PAUL, SHREYA. Surface Modification of Polypropylene Nonwovens to Improve Adhesion to Elastomers. (Under the direction of Dr. Behnam Pourdeyhimi.)

This study addresses how one can use blending, grafting and UV radiation techniques to make polar or hydrophilic polypropylene (PP) to overcome the shortcomings of the inert (hydrophobic) nature of the PP surface. For this purpose a functional monomer, glycidyl methacrylate (GMA), was chosen as the modifier. Moreover, the similarity and differences in results between the different techniques are reported.

For both blending and grafting techniques a range of weight percentage of GMA was added to the base polymer PP and it was observed that even low amounts of GMA (0.5 wt %) was sufficient to modify the surface property of the PP and produce enhanced adhesion to elastomeric polymers such as thermoplastic polyurethane (TPU) and Pebax. Increased adhesion up to 300% has been reported in this work. The physical modification of PP using UV irradiation also proved effective and has improved the hydrophilicity of PP.

The laminated samples of modified PP and elastomeric polymers were subjected to barrier and moisture transport tests. Under specific conditions of lamination, these composites have proved to be an effective barrier to water but at the same time can provide comfort property by maintaining the moisture vapor transfer through them.
Surface Modification of Polypropylene Nonwovens to Improve Adhesion to Elastomers

by
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DEDICATION

This is dedicated to my parents,
whose support and encouragement made all this possible………. 
BIOGRAPHY

Shreya Paul was born in Pune, in Maharashtra, India. She completed her school from Fatima High School, Mumbai, India in the year 1998 and high school from CHM college, Mumbai, India in 2000. She pursued her undergraduate degree from one of India’s renowned institutes of engineering, University Institute of Chemical Technology (UICT), Mumbai. She completed her Bachelor of Technology (B. Tech) degree in the department of Textile Technology in May 2004. Then she worked at Morarji Mills, Nagpur, India till 2005. After that, she joined North Carolina State University to pursue her Ph.D. in ‘Fiber & Polymer Science’ with minor in ‘Chemical and Biomolecular Engineering’. During the course of her Ph.D., she obtained the graduate certificate in Nonwovens Science and Technology. She will be joining Intel Corp., Chandler, Arizona as a Technology Development Process Engineer from March 2009.
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CHAPTER 1

1 Introduction

Polymers are reckoned as those important commercial materials without which surviving would be deemed impossible. These materials constitute one of the fast moving frontiers of everyday life. They are ubiquitous in applications including packaging, microelectronic devices, adhesion, high performance membranes, friction and wear, protective coatings, biomaterials and many more. Polyolefins, such as Polypropylene (PP) and Polyethylene (PE), exhibit the twin benefit of ease of processing and also possess excellent physical/chemical properties\textsuperscript{1}. However, they have inert surfaces and so surface modification becomes a handy tool to combine the effects of both-the original bulk property with the newly designed surface property\textsuperscript{2, 3}. The overall goal of modifying polymer surfaces is to bring about one of the two objectives: to increase the potential for surface interactions which may include adhesion promotion or to decrease the degree to which a surface reacts with a given material e.g. release or antifouling applications\textsuperscript{4}. Although the methods of polymer surface modification are extensive and may be quite complicated, in general all surface modification techniques basically share the common goal of controlling the nature and number of chemical functional groups at the polymer surface.

Generally speaking, surface modifications can be classified as physical\textsuperscript{5, 6} or chemical\textsuperscript{7, 8} methods of modification. The activities involved at physically modifying the surface can be categorized in two broad categories: the first by altering the surface layer and
the second by depositing an extraneous layer on top of the existing layer, thereby generating a sharp interface. Thus physical modification techniques use the principles of surface segregation, radiation with electromagnetic waves, oxidation with gases and many more. In wet chemical surface modification, a material is treated with liquid reagents to generate reactive functional groups on the surface. The research described here deals with the surface modification of PP polymer to enhance its adhesive properties, especially to elastomers. Amongst the chemical modifications, PP surface has been modified by different methods such as plasma treatment $^9, 10$, ion treatment $^{11}$, use of compatibilizers or blending $^{12}$, flame treatment $^{13}$, grafting $^{14, 15}$. PP has been grafted with acrylic acid$^{16, 17}$, maleic anhydride$^{18, 19, 20}$, glycidyl methacrylate (GMA)$^{21}$ and oxazoline$^{22}$. However, there has not been a lot of study using GMA and so this research work focuses on PP modification using GMA as the functional monomer. The end application of this work is to be able to make a barrier and breathable fabric using a composite structure involving elastomers and the modified PP.

The dissertation is presented here as a collection of papers and review articles. Chapters 3, 4 and 5 are articles that have been published or being prepared to be submitted to peer-reviewed journals. As a result the reader may notice some redundancy of introductory information because the papers are intended to be sufficiently independent. A short description of each is provided below to help readers navigate through this dissertation.

**Chapter 1.** Introduction to surface modification and outline of thesis.
Chapter 2. Includes review of pertinent literature. It gives detailed account of the PP structure, the need for surface modification and the different physical and chemical methods of modification. It briefly touches on these methods before focusing in detail on the two main methods of chemical modification, grafting and blending, that have been researched in this work.

Chapter 3. This chapter talks about melt–grafting of PP. PP is frequently grafted with such monomers as maleic anhydrate or carboxylic acid. But not a lot of work has been done using glycidyl methacrylate (GMA), where epoxy groups of GMA are able to react with -OH, COOH, and NH₂. This chapter focuses on the experimental methods and results obtained therein. This work has been published in *Journal of Applied Polymer Science*.

Chapter 4. This chapter includes the work done in modifying PP through blending as blending is a technique that can be used to incorporate functional groups without additional post-processing steps. PP was blended using a functional monomer containing GMA. Some experimental and simulation work have been reported as well as the improvement in adhesion to elastomers demonstrated. This work has been published in *Polymer International*.

Chapter 5. The theoretical investigations into the different modification methods to improve adhesion of PP to elastomers have been discussed in this chapter. It focuses on the atomistic
simulations and experiments to investigate the effect of the structure of both the elastomers and PP that decides the adhesion between the two polymers. This work has been prepared and is slated to be submitted to *Applied Surface Science*.

**Chapter 6.** The results from the grafting and blending reactions on PP polymeric film were leveraged to manufacture the appropriate spunbond nonwoven fabric. This chapter includes details on the specifications used to manufacture the nonwoven, the fiber properties and the fabric barrier and breathable properties. It also gives the results of adhesion of modified PP to elastomeric nonwoven fabric layer.

**Chapter 7.** In addition to the chemical methods of modification, one physical method viz. grafting by UV radiation was also studied. The experimental details and the results on PP film samples are presented in this chapter. It also has details of surface properties of these UV treated silicon samples.

**Chapter 8.** Includes summary of the present study and recommendations for future work.

### 1.1 References


CHAPTER 2

2 Literature Review

2.1 Introduction

Protection and comfort are two of the most sought after attributes in a textile garment. Comfort is the ability of a body to maintain a constant core temperature and moisture level irrespective of different environmental conditions and different rates at which the body works\(^1\). Even small deviations from normal skin and core temperatures or moisture levels can cause huge discomfort. One of the critical parameters that are considered in the manufacturing of a waterproof breathable fabric is the transmission of water vapor. It is very essential to maintain an optimum transport of water vapor, too little will cause a sense of discomfort and too much might cause dehydration.

In recent years, many attempts have been made to create breathable barrier fabrics. A breathable barrier fabric passively allows water vapor to diffuse through it, yet prevents the penetration of liquid water droplets (Figure 2.1). The amount of water vapor that passes through can be measured in terms of Moisture Vapor Transfer Rate or MVTR. It is defined as ‘the steady water vapor flow in unit time through unit area, under specific conditions of temperature and pressure’ and usually expressed in grams per square meter per day\(^2\). The definition of breathability is often confused with transmission of oxygen or carbon dioxide, but it almost always means the transmission of water vapor.
Typically, elastomeric materials have been used to achieve breathability. In general, two technologies – monolithic and micro-porous – are commonly used to achieve breathability. The monolithic technology allows the transmission of water vapor through a process called ‘activated diffusion’, i.e. through the hydrophilic groups in polymer structure, and the micro porous technology provides the passage for vapor through ‘capillary-like’ pores. In the monolithic process, the water vapor is initially absorbed in the exposed polymer surface and the amount of vapor build up is proportional to the vapor pressure. Vapor then migrates to the opposite surface. The driving force of vapor migration is the humidity gradient between the two surfaces-human body and ambience. The monolithic system is based on a chemical chain reaction between moisture molecules and the hydrophilic membrane, which consists of carbon, hydrogen and oxygen atoms linked together in long molecular chains. This property is obtained by incorporating hydrophilic group in the backbone of the elastomeric material which increases the affinity of the polymer to water and
hence provides breathability. The basis of water vapor transmission in these systems is the adsorption of water vapor through the ‘soft’ segments (i.e. polyether chains) of the polymer while water droplets are repelled by ‘hard’ segments (i.e. urethane chains). The amorphous regions in those soft segments act like intermolecular pores thus allowing the water vapor molecules to pass through but preventing the bigger liquid droplets to penetrate due to the solid membrane. Figure 2.2 depicts the monolithic principle.

![Figure 2.2: Mechanism of breathability in monolithic film](image)

The water repellent mechanism of microporous membrane is based on the size exclusion mechanism as the average size of a water droplet is around 100 µm and that of a water vapor molecule is about 0.4 nm$^4$. Although the micro-porous membrane would have an excellent MVTR, the water entry pressure is very low and capillary wicking of the challenging liquids cannot be totally avoided. In this study an attempt is made to provide an overview on breathable non-woven fabric. Detail descriptions of most commonly used
polymers (thermoplastic polyurethane) and PP are provided. To produce a robust polymeric system, an overview is provided on key techniques of polymer surface alterations and bulk polymer modification. The purpose of this study is not to provide a comprehensive review on polymer bulk or surface modification routes. The focus is primarily on PP system, therefore examples provided in this study are concentrated on PP based systems.

2.2 Types of Breathable Fabrics

Breathable fabrics can be broadly classified into the following groups:

- Densely woven fabrics
- Membranes and Coatings
- Combination of microporous and hydrophilic membranes and coatings
- Use of retroreflective microbeads
- Smart breathable fabrics
- Fabrics based on Biomimetics

2.2.1 Densely woven fabrics

Probably the first effective waterproof breathable fabric, known as Ventile, was made by closely weaving long staple cotton yarns. The yarns were then plied to improve the regularity and then they were woven using the Oxford weave. When the fabric surface is wetted by water, the cotton fibers swell transversely thus reducing the size of the pores in the
fabric and it requires a very high pressure to cause penetration (Figure 2.3). The fabric thus automatically becomes waterproof without the need for any external coating. Densely woven fabrics can also be made from synthetic microfilament yarns where the individual filaments are less than 10 µm in diameter. The use of very fine fibers and filaments in addition to dense construction results in fabrics with very small pore size compared with conventional fabrics. Whereas conventional fabrics have ~ 60 µm pore size, the one for the waterproof breathable one is ~ 10 µm.

![Figure 2.3: Densely woven fabrics (dry and when wetted with water)](image)

2.2.2 Membranes and Coatings

Membranes are extremely thin films which are made from polymeric materials and are engineered in such a way that although they have very high resistance for water droplets,
they allow the water vapor molecule to diffuse through. Coatings consist of a layer of polymeric material applied to one surface of the fabric. These coatings are much thicker than membranes which are typically 10 µm thick and similar to membranes, coatings are also classified as microporous and monolithic. The microporous coatings and membranes have hundreds of open micro pores and in hydrophilic monolithic (Figure 2.4) membranes, water vapor diffuse through the hydrophilic groups on the polymer chain. Gore-tex, introduced by W Gore, is probably the first and the best known membrane developed using expanded polytetrafluoroethylene (e-PTFE).

![Figure 2.4: Example of micro-porous membrane](image)

For coating, (Figure 2.5) those polymers are utilized which can be easily formulated into a resin or some sort of a paste for ease of application. A polymer resin can be first made
into a membrane and then laminated to a fabric. There are increasing numbers of techniques and machinery available that can be used for the lamination process. Although it is relatively simple to produce a strong bond, however the challenge is to retain the original properties of the fabric and also produce a flexible laminate.

![Figure 2.5: Example of a micro-porous coating](image)

**Figure 2.5: Example of a micro-porous coating**¹

There are numerous ways to create interconnecting pore structures in solid polymer films and coatings:

- Mechanical fibrillation (for membranes only)
- Wet coagulation process
- Thermo coagulation process (for coatings only)
- Foam coating (for coating only)
2.2.3 Combination of micro-porous and hydrophilic membranes and coatings

For combination of microporous and hydrophilic membranes and coatings, the fabrics are coated with copolymers having both hydrophilic and hydrophobic segments. The hydrophobic parts provide the resistance to liquid water droplets while the hydrophilic part allows for water vapor permeability. Few advantages of bicomponent microporous films are that it provides added strength and toughness to films, it reduces the stretch which may be caused by opening of the pores and also the moisture vapor transfer is more by mechanical means than by chemical adsorption means. The films do suffer from some drawbacks including increased cost and stiffness and reduction of breathability of the fabric.

2.2.4 Retroreflective Fabrics

A retroreflective fabric (Figure 2.6) possesses a print or coating having retroreflective pattern areas of aligned, hemispherically coated retroreflective microbeads. One patent describes how a breathable fabric was adhered to an array of dots, where each one of the dots
had coated retroreflective microbeads, in such a way that the fabric breathes from the interstices between the dots.

![Examples of retroreflective fabrics](image)

**Figure 2.6: Examples of retroreflective fabrics**

2.2.5 *Smart Breathable Fabrics*

All the above mentioned approaches of using coatings and membranes produce breathability for certain specific applications. The coatings are passive and they do not adapt to the changing environment such as temperature, humidity, pH, etc. A breathable fabric with a temperature dependent response may be desirable for certain applications where there are huge variations in temperature over a short period of time. Such fabrics are called smart breathable fabrics. One of the approaches can be to use stimuli-sensitive polymer (SSP) coatings and integrate them chemically. The challenge however is to retain their responsive behavior under such circumstances. When shape memory polymers are used and the outside temperature is low, the fabric restricts the loss of body warmth by stopping the transfer of
vapor while at high temperatures it transfers more heat and water vapor thus ensuring comfort and breathability. Shape memory polyurethane is a common shape memory polymer that is used. The mechanism is such that at lower temperatures, the coatings absorb moisture from the surrounding atmosphere and exist in a swollen state which results in the closure of microcracks. At temperatures higher than transition temperatures, the coatings exist in a collapsed state due to large number of hydrophobic interactions taking place, which result in the opening of the microcracks. Phase change materials are also an important category of polymers which are used to make smart breathable textiles. The incorporation of these phase change materials leads to improvements in thermal and moisture management.

2.2.6 Fabrics based on Biomimetics

Biomimetics is where biological mechanisms are mimicked to get desired functions. For a breathable fabric the analog of leaf stomata, which opens when the plant needs to increase water vapor intake and closes when its needs to reduce, can be used.

Amongst all elastomeric polymers, thermoplastic polyurethane (TPU) is one of the polymer that is quite often used to achieve breathable and barrier properties for the textile material. Like other monolithic materials, TPU are used with other materials such as PP. Details of TPU and PP is discussed in the subsequent sections.
2.3 Thermoplastic Polyurethanes (TPU’s)

Amongst all elastomeric polymers, Thermoplastic polyurethane (TPU) is one of the polymer that is quite often used to achieve breathable and barrier properties for the textile material. Generally, TPU is widely used in the market as it offers a wide range of properties like high tensile strength and elongation, high abrasion, chemical and UV resistance, recyclability, low temperature flexibility, clarity, etc. TPU’s come under the general category of polymers called ‘Thermoplastic Elastomers (TPE’s), which represent a special kind of polymeric materials as they combine the properties of both elastomers and thermoplastics\textsuperscript{5}. At temperatures above the softening or melting point, they have the typical properties of thermoplastics whereas below that point they show elastic deformation behavior. When they cool down, they build up a thermoreversible physical network with elastic properties. These thermoplastic elastomers can essentially be divided into two classes depending on their chemistry related morphological structure: segment or block-copolymers and polymer blends. Because of their more hydrophilic character, the polyether based copolymers are of utmost importance when considering applications for breathable films. TPE’s made up of block copolymers consist of alternating hard polyester segments and soft polyether segments. Thermoplastic polyurethanes that are based on segmented macromolecules are used for films as desired properties can be obtained through a combination of different segments and blocks. The hard and soft segments can be easily distinguished as the hard segments are built of a short diol and diisocyanate component whereas the soft segments are built of long chain diols. Usually, the flexible long chain diols are built of polyesterdiols or polyetherdiols.
TPU’s are available in varying Shore hardness values ranging from 75A and 70 D without any softening agents. The typical ones used for film applications are hardness 80 A and 50 D.

2.3.1 TPE Structure-Property Relationships

There is a very strong relationship between the structure of TPE’s and their corresponding mechanical and permeability properties. Those TPE’s which are intended for use as breathable membranes usually have polyethylene oxide (PEO) based soft segments. There is a very interesting relationship between structure and permeability, which is a function of both sorption and diffusion. The total moisture absorption is a function of PEO content and its molecular weight. Moisture permeability, which is reflected by what is called ‘water vapor transmission’, increases with PEO content and is also a strong function of the membrane thickness. TPE films for clothing should also provide a barrier for penetration of wind and water to enhance comfortability of the wearer.

2.3.2 The Challenge

However, TPUs as well as other breathable materials are quite seldom used as a single layer because of number of reasons: its discomfort (tackiness), strength (very thin films), and price. The materials/polymers that could be suitable for composite structure with TPU should possess good strength, adhesion and be easily available. Polyolefins, especially
polypropylene (PP) can be a good candidate.

Since adhesion between the elastomer and the polyolefin is now the issue, we focus here some basic definitions and concepts related to adhesion.

2.4 Adhesion and Adhesion Mechanisms

Adhesion is the force of attraction between two materials in contact with each other. It refers to the state in which two dissimilar bodies are so held together by intimate interfacial contact that mechanical force or work can be transferred through the interface\(^9\). Forces that contribute to this interfacial force include van der Waals forces, covalent bonding or electrostatic attraction. *Thermodynamic adhesion*\(^{10}\) refers to interfacial forces that are in equilibrium, associated with reversible processes such as work of adhesion, heat of wetting, etc. *Chemical adhesion* refers to adhesion at the interface due to chemical bonding. *Mechanical adhesion* is developed because of microscopic mechanical interlocking all over the interface.

It is not true to say that adhesion mechanisms involve only bond rupture and formation of new surfaces. These two phenomena do happen during a rupture of an adhesive assembly but these cannot give a measure of the fracture toughness of the assembly. The adhesive strength is basically due to two things: the cohesive force of the matrix itself and also the adhesive force between the matrix and the filler material. So in order to obtain strong interfacial attraction, intimate molecular contact at the interface is essential. But it is
not a sufficient condition. The polymer must be above a ‘critical molecular weight of entanglement’ as a polymer derives its mechanical strength from its molecular weight. Thus, in the interface region, segments of polymers interpenetrate and that leads to a strengthening of the interface. In short, there are two major notions that are believed to impact adhesive strength: one is that of a ‘connector molecule’ where chemical bonds or physisorption bind a polymer chain to an interface and which interacts with the bulk polymer surface so as to transfer the stress across the interface. The second notion, which is also strongly believed, is that it is because of the concentration of stress in the interface that the energy dissipation actually occurs.

The stress transfer by one connector polymer molecule at solid-elastomer interface is also important\textsuperscript{11}. Consider a smooth solid surface on which have been grafted long polymer chains in a manner that the grafting efficiency is low and also that they do not overlap. For such systems, it is well accepted now that the adhesion can be promoted and stress can be efficiently transferred across the interface by these surface anchored polymer chains. When the two partners of the assembly are tried to be separated, the van der Waals interactions between monomers are sufficient enough to maintain the connector chains in the stretched position. Stretching and progressive extraction from the bulk material are the two mechanisms by which the connector chains promote adhesion.

