THONGRUANG, WIRIYA. Properties of Polymer Blends Filled with Mixtures of Conductive Fillers. (Under the direction of Richard J. Spontak and C. Maurice Balik.)

The development of efficient conductive polymer composites (CPCs) remains an important endeavor in light of growing energy concerns. In the present work, high-density polyethylene (HDPE) and ultrahigh molecular weight polyethylene (UHMWPE), as well as blends thereof, are used to produce ternary and quaternary composites containing carbon black (CB), graphite (G) and carbon fiber (CF), as well as selected mixtures thereof, to discern if polymer blends and filler mixtures yield appreciable advantages over CPCs composed of single polymers and/or single fillers. Dry mixing and molding processes are examined as viable means by which to produce uniformly dispersed specimens and are consequently employed to prepare CPC samples throughout the study. The effects of polymer blend composition and filler type, concentration and composition on electrical conductivity, composite morphology, mechanical and thermal properties have been systematically investigated and correlated wherever possible to establish meaningful structure-property relationships that can be used to facilitate the rational design of efficient CPCs. Percolation threshold concentrations (PTCs) required for these fillers to achieve measurable conductivity in HDPE and specific HDPE/UHMWPE blends have been identified. Conductive polymer composites exhibiting double percolation of the conductive fillers due to volume exclusion considerations possess a noticeably reduced PTC
and afford a desirable alternative to conventional CPCs. In this case, blend composition is found to influence electrical conductivity, revealing pronounced conductivity maxima at nearly identical filler concentrations in CPCs containing CB and G. This behavior is not, however, observed for composites with CF. The conductivity of HDPE/G and HDPE/UHMWPE/G composites likewise increases when CF is added at constant filler concentration. The extent of this substantial increase is sensitive to CF length, and the concept of bridged double-percolation is proposed to explain this increase in quaternary CPCs composed of a HDPE/UHMWPE matrix filled with a G/CF mixture. Optical and electron microscopies are employed to ascertain the extent to which the polymers, and hence filler particles, are segregated, whereas dynamic mechanical analysis reveals that filler type, composition and CF length impact both the magnitude and temperature dependence of the dynamic storage modulus. Differential scanning calorimetry of the composites confirms that the constituent polymers are (i) indistinguishable in terms of their thermal signatures and (ii) virtually unaffected by the presence of any of the fillers examined in this work.
PROPERTIES OF POLYMER BLENDS FILLED WITH MIXTURES OF
CONDUCTIVE FILLERS

by

WIRIYA THONGRUANG

A dissertation submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Doctor of Philosophy

MATERIALS SCIENCE AND ENGINEERING

Raleigh

2001

APPROVED BY

Dr. A. A. Fahmy
Dr. M. A. Zikry
Dr. R. J. Spontak
Dr. C. M. Balik

Co-chair of Advisory Committee
Co-chair of Advisory Committee
DEDICATION

This work is dedicated to my parents and my wife, Jureerat Thongruang. Their love and support drive the completion of this dissertation.
WIRIYA THONGRUANG was born in Thailand on March 15th, 1968. In 1985, he graduated from Suratthani High School in southern part of Thailand. Four years later, he received a Bachelor of Science degree in Mechanical Engineering from Prince of Songkhla University. After graduating, he worked as a production engineer in the Electrical Generating Authority of Thailand (EGAT) for almost three years. In 1992, he resigned and joined faculty members in Mechanical Engineering Department, Prince of Songkhla University, Thailand. He first came to the United States to pursue a Master of Science degree in Materials Science and Engineering at New Jersey Institute of Technology (NJIT) and earned the degree in December 1996. He has continued his Ph.D. study at North Carolina State University in Materials Science and Engineering program since January 1997. In December 1999, he married his wife, Jureerat, a Chinese-Thai lady, who was born in Thailand. He and his wife have a wonderful life in Raleigh, North Carolina and really enjoy the environment in the United States.
ACKNOWLEDGEMENTS

The author would like to thank friends and colleagues at NCSU especially all of them in Riddick (M. A. Hunt, Dr. T. Banerjee, C. J. Sikes, etc.) for their help and support. In particular, I would like to express deep appreciation and thanks to the following:

Dr. C. Maurice Balik and Dr. Richard J. Spontak, my advisors for their patience to my lack of knowledge in polymer fields and English.

Dr. A. A. Fahmy and Dr. M. A. Zikry (committee members) as well as Dr. J. Kasichainula (substitute committee member) for their valuable comments, advice and time.

Dr. T. M. Hare, Dr. Y. Fahmy, Mr. R. Russell and Mr. D. Leanoard, for their advice and help during my TA works for many semesters.

The Vonkchalee family, for their warm welcome and support during my Ph.D. study and living in North Carolina.

Finally, Ms. Edna Deas, the department secretary for her advice and help during my 5 years of Ph.D. study.
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1. INTRODUCTION

1.1 Background and Applications

Conductive polymer composites containing carbonaceous fillers have been studied for years due to their ability to impart electrical conductivity, light weight, and good corrosion and ultraviolet (UV) resistance to commodity polymers. Examples of carbonaceous fillers commonly employed for this purpose include carbon black (CB), graphite (G) and carbon fiber (CF). Electrical conductivity may also be imparted to polymers by adding conductive particles composed of metals such as copper, silver and platinum. These metals, however, are more expensive and heavier than their carbon-based counterparts at similar volume-fraction concentrations. While less expensive metals such as steel may also be used for improving the conductivity of polymers, these metals are more prone to chemical interaction (especially with oxygen), often resulting in corrosion. Thus, the use of highly conductive metals as filler material for conductive polymer composites can be problematic. Conductive polymer/carbon composites, on the other hand, have been used in a variety of different applications with current focus on battery and fuel cell electrodes, anti-static materials and corrosion-resistant materials. No one researcher has made the claim to be the first to establish the electrical properties of carbon-filled polymers. Records show, however, that in 1930, composites prepared from polymer and CB were used commercially as conductive and anti-static compounds [1]. A later account reveals that the conductivity of rubber filled with CB was studied in 1957 [2].
Polymers are, for the most part, well-established as electrically insulating materials. They can typically be modified to become a good conductive material by compounding with electrical conductive fillers such as metals and carbon. The most attractive type of polymers commonly used for producing composite materials are *thermoplastics*. Commodity thermoplastics possess the advantages of low cost, light weight, low-cost manufacturing, high fracture toughness and consistent quality [3]. In addition, one more important property of thermoplastics such as polyethylene and polypropylene is their very good chemical resistance. Carbon-based fillers have been used in polymers for three main purposes: color, mechanical reinforcement and electrical conductivity. The three major types of carbonaceous fillers commonly used to make composites - CB, G and CF - are discussed in a later section. Composites of thermoplastic/carbon are easily formed into desired shapes for different applications by using conventional polymer processing strategies such as mixing and molding.

1.2 Polymer Properties

Polymers are viscoelastic materials, which means that their properties lie between those of elastic solids and viscous liquids. Upon application of external forces (or hydrostatic pressure), elastic solids of one shape adopt a new shape in response to their deformation. After removal of these external forces, the solid converts exactly to its original form. In this manner, the solid stores the energy obtained from the work done by the external forces during deformation, and this
energy is available to restore the body to its original shape when the forces are removed. In marked contrast, viscous liquid has no definite shape and flows irreversibly under the application of external forces. It is difficult, however, to classify polymers as either elastic solids or viscous liquids, since their mechanical properties are so dependent on time, temperature, strain amplitude and strain rate. At low temperatures, polymers may be glassy, exhibiting a Young's modulus in the range of $10^8$-$10^{10}$ N/m$^2$, and will break or flow at strains in excess of 5%. At high temperatures, however, the same polymer may be rubber-like with a modulus in the range of $10^6$ - $10^7$ N/m$^2$. In this state, the polymer can withstand large extensions (~100%) without permanent deformation [4]. With increasing temperature (above the melting temperature, if one exists), permanent deformation of the polymer occurs, and the polymer effectively behaves in the same fashion as a highly viscous liquid.

