiber surface mostly by physical adhesion, they usually exhibit poor durability; consequently, they can be easily removed by coming in contact with fluids or by surface abrasion. Finishes can also interfere with downstream processes such as thermal bonding if the finish is applied prior to such processes [15].

With the corona and flame treatments, although the equipment setup is simple and cost-effective, the variation in ambient conditions such as temperature and humidity (in corona treatments), and, difficulty in controlling the chemical composition of fuel and the distance between the tip of the flame and the object (in flame treatments) makes these treatments inconsistent. Even though surfaces modified by plasma treatment are fairly uniform and the surface modification is confined only to the surface, the plasma treatment carried out in vacuum, increases the cost of operation and is time consuming as well. All these methods

lead to an immediate hydrophilicity that deteriorates after a time [16, 17]. It is reported that the hydrophilic surface can be obtained by chemical surface derivatization such as graft polymerization, but polypropylene is one of the most chemically resistant polymers to chemical modifications. Therefore, normally necessary treatment conditions can lead to degradation of the polymer [15].

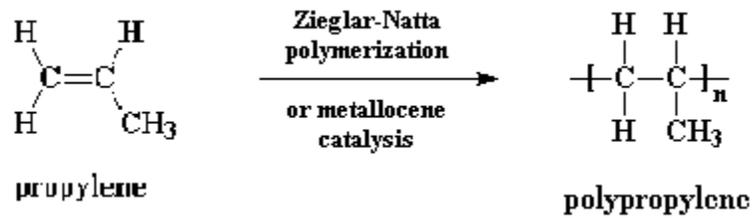


Figure 2.1: Molecules of propylene and polypropylene.

2.2. USE OF ADDITIVES AND MELT ADDITIVES IN THERMOPLASTIC POLYMER AND PP

2.2.1. Plastics Additives

An additive is a substance introduced into a polymer or applied to its surface in order to modify its properties or to enhance its performance. Additives are intensively used in the plastics industry to provide materials with different properties. Additives are generally small organic molecules or minerals introduced at low levels. They can be blended with the polymers either during or prior to melt spinning (hence the term ‘Melt additives’) for better processability, for a colorful appearance, and/or to impart functionalities like flame retardancy, repellency or hydrophilicity. Polymeric additives introduced at low levels in formulations (less than 10%) can significantly modify or improve properties. There are numerous families of additives that can be classified into three main categories [18]:

- Property extenders,
- Processing aids
- Modifiers.

Table 2.1 lists the most common additives and their functions used in commercial thermoplastics and thermosetting resins [19]:

The different polymers used as additives and modifiers in thermoplastics most commonly include [18]:

- i. Adhesion promoters and compatibilizers (e.g. block and grafted copolymers, functionalized polymers like maleated polymer and epoxydized polymers.)
- ii. Impact modifiers (e.g. acrylic polymers, butadiene-styrene copolymers)
- iii. Flame retardants (e.g. halogenated and non-halogenated polymers)

- iv. Surface modifiers (e.g. matting agents, antistatic agents, antiscratch, abrasion and surface additives)
- v. Polymer processing aids (e.g. fluoroelastomers, high molecular weight PDMS, and acrylic copolymers).

Some polymers work advantageously as additives to provide material with better benefits than standard additives. Polymeric materials provide easier handling, low migration and volatility and also lower toxicity. In most cases these materials may provide long-term performance like antistatic, printability and paint adhesion than lower molecular weight materials or greasy materials [18, 20].

2.2.2. Incorporation of Additives to PP

The addition of a small amount of the correct chemical transforms a useless material into a durable raw material suitable for use in a wide variety of applications. Various additives are used not only to impart stability during the processing and use of polypropylene, but also to modify various properties and characteristics. Beyond the need for stabilization, additives are used in PP for the following reasons [21]:

- i. To add/adjust color
- ii. To alter stiffness
- iii. To control transparency
- iv. Lower molecular weight and molecular weight distribution
- v. To impart hydrophilicity, repellency, antistatic and flame-retardancy
- vi. Decrease static buildup
- vii. Control surface properties to modify frictional and adhesion properties
- viii. Enhance whiteness
- ix. Prevent biological growth

For instance, in our study detailed below, we aim to employ low molecular weight melt additives to function as a surface modifier to impart hydrophilicity to a rather inert and hydrophobic polymer like polypropylene (PP).

2.2.3. Surface Modification with Melt Additives

To overcome the drawbacks mentioned before with the other methods, there is a growing interest in surface modification techniques by means of melt additives. A promising method to affect surface properties more permanently is the use of hydrophilic melt additives, wherein the melt additive is blended with the base polypropylene polymer and extruded. Melt additives can be blended with the polymers prior to or during melt spinning [22]. The process of melt blending the additive with the polymer has been utilized to improve the surface properties of fibers in many applications. The focus has been with the expanded use of polymers aimed for antistat, dyeing, and, flame retardant applications. However, the use of melt additives for hydrophilic-based applications has not been widely studied.

One of the major considerations for the use of surface modifying melt additives is achieving desirable properties without sacrificing the bulk properties. Melt additives become dispersed in the molten polymer during the compounding process and are bound in the polymer matrix when the polymer cools during fiber quenching. The idea is that if a surface active additive with desirable functional groups is blended in small amounts with a host polymer melt or solution, physical processes such as diffusion, spontaneous surface segregation, and shear might be used to transport the additive to the host polymer's surface during normal polymer processing to impart surface functionality (e.g., hydrophilicity) without resulting in significant changes in the bulk properties of the fiber [23].

Migration of functionalized additives dispersed in a host polymer to the surface of host polymer has long been recognized as a potential solution. This approach for surface modification is attractive for several reasons:

- i. Surface modification of polypropylene to obtain improved hydrophilicity, can be brought about with considerably low levels (1-2 wt %) of melt additives.
- ii. The process relies on physical forces to maintain additive molecules at the host polymer's surface; it is therefore not limited by the ability to control chemical reactions on a mobile polymer surface.
- iii. The surface modification process can be integrated into conventional polymer processing operations, such as solvent casting or melt extrusion, and therefore, offers processing advantages with the elimination of expensive processing equipment, fewer processing steps and lower energy consumption.
- iv. It is possible to have better control of the process and its uniformity. Provided that the additive can be made to migrate to the host polymer's surface, any functional group or perhaps even combinations of desirable functional groups can be presented at the host polymer's surface [23, 24].

Table 2.1: List of common additives and their functions.

	Additives	Function
1	Antioxidant	Protects a polymer against oxidation, whether during processing or in-service life.
2	Antistatic agent	Reduces or eliminates surface electrical charges and prevents dust pick-up etc. on polymer surfaces.
3	Biocide	Protects a plastic article against attack by bacteria, fungi, algae, moulds, etc.
4	Blowing agent	Generates gases, which will have the effect of expanding or foaming the polymer.
5	Compatibilizer	Substance, usually polymeric, which when added to a mixture of two rather dissimilar polymers, enables them to become more intimately mixed than before.
6	Coupling agent	Substance (mineral/polymer) used to treat a surface so that bonding occurs between it and another kind of surface
7	Curing agent	Promotes crosslinking in polymers
8	Fiber	Used as reinforcement for polymers, improves mechanical properties and increases length to diameter ratio.
9	Filler	Particulate additive, designed to change polymer physical properties or to lower cost.
10	Flame retardant	Substance added to reduce or prevent combustion.

Table 2.1 (continued)

	Additives	Function
11	Heat stabilizer	Prevents thermal degradation of polymer, even in absence of oxygen, during processing.
12	Impact modifier	Substance added to use up the energy of crack propagation and hence increases resistance to impact.
13	Light stabilizer	Prevents polymer degradation in outdoor use by reducing or eliminating reactions caused by visible or ultra-violet radiation.
14	Lubricant	This substance has a two-fold function. They prevent a polymer from sticking to the mould or the machinery, and reduce the melt viscosity, allowing the molten polymer to pass easily through intricate channels. They also reduce friction between polymer particles before they melt.
15	Nucleating agent	Promotes or controls the formation of spherulites in crystallizable polymers.
16	Odor modifier	Used to mask an undesirable odor, or to add a desirable one.
17	Optical brightener	Special fluorescent substances used to correct discoloration or enhance whiteness by absorbing ultra-violet radiation and emitting it as visible light.
18	Peroxide	Source of free radicals, generally for cross-linking thermosetting resins or polyolefins. Also used in the rubber industry and as polymerization initiators.
19	Plasticizer	Leads to enhanced flexibility, softness and ductility of plastics.

Table 2.1 (continued)

	Additives	Function
20	Processing aid	Counters processing problems by lowering melt viscosity and improving melt inhomogeneity.
21	Release agent	Eases the parting of plastics from its mould with either an internal additive or coating.
22	Slip agent	Form of a lubricant having insufficient compatibility to remain long in the polymer, so they migrate to the surface reducing tack. Can also perform as an antistatic agent.
23	Surfactant	Reduces the surface tension of liquids.
24	Thixotropic agent	Modifies the dependence of viscosity on shear rate, producing low viscosity at high rates, and vice versa.
25	Ultra-violet stabilizer	Prevents degradation of material exposed to harmful ultra-violet radiation.
26	Wetting agents	Aids in wetting out solid substrates, e.g. filler particle surfaces, and help their uniform dispersion in a polymer matrix without agglomeration.

2.3. SURFACE SEGREGATION OF MELT ADDITIVES

2.3.1. Migration Phenomena

Surface segregation or migration, often referred to as blooming, is an almost universal phenomenon in multicomponent systems. By component segregation, the polymer blend lowers its overall free energy by having a surface enriched in the lower energy component or low molecular weight component. In multi-component systems such as polymer-additives, one component can be preferentially segregated to the surface or interface to establish more stable mixtures. Additive migration is the process of this preferential segregation in melt additive-polymer compounds.

Obtaining preferential migration of melt additives to the surface is essential in the hydrophilic PP modifications. Both efficiency and durability of the hydrophilic melt additives in PP highly depends on the migration phenomena.

- *Efficiency:* The preferential surface segregation of the melt additive leads to increased surface concentration of the melt additive at a given mean additive concentration. The additives with strong migration tendency will be able to generate a hydrophilic surface at the low level of overall melt additive use.
- *Durability:* Additive molecules on the surface could be lost by liquid contact or abrasion. When this happens, additives in the bulk act as reservoir and may be pushed to the surface by migration and restore surface hydrophilicity. Therefore migration of the melt additive is an ideal mechanism to maintain surface hydrophilicity after multiple contacts with the water. However, it is believed that too rapid surface migration causes fast release of additives and poor durability.

Migration phenomena have been observed in polymer blends or polymer-additive systems. When a film or a fiber consists of more than two components, whether it is two polymers or

polymer and a small molecule additive, migration of the one component may happen and generate non-uniform distribution of the components. Additive concentration can be richer in the surface or vice versa as the result of the migration effect. Migration characteristics depend on the diffusion characteristics of the additive in the solid state, molecular weight, structure, purity, surface tension differences, etc. Depending on the chemical structure and composition of the melt additive and processing conditions, faster or slower migration can be observed [25]. Consequently to achieve durable surface properties, there are a number of key parameters and phenomena controlling the migration of the additive to the surface.

In the PP/Melt additive system, the tendency of the additive molecules to prefer surface results in enrichment, or increase in volume fraction of these additive components at the surface. In this case, the volume fraction of the additives may not be uniform through the PP matrix, but will vary as a function of distance from the surface. With time t , volume fraction of the melt additives ϕ_s would increase and $\phi_s > \phi_{\text{bulk}}$, by further migration after extrusion. Figure 2.2 shows the composition profile in phase segregated polymer systems illustrating the surface composition ϕ_s , the bulk composition ϕ_{bulk} , and decay length λ . The shaded area is the surface excess, z^* [26-29].

Surface segregation therefore reflects a balance of surface forces and bulk mixing thermodynamics [30]. In addition to these thermodynamic considerations, the resulting phase-separated morphology may be far from thermodynamic equilibrium, and kinetic barriers may hinder relaxation toward equilibrium, so the rate and the degree of attainment of equilibrium are affected by fine structure of polymer matrix. The effect of crystallinity is an important variable to be considered [26].

Particular interests are the absolute surface composition, the total adsorbed amount z^* , and the shape of the near-surface depth profile. The shape of the composition profile depends on the various parameters, some of which are summarized in Figure 1.1.

2.3.2. Migration and Polymer Processing

The surface-active additive is incorporated into the polymer during or prior to extrusion. Therefore, it is necessary to recognize the various stages of the extrusion and fiber forming process. The additives are dispersed homogeneously in the bulk of the polymer during the extrusion process (Figure 2.3). Solubility/compatibility with the host polymer can mainly be regulated by the nature of the hydrocarbon part of the additive, and certain case of molecular structures can result in one-phase mixtures.

Some enrichment of the polymer melt additive in the surface region of the 'liquid' fiber will have occurred during the actual fiber formation in the die. Upon cooling/quenching, when fiber crystalline structure develops, more segregation can occur and the additive may be pushed out of the crystalline regions and squeezed into the amorphous region. Further migration of the melt additive from the solidified bulk to the surface is now hindered by the polymer matrix structure. Therefore, polymer fine structures would be one factor of migration process in this stage. Processing parameters such as rate of cooling, shear rate, draw ratio not only effects additive migration during fiber formation but also after fiber formation, because of migration through different polymer fine structures developed. However, only few studies are found regarding this aspect.

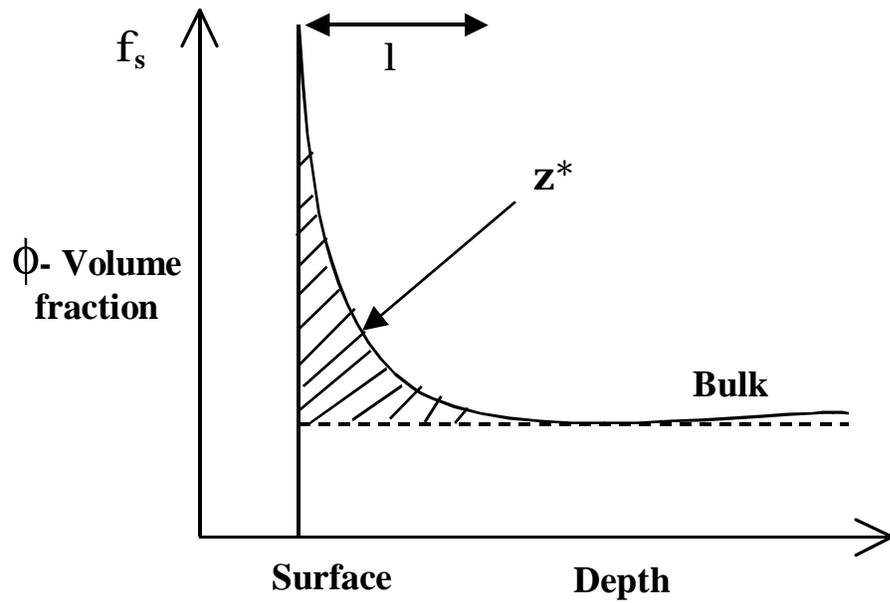


Figure 2.2: Composition depth profile of the enriched component near the surface [28].

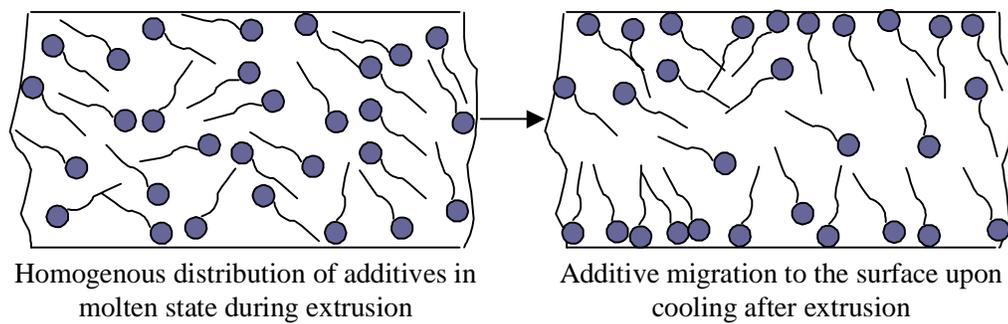


Figure 2.3: A simple figure illustrating migration of additives to the polymer surface during and after extrusion [24].

2.4. SEGREGATION MECHANISM AND ROLE OF ADDITIVE CHEMISTRY

Surface modification via surface enrichment of one of the component in a multicomponent system, such as a blend, has been of interest for numerous years [31-35]. The driving force for surface modification in such a system is largely thermodynamic, where the component with the lowest critical surface tension rises to the air-polymer interface, thereby lowering the interfacial free energy. The miscibility and mobility of the component influence the kinetic driving force toward the interface [36-38].

In general, the melt additive migration and the efficiency of surface enrichment of these additives may depend on several factors, which include:

- Diffusive mobility, which depends on the size of the additive, and polymer fine structures.
- Solubility/compatibility of the additive with the host polymer, which involve miscibility, solubility parameters or the free energy of mixing.
- Other driving factors include surface free energy and molecular weight differences, and
- Environmental factors.

2.4.1. Effect of Diffusive Mobility

The mobility of small molecules is characterized by the diffusion coefficient (D) derived from the permeation rate. Permeation of small molecules through polymers usually occurs by the solution-diffusion mechanism. The rate of migration (permeation), P is a product of the solubility (S) and the diffusion (D) coefficients [39].

$$P = D * S \dots\dots\dots (2.1)$$

The process of diffusion minimizes the Gibbs free energy and can be described by Fick's laws, where the diffusion coefficient D , proportionality constant, is related to the net flux J , of the transported quantity to their concentration gradient $\partial C/\partial X$ [39, 40];

$$J = -D * \frac{\partial C}{\partial X} \dots\dots\dots (2.2)$$

where, C is concentration of the diffusion substance, and X is the space coordinate measured normal to the section.

The characteristics of polymer and the additive that affect both the solubility and diffusivity are [39]:

- The availability of "free volume" in the polymer: Increase of the free-volume in the polymer ensures higher freedom in segment mobility accompanied by an increase of S and D .
- Self-interaction of the additive does not seem to affect the mobility, but it decreases the solubility in the polymer.
- The cohesive forces between the polymer chains (i.e., how tightly the chains are held together) are also crucial.
- Finally, while both shape and size of the additive molecule mainly affects the solubility, the latter is important from the aspect of mobility, as the free-volume brought into the polymer increases the overall free-volume.

In the present study, for example with the polymer-melt additive system, the diffusion of the melt additive within the host polymer will ensure uniform distribution of the additive and the diffusion coefficient, D , will determine the extent and rate of migration of the melt additive to the air-polymer interface which depends on the size of the additive molecules as discussed before and also on the polymer fine structures. Highly crystalline structure will hinder the mobility of the melt additive from the bulk to the surface, which may not be the case with

semi-crystalline materials, in which the movement of the additive molecules is favored through the amorphous regions. Processing parameters have a great influence on the development of the polymer structure, which consequently affects the additive migration, so balance must be reached between the processability and the final polymer properties. Additionally, polymer-additive interactions in the form of strong covalent bond formation will prevent the migration of the additive to the air-polymer interface. Therefore, polymer and additive molecular characteristics can be tailored to deliver a product with essential properties.

Clark et al. [41] studied poly (ϵ -caprolactone)/poly (vinyl chloride) (PCL/PVC) blends and found that the surface composition was dependent on molecular weight and degree of crystallinity. Moreover, it has been shown that the phase morphology depends on the polymer molecular structure, composition, and the method of blend preparation [42] and can also be influenced by a suitable choice of the substrate surface free energy [43]. The film surface segregation and morphology may also be modified by film thickness [44, 45].

Other critical factors that control the migration and segregation of the melt additives are discussed in the following sections.

2.4.2. Effect of Miscibility, Solubility Parameters, and Free Energy of Mixing

The thermodynamics of polymer blends plays a major role in the molecular state of dispersion, the morphology and adhesion of two-phase mixtures and consequently influences most properties and applications. One of the first and foremost thermodynamic questions is concerned with the equilibrium miscibility or solubility of two components in a blend. Very often, miscibility and compatibility are used synonymously. ‘Miscibility is used to describe polymer blends that have theoretical thermodynamic miscibility down to the segmental level,

and the term compatible is be used to describe polymer blends that have useful practical properties, regardless of whether they are theoretically miscible or immiscible' [46].

Miscibility is generally established from thermodynamic relationships given by the Gibb's free energy of mixing expression $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$, where resultant negative value of the free energy and heat of mixing such as $\Delta G_{\text{m}} \sim \Delta H_{\text{m}} < 0$ is associated with miscibility and polymer blends whose free energy of mixing is $\Delta G_{\text{m}} \sim \Delta H_{\text{m}} > 0$ are termed as immiscible [47].

A number of factors contribute to miscibility/immiscibility of polymer blends [46].

- Polarity – polymers with similar structure or polarity are more likely to form a miscible mixture.
- Specific interactions such as hydrogen bonding, acid-base, charge transfer, ion-dipole, donor-acceptor attractions favor miscibility
- Molecular weight – low molecular weight permits greater randomization leading to increase in the entropy favoring miscibility. Polymers of similar molecular weights are more miscible than polymer with different molecular weights even if they both have the same composition.
- Ratio and crystallinity

Most polymer pairs are not miscible and separate into two-phase systems. If they are very immiscible, the domain size is coarse, irregular, and unstable, and the interface is sharp and weak, resulting in poor properties and practical incompatibility. In many naturally compatible polymer blends, partial miscibility is the cause for their good properties. Interestingly, in our present study, optimum miscibility of the PP-melt additive will aid in the segregation and migration of the melt additives to the air-polymer interface altering the surface properties of the host polymer [46].

In a fundamental sense, the miscibility, adhesion, and interfacial properties are all interrelated thermodynamically to the interaction forces between the two components in the polymer blend. Flory-Huggins solution theory, although inadequate for some purposes, provides a useful approximation for the terms in the equation below to interpret and predict different material's behavior to determine miscibility of low molecular weight additives in polymers. Originally derived for small molecule systems, it assumed that each molecule occupied one site on a lattice. The theory was expanded to model polymer systems by assuming that the polymer consisted of a series of connected segments each of which occupied one lattice site. Assuming that the segments are randomly distributed, the free energy of mixing per mole of lattice sites for a mixture of polymer A and polymer B is [47]:

$$\frac{\Delta G_{mix}}{RT} = \left(\frac{\Phi_A}{N_A}\right) \ln \Phi_A + \left(\frac{\Phi_B}{N_B}\right) \ln \Phi_B + c_{FH} \Phi_A \Phi_B \dots\dots\dots (2.3)$$

where ΔG_{mix} is the Gibbs free energy of mixing, R is a gas constant, ϕ_i , N_i are the volume fraction and degree of polymerization of polymer i , T is temperature, and χ_{FH} is the Flory-Huggins interaction parameter related to the heat of mixing, which is positive for endothermic systems. The first two logarithmic terms give the combinatorial entropy of mixing, and each is related to the size or molecular weight of that component, while the third term is the enthalpy of their interaction. Entropy always favors mixing. But, for polymer blends with high molecular weights, the combinatorial entropy is vanishingly small, so the miscibility or immiscibility of the system mainly depends on the value of the last term, $\chi_{FH}\phi_A\phi_B$.

$\chi_{FH}=0$ indicates ideal mixing, where the enthalpy of mixing is zero. $\chi_{FH} < 0$ (a very rarely encountered situation) indicates an enthalpic driving force towards mixing. $\chi_{FH} > 0$ (which is the case in a vast majority of mixtures) indicates that the components enthalpically prefer to be surrounded by other molecules of their own kind. A larger positive χ_{FH} indicates a

stronger enthalpic driving force towards phase separation or segregation, which may drive the melt additive (in our study) to segregate and migrate to the air-polymer (PP) interface. Phase separation occurs if χ_{FH} has a sufficiently large positive value to overcome the entropic effect. The entropic effect decreases rapidly in relative importance with increasing degree of polymerization N , so that miscibility decreases with increasing N . The product $\chi_{FH} * N$ quantifies the combined effects of degree of polymerization and of intermolecular interactions on miscibility [39, 47].

According to Hildebrand, the Flory-Huggins interaction parameter χ_{FH} , can be estimated from the solubility parameters ‘ δ ’ of the polymer blend and will help in determining whether two polymers are miscible. The solubility parameter, δ is defined as the square root of the ratio of the cohesive energy density to its molar volume (V) given by $(E_{coh}/V)^{1/2}$ where E_{coh} is the cohesive energy [47].

$$C_{FH} = V_{ref} * \frac{(d_A - d_B)^2}{RT} \dots\dots\dots (2.4)$$

where V_{ref} is the geometric mean of molar volumes of both polymer segments, and δ_A and δ_B are solubility parameters for components A and B. Generally speaking the lower the difference in the solubility parameters, the more mixable and compatible are the two components. Higher solubility parameter differences (between the low molecular weight melt additive and the PP polymer in our present study) may result in the segregation and migration of the additive to the air-polymer interface dominated by component incompatibility thereby altering the surface properties.

The nature of the hydrophilic group and its length and the length of the hydrocarbon tail will determine the surface energy of the molecules, migration tendency, processing compatibility and durability. For instance, in an additive with very short hydrocarbon tail the whole

molecule can actually migrate completely out of the nonwoven fibers over time. The fast migration capability accounts for excellent fast wetting and sorbency properties achieved in industrial melt-blown sorbents, which is the preferred application for this product. Hence, immediate hydrophilicity is obtained and possible release of additives from the fiber surface to the liquid occurs, resulting in reduction in the surface tension of the liquid and thereby providing enhanced wettability. However, multiple wetting will rapidly wash out most of the additive making it less durable [3].

On the contrary, a longer hydrocarbon chain, may account for both a reduced speed of migration to the surface during the separation phase and a need for additional heating to enhance further blooming. The result is improved wetting performance and durability since the additive will not readily transfer to the fluid [3].

Surface enrichment of additives and change of the surface properties have been reported by many authors [48, 49]. William et al. [48] showed surface enrichment of glycerol monoesters in PP by contact angle measurements and XPS analysis. Yilgor et al. [49] studied the surface properties of polyamides by melt blending with silicone-urea copolymers and polydimethylsiloxane oligomers. XPS analysis of quench cooled blends revealed that due to rapid solidification of the polymer melt, the additive is trapped in the solid matrix before migrating to the polymer-air interface, whereas annealing at high temperatures resulted in substantial enrichment of the additive on the polymer surface over a period of time.

Even though surface modification by migration of the additives is a well-established fact, the mechanism of the additive-migration has not been fully understood. It has been suggested that the migration mechanism is based on the surface tension gradient, molecular weight differences and other polymer-additive interactions [50].

2.4.3. Effect of Surface Tension

One possible driving force of migration process is the differences in the surface energy between additives and the host polymer. The component with lower surface free energy is enriched at the surface in order to minimize the air/polymer surface tension [51-53]. This phenomenon of surface enrichment has been used by various authors, for example, by O'malley et al. [54] to explain selective enrichment of polystyrene in PS-b-PEO diblock copolymer films, by Bhatia et al. [55] for surface enrichment of poly (vinyl methyl ether) (PVME) in miscible PS/PVME blends, and by Tanaka et al. [56] for surface segregation of poly (dimethyl siloxane) (PDMS) in immiscible blend PS/PDMS.

Also in a recent article by Lee and Archer [50], where surface migration in polymers occurring due to the multiple mechanisms for example; the role of surface free energy and additive molecular weight was investigated. They studied the migration of polystyrene-b-poly (dimethylsiloxane) copolymer additives which has low surface energy in polystyrene hosts by using a series of narrow molecular weight distribution polystyrene and pointed out that the migration is driven by surface free energy differences between the host polymer and additive. The surface chemical composition of polymer/additive blend characterized by the dynamic contact angle and ATR-FTIR techniques provided favorable information. The findings suggest that irrespective of the host polymer molecular weight, considerable amount of additive was found to be at the air/polymer interface.

Components with higher surface energy in a polymer blend tend to move away from the surface toward the bulk phase. This process reduces the surface energy of material, and as a result the lower surface energy components accumulate onto the top-most layer. By this mechanism the hydrophilic additives with higher surface energy will be forced to migrate inside the fiber, and not to surface. Then, how do we achieve high surface energy, hydrophilic surface with the migration phenomena?

2.4.4 Effect of Molecular Weight

Kumar and Russell [57] found the chain length of the two components plays significant effect on the surface migration with lattice and off-lattice Monte Carlo simulations. The component with higher molecular weight experiences a greater conformational entropic penalty for residing near the interface, so the component with lower molecular weight migrates to the interface [23]. Two mechanisms, differences in the surface tension and molecular weight of the polymer-additive are competing with each other.

The configurational entropy per segment of polymer chains near rigid surfaces is believed to be substantially lower than in bulk polymer systems [58, 59]. Thus, the conformational entropy of a chain at the film surface is significantly smaller than that in the bulk. The difference of conformational entropy between a polymeric chain existing at the surface and in the bulk, that is, the conformational entropic penalty of a chain at the surface, decreases with decrease in the number average molecular weight (M_n). Therefore, it is reasonable to consider in polymer mixtures that the high polymer molecular weight experiences a large entropy penalty and the polymer layer near the surface would be expected to be depleted in high molecular weight polymer components and enriched in lower molecular weight ones as a result of reduced conformational entropic penalty at the blend surface. Therefore, even in systems where no substantial difference exists between polymer surface energetics, migration towards the film surface may occur by selecting polymers with different molecular weights [57]. This mechanism of surface segregation has been reported for the blend systems of PS/PS-*b*-PMMA and for the blend of high-molecular-weight PS and low molecular weight PMMA [56, 60].

Tanaka et al. [56] also investigated the effect of surface tension and molecular weight differences on the migration of poly (methyl methacrylate) (PMMA) in the polystyrene (PS) host. In the case of PMMAs with low molecular weight (1.2k to 40.5K) in PS host with molecular weight 1450K, it was found that the surface PMMA weight fraction was much

higher than the blend ratio of the PMMA even though the surface tension of the PMMA component (about 44.3 mJ/m²) is higher than that of the PS component (40.9 mJ/m²). However, the surface fraction of PMMA decreased with an increase in molecular weight PMMA. Then, the surface segregation of PS and PMMA is determined by the conflict between the surface tension and molecular weight differences. In the case of PMMA with molecular weight of 387K, the surface PMMA weight fraction became lower than the blend ratio of PMMA since surface tension driven migration phenomena become more dominant than molecular weight effect.

Similarly, in a further series of papers by Lee and Archer [23], the effect of host and polymer molecular weight on migration where surface energy differences were small was investigated in the PS/PS-*b*-PMMA system. For host molecular weight substantially higher than the copolymer additive, surface enrichment of the additive was observed. An opposite behavior was seen for polymer/additive blends with copolymer additive molecular weight higher than the host polymer, wherein, the surface was found to be depleted of MMA groups.

Finally, for the bulk composition of PS-*b*-PMMA above the critical micelle concentration, micelles in bulk that are weakly penetrated by the surrounding matrix material are formed with blends of high molecular weight PS host. The micelle segregation to the surface will therefore minimize the free energy of the system [23]. Several experimental and theoretical studies reveal strong connections between the polymer molecular weight, configurational freedom, and blend compositions near phase interfaces.

2.4.5. Synergism Effects in Polymer/Additive blends

Synergistic effects were first highlighted by Klun et al. [61] and were also discussed in a recent article by Moñoz et al. [62]. In the former case, the melt addition of fluorochemical/hydrocarbon surfactant blends was found to impart cost effective wettability to nonwoven webs based on the strikethrough, rewet, and, percent run off tests. The pairing is believed to be effective because the fluorochemical enhances the movement to the surface

for both surfactants, where they can work together to lower the surface tension of the impinging liquids.

However, the latter article addresses the same issues in terms of the processing improvement and surface characteristics. Though the addition of particles (additive) to the polymer melt looks attractive, most of the polymer blends are immiscible and incompatible which results in processing problems, questioning the performance of the melt additive in generating the desired properties. A third component like silane grafted polyethylene (HDPE-VTES) was added to the binary blend containing silicone master batch (SMB) and high-density polyethylene (HDPE) as a compatibilizer. The experimental results from MFR (Melt flow rate), DSC (Differential scanning calorimetry), tensile, FTIR (Fourier transform infrared spectroscopy), and SEM (Scanning electron microscopy) photomicrographs indicated processing and surface property improvements, with very little effect on their bulk tensile and thermal properties. In the absence of the HDPE-VTES, SMB was found to form discrete disperse domains in the HDPE matrix, while the SMB domain size was considerably lower in the presence of the compatibilizer. The addition of a third component is believed to reduce the interfacial tension between the polymer/additive phases, increasing the surface area of the dispersed phase, thus promoting adhesion and stabilizes the dispersed phase morphology.

As a result of the various migration driving factors, the migration rate and resulting surface activity will vary depending on polymer morphology, host polymer-additive surface tension gradient, molecular weight distribution of polymer and additives, the additive microstructure, additive concentration, and processing conditions such as shear rate, quenching rate, and drawing [63].

2.4.6. Effect of Environmental Factors

The migration phenomena will also be affected by environmental factors such as heat and contact surface. It is found that annealing enhanced the rate of the migration [23, 56].

Moreover, annealing at a temperature higher than the glass transition temperature (T_g) of the polymer components of the blend films is believed to produce a different structure than that prepared at temperatures below the T_g of the polymer components [64-66].

It is also observed that migration toward air/polymer interface differs from migration toward glass/polymer interface [67], and can be explained by their different interfacial energies. This implies that water related process, such as washing, laundering, even hydro-entangling, may affect migration of the additives in polymer since water/polymer interface is different from air/polymer interface.

It is worthwhile to note that surface migration is responsible for surface modification without bulk properties changes, but excessive surface migration and poor polymer-additive adhesion may also lead to poor durability of the hydrophilicity. Other considerations in the melt blending of the additives in the fiber are incorporation and processing characteristics. Incorporation at the melt state depends on the solubility of the additive with the polymer melt additive and polymer type, chemistry, polarity, molecular weight, and melting point. The melting point and the molecular weight of the additive determine its processibility during its incorporation into polymers and the processability during spinning. The surface migration characteristics can be optimized by achieving a balance between the molecular weight and the ratio of hydrophilic and hydrophobic components in the surface-active agent [24].

In summary, melt additives are a promising technology to impart durable hydrophilic surface in highly hydrophobic fibers such as polypropylene, which can lead to better performance and wider applications. However, only a few studies are reported on the subject and therefore it is necessary to understand polymer-additive interactions during the process, such as compounding, spinning and bonding, and, migration phenomena to achieve durable hydrophilic surface without impairing polymer bulk properties.

2.5. ROLE OF MELT ADDITIVE MOLECULES IN SURFACE PROPERTY ALTERATION

For the purpose of comparing the performance of surfactants in reducing interfacial tension, two distinct concepts, the efficiency and effectiveness of surfactants, have been developed [68]. It is worthwhile to note that these two characteristics may not show the same trend.

Efficiency is the bulk phase concentration of surfactant required to reduce the interfacial tension by some significant amount [68]. It is measured as the surface adsorption at the interface, so in our case it is related to the surface concentration of the melt additives and migration. However, for surfactants in liquid, equilibrium surface adsorption is achieved almost instantly. This is not the case of melt additives in polymers. Actually, surfactant surface adsorption would not be the principal model for migration of melt additives to the air/polymer interface since surface prefers lowest energy status. Water/PP interface prefers surfactant over PP, but changes in the surface adsorption may be limited by lack of mobility of the surfactants on contact with water. Still we expect that there will be some alteration, such as surfactant molecule realignment, when the PP/air interface is displaced by the PP/water interface.

Effectiveness is the maximum reduction in interfacial tension that can be obtained regardless of bulk phase concentration of surfactant. The effectiveness of a surfactant in reducing surface or interfacial tension can be measured by the amount of reduction of surface tension attained at the critical micelle concentration (CMC) [68]. CMC is the concentration of the surfactant where the amount of surfactant adsorbed on the surface reaches its maximum and any additional surfactant molecules forms self-assemblies, known as micelles, in the solution bulk. Therefore, the reduction of the tension beyond the CMC is relatively insignificant. CMC and interfacial tension of the system depend on the surfactant chemical structures and nature of the interface. We expect similar phenomena to be observed in the PP-additive system, so hydrophilicity may not continuously increase as bulk phase concentration

increases. Detection of maximum hydrophilicity obtained by given melt additives and its concentration will be critical in practical applications.

Siloxanes, fatty acid esters, non-ionic surfactants such as polyethylene glycols and tertiary amines all are candidates of surface-active additives. Non-ionic type surfactants, which are low molecular weight oligomers with an amphiphilic structure, composed of a long hydrophobic tail and a hydrophilic head group are reported as good surface active additives [24]. For example, the following classes of nonionic surfactant molecules can be used as melt additives:

- i. Mono glycerides and mono/di glycerides
- ii. Low level ethoxylates of alcohols or nonyl phenol
- iii. Low molecular weight PEG esters
- iv. Low level ethoxylates of fatty amines

2.5.1. Interfacial Adsorption of Melt Additives

Surfactants, being surface-active, adsorb on almost every surface and at almost every interface. Surfactants adsorb at the interface between oil and water. Surfactants adsorb at the interface between liquids and gases (the water and air interface, for example). Still, their behavior at a solid-liquid interface is unique. Surfactant adsorption at the solid-liquid interface is especially interesting because adsorbed surfactants form aggregates on the surface of solids that can dramatically change the properties of the interface. This is an important factor in solid-liquid dispersions, in wetting of surfaces, and in cleaning [68].

Adsorption of a surfactant at a solid-liquid interface can be good or bad. When you want the surfactant to modify the properties of the interface, as you do in wetting applications, you want the surfactant to adsorb. So it is very important, therefore, to be able to choose a surfactant system so that the surfactant adsorption is high when it is needed to control the

properties of the surface or interface, as for instance in the present study to create or impart a durable surface hydrophilicity to the host polymer PP [68].

In the section below we take the opportunity to discuss the general adsorption mechanism most commonly encountered when a gas or liquid or solute (called adsorbate) accumulates on the surface of a solid or more rarely a liquid (adsorbent), forming a molecular or atomic film (adsorbate).

The process of migration of melt additives in polymer blends will lead to preferential enrichment of the melt additive (polar oxygen containing groups) at the air-polymer interface. Termed as adsorption in other words, it generally involves the migration of a substance from one phase to the surface of an adjacent phase, accompanied by its accumulation at the interface. Adsorption is a result of the binding forces between individual atoms, ions, or molecular regions of an adsorbate and the adsorbent surface. The interaction between the adsorbate and the adsorbent may be either chemical or physical. These binding forces or interactions vary in magnitude and can be identified as follows [69]:

- Strong covalent bonds in chemisorption
- Hydrogen bonding,
- Hydrophobic bonding formed by association of hydrocarbon chains
- Weak van der Waals type of attraction contributing to physical adsorption

The net interactions between the adsorbent-adsorbate might involve more than one type of interaction, depending on the chemical structure of both components.

Adsorption will usually affect a system by altering the energetic or mechanical characteristics of the interface as, for example, by lowering the interfacial tension between two immiscible phases, and altering the wetting characteristics of a solid surface. The adsorption of a component at the interface is usually expressed as the amount of the component i in the

surface phase excess n_i^s that differs from its concentration n_i^b in the bulk phase. Suitably, the surface excess concentration of i , Γ_i is given by [68, 70],

$$\Gamma_i = \frac{n_i^s}{A} \dots\dots\dots (2.5)$$

where A is the interfacial area. In principle, Γ_i may be either positive or negative and the energy of the interface changes when interfacial adsorption occurs. It is important to know the amount of material adsorbed at the interface to understand and predict the role of surfactant adsorption. The Gibbs equation, which relates the changes in the interfacial energy of a system to the degree of adsorption of a species at the interface and the compositions of the bulk phases, forms the basis for understanding the thermodynamics of the adsorption process. Under conditions of constant temperature and pressure, the basic equation is given as [68, 70],

$$\delta\gamma_i = -\Gamma_1\delta\mu_1 - \Gamma_2\delta\mu_2 - \Gamma_3\delta\mu_3 \dots\dots\dots(2.6)$$

where γ_i is the interfacial energy, $-\Gamma_i$ is the surface excess of component i at the interface, and μ_i is its chemical potential (free energy change per mole of a specific reactant) in each bulk phase.

The change in the free energy G of a system may be given by [68, 70],

$$dG = -S dT + V dP + \gamma dA + \sum \mu_i dn_i \dots\dots\dots(2.7)$$

where G is the Gibbs free energy, S is the entropy, P is the pressure, V is the volume, and T is the absolute temperature have their usual thermodynamic definitions, and A , μ_i and n_i are defined above.

However, at equilibrium and under constant conditions of T, P, and n_i , the above equation reduces to [68, 70],

$$dG = \gamma dA \dots \dots \dots (2.8)$$

If the surface excess component 'i' is allowed to vary by adsorption, then

$$\delta\gamma = - \Sigma (n_i^s / A) \delta\mu_i = -\Sigma \Gamma_i \delta\mu_i \dots \dots \dots (2.9)$$

For a two-component system, equation 2.9 reduces the above equation to [68, 70],

$$\delta\gamma = -\Sigma \Gamma_2 \delta\mu_2 \dots \dots \dots (2.10)$$

The chemical potential of a species is related to its activity by

$$\mu_2 = \delta\mu_2^0 + RT \ln a_2 \dots \dots \dots (2.11)$$

so that

$$d\mu_2 = RT d \ln a_2 \dots \dots \dots (2.12)$$

and,

$$\delta\gamma = - \Gamma_2 RT d \ln a_2 \dots \dots \dots (2.13)$$

In low concentration surfactant system, the activity coefficient of the additive can be approximated to 1, concentration c_2 can be substituted for a_2 . The Gibbs equation is then transformed to its most common form [68, 70],

$$\Gamma_2 = - \frac{1}{RT * \frac{dg}{d \ln c_2}} \dots\dots\dots (2.14)$$

In systems where the interfacial energy can be determined (for example, liquid-liquid, liquid-vapor systems) the above equation can be used to determine the surface excess concentration of the adsorbed species [68, 70]. This information can be used as tool for characterizing a surfactant species at the molecular level and aids in the interpretation of the surface phenomena on the basis of the chemical composition and molecular structure. However, in systems with a solid polymer interface (PP-melt additive), interfacial energy cannot be measured directly, and changes in the interfacial energy can only be qualitatively studied by relating the surface chemistry/composition changes with the wettability measurements.

2.5.2. The Role of Melt Additives on Polymer Surfaces

The theory of adsorption of surfactants from an aqueous solution onto a hydrophobic surface was used to understand what may happen with a hydrophobic solid PP matrix containing melt additives with amphiphilic structures.

When aqueous surfactant solutions are brought into contact with hydrophobic polymer surface, adsorption of surfactants from aqueous solutions onto nonpolar or hydrophobic surfaces is primarily by dispersion force interactions and surfactant adsorbs onto the surface by interactions between the hydrophobic surface and the hydrophobic tail of the surfactant, while the hydrophilic head favorably interacts with water [68, 71].

Adsorption of the surfactant onto the polymer/water interface can significantly modify interfacial properties at unusually low bulk concentrations. Also, by cooperative self-association, surfactants form micelles above CMC (critical micelle concentration), where

aggregation first occurs, and both individual amphiphilic molecules and micellar clusters coexist in dynamic equilibrium.

The surfactant-surfactant and surfactant-hydrophobic surface interactions that cause aggregation can lead to changes in orientation and packing of surfactant at the surface. The orientation changes undergone by surfactant molecules adsorbed onto the polymer surface can occur in several stages [68, 71] (see Figure 2.4).

Initially (*stage one*), the surfactant starts to migrate from the solution to the surface where there are very few surfactant molecules and where consequently surfactant-surfactant interactions are negligible. Adsorption occurs because of Van der Waals interactions, principally determined by the hydrophobic moiety of the surfactant. Nevertheless, the polar groups of the surfactant may also have some interaction at the surface. At this point, the surfactant tends to lie flat (monolayer saturation) on the surface because its hydrophobic portion is positively adsorbed. Adsorption therefore, will always result in an increase in the hydrophilic character. Increase in the size of the surfactant molecule by, for example, lengthening the hydrophobic or hydrophilic chain may alter the adsorption [68, 71].

The subsequent stages of adsorption are increasingly dominated by surfactant-surfactant interactions, although it is these interactions that initially determine how the adsorption progresses when *stage two* is complete. The surfactant-polymer interactions depend on the nature of the polymer and on the hydrophilic-lipophilic balance in the surfactant. For example, when the polymer is non-polar, or when the surfactant has a short POE chain rather than long one, the hydrophilic group is only weakly adsorbed to the surface [68, 71].

The change in amount adsorbed in *stage three* of adsorption may be large, but as the concentration of the surfactant at the surface approaches CMC, the alkyl chains of the adsorbed molecules tend to aggregate. This will cause the molecules to become vertically oriented and there will be a large increase in the number of molecules adsorbed. This

increase is probably not entirely caused by the change in orientation. The lateral forces due to alkyl chain interactions in the adsorbed layer will compress the head group, and for an ethylene oxide chain this will result in a less coiled, more extended conformation. However, even in the close packed monolayer, the ethoxy chain may not be fully extended. The longer the surfactant alkyl chain the greater will be the cohesion force and hence the smaller the surfactant cross-sectional area.

This may explain why saturation adsorption increases with increasing chain alkyl chain length as well as with decreasing POE chain length [68, 71]. The interactions occurring in the adsorption layer during the *fourth and subsequent stages* of adsorption are similar to the interactions in solution, where enthalpy changes caused by increased alkyl-alkyl interactions balance those due to head group interactions. For this reason, the heat of adsorption becomes constant, although adsorption increases with increasing temperature due to increase in the surface activity. The parallel between bulk micellization and the aggregation processes occurring at the surface has been most strongly emphasized. It has been suggested that above the CMC, adsorbed surfactant forms micellar aggregates on the surface resulting from the association of the surfactant molecules already on the polymer surface, and not migrated and transported from the solution. For non-polar adsorbent, *stage four* represents the final adsorption stage [68, 71].

The Langmuir isotherm is the most common adsorption isotherm used to investigate the adsorption mechanism of nonionic surfactants.

Similarly in the case of melt additives in the PP polymer, theoretical analysis of the mechanism of adsorption/enrichment of melt additives on the PP polymer surface can be explained by analogy with the surfactant adsorption onto hydrophobic surface from aqueous solutions as explained before by interactions between the PP and the hydrophobic tail of the melt additive with the hydrophobic tail sticking into the PP matrix while the hydrophilic head may be oriented vertically into the air attracting moisture from the atmosphere leading to a

hydrophilic surface. Due to the mobility of the melt additive in the solid polymer matrix a closely packed monolayer may form, but it is difficult to tell whether or not micellar aggregates may form on the surface with the PP-melt additive system, as the association of the additive molecule will only begin when surface concentration of the melt additive reaches the CMC. While the migration of the micellar additive aggregates from the bulk of the host polymer to the surface may not be possible, they should still be able to exert their powerful effects on the interfacial tension as discussed earlier.

The efficiency and effectiveness of adsorption then will be largely dependent on the size and nature of the hydrophobe, with a lesser role being played by the hydrophile. Particularly important from the hydrophilic standpoint will be the extent of mutual repulsion among neighboring head groups, which affect both the efficiency and the effectiveness of adsorption. The nature of the hydrophobic group, i.e. the degree of branching, unsaturation, polar substitution, the presence of aromatic groups, etc. will play a major role in the adsorption characteristics of the system, primarily as a result of its effects on the conformation of the hydrophobic chain and its interaction with the polymer.

Therefore, the performance of a melt additive in terms of migration, efficiency, effectiveness, will be expected to depend on the chemical classes and the structural changes within the class.

2.5.3. Additives and its Role in Interfacial Tension Reduction

Hydrophilic melt additives are mostly surfactants modified to meet the requirements of the polymer melt process. These additives are low molecular weight oligomers and are characterized by an amphiphilic structure, composed of a long hydrophobic tail and a hydrophilic head group [24]. Amphiphilic structure is a key characteristic of the surfactant, which is responsible for preferred surface adsorption, interfacial tension reduction and micelle formation.

A huge amount of the work has been done related to the function of surfactants in liquid phase while the study of surfactant functions in the solid phase such as melt additives are rare. However, we would like to introduce some concepts developed for surfactant functions in liquid phase since surfactant actions at the interface would be principally similar except the surfactant has very limited mobility in the solid polymer matrix.

If we add a surfactant to a system of two immiscible phases (in our case hydrophobic PP and water), a surfactant is adsorbed at the interface and it will orient itself with the hydrophilic group toward the water and the hydrophobic group toward PP (if you assume, surfactant molecules are completely mobile, as inside the liquid and there is no structural hindrance by the PP structure, which is not the case of melt additive in the solid PP).