In contrast to the situation where there are chains which are tethered to the surface and where the connector chains entangle with polymer network, the structure of polymer interfaces between polymer melts is primarily controlled by the interfacial width, defined as
the average distance over which free chains can interpenetrate. For two mutually immiscible polymers, the interfacial width is controlled by Flory Huggin’s interaction parameter $\chi$ between the two polymers. To measure the adhesive strength of the interface between these materials empirically is difficult because the materials are soft and highly viscoelastic. For such scenario, the peel test can give an idea about the work of fracture of interfaces and if the test is properly executed, the practical work of adhesion can be measured. In the simplest case of a smooth and flat interface, the work of adhesion is defined as the reversible work required to separate the interface between two bulk phases 1 and 2 from their equilibrium separation to infinity. It is given by the following equation\textsuperscript{12, 13}:

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12}$$  \hspace{1cm} \text{Eqn. (2.1)}

where $\gamma_1$ and $\gamma_2$ are the surface tension of phases 1 and 2 respectively and $\gamma_{12}$ is the interfacial tension between component 1 and 2.

The above equation suggests that greater the interfacial attraction, greater is the work of adhesion. It also summarizes physico-chemical aspects of adhesion on the interface in terms of surface energy. It suggests that adhesive strength is strongly a function of the surface and interfacial energies of the system and is related to the nature of intermolecular interactions\textsuperscript{14}. Polarity of a material is also a deciding factor in hinting at adhesive strength between two surfaces. The polarity of a material can be calculated from its interfacial tension with a non-polar material. It is obtained as\textsuperscript{9}
where $\gamma^d$ is the dispersion or the non-polar part of surface energy and $\gamma^p$ is the polar part of it.

2.4.1 Mechanisms of adhesion

The first step in the formation of an adhesive bond is establishing interfacial molecular contact and this happens through wetting. Wetting can be defined as the displacement of a fluid from a solid surface by a second immiscible fluid\textsuperscript{15}. The first fluid is usually air and the second fluid is a liquid. The wetting phenomenon involves various interactions such as liquid-substrate, liquid-liquid and liquid-air and these are represented by appropriate interfacial tensions. When a liquid is in contact with a substrate, two possibilities can arise: the liquid may spread over the solid, displacing the original fluid air and finally come to a halt when the angle between the liquid-air and solid-liquid interfaces reach a certain value, called contact angle $\theta$. When there is no relative movement of the contact line with the substrate surface, this angle is referred to as static contact angle. This static contact angle and the surface tension of the liquid and the interfacial tension is related by Young’s equation as below\textsuperscript{16}:
where $\theta$ is the equilibrium contact angle, $\gamma_s$ is the interfacial tension between solid and vapor, $\gamma_{sl}$ is the interfacial tension between solid and liquid and $\gamma_l$ is the interfacial tension between liquid and vapor.

Thus the value of contact angle can characterize wetting phenomenon. A low contact angle means high wettability and high contact angle means poor wettability\(^{17}\). When the contact angle between a liquid and a solid surface is zero, the liquid will spread spontaneously without limit. However, static contact angle is an incomplete measure of wettability as it does not involve the time needed for the liquid to spread over the surface of a solid.

There are two ways in which wetting can affect adhesion. An incomplete wetting produces interfacial defects which tend to lower the adhesive strength whereas complete wetting can increase the adhesion strength by increasing the work of adhesion. The next step in ensuring a strong adhesive bond is the generation of intrinsic adhesion forces across the interface and in this the nature and the magnitude of these forces are very critical. These forces across the interface require being sufficiently strong and stable throughout the service life of the joint so that the interface does not become the weak link in the chain. The different forces which act to secure the interface are called the ‘mechanisms of adhesion’. The four main mechanisms of adhesion include: mechanical interlocking, diffusion theory, electronic
theory and adsorption theory\textsuperscript{18}.

The **mechanical interlocking** theory basically claims that the surface irregularities on the substrate are the prime source for mechanical keying or interlocking of the adhesive on the substrate. Mechanical interlocking can be improved when surfaces can be made abrasive. Techniques generating abrasive surfaces include metal plating of plastics (specific), mechanically roughened substrates and chemically roughened surfaces. The metal plating involves a chemical pretreatment followed by etching. Any form of mechanical abrasion increases adhesive strength but micro and macro level optical and electron micrographs have confirmed that it is not because of enhanced interlocking but rather due to mechanical abrading. It removes substances such as release agents, machine oil, grease, scale, etc and thus enhances wetting. Also due to smoothening of the top surface, small cracks and flaws are prevented from propagating along the interface. Chemical abrasion on the other hand can lead to formation of roughened surfaces at the interface which might be the cause for enhancement of adhesion. However, critical parameters such as time and temperature of treatment have to be very precisely controlled to not end up with a weak or friable surface.

The **diffusion theory** advocates that mutual diffusion of polymer molecules across the interface is the reason behind the intrinsic adhesion of polymers to themselves (autohesion) or to each other. Given sufficient interaction and affinity between two phases, polymer molecules can diffuse beyond the substrate interface to form entangled structures with other phase. To attain this, the polymer macroradicals should possess sufficient mobility and mutual solubility. When material is heated above glass transition temperature, the
polymer chains have the mobility to penetrate deeper by diffusion and if sufficient time is given, adhesion improves as well\textsuperscript{19}. Therefore, time and temperature are the two important parameters which can be manipulated to obtain maximum adhesion.

To have solubility the two polymers should possess equal or very similar solubility parameter ($\delta_s$) which is given by:

$$\delta_s = \left( \frac{\Delta H_v - RT}{V} \right)^{1/2}$$  \hspace{1cm} \text{Eqn. (2.4)}

where $\Delta H_v$ is the molar heat of vaporization, $R$ is the gas constant, $T$ is the absolute temperature and $V$ is the molar volume. So the solubility parameter is the indicator of the compatibility between the two polymers.

The \textbf{electronic theory} proposes that when the adhesive and the adherend have electronic band structures which are different from each other, then it is possible to have some electron transfer during contact. This would result in the forming of a double layer of electric charge as the Fermi levels would be balanced. Deryaguin et. al\textsuperscript{20} have formulated that these contacts and junction potentials will give rise to electrostatic forces which would contribute significantly to improve intrinsic adhesion. One criticism of this theory is that the electrical phenomenon observed may actually be due to the failure event and not the cause the adhesion improvement.

The \textbf{adsorption theory} is the most widely accepted and the most applicable adhesion
theory. It claims that, given that there is enough intermolecular contact at the interface, the interatomic and intermolecular forces established between the atoms and molecules of the adhesive and the substrate will result in a strong adhesion. The most common of all types of forces are van der Waals and hydrogen bonds and they are called secondary bonds. In addition, covalent bonds can also be formed at the interface. This is called as chemisorption and includes ionic, covalent and metallic interfacial bonds which are referred to as primary bonds.

There are four basis types of stresses in adhesive bonded joints. These include normal or direct stresses, shear stresses, cleavage stresses and peel stresses. Normal stresses, as the name suggests, act normal to the plane in which they act and can be further divided as tensile or compressive stress. Shear stresses, on the other hand, act parallel to the plane on which they act. Cleavage stresses arise due to offset tensile force or bending moment and the fourth type arise when either one or both the substrates involved are flexible. This research work will focus primarily on the last kind of stress along interfaces in breathable composite applications.

2.5 Polypropylene (PP)

2.5.1 PP Structure

PP falls under the category of polyolefinic or ethenic polymers which are thermoplastics and have ethylene i.e. \( \text{H}_2\text{C} = \text{CH}_2 \) as basic monomer structure. PP
homopolymer is semi crystalline in nature and the morphology exhibits a hierarchy of characteristic scales, ranging from gross reactor particle shape\textsuperscript{22, 23} to skin core structures\textsuperscript{24, 25}. One of the governing factors for the resultant morphology is the crystallizability of the chains. The degree of crystallinity is, in turn, dependent on the tacticity of the chain. PP has 3 tactic forms-isotactic (i-PP), syndiotactic (s-PP) and atactic (shown in Figure 2.7). Isotactic chains, where the methyl groups have the same configuration with respect to the polymer backbone, results from head-to-tail addition of PP monomer units and by using Ziegler-Natta catalysts. Syndiotactic, on the other hand, have an alternating configuration of the methyl groups whereas, the atactic chains do not show any consistent placement of the methyl groups.

\textbf{Figure 2.7: Different tacticities of PP}\textsuperscript{21}

On the crystallographic scale, PP is present in different forms viz. $\alpha$-form i-PP; the
polymorphic forms of i-PP: β, γ and mesomorphic; and s-PP. PP is prepared industrially by the polymerization of propylene (C₃H₆) in a low pressure process using a mixture of aluminum triethyl and titanium tetrachloride as catalysts. The reaction mechanism induces a chain having a helical structure that exhibits the same asymmetrical stereochemical configuration of carbon atoms. This leads to a macromolecule having a high degree of crystallinity. Hence, PP has considerably improved mechanical properties compared to polyethylene (PE); it has a lower density than PE, it is stiffer, harder and has a high strength than many PE grades. Also, due to its higher melting point (160 °C), it can be used for processes which involve high temperatures and it is only attacked by strong oxidizing agents. PP has high modulus and a lower coefficient of thermal expansion than PE. It can be compounded with a very broad range and amount of fillers, reinforcing agents and other polymeric materials. However, it has a hydrophobic, chemically inert surface and this restricts its applications in many operations like coating, adhesion, painting, coloring, packaging, laminating etc. The poor adhesion of PP to the surface of other materials, especially TPUs is the primary concern.

2.5.2 Need for Surface Modification

As already mentioned, PP has a hydrophobic surface due to the pendant methyl groups and a purely hydrocarbon backbone and this restricts its applications where surface polarity is required. Hence the dire need to modify PP arises. Also, the overall goal of modifying polymer surfaces is to bring about one of the two objectives: to increase the
potential for surface interactions e.g. adhesion promotion or to decrease the degree to which a surface reacts with a given material e.g. release or antifouling applications. Although the methods of polymer surface modification are extensive and may be quite complicated, in general all surface modification techniques basically share the common goal of controlling the nature and number of chemical functional groups at the polymer surface. Hence the term functional group is used generically to indicate any chemical moiety that would bring about a desired change on the surface. There is a rising need for material surface modification for basically two important reasons: first there has been a steady and fast growth in the fundamental understanding of the structure property relationship, especially between physicochemical structure and various aspects of surface performances. So the guidelines for the rational design of polymer surface modification are set. Second, there is also an increase in the availability of state-of-the-art analytical techniques, which have made it possible to modify and accurately characterize the modified surface. In theory, there are umpteen possibilities for surface modification but in reality not all are feasible. Most of the chemical reactions are in solution i.e. they are homogenous but most surfaces are heterogeneous. Also, the rates and yield of heterogeneous reactions are lower than the homogenous ones and the characterizations of the modifications are made on indirect evidences. All these possibilities and limitations have to be kept in mind when proceeding with the surface modification of any polymer.
2.5.3 Structure of Polymer Surfaces

One very important concern encountered during surface functionalization is that what exactly constitutes a ‘surface’. A schematic of this problem is been demonstrated in Figure 2.8.

![Figure 2.8: Definition of a surface](image)

Figure 2.8: Definition of a surface

We can broadly divide the surface into three different zones\(^29\): The first is a non-swollen surface; in this the functional groups are in contact with the modifying solution even though they are completely unreactive. The second deeper zone would be where there is solvent-swollen surface; this zone will be of varying depths and that would depend on the reactivity of the solvent-polymer or polymer-polymer system as much as it would depend on the temperature. The third region would be the bulk polymer. Functional groups in the bulk
polymer would not react with the solvent or soluble reagents. Importantly, functional groups in the polymers bulk will not affect the polymer’s surface properties. However, there are several ways by which polymer bulk can be modified and which would have pronounced effect on polymer characteristics. In the subsequent sections descriptions of polymer surfaces and bulk modification is discussed.

2.6 Polymer Surface Modifications

These have been studied in various fields of industrial applications using different innovative techniques which include various physical and chemical methods.

2.6.1 Physical Surface Modifications

The activities aimed at physically modifying the surface can be categorized in two broad categories: the first by altering the surface layer and the second by depositing an extraneous layer on top of the existing layer, thereby generating a sharp interface. Thus physical modification techniques use the principles of surface segregation, radiation with electromagnetic waves, oxidation with gases and many more. Knowing the inert nature of PP surfaces, to use the former method would imply to generate high energy reactive species i.e. radicals, ions, etc. In nature, fire or thunder are the only two high energy media and for practical purposes fire, plasma and corona discharges simulate these real life sources. In flame treatments, oxygen containing functionalities are introduced at PP surfaces, mainly to improve adhesion, printability or paintability. The active species formed at high temperature
are radicals, ions and molecules in excited state. In Corona treatments, the corona effect is used, which is the formation of high energy electromagnetic fields close to charged thin wires or points, with consequent ionization in their proximity\(^3\). In the ionized region, excited species such as ions, radicals, electrons and molecules are present, and these are the active oxygen-containing functionality. With cold-plasma treatments, low temperature plasmas require low pressures but functional group contains high energy photons, electrons, ions, radicals. Using plasma chemistry has its own advantages and disadvantages: the former includes the formation of chemical bonds at the interface but there can also be the possibility of high degree of cross-linking on the plasma polymerized layer. With hot plasma treatments\(^3\) plasmas generated at atmospheric pressures, reach very high temperatures and these can then be used for metallurgical operations for depositing coatings. In UV treatments, photons with low wavelength are energetic species are used to activate many chemical reactions. Most commodity polymers, especially PP\(^3\).\(^4\) have been extensively studied. Irradiation in the presence of oxygen or ozone is progressively used for improving wettability. Laser sources can be used to promote cross-linking or opposite scission effects. Lasers can have high enough intensities that can modify polymers even with high MW. They are energy and space coherent.

2.6.1.1 Flame Treatment on PP

Flame is probably the oldest plasma known to humanity. Flame treatment was mainly
employed to improve ink permeability on polymeric surfaces. Now it is an industrial process commonly used to improve the adhesion properties of polymeric substances. It can be used to oxidize the polymer surface in a controlled way to a thin layer of ~5-10nm\textsuperscript{35}. A very simple set-up (Figure 2.9), consisting of a burner and a fuel tank, is required for the process but simultaneously a very high degree of craftsmanship is also required to produce consistent results. The flame treatment brings about the oxidation of the polymer surface and this can be attributed to the high flame temperature range (1000-1500 °C) and its interactions with other excited species in the flame. The defining characteristic of the mechanism includes the formation of polymer radicals due to hydrogen abstraction.

![Figure 2.9: Schematic of flame treatment\textsuperscript{36}](image)

To obtain an efficient and reproducible flame treatment, a number of parameters including the air-to-gas ratio, gas flow rates, distance between the tip of the flame and the
object to be treated, the treatment time, nature of the gas and so forth, have to be carefully monitored. Sutherland, et al. \(^{37}\) conducted the studies of these parameters on the surface property of PP and analyzed their results using X-ray Photoelectron Spectroscopy (XPS) and contact angle measurements. They noticed that for mild flame treatments, the surface energy of PP increases with the oxygen content of the surface. The optimum air-to-gas ratio was observed to be 11:1 while the optimum flow rate was decided at 24 l min\(^{-1}\). Also, measured bond strengths were found to be well in excess of those obtained by other methods of modification. Stroud et al. \(^{38}\) performed detailed numerical modeling of the surface oxidation of the PP films and found that calculated values correlated very well with experimental data. O\(_2\) and OH play major roles in the modification of the surface and the rate determining step is the abstraction of hydrogen by the hydroxyl radical. Also, they noticed that under fuel-rich conditions, hydroxyl groups dominate the surface whereas for lean-fuel conditions just by changing the flame equivalence ratio, dominant groups change from peroxy to a combination of peroxy, alkoxy and hydroxyl. A study also determined that flame treated PP surfaces responded much more to silane-based post treatments and that increased the adhesion significantly compared to non-flame treated PP surfaces. This improvement was due to changes in surface free energy, morphology and generation of functional groups on PP surface. Flame treated PP surfaces responded better to epoxy silane rather than amino-silane in terms of adhesion strength. Flame treatments have however shown some generic drawbacks as it reduces the optical clarity of polymers.
2.6.1.2 Corona Discharge Treatment

Corona discharge is a well accepted, relatively simple and one of the most widely used continuous processes for the surface treatment of polyolefin films\textsuperscript{39,40}. This technique is especially used for improving the printability and adhesion of polyolefin films. The corona treatment setup is a very simple and a cost effective one. It consists of a high voltage-high frequency generator, an electrode and a grounded metal roll covered with an insulating material as shown in the Figure 2.10.

![Figure 2.10: Schematic of the corona discharge treatment\textsuperscript{41}](image)

The whole system works as a large capacitor, with the electrode and the grounded roll as the plates of the capacitor and the roll covering and air as the dielectric. In this system
when a high voltage is applied across the electrodes, it ionizes the air producing plasma (often identified by the formation of a blue glow in the air gap). This atmospheric pressure plasma also known as corona discharge brings about the physical and chemical changes on the polymer surface for improved adhesion and dyeability. As a result of the corona discharge, a number of chemical reactions happen at the polymer surface.

Carlsson\textsuperscript{42} and coworkers studied the effect of corona treatment on the adhesion between PP-nylon 6 10 composites prepared by in situ polymerization. They observed that adhesion between the PP and nylon markedly improved only by a brief corona discharge treatment. They noticed that the peel strength of corona treated samples was much higher compared to the untreated ones. They proposed that interfacial adhesion can be a combination of 1) mechanical interlocking 2) adsorption (mainly due to dispersion forces) 3) electrostatic attraction and/or 4) interdiffusion. They were not clear which of these factors played a major role during corona discharge but sensed that the adhesion improvement must be primarily due to surface topography changes and hence attributed them to mechanical interlocking. They also partly attributed it to the consolidation of the weak surface layers by the corona treatment. O’Hare et al.\textsuperscript{43} studied the physicochemistry of the surfaces of corona treated and untreated biaxially oriented PP films and analyzed the results using XPS and Atomic Force microscopy (AFM). They observed a higher surface energy for the corona treated films and attributed it to the presence of polar groups such as hydroxyl, peroxy, carbonyl, ester, carboxylic acid and carbonate. They also observed a change in morphology from fibrillar crystalline structure to a globular morphology. They also suggested two
mechanisms for the observed increase in surface energy: below a threshold energy of \( \sim 4 \) kJ/m\(^2\), oxidation and scission of the low-molecular-weight boundary layer present on the PP films was the dominant means for the formation of low-molecular-weight oxidation materials; above \( \sim 4 \) kJ/m\(^2\) oxidation and scission of the polymer backbone is the main process. Vassiliadi et al. 44 studied the effect of corona energy which was applied to metallized PP. They detected increased surface roughness and polarity due to the presence of oxygen groups and these changes became more pronounced with increasing the intensity of the corona treatment. Their samples were also studied for ageing effects and they noticed a 40 \% decrease in tensile strength after 216 hours of ageing. This was attributed to the plasticizing effect taking place during the ageing process. Though this technique has its distinct advantages it is also associated with certain shortcomings such as non-consistent treatment due to the variation in ambient conditions (such as temperature and humidity), a high possibility of contamination due to the treatment carried out in air and at times, lack of homogeneity/uniformity of surface modification. Another limitation of this process would be the formation of low molecular weight materials which affect adhesion in a negative way. Also the broad range of oxygenated groups that are introduced reduces the specificity of functionalities that need to be introduced into substrates. Also, it is reported that surface polar groups on corona treated polyolefins are particularly unstable. Materials should therefore be used almost immediately after corona treatment.
2.6.1.3 Irradiation

Radiations can be used in two ways: they can be directly used to alter the surface or they can also be used to sputter off target species form another substrate which can then deposit on the desired sample surface and cause the modification. These can be basically differentiated into three basic categories on the basis of their energy. High-energy radiation, mainly delivered by X-rays, γ-rays, electron beams from cobalt ($^{60}$Co) and magnesium ($^{58}$Mg) sources, are often known as ionizing radiation. Medium-energy radiation, usually obtained from UV rays, pulsed/excimer laser and plasma sources and low-energy radiation yielded by infrared, ultrasonic, microwave and visible sources can bring about desired changes in the polymer backbone depending on the irradiation time and energy of radiation. The primary role of any of these radiations is to activate the molecules on the polymer backbone, which in turn reacts with functional species present in its vicinity to render a functional surface.