To have a better understanding of the viscoelastic behavior of polymers, the idealized modulus-temperature curve for typical linear and crosslinked amorphous polymers is presented in Figure 1.1. In this graphical representation, four regions of viscoelastic behavior are defined. At low temperatures, where the modulus is relatively high, the polymer is hard and brittle and is referred to as a glassy polymer. The glassy modulus $E_1$ slowly decreases with increasing temperature. In this regime, thermal energy is insufficient to overcome the potential barriers for rotational and translational motion of segments comprising the polymer molecules. The chain segments are essentially frozen in fixed
positions and are able to undergo only very small vibrations around these fixed positions.

Figure 1.1. Variation of modulus (E) with respect to temperature for an amorphous polymer, showing the different viscoelastic regimes.

As the temperature is increased, the amplitude of vibrational motion becomes greater. Eventually the thermal energy becomes comparable to that associated with potential energy barriers to functionality rotation. At this temperature, the polymer may exhibit a low-temperature thermal transition. Once the thermal energy is of the same order as the energy barrier corresponding to translational motion, the polymer is at its glass transition temperature where short-range
diffusional motion begins and segments dynamically jump from one site to another. The rigid but brittle glass becomes softer and the modulus then catastrophically drops (by as much as three orders of magnitude) and the polymer becomes viscoelastic; i.e., the modulus becomes time and temperature dependent.

As the temperature is further increased, the polymer becomes **rubbery**. The modulus again reaches a plateau region characterized by $E_2$. Short-range diffusional motion of the polymer segments occurs faster than in the glassy region. The long-range cooperative motion of chains that would result in translational motion of complete molecules is, however, still restricted by the presence of strong local interactions between neighboring chains. These interactions are primarily chemical bonds in the case of crosslinked polymers. In linear polymers, these interactions are dispersive in nature, arising from chain entanglements. Within the rubbery plateau region, segments of chains can reorient relative to each other, but there is no large-scale translational motion. The viscoelastic responses of linear and crosslinked polymers through the rubbery plateau region are relatively identical. As the temperature is further increased, however, differences between linear and crosslinked polymers become pronounced. In the case of crosslinked polymers, the modulus changes very slightly with increasing temperature and remains relatively constant up to the temperature where chemical degradation commences. However, this behavior is quite different for a linear chain, wherein increasing temperature causes molecular motions to become increasingly large until entire polymer
molecules begin to translate. When the temperature is sufficiently high, local chain interactions no longer have sufficient energy to prevent molecular flow. The molecules slip by one another at this temperature, and the polymer starts to flow. If the temperature is increased further, the sample becomes a viscous liquid (in the absence of chemical degradation). As a result, the modulus continues to decrease systematically.

1.2.1 Linear Viscoelastic Behavior

As mentioned in the previous section, polymers are examples of viscoelastic materials possessing mechanical properties that lie between those of elastic solids and viscous liquids. Viscoelasticity is the key for understanding the molecular nature of polymers. Most of the experimental work reported on the subject of linear viscoelastic behavior is restricted to a single mode of deformation. Such measurements usually yield the Young’s modulus or the shear modulus at short time and small strain amplitude. The “10-second modulus,” for example, has been discussed by Aklonis et al. [5]. At long times and large strains, the viscoelastic behavior becomes complex and nonlinear. In defining the constitutive relations for the elastic solid, we implicitly assume that the strains are small and that there exists a linear relationship between stress and strain. The Boltzmann superposition principle [6] can be used to describe how the principle of linearity is extended to viscoelastic materials. This principle allows the state of stress or strain in a viscoelastic body to be determined from the knowledge of its previous deformation history. The basic assumption used
for this principle is that, during viscoelastic deformation in which the applied stress is varied, the overall deformation can be determined from the algebraic sum of strains from each loading step.

The linear viscoelastic formulation is based on the analogy between Hooke’s law for elastic solids and Newton’s law for viscous liquids. In the former, the stress is linearly related to the applied strain. In the latter, however, the stress is linearly related to the strain rate. These relationships for are given by

\[ \sigma_e = G \varepsilon \]  \hspace{1cm} (1.1)

for elastic behavior, and

\[ \tau_v = \eta \left( \frac{d\gamma}{dt} \right) \]  \hspace{1cm} (1.2)

for viscous behavior. In these equations, \( \sigma_e \) and \( \tau_v \) denote the elastic and viscous stresses, respectively, \( \varepsilon \) and \( \gamma \) represent strain, \( G \) is the shear modulus and \( \eta \) is the viscosity. A simple constitutive relation for the behavior of a linear viscoelastic solid is obtained by combining these two relationships; \textit{viz.},

\[ \sigma = \sigma_e + \tau_v = G \varepsilon + \eta \left( \frac{d\gamma}{dt} \right) \]  \hspace{1cm} (1.3)
To limit the extent to which mechanical testing disrupts the structure of a given polymer, a dynamic mechanical analysis is employed in which the specimen is subjected to a low-amplitude alternating strain while the stress is measured simultaneously, or *vice versa*. Such analysis is most easily performed when an oscillating sinusoidal load is applied to a viscoelastic sample at a particular frequency. Under steady-state conditions, the applied stress varies as a function of time, and the strain for an elastic material obeying Hooke’s law varies in identical fashion:

\[
\sigma = \sigma_0 \sin \omega t \quad \text{(1.4)}
\]

\[
\varepsilon = \varepsilon_0 \sin \omega t \quad \text{(1.5)}
\]

Here, \(\omega\) is the angular frequency and the subscripted 0 represents the amplitude. In linear viscoelastic behavior, the strain lags behind the stress. Thus, the variation of stress with respect to time can be rewritten as

\[
\sigma = \sigma_0 \sin (\omega t + \delta) \quad \text{(1.6)}
\]

where \(\delta\) identifies the “phase lag” (i.e., the relative angular displacement of the stress and strain). Expanding \(\sigma\) from equation 1.6 consequently yields

\[
\sigma = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta \quad \text{(1.7)}
\]
According to equation 1.7, the stress can be considered to consist of two components, one which is in phase with the applied strain ($\sigma_0 \cos \delta$) and another which is $90^\circ$ out of phase with the strain ($\sigma_0 \sin \delta$). The stress-strain relationship can therefore be defined by decomposing the modulus G into its vector product of G' and G'', which are in phase and $90^\circ$ out of phase, respectively, with the imposed strain. Thus, we immediately obtain

$$\sigma = \varepsilon_0 G' \sin \omega t + \varepsilon_0 G'' \cos \omega t$$  \hspace{1cm} (1.8)

where

$$G' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \quad \text{and} \quad G'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta$$

Hence, the phase angle $\delta$ can be usefully described by the following relationship:

$$\tan \delta = \frac{G''}{G'}$$  \hspace{1cm} (1.9)

If the complex modulus representing the dynamic mechanical properties of a viscoelastic material is introduced, the overall complex modulus $G^*$ is given by

$$G^* = G' + iG''$$  \hspace{1cm} (1.10)

The real part of the modulus $G'$, which is in phase with the strain, is often called the dynamic storage modulus because it defines the energy stored in the sample.
due to the applied strain. The imaginary part of the modulus is $G''$, which is out of phase with the strain and which defines the dissipation energy. It is often referred to as the \textit{dynamic loss modulus}. An elastic (Hookean) solid has the capability of storing all the mechanical energy due to deformation without any dissipation whatsoever. The viscous liquid, on the other hand, dissipates all the energy due to deformation without storing any of it. When viscoelastic polymeric materials are deformed, a part of the energy is stored as potential energy and another part is dissipated as heat and manifests itself in terms of mechanical damping or internal friction.