The schematics of the additive function at the polymer-water interface are given in Figure 2.5. Without additives (Figure 2.5(a)), water-PP interaction B is very weak, compared to interaction between PP molecules A, so interface molecules are not in balance and are pulled toward the bulk, which induces large interfacial tension. In Figure 2.5(b), the presence of additives with amphiphilic nature reduces this force imbalance by affinity of hydrophilic head to water and hydrophobic tail to PP molecules.

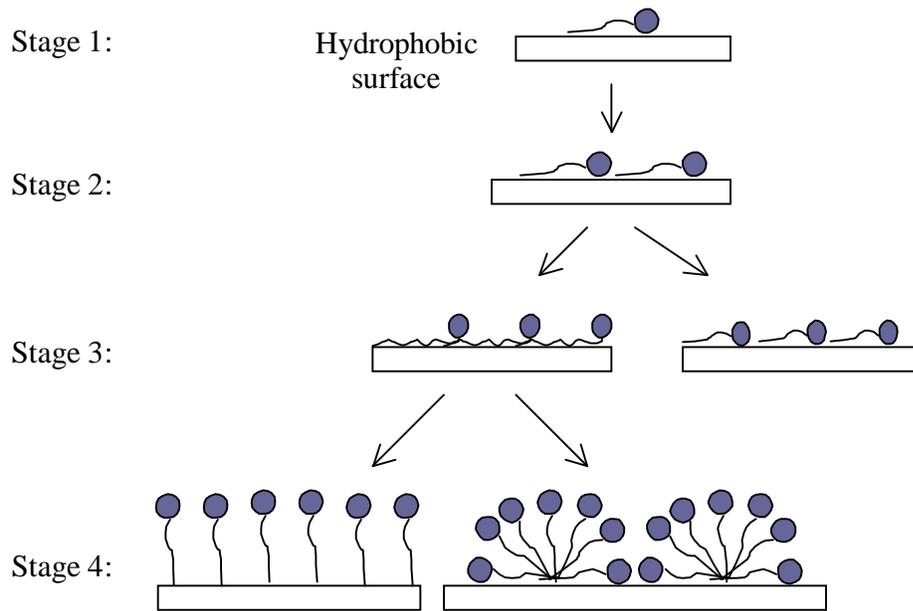


Figure 2.4: Successive stages of adsorption showing orientation of surfactant molecules at nonpolar surfaces.

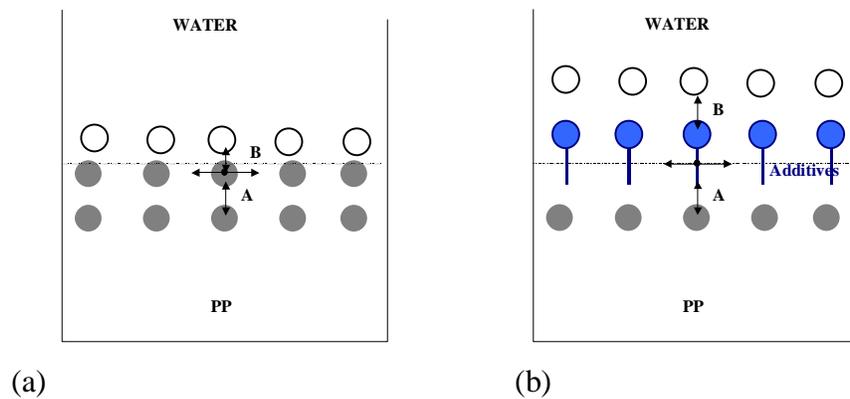


Figure 2.5: Interfacial tension reduction by melt additives (a) without additives, (b) with additives on the surface.

3. EXPERIMENTAL APPROACH

3.1. MATERIALS AND SAMPLE PREPARATION

3.1.1. Extrusion of Polypropylene Films with Melt Additives

Polypropylene (Melt flow index = 18) films containing the following ethoxylated alcohol nonionic melt additives listed in Table 3.1 have been melt extruded with a twin-screw extruder using a melt additive concentration of 2%. Polypropylene films with no melt additives have been extruded under the same conditions to produce the control sample.

The HLB, Hydrophile - Lipophile Balance, the ratio of oil-soluble and water-soluble portions of a molecule) values for the melt additives calculated based on the molecular structure using Griffins method (developed for nonionic surfactants, equation 3.1) and the oxygen to carbon mole % is also summarized in Table 3.1. The Hydrophilic-Lipophilic balance (HLB) of a surfactant is a measure of the degree to which it is hydrophilic or lipophilic. Surfactants with a low HLB are more lipid (oil) loving and those with a high HLB are more hydrophilic (water loving).

$$HLB = 20 * \frac{M_h}{M} \dots\dots\dots (3.1)$$

where M_h is the molecular mass of the hydrophilic portion of the molecule, and M is the molecular mass of the whole molecule

3.1.2. Extrusion of Spunbond Polypropylene (PP) Nonwoven Fabrics with Melt Additives

Spunbond PP nonwoven fabrics containing POE6-Stearyl alcohol melt additives listed in Table 3.1 have been produced with a melt additive concentration of 0.5-, 1-, and 2-wt% at Nonwovens Cooperative Research Center (NCRC) Pilot facilities located at North Carolina State University. Additionally spunbond PP nonwoven fabric with no melt additives has also been extruded under the same conditions to produce the control sample. The PP resin used was Sunoco PP-CP360H. The extrusion temperature is set at 240°C, melt throughput was 0.30 g/hole/min, quench air temperature 11°C, and smooth calendered with no heat. The web basis weight was controlled to reach the target weight at 50 g/m².

Table 3.1: Melt additives, their Chemical Structures, HLB's, and molar percentage of oxygen to carbon ratio.

ID	Melt additives	Chemical Structures	HLB*	O/C mole %
NP2	Nonyl Phenol Ethoxylate (NP-2) – Tergitol TM – NP2	$C_9H_{19}C_6H_4(OCH_2CH_2)_2OH$	6.8	16
NP4	Nonyl Phenol Ethoxylate (NP-4) –	$C_9H_{19}C_6H_4(OCH_2CH_2)_4OH$	9.8	22
NP6	Nonyl Phenol Ethoxylate (NP-6) - Tergitol TM – NP6	$C_9H_{19}C_6H_4(OCH_2CH_2)_6OH$	11.6	26
POE2C18	POE 2 Stearyl Alcohol – ETHAL SA-2	$CH_3(CH_2)_{16}CH_2(OCH_2CH_2)_2OH$	5.9	14
POE4C18	POE 4 Stearyl Alcohol – ETHAL CSA-4	$CH_3(CH_2)_{16}CH_2(OCH_2CH_2)_4OH$	8.7	19
POE6C18	POE 6 Stearyl Alcohol – ETHAL SA-6	$CH_3(CH_2)_{16}CH_2(OCH_2CH_2)_6OH$	10.5	23
POE3C12/C13	POE 3 C12/C13 Alcohol ---C12/C13 Chain - Bio-Soft N23-3	$CH_3(CH_2)_n(OCH_2CH_2)_3OH,$ $n=11,12$	8.9	21

* Griffins [72]

Table 3.1 (continued).

ID	Melt additives	Chemical Structures	HLB*	O/C mole %
DGMS	Distilled Glycerol Mono Stearate (D-GMS) - Starplex 90	$\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_2\text{CHOHCH}_2\text{OH}$	1.9	19
POE2C18 -Amine	POE 2 Stearyl Amine - Ethox SAM-2	$\text{CH}_3(\text{CH}_2)_{17}\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$	5.8	9
PEG400C 12Diester	PEG 400 C12 Diester – C12 Chain – Ethox DL-9	$\text{CH}_3(\text{CH}_2)_{10}\text{CO}(\text{OCH}_2\text{CH}_2)_{9.09}\text{-O-CO}(\text{CH}_2)_{10}\text{CH}_3$	10.2	29

* Griffins [72]

3.2. CHARACTERIZATION METHODS

Surface modifying melt additives aim at generating additive enriched surfaces through their migration or segregation. Characteristics of this surface will be affected by surface concentration of additives, their orientation and lateral heterogeneity of additive distribution. Surface composition and structure of the polymer-additive composite materials and their effect on surface hydrophilicity is explored using surface specific analytical methods such as XPS, ToF-SIMS, AFM, and dynamic water contact angle measurements.

3.2.1. High Performance Liquid Chromatography (HPLC)

In this study we employed ‘reverse phase chromatography’ for separation of the additive components. Liquid chromatography has been successfully used to analyze nonionic ethoxylated surfactants. The separation of the components in the additive sample depends upon the interactions with the mobile phase and the stationary phase. Therefore, the different components of the sample interact differently with the mobile phase and stationary phase particles held in the column. Depending upon the interaction, different components elute or reach the detector at different time intervals, called the ‘retention time’. In reverse phase chromatography, a polar mobile phase and non-polar stationary phase are used and its use for the separation of ethoxylated additives to examine the distribution/degree of ethoxylation has been reported.

In this study, the stationary phase used consists of a polar silica gel particles coated with non-polar C-18/C-8 hydrocarbon thus making it non-polar in nature. The mobile phase has a mixture of compounds with different polarity thus resulting in better separation of the components [73].

3.2.1.1. Analysis of Linear Ethoxylated Alcohols and Esters

For linear ethoxylated alcohols and esters (such as POE2C18, POE3C12/C13, POE4C18, POE6C18, and PEG-400C12 Diester), reverse phase HPLC analysis was used to examine the distribution of the EO chains attached to the alkyl homologs. Sample solutions (3mg/mL) were prepared by dissolving in 100% HPLC grade methanol. Water, acetonitrile and methanol were used as the mobile phase. A linear gradient, as shown in Table 3.2 was used for the separation. The separation was performed on a Waters 2695 instrument with an eluent at a flow rate of typically 1 mL/min using a C18 analytical column (typically a 250 x 4.6 mm, 5 μ m, 120 Å , AcclaimTM surfactant column) and an injection volume of typically 40 μ l. Detection was by evaporative light scattering (Waters Model ELS 2420), at 60 psi pressure and a drift tube temperature of 65 $^{\circ}$ C.

To identify the presence of residual fatty alcohol in the stearyl alcohol ethoxylates, 100 μ l of stearyl alcohol (1-Octadecanol from Sigma) was injected into the column along with POE2 stearyl alcohol.

3.2.1.2. Analysis of Nonyl Phenol Ethoxylates

For the nonyl phenol ethoxylates, sample solutions (3mg/mL) were prepared by dissolving in 100% HPLC grade acetonitrile. A linear gradient (Table 3.3) with water and acetonitrile, was used as the mobile phase at a flow rate 1ml/min and an injection volume of 50 μ l. The chromatographic separation was performed on a Waters 2695 instrument using an XbridgeTM Shield RP-18 column (3.5 μ m, 150 x 4.6 mm) with an absorbance detector (Waters 2483).

3.2.1.3. Analysis of Ethoxylated Fatty Amines

Reverse phase HPLC analysis of ethoxylated fatty amines reported by Lang et al. [74] was utilized for the separation of POE2 Stearyl amine additive. Ethoxy (polyoxyethylene) distribution was obtained using isocratic conditions with methanol as an organic modifier on a C18 column.

The sample solution was prepared by dissolving the fatty amine (10mg/mL) in 2-propanol. The HPLC chromatographic analysis was performed on a Waters 2695 instrument using a Waters Nova-Pak 60 A° C18, 4 µm, 150 x 3.9 mm column maintained at 40 °C with an evaporative light scattering detector (Waters Model ELS 2420). The detector was operated at 65 °C tube temperature and a 58-psi nebulizer pressure. An isocratic mobile phase with MeOH/H₂O (85:15) containing 25mM triethylamine and 50 mM glacial acetic acid was used with a flow rate of 1mL/min and an injection volume of 30 µl.

3.2.1.4. Analysis of Monoglyceride Additives

For analyzing monoglyceride additives for PP, the following reference standards were purchased from Sigma (St.Louis, MO, USA): 1-Stearoyl-*rac*-glycerol, glycerol and, stearic acid. The reference standards and sample solutions were prepared by dissolving 100-200ppm (w/v) and 2500ppm (w/v) respectively of each compound in ethyl acetate-chloroform (9:1, v/v). The HPLC chromatographic analysis was performed on a Waters 2695 instrument using Supelcosil™ LC-8, 3 µm, 150 x 4.6 mm column with an evaporative light scattering (Waters Model ELS 2420). The detector was operated at drift tube temperature of 65 °C and a 40-psi pressure. Acetonitrile, methylene chloride, and water-acetic acid (0.1%, v/v) were used as the mobile phase at a flow rate of 1.3mL/min as shown in Table 3.4. Injection volume was 20 µl. All the sample solutions were later filtered through 0.45 µm GH Polypropylene membrane filters before investigating by reverse phase HPLC.

3.2.2. X-ray Photoelectron Spectroscopy (XPS or ESCA)

XPS provides quantitative analysis of the atomic composition of the surface by detecting the characteristic binding energies associated with each element. The drawback of XPS is that it detects only atomic composition not molecular level information. It is useful only if additives contain atoms that are not part of substrate polymer. In case of PP-melt additive system, PP consists of only H and C while many melt additives contains oxygen. XPS measures oxygen concentration on the substrate surface and we will use this value as a representative of melt additives surface concentration at the analytical depth. The surface compositions determined from the XPS spectra were therefore used to examine the existence of oxygen on the melt blended PP surfaces.

XPS measurements were carried out in RIBER LAS-3000 spectrometer using a monochromatic Mg K_{α} X-ray source (1254 eV), an electron multiplier as the detection system and a hemispherical electron energy analyzer. The X-ray spot size (area analyzed) on the samples surfaces was approximately 3mm in diameter. A standard 75° take-off angle (the angle between the surface normal and the axis of the analyzer lens) was used for surface scans, which are believed to probe the outer 1-5 nm of the polymer surface. Elemental compositions were calculated from the areas of carbon 1s and oxygen 1s peaks in the survey spectra using appropriate relative sensitivity factors.

For quantitative analysis of the surface composition for the PP/Melt additive blends, the XPS-determined surface oxygen concentration (expressed as O/C ratio %), which is representative of the nonionic melt additives, was compared with the bulk concentration of melt additive used for PP surface modification in the blend. The experimental O/C ratio contains the contribution of each polymer to the overall O 1s and C 1s spectra, which can be expressed as,

$$\left(\frac{O}{C}\right)_{\text{experimental}} = \frac{X * O_{\text{MeltAdditive}}}{X * C_{\text{MeltAdditive}} + (1 - X)C_{\text{PP}}} \dots\dots\dots (3.2)$$

where X is the molar melt additive surface concentration in the blend and $O_{\text{MeltAdditive}}$, $C_{\text{MeltAdditive}}$ and C_{PP} are the stoichiometric oxygen and carbon atomic concentrations in pure melt additive and pure PP repeat unit, respectively. The above equation is rearranged in terms of O/C to get the value of X (actual molar melt additive surface concentration in the blend) by using stoichiometric carbon and oxygen atomic concentrations for each melt additive structure. The O/C contribution from the PP control polymer obtained by XPS due to surface hydrocarbon contamination of oxidation was subtracted from the surface O/C obtained in the melt blended PP films to get a clear indication of the surface excess of the melt additive. For example, in PP/POE2C18 blend, X is given by:

$$X = \frac{3 * O/C}{3 - 19 * O/C} \dots\dots\dots (3.3)$$

3.2.3. Water Contact angle measurements

The contact angle, θ , is one measure of wettability that refers to the response when a liquid is brought into contact with a solid surface, initially in contact with a gas or another liquid. Typically a low water contact angle means high hydrophilicity and a high water contact angle means low hydrophilicity of substrate. Water contact angle is the property of very top surface about 5 Å depth, however the depth of the substrate responsible for contact angle is hard to define.

Ideally, equilibrium contact angle is determined by the balance of interfacial tensions at the three-phase contact line (Figure 3.1). Young’s equation relates equilibrium contact angle, the surface tension of the liquid to the surface tensions of the solid/liquid interfaces and solid/air

interfaces for conditions of thermodynamic equilibrium and a perfectly flat homogeneous solid surface. It can be derived from interfacial force balances, and is given by [75],

$$\cos q = \frac{g_S - g_{SL}}{g_L} \dots\dots\dots (3.4)$$

where, θ = Equilibrium contact angle, γ_S = Interfacial tension between solid and vapor, γ_{SL} = Interfacial tension between solid and liquid, and γ_L = Interfacial tension between liquid and vapor.

When liquid has the ability to alter substrate surface on contact, contact angle changes as the function of contact time as a result of surface restructuring. Surface restructuring or contact angle relaxation (Figure 3.2) given by ‘ $\Delta\theta$ ’ is expressed as the relative change in the contact angle between two time intervals. A large ‘ $\Delta\theta$ ’ implies high relaxation and surface restructuring by reorientation of hydrophilic segment of the additive molecules towards the water phase.

The wettability of the samples was evaluated using water contact angle measurements. The system consists of a high-resolution camera and zoom microscope, a syringe, adjustable specimen stage and manually controlled lighting. A sessile drop of distilled water was dispensed and its image was captured by a video camera and displayed on a computer monitor. As contact angle is a dynamic phenomenon (change in the contact angle with time), a time scale of 1/20 second (20 images/second) is used to capture the dynamic behavior of liquid interactions on PP films, the contact angle of the water drop was determined using image analysis software and was averaged for 5 drops at each time interval. For spunbond PP nonwoven fabrics, a time scale of 10 second (1 images/10 seconds) is used to capture the dynamic behavior of liquid interactions and the contact angle of the water drop was averaged for 3 drops at each time interval.

3.2.4. Migration Study

Due to the dynamic nature of the polymer-melt additive system, the migration phenomena of the melt additives inside polypropylene film after extrusion were studied by measuring surface composition changes and hydrophilicity at different times after extrusion.

3.2.5. Water Immersion Effects and Durability Study

Exposure to water may cause realignment and loss of the additive molecules. Changes of surface properties and loss of additive molecules induced by water exposure and its recovery were studied. Hence, the durability of surface modified polypropylene films was evaluated by immersing series of samples (1g) in 200 mL of deionized water for 6, 12 and 24 hrs independently at room temperature in an incubator subjected to agitation (at 100 rpm). All the samples were later air-dried and changes in surface O/C ratio and water contact angle were observed. After drying, water exposed samples were aged under room conditions and water contact angles were measured. Recovery angle changes of contact angle during 2- or 3-week period after water exposure, were defined as,

$$q_{recovery} = q_{24hr} - q_{2-3weeks} \dots\dots\dots (3.5)$$

Where θ_{24hr} à contact angle measured at 24hrs after water exposure

$\theta_{2-3weeks}$ à contact angle measured at 2 or 3weeks after water exposure

Additive released to water from substrate during water immersion was also investigated by liquid surface tension measurement. As mentioned earlier the surface modified polypropylene films with different melt additive concentration levels were evaluated for their durability by placing the samples in water for a time period of 6, 12 and 24 hrs independently. After each soaking time, the samples were taken out and dried for a period of

24hrs and investigated for changes in the surface properties, whereas the water solutions were analyzed for changes in the water surface tension for possible additive loss with the help of a Fisher Scientific surface tensiometer working on the Du Nouy ring principle.

3.2.6. Differential Scanning Calorimetry (DSC) Analysis

To investigate the effect of heat on the surface modified polymer properties, it is necessary to know the temperature at which the polymer samples must be run. Therefore, thermal analysis of a few selected modified polypropylene substrates was carried out on 3–5 mg samples in a power-compensated Perkin Elmer Diamond DSC thermal analyzer. An indium standard was used for calibration, a heating rate of 20°C/min. was employed, and nitrogen was used as the purge gas. Samples were heated at the underlying heating rate of 20°C/min from -50°C to 200°C and the thermal transitions in the polymer such as melting and glass transition are reported.

The processing conditions and the thermal history of the polymer affect the development of fiber structure during spunbond nonwoven fabric manufacture. DSC experiments, which measure the bulk characteristics (i.e., miscibility and degree of crystallinity) are used to examine the interactions between the PP polymer and the additive at the molecular level. Similar to polypropylene film, DSC measurements were made on a power-compensated Perkin Elmer Diamond DSC thermal analyzer using 3–5 mg spunbond web samples. An indium standard was used for calibration, a heating rate of 20°C/min. was employed, and nitrogen was used as the purge gas. Samples were heated at an underlying rate of 20°C/min from -50°C to 200°C and the thermal transitions in the polymer such as melting and glass transition are reported. The degree of crystallinity of blends was evaluated by the ratio between the melting enthalpy of the blend and the melting enthalpy of the perfectly crystalline PP ($\Delta H_m = 50 \text{ cal/g}$) [76].

3.2.7. Heat Treatment Study

Increased temperature induces both softening of the polymer fine structure and alters the thermodynamic equilibrium of the additive distribution. To study the effect of heat treatment on the melt additive migration behavior and hydrophilicity, select PP films modified with nonionic melt additives were subjected to heat in the oven for nearly 3 hrs using two different temperature series (one just above T_g and the second just above the T_m of the melt additive) to explore some interesting phenomena related to the evolution of the structure of the materials during the heat treatment process. Also changes in the crystalline structure and morphology of PP films modified with 2 different melt additives subjected to higher temperatures on the surface wettability was investigated. At the end of each heat treatment step, the samples were cooled to room temperature for a period of 24hrs and examined for changes in their surface characteristics. The heat-treated film samples were then aged for a specific period of time at room temperature before further analysis.

3.2.8. Wide-angle X-ray Diffraction (WAXD)

Wide-angle X-ray scattering patterns for films of PP control and PP modified with nonionic melt additive samples both before and after thermal treatment were obtained using an Omni Instrumental X-ray diffractometer with a Be-filtered Cu-K α radiation source ($\lambda = 1.54 \text{ \AA}$) generated at 35 kV and 25 mA. The film samples were manually mounted on a sample holder prior to the examination. The samples were equatorially scanned from 2θ range = $5^\circ - 40^\circ$ using a step size of 0.1° . From the scans, the degree of crystallinity (X_c) of the various samples was deduced by estimating the contribution of the crystalline and amorphous regions to the scattering pattern area using X Powder and OriginLab software programs. Also, the crystal size was deduced using the Scherer's equation [77].

$$L = \frac{0.9 * I}{b * \cos q} \dots\dots\dots (3.6)$$

where L is the apparent crystal dimension (Å), λ is the wavelength used (Å), β is the breadth (radian) at half maximum intensity, and θ is the Bragg angle.

3.2.9. Atomic Force Microscopy (AFM)

It is possible that melt additive may produce surface heterogeneity. AFM may be a useful tool to explore heterogeneity and morphology of the surface and its impact on additive performance. Therefore, A Nanoscope III Multimode AFM (Digital Instruments) was used for imaging in tapping mode to acquire height and phase images simultaneously. Imaging was performed under a moderate to light tapping where the free amplitude of oscillation, r_{sp} was varied between 0.75 and 0.95. For imaging under ambient conditions, silicon tips (Digital Instruments) with spring constants between 25 and 100 N/m were used. Images were analyzed with the Nanoscope III software (version 5.12r3).

3.2.10. Time of Flight – Secondary Ion Mass Spectrometry (ToF-SIMS)

SIMS is the mass spectrometry of ionized particles, which are emitted when a surface is bombarded, by energetic primary particles and it results in the ejection and ionization of atoms and molecules from the surface layers of the sample, the so called secondary particles. The secondary ions are accelerated into the ToF (Time-of-Flight) mass spectrometer where they are separated according to their energy and mass/charge ratio before being detected. ToF-SIMS method is highly surface sensitive (analytical depth within the top 1nm), which can be related to the contact angle information. It also allows for the chemical mapping of the surface with high spatial resolution. The initial analysis provides only qualitative results, but calibration of the responses against those obtained from the pure samples allows for quantifying the results.

All ToF-SIMS spectra were acquired using a PHI TRIFT I instrument to raster a 100 μm x 100 μm surface area with 15 kV gallium (Ga^+) ion beam at 600 pA current with an extraction voltage set at 7500 V. Data acquisition time was set for 8 min and sample surface received an ion dose of $\sim 5\text{E}+11$ ion/ cm^2 . The mass resolution of the ToF-SIMS was sufficient to identify some of the characteristic fragment ions observed in the positive ion spectra.

3.2.11. Thermogravimetric Analysis (TGA)

Prior to the production of spunbond nonwoven fabric with the melt additives, the pure melt additives were investigated for their thermal stability to see if they can withstand the high temperatures used in the extrusion of PP films and spunbond nonwoven manufacture. Therefore, thermal analysis of a few selected pure additives was carried out on 5-10 mg samples using Perkin Elmer Diamond TGA thermal analyzer. Samples were heated at an underlying rate of 30°C/min from 25°C to 600°C in the presence of oxygen and the weight changes in an air atmosphere, which is typically a superposition of the weight loss due to oxidation, are reported.

3.2.12. Heat Calendering

The spunbond PP nonwoven webs were later heat calendered at temperatures of 100, 130 and 150°C. Calender bonding for all webs was conducted at a speed of 10 m/min with a nip pressure of 70 kN/m.

3.2.13. Hydroentangling

The spunbond PP nonwoven webs with a basis weight of about 50 g/m^2 were also hydroentangled using a 103-mesh forming PET wire belt. All the samples were initially

hydroentangled front and back (2 pass) by passing through 3 manifolds with a pressure setting of 30, 75, and 100 bars respectively. Furthermore another set of samples was hydroentangled twice (4 pass) on both front and back using the same 3 pressure manifolds. The hydroentangled spunbond PP nonwoven webs were later passed through a drying unit maintained at 100°C temperature.

3.2.14. Tensile Strength

According to ASTM standard D-5035, peak force and elongation were measured on an Instron tensile tester (Model 4400R) with a loading cell of 50-kg capacity and a gauge length of 3 in., at a constant rate of extension (crosshead speed = 30cm/min). Five specimens per sample, 1" X 6" were cut along the machine direction from each hydroentangled spunbond fabric and the force required to break the nonwoven fabric and the elongation of the fabric are reported during the measurement.

Table 3.2: Gradient program for separation of ethoxylated alcohol and ester additives.

Time (min)	% Water	% Acetonitrile	% Methanol
0	55	40	5
20	5	90	5
27	5	90	5
28	55	40	5
33	55	40	5

Table 3.3: Gradient program for separation of nonyl phenol ethoxylated additives using water and acetonitrile eluents.

Time (mins)	% Water	% Acetonitrile
0	75	25
15	25	75
20	25	75
22	75	25
30	75	25

Table 3.4: Gradient elution program for separation of Distilled monoglyceride (DGMS) [78].

Binary gradient (step)	Time (mins)	Water/Acetic acid (99.9:0.1) %, v/v	Acetonitrile %, v/v	Methylene chloride %, v/v
I	0	16	84	0
	4	0	100	0
II	12	0	70	30
	18	0	70	30
	19	16	84	0
	25	16	84	0

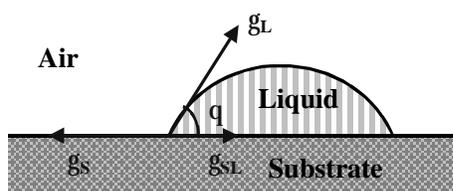


Figure 3.1: Equilibrium contact angle and interfacial tensions

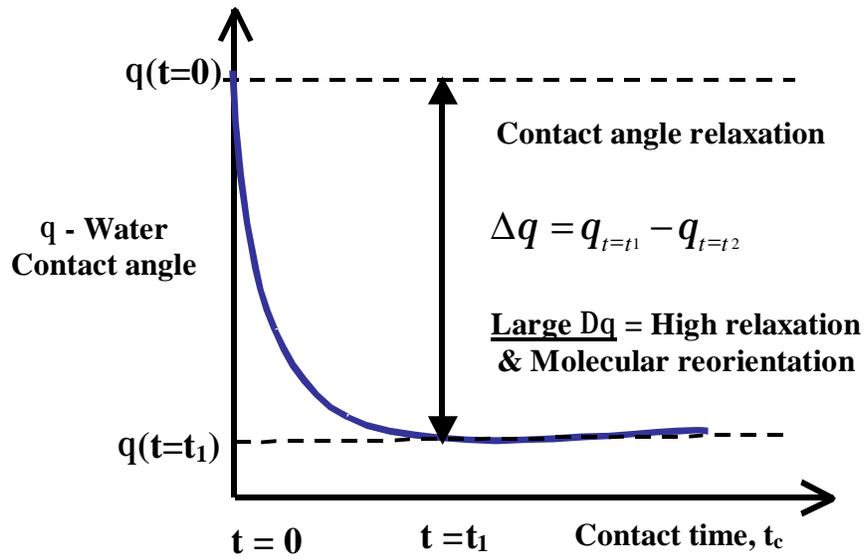


Figure 3.2: Contact angle reduction by surface realignment and release on contact with water

4. RESULTS & DISCUSSION

4.1. NONIONIC MELT ADDITIVE CHARACTERIZATION USING REVERSE PHASE HPLC

4.1.1. Stearyl Alcohol Ethoxylates

Alcohol ethoxylates are prepared by addition of ethylene oxide to aliphatic alcohols under base catalyzed conditions. The resulting product is polydisperse and has a distribution of both EO and alkyl end groups. Sometimes unethoxylated alcohol can remain after the ethoxylation reaction. Also polyethylene glycol will be present if there is any source of water. Use of an evaporative light scattering detector (ELSD) enables analysis and determination of alcohol ethoxylates distributions by gradient elution without derivatization. [79]. It is this distribution, combined with the ratio of the hydrophobe to hydrophile, that affects the chemical and application properties.

Many analytical techniques are used to characterize alcohol ethoxylates to determine both alkyl and EO distributions. A recent review discussed the use of chromatography for the analysis of alcohol ethoxylates. Alcohol ethoxylates with low degree of polymerization are characterized using gas chromatography. Though SEC (size exclusion chromatography) can analyze high mass alcohol ethoxylates, they cannot resolve individual oligomers above a mass of 600. Also thin layer chromatography can be used for separation but does not have the peak resolution of supercritical chromatography or gradient elution HPLC [80]. Typically the ethylene oxide and alkyl chain length distributions are determined by normal phase chromatography with an aminopropyl silica column and aliphatic hydrocarbon/alcohol/water mobile phases and reverse phases with C18- or C8-bonded silica and methanol/water mobile phases, respectively [80]. The use of less hydrophobic reverse phase LC columns, such as naked silica, with a reverse phase gradient results in the separation of oligomeric poly

(ethylene glycol) and alkyl phenol ethoxylates [81, 82]. Gradient elution HPLC is most commonly used to characterize alcohol ethoxylates by the number of EO units or alkyl chain lengths [80].

A C18 reverse-phase HPLC method was developed for determination of EO distribution of ethoxylated alcohols and esters. Initially samples dissolved in methanol and use of gradient mobile phase system containing water and acetonitrile with concentration of acetonitrile going from 20-80% in 5 mins, did not yield good separation due to interference effects from methanol and its absence in the mobile phase. Subsequent experiments were conducted by including a steady concentration of methanol along with water and acetonitrile as the mobile phase. Three different gradient elution approaches were implemented using water (A)/acetonitrile(B)/methanol(C) before an optimum separation of several polyoxyethylene chains was attained. The nature of separation of molecules of ethoxylated alcohols or esters depends on the type and strength of organic modifier in the mobile phase and how the hydrophobic and the hydrophilic parts interact with the stationary phase. So optimization experiments showed that a gradient program with acetonitrile concentration going from 40-90% in 20 mins gave good baseline separation of the various ethylene oxide chain components with minimal peak tailing.

The stearyl alcohol ethoxylated additives used in this study are commercial materials. Therefore, reverse phase HPLC was used to examine the distribution of EO chains attached to the C18 chains. In our analysis, as shown in the chromatogram plot in Figure 4.1, as the mobile phase polarity decreased, the retention time for the hydrophobic component of the sample or additive increased resulting in quick elution of relatively hydrophilic components in the additive. This is due to weaker interactions with the nonpolar stationary phase. The stearyl alcohol ethoxylate oligomers elute according to ethoxylate number and the retention time of the oligomers decreased with increasing ethoxylate number. All the components were separated with a run time of only 22 minutes through the column. Use of a column with an octadecyl (C-18) phase enabled satisfactory separation of a mixture of ethoxylated alcohols

comprising of around 13 EO oligomers obtained from a single C18 hydrophobe. The bulk EO distribution in the additives analyzed using HPLC revealed polydispersity with an EO distribution of around 1-13 units. The degree of ethoxylation was found to be higher in POE6 Stearyl alcohol compared to POE4-, and POE2-Stearyl alcohol as observed by an increase in the intensity of higher oligomers (such as EO chains with lengths ranging from 8-13 units) eluted before. Examination of retention behavior of Stearyl alcohol revealed traces of Stearyl alcohol in all the ethoxylated additives used in this study with a peak eluting at about 21 minutes.

The size of the peak in the resulting chromatogram is proportional to the concentration of the analyte. The size of the peak determined using several measurements such as height, width and area can be used to evaluate the concentration of the analyte. Each surfactant concentrations were calculated by dividing each component peak area by the total area under the chromatogram determined using the normalization procedure [83]. There are limitations with respect to peak area measurements determined using the normalization procedure as the analysis provides only relative amounts of the components in the analyte (additive) and not the absolute values. Based on the peak areas, the distribution of EO chain lengths in each stearyl alcohol ethoxylated additives is illustrated in Figure 4.2. All the three additives have a distinct EO distribution and both POE4 and POE6 additives have a broad distribution with POE6 containing a large portion of more hydrophilic EO chains compared to POE4 and POE2. This explains why POE6 is comparatively more hydrophilic.

4.1.1.1. Identification of Stearyl Alcohol

In order to identify the presence of residual fatty alcohol (stearyl alcohol) in the stearyl alcohol ethoxylates, 100µl of stearyl alcohol was injected into the column along with POE2 stearyl alcohol. The resulting chromatogram (Figure 4.3) of a mixture of both POE2-Stearylalcohol and Stearyl Alcohol sample confirmed the presence of stearyl alcohol by spiking (or increase in intensity) of the peak with retention time of around 21 minutes.

4.1.2. POE3C12/C13 Alcohol Additive

Separation of Bio-Soft N23-3 (mixture of C12 and C13 linear alcohols) on reversed phase was carried out and the resulting chromatogram is shown in Figure 4.4.

The POE3C12/C13 alcohol additive is believed to contain a mixture of both C12 and C13 alkyl chains and the chromatogram of POE3C12/C13 alcohol additive shows a bimodal distribution containing different lengths of the polyoxyethylene chains resulting from both the C12 and C13 alkyl homologs, unlike Stearyl alcohol ethoxylated additives where a single EO distribution associated with C-18 alkyl chain was observed.

In Figure 4.4, EO chains associated with the C12 alkyl homolog being more hydrophilic elute before EO chains from the C13 alkyl homolog. Therefore, the first peak eluted corresponds to the most hydrophilic EO chain from the C12 alkyl homolog, whereas the last peak corresponds to the least hydrophilic EO chain attached to the C13 alkyl chain. All the components were separated with a run time of only 14 minutes through the column and this accounts for the more hydrophilic nature of POE3C12/C13 alcohol compared to POE (n = 2, 4, 6) Stearyl alcohol, since the same chromatographic conditions were used for both kinds of additives. Due to overlap of the EO peaks resulting from the C12 and the C13 chains, it was not possible to identify the exact distribution of EO chains in both the C12 and C13 alkyl, but it can be predicted that there may be 1-10 EO chains and 1-5 EO chains resulting from C12 and C13 hydrophobes, respectively.

4.1.3. PEG400 C12 Diester additive

These are esters of fatty acids and polyethylene glycol, although they are generally made by direct addition of EO to the acid. They contain, besides the main diester ingredient, monoester, free acid, and free PEG. [79]

The product of ethoxylation of fatty acids of polyethylene glycol usually contains diesters (DE) of PEG as well as relative amounts of monoesters (ME) and PEG, along with diester (DE). Gradient elution chromatography using an evaporative light scattering detector applied to PEG acid ethoxylate gives peaks, in order of elution, of PEG (after 2.7 minutes, Figure 4.5), monoester, and diester (Figure 4.6) The linear gradient program conditions listed in Table 3.2 used for separation of PEG acid ethoxylate also gave EO (ethylene oxide) distribution for the mono- and the di-esters of PEG. Therefore the analyses (Figure 4.7) revealed broad EO distribution of less resolved 1-8 units for the monoester and good baseline separation of 1-11 chains of EO for the diester components. Figure 4.7 demonstrates the same EO distribution for the PEG mono- and di-ester expressed in terms of the weight fraction of each EO chain component and evidently the additive has a higher fraction of the ethoxylated diester.

4.1.4. Nonyl Phenol Ethoxylates

Ethoxylated alkylphenols are produced by alkaline-catalyzed ethoxylation of the nonyl phenols. Usually, a Poisson distribution of ethoxylated homologs is produced, with some unethoxylated nonylphenol remaining, and perhaps with some polyethylene glycol. Nonyl phenol ethoxylates belong to a group of nonionic surfactants that are collectively referred to as alkyl phenol ethoxylates. They find widespread institutional and industrial use as detergents, solubilizers, emulsifiers and wetting agents. [79]

Separation of nonylphenol ethoxylates was also achieved using reverse phase high-performance liquid chromatography on C-18 with specialty silica-based packing columns. Similar to ethoxylated alcohols and esters, a series of experiments was carried out to examine the degree of separation of polyoxyethylene chains attached to the alkyl chain. The use of AcclaimTM C-18 surfactant column with linear gradient programs summarized in Tables 4.1, 4.2, and 4.3 failed to yield any separation of the ethylene oxide chains in the nonyl phenol ethoxylated additives. The use of isocratic HPLC method with 50/50 of water/acetonitrile

mobile phase system for 30 mins AcclaimTM C-18 surfactant column seem to produce good separation of the Nonyl phenol ethoxylated (NP-4) additive in the earlier stages but was not good for the entire 30 mins. Through many failed attempts, use of 75/25 water/acetonitrile linear gradient with acetonitrile concentration going from 25-75% in 15mins (Table 3.4) yield better separation of EO components on a XbridgeTM Shield RP-18 column.

Specific lengths of the fatty and polyoxyethylene chains are critical to the performance in a specific application, thus the ability to accurately characterize these additives (NI surfactants) is crucial. The nonyl phenol ethoxylated oligomers elute according to ethoxylate number and the retention time of the oligomers decreases with increasing ethoxylate number. The chromatogram plot with all three nonyl phenol ethoxylate oligomers illustrated in Figure 4.8 shows the bulk EO distribution. The molecular composition of these additives employed for surface modification of PP given in Table 3.1 shows the nominal values of DOE (degree of ethoxylation) as 2, 4 and 6 respectively for NP2, NP4, and NP6. The bulk EO distribution in the additives analyzed using HPLC revealed polydispersity with a EO distribution of around 1-3, 1-11, 1-11 units for NP2, NP4, and NP6 respectively. Since retention time is affected by degree of ethoxylation, higher ethoxylates are more polar than lower ethoxylates, nonyl phenol ethoxylated additives elutes in order of decreasing ethoxy number under most reversed-phase conditions.

The noticeable shift in the chromatogram peaks between the NPE additives and earlier elution of relatively hydrophilic components for NP6 confirms the more hydrophilic nature of NP6 compared to NP4 and NP2. Additionally the analysis and elution of nonyl phenol at 21.58 minutes confirmed the absence of any nonyl phenol adducts in the ethoxylated additives as illustrated in Figure 4.9. While NP2 has a narrow EO distribution, both NP4 and NP6 have a broad EO distribution containing a large fraction of the more hydrophilic EO chains compared to NP2 as shown in Figure 4.10.

4.1.5. Ethoxylated fatty amine – POE2 Stearyl Amine

Reversed and normal phase high performance liquid chromatography (HPLC) methods have been developed for analysis of ethoxylated nonionic surfactants, most commonly for ethoxylated fatty alcohols, acids, sulfonates, and alkyl phenols [74].

In Figure 4.11, PEG being the most polar fraction elutes first as a single broad peak, while the more hydrophobic molecules of ethoxylates are retained on the C18 phase for a longer time leading to elution of relatively small amount of C16 (EO peak), and, C18 (with two less resolved peaks of EO) homologs in that order.

Though no attempts have been made to identify the PEG and C16 homolog peak in the current study based on the chromatography analysis reported in a previous paper by Lang et.al [74] we postulate that the peaks eluted at 1.17 and 4.97 minutes are indeed associated with the PEG and EO component associated with C16 homolog in the POE2 Stearyl amine respectively.

4.1.6. Distilled Monoglyceride (DGMS) additive

Glycerol esters of fatty acids are esters of fatty acids and glycerol. Stearic acid is the most common of the long-chain fatty acids used in their preparation. Sometimes free glycerol and stearic acid may still remain the system after the esterification process [79].

Separation of mixtures of fatty acids and monoglycerides is made possible by chromatographic techniques such as thin-layer, column, and gas, but are time consuming, does not permit complete isolation of material and require additional techniques for quantification [84]. In a recent paper by Marcato and Cecchin [78], high performance liquid chromatography utilizing a evaporative light scattering detector was shown to successfully separate commercial monostearates of glycerol in a single run. The distilled monoglyceride

used as a hydrophilic additive for PP in this study was therefore separated using a ternary gradient reverse phase HPLC procedure described in the paper reported by Marcato et al. [78].

Using glycerol, monostearate, and stearic acid as standards, the method allowed for the separation and identification of these components in the additive. All three components of interest were eluted in less than 5 minutes as illustrated in Figure 4.12. The more hydrophilic species glycerol elutes first in about 1.57 minutes, then monostearate at about 4.05 minutes and no trace of stearic acid was observed.

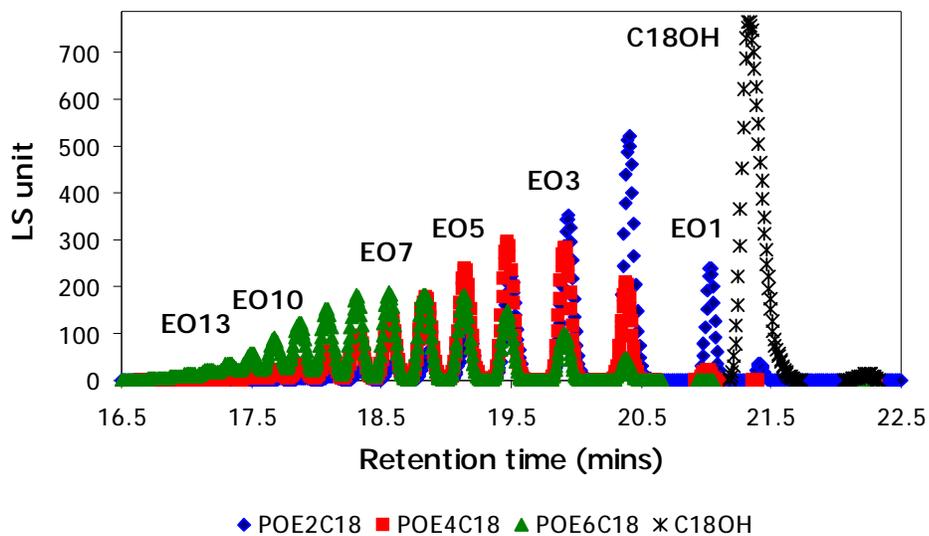


Figure 4.1: Reverse phase HPLC chromatograms of stearyl alcohol ethoxylated additives used in the surface modification of PP.

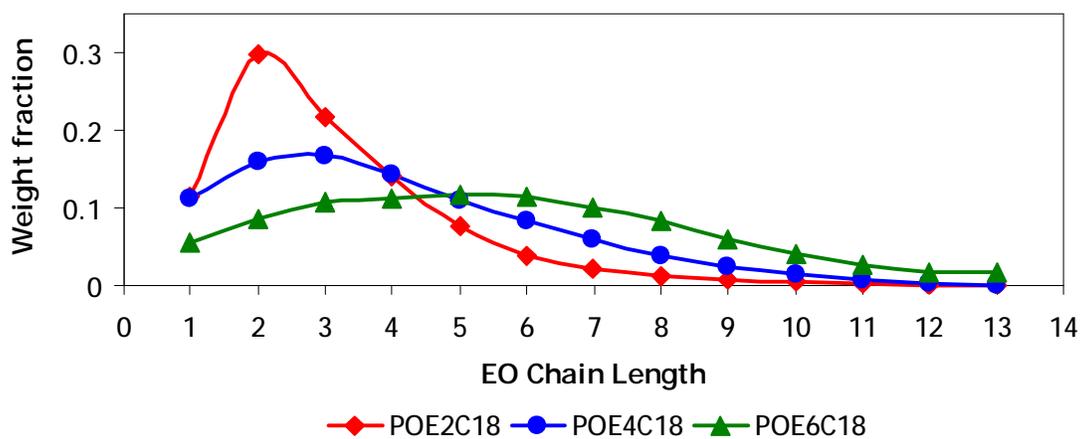


Figure 4.2: Weight fraction of each EO chain component attached to C18 alkyl chain in stearyl alcohol ethoxylated additives.

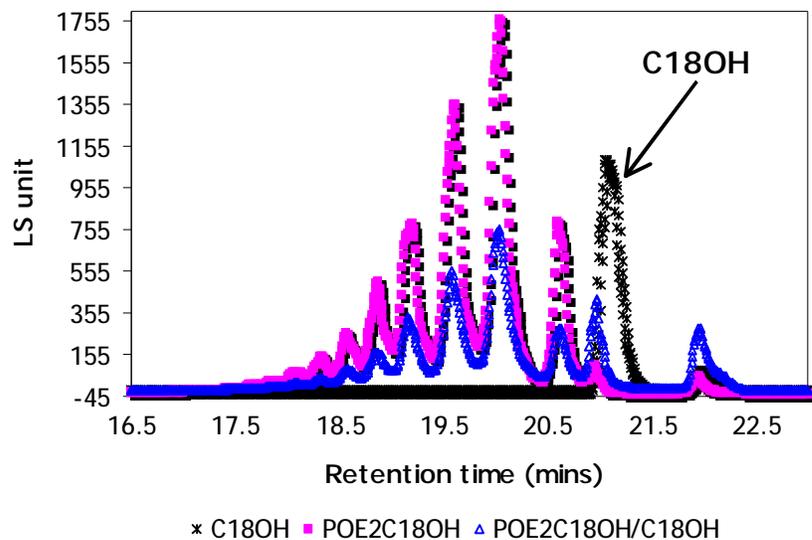


Figure 4.3: Reverse phase HPLC chromatograms of Stearyl alcohol, POE2-stearyl alcohol additive and a mixture of POE2 Stearyl alcohol additive with Stearyl alcohol.

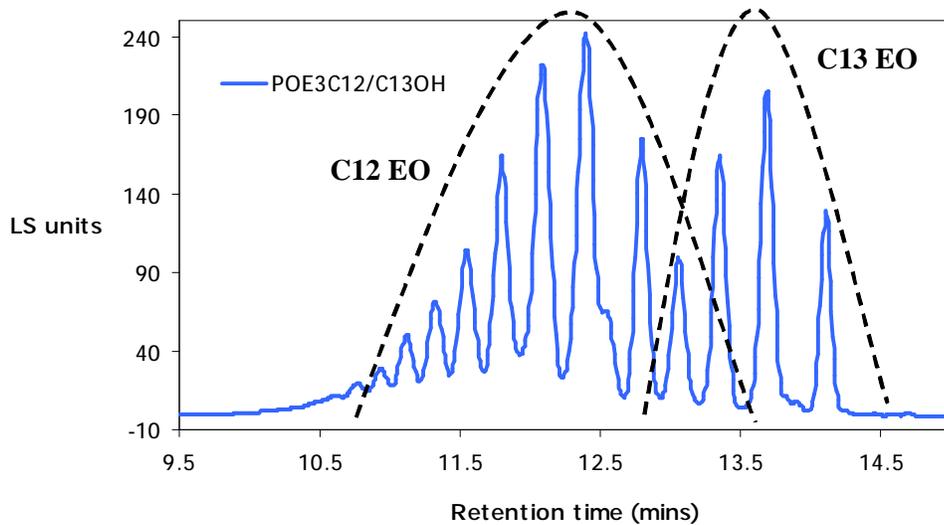


Figure 4.4: Reverse phase HPLC chromatograms of POE3C12/C13 alcohol additive used in the surface modification of PP.