Mirabedini et al. $^{45}$ studied the effect of microwave irradiation on the surface characteristics of PP and noticed a relative increase in surface energy and also a pitted structure as revealed by SEM with only 120s of the microwave treatment. The adhesion measurements revealed a change in the locus of failure from adhesive to cohesive failure within the bond line indicating that the interface was strengthened due to the irradiation treatment. Lee and coworkers$^{46}$ used low-energy hydrogen ions having light weights and deep penetration depths instead of the heavy argon ions to reduce molecular damage by ion-beam bombardment of the polymer chain. They found excellent adhesion between irradiated
PP and Polyacrylonitrile and said the main contribution was the increase in surface energy resulting from the presence of non-washable groups such as C-O, C=O and (C=O)-O. They confirmed that the improvement in surface roughness was not as important a contributing factor as the increase in the surface energy.

2.6.1.4 Plasma Treatment

Plasma is regarded as the ‘fourth’ state of matter, consisting of highly excited atomic, molecular, ionic and radical species. A gas plasma may form whenever gas is exposed to an electric field. If the field is sufficiently strong, a high percentage of gas atoms will surrender an electron or two and become ionized. The resultant ionized gas and liberated energetic electrons comprise the gas plasma or plasma. The ionized gas atoms have relatively little kinetic energy unless they are accelerated through an electric field. Upon acceleration, they bombard any surface with sufficient force to dislodge any atom from a target material. Thus, plasma effects sputtering and etching processes by momentum transfer of material and the use of reactive gases produces chemical modification as well. By controlling parameters of electric field intensity, chamber pressure, gas flow and exposure time, plasma chemistry can be utilized as a powerful tool to change any substrate’s surface chemistry (Figure 2.11).
Techniques based on plasma, that combine the advantages of conventional plasma and ion beam technologies are effective methods for modifying surface energetics of a wide variety of materials. In particular, modifying the surface energetics of materials can improve the adhesion strength, surface and coating properties as well as biocompatibility, naming a few. Briefly, plasma technique offers the following advantages for polymeric materials:

1. A good understanding of the physics and the chemistry behind plasma reap huge benefits in fields of microelectronics

2. Plasma is usually reliable, reproducible, relatively inexpensive process that can be applied to various geometries as well as different materials such as metals, polymers, ceramics and composites. These processes can be accurately monitored using in-situ plasma diagnostic devices.
3. Plasma treatment brings about an array of changes in surface characteristics ranging from chemical, tribological, electrical, optical, biological and mechanical. Judicious applications can yield dense and pinhole free coatings with excellent interfacial bonds due to the rough nature of the interface.

4. Plasma techniques can be combined with masking techniques to allow surface patterning

2.6.1.5 Plasma sources

There are several kinds of plasma sources, the most common ones being gaseous, metallic and laser based sources. Each one of these is characterized by their electron temperature, ion temperature, uniformity, electron density and such other factors. A gaseous plasma is obtained by applying a potential through a gas and the breakdown potential depends on the pressure and discharge gap width. Depending on the applied pressure, these are broadly divided into low-pressure plasma sources which include direct current, rf glow discharge (rfGD) and electron cyclotron resonance (ECR) and high or atmospheric pressure plasma sources such as corona discharge and arc plasma. A vacuum arc plasma consists of a plasma production unit and a macro-particle filter but the plasma flux is ununiform in both axial and radial directions. In a laser plasma source the plasma is generated by the interaction of high density pulses with a solid target involving laser.
2.6.1.6 **Kinds of Plasma**

There are two kinds of plasma: cold and hot. The difference is the temperature of the heavy species: it is similar to the electrons in hot plasma, while it is lower than 773K in cold plasma. Moreover, the working pressure of cold plasma is generally lower than the one of a hot plasma or atmospheric pressure: this allows the production of chemical reactive species at low temperatures.

2.6.1.7 **Plasma-surface modification techniques**

In this section the main principles and applications of plasma sputtering, etching, cleaning, implantation and deposition are mentioned.

In plasma sputtering and cleaning process, materials get removed from the surface due to chemical reactions and volatile products are formed along with some physical sputtering. Inert gases, especially Argon, are used for the surface cleaning. The simple principle of this process is that during sputtering, the negative voltage applied to the substrate and the presence of rfGD or ECR generates Argon plasma. The applied electric field accelerates the ions towards the substrate but since the energy is not very high, the argon ions do not go very deeply into the substrate and end up affecting the surface molecules only. Some of the surface atoms acquire the high energy and release from the substrate to the vacuum chamber which exposes the underlaying layers of atoms which eventually get etched. The excess surface contamination gets cleaned off by deploying sufficient sputtering
time. This process is generally used for pretreatments for subsequent implantation and deposition.

The interaction between a plasma and polymer leads to two main reactions: modification and degradation, which compete with each other. For the properties of the polymer to change due to ion beam interaction, plasma-graft co-polymerization and plasma polymerization, the modification effect has to dominate. Etching takes place when the degradation mode dominates. The rate of weight loss is a strong function of the nature of the polymer as well as the energy of the plasma. Polymers containing polar functionalities such as ether, carboxylic acid and ester groups show high plasma susceptibility whereas polyolefins, which do not have any substituents, exhibit low plasma susceptibility. The weight loss takes place only from the topmost layers of the polymer hence the polymers subjected to the etching process show similar physical and chemical properties as the original polymer. The weight loss is essentially because of bond breaking of polymers. Every time when there is a chemical etching taking place, a certain amount of physical sputtering also takes place.

In plasma implantation, elements of choice can be introduced into the surface of the material without any thermodynamic constraints. Plasma implantation into metals/alloys and polymers are very common. In plasma immersion ion implantation (PIII) of metals and alloys, the specimens are surrounded by a high density plasma and is pulse-biased to a negative potential relative to the chamber wall. In PIII, multiple processes such as simultaneous and consecutive implantation, deposition and etching are possible by varying
the instrumental parameters without breaking vacuum. Also, these implantations are usually conducted in low-temperature and the target can be cooled, thus keeping thermal deformation of specimens to minimal. In plasma implantation of polymers, a polymer is exposed to plasma with proper plasma density and treatment time and thus much functionality can be created. In a typical process, the first step is abstraction of a hydrogen from the polymer chains to create a radical at the midpoint of a chain followed by recombination of the radicals with simple radicals created by the plasma gas to form oxygen or nitrogen functionalities. Generally since polymers are hydrophobic, their conversion from hydrophobic to hydrophilic by plasma implantation leads to improved surface characteristics for adhesion strength and other pertinent properties.

Plasma deposition is a very important area as an engineered layer of desired properties, different from the bulk polymer, can be deposited on the material of interest. Some of the common techniques in this category are dual plasma deposition, plasma grafting co-polymerization, plasma polymerization, laser ablation (LA) and plasma spraying. In dual plasma technique, an rfGD or a vacuum arc plasma source is used to generate gas and metal plasma. This technique has many advantages for thin films; especially the fact that a film composed of several elements with various compositions can be fabricated in the same instrument without breaking vacuum. In addition the ion density is high as the metal vacuum arc plasma is operated in a pulse mode. The substrate being immersed in the plasma, there is a uniform deposition over a large area. In plasma polymerization, with the use of energetic plasma species such as electrons, ions and radicals low-molecular-weight molecules are
transferred to high-molecular-weight molecules. These differ from conventional polymerization involving radicals as they have different physical and chemical properties as well as different chemical compositions. Plasma polymers comprise of complicated units such as cross linked, fragmented and rearranged units from the monomers. In plasma grafting co-polymerization, polymers are first exposed to the plasma to create radicals on the surface, then they are exposed to a vapor of the monomer. Because plasma creates radicals close to the surface of the polymers, the plasma grafting co-polymerization is also restricted to the surface. In LA, the plasma plume which is generated near the surface of the target by the laser beam is transported to the substrate to produce the film. The density and the kinetic energy of the plasma plume are the critical parameters which decide the quality of the film. A high energetic plume will destroy the film. Target preparation and target morphology also affect the surface morphology of the films. In atmospheric pressure plasma spraying, the powders of the spray materials are introduced into the plasma area of the torch. Because of the high temperature and flux velocity of the plasma, the fully or partially melted powders get accelerated towards the substrate at a high speed forming a lamellar coating structure. The basic advantages with plasma spraying technique is that it can treat complex geometries and since it can handle a wide variety of materials, this technique can be extended to the areas such as corrosion resistant, high temperature and ablation resistant coatings as well as for biocompatible coatings. However it suffers from a disadvantage: it has poor adhesion between the substrate and the coating, although several measures can be taken to improve it. Figure 2.12 is the schematic representation of the different plasma methods to modify
There have been several studies in the literature of modifying polyolefins, especially PP, by using plasma techniques. Some of them are discussed below.

Cho\textsuperscript{50} studied the adhesion of paint to PP bumper surface by treating it with oxygen, water and acetylene plasmas. He tried to investigate the two reasons for failure of adhesion: ageing and wet environment. He concluded that adhesion can be improved by treating the PP bumper surface with plasma rather than use a primer. He also noticed that the adhesion
strength decreases significantly in wet environments if the PP is treated with O$_2$ or H$_2$O plasma, but does not vary much if treated with an acetylene plasma, which was attributed to the existence of reactive unsaturated hydrocarbons as well as oxidized hydrocarbons in the film deposited in acetylene plasma. Carrino et al. $^{51}$ worked with cold plasma on PP and studied wettability and adhesion. Now, the interaction between a polymeric surface and a cold plasma flow can be either an ablation, a cross-linking or a surface activation, depending on the gas and the material tested. Ablation consists of the removal from a surface both molecular layers and organic residues. This effect is part due to the continuous bombardment of a surface by plasma particles and by electromagnetic radiation and part due to fluid dynamic interactions between the gas flow and the surface. It also produces an increase in surface roughness. Crosslinked polymer is formed by the bombardment and radiation given out by plasma particles which causes the breakage of polymer macro-molecules and the simultaneous creation of free radicals. Activating a surface by means of cold plasma increases the layer energy and that leads to the capture of polar groups by the surface.

2.6.2 Chemical Surface Modifications

In wet chemical surface modification, a material is treated with liquid reagents to generate reactive functional groups on the surface. This traditional approach can be easily conducted as it does not require specialized equipment and hence can be easily conducted in any small-scale laboratory$^{52}$. Also, in comparison to plasma and other energy source surface
modification techniques, this makes easy penetration of the wet chemical through porous three-dimensional substrates as well as in-situ surface functionalization. On the other hand, these techniques are not very reproducible and produce hazardous chemical wastes and irregular surface etching.

2.6.2.1 Chemical Etching

Chemical etching is a type of a wet surface modification technique. This method involves the use of chemical etchants to convert smooth hydrophobic polymer surfaces to rough hydrophilic surfaces by dissolving the amorphous regions and/or oxidizing the surface as shown in Figure 2.13. It shows ‘grass-like’ residue due to polymer etching.

![SEM image of ‘grass-like’ surface formed due to etching](image)

*Figure 2.13: SEM image of ‘grass-like’ surface formed due to etching*  

It has been established that the amorphous phase on the interfacial layers are the ones
chiefly affected during these treatments. Chemical treatment by etching have been used traditionally for large objects that would be difficult to treat by any other means. The choice of etchant completely depends upon the type of polymer. Usually strong acids are used for such purposes. Concentrated sodium hydroxide and sulfuric acid have been used to generate carboxylic acid groups by base and acid hydrolysis of PMMA. The methyl ester side chains of PMMA have been reduced to hydroxyls. Chromic acid and potassium permanganate in sulfuric acid have been used to introduce reactive oxygen-containing moieties to PE and PP. PP surface etched with chromic acid solution was more effective than plasma etching to bring about an improvement in adhesion. Chang et al. studied the pretreatment parameters such as etching time, temperature and air agitation and found that amongst these parameters, the critical parameter is the etching time. The ultimate peel strength observed was just before the sample was over-etched. High etching time led to over etched sample where the surface strength was diminished and peel strength dropped. Thus, investigation of the surface chemistry in terms of functional group content, wettability, surface morphology and adhesive strength of etched films revealed that by controlling the reaction temperature and time, the adhesive strength can be controlled and a surface with optimum wetting and adhesive properties can be achieved. However, the main shortcoming of this process, other than using correct time of treatment, is the lack of control over the process, leading sometimes to excessive bulk degradation for highly amorphous polymers. Hence the degree of surface functionalization may not be repeatable between polymers of different molecular weight, crystallinity or even tacticity. Since the etching methods generate a range of
hazardous chemicals and many of these techniques require extended treatment in concentrated corrosive solutions, these techniques may not be very suitable for larger scale, industrial applications.

2.7 **Bulk Modification of Polymers with additives**

Most of the macromolecular substances, especially solid polymers, that are received from manufacturing processes cannot be used as received. Almost every time, small amounts of additives have to be mixed as processing aids or to improve the properties of the polymer before molding or granulating these compounds\(^{29}\). The following list of additives is the most commonly used ones and are the most beneficial to processing:

- Lubricants are used to enhance the rheological properties during manufacture and ease processing
- Stabilizers are added in melt to prevent thermooxidative degradation
- Plasticizers increase processability, flexibility and impact strength
- Antioxidants and light stabilizers are used as anti ageing additives to protect against oxygen and light during usage
- Fillers and reinforcing materials for selectively modifying certain predominant mechanical properties

Sometimes depending on the actual need and intended application of the polymer, the following agents are also added:
- Antistatic agents for protection against electrostatic charging
- Conducting additives eg. Carbon black, graphite, to decrease electrical resistance
- Flame proofing agents to decrease inflammability and combustibility
- Dyes and organic/inorganic pigments for coloring
- Blowing agents for manufacture of foams

2.7.1 Addition of stabilizers

During the manufacture of moldings and also during use, polymers can be exposed to substantial amounts of heat or elevated temperatures and temperature fluctuations. For example, many manufacturing processes reach temperatures of ~100-200 °C above the glass transition temperatures of the polymers to get them in a melt state as well as obtain the required melt viscosity. Also atmospheric oxygen and light may cause thermal chain scissions or oxidation by radical mechanisms. Many polymers undergo thermal oxidative degradation during processing. Over longer periods at ambient temperature polymers also deteriorate in the solid state through what is called autooxidation and photooxidation. When materials are exposed to UV solar radiation, the energy of this radiation is sufficient enough to initiate photochemical reaction. These unwanted degradations and oxidation processes can be suppressed by structurally modifying the polymer in processing by adding suitable additives. Usually, antioxidants come to the rescue and prevent ageing and unstable surface properties. Amines especially aromatic amines and hindered heterocyclic amines are the most commonly used to stabilizers for protecting plastics. The basic requirements for stabilizers
are that they must be effective over long periods of time, they should not volatilize, leach out or otherwise removed from plastic material. They also need to be dispensed homogenously in the polymer matrix.

2.7.2 Addition of plasticizers

Plasticizers are substances added to polymers to improve their softness, processability and stretchability. Plasticizers increase the free volume in a polymer, thus lowering the glass transition temperature which eventually influences the melting and softening temperatures. It also tends to reduce the elastic modulus and hardness of the polymers. Plasticizers are nothing but low molecular weight substances or oligomers which can change the softness or other properties as they lie in between the polymer chains, thus reducing the interactions between the polymer chains. The effects are seen in the lowering of glass transition temperatures. The basic requirements for a plasticizer is that they should be a high boiling, have a low vapor pressure and should not migrate to the surface of the polymer to avoid embrittlement of the softened products. Sometimes the plasticizers are built into the polymer chain, called ‘internal’ plasticization to irregularise the usual packing of the macromolecular chains and hence cause a decrease in the glass transition temperature. One apparent advantage of internal plasticizer is that the oligomers cannot migrate to the surface but again they are restricted in how much of these monomers could be used.
2.7.3 Addition of fillers and reinforcing materials

Fillers are solid materials that are dispersed in plastics and elastomers. There are two kinds of fillers—inactive and active. The inactive ones are used simply to make the plastic inexpensive; the active ones are more specific and try to improve mechanical properties thus reinforcing the polymer. What constitutes as fillers are small irregularly formed pieces of organic (cellulose, wood flour, carbon black) or inorganic (silica, powdered stone, chalk, talcum powder, glass beads) substances. It is very well known that the thermal and mechanical behavior of polymer is strongly influenced by factors such as type, size, content and shape of the filler. Besides, these properties have a very complex dependence on the chemical structure and the crosslink density when thermostaat resins and metallic fillers are combined.

2.8 Compatibilization

The goal of combining two or more polymers such as commercial ones or commercial and specialty polymers is to achieve a combination of favorable properties from each polymer in the blend. Compatibilization lowers the interfacial tension in a blend while also reducing the coalescence rate. However, when two immiscible polymers are blended without any compatibilization, what one would obtain is a mixture with physical properties that are worse than those of the individual polymers. Usually such blends have poor structural integrity combined with poor heat stability. On macroscopic levels, the blend
appears to be completely heterogeneous and even structurally delaminated. When a compatibilizer is indeed used, one expects a synergistic combination of the favorable properties of the parent polymers in the blend. In short, the ultimate goal in making a compatible blend is to stabilize an appropriate morphology of the dispersed phase polymer in the matrix polymer. There are several methods of compatibilization of immiscible polymer blends but these can be broadly classified into two main strategies: physical compatibilization and reactive compatibilization. The first one (also called as blending) consists of adding a pre-formed suitable substance such as a copolymer or a coupling agent to the immiscible blend, whereas, the second strategy (called grafting) involves the generation of the compatibilizer in-situ during the melt processing of the blend. These two processes will be explained in detail in the following section.

2.8.1 Polymer Blends

Even though there are a few polymer blends which obey specific sets of condition and exhibit miscibility, most commercial polymer blends are immiscible and they require compatibilization. As with metals, it is principally possible to vary the properties of macromolecules by adding one or more polymers together, but (as mentioned before) that more often than not it results in a heterogeneous mixture. These polymer blends exist as two phases, one polymer is the dominant phase called the ‘matrix’ while the other added polymer is called the ‘dispersed phase’. If two polymers are mixed together they can either form one homogeneous system or separate into two phases. Which of the two cases would occur would
depend whether the free energy of the system ($\Delta G$) increases or decreases during the mixing process. The Gibbs free energy equation is given as:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

Eqn. (2.5)

For complete miscibility or to obtain a homogeneous system, the free energy value has to be negative and incompatibility or a two phase system results when the free energy value is positive. When mixing two polymers, either in solution or melt, the condition of $\Delta G < 0$ is less frequently encountered compared to when mixing two low molecular liquids. This is due to the very low value of the entropy of mixing $\Delta S$ for high molecular weight substances. Although the entropy of mixing is positive as there is an increase in disorder due to mixing, the absolute values are still substantially lower for polymers than for low molecular weight liquids. Therefore, it is only possible to obtain a homogeneous single phase mixture when the enthalpy of mixing $\Delta H$ is sufficiently small or its magnitude is smaller than $T\Delta S$. However, this is only expected in the case of mixing very similar macromolecules. So most of the time one ends up getting a phase separated system in which the molecules of polymer A are only slightly or not at all miscible in the other polymer B. In other words, the polymer A is incompatible or partially compatible with polymer B.

There is another indicator to whether a polymer blend will be partially or fully miscible. It is based on Flory Huggin’s lattice theory. A negative value of Flory Huggins’s parameter ($\chi$) indicates good miscibility whereas a positive $\chi$ means immiscibility or
complete incompatibility. However, this theory fails for those polymer mixtures where crystallization and strong intermolecular actions occur.

2.8.1.1 Strategies for blending

The strategies to induce compatibilization include addition of a small quantity of co-solvent as the third component which would be miscible with both the phases, adding a copolymer such that, the block or graft polymer, used as a compatibilizing agent contains a minimum of two different segments such that each segment is either miscible or has significant interactions with one blend component. A sufficient amount of the added copolymer is expected to locate at the interface between the two blend components and reduce the interfacial tension, hence stabilizing the dispersion. Fayt and coworkers concluded that a block copolymer is more efficient than a graft copolymer and that a diblock copolymer is a more effective than a triblock copolymer. The third strategy is to add a large amount of a core shell polymer which, in addition to acting as a compatibilizer would act as an impact modifier. The fourth strategy includes adding a reactive compatibilizer which would modify one macromolecular species such that it would develop local miscibility regions and last but not the least strategy is to involve mechano-chemical blending.