1.3 Polymer Blending

Polymer blends are generally considered as mixtures of at least two kinds of chemically dissimilar polymers or copolymers in the absence of covalent bonds that link the constituent species. One of the primary reasons for polymer blending is to reduce cost while maintaining good properties. Polymers are selected for a blend in such fashion that each constituent will either add desirable functionality to the blended material or compensate for deficiencies of the other component. Strong interactions or even chemical reactions between different polymer chains may occur during simple mechanical blending operations such as open rolling and extrusion wherein the shearing action generates free radicals and initiates polymer degradation. These free radicals often subsequently react to form chemical crosslinks between the two components, which may serve to improve the mechanical properties of the blend.
1.3.1 Miscibility and Phase Equilibria

The two basic types of phase diagrams used to describe the behavior of most binary polymer blends correspond to upper critical solution temperature (UCST) and lower critical solution temperature (LCST) behavior. These phase diagrams are illustrated in Figure 1.2. Note that other, more complex, phase diagrams exhibiting multiple critical points have been observed in binary polymer blends, but are not considered further here. As a general rule, the enthalpy of mixing ($\Delta H_m$) tends to be positive (endothermic) for most polymer blends, so that the critical solution temperature ($T_c$) corresponds to the maximum of the binodal and spinodal curves [7]. This temperature defines the upper critical solution temperature above which the polymer and solvent are miscible in all proportions, as displayed in Figure 1.2a. Exothermic mixing (negative $\Delta H_m$) is also observed in fewer cases of polymer blends. Such mixing is often indicative of specific polymer-solvent interactions induced by hydrogen bonding and charge transfer. The $T_c$ in this case corresponds to the common minimum of the binodal and spinodal and defines the lower critical solution temperature below which the polymer and solvent are completely miscible (see Figure 1.2b).

In the binary systems detailed above, there exist three distinct regions wherein the phases are miscible (I), metastable (II) or immiscible (III). The dynamics of phase separation are adequately described by the mean-field (square-gradient) approach introduced by Cahn and Hilliard [8]. In the metastable region between the binodal and spinodal, nucleation and growth (a relatively low driving force mechanism) overcomes the activation energy required
for phase separation. Within this regime, small domains nucleate and grow without changing the composition of the phases. However, when the temperature is rapidly lowered from the homogeneous regime (in a typical UCST phase diagram) into the spinodal region, spontaneous phase separation due to spinodal decomposition (a relatively high driving force mechanism) occurs. This mode of phase separation is characterized by a propagating concentration fluctuation wave whose amplitude increases with increasing time. Thus, the spatial composition distribution associated with this phase-separation mechanism is time-dependent. Details regarding the kinetics of nucleation and growth, as

Figure 1.2. Phase diagrams for polymer solutions exhibiting (a) UCST and (b) LCST behavior. The solid and dashed lines represent the binodal (coexistence) and the spinodal (stability) curves, respectively.
well as spinodal decomposition, in polymeric blends are available elsewhere [7,9,10].

1.3.2 Thermodynamic of Mixing

The thermodynamics of mixing is the key to explaining and understanding the behavior, as well as the properties, of polymer blends and alloys. For a binary system, the Gibbs free energy of mixing (\(\Delta G_m\)) of two components is given by

\[
\Delta G_m = G_{12} - (G_1 + G_2)
\]  

(1.11)

where \(G_{12}\) is the Gibbs free energy of the mixture, and \(G_1\) and \(G_2\) are the Gibbs free energies of the individual components 1 and 2, respectively. A two-component solution is formed when the Gibbs free energy of a mixture is less than the sum of Gibbs free energies of the individual components (i.e., \(\Delta G_m < 0\)).

The useful form of \(\Delta G_m\) expressed in terms of the enthalpy (or heat) of mixing (\(\Delta H_m\)) and the entropy of mixing (\(\Delta S_m\)) at any temperature can be expressed as

\[
\Delta G_m = \Delta H_m - T\Delta S_m
\]  

(1.12)

Here, \(\Delta S_m\) typically increases upon mixing due to an increase in the number of spatial arrangements, which can be written for small molecules or atoms in terms of mole numbers (n) by
\[ \Delta S_m = -R [n_1 \ln X_1 + n_2 \ln X_2] \] (1.13)

where \( R \) is the gas constant and \( X \) is a mole fraction defined by

\[ X_1 = \frac{n_1}{n_1 + n_2} \quad \text{and} \quad X_2 = \frac{n_2}{n_1 + n_2} \] (1.14)

Flory and Huggins [11,12] independently studied the formation of solutions of a polymer in a solvent by considering the polymer molecules to be composed of solvent-like segments that occupied the same volume as individual solvent molecules. These studies introduced the notion of molecular connectivity and yielded the well-known Flory-Huggins equation of state, which is given by

\[ \Delta G_m = RT [n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi] \] (1.15)

where \( \phi_1 \) and \( \phi_2 \) denote the volume fractions of solvent and polymer, respectively, \( T \) is absolute temperature and \( \chi \) is the \textit{Flory-Huggins interaction parameter}, a temperature-dependent dimensionless quantity stemming from regular-solution thermodynamics. The \( \chi \) parameter can be decomposed into both enthalpy (temperature-dependent, \( H \)) and entropy (temperature-independent, \( S \)) contributions:

\[ \chi = \chi_H + \chi_S \] (1.16)
1.3.3 Methods of Blending

Prior to processing a polymer blend, the compatibility of the components must be carefully considered due to its effect on phase homogeneity and stability, as well as their impact on the ultimate properties of the blend. Incompatibility in a polymer blend arises from the very small entropy gained by mixing different kinds of long-chain polymers. While polymer incompatibility is the norm for most limited compatibility can occur in highly diluted solutions of a ternary system composed of two polymers and a solvent or copolymer [13]. In fact, only polymer pairs with zero or negative $\Delta H_m$ are capable of forming a single phase. Several methods have been introduced to improve the homogeneity, and consequently the properties, of polymer blends. Use of sub-micron-sized particles, compatibilizing agents, reactive processing (detailed elsewhere [9]) and stabilization are all commonly used to improve the performance of polymer blends through alloying. Processes for preparing polymer blends and alloys typically include: (1) mechanical or internal mixing, (2) solvent blending and casting and (3) fine powder mixing.

1.4 Nature of Polyethylene

Polyethylene (PE) is classified as a commodity thermoplastic material due to its volumetric production and low cost. The ethylene monomer and polyethylene structures are presented in Figure 1.3. Ethylene gas is produced by cracking higher hydrocarbons from natural gas or olefins [14]. Polyethylene has been used in many applications due to its low price and processability, as well as by its
broad range of properties relative to many other thermoplastics. In addition to the above, it exhibits good chemical resistance and light weight. These advantages have led to widespread use of polyethylene in many industrial applications, such as wire coating, pipes and containers. Two common types of polyethylene are utilized in commercial applications: low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The primary difference between the two is that LDPE possesses a branched chain structure, whereas HDPE has essentially a linear chain structure. The chain structure impacts how the molecules pack and, hence, their degree of crystallinity and overall density.