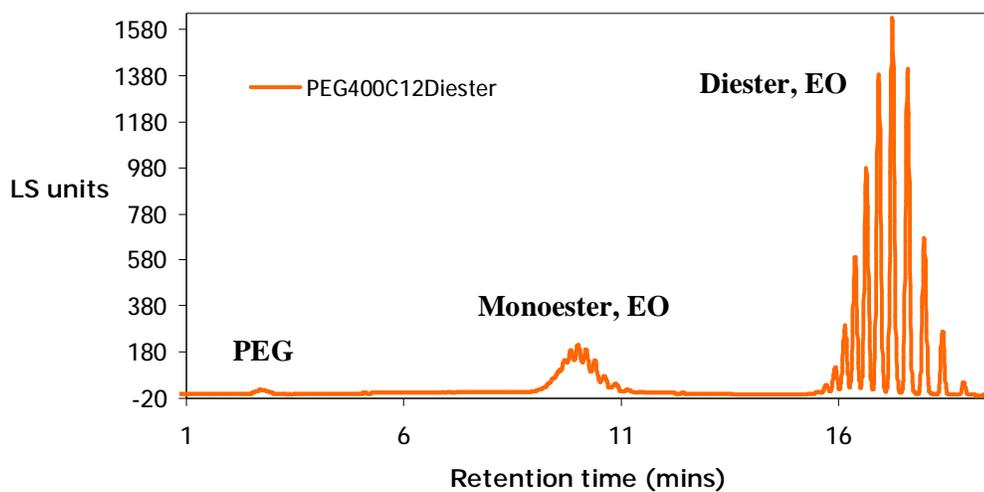


Figure 4.5: Gradient elution of Reverse phase HPLC analysis of PEG400 C12Diester additive used in the hydrophilic surface modification of PP.

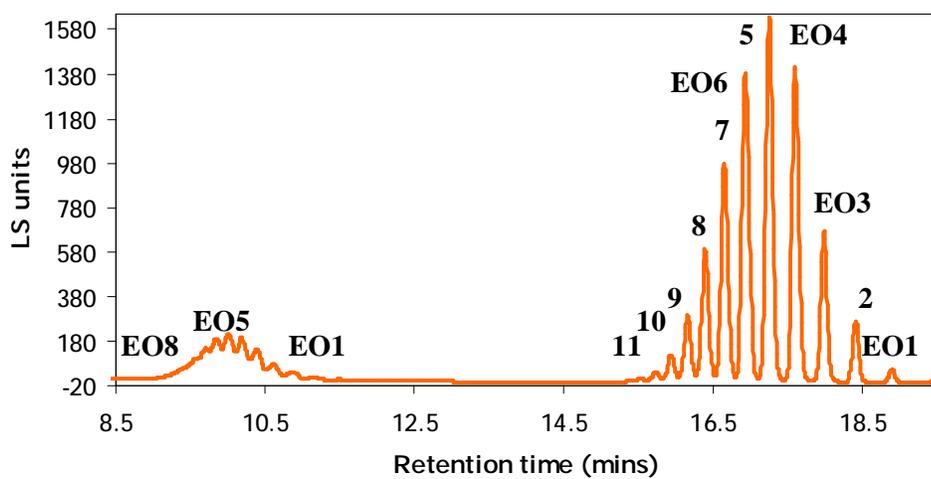


Figure 4.6: Gradient elution of Reverse phase HPLC analysis of PEG400 C12Diester additive showing peak assignments of EO chains for the mono- and di-esters of PEG.

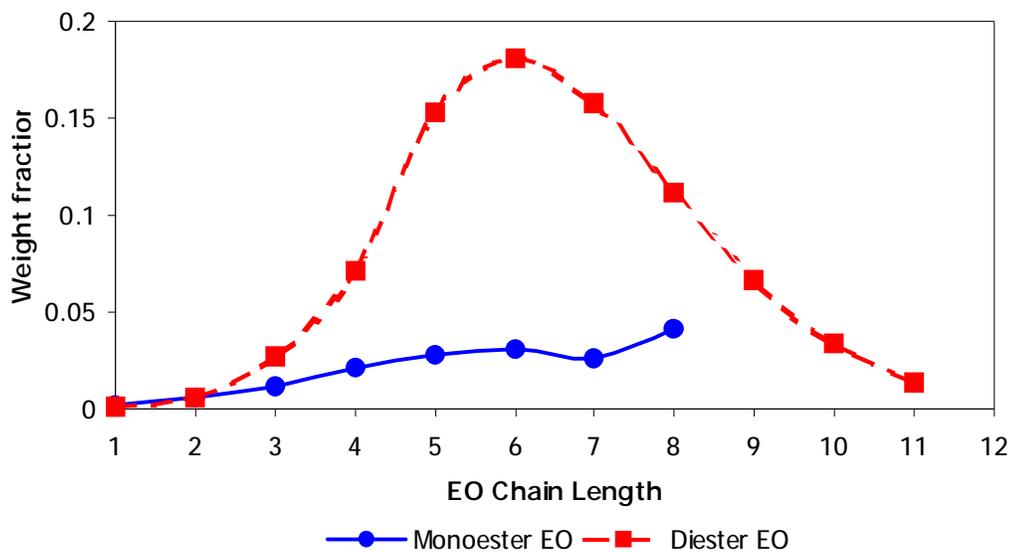


Figure 4.7: Weight fraction of ethoxylated mono- and di-ester in the PEG400 C12Diester hydrophilic additive.

Table 4.1: Gradient program for separation of nonyl phenol ethoxylated additives with mobile phase containing water and acetonitrile.

Time (min)	% Water	% Acetonitrile
0	60	40
10	40	60
13	40	60
15	60	40
20	60	40

Table 4.2: Gradient program for separation of nonyl phenol ethoxylated additives with mobile phase containing water, acetonitrile, and methanol.

Time (min)	% Water	% Acetonitrile	% Methanol
0	65	30	5
10	35	60	5
15	35	60	5
20	65	30	5
27	65	30	5

Table 4.3: Gradient program for separation of nonyl phenol ethoxylated additives with mobile phase containing water (with 0.1M ammonium acetate), acetonitrile, and methanol.

Time (min)	% Water (0.1M Ammonium acetate)	% Acetonitrile	% Methanol
0	65	30	5
10	35	60	5
15	35	60	5
20	65	30	5
27	65	30	5

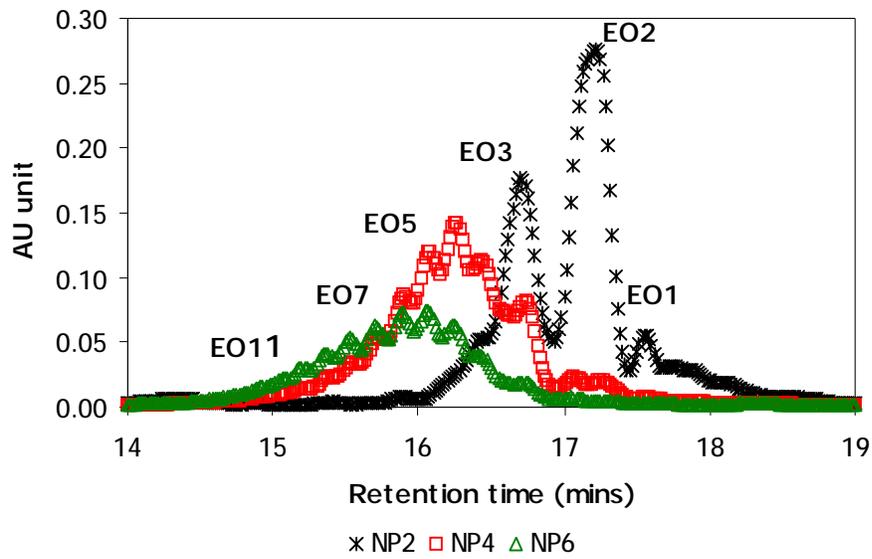


Figure 4.8: Reverse phase HPLC chromatograms of Nonyl phenol additives used in the surface modification of PP.

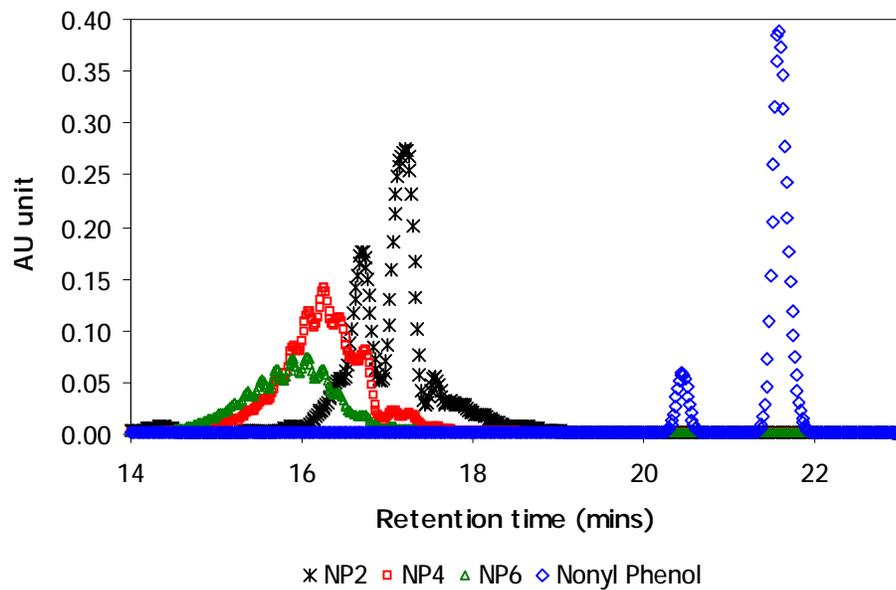


Figure 4.9: Reverse phase HPLC chromatograms of Nonyl phenol additives coupled with nonyl phenol.

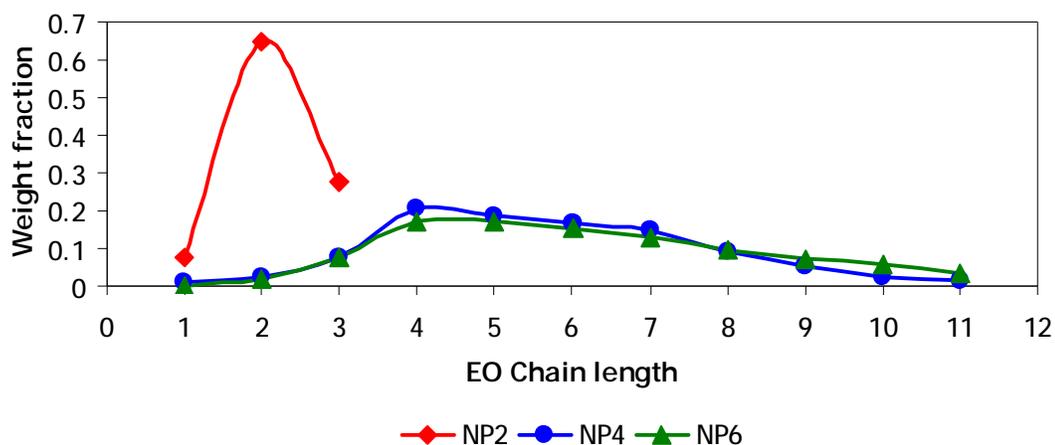


Figure 4.10: Weight fraction of ethoxylated chains attached to C15 alkyl chain in Nonyl phenol ethoxylated additives.

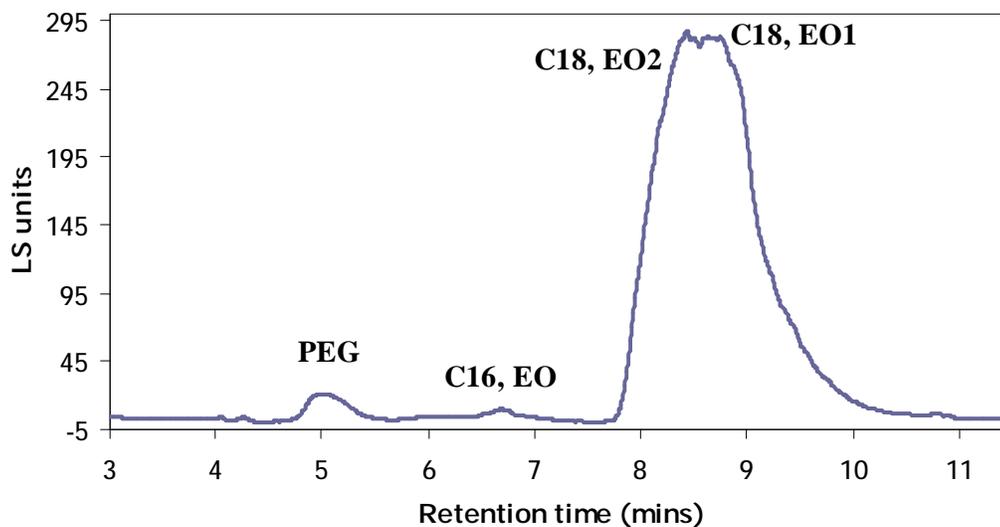


Figure 4.11: Isocratic Reverse phase HPLC analysis of POE2 Stearyl amine additive. The column is a Novapak C18 and detection is by ELS.

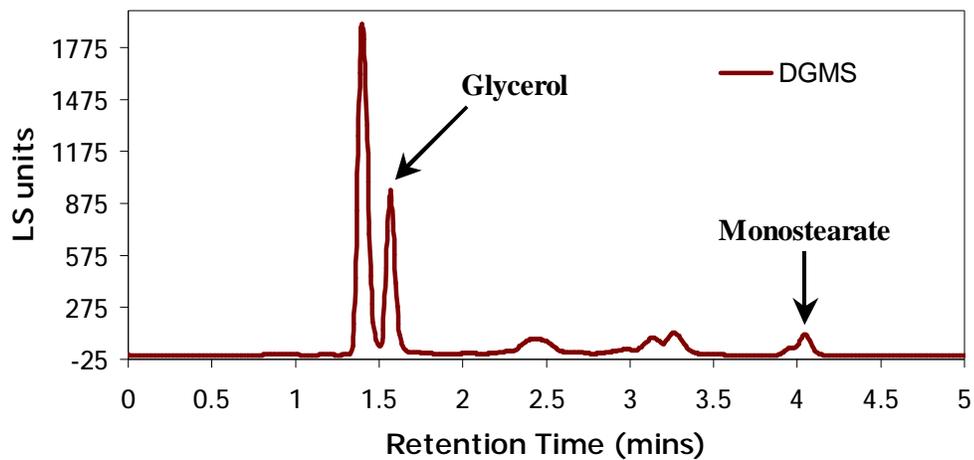


Figure 4.12: HPLC chromatogram for the distilled monoglyceride additive used for hydrophilic surface modification of PP. The column is a Supelcosil™ LC-8 and detection is by ELS.

4.2. THERMOGRAVIMETRIC ANALYSIS OF NONIONIC MELT ADDITIVES

Thermogravimetric analysis is based on the measurement of the weight changes of the material as a function of the temperature. The loss in weight over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability. Hence, thermogravimetric analysis was carried out on samples of pure additives used in the hydrophilic surface modification of polypropylene polymer to assess the thermal stability of these hydrophilic additives during the extrusion process.

Figure 4.13 shows TGA curves from 150°C to 550°C for pure POE2C18, POE4C18, POE6C18, POE3C12/C13, DGMS, POE2Amine, PEG400C12Diester additives, and for PP Control. A derivative was applied to the thermograms to get a detailed pattern of the actual behavior of the material with increase in temperature. The onset and the completion of the decomposition process was analyzed by considering different sections of the thermogram. The TGA curves of the pure additives show similar degradation pathways. Weight loss of pure additives is of extreme significance during processing of film and spunbond web formation of polypropylene (PP) materials especially in the extrusion temperature range and it is summarized in Table 4.4. The onset of degradation in pure additives is seen to begin at a temperature of about 150°C, whereas in PP Control it starts at 240°C. Most of the additives used in the polypropylene (PP) hydrophilic modification show a weight loss of about 1-2 wt % except with POE2C18 and POE3C12/C12 additives where considerable weight loss of 6-wt% and 10-wt% was estimated up until 250°C mostly associated with the loss of water and alcohol constituents in the material at high temperatures. An increase in the mass fraction of the hydrophilic part of the additive (polyoxyethylene chain) and average molecular weight of the additive improves the thermal stability by delaying the onset degradation to a higher temperature as discovered in POE6C18 and PEG400C12Diester additives respectively. This confirms that nearly all additives possess the thermal stability to withstand the spunbond and

the meltblown processing conditions (spunbond and meltblown processing temperatures for PP polymer typically range from 200°C-250°C).

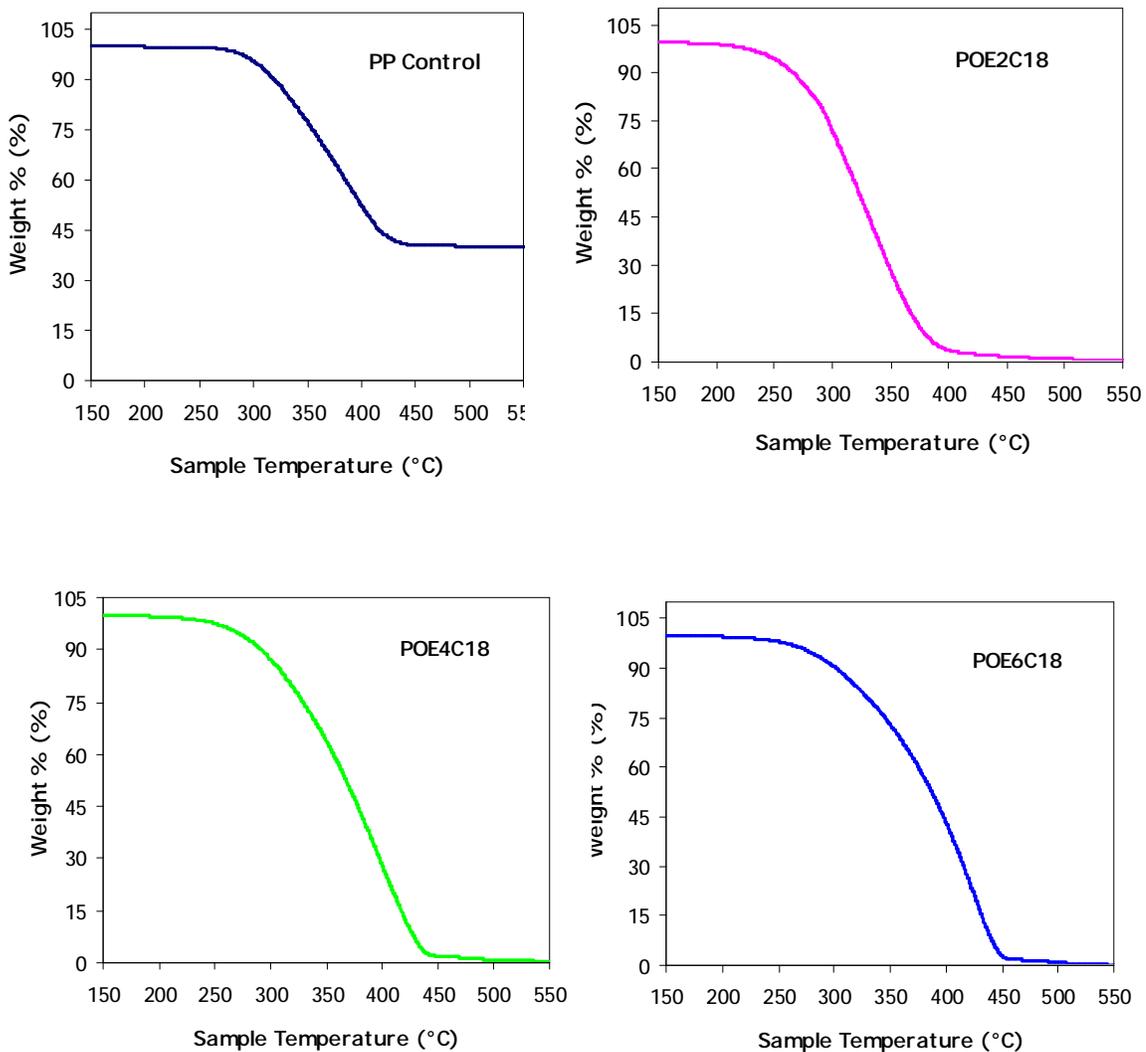
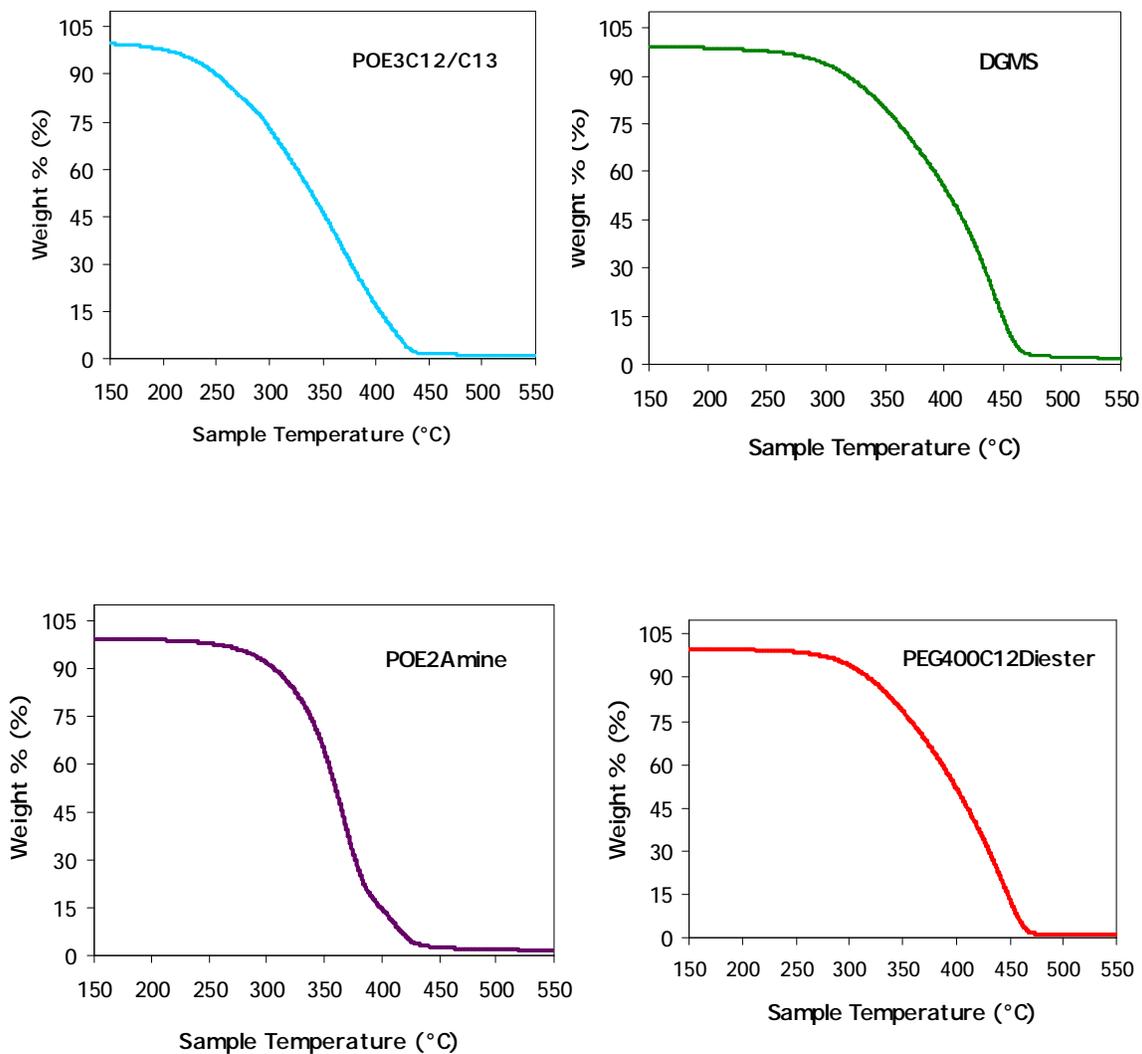


Figure 4.13: TGA curves of PP Control and pure nonionic additives used in the hydrophilic surface modification of PP.



(b) Thermal degradation behavior of POE3C12/C13, DGMS, POE2Amine, and PEG400C12Diester additives.

Figure 4.13 (continued): TGA curves of PP Control and pure nonionic additives used in the hydrophilic surface modification of PP.

Table 4.4: Weight loss data for PP Control and pure additives in the extrusion temperature range of processing polypropylene (at 240°C) for films and spunbond web formation extracted from TGA analysis.

Sample	% Sample weight loss up until 250° C
PP Control	0.41
POE2C18	5.77
POE4C18	2.38
POE6C18	1.94
POE3C12/C13	9.92
DGMS	2.28
POE2Amine	1.90
PEG400C12Diester	1.14

4.3. EFFECT OF MELT ADDITIVE CHEMISTRY ON MIGRATION AND PP SURFACE CHARACTERISTICS

4.3.1. Surface Segregation and Migration Behavior of Melt additives

Surface segregation of melt additive adsorption is governed both by the additive structure and the nature of interactions between the additive and the polymer. The additive may adsorb onto the polymer surface with one of several molecular orientations, the predominant ones being either with the head group pointing into the vapor phase (aqueous medium when a drop of water is placed) on the surface or with the head group intimately associated with a surface group on the solid. The orientation of the adsorbed surfactant (additives) molecule at the interface will determine the physical results of the adsorption process/reactivity at surface. The XPS (X-ray photoelectron spectroscopy) method gathers information from the top few monolayers (up to 5 nm) of the polymer surface.

4.3.1.1. Nonyl Phenol Ethoxylate Melt Additives

The dependence of additive migratory effectiveness on aging time was evaluated by monitoring the surface composition changes up until month 4 after extrusion and the results are illustrated in Figure 4.14.

Surface O/C ratio (%) measured with XPS analysis on Day 2 after extrusion were 9% in NP2, 4.1 % in NP4, and 3.7 % in NP6 additives containing films and it shows that blending of nonlyphenol ethoxylate additives in polypropylene polymer generated oxygen enriched surfaces by additive segregation in all three additives. It is more clearly shown in Table 4.5, where molar melt additive surface concentrations, calculated using the method described in section (3.2.2), are given. It is shown in Table 4.5 that for a bulk molar concentration of 0.65% NP2 additive, the surface NP2 concentrations for PP with 2 wt% of NP2 additive was

11.48% on Day 2 after extrusion, and decreases gradually to 2.18% after Week 3, whereas the surface NP4 and NP6 additive concentrations for PP with 2-wt% of NP4 and NP6 increases gradually with time from 1.46% and 0.81% on Day 2 to 10% and 20% on Month 4 respectively.

However, the length of hydrophilic group in nonlyphenol ethoxylate affects both the rate and the degree of additive surface segregation. NP2 modified polypropylene showed higher oxygen content immediately after extrusion indicating faster mobility of the additive due to its low molecular weight and shorter hydrophilic group length. In contrast, melt additives with longer hydrophilic chains- NP4 and NP6 showed lower surface oxygen content at Day 2, which increased over time.

At 4-month aging time, additive surface concentration represented by surface O/C ratio measured with XPS increased with the length of ethoxylate group. NP6, which has the longest hydrophilic, chain length showed highest concentration of oxygen while NP2 generate very small amount of additive enrichment. This trend can be explained by miscibility of polymer and additives.

At 4-month aging time, additive surface concentration represented by surface O/C ratio measured with XPS increased with the length of ethoxylate group. NP6, which has the longest hydrophilic, chain length showed highest concentration of oxygen while NP2 generate very small amount of additive enrichment. This segregation trend is owed to the differing compositions, prevalence and conformational changes of the molecular chain segments (both hydrophobic and hydrophilic) of the additive at the surface with time.

4.3.1.2. Stearyl Alcohol Ethoxylate & POE3C12/C13 Melt Additives

An increase in surface oxygen content measured with XPS (X-ray photoelectron spectroscopy) was observed in PP films containing POE2C18, POE4C18, POE6C18, and POE3C12/C13 melt additives as shown in Figure 4.15. It is also shown that additives in PP

film have mobility even after the film is fully solidified and the additive surface composition determined as surface O/C ratio continues to increase as a function of time after extrusion. On Day 2 surface enrichment of oxygen was highest with POE2 stearyl alcohol, whereas surface oxygen content increased over time in PP samples with POE6 Stearyl alcohol.

When the film is extruded, owing to small molecular size and high mobility, POE2-Stearyl alcohol due to its shorter hydrophilic chain migrates faster to the surface than additives with longer hydrophilic chains where migration may be hindered by polypropylene molecules. However, additives with long hydrophilic (or ethoxylated) chains due to their more polar nature, and less compatibility with the polypropylene polymer are eventually pushed out from the bulk of the polypropylene polymer. Therefore, POE6-Stearyl alcohol shows a gradual increase in the surface additive concentration due to steady and slower migration of additives to the surface.

Both POE4-Stearyl alcohol and POE3C12/C13 alcohol additives show an interesting reversal of the migration trend during aging. Initially, the surface concentration increases, reaches its maximum, and then decreases. The migration behavior of this additive is not completely understood, but it may result from a competition of various governing factors, such as surface energy minimization [50], polymer-additive phase separation [46], entropical preference of small molecules on the surface [56, 57].

Surface O/C ratio (%) of the top few monolayers (upto 5 nm or 50Å) of the polymer surface on Day 2 after extrusion were 5% in POE2C18, 3% in POE4C18, 4% in POE6C18 and 3% in POE3C12/C13 additive containing films which corresponds to a molar surface concentration of additives to 4%, 1%, 1%, and 1% respectively, which is higher than the bulk composition for PP films containing 2-wt% of these additives (Table 4.6). Therefore, the additives in polypropylene are not uniformly distributed but highly concentrated on the surface and generate additive-enriched surfaces. For a bulk molar concentration of 0.56% POE2C18 additive, the surface POE2C18 concentration was 4.04% on Day 2 after

extrusion, and increases gradually to 12.81% and 11.07% respectively after Week 3 and Month 4, respectively. The amount of additive migrating to the surface depends not only on the structure and composition of the melt additive, but also on the nature of the polymer (PP)-additive interactions.

4.3.1.3. Comparison of Segregation behavior in additives with different Hydrophobe group structure (Linear C-18 chain vs Nonyl phenol)

From an understanding of the segregation behavior of ethoxylated melt additives such as nonyl phenol- and stearyl alcohol-ethoxylates) in PP films discussed above, Figure 4.16 shows the effect of the hydrophilic chain length (EO2 vs EO6) and hydrophobe group structure (phenylene (in nonyl phenol) vs straight C-18 alkyl chain) on the migration behavior and surface enrichment.

The structure of the hydrophobe group has a large effect on the migration and surface enrichment in additives with shorter hydrophilic chains as shown in Figure 4.16 (a). Initially on Day 2, NP2 containing PP surfaces show higher additive concentration than PP surfaces containing POE2C18 additive and the segregation behavior also varied with aging time. Though different in magnitude, the migration effect was quite similar in PP films containing POE6C18 and NP6 additives indicating less hydrophobe group structure effect as the hydrophilic chain length increased. The mobility and the packing or enrichment of these low molecular weight additives at the polymer-air interface is affected by the additive-structure and PP-additive interactions given by the solubility characteristics of the components. For example, the solubility parameter of the PP polymer is $16.8 \text{ (J/cm}^3)^{1/2}$ [85] and for the C-18 hydrocarbon chain and nonyl phenol (NP) chain are $16.9 \text{ (J/cm}^3)^{1/2}$ and $18.8 \text{ (J/cm}^3)^{1/2}$ respectively calculated using Fedors group contribution method [86]. The incompatibility between the PP polymer chains and nonyl phenol hydrophobe group given by high solubility parameter difference drives the NP2 to the surface to a greater degree compared to POE2 additive with a more compatible C-18 chain. Though the NP6 and POE6C18 additive

containing PP materials have similar initial migration tendency, total surface energy changes affects the packing or structure of surface additive molecules in the top few monolayers at which the XPS response is obtained.

4.3.1.4. Other Melt Additives

To study the effect of the nature of the hydrophilic group in imparting a durable hydrophilic PP surface, polypropylene (PP) films modified using nonionic-melt additives that have different hydrophilic groups, such as distilled GMS, POE2-Stearyl amine, and PEG400C12Diester, have been characterized using XPS with time. Most evident difference between these additives is the chemical state of oxygen present in each melt additive (the polar oxygen containing groups are present in the form of ethoxylate ($\text{CH}_2\text{CH}_2\text{O}$), ester (COO), and also contains nitrogen (in POE2 Stearyl amine additive)).

The surface O/C ratio (%) derived from all the XPS spectra determined over a 4-month time period after extrusion date is illustrated in Figure 25 for surface modified polypropylene films with 2-wt% of Distilled GMS, POE2Amine and PEG400C12Diester. Surface enrichment of oxygen was found in samples with all the melt additives, but rate of migration varied over time and also depending on the nature of the hydrophilic group. On day 2, surface oxygen content was highest with distilled-GMS and it is the only melt additive along with PEG400C12 Diester where additional surface migration was observed after Day 20 (Week 3). In PP film with DGMS additive, the surface O/C ratio % rapidly increased and reaches a plateau after Week 3, whereas, surface enrichment of oxygen was seen to increase gradually for PEG 400C12 diester up until 4 months indicating slow migration behavior. Compared to D-GMS and PEG400C12Diester, moderate enrichment of melt additive was observed with POE2 Stearyl Amine and this may be due the steric hindrance associated with the tertiary amine structure leading to decreased surface adsorption.

The surface additive molar concentrations evaluated using the method described in section (3.2.2) for PP films containing 2-wt% of DGMS, PEG400C12Diester and POE2C18Amine are presented in Table 4.7 as the changes in the surface O/C ratio % was monitored using XPS over a 4- month aging period. Surface segregation behavior in PP films containing additives with same HLB values and C-18 hydrophobe chains such as POE2C18 and POE2C18Amine was compared and it was observed that initially on Day 2 higher surface additive enrichment is seen in PP films containing 2-wt% of POE2Amine than POE2C18. It can be explained by the topology or the architecture of the additive molecules, branched POE2Amine additives are driven entropically to the surface compared to linear C18 chain in POE2-Stearyl alcohol and the surface additive concentration is similar in both additive containing PP surfaces and reaches a plateau after Week 3 in enrichment. Also the absence of the nitrogen peak or atom in the top 100 Å^o (N 1s photoelectron at 399.1 eV) in POE2C18Amine additive PP surfaces shown in the XPS spectra in Figure 4.18 indicates that the additive molecules are arranged with hydrophilic EO segments pointing towards the surface through hydrophobic interactions between the C18 chain and the PP polymer chains.

4.3.2. Influence of Molecular Characteristics of Melt Additives on the Migration Behavior

Possible relationship between molecular characteristics such as hydrophilicity, molecular size, and solubility parameter and, migration behavior inside host polymeric matrix was explored.

4.3.2.1. Influence of HLB (Hydrophilic-Lipophilic Balance) of melt additive on surface mobility

Strong influence of the hydrophilicity (HLB) of the melt additive on the migration behavior and its subsequent effect on the hydrophilic properties of modified PP polymer was observed.

Figure 4.19 (a) and (b) illustrate the migration behavior of the ethoxylated additives with different HLB values. Immediate surface enrichment of oxygen was observed in low HLB melt additives after extrusion (Figure 4.19 (a)) while surface oxygen content increased over 4-month time period after extrusion for high HLB melt additives indicating slow and steady migration as clearly observed in the Figure 4.19 (b).

HLB is an empirical parameter and the mechanism by which additive surface enrichment is affected by HLB is yet not understood. A possible explanation is the influence of size of both the hydrophilic and hydrophobic chain lengths on the HLB of the additive, which also affects the overall diffusion and surface segregation in the PP matrix. In fact, Marszall [87] in his article reported the dependence of HLB of non-ionic surfactants on the size of the molecule by evaluating surfactants of different polyoxyethylene chain lengths attached to the same hydrocarbon chain and for surfactants of different hydrocarbon chain lengths attached to the same polyoxyethylene chain. It was deduced that an increase in the molecular weight of the aliphatic hydrophobic chain length (comprising of CH₃ and CH₂ groups) resulted in the decrease of HLB while increasing the molecular weight of the hydrophilic moieties (containing the EO and OH groups) increases the HLB of the surfactant.

Since HLB by itself is dependent on the molecular size (molecular weight) of the surfactant, the effect of molecular size (particularly the size/length of the hydrophilic segment of the additive on the migration and surface segregation was earlier discussed in detail in section 4.3.1 and HLB effect shown here may not be absolutely coming from HLB of the additive, but is combined effect of HLB and size of the additive.

4.3.2.2. Influence of Solubility Parameter Differences on surface mobility of additives

Solubility parameter is defined as square root of the cohesive energy density of the material is commonly used to explain the compatibility or miscibility of components in a polymer

blend. In our study the solubility parameters of the PP polymer and the low molecular weight additives were estimated using the Fedors [86] group contribution method (refer Table 4.8).

Generally speaking the lower the difference of the solubility parameter, the more mixable and compatible are the two components. Figure 4.20 (a) and (b) shows surface melt additive molar concentration vs. solubility parameter difference between additive molecules and host polymer (Polypropylene solubility parameter is 16.8 [85]). Higher solubility parameter difference produces more oxygen (or melt additives) enriched surface, which was evident from additive surface concentrations determined on Day 2 (Figure 4.20 (a) and Month 4 (Figure 4.20 (b) after extrusion. It means that surface segregation of melt additives is dominated by both additive size (hydrophile/hydrophobe) and component incompatibility represented by solubility parameter differences.

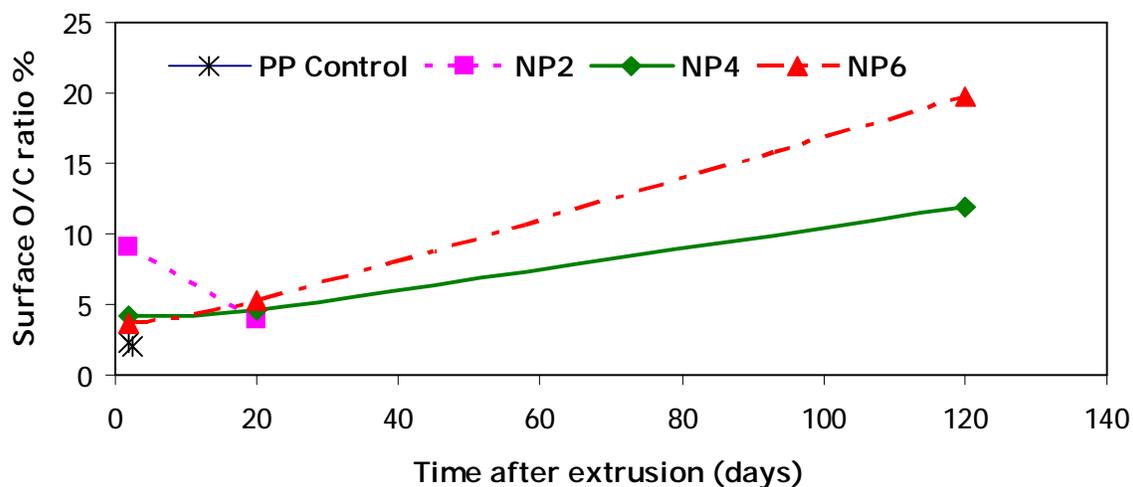


Figure 4.14: Surface O/C ratio (%) for the surface modified film using nonyl phenol ethoxylates measured at Day 2 and Week 3, Month 4 from the extrusion date.

Table 4.5: Surface concentration of nonyl phenol ethoxylated melt additives in the PP blends containing 2-wt% of the additives calculated by means of elemental O/C ratio derived from XPS analysis.

Film samples	Bulk molar concentration (%) of Melt additive	Molar Melt additive Surface Concentration in the Blend (%)		
		Day 2	Week 3	Month 4
PP + NP2	0.65	11.50	2.18	-
PP + NP4	0.51	1.47	1.85	10.01
PP + NP6	0.41	0.81	1.60	19.60

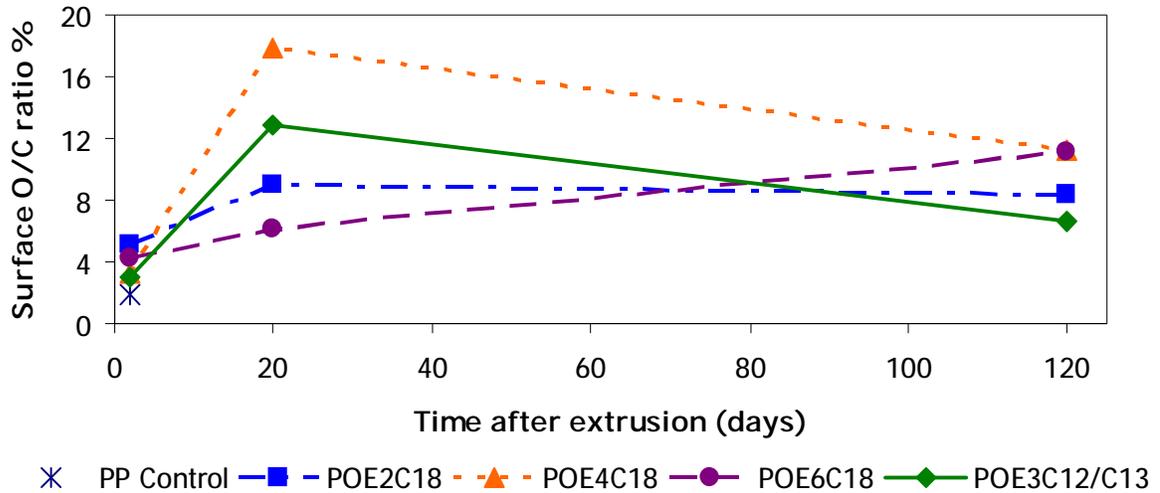
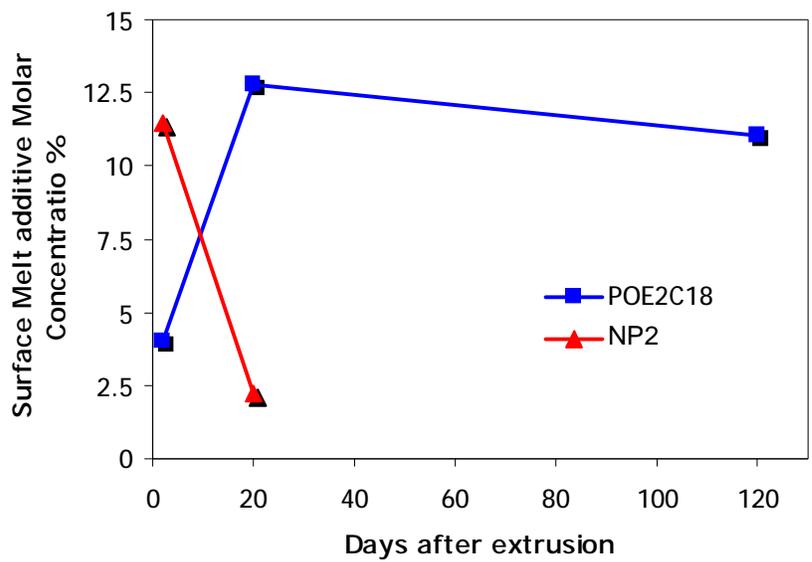


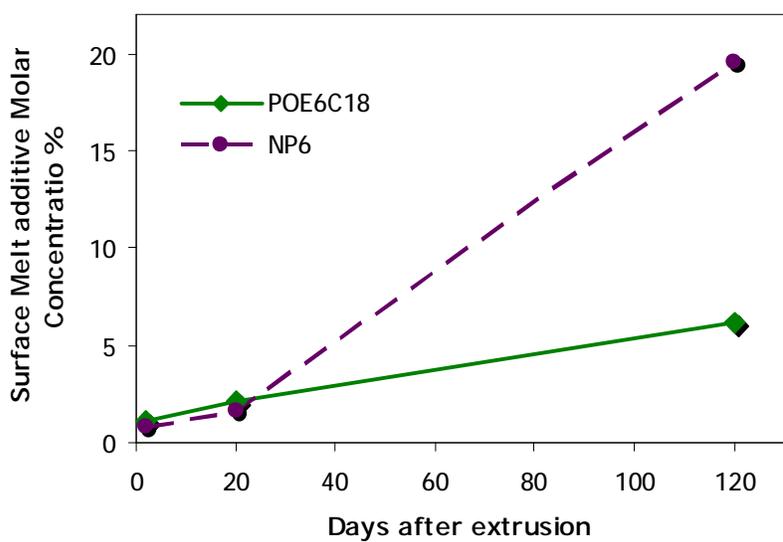
Figure 4.15: Surface O/C ratio (%) for the surface modified film using POE (n) stearyl alcohol melt additives measured at Day 2 and Week 3, Month 4 from the extrusion date.

Table 4.6: Surface concentration of ethoxylated alcohol melt additives in the PP blends containing 2-wt% of the additives calculated by means of elemental O/C ratio derived from XPS analysis.

Film samples	Bulk molar concentration (%) of Melt additive	Molar Melt additive surface concentration in the Blend (%)		
		Day 2	Week 3	Month 4
PP + POE2C18	0.56	4.04	12.81	11.07
PP + POE4C18	0.45	0.90	36.33	9.75
PP + POE6C18	0.37	1.09	2.15	6.18
PP + POE3C12/C13	0.62	0.86	14.04	4.28



(a) Surface enrichment in PP film containing 2-wt% of POE2C18 and NP2



(b) Surface enrichment in PP film containing 2-wt% of POE6C18 and NP6

Figure 4.16: Effect of hydrophilic chain length and nature of hydrophobe group on Melt additive surface enrichment.

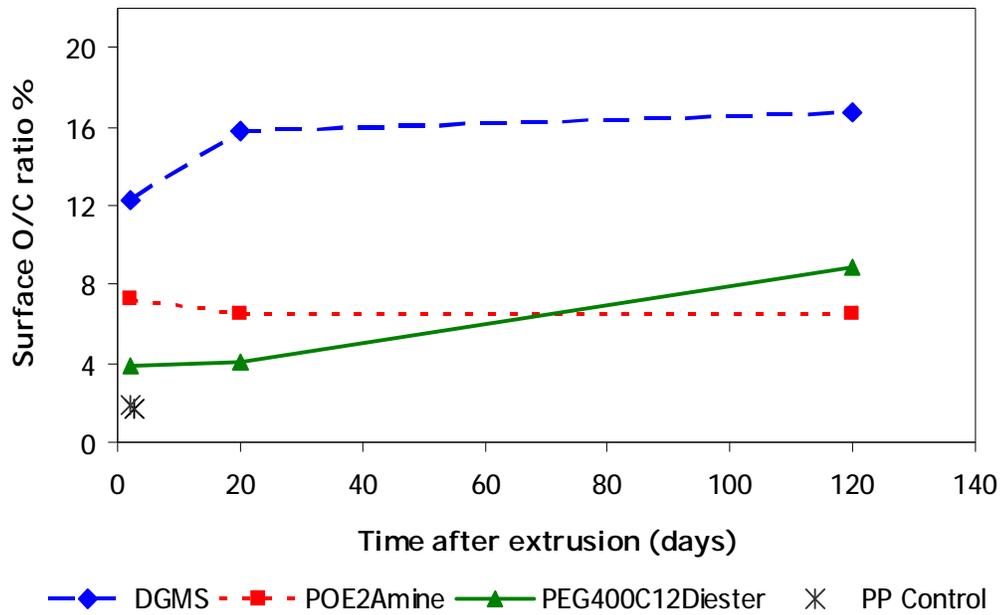


Figure 4.17: Surface O/C ratio (%) for the surface modified film using 2-wt% of Distilled GMS, POE2Amine and PEG400C12Diester.

Table 4.7: Surface concentration of other (non-ethoxylated) melt additives in the PP blends containing 2-wt% of the additives calculated by means of elemental O/C ratio derived from XPS analysis.