Blending changes the morphology of the new blended structure. Morphology depends on the concentration of different ingredients of the blend. At low concentration of either component the dispersed phase forms more or less spherical drops, then with increasing amounts of loading of this ingredient, cylinders, fibers and subsequently sheets are formed.
Thus, one can classify the morphology to be dispersed at both ends of the concentration scale-low and high, and co-continuous at intermediate concentrations. The maximum co-continuity occurs at the phase inversion concentration, $\Phi_I$, where there ceases to be any distinction between the matrix and the dispersed phase. Microrheology can be used as a suitable guide to understand the morphology of blends. The quality of compounded blend affects the processing and performance of the final blend. Layering, poor weld lines in injection molded parts, skin-core extrudate structure with low notched Izod impact strength, all indicate poor blend quality-either not adequate dispersion or poor stabilized morphology.

2.8.1.2 Advantages and disadvantages of blending

Blending of polymers is a powerful way to obtain improved property/cost performances. This strategy is usually cheaper and less-timing consuming than the development of new monomers/polymers and/or new polymerization routes. It provides materials with full set of desired properties at lowest prices and also extends the resins performance. An additional advantage is improved processability, product uniformity and scrap reduction. One drawback is that the blend or alloy cannot be recycled into its constituents.

2.8.1.3 Examples of blended PP

Polyethylene (PE) has been used to improve the low temperature impact strength of
PP. These two blends are mostly immiscible and are compatibilized by adding either ethylene-propylene rubber (EPR), ethylene-propylene-diene monomer rubber (EPDM), reactive blending or by post blending co-crosslinking. Blends of PP with elastomers such as polyisobutylene and other polyolefins such as polyethylenes have been used since a long time and these were made with the aim of improving the mechanical properties of thermal bonded non-woven fabrics. In blends of PP with elastomers, roughly 5-20% of elastomers have been used. The main elastomeric polymers that have been widely used include EPR, polyisobutylene (PIB), styrene-butadiene rubber (SBR) and such. Many EPR and EPDM elastomers show a block copolymer behavior such that when blended with PP, they form emulsion like dispersions. Sometimes a small amount of PE is added to ease processing. If the elastomeric phase gets slightly crosslinked the morphology becomes more stable. The PP/EPR blends show characteristics of good processability, dimensional stability, low shrinkage, high stiffness, tear strength and softening temperature as well as good mechanical properties, ozone resistance, fatigue and abrasion resistance. Despite the similar nature of PP and Linear Density Polyethylene (LDPE), these blends exhibit negative deviation from additivity indicating they are immiscible and that their miscibility depended on the blend composition as well as molecular weight of the LDPE. PP/EVAc blends are immiscible, hence only small amounts of ethylene-vinyl acetate copolymers (EVAc) are used and it helps in improving dyeability, flexibility, electrostatic dissipation as well as barrier properties. PP has also been blended with many engineering resins to get desired properties. In the case of PP/PA blends, there are three kinds: ones with a small percentage of polyolefins, alloys with high PA content such that it behaves as the matrix phase and blends with small amounts of
dispersed PA to increase rigidity of the resulting blend. PP/PC blends are immiscible thus only very small amounts of one into the other concentrations have been experimented with. Examples are where 5 wt% PP was added to PC to improve processability or where 10 wt % of PC was added to PP to enhance processability and crystallinity, appearance, modulus and impact strength, etc. PP has also been blended with specialty polymers to give it the edge in performance. PP blends with small amounts of Liquid Crystalline Polymers (LCP) are added for improved processability, mechanical performance which depends on the blends morphology.

2.8.2 Grafting

2.8.2.1 Techniques of grafting

The various techniques available to graft polymers or monomers on polymeric backbones include chemical, radiation, photochemical, plasma-induced and enzymatic. When grafting is initiated by chemical means it can proceed along two major paths: free radical grafting or ionic grafting. Atom transfer radical polymerization is also interesting. In free radical grafting, radicals are produced from initiators and transferred to the polymeric backbone to react with the monomer to form graft co-polymers. Radiation grafting through the ionic mode proceeds where ions are formed through high-energy irradiation. The polymer is irradiated, it forms the polymeric ion and then on reacting with the monomer, it forms a
graft-copolymer. One big advantage of ionic grafting is the high reaction rate. In photochemical grafting, the grafting process is initiated when a chromophore on a macromolecule absorbs light and it becomes excited and dissociate into reactive free-radicals. Plasma induced grafting is already discussed previously. Enzymatic grafting technique is very new and the principle involves enzymes which initiate chemical/electrochemical grafting reaction.

2.8.2.2 Controlling factors in a grafting reaction

There are a lot of variables that control the extent of the grafting reaction such as the nature of the polymer backbone, monomer, solvent, initiator, additives, temperature, etc. The backbone plays an important role as the monomer are covalently bonded to the pre-formed polymeric backbone. For example, cellulose would resist the grafting reactions in water as they are insoluble in them. The monomers’ reactivity is dependent on many factors such as their polar and steric nature, swellability of backbone in their presence and their concentration. Graft copolymerization involving a mixture of monomers is different and more complex than those involving single monomer. Grafting locations change depending on the stereochemistry of the monomers involved. Solvents in grafting reactions act as a medium by which monomers are transferred to grafting locations on the polymeric backbone. Which solvent is chosen depends on the solubility of the selected monomer, the swelling properties of the backbone, the miscibility of the solvents if there are two or more and so on. For example, the presence of water is essential for grafting carboxylic acid terminated PP
onto collagen or other protein containing materials. Initiators are an essential part of every grafting reaction so its concentration, solubility as well as function are important and can very well decide the route of grafting reaction. AIBN initiator, unlike peroxide initiators, exhibit resonance stabilization and hence gives low performance compared to the other. In terms of the concentration, beyond a certain amount the initiators do not bring about enhanced conversion of grafted monomers. Instead they may lead to higher termination rates and thus the yield of the reaction can be lower than expected. Temperature is also an important factor that controls the grafting reaction as the grafting yield increases with temperature (upto a certain extent). The positive effect of temperature can be due to the enhanced mobility provided to the monomer to move about and reach the polymer backbone. Enhanced swelling of the backbone and hence enhanced rate of diffusion of monomers in silk grafting was observed by Dilli et al. However, had noticed in the case of grafting acrylamide to cellulose acetate there was a decrease in the grafting yield with an increase in the temperature.

2.8.2.3 Routes for grafting

Grafting can be done broadly by two different routes-‘grafting from’ and ‘grafting to’. The former utilizes active chemical species already present on the surface to initialize the polymerization process. The latter route utilizes preformed polymer chains carrying reactive groups at ends or sides which are covalently coupled to the surface. Also grafting can take place on spherical substrates as well as plane surfaces (Figure 2.14). For reactive compatibilization, the functional groups are selected so that they are formed at the interface
within the processing time at the extruder. Because of the limited yield of the interfacial reaction and the high viscosity of the reaction medium, highly reactive groups are required.

![Grafting schematic on spherical and plane surfaces](image)

**Figure 2.14: Grafting schematic on spherical and plane surfaces**

2.8.2.4 Advantages and disadvantages of grafting

The advantages of reactive compatibilization include 1) The copolymer is made as needed during the melt-blending process and a separate commercialization of the copolymer is not needed. 2) The copolymer is directly formed at the interface where it has to act to reduce the interfacial tension unlike in physical compatibilization where the copolymer has to overcome the viscous forces and find its way to the interface. 3) The molecular weight of each of the two distinct polymeric segments in the copolymer is usually the same as that of the individual bulk polymer phase in which the segment must dissolve allowing, thus, for a maximum interfacial adhesion. 4) It is a very specific process with the number of graft chains, the graft chains density, the length of graft chains being very easily specified and
controlled. 5) Also care can be taken to modify only the surface properties leaving the bulk unmodified and unchanged. 6) Additionally, the covalent attachment of the graft chains with the surface leads to long term chemical stability and prevents delamination, in contrast to physical methods of modification.

There are also disadvantages associated with this process: the in-situ compatibilizer may form micelles as a separate phase that is useless for compatibilization, also there is a need to have reactive functional groups on the polymers to be compatibilized.

2.8.2.5 *Examples of grafted PP*

Norton et al. ⁶⁵ and Sha et al. ⁶⁶ in their work on the mechanism of reinforcement of the interface verified that the maximum surface density of graft molecules that can be effectively attached to the substrate surface is inversely proportional to the length of grafted chains measured by their degree of polymerization. Norton showed in his experiments that the maximum surface graft density ($\sigma$) was obtained when the length of the connector molecules (N) was small.

Grafting by UV radiation on semicrystalline polymers yields a bumped surface texture, likely due to the difference in the activation reaction between the crystalline and the amorphous regions and this creates adhesion sites by mechanical interlocking.⁶⁷ One of the good candidates for carrying out surface grafting with UV is Hydroxyethylmethacrylate (HEMA). First it is inexpensive, can be easily grafted to polyolefins by UV grafting and it contains a polar hydroxyl group that helps in imparting the desired hydrophilicity. Exposing
isotactic PP to ozone results in surface oxidation and formation of peroxides and hydroperoxides. With as little as 5 minutes of ozonation, the molecular weight of the PP drastically reduced. Cellulose fibers exhibiting stimuli (pH) sensitive was prepared by ozone induced graft polymerization.

The structure of grafted surface changes with degree and amount of grafting. Grafting density changes enormously depending on the conformation of the graft chains and also whether it is in a good solvent or a poor solvent. A mushroom structure is formed at low grafting densities, whereas at high grafting densities a stretched polymer brush results.

Maleic anhydride (MA) has been extensively used to modify PP by the grafting process. Grafting PP with MA increases its polarity thus increasing its capacity for interfacial interaction\footnote{68}. PP-g-MA has been used for various purposes: as a compatibilizer to compatibilize alloys of incompatible polymers, as a coupling agent for chemically bonding reinforcing agents to the PP matrix, as an adhesive layer in multilayered coextruded laminates, as a compactor for radioactive waste. MA in the copolymer improves the dyeability of PP fibers and PP-g-MA is also used with reinforcing agents in laminated paper substitutes. For grafting functional PP two methods hydroperoxidation and halogenation are widely used\footnote{69}. The hydroperoxidation of PP was carried out by heating in an air/oxygen current at 70-80 °C. Five oxidation variables-temperature, time, oxygen pressure and concentrations of initiator and surfactant are considered to be important factors to attain peroxide content for a desired graft level. A number of monomers such as methyl methacrylate, vinyl chloride, vinyl acetate, etc are used for the hydroperoxidation which is
believed to be restricted to surface or intercrystalline amorphous regions. Halogenation is another method used to introduce functionality into PP backbone. A chlorine atom is introduced onto PP backbone turning nonpolar PP into a polar one.

2.9 Interpenetrating Networks

Another method of compatibilizing diverse polymers involves the simultaneous or sequential polymerization of polymer networks. Blends created with this approach are called interpenetrating networks (IPN). The basic hypothesis is that the interlocking rings of polymers (referred to as catenane structures) would lead to compatibilization of diverse polymers. This approach does not require covalent bonding between the constituents, although it may occur. As the reaction of the networks proceeds, polymer chains at the interface can become interlocked leading to mechanical adhesion. Simply put, an IPN can be defined as a combination of two polymers in network form, at least one of which is synthesized and/or crosslinked in the immediate presence of the other. An IPN can be distinguished from simple polymer blends, block copolymers and graft copolymers in broadly two ways: 1) An IPN swells but does not dissolve in solvents 2) creep and flow are suppressed. IPN’s are of two types, the sequential IPN and the simultaneous IPN’s (SIN’s). The sequential process begins with the synthesis of a crosslinked polymer I. Monomer II, plus its own crosslinker and initiator, are swollen into polymer I, and polymerized in-situ. In SIN’s, there occurs a mutual solution of both monomers and their respective crosslinkers are polymerized simultaneously by noninterfering modes, such as stepwise and chain
polymerizations. There is also a third mode of IPN synthesis which takes two latexes of linear polymers, mixes and coagulates them and crosslinks both components simultaneously. This product is called as an interpenetrating elastomeric network (IEN) \(^70\).

![Figure 2.15: Schematic of Interpenetrating Networks (IPN) \(^71\)](image)

Another method of compatibilization involves crosslinking between the phases of a phase separated system. Some additional methods of compatibilization include solid-state shear pulverization. It involves the application of high shear/extension below the melt or the glass transition temperature to yield a fine powder without melting. Chain scission resulting in free radicals at the chain ends allows for the potential of block copolymer formation at the interface if a polymer blend is employed. This method was applied to PP/Polystyrene blends followed by melt mixing and the results were compared with non-pulverized melt mixed control blend \(^72\). The particle size reduction in the solid state pulverized method showed
evidence of compatibilization. High power ultrasound applied to PP/EPDM blend during extrusion yielded improved morphological stability and modest improvements in mechanical properties. The addition of organically modified clay (2-5 wt%) to PP/PS blends showed a reduction in the dispersed PS particle size.

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CHAPTER 3

3 Surface and Bulk Properties of Glycidyl Methacrylate Modified Polypropylene:
Experimental and Molecular Modeling Studies

3.1 Abstract

Modifications of polypropylene (PP) are often carried out to either functionalize them or meet specific property demands. This study considered the process of PP grafting with glycidyl methacrylate (GMA) as an intermediate step to achieve improvements in surface properties of this polymer. Abundant literature is available on this grafting process but little is known about the surface properties of the grafted PP. Present work considered both experimental and computational approaches to attain this goal. Experimentally, it was established that the melting temperature of modified PP changed with the addition of GMA, and at higher concentrations of GMA in the PP matrix, heterogeneous nucleation took place. Experimental results revealed a decrease in the surface energy (SE) as well. To discern the underlying reasons behind these changes, molecular dynamics simulations were undertaken. The computational results revealed that the changes in SE could be associated with the location of the functional group.

3.2 Introduction

Due to good mechanical properties, excellent chemical resistance, ease of
processability and relatively low cost, polyolefins, especially polypropylene (PP), have become one of the largest polymers in use today in a variety of applications\(^1\). However, due to its nonpolar nature, PP possesses poor adhesive properties limiting its application in laminates and composites\(^2, 3, 4\). Various chemical modification techniques have been employed for several decades to overcome this deficiency in PP. Melt–grafting of polar monomers is one of the many methods used to modify polyolefins\(^5\). PP is frequently grafted with such monomers as maleic anhydrate or carboxylic acid\(^6, 7, 8, 9, 10\). Glycidyl methacrylate (GMA) has been utilized as the grafting monomer for polyolefins because epoxy groups of GMA are able to react with -OH, COOH, and NH\(_2\)\(^11, 12, 13, 14\). Being grafted on the fiber surface, GMA can also improve fiber wettability and adhesive properties, or GMA can be used as an “anchor” for the further polymer/fiber modifications.

In the work reported here, we considered grafting of polypropylene with GMA and styrene monomers as an intermediate step for the improvement of PP adhesive properties. This technique was studied in details by Xie et al\(^15\) and Sun et al\(^16\). It was discerned that the presence of styrene decreased the degradation of PP during the melt-grafting process. This technique also led to the highest concentration of grafted GMA.

The primary focus of this study was to determine the optimal concentration and location of the functionalized group (i.e. GMA). Therefore, we examined the surface and bulk properties of the styrene-GMA modified PP experimentally. Additionally, we carried out molecular dynamics simulations to determine the underlying mechanisms. Molecular dynamics simulation is a powerful tool for studying microscopic properties of amorphous
polymers, as well as for predicting the properties of polymeric materials. A number of studies have used this approach\textsuperscript{17, 18, 19, 20, 21, 22, 23, 24} to compute surface energy, density profile, adhesion and compaction parameters for various polymers and their compatibility in blend systems. In the work reported here, the surface energies of PP containing different concentrations of GMA molecules and their location with respect to the surface were calculated.

### 3.3 Experimental

#### 3.3.1 Materials

For this work, polypropylene ($T_m = 160.7$ °C, $\rho = 0.91$ g cm\textsuperscript{-3}, Melt flow index = 34) was obtained from Sunoco Chemicals (USA). The rest of the chemicals required for melt-grafting, such as dicumyl peroxide (=99%), glycidyl methacrylate (=97.5%) and styrene monomers (=99.5%), were purchased from Sigma-Aldrich, Inc. (USA).

#### 3.3.2 Sample preparation

Melt-grafting of PP with GMA was carried out by charging PP pellets, styrene, GMA and initiator into the twin-screw micro-compounder (ThermoHaake Corp., USA). The reaction temperature was set and maintained constant at 175 °C. The grafting was carried out for 11 minutes at the screw speed of 100 rpm. The styrene to GMA molar ratio was kept constant at 1:1 and the initiator at 0.6 weight (wt) % or 1 wt %\textsuperscript{14}. The concentration of GMA
added ranged from 4 to 8 wt%, with 8 wt% being the maximum amount that could be loaded into the extruder.

After the designated reaction time, the polymer melt was extruded from the micro-compounder. Modified polypropylene was then purified by dissolution in hot xylene. Unmodified and modified PP were precipitated by the addition of 400 ml of acetone. The precipitated polymer containing pure and grafted PP was filtered out leaving unreacted chemicals in the filtrate. The resulting ‘cake’ was dried in the vacuum oven for 24 hours at 80° C.

3.3.3 Characterization

The amount of GMA reacted with the PP was determined by FTIR spectroscopy (Nikolet Nexus 470 FT-IR)\(^1\). For this purpose, the peak of carbonyl group appearing at 1730 cm\(^{-1}\) and the peak of the PP at 2722 cm\(^{-1}\) were taken as references. Calibrations for GMA were made using known concentrations of GMA.

The determination of total surface energy, its polar (\(\gamma_p\)) and disperse (\(\gamma_d\)) parts, was conducted via contact angle measurement using sessile drop method. Two different liquids were used: deionized water (\(\gamma_d = 22.1\) and \(\gamma_p = 50.7\) mJ m\(^{-2}\)) and ethylene glycol (\(\gamma_d = 29\) and \(\gamma_p = 19\) mJ m\(^{-2}\)). The final total surface energies were calculated by using a set of harmonic-mean equations\(^2\).

The DSC analysis was conducted on a Perkin Elmer DSC 7 differential scanning calorimeter in nitrogen atmosphere. The samples were heated at a heating rate of 20° C min\(^{-1}\).
from 25 to 180° C. The samples were maintained at 180° C for 5 min and cooled down under the same conditions.

3.3.4 Computational details

Simulation of polymers was carried out using a commercially-available MS modeling software from Accelrys, Inc. (USA)\textsuperscript{26}. A series of molecular dynamics (MD) runs and minimizations were performed with Discover module employing COMPASS forcefield\textsuperscript{27}. The minimizations were conducted using ‘Smart Minimizer’, where the process of minimization starts with the steepest descent approach followed by conjugate gradient and Newton methods. Non-bonding interactions were calculated using the group-based method with the cut-off radius of 9.5 Å.

Polymer chains with 50 repeat units were generated using ‘Amorphous-Cell’ module with periodic boundary conditions. To construct the modified PP, the functionalized group was added to the center (25\textsuperscript{th} repeat unit) of the PP chain as shown in Figure 3.1.
Figure 3.1: Structure of GMA-grafted-polypropylene

Amorphous cells of PP and its grafted version, GMA-g-PP, were constructed at the experimental density of PP. The parameters of the resulting structures are shown in Table 3.1. For each configuration 5 amorphous cells were built.

Table 3.1: Properties of the cells studied

<table>
<thead>
<tr>
<th>Concentration of GMA , %</th>
<th>0</th>
<th>0.8</th>
<th>1.3</th>
<th>1.7</th>
<th>2.2</th>
<th>3.3</th>
<th>4.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP, number of molecules</td>
<td>3</td>
<td>7</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>GMA-g-PP, number of molecules</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Average cell size, Å</td>
<td>23.13</td>
<td>32.09</td>
<td>27.32</td>
<td>25.63</td>
<td>23.34</td>
<td>20.39</td>
<td>23.60</td>
</tr>
</tbody>
</table>
These cells were then refined by running a ‘basic refine’ protocol with molecular dynamics run of 4000 fs at 298 K. To remove low or zero density areas, the cells were run through a temperature cycle – 11 stages from temperature of 298 K to 453 K and 11 stages from temperature of 453 K to 298 K – keeping pressure at 1 atm (0.0001 GPa). Finally, all cells were minimized using ‘Smart Minimizer’ to a convergence of 0.1 kcal mol\(^{-1}\) Å\(^{-1}\).