Low-density polyethylene was first commercially produced in 1939 by using autoclave (or tubular) reactors at high pressure and temperature (14,500 psi and 300°C). High-density polyethylene, on the other hand, was commercially introduced using the Phillips and Ziegler-Natta processes in 1956-1957 at low pressures and temperatures. The Phillips and Ziegler-Natta processes operate at 100-150°C and 290-580 psi with special catalysts and have been described by Young and Richardson [7,14]. Since LDPE has a branched chain structure, its degree of crystallinity, density and strength are lower than those of HDPE because of inefficient chain packing and a net reduction in intermolecular bonding forces. In contrast to LDPE, HDPE possesses very little branching, which allows the chains to pack closer together to increase crystallinity, density and strength.
Ultra-high molecular weight polyethylene (UHMWPE), another type of polyethylene in the ethnic family, is typically available with average molecular weight (MW) values between 3 and 6 million g/mol. This polymer is another example of a linear, low-pressure, Ziegler-catalyst polyethylene [15]. With such a high MW, however, UHMWPE exhibits a high viscosity molten state with very little flow potential. Fabrication of UHMWPE products is made possible by compression-molding, rather than the injection molding or extrusion processes more aptly suited for conventional thermoplastics. Products manufactured from this polymer have outstanding impact strength and abrasion resistance compared to other thermoplastics. The low coefficient of friction of UHMWPE yields a self-lubricating, non-stick surface. The molecular weight of UHMWPE is usually determined from dilute-solution viscosity, rather than by size exclusion chromatography (SEC), due to its insolubility. Richardson [14] and Stein [15] reported the approximate density range for LDPE as 0.910-0.925 g/cm³, HDPE as 0.941-0.965 g/cm³ and UHMWPE as 0.93 g/cm³. Unfortunately, the cost of UHMWPE is relatively high compared to LDPE and HDPE, which tends to limit its

Figure 1.3. Chemical structures of ethylene monomer and polyethylene.
commercial use. While the cost of UHMWPE is decreasing as more applications find use for this polymer, it is currently used as an additive to improve the mechanical properties of other polymers.

1.5 Nature of Carbon Black, Graphite and Carbon Fiber

Carbon black (CB), graphite (G) and carbon fiber (CF) have been used as polymer additives by design engineers for the primary purposes of color modification, mechanical reinforcement and electrical conductivity. In the present research, however, we focus mainly on the electrical and reinforcement properties of these three common carbonaceous additives. The size of individual filler particles or fibers, the aggregate morphology and the degree of dispersion are the key for controlling the electrical and mechanical properties of conductive polymer composites. The following sections discuss the behavior of these additives in more detail.

Carbon black particles typically consist of nearly pure carbon that takes the form of “grape-clusters” in which particles are fused together in irregularly-shaped aggregates. Within each discrete particle, carbon atoms are arranged in imperfect graphite layers. The arrangement of carbon atoms and layers is referred to as its microstructure [16]. The layers are arranged within each particle (growth center) with some degree of parallelism between adjacent layers in small regions, and are often continuous from one particle to the next within an aggregate [17]. The microstructure layer within a particle can be observed by a high-resolution electron microscopy [23]. However, electron micrographs may
not represent the actual arrangement of layers or the number of layers due to imaging complications [18]. Nearly all CB is produced from petroleum oil by the furnace process [19]. The black product from this process is the fluffy form, with a bulk density of about 0.15 g/cm$^3$. Typical furnace CBs are composed of spherical particles with diameters ranging from 10-100 nm and surface areas from 25-1500 m$^2$/g [20]. However, most of the CB that is commercially produced is spherical pelletized black with a diameter of about 0.3-1.0 mm and a higher density that is easier to handle than the fluffy form. Special modifications of the oil furnace process are used to make highly electrical conductive CB, such as Vulcan XC-72, Acetylene [21] and Ketjenblack [22]. Different grades of conductive CB are distinguished chiefly by their surface area, which is determined by gas adsorption methods [22,23]. The structure of CB is determined from its aggregate size, shape and the number of particles per aggregate. Primary aggregates of CB comprised of many particles with considerable branching and chaining are referred to as high structure CB. In contrast, compact aggregates with few primary particles are considered as low structure CB. Both of these structures are portrayed in Figure 1.4.

High-structure CB particles are more easily dispersed because the greater distance separating aggregate centers weakens the attractive forces between neighboring aggregates. However, perfect dispersion is not always necessary or even desirable as is the case of conductive polymer composites. The primary particle size of the black also controls the size of CB aggregates. As the primary particle size decreases, the primary aggregate size likewise becomes smaller.
As a result, more aggregates per unit weight of carbon black are distributed throughout the fixed volume of a polymer matrix. Therefore, the combination of fine particle size and the accompanying small aggregates improves the electrical conductivity when dispersed in plastics. In addition, high structure carbon black creates irregular shapes from branching and chaining that provides more potential pathways for electron transfer throughout the composite, thereby improving electrical conductivity.

Graphite is another common carbonaceous filler and represents one of the two recognized crystalline forms of carbon existing in nature (diamond is the other). It possesses a layer type-hexagonal structural with three-dimensional ordering. Each layer consists of strong covalent carbon-carbon bonds (~525 kJ/mol). The inter-layer bonds, however, are van der Waals bonds and are much weaker (<10 kJ/mol). This substantial difference between intra- and inter-layer
bonding causes the properties of G to be highly anisotropic. The structure of G is denser than the structure of CB and is vertically oriented. Graphite is commercially prepared by controlling the heat applied to cellulose or carbon fibers.

Figure 1.5. Crystallographic arrangements of carbon atoms in three carbon structures (reproduced from ref. [20] with permission of the Society of Plastic Engineers).

Carbon fibers are produced by many different processes and their structures and properties vary considerably. The high-modulus carbon fiber was marketed by Union Carbide in 1959. These particular fibers were produced from pyrolysis of a rayon precursor yarn [24]. However, there are two well-known types of carbon fiber in common use: PAN-based and pitch-based fibers. The difference between these two fibers is the type of precursor material used. The PAN-based CF uses a polyacrylonitrile fiber precursor, the details of which have been reported elsewhere [25]. The pitch-based fiber is a by-product of the petroleum and coal-coking industries, and is designed to have better impact toughness. As the organic precursor is decomposed, the steps of carbonization (i.e., gradual
structural reordering) and graphitization at high temperature lead to fiber formation. Hot stretching may be needed to increase the modulus and strength by developing preferred orientation in the fibers and reducing porosity.

1.6 Carbon-Doped Single Polymer and Polymer Blends

Polymers are generally good insulators, exhibiting electrical conductivities of about $10^{-19}$-10$^{-15}$ (Ω-cm)$^{-1}$. It is possible, however, to obtain higher electrical conductivities in polymers while retaining their desirable properties. Such improvement can be routinely achieved by adding highly conductive materials such as metals, CB, G and CF to the polymer matrix. Such physical modification yields composite materials with electrical properties similar to those of conductive agents while retaining the mechanical and chemical resistance properties of the polymers. In addition, incorporation of inorganic additives to polymers may promote an overall improvement in mechanical properties. The presence of very high concentrations of such fillers in a polymer matrix may, however, promote a drastic reduction in mechanical properties due to insufficient wetting of the filler. The resistivity range of polymer composites containing conductive carbonaceous fillers is identified by the shaded area of Figure 1.6.

The various steps involved in dispersing carbon black in a polymer have been discussed by Boonstra et al. [26]. In that study, the molten polymer is first forced into the interstices of the CB agglomerates and aggregates. This step is called the incorporation stage. Voids and air pockets are eliminated during this stage. Next, filler agglomerates are pulled apart by shear or extensional flow in the
deagglomeration stage. Then, the individual aggregates are distributed throughout the polymer by random mixing. Finally, the inter-aggregate separation is determined by diffusion of the aggregates. However, this may differ in mechanical mixing and molding processes, in which random dispersion of aggregates takes place during mechanical mixing. Deagglomeration and diffusion may also occur during molding. The degree to which CB and G disperse is expected to be similar due to their particulate nature. Dispersion of CF in a polymer matrix is, however, more difficult due to its high aspect ratio, and may proceed by a different mechanism than the one described above.

![Figure 1.6. Resistivity range of conductive polymer composites containing CB (reproduced from ref. [20] with permission of the Society of Plastic Engineers).](image)

In the case of a single polymer matrix, fillers may be distributed evenly in the matrix phase since there is no spatial variation in the viscosity of the polymer. In
a matrix composed of a polymer blend, however, there are three possible ways for a filler to distribute within the matrix: (1) it may be distributed evenly, (2) it may preferentially reside in one of the two polymer phases or (3) it may reside at only the polymer interface. Studies of immiscible polymer blends containing carbonaceous fillers in which the fillers selectively reside and form a conductive network within one polymer phase have been reported [27-29]. These ternary composites exhibit a much higher electrical conductivity relative to a single polymer matrix at the same conductive filler loading level. Volumetric constraints in this case force the filler to occupy a smaller volume and pack more tightly, thereby increasing the number of filler contacts and increasing the overall conductivity of the composite.