Film samples	Bulk molar concentration (%) of Melt additive	Molar Melt additive Surface Concentration in the Blend (%)		
		Day 2	Week 3	Month 4
PP + GMS	0.56	14.66	27.84	33.23
PP + POE2Amine	0.56	16.63	12.26	12.26
PP + PEG400C12Diester	0.26	0.53	0.59	2.25

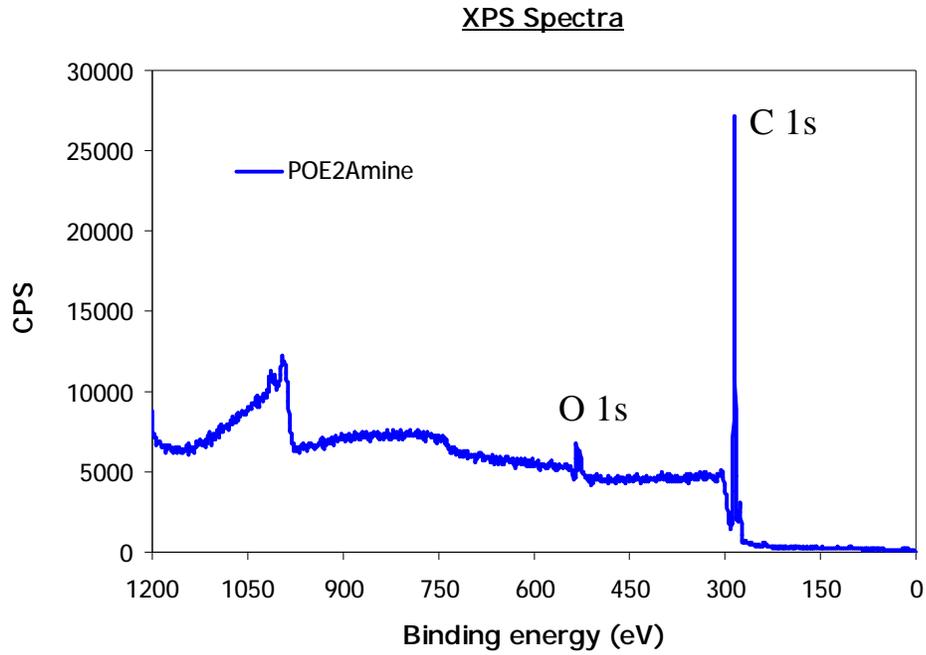
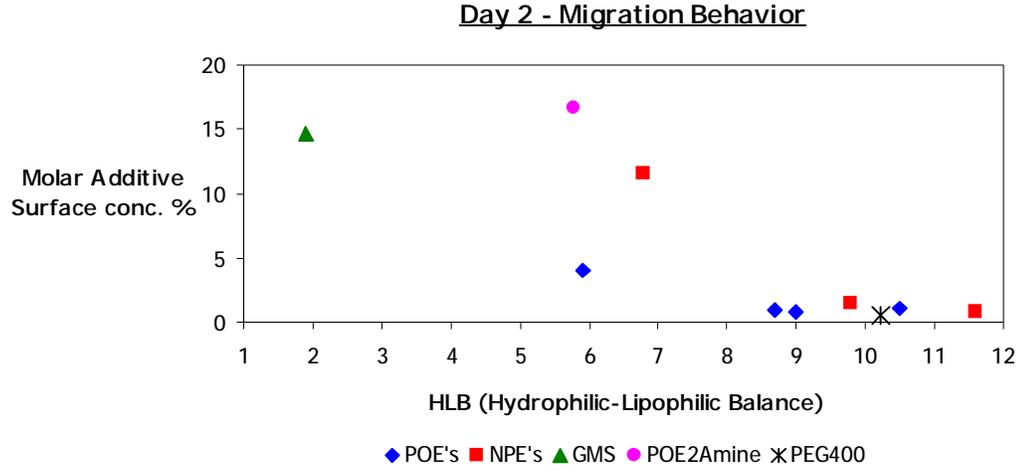
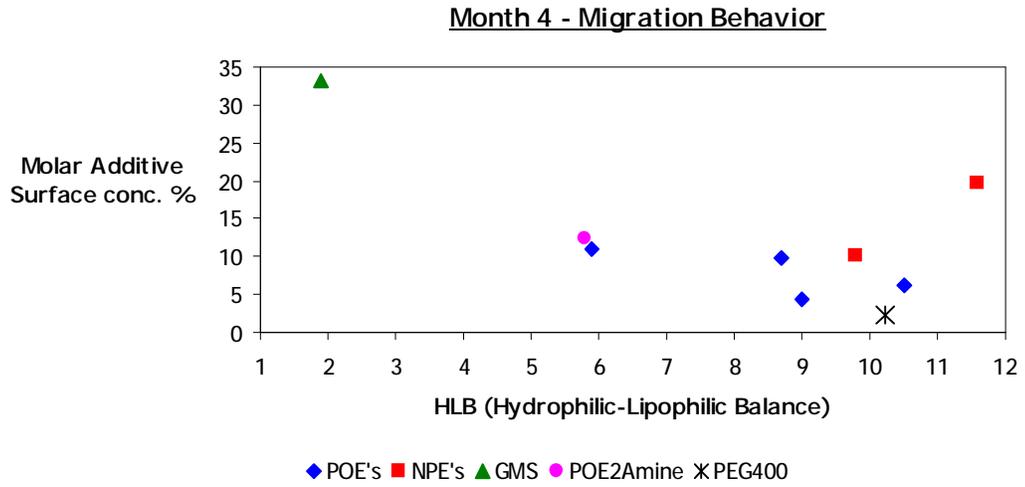


Figure 4.18: Example of XPS spectrum for PP film containing 2-wt% of POE2-Stearyl amine measured at Month 4 after extrusion.



(a) Effect of HLB of melt additives on migration behavior at Day 2

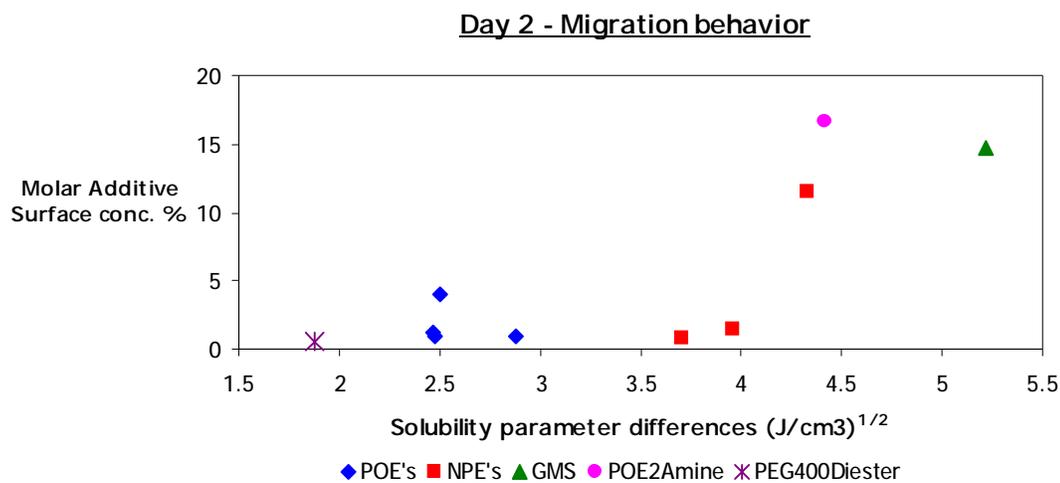


(b) Effect of HLB of melt additives on migration behavior at Month 4

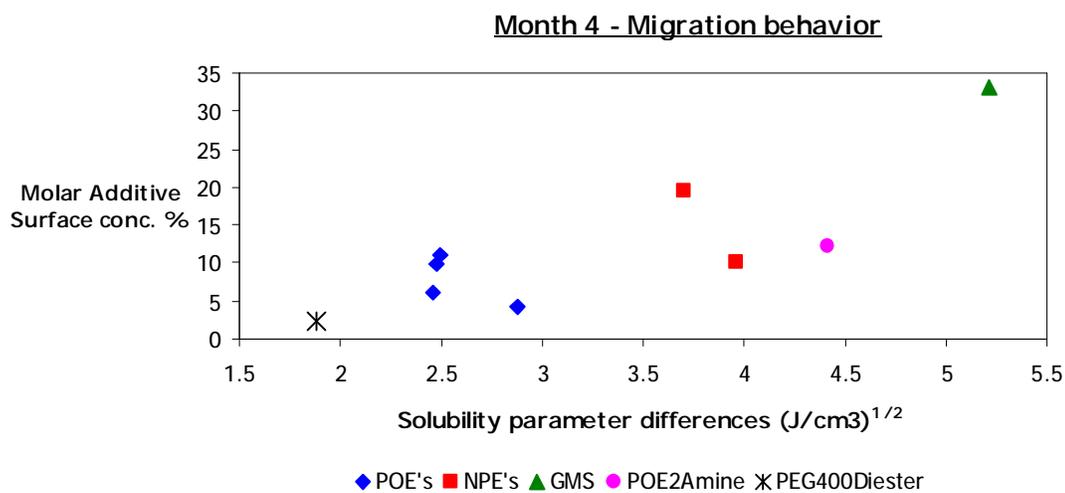
Figure 4.19: Surface melt additive molar concentration (%) for PP modified using melt additives with different HLB values

Table 4.8: Solubility parameters for PP Control and pure additives estimated using Fedors group contribution method.

Sample	Solubility Parameter (J/cm³)^{1/2}
PP Control	16.8 [85]
NP2	21.13
NP4	20.76
NP6	20.51
POE2C18	19.30
POE4C18	19.28
POE6C18	19.26
POE3C12/C13	19.73
DGMS	22.02
POE2C18-Amine	21.22
PEG400C12Diester	18.68



(a) Effect of Solubility parameter on migration behavior at Day 2



(b) Effect of Solubility parameter on migration behavior at month 4.

Figure 4.20: Surface melt additive molar concentration (%) for PP modified using melt additives as a function of solubility characteristics of components in the blend.

4.4. SURFACE WETTABILITY

4.4.1. Dynamic Water Contact Angle Measurements and Wettability Changes with Aging Time

The process of additive migration and adsorption onto the polymer surface is often of technological importance for macrosurfaces, especially in the control of wetting or nonwetting properties of materials, adhesion, and, the control of fluid flow through porous media. One thermodynamic measure of a liquid's ability to flow on another material (solid polymer surface in this case) is its surface wettability. The process of melt blending the additive with the polypropylene modifies the surface by increasing the surface energy of the solid substrate due to migration of surface-active additive molecules from the bulk to the polymer surface. The effect of additive migration on the surface wettability is analyzed using contact angle measurements [64, 65].

4.4.1.1. Nonyl Phenol Ethoxylated Melt Additives

Figure 4.21 represents the water contact angle measurements for the surface modified PP films with the nonionic melt additives NP2, NP4 and NP6 observed after day 3, Week 3, and month 4 after extrusion. The contact angle of PP Control is around 90° indicating its hydrophobic nature. In NP4 and NP6 samples, the reduction of contact angle representing higher surface hydrophilicity was observed and it could be explained by additive surface enrichment showed in Figure 4.21. Immediate reduction of water contact angle was achieved and water contact angle continue to decrease over time as the surface oxygen content increases. Also the high surface hydrophilicity in PP blends with NP4 and NP6 might be due to molecular reorientation of the additive at the polymer/water interface or may be due to additional additive migration to the surface that occurs in the presence of polymer/water interface. The existence of water-surface interactions is clearly demonstrated by a very

prominent dynamic behavior as witnessed in NP4 and NP6 blends of PP when observed with the dynamic contact angle behavior illustrated in Figure 4.22.

In section 4.3.1.1 we reported high initial surface enrichment of NP2 additives, with 11.5% molar surface concentration at day 2, as reported in Table 4.5. However, initial higher additive surface enrichment of NP2 additive did not contribute surface hydrophilicity. PP film modified with NP2 was hydrophobic showing a high water contact angle within the 4-month period regardless of surface O/C ratio. One possible reason for the discrepancy between surface oxygen content and hydrophilicity is the difference in the analytical depth. It is commonly believed contact angle is determined predominately by top monolayer of molecules while oxygen content measured by XPS probes down to 5nm material depth. Therefore, existence of polar oxygen molecules in top 5 nm does not always lead to higher oxygen content on top surface, which is more relevant to contact angle and surface polarity.

4.4.1.2. Stearyl Alcohol Ethoxylated Melt Additives

The dynamic water contact angle for PP control and PP modified using ethoxylated melt additives such as POE3C12/C14, POE2C18, POE4C18 and POE6C18, for a contact time of 1 min is illustrated in Figure 4.23. Due to dynamic nature of the interactions between the PP/additive surface and testing liquid, a liquid droplet spontaneously spreads on top of a flat substrate by interaction between the drop and the surface, where the contact angle, θ , relaxes in a time dependent manner from a possible maximum angle to its equilibrium angle; $\theta > 0$ in the case of partial wetting or zero if the liquid wets the solid completely. An interfacial force may drive the front spontaneously towards equilibrium. Indeed, when a drop of water was placed on the PP/POE2C18 surface, its contact angle immediately started to decrease by complete wetting of the sample within the first 5 seconds of contact with water.

Figure 4.24 represents advancing water contact angle measurements for PP Control and surface modified polypropylene films with POE3C12/C14, POE2-, POE4- and POE6-Stearyl

alcohol measured after Day 3, Week 3, and Month 4 from extrusion determined using the dynamic water contact angles observed over a one minute time period. The figures clearly demonstrate a reduction in the water contact angles observed over a 4-month aging period. Particularly, PP sample with POE2C18 melt additive provides a better performance in the creation of a hydrophilic surface, and it is in good agreement with the molar melt additive surface concentration which is found to be consistently higher in PP surfaces containing POE2C18 additives determined over a 4-month aging time reported in Table 4.6. Additionally, complete wettability with POE2C18 surfaces might be due to the favorable conformations of the POE2-chain at the surface leading to a decrease in the water contact angle by interactions between the hydrophilic segment (POE chain) of the additive and water thereby demonstrating higher contact angle relaxation within 5 seconds of water contact as illustrated in Figure 4.23.

POE2-Stearyl Alcohol effectively works in improving the surface hydrophilicity by completely wetting the surface (reaching '0' degree contact angle) within 5 seconds of contact with water, in spite of its lower hydrophilic nature, and, in contrast to the NP2 additive with a C15 hydrocarbon chain length comprised of a phenylene which restricts the mobility and alignment of the hydrophilic segment to interact favorably with water, subsequently leading to lower hydrophilicity (higher contact angle). The unique behavior of POE2C18 additive can be related to its smaller length of the hydrophilic group and low molecular weight making it much easier to migrate to the surface thermodynamically favoring higher surface enrichment of additive leading to decrease in the water surface tension, and imparting durable hydrophilicity. Improved surface wettability in sample with POE6-Stearyl alcohol compared to POE4-Stearyl alcohol may be due to the more hydrophilic (higher HLB) nature of POE6-Stearyl alcohol.

Segregation/migration behavior discussed in earlier section 4.3.1 confirmed that when the hydrophile chain length such as EO2 as in POE2C18 and NP2 additives is short the structure of the hydrophobe itself affected the migration and possibly the molecular arrangement at the

surface and its corresponding surface composition. Also we have seen that due to the miscibility or compatibility given by high solubility parameter differences between the aromatic nonyl phenol hydrocarbon and the PP polymer chains compared to linear C-18 chain in POE2C18 additives, the bulky nonyl phenol is pushed out of the bulk to the PP surface possibly with the phenylene group either lying flat on the surface interacting with PP or sticking outside perpendicular to the surface into the air, while hydrophilic EO chain segments lie beneath the surface. In fact the presence of aromatic phenylene group and other hydrocarbon molecular fragments and the absence of hydrophilic POE chain segments was confirmed by the qualitative ToF-SIMS analysis (section 4.6.2) of the top PP surface containing 2-wt% of NP2 additive. It is in fact due to this molecular arrangement and bulky nature of the nonyl phenol hydrocarbon chain that the surface exhibits a higher contact angle compared to PP with POE2C18 surfaces which were saturated with the hydrophilic POE chains, with the C18 hydrocarbon chain favorably interacting with PP polymer chains due to their good compatibility and lower solubility parameter differences.

As the hydrophile chain length increases for example with EO6 chain in the POE6C18 and NP6 additives, the miscibility increases between the additive and the PP hydrocarbon chains and therefore, the molecular configurations differs from those of the PP surfaces containing shorter hydrophilic chain lengths. Now both the hydrocarbon (both C18 and the nonyl phenol chain) chain along with longer hydrophilic EO6 chain either aligns, themselves parallel to the surface or with just hydrophilic EO6 chain end at the surface while the hydrocarbon chain is anchored inside to the PP matrix. Both configurations will therefore result in surface enrichment of oxygen or melt additive and this is demonstrated from both the XPS analysis of POE6C18 and NP6 additive surfaces examined on Month 4 and the presence of the POE (polyoxyethylene) chains on the top surfaces revealed by the ToF-SIMS analysis discussed in section 4.5.4, this arrangement leads to a hydrophilic surface by significant reduction in the water contact angles.

4.4.1.3. Other Melt Additives

Figure 4.25 and Figure 4.26 represents advancing water contact angle measurements for PP Control and surface modified polypropylene films with Distilled GMS, POE2Amine and PEG400C12Diester measured after Day 3, Week 3, Week 4, and Month 4 from extrusion determined using the dynamic water contact angles observed over a one minute time period.

Distilled-GMS improved the surface wettability moderately and much better than POE2–Stearyl Amine. It can be related to its ability to migrate to the surface more easily than POE2-Stearyl Amine and therefore changing its surface characteristics. Also the higher contact angle observed with PEG400C12 Diester, may be due to its large molecular size and relatively high molecular weight thus making it difficult to diffuse to the surface and, therefore, neither migrates to the surface nor alters the surface hydrophilicity. Even though similar levels of surface oxygen are found in both POE2 Stearyl Alcohol and POE2 Stearyl Amine, relatively little changes in the contact angle is observed over time with POE2-Stearyl amine and does not provide satisfactory results concerned with surface hydrophilicity. It may be due to the inability of the ethoxylated tertiary amine to migrate to the surface to alter the surface properties, and whatever small changes in the contact angle over the control is seen was due to the migration of small amounts of oxygen to the surface. Therefore, we notice that hydrophilic moieties of the melt additive containing the OH group function better than the one containing the COO group in improving the surface hydrophilicity. Other factors such as the nature and length of the hydrophobic group, i.e. the degree of branching, unsaturation, polar substitution, the presence of aromatic groups, etc. will play a major role in the adsorption characteristics of the system.

4.4.2. Surface Dynamics and Water Contact Angle Relaxation

Surface segregation of the melt additives has been confirmed by X-ray photoelectron spectroscopy (XPS) and since these modified PP/additives surfaces are very active, the

orientation of the segregated molecules depends on the nature of the interface. Therefore the surface restructuring and the dynamic nature of interactions when the modified PP/additive film comes into contact with water, was investigated by water contact angle relaxation [88-92].

The water contact angle relaxation for PP films modified using nonionic melt additives for a contact time of 55 seconds is illustrated in Figure 4.27. From the chart it is evident that water contact angle decreases steadily over time indicating increase in surface hydrophilicity. Especially with PEO2-StearylAlcohol, regardless of small changes in the surface composition observed over time, the contact angle significantly dropped and remained consistently lower by complete wetting of the sample within the first 5 seconds of contact with water.

The reduction of contact angle induced by water contact observed in some additives may be explained by segmental motion of polymer chains at the surface of the films causing surface molecular reorientation when the film comes in contact with water [93]. As illustrated in Figure 4.28, contact of water may induce hydrophilic head of the additives to the water phase if it is not already aligned. As a result water contact angle will drop as contact time increases. If additives has high mobility and are poorly anchored in the PP matrix, it may be released to the water, which causes reduction of water surface tension, resulting in further contact angle reduction.

A conformational reorientation of the hydrophilic segment of the melt additive is greatly influenced by the hydration power of the water environment, and the time required for the orientation might depends on the state of hydration. The time dependence of the relative contact angle was then measured in order to estimate the time required for the rearrangement of the surface structure. A liquid drop spontaneously spreads on top of a flat substrate by interaction between the drop and the surface, where the contact angle, θ , relaxes in a time dependent manner from a possible maximum of 180° to its equilibrium angle; $\theta > 0$ in the

case of partial wetting or zero if the liquid wets the solid completely. An interfacial force may drive the front spontaneously towards equilibrium. Indeed, when a drop of water was placed on the PP/POE2C18 surface, its contact angle immediately started to decrease as shown in Figure 4.27.

The contact angle relaxation as a function of time was monitored for the following time period, $t = 0-55$ sec. All of the surfaces exhibited a characteristic contact angle relaxation and as shown in Figure 4.29, these tendencies are more clearly expressed when the relaxation is summarized for the time intervals, $\Delta\theta$ ($\theta_{t=0} - \theta_{t=55}$). The additive realignment and release on water contact, measured with contact angle relaxation is highly dependent on additive structures. It is worth noting that PP/POE2C18 showed the largest decrease in relative contact angle, particularly within 5 seconds of spreading as observed in Figure 4.27. This can be ascribed to the fastest restructuring of the surface achieved among all the melt additives. Accordingly, the contact angle relaxation directly affects the surface properties sensed by the sessile drop contact line of the wetting liquid indicating that the time and rate constants of the restructuring process are comparable between both measurements. The mobility of the hydrated POE chains decreased with the chain length; therefore, the surface having the shortest POE chains will exhibit rapid contact angle relaxation, which is what was observed with PP/POE2C18 surface. The POE chain distribution identified using reverse phase-HPLC analysis confirms that the contact angle relaxation observed in PP films containing ethoxylated melt additives is due to the presence and mobility of the shorter hydrophilic (POE) chains at the surface. It was observed that the time required for the modified PP substrate surface to attain aqueous equilibrium wetting characteristics was less than a few minutes. Also higher contact angle relaxation was revealed in more hydrophilic surfaces such as PP films containing POE2C18, POE3C12/C13, NP4 and NP6 additives. From the results obtained above, one can conclude that the interaction of the PP/Melt additive surfaces with water provides a strong driving force to reduce the interfacial free energy by reorientation of the hydrophilic component of the additive to interact optimally with the water phase.

Surface Hydrophilicity

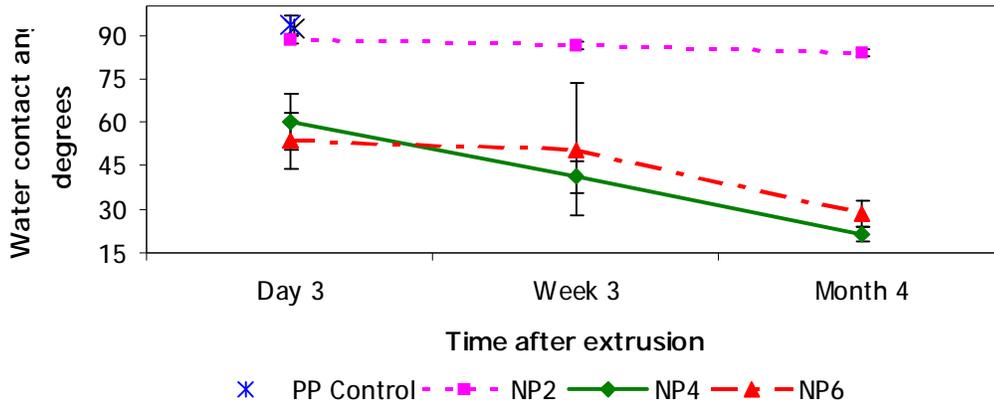


Figure 4.21: Equilibrium water contact angle measurements for the surface modified polypropylene films with NP2, NP4 and NP6 ethoxylate melt additives after day 3, Week 3, and Month 4 from extrusion.

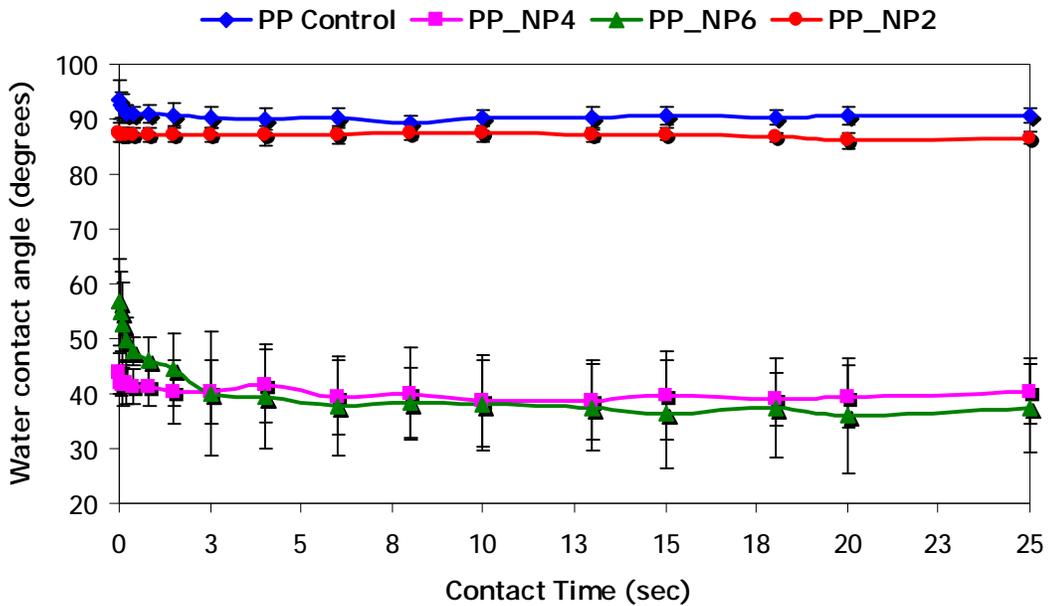


Figure 4.22: Dynamic water contact angle measurements for films of PP control and PP modified with NP2, NP4 and NP6 determined after 5 weeks aging for contact of water droplet for 25 seconds.

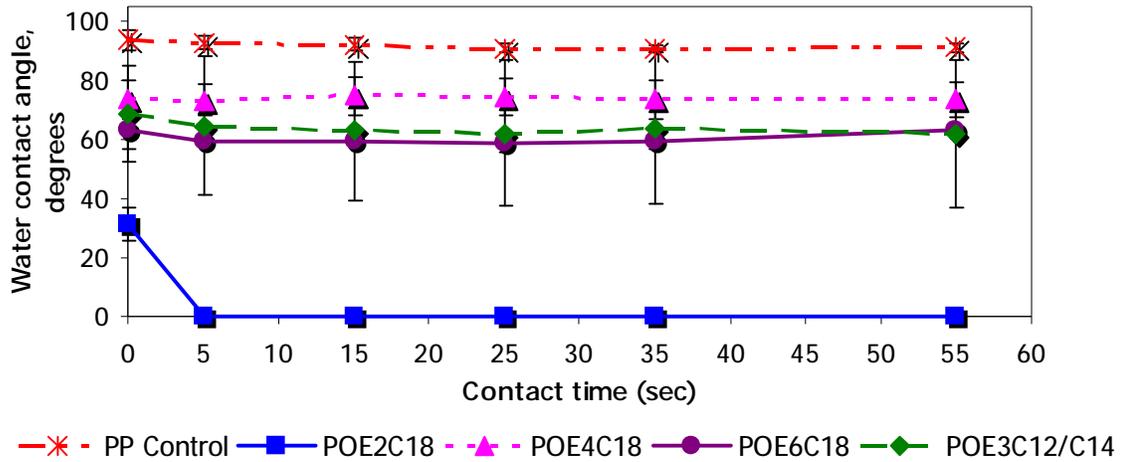


Figure 4.23: Dynamic water contact angle measurements with water contact time of 1 min for surface modified polypropylene films with POE3C12/C13, POE2-, POE4-, and POE6- Stearyl alcohol determined after Week 3 from extrusion.

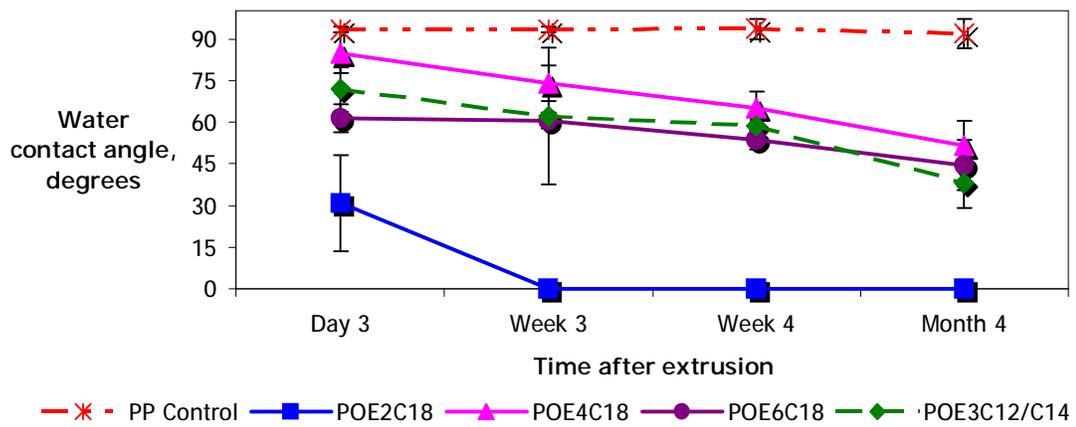


Figure 4.24: Advancing water contact angle for the surface modified polypropylene films with POE3C12/C13, POE2-, POE4-, and POE6- Stearyl alcohol after Day 3, Week 3, Week 4, and Month 4 from extrusion.

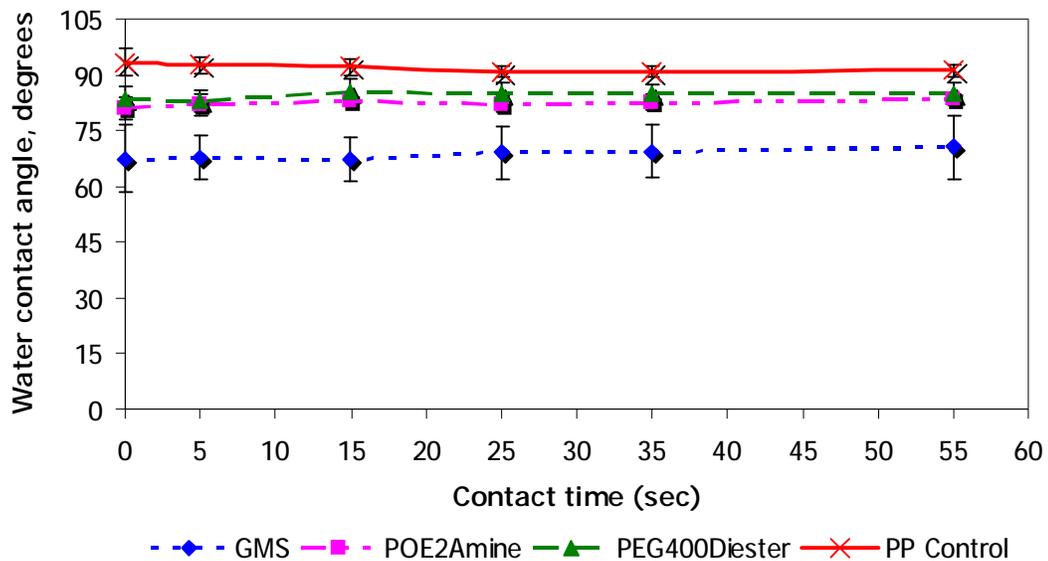


Figure 4.25: Dynamic water contact angle measurements with water contact time of 1 min for surface modified polypropylene films with DGMS, POE2-Stearyl Amine, and PEG400C12Diester determined after Week 3 from extrusion.

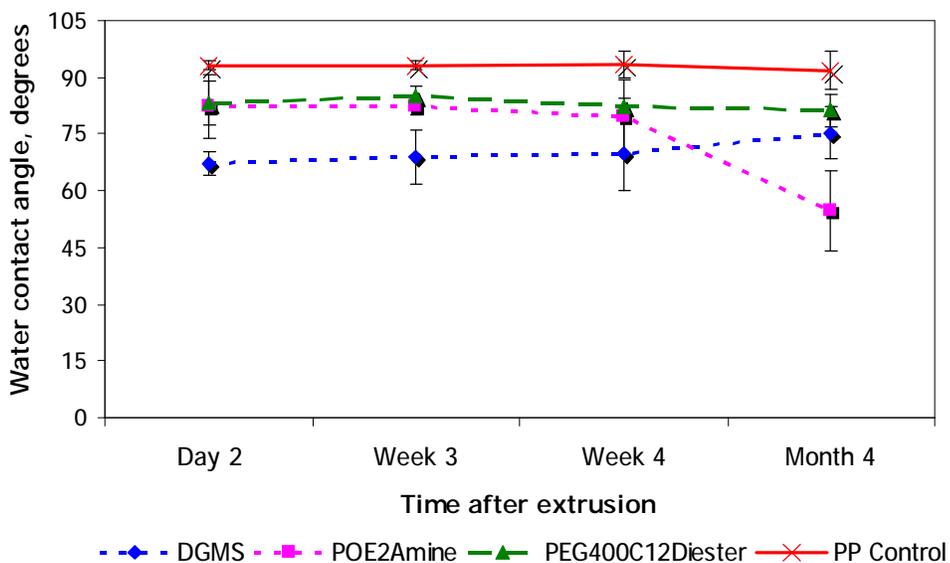


Figure 4.26: Advancing water contact angle measurements for surface modified polypropylene films with DGMS, POE2-Stearyl Amine, and PEG400C12Diester after Day 3, Week 3, Week 4, and Month 4 from extrusion.

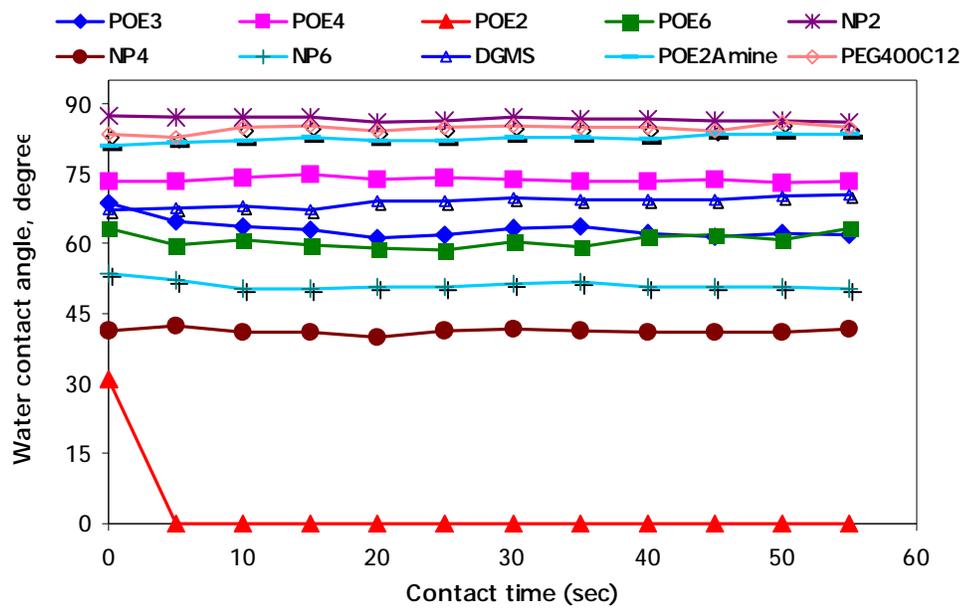


Figure 4.27: Dynamic Water Contact angle measurements examined for PP films modified using nonionic melt additives at Week 3 after extrusion.

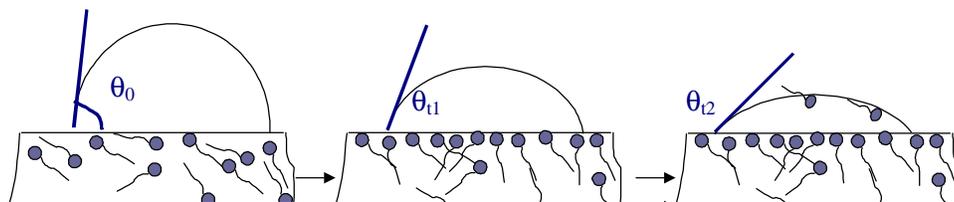


Figure 4.28: Schematics of contact angle reduction on the contact of water by Realignment and release of additives.

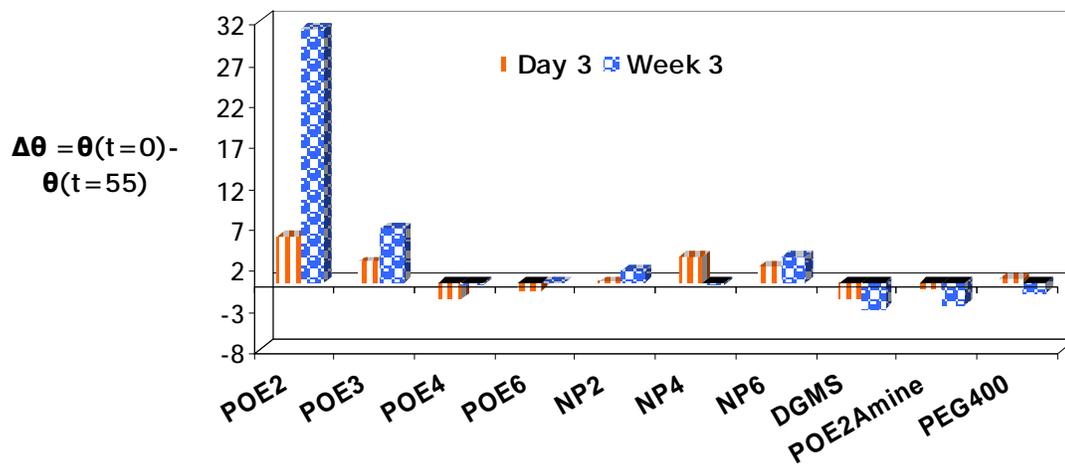


Figure 4.29: Contact angle relaxation for the respective time intervals for PP films modified with nonionic melt additives.

4.5. WATER IMMERSION TEST OF SURFACE MODIFIED PP SUBSTRATES

4.5.1. Water Immersion Durability

4.5.1.1. Nonyl Phenol Ethoxylated Melt Additives

Changes in the surface composition measured before and after 6 hr water immersion for the surface modified PP films with nonyl phenol ethoxylated melt additives is illustrated in Figure 4.30.

Surface properties changed after water immersion of modified PP films and typically two types of behavior were observed. Water immersion caused considerable decrease in the surface oxygen concentration in PP films containing more hydrophilic NP4 and NP6 additives indicating loss of additive molecules from the surface, and interestingly enough slight increase in oxygen concentration was observed for PP films modified using NP2 additives and it might be due to its lower hydrophilic nature associated with the bulkier aromatic nonyl phenol hydrophobe group and shorter hydrophilic chain length, EO2. As discussed in section 4.3.1, due to lower miscibility or compatibility of nonyl phenol hydrocarbon chain with PP, the additive molecules may be packed with nonyl phenol pushed outside the PP matrix either lying flat on the surface or with the phenylene ring facing outwards towards the the air/polymer interface and hydrophilic chain length anchored into the PP polymer. Since thermodynamically, modified PP/additive surfaces prefer polymer/water interface over polymer/air interface and water immersion may cause additional migration induced by water/film interface and possible rearrangement of the molecular chains with hydrophilic POE (polyoxyethylene) chains optimally interacting with the water phase. Depending on the hydrophilic nature of the additives, some loss of surface additive molecules occurs in more hydrophilic additives such as NP4, and NP6, and increase

in surface oxygen enrichment in NP2 additive surfaces due to additional migration or rearrangement of the additive molecules.

The results from the surface wettability measurements illustrated in Figure 4.31 are in good agreement with the surface oxygen content examined using XPS. NP4 and NP6 additive surfaces demonstrated increase in the water contact angle after 6 hr, 12 hr, and 24 hr water immersion indicating loss of surface hydrophilicity by release of top layer additive molecules by water immersion. However, the small increase in oxygen content in NP2 surfaces after 6hr water immersion only decreased the water contact angles to a certain extent and no significant improvement in the PP surface hydrophilicity was observed after 6 hr, 12 hr, and 24 hr water immersion.

4.5.1.2. Stearyl alcohol ethoxylated melt additives

Water immersion of PP films containing stearyl alcohol- and dodecyl alcohol- ethoxylates caused significant decrease in the surface oxygen concentration in POE6C18 surfaces, and increase in surface oxygen concentration in PP films with POE2C18, POE4C18, and POE3C12/C13 additives (Figure 4.32). PP/additive surface responses to prolonged exposure to water were affected by the additive structure, such as the length and nature of the hydrophile and hydrophobe, respectively.

Moreover the results from the surface wettability measurements illustrated in Figure 4.33 were in good agreement with the surface oxygen content examined using XPS after 6hr water immersion for water-immersed samples PP films containing stearyl alcohol ethoxylates. As explained before, POE6C18 additive being more hydrophilic in nature, PP films incorporated with POE6C18 additive demonstrated loss of surface hydrophilicity resulting in increase in the water contact angle after 6hr and 24hr water immersion, and, PP films with POE2C18 and POE4C18 additive became highly hydrophilic by significant reduction in the water contact angle after 6, 12, and 24 hr water immersion. Particularly, POE2C18 additive

surface showed a 0 degree water contact angle even after 24hr water immersion. However, the POE3C12/C13 additive surfaces became less hydrophilic by increase in water contact angle after water immersion, though an insignificant increase in the surface oxygen content was observed after 6 hr water immersion.

With the objective of confirming whether or not the loss of surface oxygen concentration or in other words the loss of surface additive molecules happens during water immersion, the water samples utilized for soaking the PP films containing 2-wt% of POE2C18 and POE6C18 additives were analyzed for changes in the water surface tension (Figure 4.34) using a tensiometer working on the Du Nuoy ring principle. The figure clearly shows evidence for release (or loss) of surface additive molecules into water represented by reduction in the surface tension of water with immersion time which is in good agreement with the decrease of surface oxygen concentration examined using XPS. The surface tension analysis reported also supports the assumption made in section 4.4.2 that additives with poor anchoring capabilities may actually release into the water droplet placed on the PP film further decreasing the water contact angle by reduction in the water surface tension.

4.5.1.3. Other Melt Additives

Surface O/C ratio (%) derived from the XPS spectra measured before and after 6 hr water immersion for the PP modified with Distilled GMS, POE2-Stearyl Amine, and PEG400C12Diester additives is illustrated in Figure 4.35. A considerable increase in the surface oxygen content was observed for PP films modified using POE2-Stearyl Amine and Distilled GMS. This behavior is a result of their lower hydrophilic nature and thermodynamically driven migration and reorientation of the polar segment of melt additive in the presence of water. For 6 hr water immersion, the results from surface wettability measurements illustrated in Figure 4.36 are well supported by the surface composition changes. No significant changes in both surface composition and wettability were observed in PEG400C12 surfaces. While hydrophobic surface recovery was witnessed in DMGS

surfaces after 24 hr immersion, the POE2-Stearyl amine surfaces became more hydrophilic with immersion time.

4.5.1.4. Influence of HLB

The changes in the surface composition and surface wettability after 6 hr water immersion for melt additives with different HLB values are illustrated in Figure 4.37 ((a) and (b)). So the X-axis represents The positive values (on the Y-axis) in the Figure 4.37 (a) indicates increase in surface oxygen content observed in low HLB melt additives and negative values indicate decrease in surface oxygen content or loss of additive observed with high HLB melt additives. Correspondingly in Figure 4.37 (b) we observed increase in surface hydrophilicity (negative values on the Y-axis) with low HLB melt additives and decrease in surface wettability (positive values) in high HLB melt additives after 6hr water immersion which is well supported by their respective surface composition changes.

4.5.2. Surface Recovery – Water Immersion

4.5.2.1. Nonyl Phenol Ethoxylated Melt Additives

Aging of the water immersed samples showed some evidence of additional additive migration to the top surface, which caused contact angle changes as shown in Figure 4.38. Both NP4 and NP6 had positive recovery angles, which indicate that aging of water soaked samples increases surface hydrophilicity. In case of NP2, a slight negative recovery angle is observed indicating aging had little impact on improving hydrophilicity.

4.5.2.2. Stearyl Alcohol Ethoxylated Melt Additives

Water immersion of PP films containing POE2C18 and POE4C18 additives caused improvement in surface hydrophilicity whereas wettability decreased with POE6C18 and POE3C12/C13 surfaces as observed previously in Figure 4.33. Aging of POE6C18 surfaces shows good (positive) recovery by significantly improving the surface wettability in 6hr immersed films through additional migration of additive from bulk to the surface (Figure 4.39), while no significant recovery was observed by negative recovery changes in 12 hr water soaked POE6C18 film surfaces and those of POE3C12/C13 surfaces soaked for 6 & 12 hrs.

As usual POE2C18 surfaces demonstrate excellent durability by exhibiting a zero degree contact angle even after 24 hr water immersion and aging. POE4C18 surfaces became more hydrophilic with aging especially with 12 hr immersion while aging had little effect on water contact angle changes in 6 hr water immersed PP films.

4.5.2.3. Other Melt Additives

Water immersion caused increase in surface hydrophilicity for PP films incorporated with DGMS and POE2Amine and loss of wettability in PEG400C12 additive surfaces as shown in Figure 4.36. Figure 4.40 shows the aging effect on the recovery of water contact angles of modified PP surfaces. Continued increase in surface hydrophilicity with aging was observed in POE2Amine surfaces given by positive recovery angle and also positive recovery of water contact angle in 6 hr immersed PEG400C12 surfaces indicates significant recovery of lost wettability by regeneration of surfaces by continued segregation of additive molecules from bulk to surface.

Though water immersion improved surface wettability in GMS additive surfaces, negative recovery angles suggests hydrophobic surface recovery with aging due to reorientation of the hydrophobic segments at the polymer/air interface.

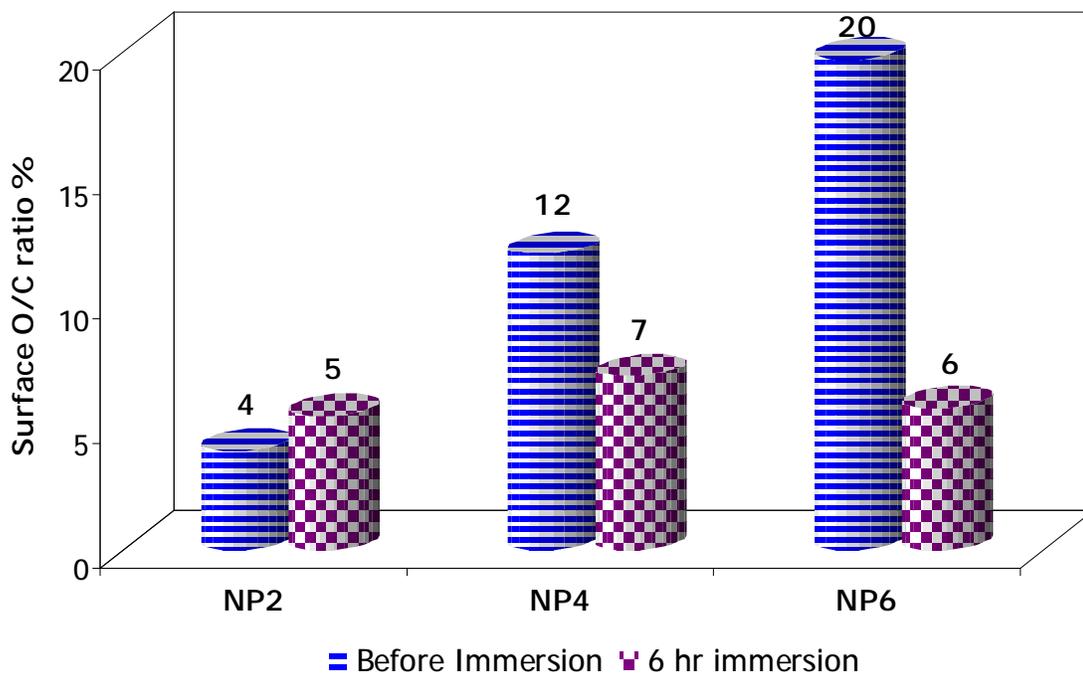


Figure 4.30: Surface O/C ratio (%) for the surface modified substrates with nonyl phenol ethoxylated melt additives before and after 6 hr water immersion

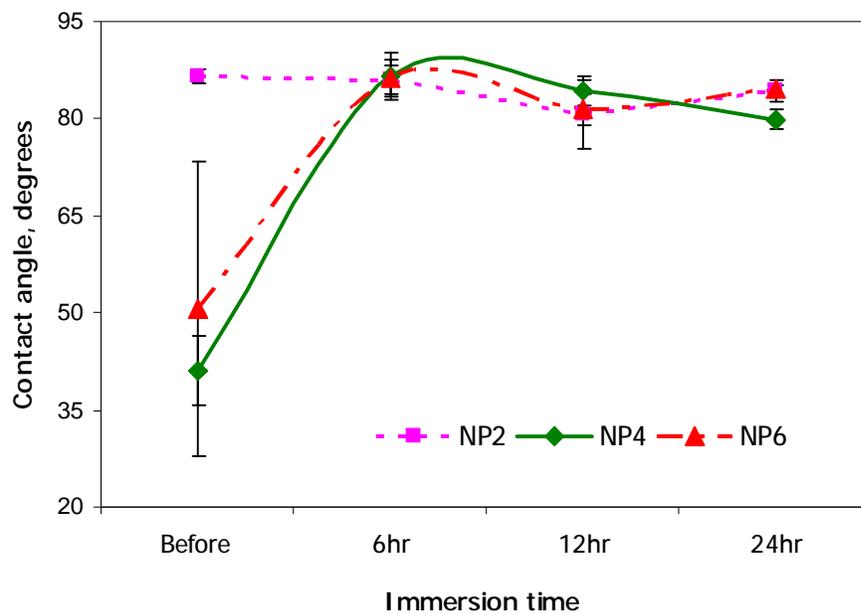


Figure 4.31: Equilibrium water contact angles before and after 6 hr, 12 hr, and 24 hr water immersion for the surface modified substrates with nonyl phenol ethoxylated melt additives.