Ready bulk samples were relaxed for 50 ps via NVT (constant concentration, volume and temperature) MD simulation. Snapshots of the trajectory were taken every 0.025 ps during the last half of the run. The snapshot with the lowest potential energy was minimized to a convergence of 0.1 kcal mol\(^{-1}\) Å\(^{-1}\). The generated bulk samples were used to form film cells and to calculate the cell parameters.

To create the thin films, one edge (z direction) of the minimized bulk samples was extended to 100 Å, so that the polymer chains no longer interact with its image along this direction. These newly-formed films were subjected to the energy minimization run followed by 50 ps of MD simulation at 298 K. The trajectory snaps were taken during last 25 ps and a cell with minimum potential energy was further minimized. In some cases however, the dynamics were conducted at 600 K to ‘shake’ the cell out of unfavorable local minima. The resultant film cells were used for the calculations of surface energies and density profiles.

The surface energies were calculated as the difference of potential energies of the thin film (\(E_{film}\)) and its corresponding amorphous cell (\(E_{cell}\)) divided by surface area (2A) created upon formation of the thin film as given by the equation below:\(^{18}\):
\[ \gamma = \frac{(E_{film} - E_{cell})}{2A} \]  

Eqn (3.1)

3.4 Results and discussion

3.4.1 Experimental results

The grafting process yielded a series of functionalized PP. The results are shown in Table 3.2.

Table 3.2: Grafting efficiency and surface energies of GMA modified polypropylene

<table>
<thead>
<tr>
<th>GMA added %</th>
<th>GMA grafted %</th>
<th>Total surface energy mJ m(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>27.6 ± 0.4</td>
</tr>
<tr>
<td>4</td>
<td>0.45</td>
<td>25.0 ± 0.8</td>
</tr>
<tr>
<td>8</td>
<td>0.81</td>
<td>23.0 ± 0.4</td>
</tr>
<tr>
<td>6</td>
<td>1.31</td>
<td>23.2 ± 0.8</td>
</tr>
<tr>
<td>6*</td>
<td>1.90</td>
<td>25.0 ± 0.6</td>
</tr>
</tbody>
</table>

* - with 1% wt of initiator

Due to limitations of the present experimental apparatus, the highest concentration of GMA grafted onto PP was only 1.9% wt. Nevertheless, the table depicts that there is a
maximum concentration of GMA molecules that can be introduced onto PP chain without changing the initiator concentration. Similar observations were made by Xie et al\textsuperscript{15}. The addition of the initiator resulted in an increase in grafting efficiency but at the expense of PP degradation by the initiator. The presence of GMA in PP matrix decreased the SE wherein a minimum was obtained at about 0.8 wt\%. These results might indicate the change in miscibility of the grafted and unmodified PP molecules\textsuperscript{28}. To confirm this, samples were analyzed by DSC.

The effect of grafting on crystallinity (X\textsubscript{c}), crystallization (T\textsubscript{c}) and melting (T\textsubscript{m}) temperatures were determined by DSC. The results are shown in Table 3.3.

\textbf{Table 3.3: Melting (T\textsubscript{m}), crystallization (T\textsubscript{c}) temperatures and crystallinity (X\textsubscript{c}) of GMA grafted polypropylene}

<table>
<thead>
<tr>
<th>GMA grafted, %</th>
<th>T\textsubscript{m}, °C</th>
<th>T\textsubscript{c}, °C</th>
<th>X\textsubscript{c}, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>160.7</td>
<td>113.6</td>
<td>50</td>
</tr>
<tr>
<td>0.6</td>
<td>157.9</td>
<td>116.6</td>
<td>63</td>
</tr>
<tr>
<td>0.9</td>
<td>162.2</td>
<td>117.2</td>
<td>71</td>
</tr>
<tr>
<td>1.4</td>
<td>162.0</td>
<td>119.4</td>
<td>62</td>
</tr>
<tr>
<td>1.9</td>
<td>160.5</td>
<td>118.5</td>
<td>48</td>
</tr>
</tbody>
</table>

The DSC analysis of PP-g-GMA showed that the T\textsubscript{c} of modified polyolefin were higher than virgin PP. This indicates that grafted GMA molecules provided additional sites for PP during the crystallization process. The melting temperatures of the grafted PP were
higher as well, with the exception of one sample containing 0.6 wt% of GMA. The melting temperature of this sample was observed to be 157.9º C, which is lower than the original PP polymer. Somewhat similar results were obtained by Liang et al\textsuperscript{29} and Pesetskii and Makarenko\textsuperscript{30}. The former observed an increase in $T_m$ value. The results were elucidated by the heterogeneous nucleation effect of GMA. Pesetskii and Makarenko also observed a decrease in the $T_m$ of the samples explaining it by the difference in melt viscosities and grafting efficiency. However, the surface energies or the degree of grafting were not determined.

Taking into consideration the results obtained by Krump et al\textsuperscript{28} stating that the surface energy of well-miscible polymer blends tend to decrease, then the PP chains containing up to 0.6% wt of GMA should possess good miscibility in an unmodified PP matrix. This sample had a lower surface energy and lower $T_m$ compared with ungrafted PP. However, the surface energies of the samples with a GMA content of 0.9 wt% and higher began to increase (see Table II). Also, the $T_m$ for these samples was higher than that of the virgin PP, i.e. heterogeneous nucleation was observed\textsuperscript{29}. These observations may imply limited miscibility of GMA-grafted molecules (above 0.9 wt%) with ungrafted PP.

It must be noted that the sample with 1.9 wt% was also an exception. The increase in the amount of initiator to 1 wt% led to a decrease in the viscosity of PP\textsuperscript{15} and hence a decrease in melting temperature was observed.
3.4.2 Atomistic simulation

To reaffirm the changes in the bulk properties of PP-g-GMA and also to perceive the effect of high wt% of GMA grafted, we turned to computational methods. The modified PP chains were constructed based on the results observed by O’Rourke-Muisener et al\textsuperscript{31}. They have concluded that the best architecture for the polymer having a polar functional group is when this group is placed at the center of the chain backbone. With this in mind, it is expected that the results from the computation will be slightly different from the experimental results because grafting occurred at random locations of the chain in addition to the slight variations in the structure of functional group. However, the phenomena observed experimentally should be also discerned computationally.

We began our analysis with the calculation of surface energy (SE) of the functionalized polypropylene by using eq. (1) and comparisons with the results obtained experimentally. The data are presented in Figure 3.2. As can be seen from this figure, the values of surface energy obtained via MD simulation were quite close to experimental values. A small decrease in the SE values was observed at the GMA concentration of 1.7 wt%, which is a bit higher than one observed during the experiments. The values of surface energy at lower concentrations of the GMA (lesser than 1.3 wt%) were not possible to obtain as the cell sizes were relatively large to construct ‘thin films’ and the correlation (1) was not applicable. However, MD simulations allowed us to project the SE values up to 4.4 wt% and higher. The MD simulation results show that the major changes in surface energy occurred up to GMA concentration of 3 wt%.
Figure 3.2: The values of surface energy of modified polypropylene and comparison of the data obtained from the experiments and molecular dynamics simulations

To determine if the changes in the SE values can be associated with the location of the functionalized group (epoxy), an analysis of the density profiles of the films along z direction was conducted. eq. (2) was employed to obtain the position of interface and its thickness:

$$\rho(z) = \frac{1}{2} \rho_{bulk}(z) \left[ 1 - \tanh \left( \frac{2(z-h)}{w} \right) \right]$$

Eqn (3.2)

where $\rho(z)$ is the density at position $z$, $\rho_{bulk}(z)$ is the bulk density, $h$ is the position from the interface, and $w$ is interfacial width.
Since the size of the cells was different, the ratio of distance of epoxy group from center of mass (c.m.) to the distance from the c.m. to the surface was calculated by:

\[ R(z) = \frac{l(z)}{h+w} \]  

Eqn (3.3)

where \( l \) is the distance of epoxy group from c.m. along z direction. The results of the calculation are shown in Figure 3.3. The data represented are the average of five cells.

This figure exhibits that the polar groups depleted from the surface. With an increase in its concentration, the high energy group drives away from the surface. At the concentration of 1.7 wt\%, the location of the epoxy group was near at the center of mass. At this point, the surface energy was also observed to be the lowest. At 2.2 wt\%, the epoxy group was found to be closer to the surface again. Perhaps it can be attributed to the rearrangement of this group to minimize its energy within PP due to its immiscibility with the rest polymer matrix, as it was observed during the experiments.
3.5 Conclusions

The influence of the concentration of GMA molecules on the properties of PP polymer was investigated in this work. Experimental results indicated an initial decrease in surface energy. Thermal analysis showed that at low concentrations of GMA in the PP matrix melting temperature was lower than that of unmodified PP. At a GMA concentration of about 0.9 wt% and higher, heterogeneous nucleation was observed as indicated by the values of Tm. MD simulation confirmed our experimental observations. The variation in surface energy could be attributed to the location of the functional group. The epoxy group was observed to be closer to the surface at lower concentrations of functional group which
suggests that further modifications of polymer/fibers could be more effective at these concentrations.

3.6 Acknowledgment

The authors would like to thank the industrial members of Nonwovens Cooperative Research Center (NCRC) for the financial support.

3.7 References


(3) Tu, X.; Young, R. A.; Denes, F. Cellulose 1994, 1, 87-106.


CHAPTER 4

4 Blending polypropylene with glycidyl methacrylate containing polymer to improve adhesion to elastomers

4.1 Abstract

BACKGROUND: Polypropylene is one of the widely used polyolefin but gets restricted in surface applications due to its non-polar nature. Surface properties of films made of polypropylene (PP) were modified to improve their adhesion to elastomeric polymers such as thermoplastic polyurethane (TPU) especially to Pebax® (Polyether-block-amide).

RESULTS: Surface modification of PP was brought about by blending it with glycidyl methacrylate (GMA) containing polymer to increase its surface energy (SE). Films of modified PP were analyzed to determine the blending efficiency and characterized by contact angle measurements, differential scanning calorimetry (DSC), X-Ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Molecular dynamics simulations were done to determine surface and bulk properties of PP blended with GMA. The computational results correlated very well with the experimental data and revealed that the changes in the surface energy can be linked to the position of the functional group within the sample. T-Peel tests indicated a 2.4 times increase in adhesion to Pebax and only 1.7 times increase in adhesion to TPU compared to unmodified PP.

CONCLUSION: Thus the surface energy values and enhanced adhesion proved that polypropylene was successfully modified and its surface made more polar.
4.2 Introduction

Polyolefins, specifically polypropylene (PP), have excellent bulk physical and chemical properties and therefore, are used in a variety of applications. However, the performance of polymeric materials relies to a large extent upon their surface properties and in many applications such as coating, bonding, metallization, printing, and adhesion between two layers surface property plays a very significant role. PP being hydrophobic and chemically inert has low surface energy and hence shows poor adhesion, especially to elastomers. Thus, PP surfaces are frequently modified to overcome this problem. These modifications are generally classified into two groups: physical and chemical. Some of the physical (structural) modifications can be incorporated by changing the spinning, drawing and relaxation treatment conditions so that the supramolecular structure is changed. In addition, the cross-section can be changed to bring about significant alteration in properties such as increased surface area. The chemical modifications of PP surface has been investigated by different methods such as plasma treatment, ion treatment, use of compatibilizers or blending, flame treatment, grafting etc. Grafting is one of the frequently used chemical compatibilization methods to functionalize polypropylene. PP has been grafted with acrylic acid, maleic anhydride, glycidyl methacrylate (GMA) and oxazoline. However, grafting is usually accompanied by undesirable side reactions such as branching and cross-linking which cause degradation of the polymer backbone. In addition, removing the residual monomer and initiator from the final product becomes difficult and sometimes challenging. Therefore, blending is a technique that can be
used to incorporate functional groups without additional post-processing steps. For years, polymer blending has been receiving attention from both the scientific and industrial communities as it is an efficient method that offers low-cost substitute to the development of entirely new materials 20.

The objective of this study was to investigate blending of PP with a GMA containing polymer as a way to improve adhesive properties of PP. The epoxide group in GMA was found to be very effective to bring about the modification process. While the GMA grafting procedure is often preferred, the process of blending has not received much attention. In this work, the effect of GMA concentration on polymer surface energy (SE) and the location of functionalized group in PP matrix were examined. The latter was obtained via molecular dynamics (MD) simulation. The MD simulation is a powerful tool for studying and predicting the microscopic properties of amorphous polymers. A number of studies have used this approach 21, 22, 23 to compute surface energy, density profile, adhesion and compaction parameters for various polymers and their compatibility in blend systems.

4.3 Experimental approach

4.3.1 Materials

Polypropylene (grade CP36OH) was obtained from Sunoco Chemicals (PA, USA). This polymer has a narrow molecular weight distribution, with a melting point ($T_m$) of 160° C, density of 0.91 g cm$^{-3}$, a Melt Flow Index (MFI) of 34 dg/min and crystallinity of about
50%. Polyethylene–block-glycidyl methacrylate (PE-b-GMA) was chosen as a functional polymer. This PE-b-GMA (Lotader AX 8840) was obtained from Arkema (PA, USA) with total content of 8 weight (wt) % GMA. This polymer has MFI of 5 dg/min, $T_m$ of 109° C, and a density of 0.94 g cm$^{-3}$.

Thermoplastic polyurethane films of 0.13 mm thickness, with ether-based soft blocks, were obtained from BASF (MI, USA). Pebax, (commercial grade MV 3000) obtained from Arkema, is a thermoplastic elastomer/flexible polyamide without plasticizer. It consists of a regular chain of rigid polyamide segments and flexible polyether segments. The thickness of these films was 0.13 mm. The soft blocks had a melting temperature ranging from 40-90° C and the hard blocks melted over a range of 140-160° C.

4.3.2 Experimental Procedure

The blends of PP and PE-GMA were obtained by mixing the two polymers in 100 cm$^{-3}$ xylene at ~120° C. The amount of functional polymer was added in a way to achieve 0.5, 1, 1.5, 2, and 4 weight (wt) % of GMA. This solution was then precipitated by adding 400 cm$^{-3}$ acetone, and filtered using vacuum. The resulting cake was dried for 24 hours in vacuum at a temperature of 80° C. The films were obtained by compression molding at 170° C and a pressure of 1.034 MPa. Each film was ca. 0.1 mm thick.
4.3.3 Analytical Methods

Total surface energy (SE), its polar ($\gamma_p$) and disperse ($\gamma_d$) parts were determined by static contact angle measurements using sessile drop method. Two different liquids were used: water ($\gamma_p = 50.7$ and $\gamma_d = 22.1$ mJ m$^{-2}$) and ethylene glycol ($\gamma_p = 19.0$ and $\gamma_d = 29.0$ mJ m$^{-2}$). SE was calculated using the contact angle values with the above mentioned liquids in the harmonic-mean equation $^{24}$. The results are an average of 10 readings.

The surfaces of the unmodified and modified PP films were analyzed with X-ray photoelectron spectroscopy (XPS). The samples were irradiated using Mg Kα (1253.60eV) rays. The unique set of binding energies of each element was used to identify and determine the concentration of the element on the surface.

The thermal analysis of the pure and blended polymers was performed with a Perkin-Elmer Diamond DSC-7 differential scanning calorimeter. Evaporated nitrogen, with a feed rate of 20 cm$^3$/min, was used as the purge gas. The samples, with weights of 0.003 to 0.005 mg, were run at temperatures ranging from –50° C to 180° C and a heating rate of 20° C min$^{-1}$. The total crystallinity of the sample was characterized as a ratio of heat of fusion of the present PP sample to that of 100 % crystalline polymer.

Scanning electron microscopy (SEM) was employed to study the microstructure of the modified PP films. To analyze film cross sections, the samples were fractured in liquid nitrogen. The cryofractured polymer samples were gold sputtered for 2 minutes and the morphology across the cross section was investigated.

To obtain changes in adhesion, T-Peel test (ASTM D1876-01) was conducted. The
modified PP films (0.1 mm thick) were laminated with TPU and Pebax films (~0.1 mm thick) at 140° C for 1 minute and 1.03 MPa pressure. The final thickness of the laminate was ~0.2mm. Sample size of the specimens for the test was 25 mm x 152 mm.

4.3.4 Computational Details

The MD simulations were performed by using a modeling software from Accelrys, USA. All runs were done by using the Discover package by employing the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force fields. The minimizations were performed using the ‘Smart Minimizer’ that begins a minimization process with the steepest descent approach followed by the conjugate gradient method and Newton method. Non-bond interactions were calculated using the group based method with a spline fit cut off radius of 9.5 Å.

PP and PE-b-GMA chains were generated with 50 and 75 repeat units, respectively. To construct the PE-b-GMA, the functional group was added to the 35th atom of the chain. The amorphous cells of each PP, PE-b-GMA, and their blends were constructed using the ‘Amorphous Cell’ package at their experimental densities. The edge length of these cells varied from 19.63 to 31.15 Å. To obtain a statistical average, five amorphous cell samples of each system were built.

The cells were first refined by running a ‘basic refine’ protocol with molecular dynamics run of 4000 fs at 298 K (25° C). To remove low density areas, the cells were run through a temperature cycle of 11 stages from 298 to 453 K (25 to 180° C) and back to 298
K (125° C) keeping pressure at 0.1 MPa. Finally all cells were minimized using ‘Smart Minimizer’ to a convergence of 0.1 kcal mol\(^{-1}\) Å\(^{-1}\).

Equilibrated bulk samples were generated by running NVT (constant concentration, volume and temperature) dynamics for 50 ps. Snapshots of the trajectories were taken during the last half of the run every 0.025 ps. The snapshot with the minimum potential energy was selected and further minimized with conjugate gradient and Newton minimizer to a convergence of 0.1 kcal mol\(^{-1}\) Å\(^{-1}\).

Thin films were generally constructed from the amorphous cells by elongating one of the periodic boundary conditions (at z direction). The periodic boundary condition along the z direction was extended to 100 Å. These new thin films were minimized followed by 50 ps of MD simulation at 298 K (25° C). The trajectory snaps were taken during the last 25 ps and the snapshot with the lowest potential energy was further minimized. In some cases, however, the dynamics were conducted at 600 K (573° C) to ‘shake’ the cell out of unfavorable local minima. The resultant films were then used to calculate surface energy and density profiles.

The surface tension was calculated from the energy difference between the thin film \((E_{film})\) and the bulk cell \((E_{bulk})\) divided by the surface area created upon formation of thin film as given by equation (1)\(^{22}\):

\[
\gamma = \frac{E_{film} - E_{bulk}}{2A}
\]

**Eqn (4.1)**
where surface area is 2A as two surfaces are formed upon creating thin films.

To determine the position of the epoxide groups of GMA, the analysis of the density profiles of the films along the z direction was done and equation (2)\textsuperscript{27} was employed:

\[
\rho(z) = \frac{1}{2} \rho_{\text{bulk}}(z) \left\{ 1 - \tanh \left[ \frac{2(z-h)}{w} \right] \right\}
\]

Eqn (4.2)

where \(\rho(z)\) is the density at position \(z\), \(\rho_{\text{bulk}}(z)\) is the bulk density, \(h\) is the position from the interface and \(w\) is interfacial width.

Since the size of the cells were different, the ratio of distance of epoxy group from center of mass (c.m.) to the distance from the c.m. to the surface \((h + w)\) was calculated by:

\[
R(z) = \frac{l(z)}{h+w}
\]

Eqn (4.3)

where \(l\) is the distance of epoxy group from c.m. along z direction.