1.7 Brief History of Conductive Polymer Composites

Table 1 shows the historical development of conductive polymer composites. These composites have been produced from a wide variety of different polymers and fillers. From these studies, it has been found that the types of polymers and fillers, as well as the processing and measuring methods used to prepare and characterize them, affect the threshold concentration or conductivity.
**Table 1.1.** Historical development of conductive polymer composites.

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1930</td>
<td>The earliest polymer/CB composites were introduced to the market as conductive and anti-static compounds.</td>
<td>1</td>
</tr>
</tbody>
</table>
| 1957 | Electrical properties of rubber/CB composites.  
  *Result*: concept of conducting electrons through CB particles was discussed. | 2 |
| 1965 | Carbon fibers made by Union Carbide were introduced to the market. | 24 |
| 1968 | Studies of immiscible polymer blends filled with carbon-based fillers. | 27, 28, 29 |
| 1981 |  |  |
| 1988 | Electrical Conductivity of HDPE/CB/CF.  
  *Exp.*: plastograph/compress-molded, ohmmeter.  
  *Result*: tremendous effect of CF on conductivity was found above threshold concentration of HDPE/CB.  
  \[ \sigma = 0.01 \, (\Omega \cdot \text{cm})^{-1} \text{ at } 2.2 \, \text{vol}\% \text{ CB and } 11 \, \text{vol}\% \text{ CF.} \] | 30 |
  *Exp.*: solution, 4-pt probe in He(l).  
  *Result*: percolation was found at 0.02 vol\% G. | 31 |
<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td>Electrical and dielectric properties of PE/CB.</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td><em>Exp.</em>: compression-molded, standard resistivity measurement with aluminum layer.</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Result</em>: insulator-conductor transition in the range of 0.25-0.65 vol% CB. UHMWPE has a lower transition than normal MW PE.</td>
<td></td>
</tr>
<tr>
<td>1991</td>
<td>Dispersion of CB into, and measurement of the electrical conductivity of, HDPE/PP, PP/PMMA and HDPE/PMMA composites.</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td><em>Exp.</em>: melt mixing+molding, electrometer &amp; digital meter with silver paste.</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Result</em>: uneven distribution of CB in blends and evidence for double percolation was established.</td>
<td></td>
</tr>
<tr>
<td>1992</td>
<td>An effective medium percolation approach in epoxy with either CB or G.</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td><em>Exp.</em>: equation was introduced to fit the resistivity data.</td>
<td></td>
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<tr>
<td></td>
<td><em>Result</em>: the number of contacts per particle is greater for CB than G.</td>
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<tr>
<td>Year</td>
<td>Event</td>
<td>Ref.</td>
</tr>
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<td>------</td>
</tr>
<tr>
<td>1992</td>
<td>Electrical conductivity of CF-reinforced polychloroprene rubber.</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td><em>Exp.</em>: cement &amp; mill mixtures, 4-pt probe for high $\sigma$ and high</td>
<td></td>
</tr>
<tr>
<td></td>
<td>resistance meter for low $\sigma$.</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Result</em>: Mill mixing caused more CF breakage than cement mixing.</td>
<td></td>
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<tr>
<td></td>
<td>Critical concentration $\phi_c$ from cement mixing and mill mixing</td>
<td></td>
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<tr>
<td></td>
<td>are 5-10 phr (part per hundred) and 20-25 phr, respectively.</td>
<td></td>
</tr>
<tr>
<td>1993</td>
<td>Electrical conduction of CF filled polychloroprene rubber.</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td><em>Exp.</em>: cement &amp; mill mixtures, 4-pt probe for high $\sigma$ and high</td>
<td></td>
</tr>
<tr>
<td></td>
<td>resistance meter for low $\sigma$.</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Result</em>: suggested hopping mechanism for conduction and number of</td>
<td></td>
</tr>
<tr>
<td></td>
<td>the electron increases with CF concentration and aspect ratio.</td>
<td></td>
</tr>
<tr>
<td>1993</td>
<td>I-V Characteristics of HDPE/CB composites.</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td><em>Exp.</em>: Brabender mixing, a pulsed voltage technique with silver</td>
<td></td>
</tr>
<tr>
<td></td>
<td>paint.</td>
<td></td>
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<tr>
<td></td>
<td><em>Result</em>: at 28% CB, $\sigma = 0.02$ ($\Omega$-cm)$^{-1}$ and showed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ohmic behavior of I-V data.</td>
<td></td>
</tr>
<tr>
<td>1994</td>
<td>Electrical conductivity of PE/CF.</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td><em>Exp.</em>: molten mixing + casting, typical I-V measurement.</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Result</em>: at 30 vol% CF, $\sigma \sim 1$ ($\Omega$-cm)$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td>Year</td>
<td>Event</td>
<td>Ref.</td>
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<tr>
<td>------</td>
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</tr>
</tbody>
</table>
| 1996 | Conductive PP/PA blends containing CB.  
*Exp.:* dry mixing + Brabender mixing, electrometer with silver or nickel paint.  
*Result:* resistivity decreased about 10 orders of magnitude by using the blend compared to parent polymers. Double percolation was discussed for this system. | 39 |
| 1997 | Electrical transport measurements for polymer/CB.  
*Exp.:* N/A, dc resistivity measurement.  
*Result:* at 40 vol% CB, \( \sigma = 1.0 \, (\text{Ω-cm})^{-1} \). | 40 |
| 1997 | Electrical properties of HDPE/CB.  
*Exp.:* Brabender, 4-pt probe technique.  
*Result:* at 35 wt% CB, \( \sigma = 0.85 \, (\text{Ω-cm})^{-1} \) with untreated and 0.92 (Ω-cm)^{-1} with treated (gasified) CB. | 41 |
| 1997 | Electrical properties of UHMWPE/CB.  
*Exp.:* hot pressing, multimeter.  
*Result:* CB found localized at the interface of UHMWPE.  
The onset of conductivity starts at \( \sim 0.5 \) wt% CB and \( \sigma \sim 10^{-5} \, (\text{Ω-cm})^{-1} \). | 42 |
| 1998 | Conductive epoxy/CF composites.  
*Exp.:* hand-mix + cure, ammeter with silver coat.  
*Result:* percolation threshold at \( \sim 6 \) vol% CF. | 43 |
<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1998</td>
<td>CB-filled immiscible blends of PVDF/HDPE.</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Exp.: Haake internal mixer+hot pressing, multimeter with silver paint.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Result: percolation threshold at ~0.037 vol% CB with 50/50 PVDF/HDPE. Conductivity increases by a factor of 10 at 10% CB and 50/50 blend compared to the parent composites.</td>
<td></td>
</tr>
<tr>
<td>1998</td>
<td>Mechanical and electric properties of UHMWPE/CB.</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Exp.: solution, I-V measurement.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Result: CB loading up to 90 wt% CB can be made and $\sigma =1(\Omega\text{-cm})^{-1}$ was obtained. Electrical conductivity decreased with increasing draw ratio.</td>
<td></td>
</tr>
<tr>
<td>1999</td>
<td>Processing effects on PET/CF conductivity.</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>Exp.: Brabender mixing</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Result: conductivity decreases with increasing rotor speed and time.</td>
<td></td>
</tr>
<tr>
<td>1999</td>
<td>Electrical properties of epoxy/Cu.</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>Exp.: molded + cure.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Result: percolation threshold at ~25 vol% Cu.</td>
<td></td>
</tr>
</tbody>
</table>
1999  Reduced percolation thresholds of immiscible EVA/HDPE blends containing CB.