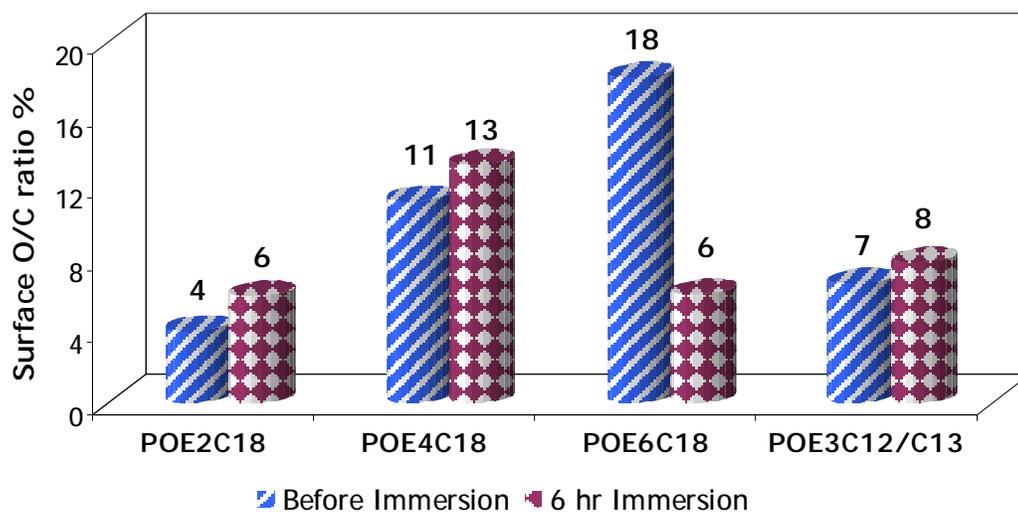


Figure 4.32: Surface O/C ratio (%) for the surface modified substrates with stearyl alcohol- and dodecyl alcohol-ethoxylate melt additives before and after 6 hr water immersion.

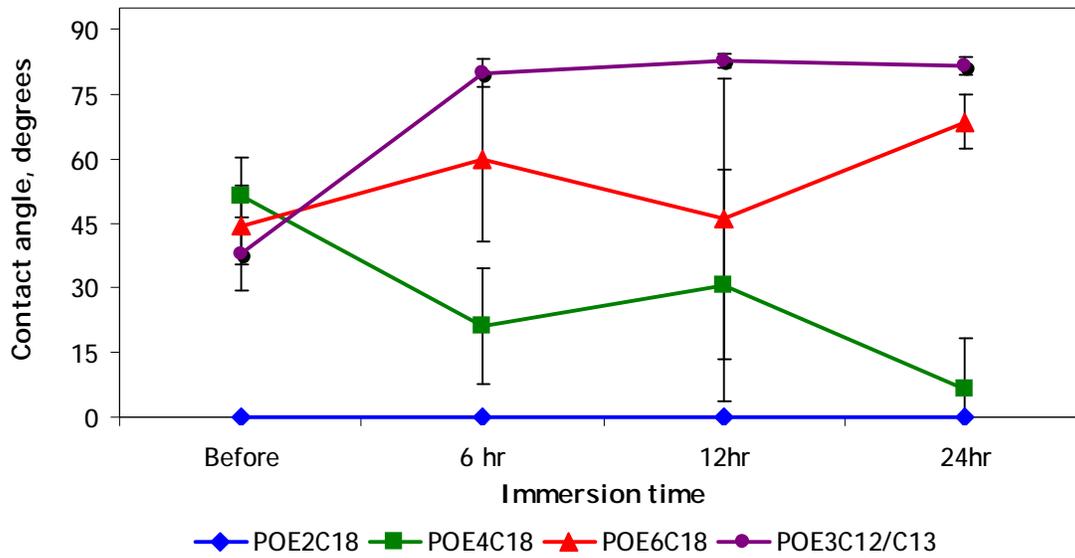


Figure 4.33: Equilibrium water contact angles before and after 6 hr, 12 hr, and 24 hr water immersion for the surface modified substrates with stearyl alcohol and dodecyl alcohol ethoxylated melt additives.

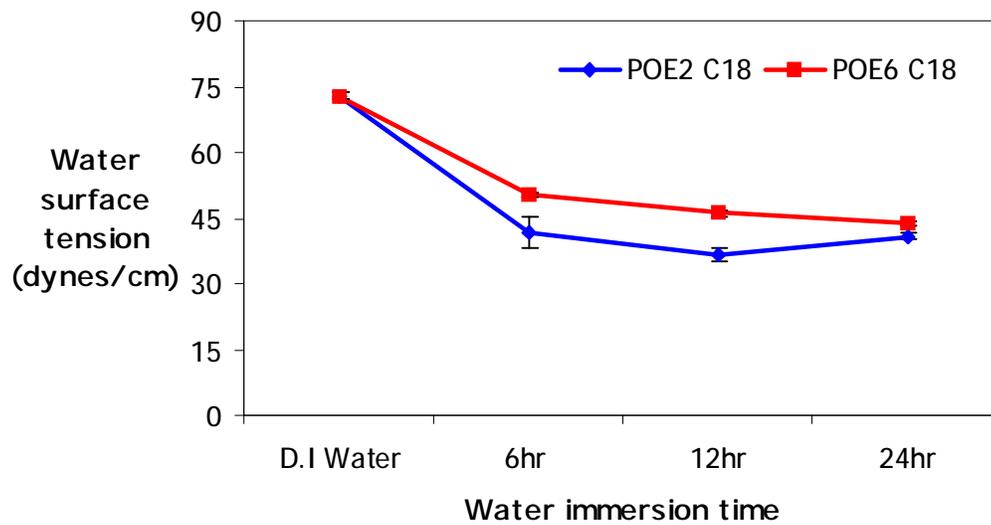


Figure 4.34: The surface tension (dynes/cm) of water before and after soaking of PP films modified with 2-wt % of POE2C18 and POE6C18 for 6 hr, 12 hr, and 24 hrs.

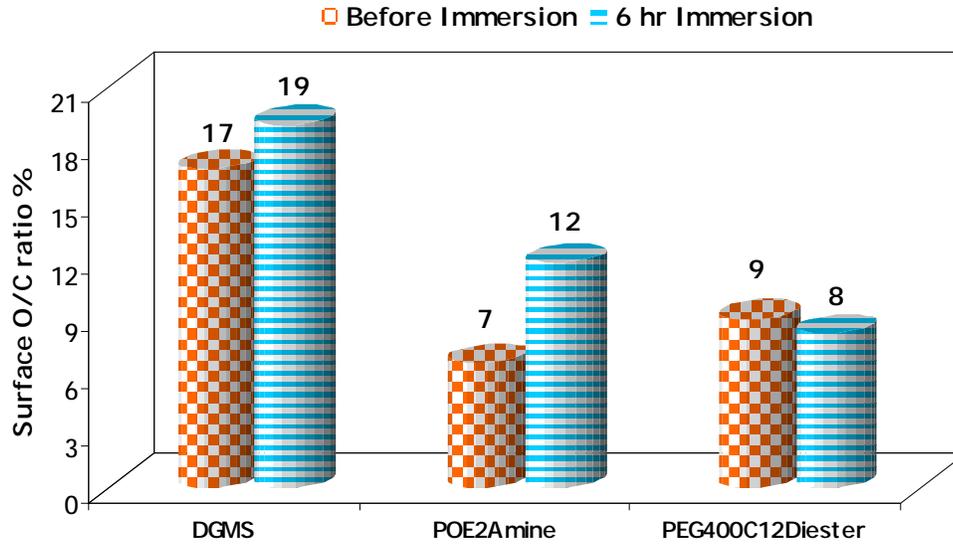


Figure 4.35: Surface O/C ratio (%) for the surface modified PP substrates with Distilled GMS, POE2-Stearyl amine and PEG400C12Diester melt additives before and after 6 hr water immersion.

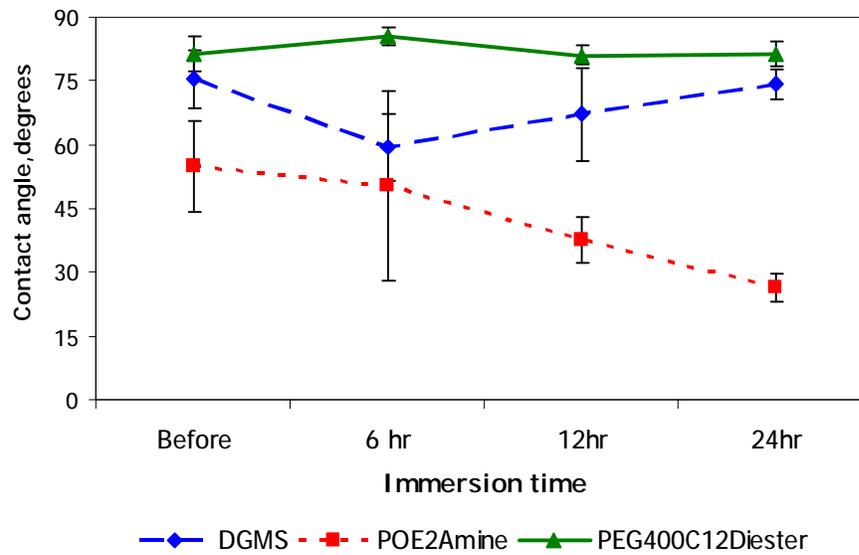
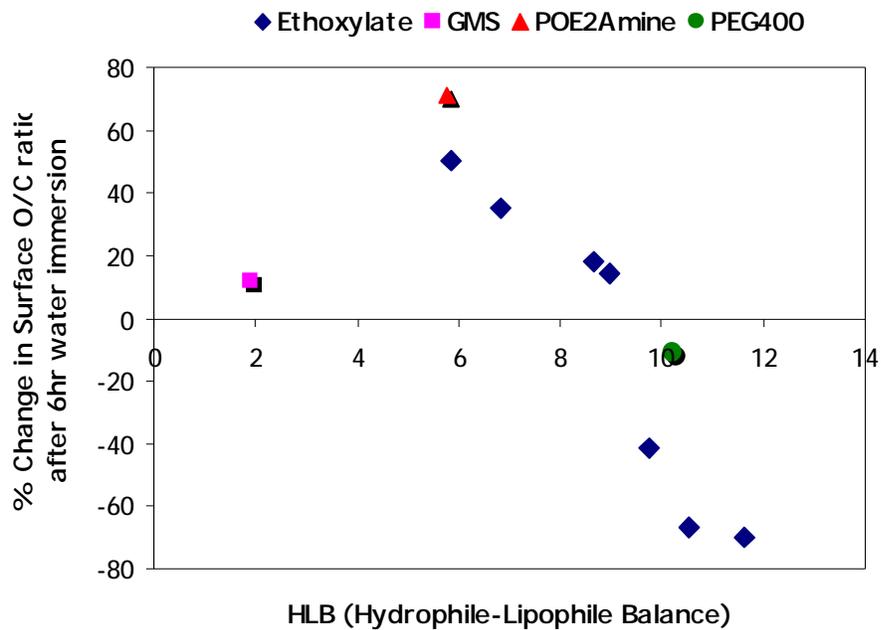
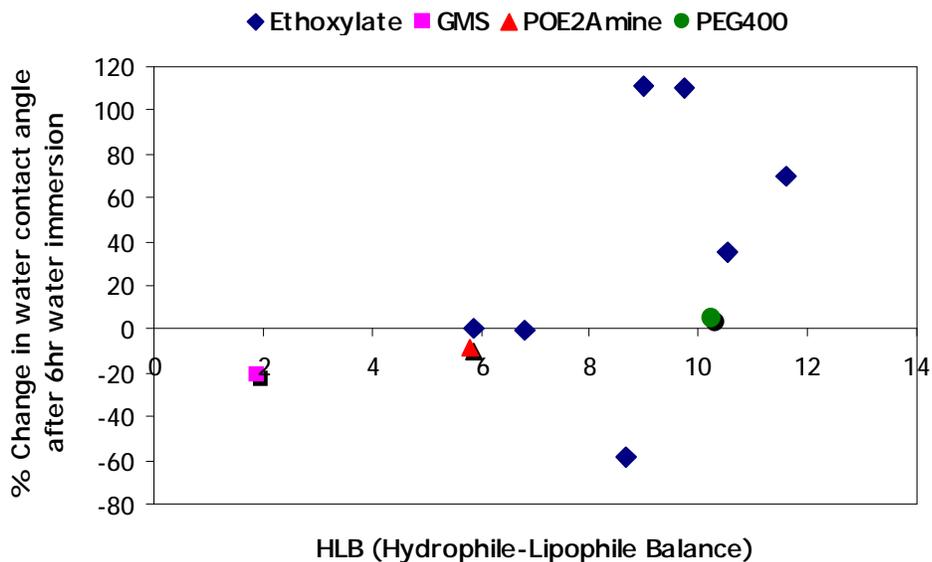


Figure 4.36: Equilibrium water contact angles for the surface modified PP substrates with Distilled GMS, POE2 Stearyl amine and PEG400C12Diester melt additives before and after 6 hr, 12 hr, and 24 hr water immersion.



(a)



(b)

Figure 4.37: Changes in the Surface O/C ratio % (a) and Water contact angle (b) of PP films modified using melt additives with different HLB values before and after 6 hr water immersion.

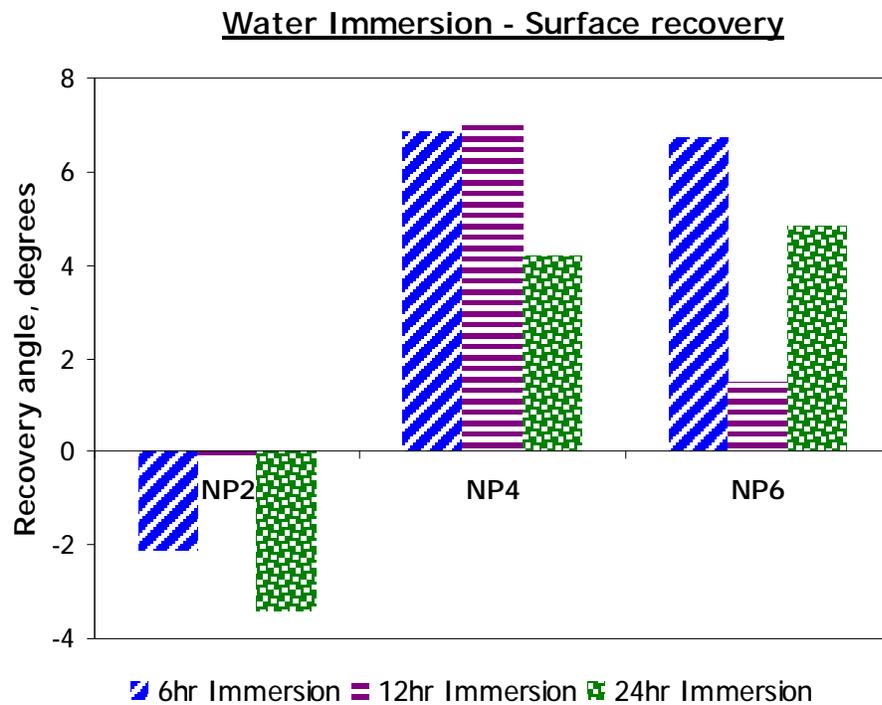


Figure 4.38: Recovery of water contact angles in PP films with nonyl phenol ethoxylated melt additives by aging samples after 6 hr, 12 hr, and 24 hr water immersion

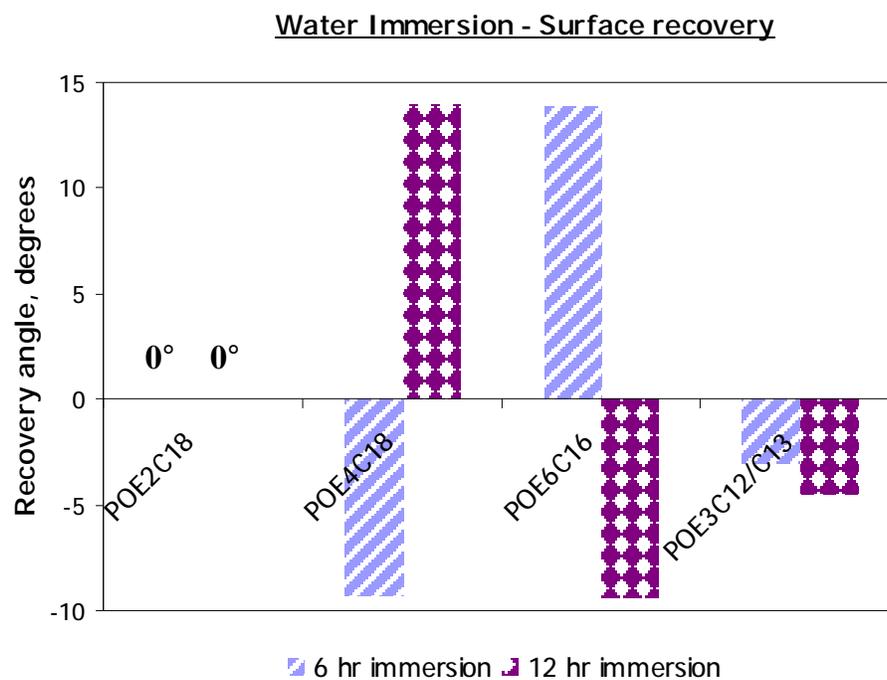


Figure 4.39: Recovery of water contact angles in PP films with stearyl alcohol ethoxylated melt additives by aging samples after 6 hr and 12 hr water immersion.

Water Immersion - Surface recovery

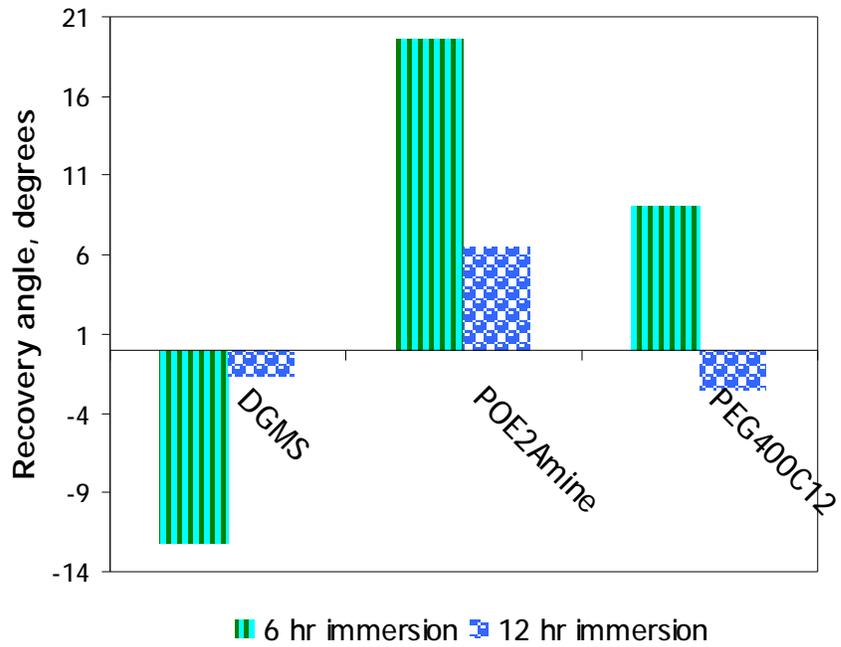


Figure 4.40: Recovery of water contact angles in PP films with DGMS, POE2Amine and PEG400C12Diester additives by aging samples after 6 hr and 12 hr water immersion.

4.6. ADVANCED MICROSCOPIC ANALYSIS OF SURFACE MORPHOLOGY AND ADDITIVE DISTRIBUTION

4.6.1. Surface Morphology and Roughness using Atomic Force Microscopy (AFM)

The surface topography on the modified PP surfaces was obtained from the height images shown below in Figure 4.41.

Surface heterogeneity and microphase separation are important determinants in the surface topography, which affects several surface characteristics. The height image of PP control shows a typical spherulitic crystalline structure indicating initiation of crystallization from several nuclei distributed on the sample surface. In PP films with nonionic additives, the surface becomes less structured due to migration of additives from the bulk to the surface and therefore, the surface topography is rough and dominated by the presence of a variety of non-uniform features (both bumps and depressions) seen as bright tall spots. A closer look on the 3D surface plots (Figure 4.42) of the height images suggests that the crystalline morphology itself is preserved. It is a well known fact that the crystallinity and the morphology of semicrystalline polymers depend strongly on the thermal history and DSC thermal analysis of PP Control and PP films containing nonionic additives discussed in section 4.8.1 reveals slight changes in the PP crystallinity in films with the additives but not the melting temperature T_m .

Surface roughness statistics were also obtained using the 'Roughness Analysis' feature of the software. The roughness parameters are estimated by the analyzing the topography scans of the sample's surface. The RMS (root mean square) roughness (standard deviation of the z-values within the given area) values for 50 x 50 μm^2 area of PP control and modified PP films obtained from AFM height images on these surfaces are presented in Table 4.9.

Wenzel [94, 95] first discussed the effect of the surface roughness on contact angle. He noticed that the actual surface area of the rough surface would be larger than that of a smooth surface with the same geometric area. Surface tension is defined as energy per unit area, so actual area is considered instead of the geometrical area in surface phenomena. He modeled the contact angle on a rough surface by introducing a roughness factor, ϵ , which is defined as the ratio of the true surface area to the planar projected area of the surface.

$$\bar{\epsilon} = \frac{A_{act}}{A_{proj}} \dots\dots\dots (4.1)$$

where, A_{act} : actual surface area, A_{proj} : geometric(projected) surface area

Then, the contact angles on rough surfaces become,

$$\cos q_w = \bar{\epsilon} \cos q_{true} \dots\dots\dots (4.2)$$

θ_w is called the Wenzel contact angle, which is the equilibrium contact angle on a rough solid surface.

Using the statistics obtained through the roughness analysis, the real contact angles of modified surfaces was obtained using roughness factor considered by Wenzel and are summarized in Table 4.9 below. Overall, it shows roughness has little effect on measured contact angle, so contact angle reduction by addition of melt additives is the result of surface composition changes, not of alteration of surface morphology.

The alteration of the additive containing PP surfaces can be verified through AFM images (Figure 4.43). While water immersion induce little changes in the PP control surface, significant reduction of surface roughness accompanying with erosion of irregular surface

features (bumps, etc) were observed in additive containing PP surfaces after water immersion.

4.6.2. Molecular Composition Analysis using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

Figure 4.44 illustrates the surface analysis for PP films modified with nonyl phenol ethoxylate (NP2, NP4, and NP6) melt additives. The positive ion spectra in the figure below show the chemical composition of the very top layer of the modified samples from the ToF-SIMS analysis. The positive ion spectrum exhibited characteristic fragmentation patterns, and they are mostly dominated by fragments composed of C_xH_y and $C_xH_yO_z$ groups as shown in Figure 4.44. The fragments C_xH_y ($C_3H_5^+$ ($m/z=41$), $C_3H_7^+$ ($m/z=43$)) and $C_xH_yO_z$ ($C_2H_5O^+$) could be assigned to the fragmentation of the molecules from the PP polymer and POE (polyethylene oxide unit in the hydrophilic part of the melt additive), respectively. The identification of the $C_2H_5O^+$ ($m/z=45$) fragment is attributed to the phase segregation of the melt additive, which has a low solubility parameter compared to PP polymer. Also it can be seen that there is no $C_2H_5O^+$ fragment in NP2 sample indicating absence of the melt additive (or poor orientation of the hydrophilic segment) at least within the top 1nm of the polymer surface, however oxygen enriched surface was observed within the top 1-5 nm of the surface determined by XPS method. (refer Figure 4.14). On the other hand, the $C_2H_5O^+$ ($m/z=45$) fragments seen in the spectra of NP4 and NP6 PP films indicate the presence or the migration of the melt additives to the air-polymer interface and they are more intense for the NP6 sample compared to NP4 sample. This was in agreement with the content of the ethoxylated segment, which is higher in NP6 melt additive than NP4.

It is believed that the presence of a segregated NPE chain will greatly influence the surface composition of the modified PP films and subsequently the presence and orientation of the hydrophilic segment will affect the water contact angle measurements. Therefore referring to Figure 4.21 the equilibrium water contact angle observed over a 4-month time period after

extrusion showing hydrophobic nature or higher contact angle for NP2 (absence of polar oxygen containing group at the surface) sample and decreasing contact angle or improved surface hydrophilicity for NP4 and NP6 over time.

4.6.3. Surface Analysis and Top Surface Additive Distribution using ToF-SIMS Imaging

Quantitative X-ray photoelectron spectroscopy cannot give absolute information about the exterior surface functionalities on a fiber surface, because this technique includes subsurface contributions (up to 5nm), while contact angle measurements are affected by interactions between the functionalities on the outer fiber surface [about the outermost atom layers of a surface (0.5 to 1 nm)] and the test liquid. Unfortunately the difference in analytical depth is the main reason why the surface wettability measurements cannot be fully explained from the elemental composition obtained from XPS.

Surface characterization from ToF-SIMS method has its own unique advantages compared with XPS due to its high molecular specificity, extreme surface sensitivity (about 1nm), and high-mass resolution, and therefore qualitative interpretation from ToF-SIMS are most suitable for characterizing the changes in the surface “nature” with a high degree of accuracy and can be confidently related to the changes in the water contact angles measurements.

Figure 4.45 shows the ToF-SIMS positive ion spectra of PP surfaces containing 2-wt% of POE2C18 (Figure 4.45 (a)) and POE6C18 (Figure 4.45 (b)) additives for bombarding with (Ga⁺) ion beam. In the spectra, characteristic secondary ions are detected and the mass range upto $m/z = 100$ are dominated by fragments associated with both additive as well PP polymer chains. The signals at 15, 27, 43 and 45 m/z result from the hydrophobe and the hydrophile segments of the additive, while those at 41, 43, 55, 68 and 83 m/z are characteristic of molecular fragments associated with the PP polymer chains. The Table 4.10 summarizes the

suggested composition of the characteristic positive secondary ions identifying the presence of the hydrophilic POE (polyoxyethylene, $\text{CH}_2\text{CH}_2\text{O}$) chain segment at 45 m/z.

The surface distribution of the additives particularly the hydrophilic POE chain segment is therefore determined by mapping of the molecular fragment $\text{C}_2\text{H}_5\text{O}^+$ (POE chain) at identified $m/z = 45$ on the modified PP surfaces, since it is believed that the presence of a segregated stearyl alcohol ethoxylated chain will greatly influence the surface composition of the modified PP films and subsequently the presence and orientation of the hydrophilic segment (POE chain) will affect the water contact angle measurements. The distribution of the hydrophilic POE (polyoxyethylene) segment of the additive on the very top surface mapped by using the ToF-SIMS technique in the imaging analysis mode is illustrated in Figure 4.46. It can be seen that there is little/no POE fragment in the PP polymer, while the presence of the significant amount of POE fragments observed in PP films with POE2- and POE6-C18 additives indicate the presence or the migration of the melt additives to the air-polymer interface and they are more intense for the POE2 sample compared to POE6 sample.

Hence the ToF-SIMS imaging confirms that the presence of higher concentration of hydrophilic segment within the top 1nm of the polymer surface in PP modified with POE2C18 additive is the reason for its complete wettability.

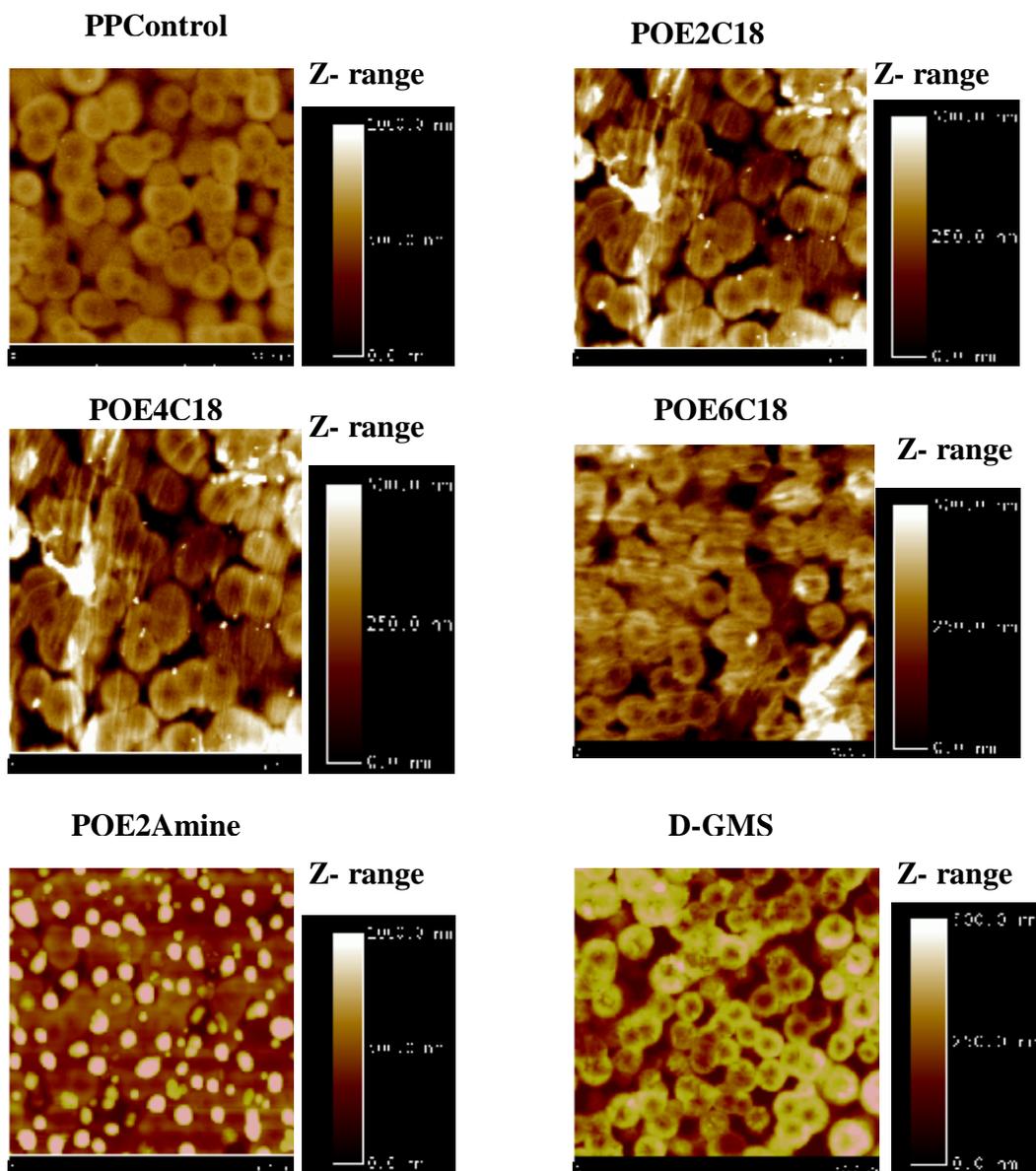


Figure 4.41: AFM height (topography) images of PP Control and PP modified using POE (n=2,4,6) C18, POE2Amine, and D-GMS) in air. All the images are 50 x 50 μm and z-scale varies with the sample and included above

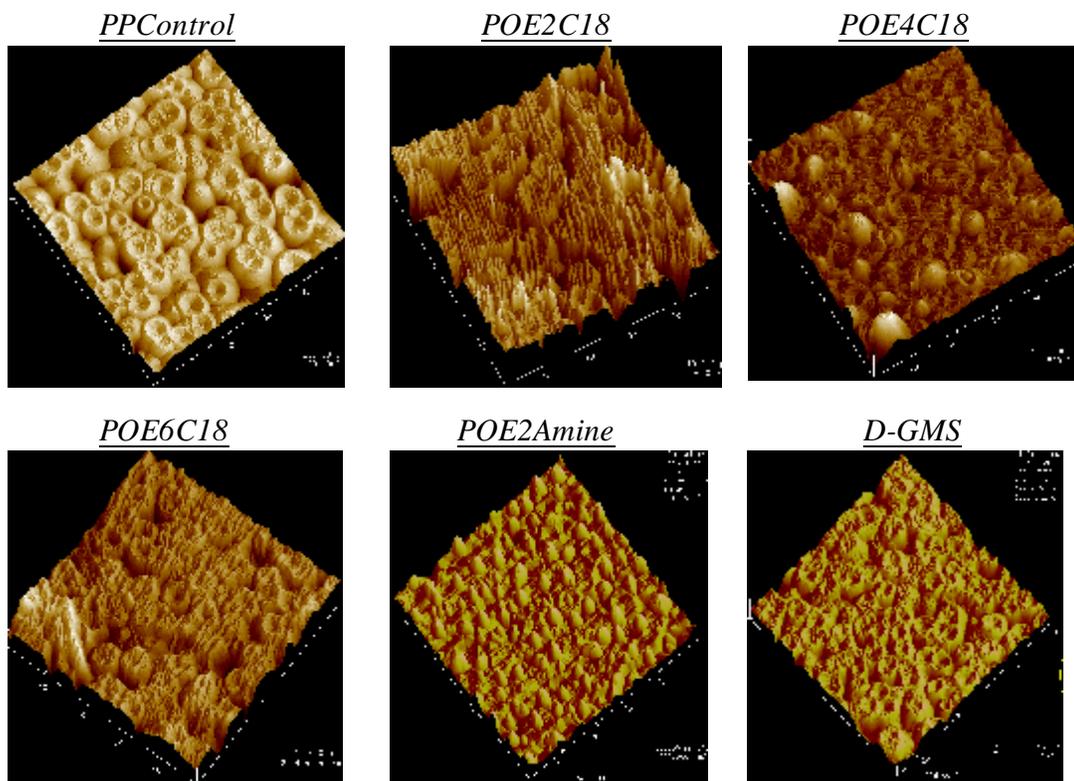


Figure 4.42: 3D Surface plots of PP control and Modified PP films obtained from AFM height images in the tapping mode

Table 4.9: Estimated Wenzel contact angle of PP control and modified PP films obtained from the roughness analysis statistics.

Sample	RMS Roughness values (nm) on 50 x 50 nm ²	Roughness factor, ϵ	Q_{measure}	θ_{true}
PP Control	128	1.0124	92	92
PP + POE2C18	137	1.0176	11	15
PP + POE4C18	358	1.0576	45	48
PP + POE6C18	111	1.0104	35	35
PP +POE2Amine	274	1.0932	55	58
PP + DGMS	143	1.02	75	76

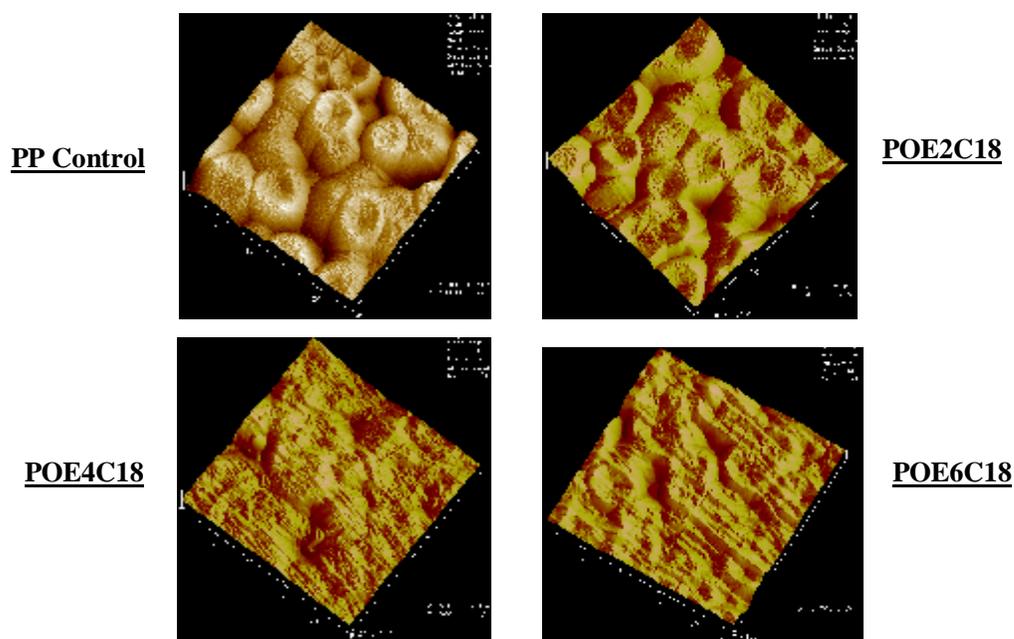


Figure 4.43: 3D Surface plots of PP control and modified PP films obtained from AFM height images after 6hr water immersion.

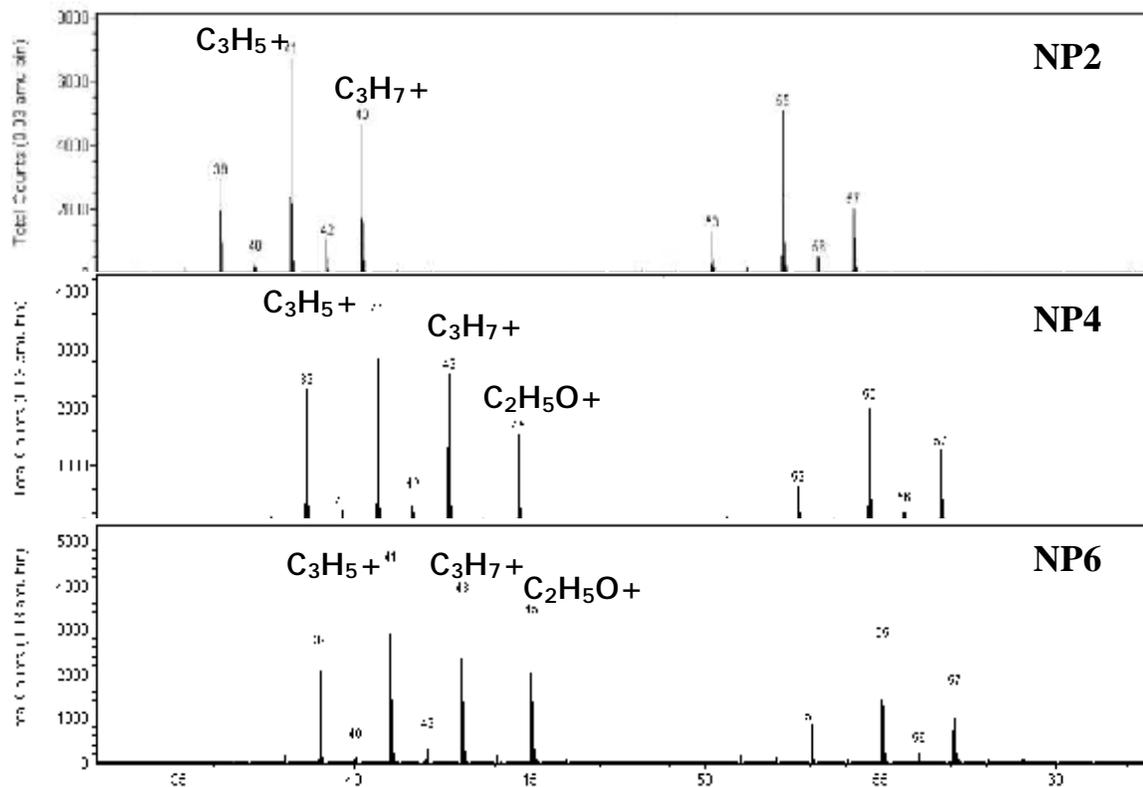
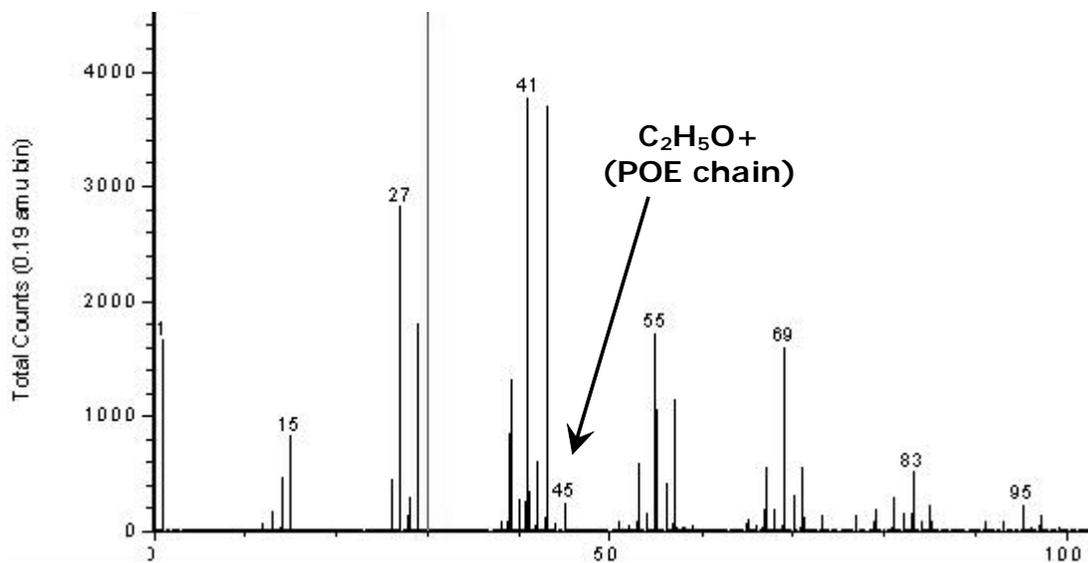
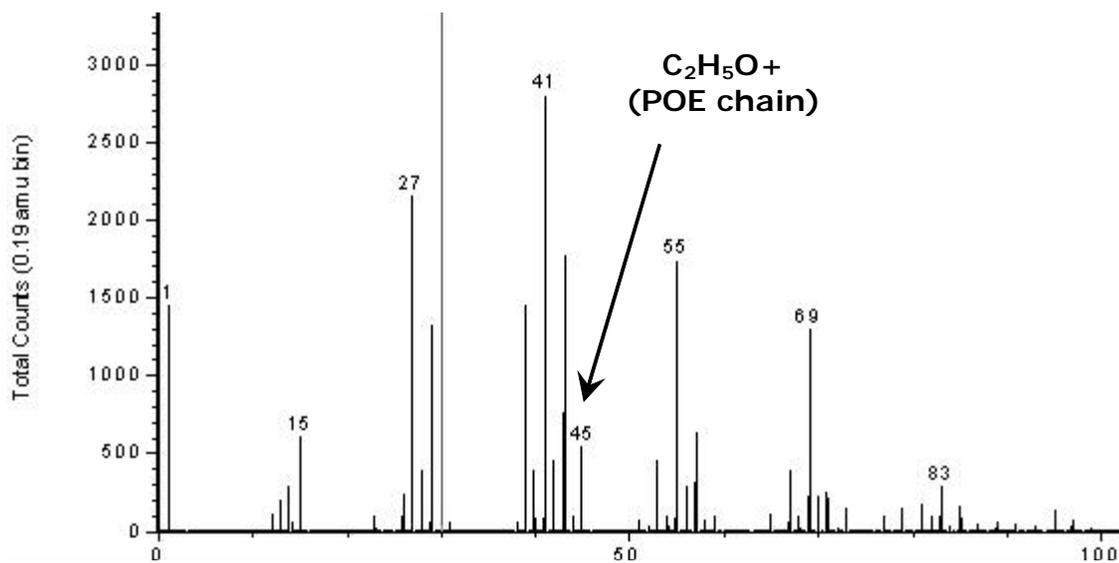


Figure 4.44: ToF-SIMS positive ion mass spectra for surface modified PP films with nonyl phenol ethoxylate (NP2, NP4, and, NP6) melt additive.



(a) Spectra for PP film containing 2-wt% of POE2C18 additive



(b) Spectra for PP film containing 2-wt% of POE6C18 additive

Figure 4.45: ToF-SIMS positive ion mass spectra for surface modified PP films with POE2- and POE6-Stearyl alcohol melt additives.

Table 4.10: Suggested structure of the characteristic positive secondary ions emitted from PP containing 2-wt% of POE2C18 and POE6C18 additives.

Sample	Mass	Fragment Composition
PP + 2-wt% of POE2 C18	15	CH ₃ ⁺
	27	C ₂ H ₃ ⁺
	41	C ₃ H ₅ ⁺
	43	C ₂ H ₃ O ⁺ , C ₃ H ₇ ⁺
PP + 2-wt% of POE6 C18	45	C ₂ H ₅ O ⁺
	55	C ₄ H ₇ ⁺
	69	C ₅ H ₉ ⁺
	83	C ₆ H ₁₁ ⁺

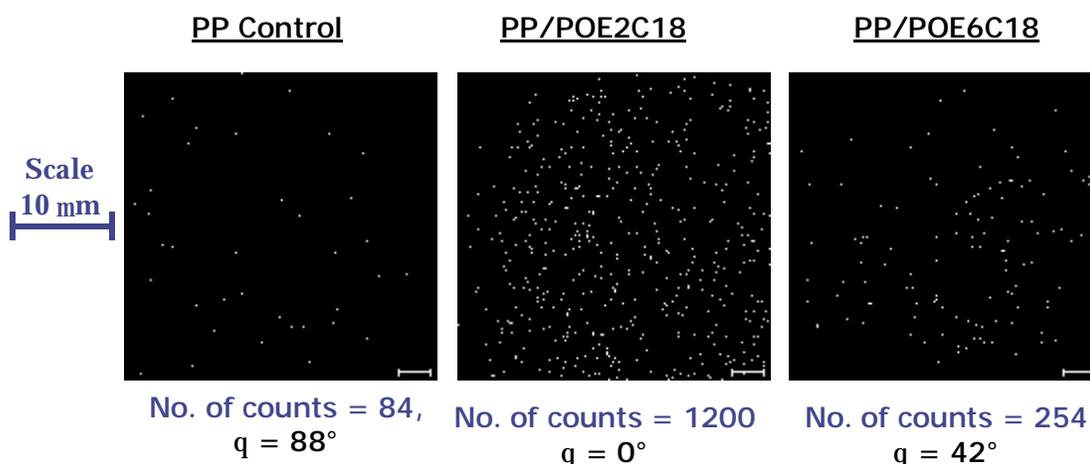


Figure 4.46: Characteristic secondary ion image of C₂H₅O⁺ (POE chain, m/z = 45) fragment in PP control and surface modified PP films with stearyl alcohol ethoxylate (POE2 and POE6) melt additive of 100 μm x 100 μm area. In the subscript of each map the maximum no. of counts per pixel and equilibrium water contact angles are given.

4.7. RELATIONSHIP BETWEEN SURFACE COMPOSITION AND STRUCTURE AND SURFACE WETTABILITY

For the case of PP polymer/Melt additive systems, which are barely compatible, the analytical estimates are provided for

- Amount of additive that saturates a polymer surface at a given time and
- For the phase distribution in such a system, and,
- How the additive distribution and structure influences the overall surface wettability.

4.7.1. XPS vs Contact Angle

In the course of our work we made an assumption that higher surface melt additive concentration, represented by higher oxygen content on the surface will make the surface more hydrophilic. Although considerable segregation resulted in additive enriched surfaces, there is no direct relationship between melt additive concentrations present on the surface and its surface hydrophilicity. Figure 4.47 shows the plots for water contact angle measurements versus surface additive concentration calculated from XPS analysis of PP films modified using 2-wt% of stearyl-and dodecyl-alcohol ethoxylated additives (a), nonyl phenol ethoxylated additives (b) and other nonionic melt additives (c) determined after Day 2, Week 3, and Month 4 after extrusion. Although some correlation i.e. lower contact angles for surfaces with considerable additive concentration were seen with few additives, essential differences exist in most PP/additive film surfaces. The interaction of the molecules of additive themselves and those of the polymer-additive changes the mobility and the apparent solubility of additive but the response of the modified surfaces and their structure when brought into contact with external media such as water and heat also affects the surface wettability. It must also be noted that XPS measures surface composition within the top 1-5 nm of the polymer surface, the polymer/additive structure may be very different on the top surface and it is the top structure that is believed to affect the contact angle data. Therefore,

surface wettability cannot be fully explained by additive concentrations at the analytical depth of XPS.

The decrease in the contact angle indicated that the chemical and physical surface properties differed due to the variety or amount of polar surface groups, especially the type of polar oxygen-containing groups for example, C-OH, or COOH, or C-O-C does seem to influence the extent of surface modification.