### 4.4 Results and discussion

#### 4.4.1 Effect of Addition of PE-b-GMA on Properties of PP

The averaged surface energy (SE) values from five replicates are shown in Table 4.1.
Table 4.1: Values of surface energy obtained experimentally

<table>
<thead>
<tr>
<th>GMA concentration in PP (%)</th>
<th>Surface Energy (SE) mJ/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>27.55 ± 0.42</td>
</tr>
<tr>
<td>0.5</td>
<td>26.83 ± 0.47</td>
</tr>
<tr>
<td>1.0</td>
<td>26.19 ± 0.81</td>
</tr>
<tr>
<td>1.5</td>
<td>26.90 ± 0.29</td>
</tr>
<tr>
<td>2.0</td>
<td>27.11 ± 2.00</td>
</tr>
<tr>
<td>4.0</td>
<td>27.23 ± 0.94</td>
</tr>
</tbody>
</table>

It was observed that with the addition of GMA, SE of the films initially decreased to a minimum value of about 26.19 mJ/m² and then increased with higher concentrations of GMA in the sample. This initial decrease might indicate rather good miscibility amongst the functional polymer and the base polymer. Additionally, the minimum value of SE could be attributed to the point where the onset of phase separation is triggered. With the subsequent increase in surface energy, the blend behaved as a phase separated system with the functional polymer uniformly dispersed in the PP matrix. To confirm these observations and the phenomenon of phase separation, molecular dynamics modeling was performed and the blended samples were also analyzed using SEM and DSC.

4.4.2 Phase Separation

Experimentally, the onset of phase separation was observed by using SEM. The SEM micrographs of the cross sections of films of samples having 1, 1.5, 2 and 4 wt% of GMA
are shown in Figure 4.1. As can be seen from this figure, the blends with 1 and 1.5 wt % of GMA (Figure 4.1A and 4.1B) appeared to be homogeneously mixed. At 2 wt %, sharp edges as well as small globules of PE-b-GMA can be seen in the image (Figure 4.1C). At 4 wt % of GMA in sample (Figure 4.1D), the phase separation of the functional phase is clearly evident as the GMA now forms large distinct globules. However, SEM images cannot exactly indicate when phase separation began and what the properties of the blends are. Therefore, thermal analysis of the samples was undertaken.

The data extracted from DSC curves by running the heating and the cooling scans of the pure and modified films are shown in Table 4.2. Table 4.2 lists the values of the melting temperature ($T_m$), the crystallization temperature ($T_c$), and the degree of crystallinity ($X_c$).

As can be seen from this table, $T_m$ of pure PP is 160.7°C; whereas that for the blended samples had $T_m$ within 161.1 to 162.2°C. This increase in melting temperature may be due to the heterogeneous nucleation effect of the GMA on PP, which was observed by other researchers also. The data in Table 2 also indicates that the crystallinity of the PP blend decreased. The introduction of the GMA as PE-b-GMA into the PP matrix resulted in the reduction of the regular packing of PP chains leading to lower crystallinity in comparison with the pure PP sample. Besides this, PE-b-GMA has higher viscosity, i.e. higher molecular weight, than PP polymer. This, in turn, further reduces the possibility to form nuclei due to the loss of molecular mobility.
Figure 4.1: SEM images of the cross-sections of the films of modified PP A) 1.0 wt % B) 1.5 wt % C) 2.0 wt % and D) 4.0 wt % of GMA added
Table 4.2: Melting ($T_m$) and crystallization ($T_c$) temperatures, the degree of crystallinity ($X_c$) for pure and blended samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$, °C</th>
<th>$T_c$, °C</th>
<th>$X_c$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0%</td>
<td>160.7</td>
<td>113.6</td>
<td>54.3</td>
</tr>
<tr>
<td>1.0%</td>
<td>162.2</td>
<td>110.2</td>
<td>52.7</td>
</tr>
<tr>
<td>1.5%</td>
<td>161.1</td>
<td>111.6</td>
<td>53.3</td>
</tr>
<tr>
<td>2.0%</td>
<td>161.9</td>
<td>110.3</td>
<td>52.7</td>
</tr>
<tr>
<td>PE-b-GMA</td>
<td>103.0</td>
<td>89.7</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.2 shows the heating thermograms for the samples with 1.5 and 4 wt % of GMA.

![DSC heating curve for 1.5 wt % and 4.0 wt % blended samples](image)

Figure 4.2: DSC heating curve for 1.5 wt % and 4.0 wt % blended samples
This figure discerns that the phase separation phenomenon could be triggered below or about 1.5 wt % GMA. The 1.5 wt % blend behaves as if it is homogenous because the primary peak was observed at 160° C and no peak was observed at about 103 °C, which is \( T_m \) of PE-b-GMA. However, a secondary peak at 145° C indicated the presence of different type of PP crystals in the blend. This implies that the phase separation process may have been triggered firstly by the formation of different types of crystals. No such secondary peaks were observed at 0.5 or 1 wt % of GMA added. In the samples with 4.0 wt % of GMA, we clearly saw the presence of two separate peaks, one observed at the \( T_m \) of PP and the other at \( T_m \) of PE-b-GMA.

4.5 Molecular Dynamics (MD) Simulation

To confirm and explain the possible reasons for the above observations, several runs of molecular dynamic simulations were conducted. Cells having 0, 1.3, 1.7, 2.4, and 4 wt % of GMA were constructed. The simulations for GMA concentrations less than 1 wt % were not possible because the size of the cells became too large to construct ‘thin film’, thus causing an error in calculations.

As can be seen from Figure 4.3 at low concentrations of GMA in the sample, SE reduced compared to that of the pure polymer. Subsequently, as the concentration of GMA in the polymer increased, the values of SE increased as well. It is to be noted that the modified PP chains were constructed based on the results observed by O’Rourke-Muisener et al.\(^{32}\) who stated that the best architecture for a polymer having a polar functional group is when this
group is placed at the center of the chain backbone. With this in mind, it is expected that the results from the computation will be slightly different from the experimental results, the absolute values of SE obtained via MD simulation were slightly higher than experimental values obtained \(^{33}\). When the experimental and simulation data were plotted together (as shown in Figure 3) similar trends in SE values were observed. The data showed a V-shape trend i.e. an initial decrease, a minimum followed by subsequent increase.

![Plot of experimental and simulation values of surface energy versus Percentage GMA in sample](image)

**Figure 4.3: Plot of experimental and simulation values of surface energy versus Percentage GMA in sample**

The position of the functional group (i.e. epoxy) with respect to the surface was calculated using equation 2. Figure 4.4 shows the results of this calculation. At low concentrations of GMA in the sample, the epoxy group was positioned close to the surface.
With the addition of more GMA into the system, this group had a tendency to sink and move close to the bulk of the polymer. At 1.7 wt %, the epoxy group resided closest to the center of the polymer cell. Subsequently, with addition of higher amounts of GMA in the sample, the functional group re-emerged at the surface. This could be an indirect indication of phase separation phenomena wherein functional (polar) groups instead of moving closer to the polymer bulk, reappeared at or near the surface.

![Figure 4.4: Position of epoxy group with respect to the surface](image)

Using MD simulation, the Flory-Huggins parameter ($\chi$) was calculated. The results can be viewed in Figure 4.5. In this figure the negative value of $\chi$ shows that there is good compatibility between the base polymer and the functional polymer at 0.8 wt % of GMA.
added. However, the addition of higher amounts of PE-b-GMA lead to an increase in the $\chi$ value. Positive $\chi$ values at about 1.3 wt % of added GMA indicate the existence of a phase separated system.

![Figure 4.5: Plot showing Flory Huggin’s interaction parameter versus % GMA in sample](image)

Since simulation data represents the initial monolayers, conducting an XPS, which is a surface chemical analysis technique, was thought to be appropriate. It is worth noticing that the XPS data shown in Figure 4.6 showed a similar trend to the surface energy values listed in Table 4.1. With initial amounts of GMA in sample i.e. 0.5 wt %, the Oxygen to Carbon (O/C) ratio is high. With the addition of GMA to about 1.0 wt %, a minimum in O/C ratio was observed confirming that SE values could be related to the position or concentration of
oxygen at the surface. It must be noted that the “O” we detected does not correspond to only the epoxide group in modified PP but also to all oxygen available in PP (including the additives added during the manufacturing of the polymer).

![Figure 4.6: O/C ratio versus Percentage of GMA in sample obtained from XPS](image)

4.5.1 Results from Adhesion tests

Figure 4.7 shows the experimental results for modified samples laminated with Pebax and TPU. The trends for the Peel test are the same as the surface energy. The addition of low concentration of GMA lead to an increase in the adhesion, but at around 1.5 to 1.7 wt %, where the phase separation is likely to have started, a decrease in the adhesion is observed. The reason is likely to be the sinking epoxy group and its absence in the initial monolayers of
the sample. As phase separation is almost complete (above 2.0 wt % blend), the GMA rises again to the surface and correspondingly the adhesion strength. One must note that Pebax responds better to the modifications of PP than TPU. This, in turn, indicates that these two elastomers adhere to PP surface differently and therefore, different functional groups would be needed to further increase TPU or Pebax’s adhesion to PP.

![Figure 4.7: Plot showing % increase in adhesion of films of modified PP with TPU or Pebax](image)

**Figure 4.7: Plot showing % increase in adhesion of films of modified PP with TPU or Pebax**

### 4.6 Conclusions

The influence of the concentration of GMA molecules on the properties of blended PP polymer was investigated in this work. The experimental results indicated a V-shape
curve for the surface energy, an initial decrease in surface energy, followed by a minimum and then the subsequent increase with higher additions of GMA in the sample. XPS data follow the same trend and can be used to correlate with the surface energy data. SEM images and thermal scans showed that collectively, for GMA blended PP samples, the melting temperature ($T_m$) was higher than that of the unmodified PP. This effect could be explained by heterogeneous nucleation. MD simulation confirmed our experimental observations. Additionally, the variation in surface energy could be attributed to the location of the functional group.

4.7 Acknowledgements

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4.8 References


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CHAPTER 5

5 Polypropylene surface modification to improve its adhesion to polyether-block-amide and thermoplastic polyurethane: Theoretical investigations

5.1 Abstract

Elastomers and polyolefins are widely used in everyday life because of their unique properties. However, these two polymers are incompatible and cannot be used together in a composite. In this work, atomistic simulation and experiments were used to investigate the effect of the structure of elastomers as well as the effect of polyolefin modification on the adhesion between two polymers. Polypropylene (PP) was selected for this purpose, which was modified with glycidyl methacrylate (GMA) via grafting. GMA was used as an anchor for the modification with polyacrylic acid (PAAc) and polyacrylamide (PAAm). The interfaces of PP/thermoplastic polyurethane (TPU) and PP/polyether-block-amide (Pebax®) were simulated, and the work of adhesion, density profiles, and the depth of penetration were calculated. The results showed that unmodified PP adheres better to TPU when compared to Pebax®. The situation differed when the polar group or polymers were introduced to the system studies.
5.2 Introduction

Elastomers such as thermoplastic polyurethane (TPU) and polyether-block-amide (Pebax®) are very widely used as films or coatings for various materials. Due to the capabilities of these polymers to transmit moisture vapor, i.e. be ‘breathable, they are frequently used in protective and medical garments, sportswear apparel, etc. 1, 2, 3. Both TPU and Pebax consist of soft segment (SS) and hard segments (HS), and it is due to the SS that moisture transmission is possible. Incorporation of a hydrophilic SS such as ether, hydroxyl, and carboxyl groups, increases the affinity of polymer to water4. Thus, by altering the SS water vapor permeation can be increased or decreased.

To create ‘breathable’ composites, TPU or Pebax® are typically hot laminated onto fabrics. The latter can be made from different polymeric materials including popular polyolefins – polypropylene (PP). This semi-crystalline polymer has very good mechanical and thermal properties as well as excellent chemical and moisture resistance. PP is also easy to process and very inexpensive. However, due to its nonpolar nature, PP has poor adhesive properties5, 6, 7, this especially concerns adhesion to elastomers, which are polar polymers.

The purpose of this article is to provide interface engineering strategies to enhance the adhesion of the polyolefin to elastomers utilizing molecular dynamics (MD) simulation. A number of studies have used this approach8, 9, 10, 11, 12, 13, 14, 15 to compute surface energy, density profile, adhesion, compaction parameters for various polymers and their compatibility in blend systems.

Two strategies can be employed to improve adhesion between elastomers and polyolefins: modify TPU/Pebax® or PP. The former method requires the modification of
elastomer by incorporating less polar polymers/particles and by grafting. Several studies were undertaken to alter adhesive properties of TPU\textsuperscript{16, 17, 18, 19}; however, TPU modification can lead to a decrease in its important property of water vapor transmission\textsuperscript{17}. To the best of our knowledge there is no information available on the modification of Pebax\textsuperscript{®}. Therefore, this work was concentrated on the second method, i.e. the modification of PP.

Various chemical modification techniques have been employed to increase the polarity of polyolefins\textsuperscript{20}. Melt–grafting with polar monomers is one of the many methods used to modify PP. PP is frequently grafted with such monomers as maleic anhydride or carboxylic acid\textsuperscript{21, 22, 23, 24, 25}. For our studies glycidyl methacrylate (GMA) was used as the grafting monomer for PP because the epoxy groups of GMA are able to react with -OH, COOH, and NH\textsubscript{2}\textsuperscript{26, 27, 28, 29}. Being grafted on the fiber surface, GMA can also improve fiber wettability and adhesive properties, or in other words, GMA can be used as an “anchor” for the further polymer/fiber modifications\textsuperscript{30, 31}. Thus, such polymers as polyacrylic acid (PAAc), polyacrylamide (PAAm), polyvinylalcohol, etc. can be anchored via GMA to the surfaces of nonpolar polymers like PP. Consequently, a similar strategy - the construction of PP chain containing GMA and the addition of various polar polymers to this functional group - was utilized and analyzed for improvement in the adhesion to elastomers throughout this study.
5.3 Experimental Approach

5.3.1 Materials

For this work, polypropylene \( (T_m = 160.7 \, ^\circ\text{C}, \, \rho = 0.91 \, \text{g cm}^{-3}, \, 34 \text{ of Melt Flow Index}) \) was obtained from Sunoco Chemicals (USA). The rest of the chemicals required for melt-grafting, such as dicumyl peroxide (99%), glycidyl methacrylate (97.5%) and styrene monomers (99.5%) were purchased from Sigma-Aldrich, Inc. (USA). These were used as received.

TPU films of 0.13 mm thickness, with polyether-based soft blocks (POE), were obtained from BASF (MI, USA). Pebax® film (commercial grade-MV 3000) containing polyamide 12 (PA12) as hard segments and POE as soft was obtained from Arkema. The thickness of the film was 0.13 mm. POE had a melting temperature \( (T_m) \) between 40 – 90 \(^\circ\text{C}\) and PA12 melted at 144 \(^\circ\text{C}\).

5.3.2 Grafting procedure

Melt-grafting of PP with GMA was carried out by introducing PP pellets, styrene, GMA and dicumyl peroxide (DC) into the twin-screw micro-compounder (ThermoHaake Corp., USA). The following concentrations of the reactants were charged: 1 weight (wt-) % of DC, 6 wt-% of GMA, and 1:1 ratio of styrene to GMA. The reaction was carried out for 11 min at a temperature of 175 \(^\circ\text{C}\). After the designated reaction time, the polymer melt was
extruded and purified by dissolution in hot xylene. Unmodified and modified PP polymer were precipitated by the addition of 400 ml of acetone. The precipitated polymer was then filtered and dried in the vacuum at 80 °C for 24 hours.

5.3.3 **Analytical methods**

The amount of GMA reacted with the PP was determined by FTIR spectroscopy (Nikolet Nexus 470 FT-IR)\(^\text{32}\). For this purpose, the peak of carbonyl group of GMA appearing at 1730 cm\(^{-1}\) and the peak of PP at 2722 cm\(^{-1}\) were taken as references. Calibrations for GMA were made using known concentrations of GMA.

The total surface energy was determined by contact angle measurement using sessile drop method. Two different liquids were used: water (\(\gamma_d = 22.1\) and \(\gamma_p = 50.7 \text{ mJ m}^{-2}\)) and ethylene glycol (\(\gamma_d = 29\) and \(\gamma_p = 19 \text{ mJ m}^{-2}\)). The total surface energies were calculated by using these contact angle values in a set of harmonic-mean equations\(^\text{33}\).

To measure adhesion strength, a composite of the polypropylene and elastomers was prepared by laminating the two films at a temperature of 140 °C for 1 min. The peel strength was then measured according to ASTM standard (D1876-01).

5.3.4 **Computational Details**

Simulation of the polymeric system was carried out using commercially-available modeling software from Accelrys, Inc. (USA)\(^\text{34}\). A series of molecular dynamics (MD) runs and minimizations were performed with Discover module employing COMPASS.
forcefield\textsuperscript{35}. The minimizations were conducted using ‘Smart Minimizer’, where the process of minimization starts with the steepest descent approach followed by conjugate gradient and Newton methods. Non-bonding interactions were calculated using the group-based method with the cut-off radius of 9.5 Å.

5.3.4.1 Construction of PP polymer molecules

The GMA-modified polypropylene chains were constructed according to the study by Xie et al.\textsuperscript{36}. The chains with 50 repeat units were generated using ‘Amorphous Cell’ module. To construct grafted PP molecule, the functionalized group was added to the center (25\textsuperscript{th} repeat unit) of one PP chain as shown in Figure 5.1a. The GMA concentration of 2.2 wt-% was achieved by constructing 5 amorphous cells each with 2 polymer chains of virgin PP and 1 molecule of grafted PP (PP-g-GMA).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure5.1.png}
\caption{Structures of a) GMA-g- PP; b) thermoplastic polyurethane (TPU); c) polyether-block-amide (Pebax)}
\end{figure}
These cells were refined at first by running a ‘basic refine’ protocol with molecular dynamics (MS) run of 4000 fs at 298 K. To remove low or zero density areas, the cells were run through a temperature cycle – 11 stages from temperature of 298 K to 453 K and 11 stages from temperature of 453 K to 298 K – keeping pressure at 1 atm (0.0001 GPa). Finally, all cells were minimized using ‘Smart Minimizer’ to a convergence of 0.1 kcal mol\(^{-1}\) Å\(^{-1}\).

Ready bulk samples were relaxed for 50 ps using a time step of 1 fs via NVT (constant concentration, volume and temperature) MD simulation. Snapshots of the trajectory
were taken every 0.025 ps during the last half of the run. The snapshot with the lowest potential energy was further minimized to a convergence of 0.1 kcal mol$^{-1}$ Å$^{-1}$.

To create the thin films, one edge (z direction) of the minimized bulk samples was extended to 100 Å, so that the polymer chains no longer interact with its image along this direction. These newly-formed films were subjected to the energy minimization run followed by 50 ps of MD simulation at 298 K. The trajectory snaps were taken during last 25 ps and the cell with minimum potential energy was further minimized. In some cases however, the dynamics were conducted at 600 K to ‘shake’ the cell out of an unfavorable local minima.

To simulate grafting onto GMA with PAAc and PAAm, the GMA epoxy ring was opened and PAAc or PAAm of 9 repeating units were attached to the PP chain as shown in Figure 5.2. Afterwards, these samples were minimized and relaxed via NVT MD simulation for 50 ps. The snapshots of the trajectory were taken every 0.025 ps during the last half of the run. The snapshot with the lowest potential energy was minimized to a convergence of 0.1 kcal mol$^{-1}$ Å$^{-1}$. 
Figure 5.2: (a) Mechanism of attachment of PAAc and PAAm to PP-g-GMA (b) Structure of PP-g-GMA
5.3.4.2 Construction of TPU and Pebax polymer molecules

The polymeric chains of ‘breathable’ thermoplastic polyurethane (TPU) were constructed according to Dolmaire et al. 37 (Figure 5.1b). These chains consisted of 5 blocks of HS and SS. The Pebax® polymeric chains were constructed in a similar way, the only difference being HS. HS of Pebax® was polyamide 12 (PA12); the structural formula of Pebax® is given in Figure 1c. Five amorphous cells with the initial densities of 1.18 g cm$^{-3}$ and 1.01 g cm$^{-3}$ were built for TPU and Pebax®, respectively. Cells of TPU and Pebax® with minimum potential energy were selected for the further refining, minimization, and dynamics steps. These steps were the same as described for PP amorphous cells with the exception of the dynamic temperature and the method for non-bonding interactions. The former was kept at 423 K. Due to a big difference in the nature of HS and SS of the elastomers, the method for non-bonding interactions was switched to ‘Cell Multipole’, which was proven to be reliable in analyzing polymeric cells 38.