    Exp.: Brabender, 2-pt probe technique with silver paint.
    Result: percolation threshold at ~3.6-4.2 wt% CB in 68/32 EVA/HDPE blend. At 4.8 wt% CB, conductivity is more than 10 order of magnitude higher compared to the parent composites.

1999  Morphology and percolation conductivity of polymer blends (PP/PE, PP/POM, PE/POM) containing CB.

    Exp.: extruder, 4-pt probe.
    Result: CB distributed in 3 different ways caused by different surface energies: randomly within polymer matrices, in one of polymer components, and at the interface of the two polymers.

1999  Electrical properties of HDPE/CB and LDPE/CB.

    Exp.: Brabender, 3-electrode electrometer with silver paste.
    Result: high crystallinity HDPE forms a more continuous conductive path compared to LDPE matrix.

1999  Polymer composites of Nylon 6/CB.

    Exp.: internal mixer + compression molding, 2-pt probe with silver leaf.
    Result: percolation threshold at ~9 wt% CB.
<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>CB-filled PP/UHMWPE blends.</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td><em>Exp.</em>: internal melt mixing, multimeter with silver paint.</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Result</em>: CB was found localized in PP matrix and at the interface of two polymers.</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>Electrical properties and processing effects on HDPE/CB conductivity.</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td><em>Exp.</em>: twin-screw extruder, high resistance meter (low $\sigma$) and 4-pt probe multimeter (high $\sigma$).</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Result</em>: at 31 wt% CB, $\sigma$ from low shear screw is about 1.6 times higher than the high shear screw.</td>
<td></td>
</tr>
<tr>
<td>2001</td>
<td>Effects of polymer matrix (polar &amp; non-polar) and processing on the conductivity of polymer blends containing CB.</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td><em>Exp.</em>: hot pressed and melt blended, 2-pt probe with gold deposited.</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Result</em>: hot-pressed films have lower threshold concentration than melt-blended films. The lower threshold concentration was found with the polar polymer hosts.</td>
<td></td>
</tr>
</tbody>
</table>
1.8 Research Goals

In the present study, high-density polyethylene (HDPE) and ultra-high molecular weight polyethylene (UHMWPE) are used to prepare conductive polymer composites consisting of polymer blends with three different carbonaceous fillers: CB, G and CF. Use of polymer blends and a filler mixture is expected to increase the composite conductivity especially when the threshold concentration is reached, and localization of the filler within one polymer phase occurs. The effects of polymer blend composition, filler type and filler concentration on the electrical, mechanical, thermal and morphological properties of the composites are studied and systematically correlated.

1.9 References


2. EXPERIMENTAL

2.1 Introduction

Many processes for making polymer/filler composite films have been developed to achieve composite films of reasonably high uniformity. Such composites often exhibit enhanced mechanical properties, depending on the concentration of filler particles. Processes by which to prepare filled polymer composites include, but are not limited to, internal mixing and solvent blending. These processes, however, require large amounts of precursor materials and are also known to have high-cost operating penalties.

Composite films in the present study have been prepared from an inexpensive 2-step process of mixing and molding. Films containing high filler loading levels, which may be non-uniform due to incomplete mixing, have been tested for reproducibility using electrical conductivity as the standard measurement prior to further analysis. The solvent blending process has only been used to compare the miscibility and co-crystallization of UHMWPE/HDPE blends with those made from the simpler mixing and molding process.

2.2 Materials

Two types of polyethylene, HDPE and UHMWPE, were used in the present study for making composite films composed of different blends and fillers. Carbonaceous fillers (CB, G and CF) were added to these polymers and their blends to increase their electrical conductivity and enhance their mechanical
properties. The salient properties of these materials are listed in Tables 2.1 and 2.2.

**Table 2.1.** Relevant properties of the HDPE and UHMWPE employed here.

<table>
<thead>
<tr>
<th>Properties</th>
<th>HDPE</th>
<th>UHMWPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>--</td>
<td>Gur 4130</td>
</tr>
<tr>
<td>Supplier</td>
<td>Celanese</td>
<td>Celanese</td>
</tr>
<tr>
<td>$M_w$ (kg/mol)</td>
<td>&lt; 200</td>
<td>3,000-5,000</td>
</tr>
<tr>
<td>Mass density $\rho$ (g/cm$^3$)</td>
<td>0.964</td>
<td>0.93</td>
</tr>
<tr>
<td>Melting Temp. $T_m$ (°C)</td>
<td>133-134</td>
<td>133</td>
</tr>
<tr>
<td>Particle Size (µm)</td>
<td>30-90</td>
<td>100-150</td>
</tr>
<tr>
<td>Melt Flow Index (g/10min)</td>
<td>7.5$^a$</td>
<td>&lt; 0.1$^b$</td>
</tr>
<tr>
<td>Vol. Resistivity ($\Omega$-cm)</td>
<td>--</td>
<td>&gt; $10^{15}$</td>
</tr>
</tbody>
</table>

Test method: $^a$ASTM D1238 and $^b$DIN 53735

Films containing a high concentration of graphite or carbon fiber were tested for uniformity and reproducibility by measuring the electrical conductivity of samples that were cut in half, stacked and repeatedly re-molded (the "Baker's method"). While lacking a high shear field, this process can be used to perform the same function as that of internal mixers (such as the screw, Banbury and Brabender types), which are commonly used to produce polymer blends and composites.
Table 2.2. Relevant physical properties of the carbonaceous fillers used here.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Carbon Black (CB)</th>
<th>Carbon Fiber (CF)</th>
<th>Graphite (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>V-XC 72</td>
<td>34-700 (PAN)</td>
<td>4424</td>
</tr>
<tr>
<td>Supplier</td>
<td>Cabot</td>
<td>Goodfellow</td>
<td>Asbury</td>
</tr>
<tr>
<td>Mass Density $\rho$ (g/cm$^3$)</td>
<td>1.92 (dense)</td>
<td>2.25</td>
<td>2.24</td>
</tr>
<tr>
<td>Primary Particle Size (nm)</td>
<td>20</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Aggregate Size ($\mu$m)</td>
<td>1</td>
<td>--</td>
<td>40</td>
</tr>
<tr>
<td>Diameter ($\mu$m)</td>
<td>--</td>
<td>7</td>
<td>--</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>--</td>
<td>0.25 and 1.0</td>
<td>--</td>
</tr>
</tbody>
</table>

2.3 Preparation of Composite Films

2.3.1 Mixing and Molding

As-received powders of HDPE, UHMWPE or their physical mixtures were dry-mixed with as-received fillers in a small mechanical mixer operating at relatively high speed to achieve a uniform dispersion. A rectangular metal mold with a cavity area of 40×120 mm$^2$ was sprayed with non-silicone mold release to eliminate crazing and adhesion of the film to the mold. Polymer/filler mixtures were subsequently spread in the mold before heating in a hydraulic press. The hydraulic press (model-C, Carver) and the metal mold are shown in Figure 2.1.

The platens of the hydraulic press were equipped with electric heaters and a water cooling system. The mold and its contents were heated (at ca. 10°C/min)
to 170°C (HDPE/filler) or 190°C (UHMWPE/HDPE/filler) before applying a pressure of 7.2 MPa and holding for 3 min at this condition to ensure complete polymer melting. The mold was cooled with cold water (-20°C/min) to inhibit further migration of polymer (which may excessively wet the filler surfaces and lower the conductivity).

![Figure 2.1. Photographs of (a) the Carver press and (b) the metal mold set.](image)

**2.3.2 Film-Making Difficulties**

Composite films prepared from as-received CB particles were difficult to process due to the high volume expansion of dense CB pellets during mixing. As-received CB pellets expanded more than 6x their original volume after mixing, thereby hindering the preparation of composite films at high concentrations of CB. The maximum CB loading level achieved here, while retaining reasonably good mechanical properties, was 35 wt%. Films containing higher loading levels
were discontinuous and brittle. In contrast, G and CF did not expand much after mixing, and their maximum concentrations were 75 and 20 wt%, respectively.