4.7.2. Other Surface Structure Effects

On the basis of characterization of surfaces using other analytical techniques such as ToF-SIMS (Time of Flight – Secondary Ion Mass Spectrometry), and SEM-EDS (Scanning Electron Microscopy – Energy Dispersive X-ray Analysis, results in Appendix 4) that characterize the chemical composition at different analytical depths, information regarding surface and bulk composition is obtained to get an understanding of the evolution of the concentration profile across the interface as result of the additive segregation and also to understand the complex polymer-additive structure. The analytical depth of SEM-EDS is about 10-15 μm and this coupled with XPS can provide information about the additive distribution in the polypropylene (PP) matrix. Another complimentary technique such as ToF-SIMS, which characterizes the surface at about 1nm depth, is utilized to relate to the surface hydrophilicity.

The subsurface material composition determined using SEM-EDS analysis confirmed that the composition at the surface is not the same as the bulk and bulk composition remained unchanged by incorporation of additives. Interestingly, ToF-SIMS proved to be a valuable method in identifying the molecular structure on the very top surface. SIMS analysis in the imaging mode confirmed uniform surface coverage of additive molecules and segregation of the hydrophilic chain and this observation was shown to have good correlation with the surface wettability data. For that reason, PP films containing 2-wt% of POE2C18 additive in

bulk were increasingly hydrophilic due to segregation of POE2C18 molecules and presence of significant amount hydrophilic segments (polyoxyethylene, POE) dominant at the outermost layer.

4.7.3. Surface Dynamics and Contact Angle

Additionally, the dynamic nature of surface interactions studied using contact angle relaxation phenomena demonstrated surface restructuring by reorientation of the hydrophilic segment upon contact with water. Once the surface is exposed to water, the surface reconstruction occurs quickly, and the wetting behavior of water changes drastically. Then, a polymer, which is hydrophobic at the polymer-air interface, can become highly hydrophilic upon contact with water due to surface dynamics in highly hydrophilic surfaces. While, the presence of the hydrophilic segment of the additive on the top surface accounts for increased hydrophilicity due to optimal interactions by intermolecular hydrogen bonding, the absence of oxygen, or the hydrophilic part of the additive on the very top surface leads to slower change in hydrophilicity .

Contact angle is a top surface phenomena and interactions between the functionalities on the outer fiber surface and test liquid, affect the measurable contact angles. So the decrease in the contact angle indicated that the chemical and physical surface properties not only depended on the amount of polar surface groups, especially the polar oxygen-containing groups on the surface of surface modified films determined using XPS (this technique includes subsurface contributions), but also on the exterior surface functionality examined using ToF-SIMS, and, the rate of surface additive alignment and release studied using contact angle relaxation.

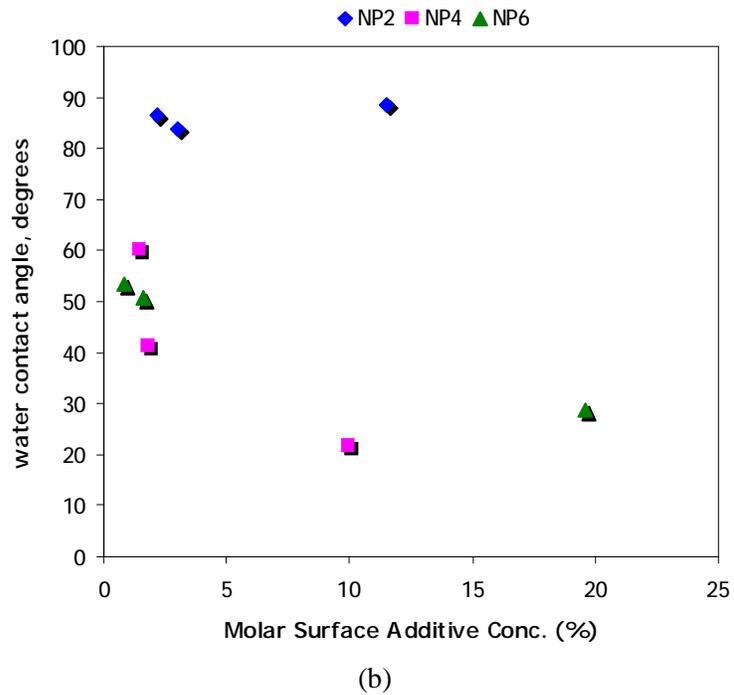
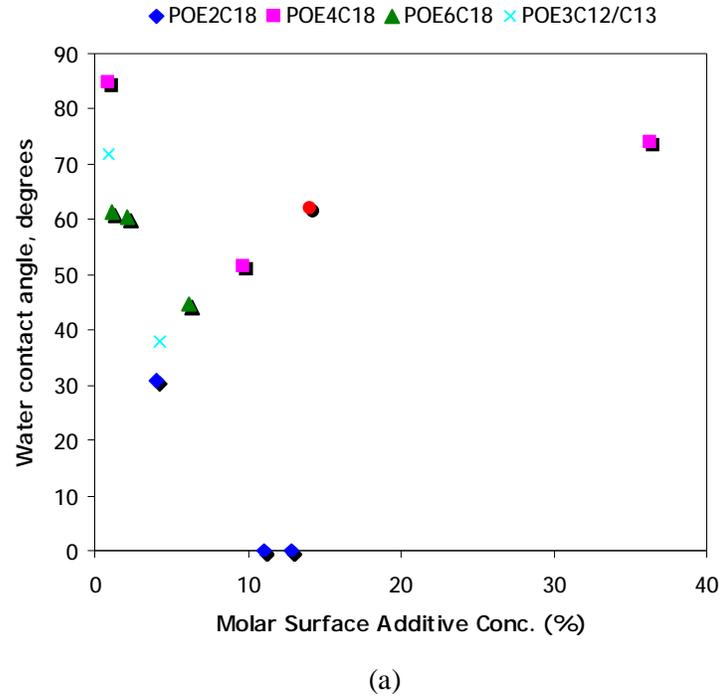
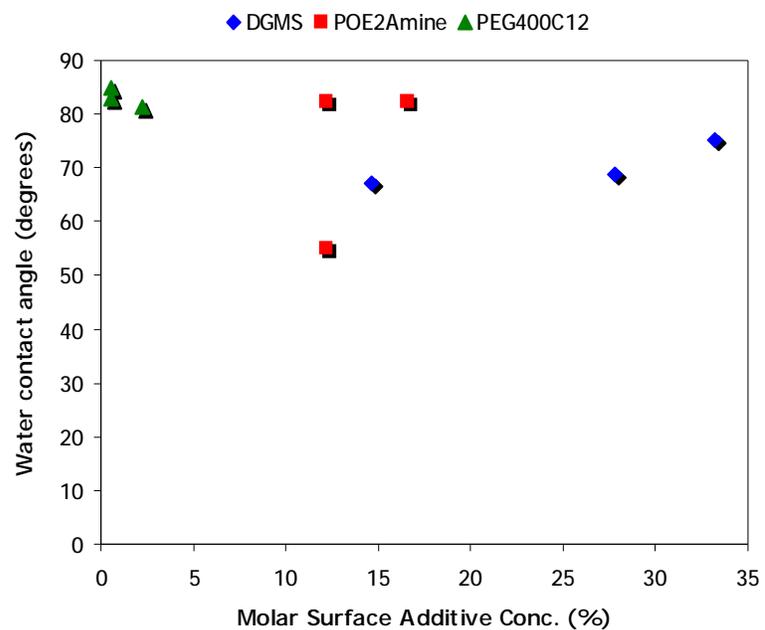


Figure 4.47: Plot of XPS surface additive molar concentration (%) vs Advancing water contact angles for PP films modified using 2-wt% of stearyl and dodecyl alcohol ethoxylates (a), nonyl phenol ethoxylates (b) and other (c) nonionic melt additives.



(c)

Figure 4.47 (continued): Plot of XPS surface additive molar concentration (%) vs Advancing water contact angles for PP films modified using 2-wt% of stearyl and dodecyl alcohol ethoxylates (a), nonyl phenol ethoxylates (b) and other (c) nonionic melt additives.

4.8. HEAT TREATMENT OF SURFACE MODIFIED PP FILMS

4.8.1. Thermal Analysis Using Differential Scanning Calorimetry (DSC)

Table 4.11 summarizes the thermal properties observed by DSC for the pure melt additives and modified polypropylene films with the melt additives. The melting temperatures from the DSC thermograms were used to determine the temperature at which the samples should be run to investigate the effect of heat treatment. Based on the performance of the melt additives evaluated in terms of their migration behavior, surface hydrophilicity, durability and surface recovery following water immersion, a few melt additives were selected to investigate the effect of heat treatment on the resultant surface composition and hydrophilicity of the modified PP substrates. These melt additives varying in kind and composition included low HLB melt additives, which resulted in immediate surface enrichment and increase in surface hydrophilicity even after subsequent periods of water immersion, and, high HLB melt additives whose surface migration increased over time resulting in enhanced surface hydrophilicity.

From Figure 4.48 it is evident that all the modified polypropylene films with the melt additives exhibited broad and distinct melting point endotherms in the DSC indicating a phase segregated polymer blend. A summary of the thermal properties in Table 4.11 showed that the PP melting temperature (T_m) is not affected by incorporation of the nonionic melt additives, though a slight increase in PP crystallinity was observed in PP films with POE2C18 and POE2Amine additives.

The DSC thermogram scans illustrated in Figure 4.48 (left) for the melt additives showed a broad melting range indicating polymer crystals that coexist and come in a range of sizes and with various degrees of perfection. While the DSC scans for the modified polypropylene substrates illustrated in Figure 4.48 (right) reveal the phase-separated nature of the polymer blends because of distinct melting endotherm peaks with the polypropylene polymer being

the obvious melting point peak due to its higher composition in the blend. It should be noted in the DSC thermogram in Figure 4.48 (right) that the melting point contributed by the smaller crystalline fractions increased indicating some degree of interaction between the polypropylene polymer and the melt additive. The melting temperature and percent crystallinity of polypropylene showed no appreciable changes in the melt-blended films. These DSC results are a good indication that thermal properties and crystallinity of the base PP polymer are not influenced by the addition of nonionic melt additives.

4.8.2. Effect of Heat treatment

Based on the results obtained from the DSC analysis of melt additive-polypropylene blend films, two different temperature series i.e. one at 30°C (above T_g of polypropylene) and the second at 80°C (just above the T_m of the melt additive) were chosen to investigate the effect of heat treatment on these modified PP substrates. Based on an understanding of the definitions of T_g and T_m , the glass transition is a second order transition that occurs in the amorphous polymer domains when they go from rigid glassy state into the soft rubbery state, and melting is first order transition where the highly ordered crystalline melts and transfer to the liquid state from solid state. It allowed us to explore some interesting phenomena, such as phase transformations, that occur in a polymeric material namely the solid-solid interactions at 30°C and the liquid-solid interactions at 80°C.

4.8.2.1. Without aging

After heat-treating polymer samples in the oven at 30°C and 80°C for 3hrs were immediately brought to room temperature and investigated for changes in the surface composition and hydrophilicity. Figure 4.49 below illustrates the water contact angles (a) and the surface oxygen content (b) of the modified PP substrates before and after heat treatment at 30°C and 80°C.

For heat-treated samples at 30°C, an increase in the water contact angle or loss of surface hydrophilicity was observed in modified PP substrates with DGMS, POE4StearylAlcohol, and POE6StearylAlcohol. In substrates with POE2-StearylAmine and POE2-StearylAlcohol slight increase in surface wettability (decrease in water contact angle) was observed. The observations were well supported by their respective decrease and increase in the surface oxygen content presented in figure 4.49 (b). Decrease in surface oxygen and loss of hydrophilicity is more apparent after heat treatment at 80°C.

The behavior is still not understood well and one possible rationale might be due to restricted mobility of molecular chains in the amorphous regions of PP at heating (above T_g and below T_c) [96].

4.8.2.2. Surface recovery (With 2-3 weeks aging)

Aging of the 80°C heat-treated samples containing melt additives induced reduction of water contact angle and improvement of surface hydrophilicity (Figure 4.50). The observations indicate that heating the samples above the T_m of the melt additive may have resulted in one phase or homogenous mixture. On cooling and subsequent sample aging, incompatibility between additives and polymers may have resulted leading to phase segregation and surface migration of the melt additive.

4.8.3. Heat Treatment induced Phase Transitions and their Influence on Surface Wettability

Application of heat induces molecular alterations and the material undergoes phase transformation resulting in changes in the crystal structure, crystallinity, and molecular orientation. In this study, the mechanisms are sought for the changes in polypropylene (PP) morphological structure caused by thermal treatment. It is a general understanding that polymer molecules and segments at surfaces and interfaces exhibit motions and relaxations,

and morphology changes require the existence of chain mobility in the crystal phase, and that the thermal treatment temperature is sufficient enough to activate this relaxation. One component of interest in this study is the role of the diffusive mobility of the melt additives on the surface wettability of PP at different heat treatment temperatures.

PP films containing 2wt % of POE2-Stearyl alcohol and POE6-Stearyl alcohol additives are chosen and films were thermally treated for 3 hours at 100°C, 130°C and 150°C. Structural changes of polypropylene (PP) polymer during thermal treatment are monitored both by DSC (Differential Scanning Calorimetry) and WAXD (Wide Angle X-ray Diffraction) techniques. The influence of thermal treatment of modified PP films with melt additives on the surface wettability was investigated.

Crystallinity measured by both DSC and WAXD summarized in Table 4.12 exhibits similar trends in the dependence on the applied treatment. A comparison of the results shows rather a good correlation except for crystallinity of heat-treated samples at 130°C. A distinctive feature is the increase in PP crystallinity with heat treatment temperature except in PP films treated at 130°C where a marked decrease in crystallinity was noticed by DSC tests. To explain the obtained results, it is necessary to bear in mind the several inherent facts related to the individual measuring techniques used and that both these techniques emphasize different aspects. WAXD crystallinity uses the intensity of the diffracted x-ray beam and is evaluated as the ratio of the intensity caused by the crystalline part and the total intensity. Therefore WAXD crystallinity is influenced by both the fraction of the crystalline material and the sizes and perfection of the individual crystals (crystallites). Very small crystallites do not contribute to the crystallinity results. DSC crystallinity is proportional to the heat energy required for melting of the crystallites. The absolute value of crystallinity is calculated using the known value for 100% pure crystalline material. DSC melting point, measured by DSC, is identified with the maximum of melting endotherm. It depends on the size and perfection of the crystallites: the higher the size and the more perfect the crystallites, the higher the melting point.

Figure 4.51 ((a), (b), and, (c)) shows the DSC curve obtained from the heat treated PP Control films at 100, 130, and 150°C. The PP films heat-treated at high temperature, 150°C, show a very narrow melting range and an increased melting temperature and crystallinity. However, DSC scans for heat-treated PP films at 100°C and 130°C show a double melting peak character i.e. the appearance of small melting peak before the main melting peak of PP melting. Previous papers [97-99] have demonstrated that this is particularly observed in isotactic-polypropylene crystallized from the smectic phase. It suggests that the untreated PP films both control and the melt blended (with hydrophilic additives) have a smectic phase which is a metastable phase widely known to exist in iPP films melt extruded and rapidly quenched to room temperature giving an intermediate state between ordered and amorphous phase. [96,100-102]. This phase is stable at room temperature, but is known to transform into the monoclinic iPP phase (α -PP) on heating to temperatures above 70–80°C [102, 103] giving a three-phase system (amorphous-smectic-monoclinic)

The WAXD diffractograms illustrated in Figure 4.52 and 4.53 also confirmed changes in the crystalline structure of PP films heat treated at 100, 130, and 150°C for 3hrs.

Structural organization and morphology in PP (in Control film and those melt blended with additives) was influenced by thermal treatments as observed in Figure 4.52 and 4.53. Untreated PP Control film (Figure 4.52) and films containing 2 wt% of POE6C18 (Figure 4.53) additive shows a characteristic smectic structure, whereas the heat treated PP films undergo a dramatic change in the crystalline morphology. New crystalline peaks appear that are not observed in the control as well as melt blended PP films. The diffraction pattern for heat-treated PP films clearly shows the formation of crystals during thermal treatment that are clearly of the monoclinic α -structural modification [104]. As the treatment temperature is raised the crystal perfection increases as evidenced by the increase in the sharpness of the crystalline peaks, that this increase can be attributed to an increase in the size and perfection of the crystalline regions. (Table 4.13 and Table 4.14) and the results indicate an accelerated

increase in the crystal dimensions and perfection with temperature. The changes in crystallinity of heat-treated PP films follow the same trend as that found for DSC.

During the DSC thermal analyses it was noted that the onset of crystallization temperature for PP polymer was around 126°C, therefore, thermal treatment of PP films at 130°C might possibly melt the imperfect PP crystals and subsequent cooling will lead to reorganization and recrystallization of chains. The WAXD diffractograms of the heat treated samples shown before also demonstrated that thermal treatment of PP at elevated temperatures has serious consequences on its microstructure, produces a gradual smectic to monoclinic phase transition, resulting in increase in both crystallinity and crystal size. However, it is also possible that the smectic phase is not completely transformed into the monoclinic phase, and the mesophase or the small melting endotherm witnessed in the DSC thermogram might actually have a lower ΔH_f (heat of fusion) compared to the ΔH_f of 100% crystalline PP which is used to calculate the overall χ_c (crystallinity). It may be reason why the overall PP crystallinity is lower for PP films treated at 130°C when in fact the χ_c of small T_m peak may be higher.

Although it is well known that segregation or migration is dependent on crystallinity [105, 106], the amount of crystallinity, crystal structure and orientation, were anticipated to have a significant effect on the segregation behavior of additive melt blended into polypropylene. The DSC and the WAXD measurement techniques described above are complementary methods for identifying the structure of a semi-crystalline polymer and therefore used for predicting possible migration of additives in the PP polymer matrix.

Structural changes in the PP polymer caused by heat treatment affected surface wettability of PP films modified using 2% of POE2C18 and POE6C18 additives as illustrated in Figure 4.54 (a) and (b) respectively. Heat treating the PP films containing 2% of POE2C18 additive (Figure 4.54 (a) and also Figure 4.55 (a) at 100°C, 130°C, and 150°C resulted in significant reduction in the surface hydrophilicity (straight line is the contact angle before heat

treatment) and no improvement in the surface wettability was observed with aging the films for a 2 week time period except for heat treated film at 100°C where some reduction in water contact angle was observed after one week sample aging after which hydrophobic surface recovery was noticed. Similar behavior was seen in heat-treated PP films containing 2wt% of POE6C18 additive (Figure 4.54 (b) and Figure 4.55 (b)) where surface wettability decreased by thermal treatment at 100°C and 150°C. However, heat treating the PP films modified with 2wt% of POE6C18 additive at 130°C showed remarkable improvement in the surface hydrophilicity with zero (‘0’) degree contact angle demonstrating complete wettability of the surface. Since migration/segregation of additives occurs through diffusive mobility of the molecules within the amorphous phase, PP crystallinity calculated using the DSC technique showed increased crystallinity with heat treatment temperature except at 130°C where the crystallinity was seen to be lower than the untreated (not heat treated) PP films. Increase in PP crystallinity will hinder the mobility or the migration of the additive to the surface thereby reducing the surface wettability as confirmed by the water contact angle measurements. And PP films (Control and modified films) heat-treated at 130°C containing a higher amorphous fraction (free volume) in the PP matrix will enhance the diffusive mobility of the surface-active additive molecules. Increased diffusive mobility will increase the surface concentration of additive molecules and therefore has greater surface modifying potential (particularly wettability) and this is what is anticipated to occur in PP films containing 2wt% of POE6C18. However, no change in the surface wettability was observed for heat treated PP film with 2wt% of POE2C18 additive at 130°C, and a possible explanation might be due to decrease in the bulk additive concentration with increased solubility of the POE2C18 additive with the PP molecular chains at 130°C, and therefore resulting in low migration potential or no additive molecules to migrate.

Table 4.11: Thermal Properties of pure Melt Additives and modified Polypropylene film with select melt additives as revealed in their Heating DSC Scans.

Sample	T _m (°C)	T _m (°C)	T _m (°C)	T _m (°C)	Crystallinity, c _c %
	(Melt additives)			(PP)	
DGMS	64.5				
POE2C18	4.02	26.32	53.27		
POE4C18	1.87	15.26	45.81		
POE6C18	45.09				
POE2Amine	55.18				
PP Control				161.95	43.06
PP + DGMS	52.36	65.5	73.16	161.87	44.68
PP + POE2C18	46.82	73.17		163.39	43.20
PP + POE4C18	-2.06	1.37	41.15	161.47	33.03
PP + POE6C18	40.3	73.19		161.69	37.80
PP + POE2Amine	49.97	73.16		162.64	41.53

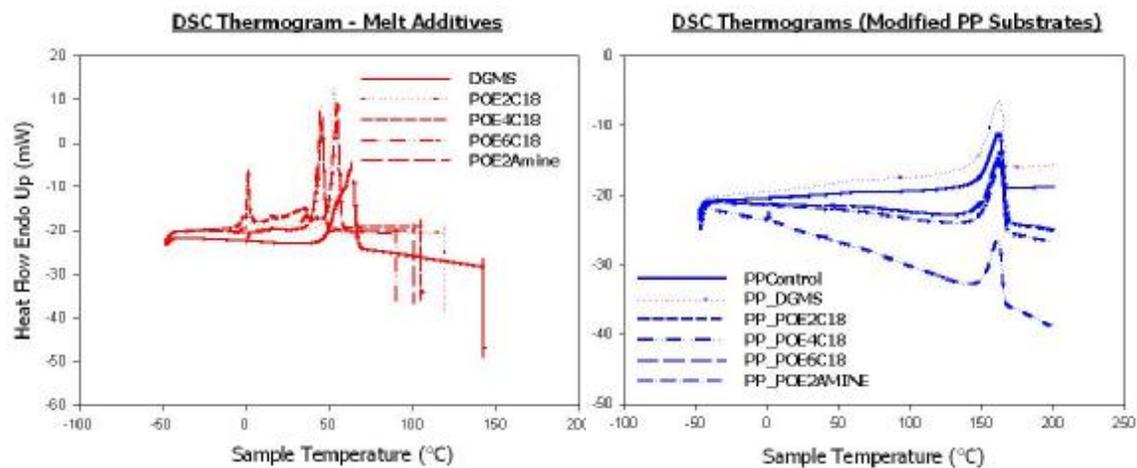
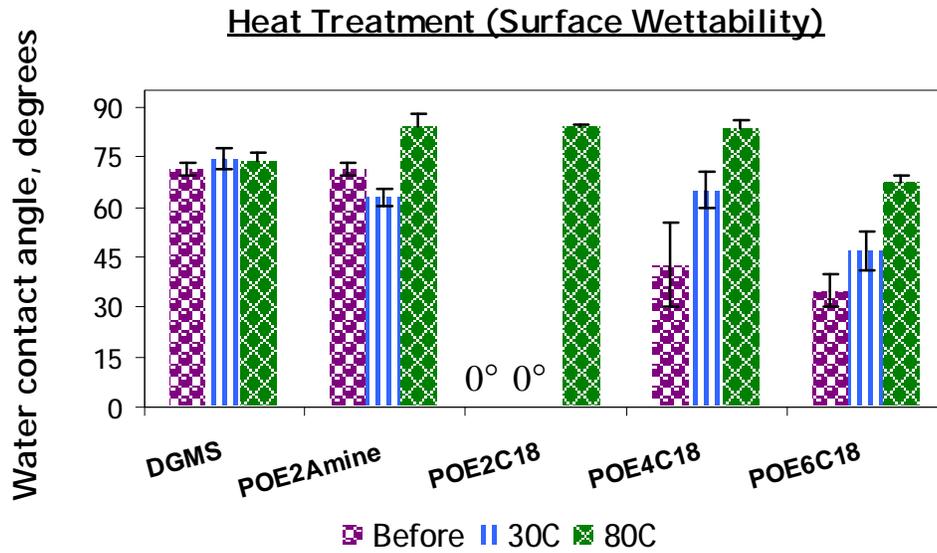
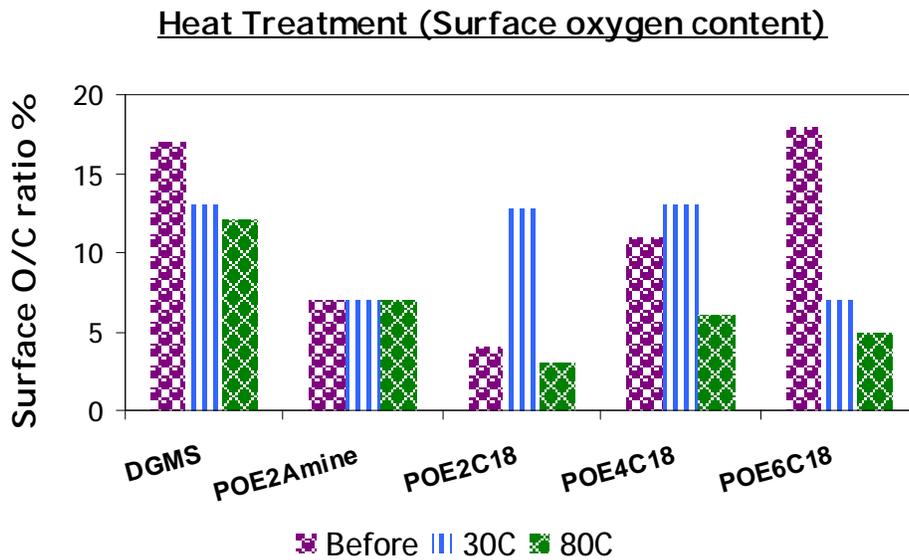


Figure 4.48: DSC Thermograms of melt additives (left) and modified PP substrates with the melt additives (right).



(a) Surface wettability changes before and after heat treatment of modified PP films



(b) Surface composition changes before and after heat treatment of modified PP films

Figure 4.49: Surface Hydrophilicity (a) and surface oxygen (b) content before and after heat-treating the samples at 30°C and 80°C without aging the samples.

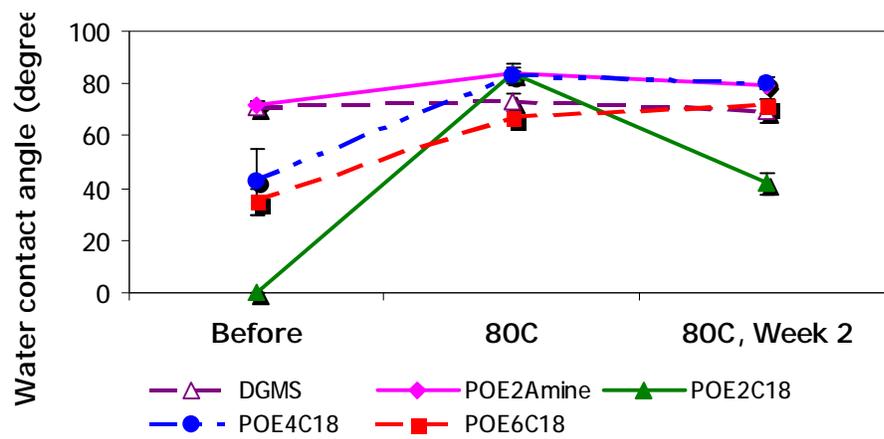
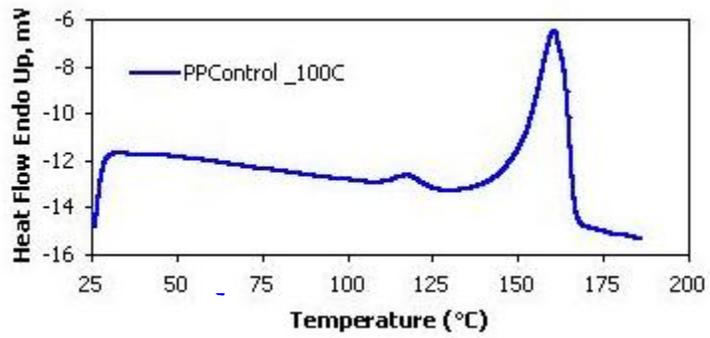


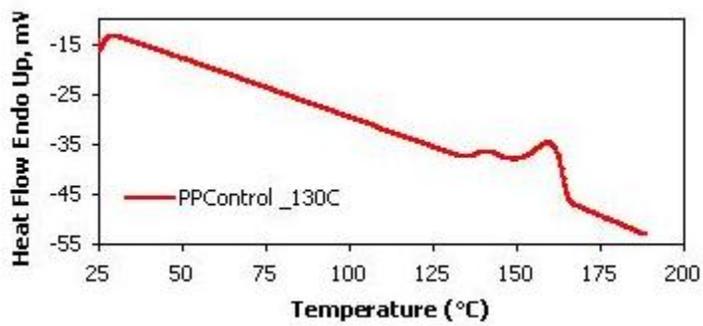
Figure 4.50: Surface hydrophilicity of heat-treated samples at 80°C after 2-3 week sample aging.

Table 4.12: DSC and WAXD results showing the influence of thermal treatment on the PP crystallinity.

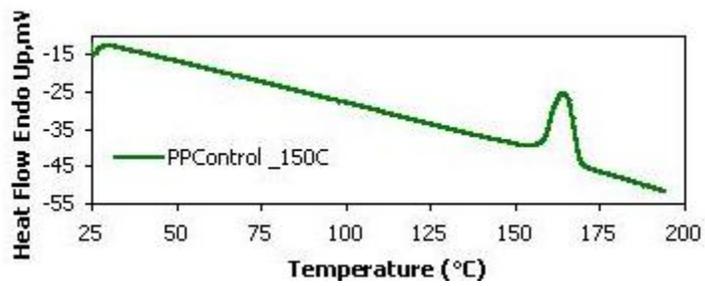
Film Sample	Treatment temperature, (°C)	Melting temperature, T_m (°C)	Crystallinity, c_c (%) – DSC	Crystallinity, c_c (%) - WAXD
PP Control	Untreated	159.82	33.71	33.64
	100°C	118.1, 160.93	39.80	38.07
	130°C	141.36, 160.71	27.87	48.67
	150°C	164.58	51.25	54.03
PP_POE2C18 (2%)	Untreated	159.46	42.68	49.42
	100°C	117.54, 159.97	38.75	36.29
	130°C	141.61, 160.89	25.11	47.06
	150°C	166.48	47.22	54.77
PP_POE6C18 (2%)	Untreated	160.05	34.68	40.04
	100°C	117.36, 160.6	39.72	41.48
	130°C	141.48, 161.59	22.69	49.47
	150°C	165.59	51.40	53.97



(a)



(b)



(c)

Figure 4.51: Example of curve obtained by DSC for heat-treated PP control films at 100°C (a), 130°C (b), and 150°C (c) for 3hrs.

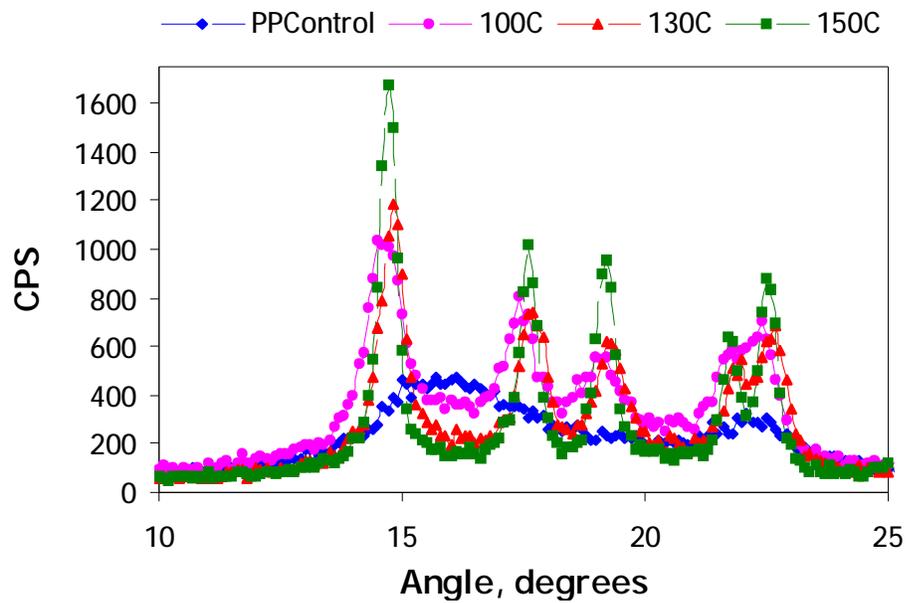


Figure 4.52: WAXD diffractograms for PP Control film and heat treated PP Control films at 100, 130, and 150°C for 3hrs.

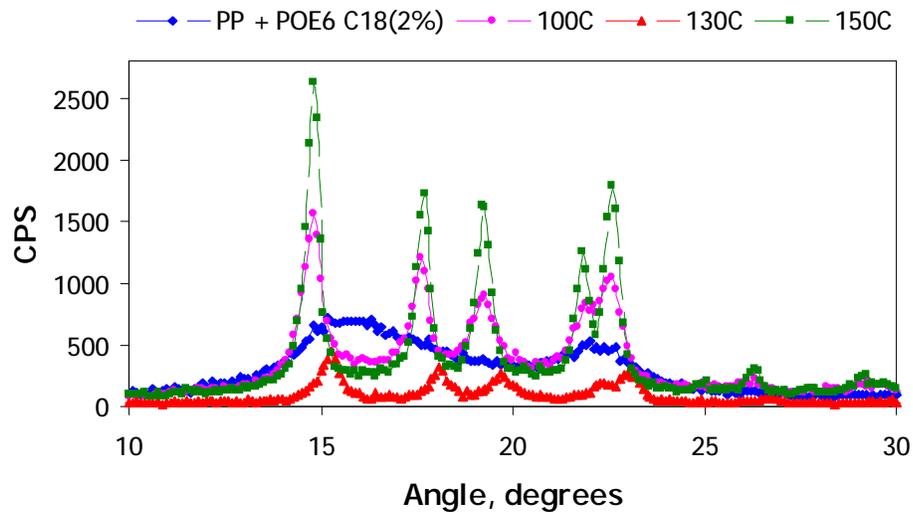


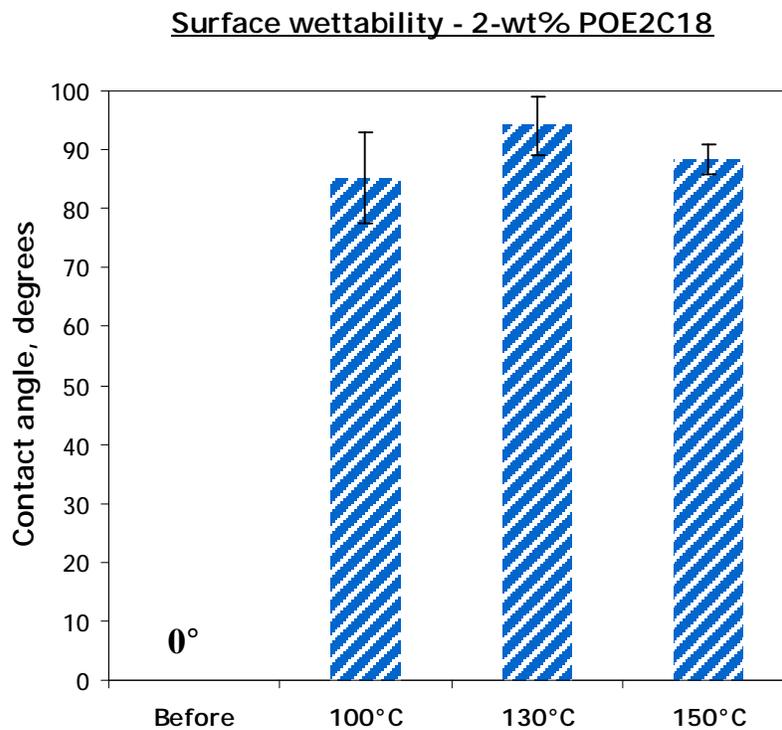
Figure 4.53: WAXD diffractograms for PP film modified with 2-wt% POE6C18 and the same film heat treated at 100, 130, and 150°C for 3hrs.

Table 4.13: Crystallite size derived from WAXD diffractograms of films of PP control before and after heat treatment at 100, 130, and 150°C for 3hrs.

Sample	Angle (2 θ)	Interplanar spacing, d (°Å)	Crystal thickness or size (°Å)
PP Control	15.80	5.61	18.24
	22.21	4.00	23.75
PP Control (100°C)	12.46	7.10	85.08
	14.71	6.02	52.05
	17.17	5.16	49.59
	19.10	4.65	41.75
	22.04	4.03	59.62
	13.32	6.65	142.30
PP Control (130°C)	14.81	5.98	87.24
	16.31	5.43	114.95
	17.63	5.03	93.72
	19.27	4.61	90.89
	22.28	3.98	57.81
	14.70	6.02	187.26
PP Control (150°C)	17.60	5.04	192.03
	19.18	4.63	210.31
	21.75	4.08	211.16
	22.54	3.94	181.68

Table 4.14: Crystallite size derived from WAXD diffractograms of films of PP modified with 2-wt% POE6C18 before and after heat treatment at 100, 130, and 150°C for 3hrs.

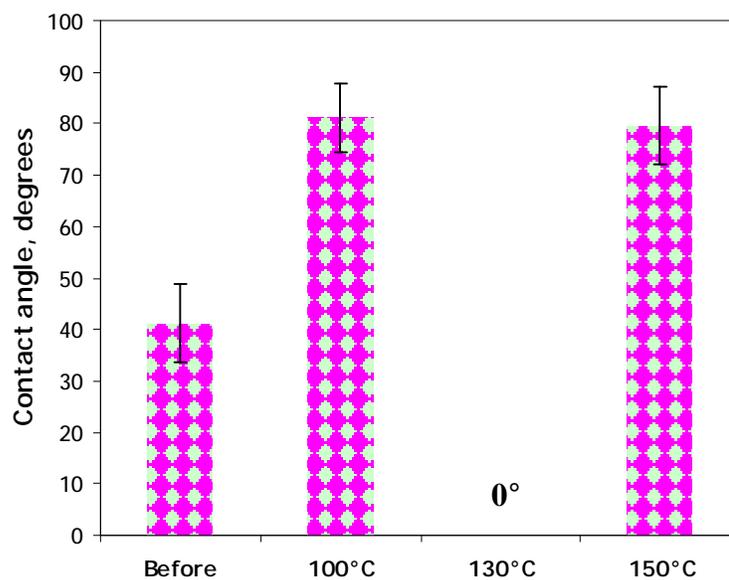
Sample	Angle (2 θ)	Interplanar spacing, d (°Å)	Crystal thickness or size (°Å)
PP + 2% POE6C18	9.68	9.14	24.61
	16.02	5.53	17.49
	21.82	4.07	20.04
	28.06	3.18	25.01
PP + 2% POE6C18 (100°C)	13.45	6.58	153.33
	14.78	5.99	90.91
	16.22	5.46	88.45
	17.57	5.05	87.40
	19.23	4.62	94.21
	22.23	3.99	60.47
PP + 2% POE6C18 (130°C)	15.24	5.81	153.39
	18.10	4.90	185.81
	19.73	4.50	129.86
	22.31	3.98	165.73
	23.06	3.85	134.15
PP + 2% POE6C18 (150°C)	14.78	5.99	184.69
	17.67	5.02	181.87
	19.26	4.61	187.33
	21.82	4.07	219.26
	22.62	3.93	180.81



(a)

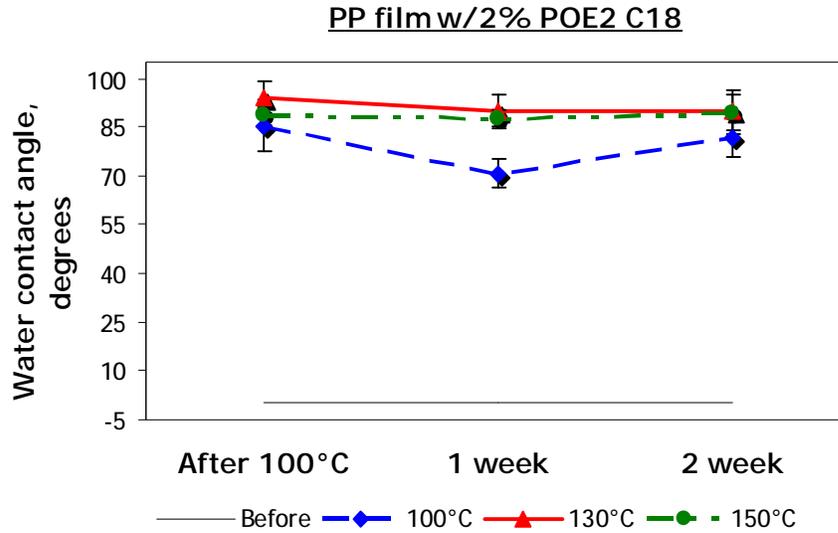
Figure 4.54: Surface Hydrophilicity of PP films containing 2-wt% of POE2C18 (a) and 2-wt% of POE6C18 (b) before and after heat-treating the samples at 100°C, 130°C and 150°C for 3hrs.

Surface wettability - 2-wt% POE6C18

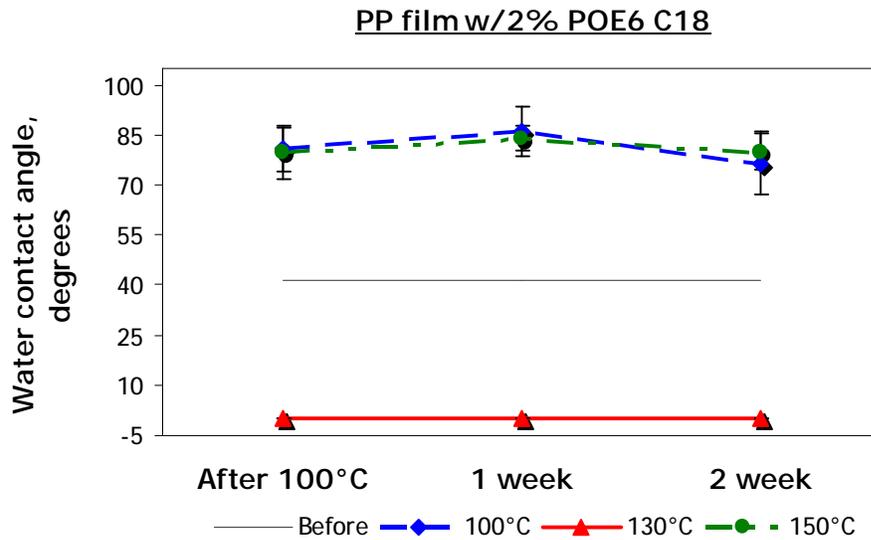


(b)

Figure 4.54 (continued): Surface Hydrophilicity of PP films containing 2-wt% of POE2C18 (a) and 2-wt% of POE6C18 (b) before and after heat-treating the samples at 100°C, 130°C and 150°C for 3hrs.



(a) Aging effect of thermally treated PP films with 2% of POE2C18 additive.



(b) Aging effect of thermally treated PP films with 2% of POE6C18 additive.

Figure 4.55: Advancing water contact angle measurements of heat treated PP films modified using 2wt% of POE2C18 (a) and POE6C18 (b) additives at 100, 130, and 150°C for 3hrs, also includes data of heat treated samples aged for 1-week and 2-week time periods.

4.9. EFFECT OF MELT ADDITIVE CONCENTRATION ON THE SURFACE CHARACTERISTICS OF MODIFIED PP FILMS

Earlier ten melt additives of different chemistries with a concentration of 2 wt% were compounded and extruded with the PP polymer as a film and investigated for their surface modifying effectiveness. As the additive molecules are surfactant based, we believe that just like in surfactant solutions, increasing the additive concentration will lead to a further decrease in the surface tension and maximum reduction is obtained only when CMC (critical micelle concentration) is reached. Also the composition will influence the processability and the miscibility between the two components in a polymer blend, which may affect its overall performance. Hence from the practical point of view, we want to obtain maximum hydrophilicity at the lowest possible additive concentration. Based on the performance of the melt additive in imparting a durable hydrophilic PP surface two melt additives were selected and polymer films with melt additive concentration of 0.5-3 wt% were produced and investigated for studying concentration effects with respect to changes in the surface properties (composition, wetting, surface energy) as a function of time, temperature and concentration, and durability against contact with water.

4.9.1. Surface Migration

The surface migration behavior of modified PP films extruded using additive concentration of 0.5-3 wt% with additives POE2-Stearyl Alcohol and POE6-Stearyl Alcohol was monitored over a four month time period after extrusion using X-ray photoelectron spectroscopy is illustrated in Figure 4.56 (a) and (b) respectively to study the concentration effects on the surface composition changes.

The surface enrichment of melt additive in PP films with POE2C18 additive gradually increased with additive concentration in bulk. However, the surface oxygen concentration in PP film samples with POE6C18 additive showed irregularities with respect to the increase in additive concentration with maximum additive enrichment obtained with 2 wt% bulk concentration for samples aged for 5 days as well as 3 weeks and surface additive was found to be highest with 1 wt% bulk additive concentration for samples aged for 4 months. The changes in the surface composition are more prominent in PP samples with POE2-Stearyl Alcohol additives as indicated by their higher surface additive concentrations. In PP samples with both POE2C18 and POE6C18 additives, the sample aging induced significant surface modification as observed by their ongoing migration behavior.

4.9.2. Surface Wettability

The advancing water contact angle measurements of modified PP films extruded with additives POE2 Stearyl Alcohol and POE6 Stearyl Alcohol using additive concentration of 0.5-3-wt% investigated over a four month time period after extrusion using X-ray photoelectron spectroscopy is illustrated in Figure 4.57 (a) and (b) respectively.

Water contact angle measurements were highly sensitive to increase in the additive concentration in PP samples with POE2C18 additive unlike POE6C18 additive as indicated by their increased (or complete) wettability with just 1 wt% over the 4-month period after extrusion. The increased wettability of PP samples with POE2C18 additive is well supported by the higher surface oxygen concentration observed over time than its counterpart POE6C18 additive owing to its easier and faster migration capability. A similar but a gradual enhancement in the surface hydrophilicity over time was observed in PP samples with an increase in the POE6C18 additive concentration. It is also important to note that samples with 1-3 wt% reached a similar contact angle measured 4 months after extrusion.

Though the additives POE2C18 and POE6C18 have similar compositions, the differences in their behavior are more clearly evidenced by contact of liquid water droplet on the respective PP/POE2C18 and PP/POE6C18 surfaces from the dynamic contact angle measurements. So the contact angle relaxation as a function of time for the PP samples with the above mentioned two additives extruded using 0.5-3 wt% was monitored for the following time periods, $t_1 = 0-5$ sec, $t_2 = 0-25$ sec, and $t_3 = 0-55$ sec and summarized for the respective time intervals, $\Delta\theta$ (θ_{t_1} , $\theta_{t_1}-\theta_{t_2}$, $\theta_{t_2}-\theta_{t_3}$) as represented in Figure 4.58.

Almost all surfaces exhibited a characteristic contact angle relaxation with a very rapid change at the beginning (t_1) indicating that a water droplet initially spreads faster on all surfaces, while the later relaxation is appreciably slower (zero in PP/POE2C18 samples with 1-3 wt% because of complete wetting). Even as discussed in our earlier reports, in spite of similar additive compositions, PP/POE2C18 showed the largest decrease in relative contact angle, particularly within five seconds of spreading in the region of θ_{t_1} , which can be ascribed to the fastest restructuring of the surface structure (observed with low concentration of 1-wt %) compared to POE6C18 additive. The mobility of the hydrated POE chains decreased with increase in the chain length; therefore, the surface having the shortest POE chains will exhibit rapid contact angle relaxation, which is observed with PP/POE2C18 surfaces where the POE2C18 additive contains a higher fraction of the shorter POE chains confirmed by the reverse phase HPLC analysis (section 4.1). From the results obtained above, one can conclude that the interaction of the PP/Melt additive surfaces with water provides a strong driving force to reduce the interfacial free energy by reorientation of the hydrophilic POE component to interact optimally with the water phase, though it is not known whether or not micelle formation is favored due to saturation of POE2C18 additive molecules on the surface.

4.9.3. Water Durability Studies

The durability of PP film sample modified with 0.5-3-wt% of POE2C18 and POE6C18 additives was investigated over various water immersion times. The samples were removed from the water and air-dried for 24hrs at room temperature and evaluated for changes in the surface properties (specifically surface composition & wettability). Additionally the water samples were later tested for differences in the water surface tension for any indication of additive loss during immersion. After the water immersed samples were investigated for surface property changes, the PP films were aged between a time period of week 2 or 3 and later tested for surface recovery by water contact angle measurements especially for PP samples which demonstrated loss of additive.