5.3.4.3 Construction of polymer layer

A polymer layer was constructed by bringing films of polyolefin and elastomer together. The periodic boundary conditions of final structure were equal to the ones of PP. The layer of PP and elastomer was minimized by ‘Smart Minimizer’ and subjected to 150 ps MD simulation at 423 K. The snapshots of the trajectory were taken every 0.05 ps during the last half of the run. The snapshot with the lowest potential energy was minimized to a convergence of 0.1 kcal mol$^{-1}$ Å$^{-1}$. 
5.3.4.4  Calculation of surface energy ($\gamma$), work of adhesion ($W_A$) and solubility parameter ($\delta$)

The surface energies were calculated as the difference of potential energies of the thin film ($E_{film}$) and its corresponding amorphous cell ($E_{cell}$) divided by surface area (2A) as given by the equation below:

$$\gamma = \frac{(E_{film} - E_{cell})}{2A}$$  \hspace{1cm} Eqn (5.1)

The work of adhesion per unit area ($W_A$) was determined from the difference in energy between the layered system and the sum of energies of the two separated thin films which were used to create the interface:

$$W_A = \frac{(E_{film1} + E_{film2}) - E_{layer}}{2A}$$  \hspace{1cm} Eqn (5.2)

The SS of elastomers or the chains of polyethyleneoxide (POE) of 33 repeat units (RU), PAAc and PAAm of 9 RU, PA12 of 1 RU and 5 amorphous cells for each case with cell sizes between of 18-20 Å were constructed using ‘Amorphous Cell’ module. These cells were used for further refining, minimization, and dynamics steps as described in “Construction of PP polymer molecules”. At the end of this procedure, the cohesive energy densities and
solubility parameters ($\delta$) provided by the software were collected and averaged for each polymer.

## 5.4 Results and Discussion

### 5.4.1 Bulk properties of amorphous cells

Our analysis began with the calculation of surface energy (SE) of the unmodified and functionalized PP cells using eq. (1). The values of SE obtained via MD simulation were 27.4±1.9 and 30.7±2.3 erg cm\(^{-2}\) for GMA-modified and virgin PP, respectively. The sample prepared according to the recipe in the experimental section yielded in 1.9 wt-% of GMA-g-PP. The experimental values of SE of as-received PP and modified PP were 27.6 ±0.4 and 25.0±0.6 erg cm\(^{-2}\), respectively. As can be seen, there is a small difference between theoretical and experimental values. But one needs to consider the fact that for MD simulations the ‘ideal’ GMA-containing PP chains were used – with polar group placed at the center of the chain backbone\(^40\); whereas during experiments grafting occurred at random locations of the chain in addition to the slight variations in the structure of functional group. Therefore, the differences between simulation and experiment are expected.

### 5.4.2 Adhesion to polypropylene

Figures 5.3 and 5.4 discern the density profiles of the interfaces of PP-TPU and PP-
Pebax®. These density profiles are plotted along the thickness of the composites (i.e. along z-direction). Figure 5.3 also shows that HS of TPU is retained at the PP surface due to its aromatic nature; Figure 5.4, on the other hand, demonstrates that HS of Pebax® diffused into PP at the density front of elastomer. This, in turn, shows that in case of TPU, the PP chains interact with less polar components of TPU chain, i.e. SS, but the case is reversed with Pebax®. Thus, Pebax® is going to have stronger electrostatic interactions with PP if any polar groups are present in it.

![Density profile along z-direction for TPU/PP interface](image)

**Figure 5.3: Density profile along z-direction for TPU/PP interface**
Figure 5.4: Density profile along z-direction for Pebax/PP interface

From the depth of diffusion of two components, the thickness of penetration of TPU and Pebax® into PP was found to be 8.3 and 7.5 Å, respectively. The primary reason for slightly better diffusion of TPU molecule into PP matrix is its low glass transition temperature and, thus better mobility, of SS (polyoxyethylene or POE). The values of penetration also indicated that the adhesion or work of adhesion ($W_A$) is expected to be higher for the TPU-PP layer because unmodified PP is electrostatically neutral and adhesion was achieved only through mechanical interlocking. To confirm this, $W_A$ was calculated.
Figure 5.5 demonstrates the values of $W_A$ for the TPU-PP, Pebax®-PP, TPU-(PP-g-GMA), and Pebax®-(PP-g-GMA) interfaces. As can be seen from this figure, the adhesion between TPU and PP was better than between Pebax® and PP; whereas incorporation of GMA led to an increase in $W_A$ for the layer containing Pebax®. Figure 5.6 showing experimental data confirmed the results obtained from MD simulation. The TPU film had better adhesion to unmodified PP polymer. After grafting reaction, which resulted in 1.9 wt% PP-g-GMA, the adhesion or peeling strength was better for the system of Pebax®-(PP-g-GMA) than for TPU-(PP-g-GMA).
5.4.3 Adhesion to polypropylene modified with PAAc and PAAm

To improve adhesion to elastomers further, the surface of the PP-g-GMA cells was modified by attaching such polymers as polyacrylamide (PAAm) and polyacrylic acid (PAAc) as shown in Figure 5.2.

Solubility parameter (δ) is an important factor, closely related to surface tension and polymer miscibility. It is suggested that polymers having similar or close δ values have a tendency to adhere better to each other. Therefore, δ of PAAm and PAAc as well as their difference with δ’s of HS of Pebax® and SS of TPU were evaluated and listed in Table 5.1. The latter two were evaluated because they first came in contact with PP and thus determine polyolefin/elastomer compatibility.
Table 5.1: Solubility parameter (δ) and difference in solubility parameters (Δδ) between POE or PA12 and PAAc or PAAm

<table>
<thead>
<tr>
<th></th>
<th>δ (J/cm³)⁰.⁵</th>
<th>Δδ (J/cm³)⁰.⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PAAc</td>
<td>PAAm</td>
</tr>
<tr>
<td>POE</td>
<td>20.3</td>
<td>12.1</td>
</tr>
<tr>
<td>PA12</td>
<td>17.4</td>
<td>10.8</td>
</tr>
</tbody>
</table>

The values listed were slightly lower than reported in literature. However, one must note that the values of δ change with molecular weight³⁸ and since δ were calculated for low molecular polymeric chains, lower δ were expected. Nevertheless, Δδ indicated that Pebax® has better compatibility with PAAc-modified PP as difference between solubility parameters was least, whereas TPU adhered better with PAAm-modified polyolefin. Calculated W_A’s (Figure 5.7) validated this allegation. The values of W_A were significantly higher after modification with PAAc or PAAm confirming suitability of proposed modification.
Figure 5.7: Work of adhesion calculated from MD simulation for polyolefin/elastomers system after GMA-g-PP modification with PAAc and PAAm

5.5 Conclusions

The adhesive properties of PP to TPU and Pebax before and after modifications with polar group/polymers were investigated using atomistic simulation and experiments. The results showed that due to slightly better penetration of POE (soft segment of TPU), the work of adhesion of TPU to unmodified PP was higher than Pebax. The same results were observed experimentally via T-Peel test. With the addition of GMA to PP matrix, electrostatic interactions with hard segment of Pebax® triggered better adhesion of PP to this elastomer. Due to lesser difference in values of solubility parameter between PAAm and TPU, the work of adhesion was found to be better for TPU and PP modified with PAAm, and
for the same reason the adhesion between Pebax® and PP modified with PAAc.

5.6 References


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6 Fiber and Fabric Properties of Modified Spunbond Polypropylene Nonwovens

6.1 Spunbonding Process

The Spunbond process, which was commercialized in mid 1960’s, has received considerable attention from the market as the product meets almost all of the market requirements. The spunbonding process can be formally defined as a nonwoven manufacturing system involving the direct conversion of a polymer into continuous filaments, integrated with the conversion of the filaments into a random-laid, bonded nonwoven fabric. They can also be generally defined as continuous-filament fibrous structures, prepared from synthetic polymers which can be made in the form of fabrics, sheets and tapes. The novel and unique feature of the spunbond process is the direct conversion from polymer (generally pellets) into finished fabric in one integrated step.

The spun bonding process is very similar to a melt spinning process, though unique in the fact that it links innovative polymer, technological and fiber research, thus imparting web bonding, cohesiveness and integrity to the structure. The spun bonding process includes extrusion, followed by non-isothermal extensional flow of the melt which is ultimately followed by molecularly oriented crystallization. The inherent properties of the filaments are
of utmost importance as they decide the final property of the web and so the kinematics and development of morphology in the filaments are studied extensively. The understanding of the influence of spinline dynamics on the structure of filaments can help in manipulating process conditions to achieve desired properties in filaments. The spun bonding systems, with production speeds ranging from 30 and 300 m/min, are the most productive of all the non-conventional methods of textile fabric formation.

6.1.1 History of the Spunbond Process

Spunbonding technology started during the 1940’s and the 1950’s when it was first seen as an extension of the existing concept of staple fiber nonwoven production. The first patent for the spun bonding process was seen as early as in the 40’s when Slather and Thomas of Corning Company filed a patent to produce glass wool\(^2\). Freudenberg of West Germany and DuPont of USA were the first company to have commercially manufactured spunbond nonwovens from synthetic polymers in the 1950’s and 1960’s. In 1965, DuPont commercialized their polyester product called ‘Reemay’. ‘Typar’ made of polypropylene and ‘Tyvek’\(^3\) made from flash spun polyethylene followed Reemay. During the same time, Freudenberg introduced ‘Lutravil’- a spunbonding process for manufacturing mixed polyamides. Within five years of this, Lurgi Kohle and Mineral-oltechnik GmbH of Germany introduced their first spunbonding process called ‘Docan’. Reifenhauser GmbH of Germany, introduced ‘Reicofil’\(^3\) in 1984 for fabricating webs especially from PP. During the 1990’s
equipment suppliers such as Kobelco, Nordson, STPI, ISBT (now Reiter), Hills, Inventa-Fisher and many others opened complete spunbond lines which helped hygiene and medical suppliers switch profitably to spunbond process. In 2000’s, Reifenhauser alongwith Nordson offered bico-spunbond using Hills bico-technology. Thus the spunbond technology rapidly evolved making it a profitable and marketable technology.

6.1.2 Market for Spunbond Nonwovens

Nonwovens are generally categorized by end use applications into disposables or durables. Spunbond fabrics are used in all market areas but the sectors where it is significantly used are automotives, geotextiles, hygiene and packaging sectors. One of the major uses in the automotives sector is as a backing for tufted automobile floor carpets. These are also used for trim parts, trunk liners, interior door panel and seat covers. In the area involving geotextiles, spunbond webs are used for erosion control, railroad beds stabilization, canal and reservoir lining, highway cracking prevention, roofing, etc. These webs are extensively used for hygiene products, as coverstock for diapers and incontinence products. The properties of spunbond webs such as breathability, lint free structure, sterilizability and impermeability to bacteria are responsible for widespread medical use. Spunbonds are widely used as packaging materials where paper products and plastic films are not satisfactory. These include metal-core wrap, medical sterile packaging, floppy disk liners, high performance envelopes and stationary products. Spunbonds are already widely used for
markets including furniture, bedding, clothing interlining, shoes and leather products. Global spunbond production has increased to more than 40% during the decade of 1990’s and it is expected to grow approximately 6% per year through 2010⁴.

6.1.3  The Spunbonding Process

The primary factor in the spunbond process is the controlling of 5 major operations: filament extrusion, drawing, quenching, lay down and bonding.

A typical spun bonding process consists of several integrated steps during the conversion from polymer pellets to fabric. The major elements are: Polymer Feed, Extruder, Fiber Spinning, Quenching/Attenuation Zone, Web Formation, Bonding and finally Slitting/Winding. The polymer feed in the form of pellets or powder form are conveyed from the silos to the extruder where they are mixed with various additives such as stabilizers, color masterbatches, resin modifiers and such. This blend then melts within the barrel of the extruder. Sometimes, vented twin-screw extruders are also used to dry the polymer as it melts. The polymer melt is then passed through a metering pump (which is a positive displacement constant volume device that controls a precise volumetric flow rate of the molten polymer) and then through a conduit which has a filter attached. It ultimately leads to a distribution section that provides uniform flow to the die block assembly. The die block assembly is one of the most crucial element in the spunbonding system. From the feed distribution system, the polymer melt is directed to the spinnerets. The spinneret is a block of metal with several orifices. The orifices are usually circular in shape though they can be of
varying shapes. For commercial production, two or more of these are used together to increase the coverage of the fibers. The molten resin gets forced out of these tiny holes to form continuous filaments.

![Figure 6.1: Polymer melt spinning out of a spinneret](image)

There are three very critical steps in the production of a nonwoven fiber: filament spinning, drawing and deposition. For the spinning process, there are again three different techniques that can be used. These include melt spinning, dry spinning and wet spinning. Amongst them, melt spinning is easy to perform and is economically feasible. The quenching zone consists of quench chambers or chimneys through which the continuous filaments travels and when cold air is targeted at them, the filament bundle cools down sufficiently to cause solidification. Efficient quenching of the filaments is important as insufficient cooling can lead to fiber roping and the fibers may not form a uniform web. Air stream then leads the solidified fiber bundles through a tapered conduit where a second stream of high velocity air
is directed at them parallel to their flow in order to cause stretching of the filaments. This mechanical stretching and drawing action helps in orienting the polymer chains within the fiber. At the web formation section, the filaments get deposited in a random manner on a moving belt. Vacuum applied below the belt performs two functions: it assists in the forming of the web and it also helps in removing extra air used in the extrusion/drawing process. In order that the web achieves maximum uniformity and cover, individual filaments must be separated before reaching the belt. So in some processes, an electrostatic charge is placed while in others deflector plates are used to lay down the filament sheet in a random manner on the forming belt. Compaction rolls are also used to provide integrity to the webs by increasing the cohesion between the filaments. The web is then delivered to the bonding section where one of the several methods of bonding can be used such as calendering, hydroentangling, needlepunching, ultrasonic bonding, through air bonding, stitch bonding or chemical bonding.

The schematic diagram of a Spunbond process is shown below.
6.1.4 Process variables

The variety of process variables that are available at each step of the spun bonding process give the much needed flexibility to modify the product specifications according to the end use. The four principal factors that can be varied are fiber properties, web-formation characteristics, bonding systems and finishing treatments.

The resin type that is used to manufacture the spunbond fabric decides the properties of the final fabric produced as it has a deep influence on it. The choice of the resin is an important parameter that is available in designing the spunbond fabric. The options available for resins are Polypropylene, Polyester, Nylon, Polyethylene, etc. In general, fiber grade resins are the ones which are utilized for spunbond fabrics. These resins have higher
uniformity and quality than general purpose resins and are understandably more expensive. In addition to resins, a wide range of resin additives and colorants can also be added.

The web formation variable inherently includes varying filament cross section, fabric weight as well as fiber orientation. Most filaments are circular in cross section, although spinnerets with modified orifice shapes can also be used to vary fabric hand, appearance, luster, stiffness as well as other fabric properties. The weight of the fabric can be altered to produce either heavy weight fabrics for greater strength and more covering power or light weight fabrics to improve hand and feel. Fiber orientation too has a tremendous influence on fabric properties. With spunbond fabrics, the filament orientation is random giving an isotropic fabric. However, it is possible to have a slight bias in the fiber orientation to give strength or increase some other property in a particular direction.

In terms of flexibility with bonding methods, thermal bonding is usually applied on spunbond fabrics. It can be of two types: area bonded or point bonded. In this type of bonding technique, filaments in the web are fused at the cross sections using direct action of heat and pressure. Needlepunching, which is a form of mechanical bonding technique, can also be employed as one of the bonding techniques. It involves using barbed needles that penetrate the fiber web many times and with each penetration, fiber tufts from the web surface are collected by the barbs and deposited well within the fiber web. Repeating this procedure many times leads to a strongly bonded fabric.

Finishes that can be applied to improve certain characteristics of the fabric include calendering for smoothness, embossing for decorative reasons, flame retardancy, coloration
for dyeing, printing for decorative purposes and many more.

6.1.5 Fabric characteristics

Spunbond webs offer a wide range of characteristics ranging from very light and flexible structures to very heavy and stiff structures.

1. Fabric strength: Fabric strength implies tensile strength, elongation, and modulus, tear strength, burst strength or abrasion resistance. Spun bond fabrics usually have high strength-to-weight ratios compared to other nonwoven, woven or knitted structures. Area bonded spunbonds have high tear strength. They have high in plane shear resistance.

2. Basis weight: These have basis weights in the range of 5 to 800 gsm and are typically in 10-200 gsm range.

3. Fiber Diameter: Fiber diameters range from 1-50 µm but are typically 15-35 µm.

4. Web thickness: Usually ranges from 0.1-4.0 mm, typically between 0.2-1.5 mm.

5. Balance: As these are randomly formed on an aerodynamic system, spunbond webs have isotropic structures with equal properties in all directions.

6. Softness: These include tactile properties, bending, rigidity, hand, drapeability and smoothness. These generally have low drapeability and show good fray and crease resistance.

7. Fabric uniformity: Uniformity of a fabric contributes to properties such as fabric’s opacity, covering power and formation of filament lay down. Spunbond fabrics
usually have poor to moderate uniformity, with high opacity per unit area. Increased production speeds necessitate precise system control for uniform lay down of filaments. Most spunbond webs are layered structures where more the number of layers, more is the basis weight. Ropiness, cloudiness and basis weight variation result from non-uniform lay down.

8. **Fabric absorbency**: These include liquid absorbency rate, absorbent capacity, wicking rate, liquid retention and oil or water absorbency. Usually spunbond fabrics are made from hydrophobic or semi-hydrophobic polymers and are as such effective oil absorbents. These need to be hydrated with surfactants or their surface modified to improve wetting with water. Wicking action improves with improving the fineness of the fibers. Also they have high liquid retention capacity due to high void content.

9. **Chemical/ Thermal resistance**: These depend on the polymer used for web formation. Generally these have good chemical resistance, thermal resistance is highest if PET is the polymer used but decreases respectively with nylon, PP and PE.

### 6.1.6 Spunbond Product Advantages and Disadvantages:

There are a large number of characteristics that are included in this. The more prominent ones are strength, softness, uniformity, absorbency, chemical and thermal resistance and so on. Spunbond fabrics, in general, are considered to have high strength (tensile, elongation, tear, etc) which is partly due to the tough resins that are used to produce them. The bonding methods employed also help in improving strength. Softness parameters
that include bending rigidity, hand, drapability and smoothness are said to be low in spunbond fabrics. Opacity, covering power and formation are included in the uniformity parameter. Spunbond fabrics usually have poor to moderate uniformity and more so when they are spun at higher speeds. Straight filaments and not crimped fibers are another disadvantage that spunbond fabrics have that lead to more non-uniformity. The absorbency of any fabric is made up of two elements: the inherent absorbency of the fibers and the overall absorbency of the entire fabric. Spunbonds are generally spun from hydrophobic polymers hence, in general these fabrics show low absorbency. However, there is a limited amount of absorbency owing to the fibrous nature of the fabric. Since the spunbonds are made of high grade polymers which are themselves chemically resistant, thus the entire fabric becomes resistant to chemical. Thermal resistance depends on the melting point of the polymers from which the fabrics are made.

6.1.7 Spunbond Process advantages and disadvantages:

Out of all the important parameters that would count under this category, only the most important and relevant ones are selected. In terms of capital investment, a lot of investment is required. The overall capital investment includes fixed investment, working capital, facilities cost, etc. With focus on product quality and quality assurances growing day by day, nonwoven process have the advantage that these processes can be strictly controlled. The spunbond process is also versatile as the fabric weight, bonding characteristics, web configuration and finishing possibilities can be efficiently altered to change the product.
codes. Spunbonds can be manufactured in bulk and so can meet the huge market demand for them.

6.2 Experimental

6.2.1 Material

Polypropylene (grade CP36OH) was obtained from Sunoco Chemicals (PA, USA). This polymer has a narrow molecular weight distribution, with a melting point ($T_m$) of 160° C, density of 0.91 g cm$^{-3}$, a Melt Flow Index (MFI) of 34 dg/min and crystallinity of about 50%. Polyethylene–block-glycidyl methacrylate (PE-b-GMA) was the functional polymer. This PE-b-GMA (Lotader AX 8840) was obtained from Arkema (PA, USA) with total content of 8 weight (wt) % GMA. This polymer has MFI of 5 dg/min, $T_m$ of 109° C, and a density of 0.94 g cm$^{-3}$. Meltblown Pebax fabrics of 130 gsm were used for the lamination.