2.3.3 Solvent Blending

Solvent-blended films of 50/50 w/w HDPE/UHMWPE were prepared from Decalin® (decahydronaphthalene) at 2% (w/v) concentration and 150°C to investigate the miscibility and co-crystallization behavior of HDPE and UHMWPE, and to compare this processing technique to dry-mixing and molding. The results of this analysis are provided in Appendix A. The solvent blending process was used to enhance phase miscibility compared to other blending processes.

2.4 Characterization

2.4.1 Electrical Resistivity

A four-point probe apparatus, shown in Figure 2.2, was used to measure the resistivity of the filled polymer films produced in the present study. This technique was preferred to the two-point probe technique (used to measure the resistivity of semiconductors) due to the spreading resistance encountered in the two-probe method by the current flowing from the small tip of the metal probe to the material being tested [1]. This problem was overcome by the four-point probe technique.
Figure 2.2 Photograph of the four-point probe instrument.

The four-point probe technique was originally proposed by Wenner [2] in 1915, and Valdes [3] later adopted this technique to measure the resistivity of semiconductor wafers. With this technique, all four probes were generally aligned with equal probe spacing. Two probes were used to carry the current and the other two measured the voltage, as depicted in Figure 2.3. The contact and spreading resistances from this technique were negligible because two voltage probes draw very small current due to the high impedance of the voltmeter or no current with the potentiometer [1]. To eliminate contact resistance from the measurement, surfaces of the material under test may be treated or deposited with highly conductive metals such as silver or gold before measuring the resistivity. In this present study, however, the resistivity of the composite films was measured without any surface treatment.
The resistivity $\rho$ of the sample obtained from the measurement was calculated from the following relationship:

$$V = \frac{\rho I}{2\pi r}$$  \hspace{1cm} (2.1)

where $V$ is the potential across the two voltage probes, and $r$ denotes the distance between the electrodes that carry the current $I$. The current was typically carried in the two outer probes and the voltage was measured across the two inner probes. The probe spacing ($s$) was the same for all four probes. If the sample thickness was less than the probe spacing, the resistivity relationship reduced to...
\[ \rho = 4.532 \ t \left( \frac{V}{t} \right) \]  \hspace{1cm} (2.2)

where \( t \) represents the sample thickness. This equation should be modified by correction factors to account for the lateral sample dimensions and placement of the probes relative to the sample edges, as proposed by Albers and Berkowitz [4]. For very thin samples \( (t \leq s/2) \), however, both correction factors were unity.

The four-point probe device used in the present study was the FPP-5000 model manufactured by Veeco®, which is rated to measure resistivities from \( 4.19 \times 10^{-5} \) to \( 1.71 \times 10^{3} \) \( \Omega\)-cm. This microprocessor-based device simplified resistivity measurements by providing direct readout upon entering the specimen thickness. The resistivity obtained from this instrument was corrected for sample geometry. This correction factor is a function of the ratio of the diameter (D) or width (W) of the sample and the probe spacing (s) [5]. Molded films from this study were cut to 40\( \times \)40 mm\(^2\) for the conductivity study. By knowing the sample size and probe spacing (15.6 mm) from Veeco®, the geometric correction factor obtained from the chart provided was 0.983. Thus, the resistivity equation utilized throughout the present study was given by

\[ \rho = 4.455 \ t \left( \frac{V}{t} \right) \]  \hspace{1cm} (2.3)

The film conductivity (\( \sigma \)) was simply the reciprocal of the resistivity; viz.,
\[ \sigma = \frac{1}{\rho} \]  

(2.4)

2.4.2 Morphological Studies

2.4.2.1 Optical Microscopy

A reflection optical microscope (BH-2, Olympus) equipped with a digital camera (HC-300Z, Fuji) was used to acquire images of the composite films in the present study. Composite specimens were lightly polished on a polishing wheel (Spectrum System™ 2000, Leco®) to ensure smooth surfaces. For this purpose, SiC papers of 1200 and 4000 grit were used along with a polishing cloth. Water was used to eliminate heat, and fine particles (0.3 µm) of alumina mixed with water were periodically applied to the cloth during polishing. Optical microscopy was also used to study the magnitude of CF breakage promoted by the mixing and molding processes. Two methods, illustrated in Figure 2.4, were used to separate the fibers from the polymer after dry-mixing and molding.
In Method-1, dry-mixed PE and CF were placed in water and stirred. The high-density CF particles were separated from the low-density polymer particles via sedimentation. The CF was extracted and dried on a glass slide before imaging. Carbon fibers in the molded films, however, were extracted from the polymer matrix by Method-2. The polyethylene in the composite films was dissolved in hot Decalin® (at 150°C), and fibers were extracted from the dilute solution of PE/Decalin® before drying on a glass slide and imaging.

2.4.2.2 Scanning Electron Microscopy (SEM)

A variable pressure SEM (S-3200N, Hitachi) was used to ascertain the morphology of the HDPE/G/CF composites. Images acquired from this SEM
were collected from specimen surfaces in contact with the mold after polishing, as well as from surfaces fractured in liquid nitrogen. The specimens were stained with chlorosulfonic acid (HSO₃Cl) to enhance contrast between the polyethylene matrix and carbon fillers. The acid reacted with and stained the amorphous phase of polyethylene [6,7].

2.4.2.3 Transmission Electron Microscopy (TEM)

Energy-filtered TEM was used to image the CB particles in several polyethylene blends at higher spatial resolution. Specimens were cryoultramicrotomed at –140 °C (Ultracut S, Reichert-Jung) to obtain thin sections suitable for TEM imaging. Images were acquired on a Zeiss EM902 electron spectroscopic microscope operated at 80 kV and 0 eV energy loss.

2.4.3 Dynamic Mechanical Analysis (DMA)

The mechanical properties of molded films were measured by dynamic mechanical analysis (DMA-983, TA Instruments). The programmable DMA-983 (shown in Figure 2.5) was able to detect polymer relaxation behavior similar to the torsion pendulum and rheovibron instruments [8,9] by applying a sinusoidal force (driven signal) to a specimen and causing the specimen to undergo oscillatory motion at a fixed deformation (strain) [10]. Energy dissipation or loss in the sample caused the resulting strain to be out of phase with the applied stress. This phase shift or lag defined the phase angle. From a combination of
the sample geometry, the driver signal and the phase angle, the dynamic storage modulus \( (G') \), loss modulus \( (G'\prime) \) and tan \( \delta \) \( (= G''/G') \) could be determined.

Figure 2.5. The instrument used to perform dynamic mechanical analysis (DMA-983, TA Instruments).

The DMA-983 consists of a mechanical oscillator, driver and oven connected to a computer that operated the instrument and analyzed the data. The heart of the instrument was a set of arms mounted on low-friction flexure pivots, as illustrated in Figure 2.6. A solid sample of known dimensions was clamped vertically and perpendicularly between the two arms and then driven by an electromechanical transducer to maintain constant amplitude and frequency. A fixed frequency of 1 Hz was used throughout the present study. Temperature can be varied during analysis to obtain a temperature sweep.
Samples measuring about 0.5 mm thick were cut to 13×40 mm² to obtain a proper specimen size for this DMA. All specimens were annealed at 90°C for 1 h to remove residual stresses before analysis. Samples were scanned at 5°C/min from ambient temperature to 120°C. The viscoelastic properties of the specimen were related to the specimen strain in terms of the angle of deformation $\phi$, and to stress in terms of the opposing moment. The displacement ($X$) induced during the test shown in Figure 2.6 consisted of three additive contributions:

1. Sample flexible deformation ($X_f$): Arm displacement is due to bending at the clamp-sample junction.
2. Sample shear deformation ($X_s$): Arm displacement arises from planes of material uniformly displaced parallel to the arms.