4.9.3.1. Surface Properties – Water Immersion

The water immersion of PP film samples modified with POE2C18 and POE6C18 additives using 0.5-3 wt% has resulted in loss of surface oxygen (or loss of additive) for most samples as clearly illustrated (Figure 4.59) by negative changes in the surface O/C ratio % (determined by XPS). However, 0.5% POE2C18 with 6hr water immersion, 2% POE2C18 with 12 hr water immersion, and 2% POE6C19 with 6hr5 water immersion showed increases in surface oxygen concentration as the result of water immersion. It is not clearly understood why these particular samples perform in a different way from the other PP/melt additives materials. As discussed previously, thermodynamically PP/additive surface prefers to have a water interface rather than an air interface due to energetically favored orientation of hydrophilic component of additive towards water, and having the water interface will therefore lead to increased additive migration capability. However, if the additive has weak anchoring capabilities to the PP matrix or has high affinity for the water, this will result in loss of surface additive molecules into the water.

It was also our intent to see how the changes in the surface compositions of water soaked samples will affect their respective surface wettability. Figure 4.60 shows the % changes in the surface hydrophilicity for the same set of PP samples discussed above. Clearly water immersion of PP films modified with POE6C18 additive with 0.5-3 wt% has resulted in an increase in water contact angle or loss of surface hydrophilicity which is in good agreement with decrease (or loss) in the surface oxygen composition represented in Figure 4.59. However, in spite of loss of surface additive molecules (loss of surface oxygen as noticed using XPS), only small changes in the surface hydrophilicity was observed in PP films modified with POE2C18 additive using 0.5-3 wt% confirming yet again the favorable interactions between the POE2C18 additive and the liquid water droplet.

Additionally, the water samples utilized for soaking the modified PP samples with 0.5-3 wt% of POE2C18 and POE6C18 additives were analyzed for changes in the water surface tension (Figure 4.61) using a tensiometer working on the Du Nuoy ring principle. The results clearly shows evidence for release (or loss) of surface additive molecules into water represented by reduction in the surface tension of water which is in good agreement with the decrease of surface oxygen concentration determined using XPS.

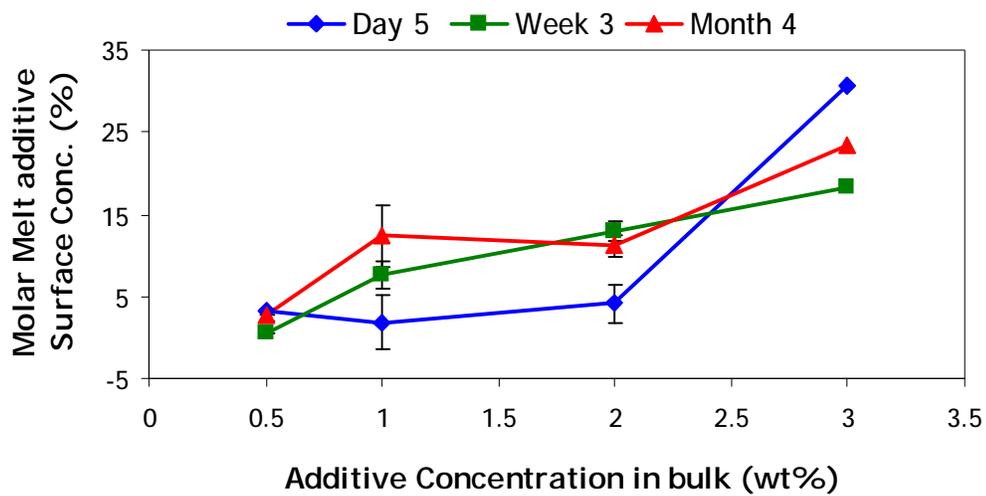
4.9.3.2. Surface Recovery – after water immersion

PP films modified with POE2C18 additive showed surface recovery of lost additive molecules demonstrated by a reduction in the water contact angle (increase of surface hydrophilicity) particularly in 2 and 3 wt % materials as summarized 4.14. However, a slow recovery of the lost surface additive molecules was noticed in PP films blended with with 1-wt % POE6C18 additives and significant hydrophilic recovery in PP films containing 2- and 3-wt%.

4.9.4. Thermal Analysis (DSC) - PP Crystallinity (%)

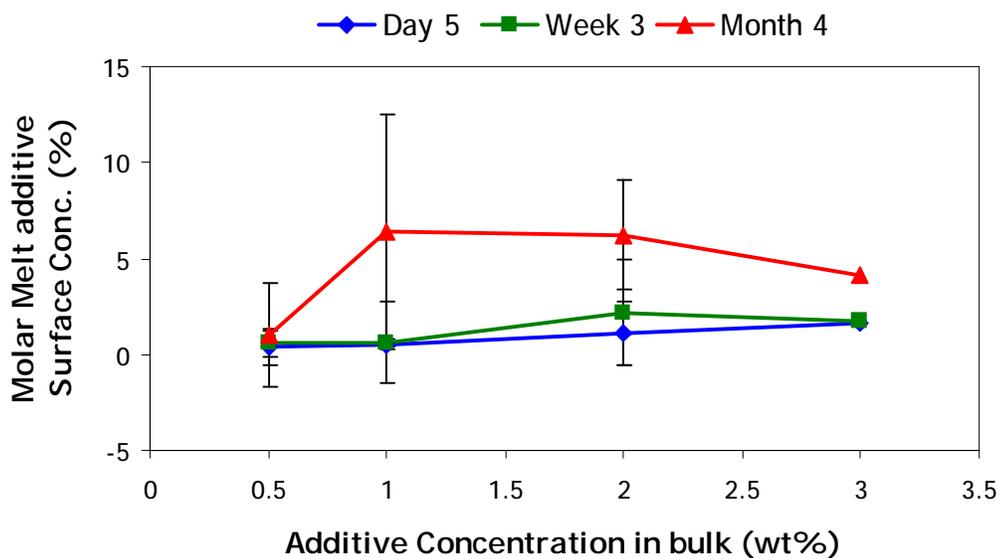
Table 4.16 presents a summary of the thermal properties observed by DSC for the melt additives and modified polypropylene substrates POE2C18 and POE6C18 additives using 0.5-3 wt%. From table 4.16 it is apparent that modified polypropylene materials with the POE2C18 and POE6C18 additives using 0.5-3-wt% exhibited distinct (mostly two) melting points characteristic of PP polymer and the melt additive revealing the phase-separated nature of these melt blended. Also as the additive concentration is increased, the melting point of the additive in PP films with both POE2C18 and POE6C18 increased with additive concentration as low as only 1 wt%, indicating commencement of interaction between the polypropylene polymer and the melt additive, brought about by thermally induced crystallization between the two molecular chains. In fact, an increase in the overall % crystallinity, χ_c of the PP polymer in materials with POE2C18 additive compared to materials with POE6C18 additive is an indication of higher degree of interaction between the polypropylene polymer and the POE2C18 additive which may be the reason for their surface modifying efficiency for hydrophilic based applications.

POE2-Stearyl Alcohol



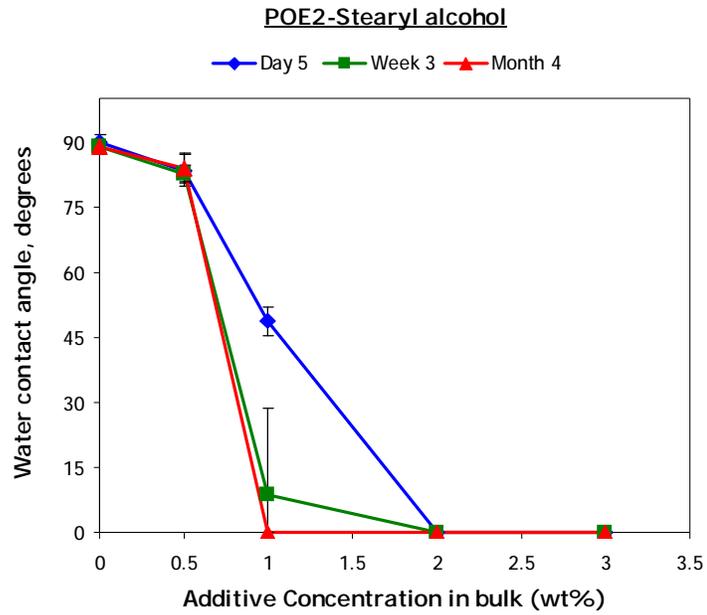
(a)

POE6-Stearyl Alcohol

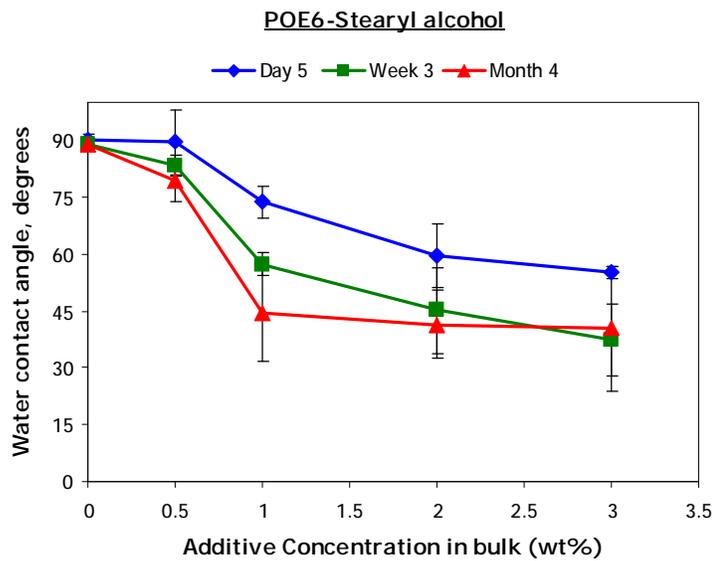


(b)

Figure 4.56: Surface concentration of POE2C18 (a) and POE6C18 (b) melt additives in the PP blends containing additive concentration of 0.5-3-wt% calculated by means of elemental O/C ratio derived from XPS analysis after Day 5, Week 3 and Month 4 from extrusion.



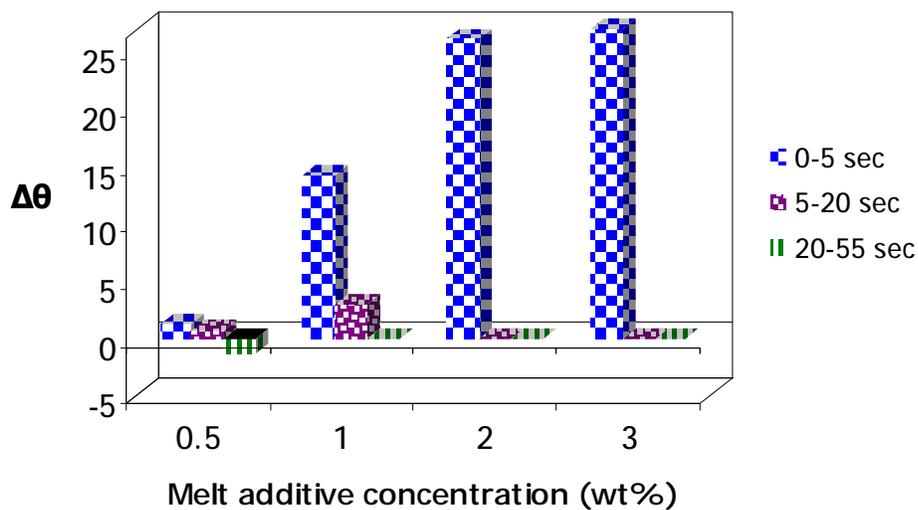
(a)



(b)

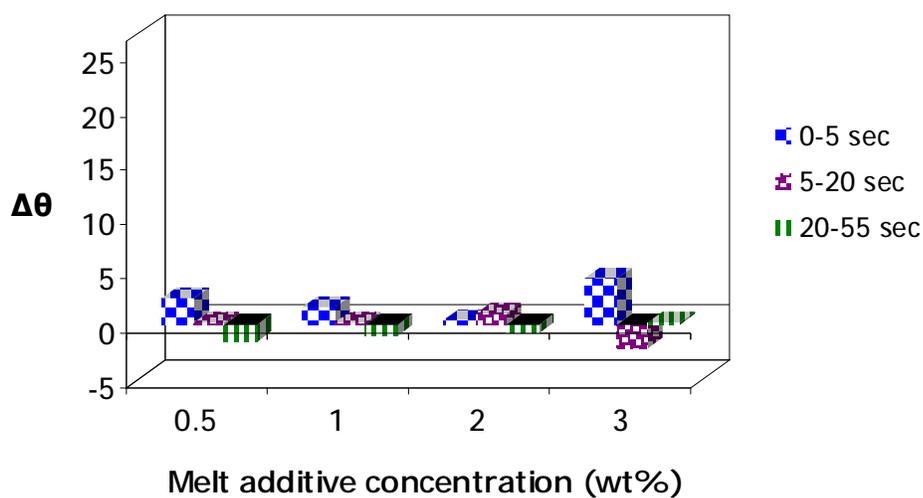
Figure 4.57: Advancing water contact angles of PP films modified using POE2Stearyl alcohol (a) and POE6 Stearyl Alcohol (b) with additive concentration of 0.5-3 wt% determined using XPS after day 5, week 3 and month 4 after extrusion.

Contact angle relaxation - PP w/POE2 C18



(a)

Contact angle relaxation - PP w/POE6 C18



(b)

Figure 4.58: Contact angle relaxation determined from Dynamic water contact angle measurements investigated after Week 3 after extrusion for the respective time intervals for PP modified using 0.5-3 wt% of POE2C18 (a) and POE6C18 (b) melt additives.

Water durability - Surface composition

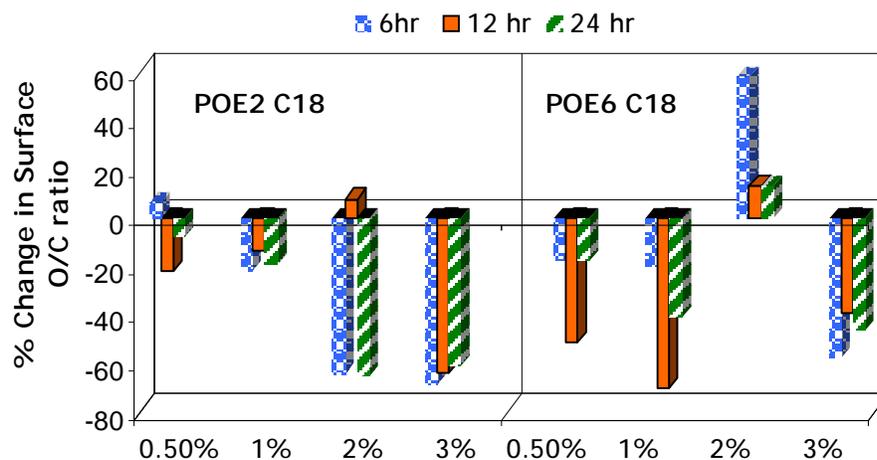


Figure 4.59: % Changes in the surface oxygen content after 6, 12, and 24 hr water immersion for PP films modified with POE2C18 and POE6C18 additives using 0.5-3 wt%.

Water durability - Wettability

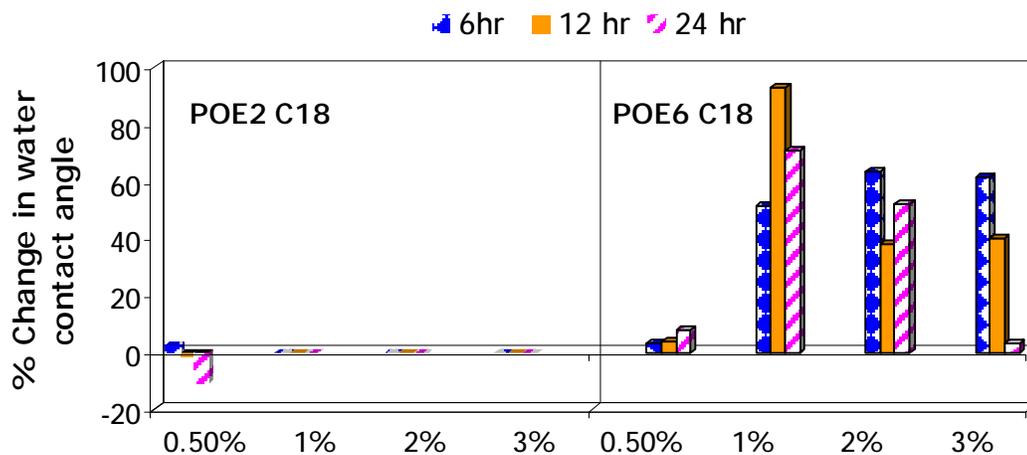


Figure 4.60: % Changes in the surface wettability after 6, 12, and 24hr water immersion for PP films modified with POE2C18 and POE6C18 additives using 0.5-3 wt%.

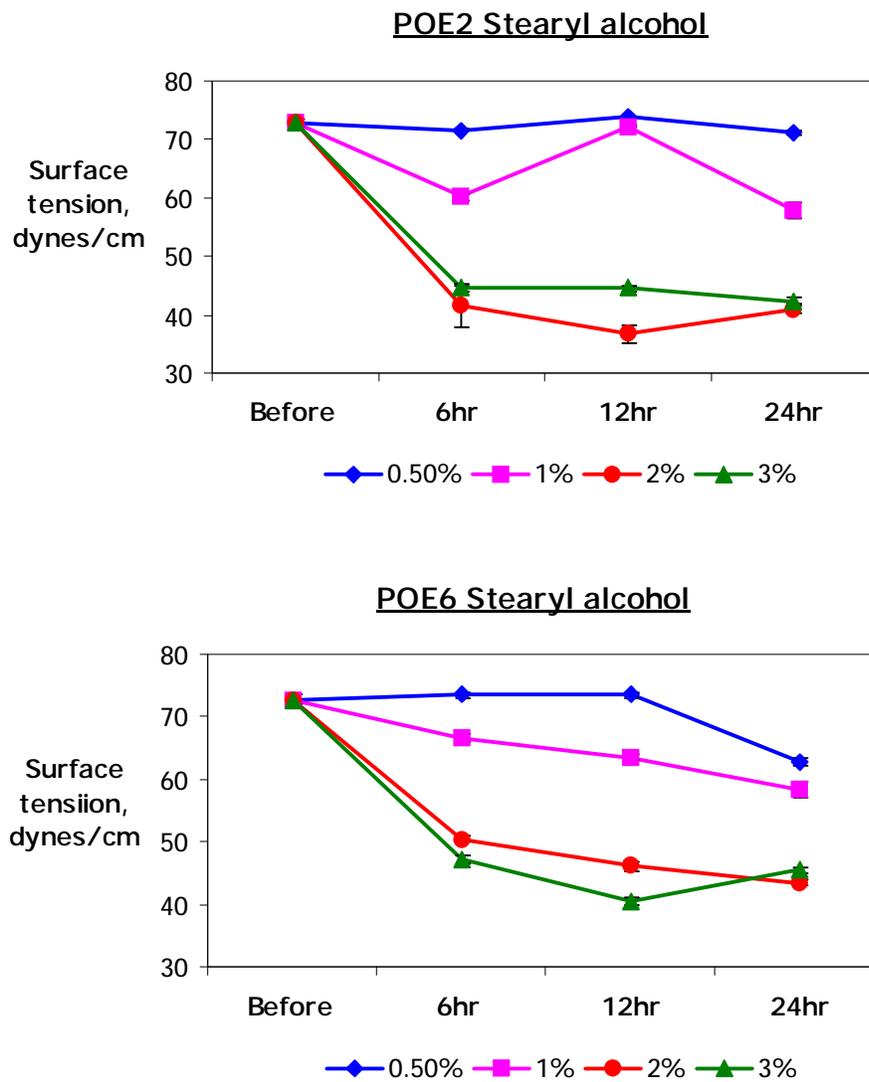


Figure 4.61: The surface tension (dynes/cm) of water before and after soaking of PP films modified with POE2C18 and POE6C18 additives using 0.5-3-wt% for 6hr, 12hr, and 24hrs.

Table 4.15: Advancing water contact angles of PP films modified with POE2C18 and POE6C18 additives using 0.5-3-wt%. Changes before immersion, after 6, 12, and 24hr water immersion and also after aging the water soaked films for week 2-3 water soaked samples. (Standard deviation (σ) is reported for measurements obtained from 10 water droplets).

Surface recovery – water immersion								
	Conc. in bulk (wt %)	Before	6 hr	Week 2-3	12 hr	Week 2-3	24 hr	Week 2-3
PP + POE2C18	0.5	84	86	85	83	84	75	77
		$\sigma=3$	$\sigma=3$	$\sigma=7$	$\sigma=4$	$\sigma=2$	$\sigma=9$	$\sigma=7$
	1	0	41	51	16	49	63	79
		$\sigma=0$	$\sigma=28$	$\sigma=11$	$\sigma=34$	$\sigma=7$	$\sigma=21$	$\sigma=7$
	2	0	0	0	33	0	0	0
		$\sigma=0$	$\sigma=0$	$\sigma=0$	$\sigma=36$	$\sigma=0$	$\sigma=0$	$\sigma=0$
3	0	31	0	0	0	0	0	
	$\sigma=0$	$\sigma=33$	$\sigma=0$	$\sigma=0$	$\sigma=0$	$\sigma=0$	$\sigma=0$	
PP + POE6C18	0.5	79	82	86	82	84	86	77
		$\sigma=5$	$\sigma=5$	$\sigma=2$	$\sigma=3$	$\sigma=3$	$\sigma=3$	$\sigma=3$
	1	44	67	58	86	80	76	78
		$\sigma=13$	$\sigma=13$	$\sigma=37$	$\sigma=2$	$\sigma=9$	$\sigma=12$	$\sigma=12$
	2	41	68	68	57	25	63	0
		$\sigma=9$	$\sigma=11$	$\sigma=5$	$\sigma=37$	$\sigma=8$	$\sigma=26$	$\sigma=24$
3	40	65	54	57	16	42	0	
	$\sigma=17$	$\sigma=17$	$\sigma=22$	$\sigma=24$	$\sigma=4$	$\sigma=21$	$\sigma=20$	

Table 4.16: Thermal Properties of Melt Additives and modified Polypropylene substrates with POE2C18 and POE6C18 additives using 0.5-3-wt% as revealed in their Heating DSC Scans.

Sample	T_m(°C)	T_m(°C)	T_m(°C)	T_m(°C)	c_c (%)
	(Melt additives)			(PP)	
POE2C18	4.02	26.32	53.27		
POE6C18	45.09				
PP Control				159.82	33.71
	PP + POE2 C18				
0.5 %			59.08	158.84	41.88
1 %			62.88	160.44	38.68
2%			44.97	159.46	42.68
3%			45.86	157.22	34.16
	PP + POE6 C18				
0.5 %	3.9	30.27	50.06	160.58	38.28
1 %			62.3	160.68	34.62
2%			39.01	160.05	34.68
3%			39.18	161.5	37.91

4.10. CHARACTERIZATION OF SPUNBOND POLYPROPYLENE NONWOVEN FABRICS WITH MELT ADDITIVES

Spunbond PP nonwoven fabrics were produced with select melt additives to investigate how surface modification with hydrophilic melt additive transfers to surface hydrophilicity in fabrics. A possible issue that might encounter when relating results obtained with film-based system to fiber-based system is the surface area to volume ratio. Fibers have greater surface area per unit mass of the materials than film and it increases as fiber diameter decreases. Moreover, high shear forces during spunbond nonwoven web formation produces high degree of orientation and crystallinity in the spun fibers unlike film extrusion [107, 108]. The segregation behavior and surface characteristics such as hydrophilicity are observed and compared with film results. The effect of web-bonding methods on the performance of melt additives and surface wettability was investigated. Additionally, the effect of melt additives on the fabric tensile strength is also reported.

4.10.1. Additive Segregation in Spunbond PP nonwoven Fabrics

The surface migration behavior of modified PP films and spunbond nonwoven fabrics extruded with POE6-Stearyl alcohol using additive concentration of 0.5-3-wt% characterized using X-ray photoelectron spectroscopy is illustrated in Figure 4.62. The dependence of additive migratory effectiveness on aging time was evaluated by monitoring the surface composition changes up until 4 months after extrusion.

The results in Figure 4.62 demonstrate gradual increase in the surface oxygen concentration in PP films with POE6-Stearyl alcohol gradually with time and additive concentration, while in spunbond fabrics even though considerable surface oxygen was found in fabrics with 2wt% of POE6C18, the aging effect was less pronounced. One must therefore speculate that

it is due to the high surface-to-volume ratio (S/V ratio (fiber) = $0.40\text{-}0.45 \mu\text{m}^{-1}$, S/V ratio (film) = $0.008\text{-}0.03 \mu\text{m}^{-1}$) and the crystalline orientation during fabric formation, the modification with melt additives is less effective in nonwoven fiber webs affecting the segregation phenomena.

4.10.2. Surface Wettability in Spunbond PP nonwoven Fabrics

Figure 4.63 shows the effect of surface modification with 0.5-2 wt% of POE6-Stearyl alcohol melt additive on wettability of PP films and spunbond nonwoven webs. Wettability is mostly affected by surface morphology and hydrophilicity at the surface of polymer. Increase in surface wettability of modified PP films is demonstrated with significant reduction in the water contact angles with sample aging. Characterizing wettability of nonwoven webs is a complicated matter since contact angle represents surface wettability only when substrate surface is smooth, which is not the case of nonwoven fabrics. Therefore, contact angle reported here is only apparent value affected both by surface energy and web pore structures. Modified PP spunbond webs exhibited high water contact angle, which agrees with additive migration tendency. Lower surface additive concentration obtained in webs combined with rough fabric surface results in high apparent contact angle. Again, contact angle results indicate fabric surface modification may require higher additive concentration to impart hydrophilicity [109].

The process differences that exist in the making of fibers and films cause the surface composition and characteristics, as well as morphology, of fibers and films, to be different. Accordingly, it was of fundamental interest to know what differences, if any, existed in the surface wetting behaviors of fibers and films produced from the same basic polymer, and how these could be explained by the differences existing in the physical and the morphological properties. Because surface morphology also affects the material's wettability, remarkable differences in the water contact angles of modified PP films and spunbond fabrics were observed. The modified spunbond fiber web has a much higher water contact

angle than the modified plane PP film due to the high surface roughness. Here the phenomenon is in agreement with the commonly known experience, i.e., for a hydrophobic material the contact angle increases with the surface roughness, while for a hydrophilic material the contact angle decreases with the surface roughness [94].

Also the analysis of dynamic water contact data (not shown here) indicated that the film had a much greater time dependent interaction with water than did the fiber. It is speculated that these differences in the behavior arose from the structural differences formed during processing, where the film structure, as compared to fiber, is less crystalline or had more voids. The values of crystallinity in the modified PP films and spunbond fabrics measured by DSC techniques discussed in the following section confirmed the latter result: the values being 35% in film (2wt% POE6C18) and 42% in fiber for PP sample with 2wt% POE6C18 additive.

4.10.3. Thermal Analysis (DSC) of Spunbond PP nonwoven fabrics

DSC was carried out to examine the crystallinity changes in the PP polymer by modification with nonionic surfactant additives. Melting enthalpy (ΔH_f) was obtained from area under a peak of DSC thermogram, and crystallinity was calculated from ΔH_f of 100% crystalline PP, 50 cal/g [76]. The results are summarized in the Table 4.17.

Under the processing conditions employed, a slight increase in crystallinity (χ_c) was observed for PP compounded and extruded with 2-wt% of POE6C18 even though the melting temperature (T_m) decreased. It can be explained by greater mobility of the polymeric chains with lower molecular weight as a consequence of presence of oligomeric additives and degradation. During the extrusion process, thermal or mechanical degradation occurs and there is a high concentration of entanglements that (due to the macromolecular nature of PP), restrict crystallization; the introduction of small molecular weight molecules and the release of strained or entangled sections of the macromolecules from degradation enables further

crystallization by the rearrangement of these freed macromolecular segments (χ_c increases). However, imperfections in crystals can result in lower melting temperatures, which is the case with spunbond PP spunbond web modified using 2% of POE6C18 additive.

4.10.4. Effect of Hydroentangling Process on Surface Hydrophilicity

The changes in the surface characteristics particularly surface wettability were also caused by the bonding methods that follow the spunbond web formation stage. Therefore, the effect of hydroentangling on the surface hydrophilicity of modified spunbond PP webs with 1-wt % (top chart) and 2-wt% (bottom chart) of POE6C18 was investigated using water contact angle measurements and presented in Figure 4.64. The amount of surface hydrophilicity recovered with sample aged over a 2-month time period is also shown in the Figure 4.64.

The topical hydrophilic finishes cannot survive the high-pressure water jets of hydroentangling, which effectively strips any finishes off the fiber. Therefore, it is highly desired for spunbond fabrics containing the nonionic additives to remain hydrophilic even after the impact of intense water jets during hydroentangling. Hydroentangling has resulted in marginal loss of surface hydrophilicity in 4-pass spunbond PP web with 2% POE6C18 additive. However, as demonstrated in the modified PP films with additives, for considerations under prolonged exposure to water results in additional segregation of additive to the surface leading to improved surface hydrophilicity, which is mostly the case observed in some spunbond fabrics containing 1- and 2-wt% POE6C18 additive. The water contact angles decreased for most hydroentangled samples (with the exception of 4-pass spunbond fabric with 2% POE6C18 additive). Aging the fabric samples (other than hydroentangled spunbond PP fabrics containing 2% POE6C18 additive) for a period of 1 month, during which time hydrophobic surface recovery was witnessed. On the whole 2% POE6C18 additive surfaces showed good recovery by significant decrease in contact angles with aging time.

4.10.5. Effect of Heat Calendering Process on Surface Hydrophilicity

The bonding process such as thermal bonding may expose the fibers to extreme conditions such as heat and high temperatures. It is well known that heat will facilitate the migration of the additives to the surface. Thus, heat exposure in the heat calendering process may lead to a higher concentration of the melt additives on the surface.

To effect of heat calendaring on surface hydrophilicity was investigated by passing the spunbond nonwoven webs between heated calendar rolls at a calculated speed and predetermined temperature under precise pressure. Figure 4.65 illustrates the changes in the surface hydrophilicity of heat calendered spunbond PP nonwoven webs containing 1-wt% and 2-wt% of POE6-Stearyl alcohol at temperatures of 100, 130, and 150°C. The heat-treated spunbond fabric samples were also monitored for changes in contact angle with aging time.

Application of heat helps in the blooming of additive to the surface resulting in increase in wettability of spunbond PP fabrics containing both 1-wt % and 2-wt% of nonionic POE6C18 additive unlike with modified PP films where heat treatment reduced surface hydrophilicity. Particularly, heat-treating the modified PP film containing 2-wt% of POE6C18 for duration of 3 hrs at 130°C resulted in complete wettability (Figure 4.66). Also behavior consistent with the film, the spunbond PP web containing 2wt% of POE6C18 under 130°C significantly improves the surface hydrophilicity by reducing the water contact angle from 120° (hydrophobic) to 0° (achieving complete wettability). Usually the higher the temperature, greater the loss of surface hydrophilicity except at 130°C, so the appropriate blooming acceleration temperature of additive segregation leading to complete wettability is 130°C. Surface wettability of spunbond fabrics with 2-wt% of POE6C18 is more sensitive to temperature changes compared to 1wt% of same additive. Also aging the samples for a almost a month's time lead to small reduction in the water contact angle, while the contact angle increased when the heat treated samples were aged for 2 months. This may be due to rearrangement of the additive molecules.

From my understanding, the remarkable changes in the surface wettability, as a result of samples (modified PP substrates, both films and spunbond fiber webs) heat-treated at 100, 130 and 150°C might be due the variations in crystallization behavior as the additive containing PP samples are cooled to room temperature after they have heat treated. The structural reorganization during heat treatment is almost the same for PP films (exposed to heat for 3hrs) and spunbond webs (passed through heat flat calendar rolls under specific pressure) as confirmed by complete wettability in heat-treated samples with 2wt% POE6C18 at 130°C.

It is well known fact that additives added to a polymer melt strongly influence the crystallization process. Many substances promote nucleation [110] as a result of which, significant changes in the morphology and the supermolecular structure of the polymer are observed. In several cases, additives result in different polymorphic forms of polypropylene being formed [111]. During extrusion (film or fiber spinning), the crystallization process occurs in a complex non-isothermal way under varying stress conditions. Under such conditions the crystallization process depends on the cooling rate and molecular orientation [112]. So a structure comprising of three phases is formed. The proportion of these particular phases, namely the amorphous phase, mesophase and crystalline phase, depends on the formation parameters as well on the kind of the additive used.

Earlier DSC thermal analysis has revealed slight increase in the PP crystallinity, which may be caused by recrystallization during processing. Also sample cooling following heat treatment may produce results for the levels of crystallinity in modified PP materials. The small increase in the PP crystallinity from DSC results suggests nucleating effect of crystalline additive components on PP. Therefore the anomalous segregation behavior of additive in PP is related specifically to the fine blend structure development at these temperatures [113].

The origin of the multiple and broad melting peaks in PP commonly observed during DSC analysis has been attributed to factors such as crystallization temperature [114-117], heating rate, orientation [116], the presence of different crystal modifications (α , β and γ -forms) and the transformation of the different structures [115, 118-120]. Other reasons for multiple melting in polymers include the reorganization of metastable crystals [119], different crystal sizes, lamella thickening and the formation of new (secondary) crystals through annealing of specimens [115, 118, 121].

Possible differences in the behavior of heat-treated materials at temperatures 100, 130, and 150°C can be attributed to the recrystallization and reorganization processes of the molecular chains during slow heating of a sample. Depending on the temperature, recrystallization (especially at 150°C in this study) includes partial or complete melting of crystals whereby deformed chain segments are replaced by a new set of undeformed molecular chains that nucleate and grow until the original chains are entirely consumed. The partially melted chain segment acquires mobility to rearrange and to attach in a more ordered configuration thereby improving the crystal structure. In comparison, reorganization is the structural changes of non-equilibrium crystals occurring in the sample in the solid-state (solid–solid transitions which occur at 100° and 130°C).

Therefore, as the PP/additive materials are cooled after heating at 100 and 130°C, due to the structural changes, the non-equilibrium crystals expel the trapped additive molecules not interacting with the crystal phase on heating such as through sliding diffusion. And 130°C is especially more advantageous for enhancing the diffusive mobility of the additive and this is true especially in PP with 2wt% of POE6C18.

4.10.6. Fabric Tensile Strength

The mechanical properties in the majority of PP homopolymers, apart from processing conditions, are influenced by their rheological and crystallization behavior. Both factors are

determined by the molecular structure: for instance, the chain structure or stereoregularity and the chain length or molar mass distribution (MWD) [122]. The degree of crystallinity in iPP is, thus, an important parameter that characterizes its physical and mechanical properties. PP polymers is compounded and extruded with oligomeric nonionic melt additives to enhance wettability. Filling a semi-crystalline polymer with low molecular weight molecules can influence its bulk properties (such as tensile properties) in different ways. In addition to the additive component properties, the mechanical characteristics of the modified PP polymer are influenced by the interactions between PP and additive molecules, morphology and properties of the interface, e.g., crystallite orientation and chain dynamics. [123-127] Moreover, the additives can influence the polymer crystallization, thereby increasing or decreasing the crystallinity. [127-129]. Therefore, the effect of melt additives on bulk mechanical properties of the web was investigated by measuring the tensile properties hydroentangled spunbond PP webs with different add-ons of POE6-Stearyl alcohol additive.

As spunbond nonwoven webs do not have much fiber integrity, the hydroentangled webs were tested for their tensile strength and Table 4.18 below shows the fabric breaking force of the PP Control and PP with 0.5-2-wt% of POE6C18 additives fabrics along the machine direction. We can see that there is no remarkable change in the tensile properties in the machine direction. It is evident that none of the modified fabrics show any reduction in their tensile properties. The inclusion of melt additives show little influence on the polymer crystallization as confirmed by the DSC thermal analyses and nonionic POE6C18 additive effectively enriched the PP surface and had less influence on the bulk property of the spunbond PP fabrics.

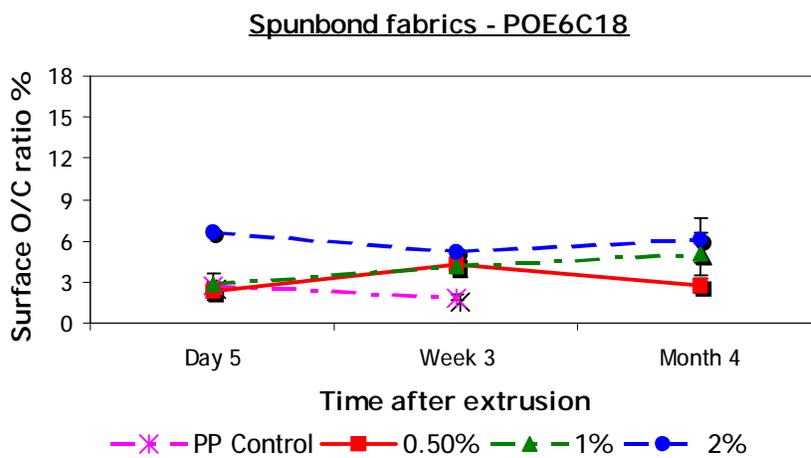
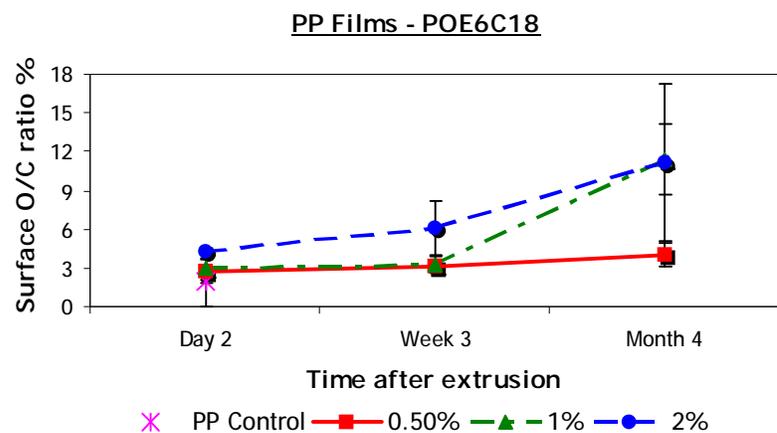


Figure 4.62: Surface O/C ratio % of PP films (top picture) and spunbond fabrics (bottom picture) modified using POE6 Stearyl Alcohol with additive concentration of 0.5-2 wt% determined using XPS over a 4 month time period after extrusion.

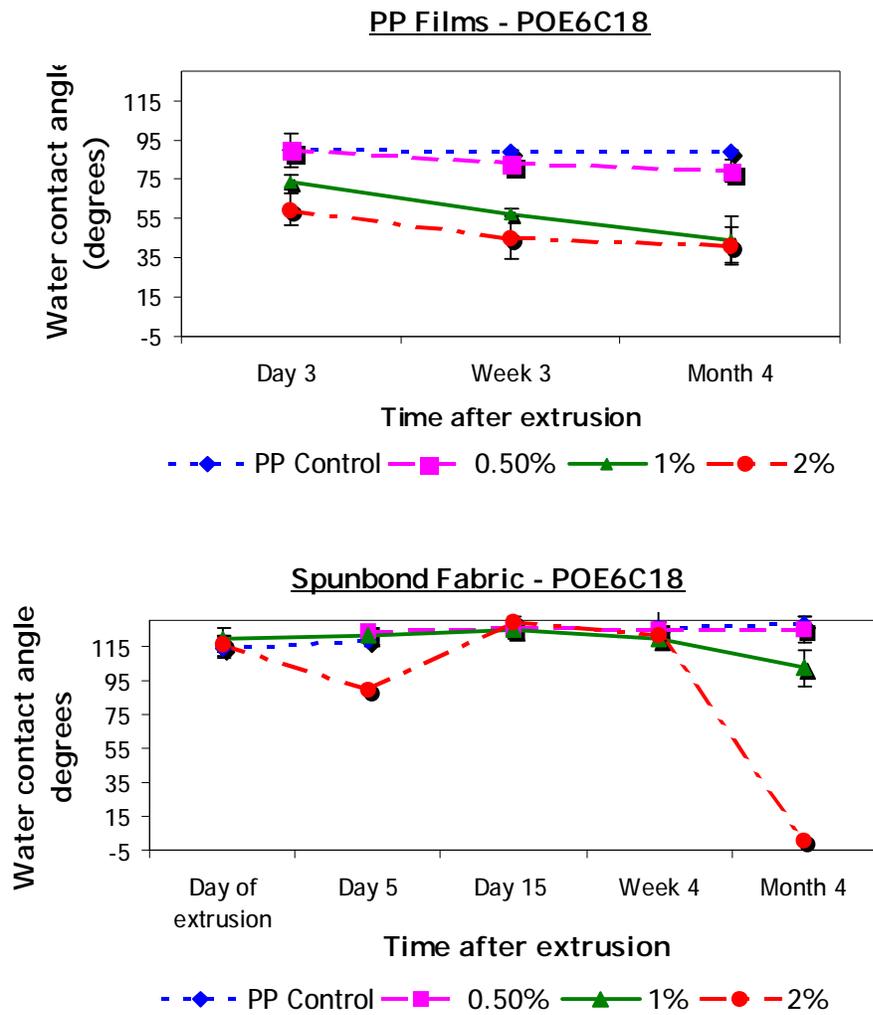


Figure 4.63: Advancing water contact angle measurements for PP films (top picture) and spunbond nonwovens (bottom picture) modified using POE6 Stearyl Alcohol with additive concentration of 0.5-2 wt% observed over a 4 month time period after extrusion.

Table 4.17: Melting temperatures and crystallinity of spunbond webs of PP control and PP modified using 2wt% POE6-Stearyl alcohol.

Sample	T_m (°C)	Crystallinity, C_c (%)
Spunbond PP Control fabric	166.1	41
Spunbond PP fabric + 2-wt% of POE6C18	161.9	42
PP Control film	159.8	34
PP film + 2-wt% of POE6C18	160.1	35

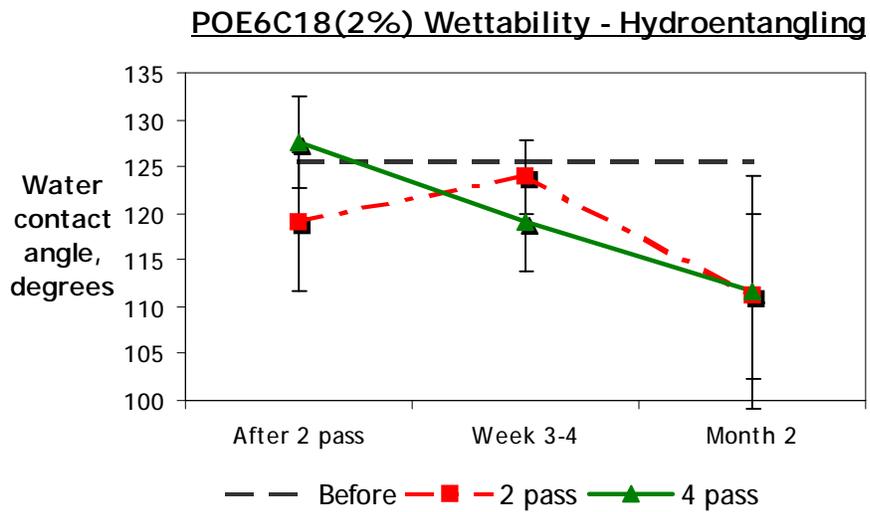
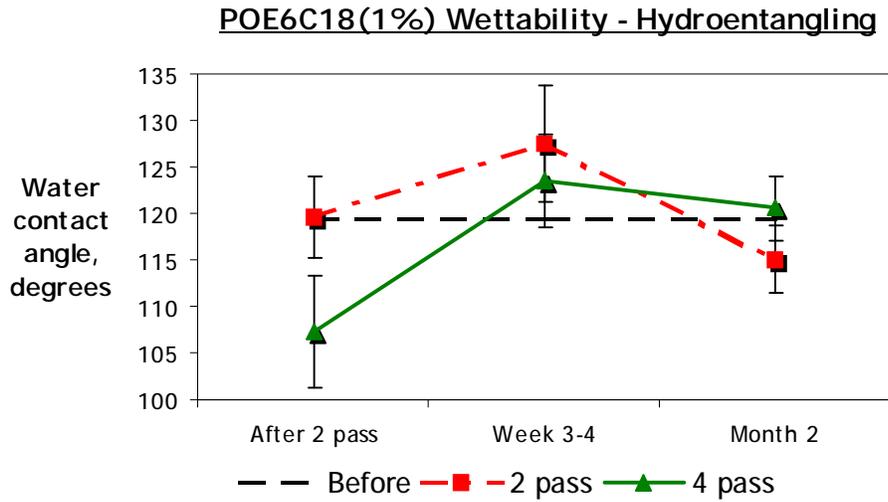
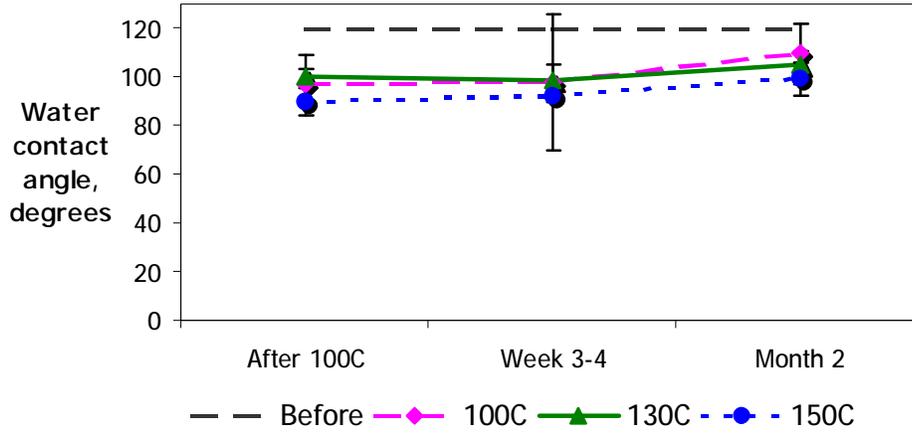


Figure 4.64: The advancing water contact angles measurements of spunbond PP fabrics modified with 1 wt % (top) and 2wt% (bottom) POE6C18 additive examined before and after hydroentangling under 2 pass and 4 pass conditions. Also depicts the changes in the contact angle of the hydroentangled webs after aging for a period of 2 months.

POE6C18 (1%) Wettability - Heat Calendered



POE6C18 (2%) Wettability - Heat Calendered

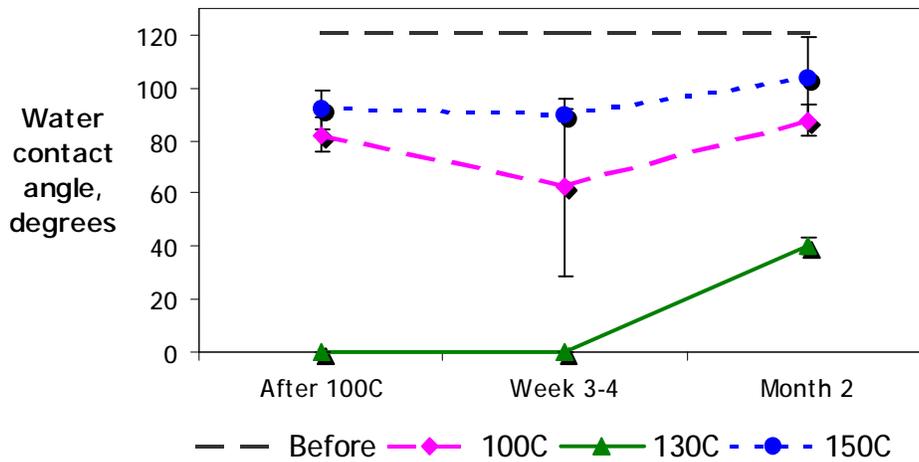


Figure 4.65: The advancing water contact angles measurements of spunbond PP fabrics modified with 1 wt % (top) and 2wt% (bottom) POE6C18 additive examined before and after heat-treating the webs at 100, 130, and 150°C. Also depicts the changes in the contact angle of the heat calendered webs after aging for a period of 2 months.