6.2.2 Nonwoven Production

Nonwoven fabric samples were manufactured in the Partner’s lab of NCRC (Raleigh NC). The polymers used were PP (Sunoco) and functional polyethylene (Arkema). The fabrics were made by blending pure PP and 0.5 wt% functional polymer. Spunbonding process was used to make the fabric. The temperature used was 230-240 °C. Fabric gsm’s of 20, 40 and 60 were collected by varying the conveyor belt speed.
6.2.3 Lamination

To measure the changes in adhesion, the modified PP nonwovens were laminated to Pebax (Arkema) nonwovens at various temperatures ranging from 120 to 155 °C for 1 minute at pressure of ~150 psi. For the hydrostatic head test, modified PP nonwovens and Pebax were laminated at temperatures ranging from 115 to 150 °C for lamination times of 20 seconds and 1 minute.

6.2.4 Analytical techniques

After spunbond PP were formed, the surfaces of the fibers were analyzed with X-ray Photoelectron Spectroscopy (XPS). XPS is a surface (1-10 µm) chemical analysis technique that can analyze the chemistry of the surface of the material. The surface analysis is done by irradiating the sample with monoenergetic soft X-rays and then analyzing the energy of the detected electrons. The samples were irradiated using a Mg Kα (1253.60eV) rays. The unique set of binding energies of each element is used to identify and determine the concentration of the element on the surface.

To obtain changes in adhesion and to find the optimum bonding temperature, T-Peel test (ASTM D1876-01) was conducted. The MTS Q tester with a 5 lb load cell was used. The gauge length and the extension rate were set to 1” and 1” per minute, respectively. The tensile strength of the single fibers were also tested using the Instron with a 5 lb load cell (ASTM D 638).
Laminated samples of Pebax and PP fabrics with a size of 6” by 6” were tested for barrier property by performing the Hydrostatic Head test according to the testing method AATCC 127-2003. All tests were performed on Textest FX 2000(Figure 6.3).

![Figure 6.3: Hydrostatic head tester](image)

For this test the samples were put atop a column of water and the pressure of water, in cm, at which the third water bubble appeared on the fabric surface, was noted down as the hydrostatic pressure head. For a fabric to be considered as a barrier, it should have a hydrostatic head value of at least 100 cm.

The samples that passed the barrier test were also tested for MVTR. The tests were performed using the Mocon instrument (Figure 6.4) according to ASTM D 6701. The results are the average of 6 specimen. The values are obtained in units of gms/m²/day.
6.3 Results and Discussion

6.3.1 XPS Analysis

The results from XPS for fibers of modified and as-received PP polymers are shown in Figure 6.5. XPS analysis clearly indicates the presence of oxygen in unmodified PP which is due to additives and partial oxidation during processing. The survey scan of XPS shows that the surface of modified spunbond PP fibers have more oxygen as compared to the pure PP fiber. This shows that the modification has made the surface of PP more polar.
Thus, spunbonding enriches the surface of the modified fiber with functionalized groups (i.e. GMA) which could lead to the improvement of PP adhesive properties.

6.3.2 Fiber Tensile Strength

The strength of the fibers containing GMA and that of pure PP are shown in Table 6.1. It was noticed that the strength of the modified PP fiber is less than that for pure PP fibers. Additionally, PE, the base polymer in PE-GMA (Lotader sample), has lower tensile properties and thus it can also affect the final property of the fiber. The presence of GMA also might hinder the orientation of the PP chains and that leads to lowered crystallinity.
Table 6.1: Tensile strength of Pure PP and modified PP

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Strength (lbf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PP</td>
<td>2.95 ± 0.29</td>
</tr>
<tr>
<td>Modified PP</td>
<td>2.28 ± 0.84</td>
</tr>
</tbody>
</table>

6.3.3 Fabric Peel Strength

Results of the lamination of the Pebax fabric with PP nonwoven fabrics are shown in Figure 6.6. It was observed that the peel strength initially increases as the temperature increased, reached a maximum point and then decreased. The maximum was observed at about 125 °C. It is worth noting that at this temperature adhesion of Pebax to modified PP was much higher than with unmodified PP. Thus, the modification brought about by blending functional monomer with PP during spunbonding brought a significant improvement in adhesion to elastomer fabric.
6.3.4 **Barrier and MVTR Properties**

For the fabric/composite to be considered as a barrier, the samples need to have a hydrostatic head of at least 100 cm. The tests were done with a Pebax fabric as the elastomer layer. The spunbond PP had a basis weight of 60 gsm. The results of the barrier test with Pebax are as shown in Figure 6.7.
Figure 6.7: Barrier property of blended PP with Pebax fabric

All samples were laminated for two different time periods. The samples laminated at 130 – 135 °C and higher passed the test. This temperature range observed was closer to the softening or melting point of Pebax which might mean that elastomeric fibers can fuse together and reduce the porosity of the composite. But this would also reduce the MVTR of the sample. Therefore, the time of lamination was reduced to 20 seconds and the barrier property was then assessed. The samples above 130 °C and up to 140 °C passed the test and the rest failed. Only those samples which passed the barrier test were then tested for the moisture vapor transfer rate.

The results of the moisture vapor transfer rate are shown in Figure 6.8. The units are given as gms/m²/day.
The results indicate that with present system the maximum MVTR of about 900 gm/m²/day could be reached. MVTR remained constant at the temperatures of 125 – 130 °C and then it deceased with increase of the temperature. It is worth noting that there is no difference in the results with different lamination time: the results were almost identical. One must also mention that for these experiments Pebax nonwoven containing hydrophobic soft segments were used. Thus, high MVTR values were not expected, but these data can be used as a starting point or as a minimum MVTR possible to achieve for this kind of system. With more hydrophilic Pebax fabric as the next step, high MVTR of the composite fabric can be reached.

Figure 6.8: MVTR of blended PP with Pebax fabric
6.4 Conclusions

The modified spunbond PP fabric was manufactured and the fiber and fabric properties were tested. The drawing process, inherent during the fabric manufacture leads to exposure of the polar functionalities from the bulk and brings them to the surface. This apparent transformation leads to increased peel strength with the elastomeric polymers and fabric layers. The fabric samples beyond 135 °C lamination temperature pass the 100 cm barrier tests and prove to be an effective barrier. Similarly the samples laminated at 125 and 130 °C show the highest MVTR value. Thus modification using functional monomer brings about significant changes in surface property which leads to enhanced adhesion. The laminated samples also prove to be a barrier fabric while having modest MVTR values.

6.5 References

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CHAPTER 7

7 Modifying Polypropylene using UV Grafting Method

7.1 Introduction

Synthetic polymers possess desirable properties such as high strength and resistance to acids and alkalis, reducing and oxidizing agents and are thus extensively used. However, their hydrophobicity, possesses another challenge to them which restricts their applications in fields, ranging, for example, from adhesion, protection of surface from corrosion to improving their biocompatibility. Hence surface treatments or surface modifications are carried out to produce hydrophilic groups such as carbonyl, carboxyl and hydroxyl groups on polymer surfaces\(^1\), \(^2\). Among several approaches, UV-initiated graft copolymerization is very popular as it combines low cost of operation, mild reaction conditions, controlled and stable introduction of grafted chains and also potentially reduces any negative effects on bulk polymer\(^3\), \(^4\), \(^5\). The modification can bring about several favorable properties such as enhancement in hydrophilicity, increase in wettability, wicking, printing and even protein absorption.

UV irradiation falls under the broad category of radiation effect on polymers and this area has been of high interest\(^6\), \(^7\), \(^8\). The primary types of radiation are either high energy,
ionizing radiation such as those obtained from gamma or neutron sources, or ultraviolet radiation from arc lamps, excimer lasers or synchrotron sources. A major difference between these two types of radiation is the initial or primary event following absorption of the radiation. In ionizing radiation, the initial absorption is typically a spatially random process which leads to the production of a free radical or ionic species. Ultraviolet (UV) absorption, on the other hand, is a molecular site specific process and often leads to electronically excited states. Subsequent steps of side group or main chain scission and crosslinking is common to both the types of radiation.

Classical sources for UV radiation include mercury and xenon arc lamps\textsuperscript{9}. These provide the advantage of broad band excitation for spectroscopic studies. For radiation, even small amounts of them can induce significant changes in the physical or mechanical properties of a polymer. In certain cases, even a few crosslinks or scission sites per molecule can dramatically affect the strength of a polymer. The molecular changes occurring in polymers due to radiation-induced chemical reactions can be classified as either chain crosslinking which leads to increase in molecular weight or chain scission which leads to decrease in molecular weight. In addition to these possibilities, irradiating a polymer can give rise to small molecule products, resulting from bond scission followed by abstraction or combination reactions.
7.1.1 Grafting methods

Photografting methods using UV can be divided into two main categories\textsuperscript{10}: One-step or Simultaneous method and Two-step method. Some of the traditional one-step processes include vapor process\textsuperscript{11},\textsuperscript{12}, liquid process and continuous process\textsuperscript{13},\textsuperscript{14},\textsuperscript{4}. The advantage of the vapor process is high grafting efficiency but is accompanied by slow rate of grafting reaction. In the liquid process, both the rate of grafting and the grafting efficiency are less. The continuous process demonstrates high grafting rates. However, all these methods cannot be feasibly used in the industry as these need an inert (N\textsubscript{2}) atmosphere because of the strong inhibition effect of oxygen. The two-step grafting method involves coating or application of the photoinitiator on the polymer surface first followed by application of the monomer solution which is then UV irradiated. There are two important microstructure factors which affect the final properties of the grafted polymer and they are the grafting density and the graft polymer chain length. These two parameters are difficult to control in traditional UV grafting methods but Ma et al.\textsuperscript{15},\textsuperscript{16} have developed a novel two-step method.

Depending on the source, UV irradiation method includes near UV irradiation and vacuum UV (VUV) irradiation\textsuperscript{17}. UV energy, with the aid of photoinitiator or photosensitizer, has been extensively used to produce surface grafted polymers. The importance of studying the effect of irradiation from a VUV source lies not only in the fact that this energy source can be applied for surface modification in addition to the regular UV source but is also important in space technology as it would indicate the durability of polymeric materials which have been treated with this effect. Research has shown that
fluorinated polymers often rupture on exposure to VUV while PET and PE do not. VUV can also be utilized on polycarbonate sheets to improve the interfacial bonding between metal deposit and polymer substrate.

The grafting initiation using UV radiation technique falls in one of the two categories\textsuperscript{18}: free-radical grafting or ionic grafting. In free-radical grafting the irradiation of polymer surfaces causes homolytic fission which forms free radicals on the polymer. Hence, in this method of grafting presence of an initiator is not essential. One important factor though is the medium such as air or inert gas. Grafting proceeds in 3 different ways: pre-irradiation, peroxidation and mutual irradiation technique. In the ionic mode of grafting ions formed through high energy radiation proceeds the grafting reaction. Ions can be anionic or cationic. The polymer gets irradiated to form the polymeric ion which then reacts with the monomer to form the grafted co-polymer. High rates of reaction are one of the advantages of this mode.

7.1.2 \textit{Photoinitiators for UV grafting}

The most commonly used photoinitiator for surface grafting is benzophenone and its derivatives\textsuperscript{19}. The functionality of benzophenone arises when it absorbs a UV photon, gets excited to the short-lifetime singlet state and relaxes to a more stable triplet state. In the triplet state it can abstract a hydrogen atom from a polymer substrate with C-H bonds and create an active site for further surface modifications. The one drawback of benzophenone
and most of its derivatives are they are not water soluble; therefore they can only be used in organic solvents. This increases costs and induces environmental problems and limits its industrial usage. The development of water soluble photoinitiators has been slow and difficult. Acetone, one of the cheapest and simplest aliphatic ketone can be used as a photoinitiator but it has low photoinitiating efficiency. Other aliphatic ketones, such as butanone, heptanone and pentanone can be used instead of acetone as shown by Wang and Brown. This finding has broadened the range of photoinitiators for UV grafting from traditional aromatic ketones to aliphatic ones.

7.2 Experimental

7.2.1 Materials

Polypropylene (grade CP36OH) was obtained from Sunoco Chemicals (PA, USA). This polymer has a narrow molecular weight distribution, with a melting point ($T_m$) of 160°C, density of 0.91 g cm$^{-3}$, a Melt Flow Index (MFI) of 34 dg/min and crystallinity of about 50%. Silicon wafers, deionized water, hexane, benzophenone, methanol, heptane, GMA were also used. All chemicals were of analytical grade and were used as received.

7.2.2 Sample preparation

The silicon wafers were first coated with PP layer using a spin coater. To prepare for
the silicon wafers were first purged with an inert gas to remove any solid particles that would have deposited on them. They were then treated with UV Ozone (UVO) treatment for 5 minutes to clean the surface further of any contamination. An IR lamp was shone on the wafers for 5 minutes to warm the surface and make it receptive to further surface treatments. A drop of 1% solution of PP in xylene was put on the silicon wafer, which was stuck onto a sample holder using vacuum. The whole system was purged with nitrogen gas and then the spin coater was rotated at 3000 rpm for 30 seconds. After the silicon wafers were spin coated with PP, they were treated with UV light to enable GMA grafting.

The method of depositing GMA on PP coated silicon wafers is as follows: PP films spin coated on silicon wafers were presoaked for 15 minutes in 5 ml solution of 1 mM Benzophenone in heptane (for entrapping). Thereafter the samples were taken out and immediately immersed 2 times for 1 min in 5 ml methanol. Then samples were quickly wiped with filter paper in order to remove the adhering solvent and were then immediately immersed into a sample holder such that when GMA was added to the holder, it maintained a constant thickness of 1 mm during the UV treatment. This sample holder, with the PP coated wafer sample inside, was then exposed to UV light for 15 mins (UV illumination system equipped with a high pressure mercury lamp and a glass filter $\lambda > 300$ nm with an intensity of 50 mW/cm$^2$ was used). After 15 minutes of irradiating, the samples were taken out and immediately washed sequentially with 80 ml of water under stirring, first for 30 min at room temperature (RT), second for 60 min at 60 °C and third for 30 min at RT. The wafers were then dried overnight at 50 °C. These treatments were carried out in 2 ways, one had the PP
films pretreated with UV Ozone before the grafting and the other did not have any pretreatment. The difference in the results are indicated below. The efficiency of the grafting reaction was tested using FTIR techniques and water contact angle.

7.2.3 Analytical techniques used

The amount of GMA reacted with the PP was determined by FTIR spectroscopy (Nikolet Nexus 470 FT-IR). For this purpose, the peak of carbonyl group appearing at 1730 cm\(^{-1}\) and the peak of the epoxide groups at 850-910 cm\(^{-1}\) were taken as references.

Total surface energy (SE), its polar (\(\gamma_p\)) and disperse (\(\gamma_d\)) parts were determined by static contact angle measurements using sessile drop method. Two different liquids were used: water (\(\gamma_p = 50.7\) and \(\gamma_d = 22.1\) mJ m\(^{-2}\)) and ethylene glycol (\(\gamma_p = 19.0\) and \(\gamma_d = 29.0\) mJ m\(^{-2}\)). SE was calculated using the contact angle values with the above mentioned liquids in the harmonic-mean equation. The results are an average of 10 readings.

7.3 Results and Discussion

The FTIR result is shown in the Figure 7.1. The FTIR scans of the pure PP showed traditional peaks at around 3200 cm\(^{-1}\). The sample with UVO pretreatment shows significant peaks of carboxyl group at around 1730 -1760 cm\(^{-1}\) which are present in the GMA molecule. The sample without the UVO pretreatment however shows less significant peaks in those
regions. Similarly peaks around 850 – 910 cm\(^{-1}\) indicating presence of the epoxide group are significantly present in the UVO pretreated samples whereas they are not so significant in samples without the pretreatment. These observations infer that the UV grafting of GMA onto PP is effective and significant with the UVO pretreatment method which cleans the surface of the PP and also prepares it to be more receptive to the next modification step.

![Figure 7.1: FTIR peaks showing difference in UVO pretreated and non-pretreated samples](image)

Figure 7.1: FTIR peaks showing difference in UVO pretreated and non-pretreated samples
The results of the static contact angle tests are as shown in the Figure 7.2. This data corroborate the fact that modification by UV does bring significant changes in surface properties. The static contact angle for pure silicon wafer without any treatment or coatings on it was 43°. The same for a PP coated wafer sample was 94.4°. Surprisingly the UV grafting of GMA without the UVO pretreatment resulted in a contact angle which was very similar to that of a pure PP coated sample, 94.6°, whereas with the UVO pretreatment there seemed to be a marked change in surface properties with contact angle lowering down to 77.6°. Thus UV grafting of GMA on PP coated silicon wafers with the addition of the UVO pretreatment caused substantial change in the surface property. It made the surface more hydrophilic than the starting material.

7.4 Conclusions

This work showed that there can be effective surface modification by UV grafting
method provided it is followed by a UVO pretreatment. This pretreatment removes any particles from the surface that would cause any hindrance to the next modification step, in addition to preparing the sample to be more receptive to the treatment step ahead. Both the contact angle and the FTIR results confirm this fact.

7.5 References


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CHAPTER 8

8 Future Work

8.1 Introduction

PP as a saturated hydrocarbon has a very low surface energy and hence modification, as shown in this research work, becomes very significant. An additional method of modification, than what has already been mentioned, is by using polar monomers. This route changes the low cost commodity polymer to a value added one that can be used for various applications such as medicine, textiles, concrete and so on. One way of getting modification is using free-radical graft polymerization. Three types of initiators can be used-water soluble initiator\(^1\), the redox initiator\(^2\) and the oil-soluble initiator\(^3\) \(^1\). Wang et al.\(^4\) compared the three typical grafting systems and came up with the observation that oil-soluble initiating systems were more effective in surface grafting PP fibers as they formed very little homopolymers.

Another way of modifying PP would be what Rao et al.\(^5\) had used. They had grafted a mixture of acrylamide and acrylic acid onto PP fibers and a mixture of acrylic acid and methacrylic acid onto PP by radiation method. They inferred that the mixture of acrylamide and acrylic acid was more effective in bringing about modification than plain acrylamide. PP can be also modified by blending it with other polymers. Sherman\(^6\) studied the blending of PP with HDPE and exploited the huge difference in melting point of the two polymers to
produce a uniaxial reinforcement of HDPE with PP. After blending, annealing followed
tensile drawing which lead to an increased tensile modulus of the blend. A PP membrane that
has hydrophilic surfaces and asymmetric porous structure is based on newly developed
hydroxylated PP (PP-OH) \(^7\). It has a brushlike microstructure, high molecular weight, high
melting point and relatively high concentration of hydroxyl groups. The PP-OH polymer acts
as the surface modifier of the asymmetric PP membrane with flexible functional groups
located on the membrane surface.

Microporous hydrophobic PP membranes\(^8\) were modified by chemical modification
technique to impart permanent hydrophilicity. The two stage modification process includes
hydroxylation of the membrane by treating with aqueous potassium peroxydisulfate and then
subjecting these hydroxylated membranes to grafting acrylamide using ceric ammonium
nitrate as an initiator. These acrylamide grafted PP membranes can be subsequently partially
hydrolyzed to have carboxyl functional groups. A novel method of grafting a sugar-
containing monomer on PP microporous membrane under UV radiation was also studied \(^9\).
The water contact angle substantially reduced and the modified membranes also showed
higher water and protein solution fluxes.

In addition to all these chemical methods of modification, physical methods can also
be effectively utilized. The CCl\(_4\) plasma treatment of PP films was investigated from the
viewpoint of improving its hydrophilicity\(^10\). It was observed that the CCl\(_4\) plasma treatment
was effective as the advancing contact angle was reduced from 99° to 81° and the surface
energy also improved from 27.2 to 38.9-67.7 mJ/m\(^2\). The modification by the plasma reached
upto 36-49 Å deep and was reasoned that the improved hydrophilicity could be due to increased chlorine, oxygen and aluminium functionalities. In order to improve surface properties, acrylic acid has been grafted to PP films and this treatment has been followed by irradiation with $\gamma$-rays. The amount of grafting however does not relate directly to the irradiation dose. One study did show that the rupture strength and ultimate elongation strength of the samples did drop down several times with the increase in radiation doses.

8.2 References