Heat Treatment - PP + 2-wt% POE6C18

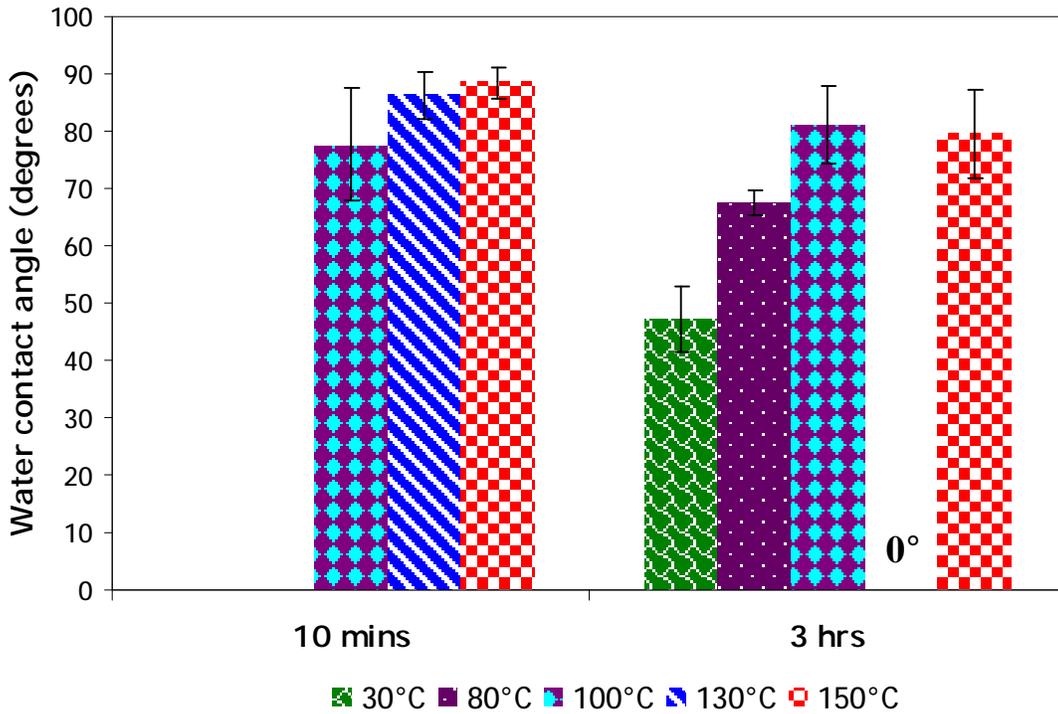


Figure 4.66: The advancing water contact angles measurements of modified PP films with 2wt% POE6C18 additive examined after heat-treating the films at 30°C, 80°C (for 3hrs), 100, 130, and 150°C (for 10mins as well as 3 hrs). The water contact angle of modified PP film with 2-wt% POE6C18 is 42°(σ=7.67).

Table 4.18: Mean breaking force tensile strengths of hydroentangled (4 pass) PP control and PP with 0.5-2-wt% of POE6C18 additive fiber web samples with their standard deviations.

Sample	Breaking force (lbf)
PP Control	11.62 (σ = 0.99)
PP + 0.5-wt% POE6C18	11.07 (σ = 1.37)
PP + 1-wt% POE6C18	12.32(σ = 0.93)
PP + 2-wt% POE6C18	14.01(σ = 1)

5. CONCLUSIONS

Polymer surface modification through the use of nonionic melt additives showed that various factors have strong influences on the surface formation, surface compositions and surface properties of the PP systems. These are amount of the additive used, type and nature (structure) of the additive, additive architecture, length and/or sizes of both hydrophobic and hydrophilic groups and their conformations, as well as their relative strength, represented by HLB (hydrophilic-lipophilic balance).

All of the above-mentioned key parameters showed significant effect on the surface properties as observed by their migration behavior and surface hydrophilicity. More specifically, the following conclusions were drawn from the experimental results:

- XPS analyses revealed surface enrichment of melt additives and this mostly lead to a hydrophilic surface by reducing the water contact angle over time.
- Melt additive surface concentration changes as a function of time indicated on-going migration behavior after extrusion. Surface activity of the modifying additive molecules and the extent of PP surface modification were interpreted in terms of additive molecular characteristics.
 - Hydrophilic chain length showed significant effect on the segregation behavior of the melt additives.
 - § Additives with shorter hydrophilic chain length (low HLB) lead to immediate surface enrichment but overtime higher surface additive concentration was found in melt additives with longer hydrophilic chains (high HLB).
 - § The hydrophobe group structure and hydrophilic end group type of the additive does seem to have a strong influence on the surface properties.

- Quantitative XPS alone cannot fully explain hydrophilicity of the surface because of the differences in the analytical depth and changes in the surface when in contact with testing fluid. ToF-SIMS analysis enabled identification of the melt additive distribution on the top surface, and contact angle test relaxation showed alteration of surface structures when substrate contacted with water.
 - Substantial reduction in the water contact angles over time indicated that the increase in wettability was dependent on the polarity of the modified surface achieved through melt additive surface segregation. In particular melt blending additive POE2-Stearyl Alcohol considerably reduced the PP surface hydrophobicity by complete wetting of the surface due to reorientation of the hydrophilic segment on contact with water. Top surface additive structure analyzed using ToF-SIMS has directly shown to affect the surface properties and has good correlation with the water contact angle measurements.

- Based on the water durability tests, the following conclusions were drawn from the analysis: Immersion into the water changes surface properties and this depended on the type of melt additive and the immersion time.
 - Realignment of additive molecules and additional (or increased) migration on water contact in low HLB melt additives such as POE2-Stearyl alcohol, POE4-Stearyl Alcohol, and POE2-Stearyl Amine increased the melt additive surface enrichment and reduction in the water contact angle. This leads to a hydrophilic surface by reducing the water contact angle over time.
 - In high HLB melt additives for example, with NP4, NP6 and POE6-Stearyl Alcohol, reduction in the melt additive surface enrichment resulted in the increase in the water contact angle and decreased surface hydrophilicity due to loss of surface additive molecules.
 - Reduction in the surface tension of water confirmed loss of surface additive molecules.
 - Aging of sample altered surface properties after water immersion.

- As for the effect of concentration, the minimum additive concentration to affect changes in the surface properties is 1 wt% and surface wettability enhanced with increasing concentration. To be more specific PP with POE2C18 additive is highly sensitive to changes in the additive concentration. It has highest degree of migration over time compared to PP films containing POE6C18 additive. With only as low as 1 wt% of POE2C18, almost complete wettability is obtained in just about 3 weeks time after extrusion. Improved hydrophilicity is achieved in samples with POE6C18 additive as the concentration is increased from 1-3 wt%.
- Surface characteristics of spunbond PP nonwoven fabrics containing melt additives shows that:
 - Low additive surface enrichment and high water contact angles in fabrics is largely attributed to their physical structures including molecular packing and orientation, crystallinity, and surface morphology.
 - High additive add-on is necessary in fabrics to bring out the level of surface wettability.
- The surface wettabilities of spunbond fabrics containing the melt additives subjected to bonding method such as hydroentangling showed that the use of high-pressure water jets in the hydroentangling process did not significantly change the surface hydrophilicity, but surface wettability improved with sample aging through further additive migration from bulk.
- Thermal treatment at increased temperatures for example heat calendaring expedited the additive blooming to the surface causing significant improvement in surface wettability. Thermal activation of the molecular chains in the amorphous regions resulted in changes in the crystallinity, crystalline structure and morphology, which significantly affected the segregation and surface wettability. Based on the heat treatment data, PP materials (both films and fabrics) containing 2 wt% of POE6C18

additive subjected to 130°C is an ideal combination to bring complete wettability by segregation of polar functional molecules.

- DSC thermal analysis of the modified PP films showed that the incorporation of melt additives does not influence the polymer bulk properties through little changes in the T_m and PP crystallinity. Additionally the fabric tensile properties remained unchanged even with increase in the concentration of the additive.

Knowledge of these effects can be ultimately used to establish principles for additive selection and for optimizing processing conditions to enhance the transport of surface functionalizing additives in polymeric hosts.

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APPENDICES

Appendix A: Surface chemical composition analysis (XPS)

To gain greater insight into the surface composition of films of PP blended with the 2-wt% of the hydrophilic melt additives, high-resolution spectra were successively acquired in the regions of C1s and O1s core levels.

A detailed analysis of the C1s and O1s spectra of the PP films modified with 2-wt% of nonionic melt additives examined using XPS on month 4 after extrusion summarized in the Table A.1 reveals multiple components, which are related to atoms in different chemical environments. Both the carbon and the oxygen signal could be synthesized by two or three components in accordance with the chemical structure of the film-forming compounds. As an example, carbon and oxygen signals of the PP films modified using 2-wt% of POE4C18 and DGMS additives are displayed with their components in Figures A.1 and A.2.

Following the procedure described in a previous work [130], the C1s and O1s signal were deconvoluted into Gaussian peak components and evaluating the areas of these peaks allowed to obtain more quantitative information on the surface segregation of additive molecular segments as reported in Table A.1. The peak fitting and knowledge concerning relative peak positions in the C1s and O1s signals were obtained from results reported in the literature [130, 131].

In particular C1s spectra of the PP containing POE4C18 additives shows three main peaks; one centered at about (C-C/C-H) 284.8 eV, is associated to hydrogenated blocks while the less intense second, and third which are centered at about 286.1 eV (C-O), and 286.8 eV (C=O) is related to carbon atoms bonded to oxygen in the POE (polyoxyethylene, CH₂CH₂O) segments in the additive or surface contamination or oxidation of carbon atoms as expected in the PP polymer [88, 89]. Likewise, concerning oxygen, the spectra also consists of three peaks; one, centered at about 533.6 eV (O-C) is assigned to oxygen atoms in polyoxyethylene chain segments in the additive and the second, centered at about 532.4 eV

(O=C), is ascribed to oxygen associated with oxidation of the methyl groups in the PP polymer, and the third, centered at 531.9 eV (O-C=O) is related to the carboxylic groups found in acids and esters.

Considering the chemical structure of the PP polymer and alkyl ethoxylate melt additives (i.e. POE's) we could assign signals at 286.1 eV (C-O) originating from the ethylene oxide units and 286.8 eV (C=O) to the surface oxidation of the methyl groups from the PP polymer backbone or the hydrocarbon part of the additive. In accordance with that, the chemical state, and consequently, the binding energy corresponding to the ether groups of the EO units and the oxidized methyl groups of the polymer (and/or additive) are 533.6 eV (O-C) and 532.4 eV (O=C) respectively. So the chemical composition of PP modified with the POE melt additives is well reflected in the quantitative XPS analysis.

PP samples with additives POE4C18 and POE6C18 display a significantly increased intensity corresponding to C-O and C=O at 286.1 eV and 286.8 eV respectively compared to PP sample with POE2C18. Qualitatively speaking even though these additives are chemically similar they largely vary in their elemental composition particularly the weight % of the O/C, which may have resulted in higher oxygen (or additive) enriched surfaces as indicated by XPS results. PP film modified with DGMS additive shows a relatively small amount of the O-C=O group characteristic of esters as found in glycerol monostearates. More importantly, surface enrichment of the additives is also driven by factors such as the molecular size (or weight) of the additive, solubility parameter differences and the HLB (hydrophile-lipophile balance), which have been discussed in detail in section 4.3.2.

As previously discussed the surface segregation of nonionic melt additives segments occurs because of the thermodynamic immiscibility of additives in PP and the high surface enrichment (segregation) of additive initially after extrusion is driven by the low molecular weight (size of hydrophilic segment) of the additive whereas the energetic balances given by miscibility changes drives the high molecular weight additives to the surface with time.

Table A.1: Relative composition of various components (Atomic %) of C1s and O1s peaks of XPS spectra obtained on Month 4 after extrusion from modified PP polymer films.

Sample	C1s (type)				O1s (type)	
	C-C	C-O	C=O	O-C=O	O=C	O-C
	284.8 eV	286.1 eV	286.8 eV	531.9 eV	532.4 eV	533.6 eV
PP Control	88.57	1.20	-	-	4.17	-
PP + POE2C18	90.13	0.03	2.17	-	1.82	-
PP + POE4C18	82.07	0.39	7.49	1.06	5.02	3.96
PP + POE6C18	85.65	0.05	4.44	-	0.58	1.07
PP + POE3C12/C13	89.36	4.46	-	-	4.20	-
PP + NP2	-	-	-	-	-	-
PP + NP4	82.45	-	6.91	-	5.20	-
PP + NP6	56.16	-	5.77	-	3.78	7.64
PP + DGMS	78.46	-	7.19	0.01	7.67	-
PP + POE2Amine	89.12	-	4.74	-	6.02	0.12
PP + PEG400- C12Diester	88.77	-	3.08	-	2.47	-

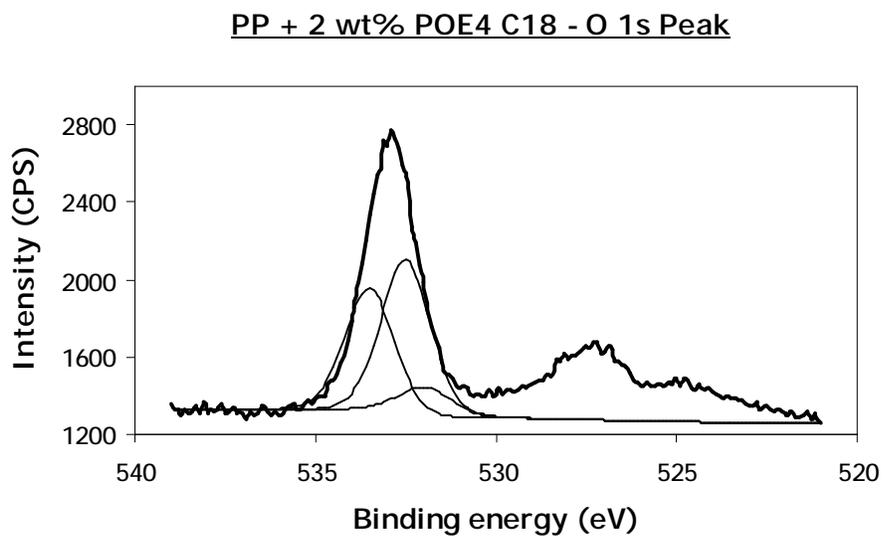
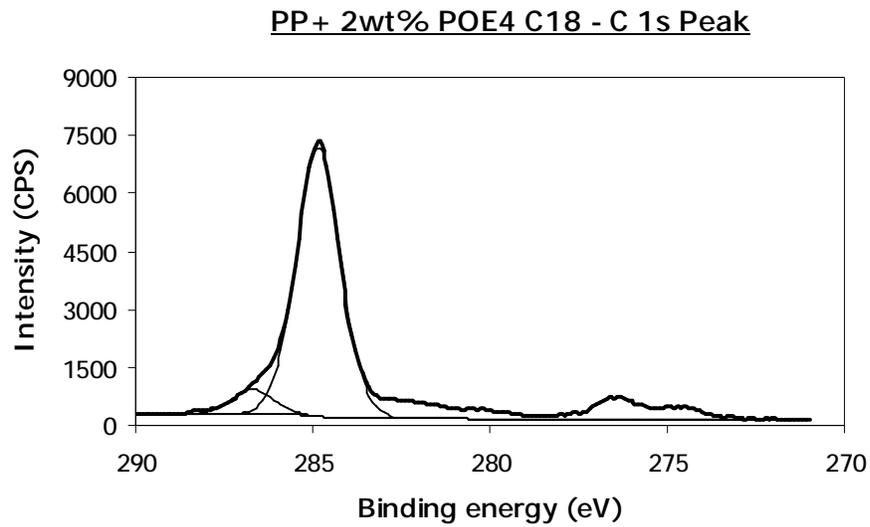


Figure A.1: An example of high resolution C 1s (top) and O 1s (bottom) XPS signal deconvoluted for PP film melt blended with 2 wt% of POE4-Stearyl alcohol additive.

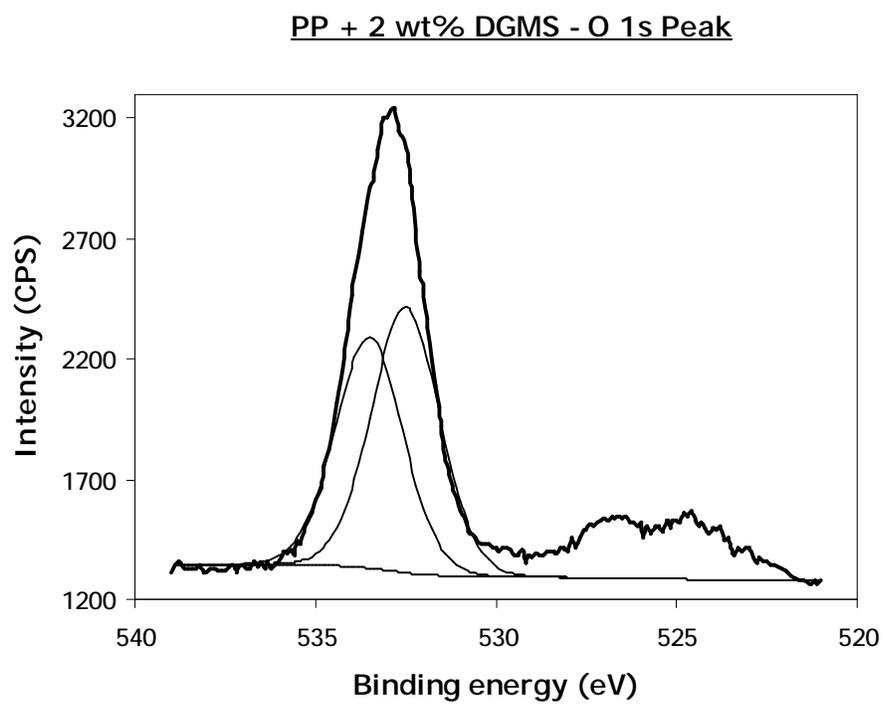
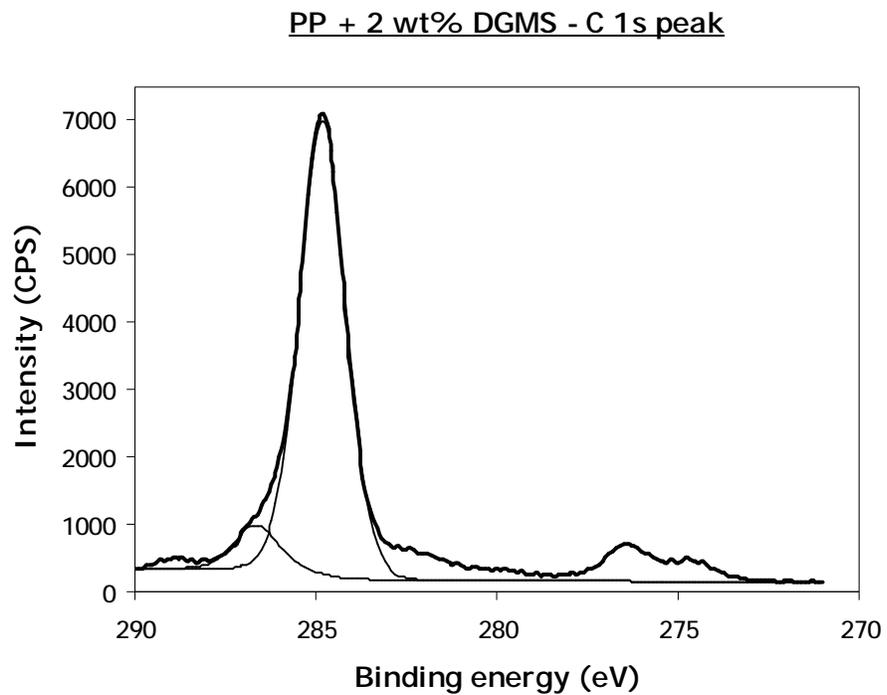


Figure A.2: Example of high resolution C 1s (top) and O 1s (bottom) XPS signal deconvoluted for PP film melt blended with 2 wt% of Distilled glycerol monostearate.

Appendix B: Contact Angle Hysteresis in the Wetting of Polypropylene (PP) Films Modified with Nonionic Melt Additives

Contact angle hysteresis is the difference between the measured advancing and receding contact angles, i.e. $H = \theta_a - \theta_r$. Advancing and Receding contact angles are obtained from the contact angle measurements, which are measured when the three-phase line is in controlled motion. Then the advancing angle is the contact angle when the three phase line is moving over and wetting the surface or "pushing" away the gas phase, while the receding angle is the contact angle when the three phase line is withdrawn over a pre-wetted surface or "pushing" away the liquid phase. The contact angle can be determined in several ways and the best technique is perhaps the Wilhelmy plate technique performed with a Tensiometer. The advancing and receding contact angles determined in this study are obtained by capturing the image of liquid water droplet dispensed on a film placed on the goniometer tilted to a specific angle (Figure B.1).

Advancing contact angles being greater than the receding leads to wetting hysteresis. Several factors for example, surface contamination, surface roughness, and time-dependent interactions of the liquid with the solid surface have been mentioned as being responsible for this phenomenon [132, 133]. The study of hysteresis on surfaces that are not homogeneous showed that existence of domains on the surface present barriers to the motion of the contact line. Domains in chemically heterogeneous surfaces represent areas with different contact angles. For example when wetting with water, hydrophobic domains will pin the motion of the contact line as the liquid advances thus increasing the contact angles. When the water recedes the hydrophilic domains will hold back the draining motion of the contact line thus decreasing the contact angle. Therefore, when testing with water, advancing angles will be sensitive to the hydrophobic domains and receding angles will characterize the hydrophilic domains on the surface. And in situations where surface roughness generates hysteresis the actual microscopic variations of slope in the surface create the barriers, which pin the motion of the contact line and alter the macroscopic contact angles [134, 135].

The hysteresis values for the polypropylene films modified with nonionic melt additives are given in Table B.1. Among these materials, PP films containing the melt additives had the highest hysteresis (except in PP films with POE2C18 and NP4 additive) and PP control had the lowest value. The relatively high values of PP films modified with additives reflect their ability to absorb/adsorb water molecules. A material which either interacted with a fluid spontaneously or did not interact much with it even after a period of contact will usually show a low value of hysteresis, which is exactly the case observed in PP films with POE2C18 & NP4 additives, and, PP control film with contact angle hysteresis of 'zero' and 3.44 respectively. A low value for polypropylene indicated that the surface was composed of hydrocarbon entities and, therefore, had little if any attraction for water [132, 136]. On the other hand, a material, which had the potential to interact but required contact with fluid over a length of time, should usually give a high value and this is witnessed in some PP films with nonionic melt additives. Chemical composition, molecular packing and orientation, and surface morphology were the factors expected to affect the nature and the speed of interaction.

The hysteresis values for the polypropylene films modified with 0.5-3-wt% of POE2C18 and POE6C18 nonionic melt additives determined from the dynamic water contact angle measurements are given in Table B.2. Among these materials, PP films containing the higher additive bulk concentration melt additives showed the least hysteresis for POE2C18 surfaces indicating spontaneous interaction with the water droplet and relatively higher hysteresis in POE6C18 surfaces suggesting slow interaction of surface with the fluid.

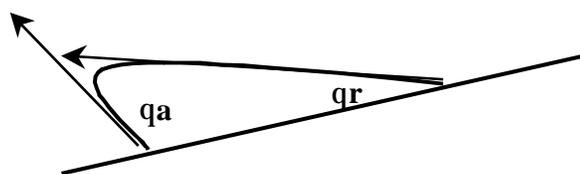


Figure B. 1: Advancing and Receding contact angles

Table B. 1: Contact angle hysteresis of surface modified PP films with the following nonionic melt additives estimated after 18 months from extrusion.

Sample	$q_{\text{advancing}}$, degrees	q_{receding} , degrees	Hysteresis, $H = (q_{\text{advancing}} - q_{\text{receding}})$
PP Control	85.49	82.05	3.44
PP_NP2	87.29	81.85	5.43
PP_NP4	0	0	0
PP_NP6	67.39	53.16	14.23
PP_POE2C18	0	0	0
PP_POE4C18	49.39	32.34	17.05
PP_POE6C18	36.57	24.72	11.85
PP_POE3C12/C13	62.89	49.61	13.28
PP_DGMS	85.90	79.66	6.23
PP_POE2Amine	63.34	54.16	9.18
PP_PEG400C12Diester	94.12	86.43	7.68

Table B.2: Contact angle hysteresis of surface modified PP films with the 0.5-3wt% of POE2C18 and POE6C18 additives.

Sample		Q _{advancing} , degrees	Q _{receding} , degrees	Hysteresis, H = (Q _{advancing} - Q _{receding})
	0.5 %	90.69	82.60	8.1
PP +	1 %	41.64	27.30	11.5
POE2 C18	2 %	0	0	0
	3 %	0	0	0
	0.5 %	83.74	67.93	15.8
PP +	1 %	52.22	41.93	10.3
POE6 C18	2 %	40.16	27.64	12.5
	3 %	44.57	34.41	11.4

Appendix C: Surface Energy of Modified Polypropylene Substrates

A more elaborate analysis is required to characterize the thermodynamics of the solid surface. One such characteristic parameter is the surface free energy of the solid substrate. The interfacial or surface tension arises from an imbalance in forces of the molecules at the interface. Since different molecular structures lead to various types of intermolecular interactions, sources of surface tension are not a single factor. As a matter of fact, it is a combination of different surface energy components induced by various molecular interactions. Various methods are used but the same basic principle applies for each. The solid is tested against a series of liquids and contact angles are measured. Different approaches are mainly used for determining the energy of solid substrates Fowkes [137] proposed that the surface tension of a material could be broken down into separate components originating from different kinds of intermolecular forces:

$$g = \sum_j g^j = g^{LW} + g^{AB} \dots\dots\dots (C.1)$$

Components are:

- Lifshitz-van der Waals Interactions component (Dispersion component or nonpolar components) γ^{LW} : van der Waals interactions are general attractive interactions between a pair of neutral atoms, and are universal interactions between atoms or molecules.
- Polar or Acid-base interactions γ^{AB} : The interactions between electron donors and electron-acceptors. However, electron-acceptor (Lewis acid) and electron-donor (Lewis base) interactions are essentially asymmetrical, so polar component can be divided into two components, γ^+ (acidic or electron-acceptor component) and γ^- (basic or electron-donor component). Then, $g^{AB} = 2\sqrt{g^+g^-}$

Even though surface energy of the substrate is one good indicator of surface hydrophilicity, it is necessary to obtain individual surface energy component to explain water-polymer interactions. It is possible that two materials have same surface energy but one can be polar and one can be non-polar. Interfacial tension with polar liquid (water) of those two materials will not be the same.

Surface energy of PP without melt additives consists of only LW component. We expect the presence of the melt additives to introduce the polar component of surface energy in PP and it will reduce water-polymer interfacial tension and reduces contact angle. Surface energy of the PP-additive films and their individual components can be calculated by following method.

The interfacial tension between solid-liquid can be written

$$g_{SL} = g_{SL}^{LW} + g_{SL}^{AB} = g_L^{LW} + g_S^{LW} - 2\sqrt{g_L^{LW} g_S^{LW}} + 2\left(\sqrt{g_S^+ g_S^-} + \sqrt{g_L^+ g_L^-} - \sqrt{g_S^+ g_L^-} - \sqrt{g_S^- g_L^+}\right) \dots\dots\dots (C.2)$$

Fowkes and Van Oss et al.[137] showed the free energy change due to Lifshitz-van der Waals interaction and acid-base interactions, ΔG_{SL} , by wetting or adhesion can be written as;

$$\Delta G_{SL} = g_{SL} - g_S - g_L = -2\sqrt{g_S^{LW} g_L^{LW}} - 2\sqrt{g_S^+ g_L^-} - 2\sqrt{g_S^- g_L^+} \dots\dots\dots (C.3)$$

By Young's equations, ΔG_{SL} is also,

$$\Delta G_{SL} = -g_L(1 + \cos q) \dots\dots\dots (C.4)$$

Using, OCG (Van Oss-Chaudhury-Good) equations for relationship between solid and liquid surface energy and its individual components and contact angle gives us,

$$(1 + \cos \theta) \gamma_L = 2 \left(\sqrt{g_s^{LW} g_L^{LW}} + \sqrt{g_s^+ g_L^-} + \sqrt{g_s^- g_L^+} \right) \dots \dots \dots (C.5)$$

Contribution of each component to total surface tension can be measured by contact angle values of three different liquids, which have known surface energy of each component and solving equation (28). Also Wu [30] utilized a similar approach but used a harmonic mean equation to sum the dispersive and polar contributions. Contact angles against two liquids with known values of γ^{LW} and γ^P are measured. The values for each experiment are put into the following equation;

$$(1 + \cos \theta) \gamma_L = 4 \left(\frac{g_L^{LW} * g_S^{LW}}{g_L^{LW} + g_S^{LW}} + \frac{g_L^P * g_S^P}{g_L^P + g_S^P} \right) \dots \dots \dots (C.6)$$

where γ_L refers to surface tension (surface free energy), the subscripts L and S refer to liquid and solid, and the superscripts lw and p refer to dispersive and polar components. You then have two equations with two unknowns and can solve for γ_s^{LW} and γ_s^P .

Examples of some of the known liquids surface energy and polypropylene surface energy are given in Table C.1 with their individual surface tension components.

In the present study, thermodynamic parameters such as the surface energy of the modified PP substrates was determined from measured contact angles and surface polarities by using two liquids of known surface energies such as water and glycerol with the help of the Harmonic mean equation given in equation C.6.

Polypropylene is a highly non-polar material, and from the earlier observations, melt blending of PP with the melt additives and subsequent migration of the additive to the polymer surface has altered the surface composition by increasing the polar amount of oxygen groups, which significantly improved the surface wettability with certain melt

additives. With the help of Harmonic mean equation, thermodynamic parameters, such as the surface tension (γ) of the modified PP substrates was estimated from measured contact angles and surface polarities by using two liquids of known surface energies such as water and glycerol deposited on the PP films.

The surface tension (γ) of a material is a combination of different surface energy components induced by various molecular interactions resulting from both nonpolar (dispersive, γ^D) and polar interactions (γ^P). Surface energy of PP without melt additives comes equally from the dispersive and nonpolar components. The introduction of the melt additives has greatly increased the polar component of surface energy in PP as shown in Table C.2 and this promoted wetting of the polymer surface by reducing the water-polymer interfacial tension resulting in the reduction in the water contact angle.

Melt blending of additive with the polypropylene polymer introduced a wide variety of oxidized functional groups onto the surface of the treated polymer. The variation in the polar contribution to the surface energy suggests that there may be different chemical species introduced onto the surface depending on the additive. These oxidized functional groups mostly included C-O, C=O, and O-C=O, as examined using XPS analysis described in section 4.3.2 by curve fitting of high resolution C 1s and O 1s peaks, and they are responsible for the change in the polymer surface properties.

Table C.1: Liquids and PP surface energy and its individual component contributions [137]

	g	g^{LW}	g^{AB}	g^+	g^-
Polypropylene	25.7	25.7	0	0	0
Hexane	18.4	18.4	0	0	0
Cyclohexane	25.5	25.5	0	0	0
Benzene	28.9	27.1	0	0	2.8
Ethanol	22.4	18.8	2.6	0.019	68
Ethylene glycol	48.0	29.0	19.0	1.92	47.0
Glycerol	64.0	34.0	30.0	3.92	57.4
Water	72.8	21.8	51.0	25.5	25.5

Table C.2: The total surface energy (γT), and its polar γ^p and dispersive γ^d components, of PP control and surface modified PP films with the nonionic melt additives.

Sample	g^D (dynes/cm)	g^P (dynes/cm)	$g^{Total} = g^D + g^P$
Polypropylene (PP)	11.77	12.46	24.23
PP_POE2C18	16.45	57.49	73.94
PP_POE4C18	9.05	42.46	51.51
PP_POE6C18	6.39	54.01	60.40
PP_POE3C12/13	-1.64	105.20	103.56
PP_POE2AmineC18	-4.51	105.18	100.68
PP_DGMS	1.46	36.98	38.43
PP_PEG400C12	4.55	25.93	30.48

Appendix D: Elemental Composition using Scanning Electron Microscopy – Energy Dispersive X-ray Analysis (SEM-EDS)

SEM-EDS measurements were carried out in Hitachi S-3200N scanning electron microscope. An Oxford Isis EDS system was used for the elemental analysis and a SiLi detector with an accelerating voltage of 20 keV range is used. Also for surface and cross-sectional elemental mapping, a Robinson backscatter detector is utilized. In scanning electron microscopy, (SEM) an electron beam is scanned across a sample's surface. Interaction of the primary electron beam with atoms in the sample causes shell transitions, which result in the emission of an X-ray. The emitted X-ray has an energy characteristic of the parent element. Detection and measurement of the energy permits elemental analysis (Energy Dispersive X-ray Spectroscopy or EDS). EDS can provide rapid qualitative, or with adequate standards, quantitative analysis of elemental composition with a sampling depth of 10-15 μm . These X-rays were also used to obtain maps or line profiles of the surface and the cross-section, showing the elemental distribution in a sample surface.

The SEM-EDS method is much less surface selective technique than XPS, because analysis depth is three orders of magnitude greater than XPS. Depending on the nature of the material it analyzes the top 10-15 μm of the polymer surface, which is too deep to relate to contact angle information. However, it can provide valuable information of the melt additive distribution in the polymer.

Composition and Melt additive Distribution in PP films containing 2-wt% of nonionic additives

Surface examination of the modified PP substrates using SEM-EDS revealed the existence of 'C' and 'O' elements as observed in the Energy-Dispersive X-ray line spectra. Table D.1 summarizes the O/C Mole % as identified by SEM-EDS and XPS analysis. The smaller mole percentage of the O/C reported from XPS analyses compared to EDS is due to the different

depths at which each response is obtained. Comparison of the O/C mole % obtained from XPS and EDS analyses indicated higher surface enrichment of the additives for PP modified with POE4C18, POE6C18 and D-GMS, and, present study using SEM-EDS suggests to an enriched POE segment away from surface. The mole % from SEM-EDS generally includes contribution from the top few layers of the subsurface and the analysis depth for EDS is three orders of magnitude higher than XPS. The mole % for POE6C18 and DGMS from SEM-EDS analyses is smaller than that obtained using XPS, which indicate hydrophilic ethoxylate group in melt additives are surface concentrated. Higher O/C mole % obtained with SEM-EDS analysis in POE2C18, and POE4C18 additives than what is obtained with XPS analyses indicates high concentration of additives in sub-surface. These higher concentrated subsurface melt additives may be responsible for high contact angle relaxation when contact with water.

However, in SEM-EDS analysis, 'C' and 'O' elements are detected below 1 KeV and anything obtained below 1 KeV suggests a non-linear response and is not truly representative of the sample. The slight deviation in the results from XPS and SEM-EDS may be due to insufficient charge neutralization associated with non-conductive samples such as PP polymer. The percentages indicated below represent only the atomic percents of elements detected in 2 individual scans and not the atomic percent present in the sample.

The back-scattered electron images (BSE) of both the surface and cross sections of films of PP Control and PP modified using POE (n=2, 4, 6) C18 melt additives is shown in Figure D.1. The PP/additive mixture is fairly homogeneous and varies somewhat in appearance from sample to sample as shown below. Particles rich in elements such as carbon and oxygen are shown in red and green colors respectively in the middle and right section of the images. The origin of non-uniformity in the cross-sectional surface features and elemental distribution are a result of the sectioning of the sample using a razor blade during sample preparation.

Composition and Melt additive Distribution in PP films containing 0.5-3 wt% of POE2C18 and POE6C18 additives

Surface examination of the PP substrates modified with 0.5-3 wt% of POE2C18 and POE6C18 additives using SEM-EDS revealed the existence of 'C' and 'O' elements as observed in the Energy-Dispersive X-ray line spectra during the experimental run. Figure D.2 and Table D.2 shows a summary of the chemical composition (O/C Mole %) determined by XPS and SEM-EDS analysis. The analytical depth for SEM-EDS is about 10-15 μm of the polymer surface (perhaps subsurface), which is 3 orders of magnitude higher than that for XPS, so information obtained from both these methods is utilized to provide an understanding of the melt additive distribution from bulk to the surface in the modified PP polymer.

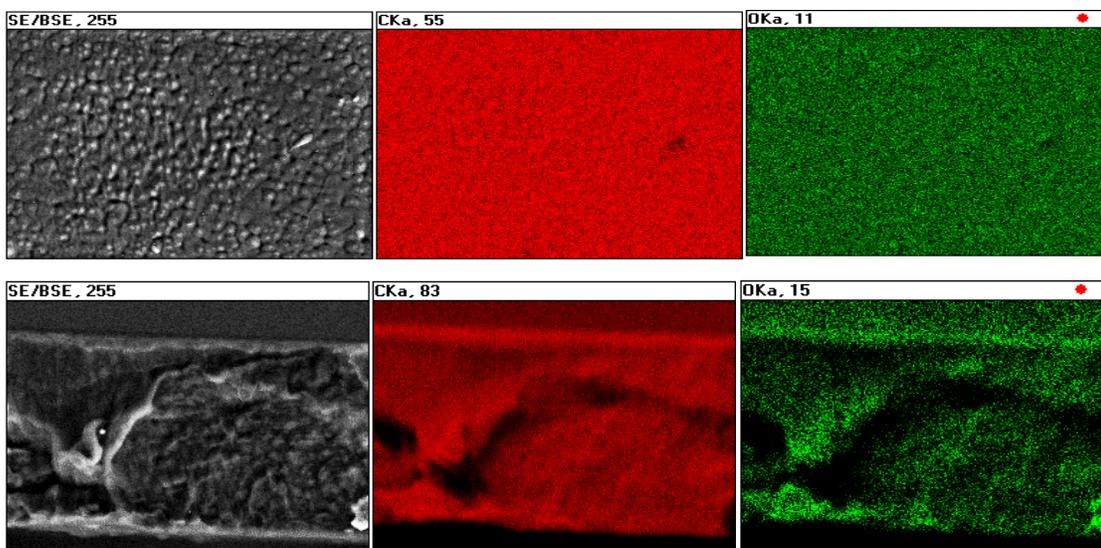
As shown in Figure D.2, PP control (w/o additive) has the same amount of oxygen on the surface as well as in the subsurface) indicating similar composition through the polymer, which may be due to presence of added impurity/additive. In PP samples with 0.5 wt % POE2C18 additive, surface (conc. too low) and subsurface oxygen composition didn't change, but an increased surface oxygen content (surface migration of additive) over bulk was observed with both 1 wt % and 2 wt% additive, while with 3 wt% an equal amount of oxygen was detected both within the top few monolayers of surface and in the subsurface. A very similar behavior was observed in PP samples with POE6C18 additive, where surface oxygen composition was relatively higher over the bulk in samples with 0.5 and 1 wt%, whereas in PP samples with 2 and 3 wt% additive, fairly equal amount of oxygen was found both on the surface and in the subsurface.

Comparison of oxygen composition from XPS with the SEM-EDS measurements suggests high enrichment of POE segment on the surface in PP samples with 1- and 2-wt % POE2C18 additive, and, rather high concentration of hydrophilic ethoxylate group away from surface in (sub-surface/bulk) in PP samples with 0.5-3 wt% POE6C18 melt additive. This may be the

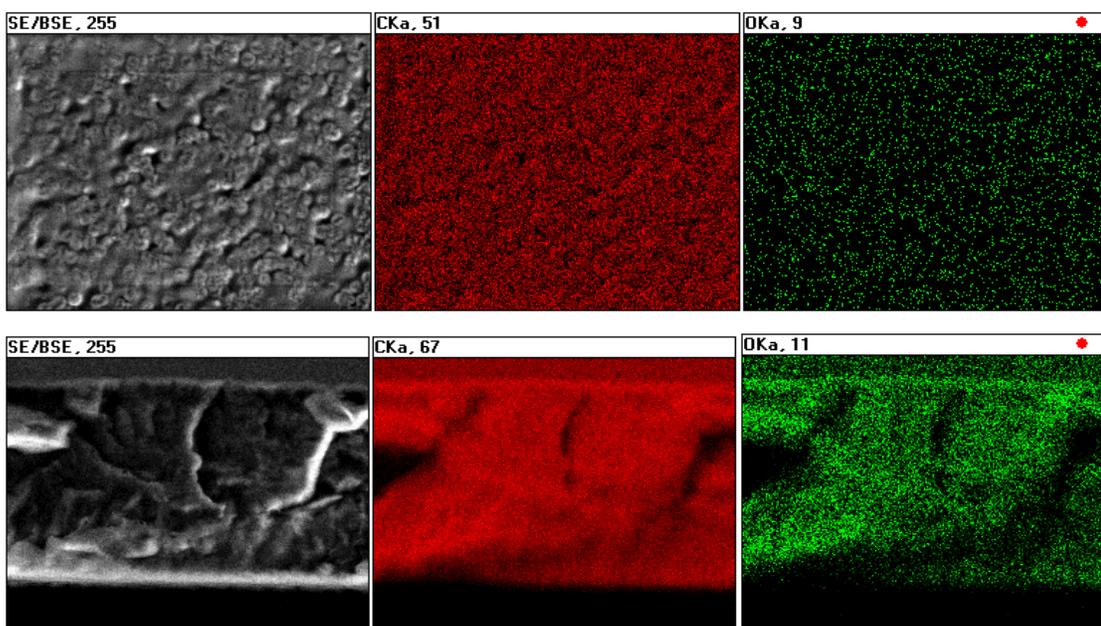
reason why POE2C18 additive is more effective than POE6C18 in enhancing the surface wettability of modified PP polymer.

Table D.1: Surface Elemental analysis as examined using XPS and SEM-EDS for PP modified using melt additives.

Melt Additive	O/C mole % (XPS)	O/C mole % (SEM) 10-15 nm	Mole % of additives (XPS)	Mole % of additives (SEM)
PP Control	10	10	-	-
PP + POE2C18	4	12	29	86
PP + POE4C18	11	13	58	68
PP + POE6C18	18	12	78	52
PP + D-GMS	17	10	90	53

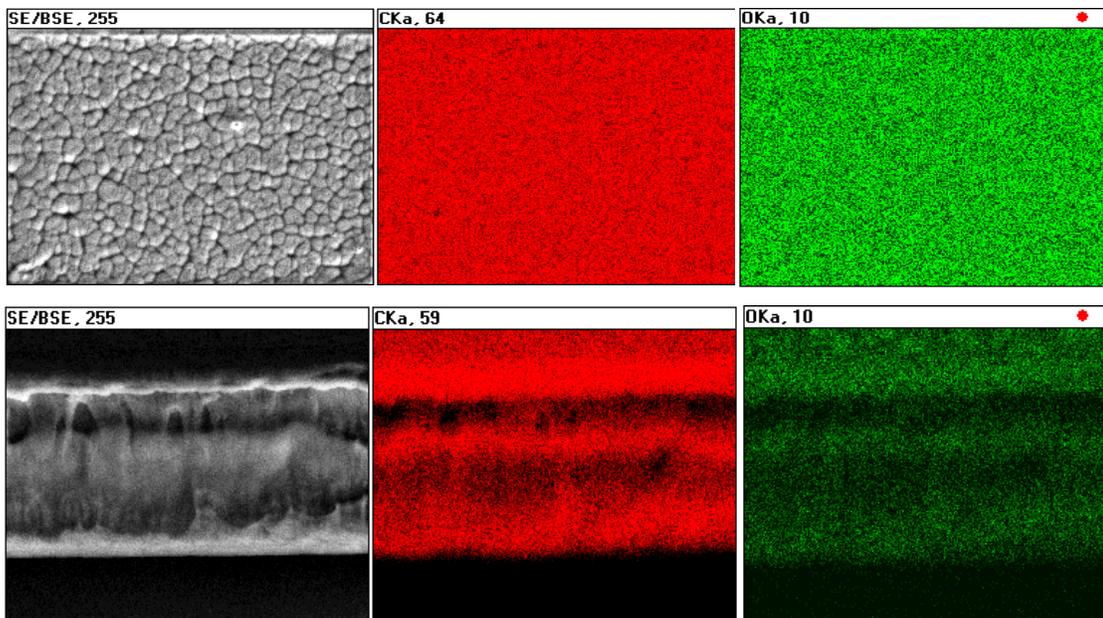


(a) PP Control Surface (top) & Cross-section (bottom)

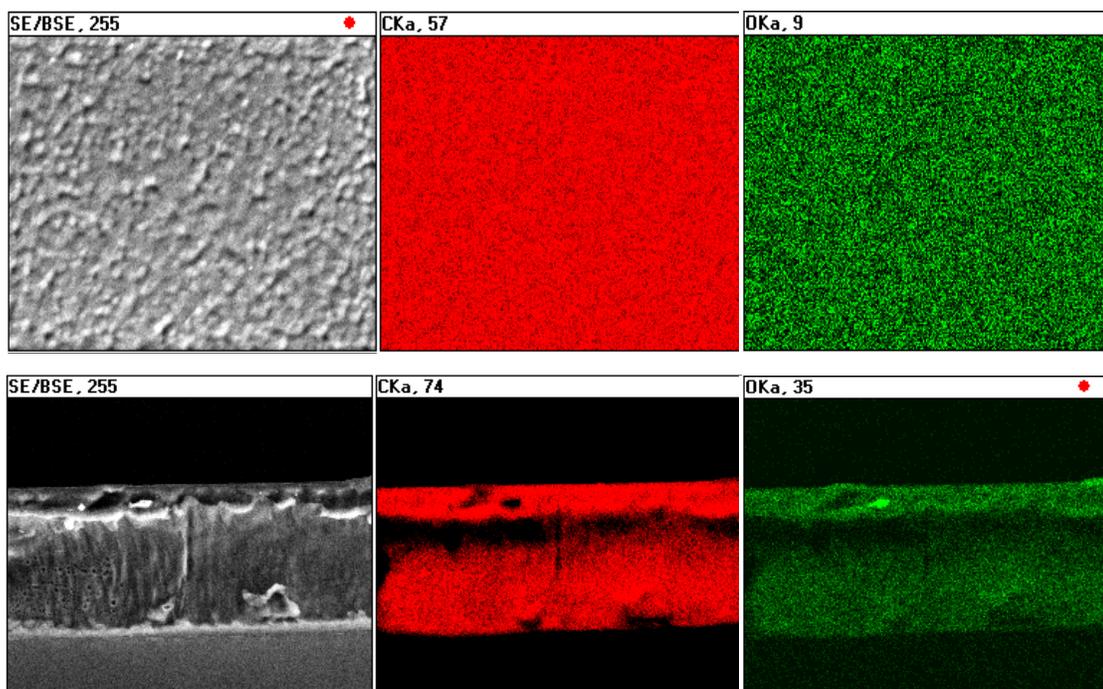


(b) PP + POE2C18 Surface (top) & Cross-section (bottom)

Figure D.1: Back-Scattered electron images of PP Control and modified PP films for surface and cross-sectional elemental mapping.



(c) PP + POE4C18 Surface (top) & Cross-section (bottom)



(c) PP + POE6C18 Surface (top) & Cross-section (bottom)

Figure D.1 (continued): Back-Scattered electron images of PP Control and modified PP films for surface and cross-sectional elemental mapping.

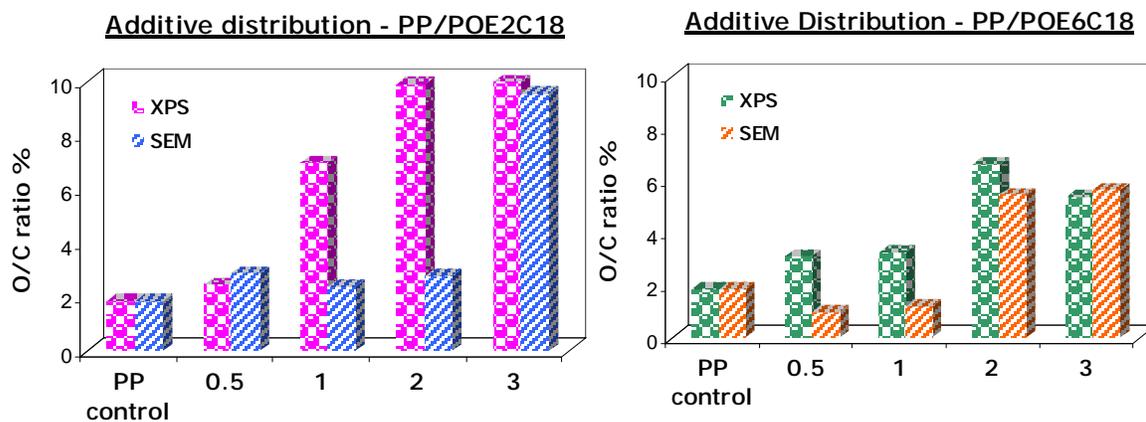


Figure D.2: Surface oxygen composition analysis as examined using XPS and SEM-EDS for PP film modified using POE2C18 and POE6C18 melt additives with 0.5-3 wt%.

Table D.2: Surface Elemental analysis as examined using XPS and SEM-EDS for PP film modified using POE2C18 and POE6C18 melt additives with 0.5-3 wt%.

Sample	Conc. in Bulk (wt %)	Mole % (XPS)	Mole % (SEM)
		1-5 nm	10-15 nm
PP + POE2 C18	0.5	21	21
	1	50	14
	2	71	21
	3	79	71
PP + POE6 C18	0.5	13	4
	1	13	4
	2	30	26
	3	22	26