3. An extra displacement ($X_c$): This displacement is linearly proportional to the force $F$, arising primarily from flexure pivot distortion.

The displacements for each of these deformations were

\[ X_f = \frac{F L^3}{12 EI} \quad (2.5) \]

\[ X_s = \frac{\alpha F L}{A G} \quad (2.6) \]

\[ X_c = F J_c \quad (2.7) \]

$F =$ force acting parallel to the long dimension of the arm

$I =$ moment of inertia of the sample cross section

$J_c =$ instrument compliance

$E =$ tensile modulus

$G =$ shear modulus

$\alpha =$ shear distortion factor

$A =$ sample cross section area

$L =$ length

The simple form of the displacement $X$, however, can be written in terms of the distance between arm centers $B$ and the angles $\phi$ and $\theta$ so that
$$X = L \sin \theta = B \sin \phi = B\phi \quad (2.8)$$

The modulus obtained from the DMA-983 was calculated by combining the results of equations that (i) describe the physical instrument with parameters derived from viscoelastic beam-bending theory and (ii) correct for sample geometry. Either the dynamic shear modulus ($G$) or tensile modulus ($E$), which are related through Poisson's ratio ($\nu$), can be obtained in this fashion:

$$E = 2 (1 + \nu) G \quad (2.9)$$

### 2.4.4 Differential Scanning Calorimetry (DSC)

Thermal calorimetry was performed on a Perkin-Elmer DSC-7 at heating and cooling rates of 20°C/min. Specimens were annealed at 90°C for 1 h prior to analysis. With this calorimeter, the melting temperature, crystallization temperature, heat of fusion and phase behavior (miscibility and co-crystallization) of polymers were ascertained. In addition, the effect of adding carbonaceous fillers on the thermal properties of the polymer matrix was also examined.

### 2.5 References


3. CORRELATED CONDUCTIVITY AND MECHANICAL PROPERTY ANALYSIS OF HIGH-DENSITY POLYETHYLENE FILLED WITH GRAPHITE AND CARBON FIBER

Wiriya Thongruang¹, Richard J. Spontak¹,² and C. Maurice Balik¹*

¹Departments of ¹Materials Science and Engineering and ²Chemical Engineering
North Carolina State University
Raleigh, NC 27695, USA

Running Header: Polyethylene with Graphite and Carbon Fiber
Keywords: HDPE, polymer composite, percolation threshold, conductivity, viscoelasticity

(submitted to Polymer)

3.1 Abstract

The development of conductive polymer composites remains an important endeavor in light of growing energy concerns. In the present work, graphite (G), carbon fiber (CF) and G/CF mixtures are added to high-density polyethylene (HDPE) to discern if mixed fillers afford appreciable advantages over single fillers. The effects of filler type and composition on electrical conductivity, composite morphology and mechanical properties have been examined and correlated to establish structure-property relationships. The threshold loading levels required for G and CF to achieve measurable conductivity in HDPE have

*To whom correspondence should be addressed (E-mail: balik@ncsu.edu).
been identified. Addition of CF to HDPE/G composites is found to increase the conductivity relative to that of HDPE/G composites at the same filler concentration. This observed increase depends on CF length and becomes more pronounced at and beyond the threshold loading of the HDPE/G composite. Scanning electron microscopy is employed to elucidate the morphology of these multicomponent composites, whereas dynamic mechanical analysis reveals that filler concentration, composition and CF length impact both the magnitude and temperature dependence of the dynamic storage modulus.

3.2 Introduction

Carbonaceous fillers are regularly employed in the production of polymer composites to enhance electrical conductivity and mechanical properties, as well as maintain light weight and corrosion resistance. Conductive carbonaceous fillers of current commercial relevance include carbon black (CB), graphite (G) and carbon fiber (CF), which differ greatly in both structure and form. Conductive polymer composites are used in a wide variety of industrial applications such as battery and fuel cell electrodes, antistatic media and corrosion-resistant materials. Consider, for example, the utility of CB particles, which have been routinely added to polyethylene (PE) and other polymers over the past quarter century for four main purposes: improved electrical conductivity, mechanical properties, color and UV stability [1-6]. Miyasaka et al. [7] report that the conductivity of PE/CB composites jumps by as much as ten orders of magnitude at a critical concentration of CB, which they designate as the threshold
concentration for CB percolation [8-10]. Since 1990, numerous studies [11-30] have investigated PE/CB composites to identify the factors responsible for improved electrical and mechanical properties. While we have focused exclusively on PE/CB composites here, the electrical properties of other polymers have also been improved through the addition of CB [31-35].

Graphite is another carbonaceous filler that has been incorporated into PE for electrical conductivity purposes [36]. The electron transport mechanism in PE/G composites has been examined [37] by dc conductivity analysis. Deviation from percolation theory at low graphite concentrations has been attributed to tunneling conduction between adjacent particles. Addition of G to thermoplastics generally combines the electrical properties of G with ease of processing, and may likewise promote attractive electrochemical, physical, mechanical and economic considerations [38]. Navarro-Laboulais et al. [39] have added G to high-density polyethylene (HDPE) and have applied percolation theory to study the impedance and resistance of their HDPE/G composites. Yi et al. [40] have demonstrated that the current-voltage behavior of HDPE/G composites is non-ohmic regardless of G concentration and probe contact pressure. Since G is available in different sizes and shapes, the importance of these factors on conductivity have been investigated by Nagata et al. [41]. By modifying low-density polyethylene (LDPE) with both plate-like and spherical G, they have found that the conductivity of the LDPE/G composite with spherical G increases with decreasing particle size, while the conductivity of the composite with plate-like G increases linearly with increasing particle size. Song et al. [42] have also
identified another non-negligible consideration in HDPE/G composites, namely, the dependence of the self-heating on the magnitude of the applied electric field.

High-aspect-ratio CF has also been added to polymers to enhance both electrical conductivity and mechanical reinforcement. In this case, however, CF length dispersity and composite anisotropy play crucial roles in property development [43]. In some cases, electrical and thermal conductivities have been found [44,45] to exhibit significant biaxial orientation due to the anisotropy of the CF. In such biaxially oriented CF composites, long fibers induce higher electrical conductivity. Short carbon fibers blended with PVC, on the other hand, display excellent electrical properties at very low fiber concentrations (~1.0 phr) [46]. In polyester/CF composites, the conduction threshold concentration has been measured [47] to be 1-2 wt% CF.

These previous works have addressed polymer composites containing a single filler, mostly CB. This is due to the cost, small particle size (high surface area) and aggregation behavior of CB, the latter two of which are responsible for the relatively low loading levels needed to achieve desired conductivities. It is difficult, however, to prepare well-dispersed polymer/CB composites containing more than 35 wt% CB with simple mixing techniques. To overcome this limitation, Calleja et al. [48] have prepared HDPE composites with mixtures of CB and CF using conventional mixing and molding processes. In these samples, the CF provides charge transport over large distances, whereas the CB particles serve to improve interfiber points of contact. This synergy is illustrated in Figure 3.1, which demonstrates that the connectivity of a G network is improved by
adding CF to a polymer/G composite. Without CF, a higher concentration of G is needed to create a conductive path throughout the entire composite film. The present work is motivated by the lack of a systematic study of polymer composites composed of a mixture of G and CF, as well as by the difficulty of blending CB with polymers at high loading levels. Composites of HDPE with G and CF fillers have been prepared for comparison with composites containing G/CF mixtures. The morphological features, electrical conductivity, mechanical and thermal properties of these conductive polymer composites are examined as functions of filler type, composition and concentration.

3.3 Experimental

3.3.1 Materials

High-density polyethylene with $M_w$ less than 200,000 g/mol was obtained in powder form from Celanese. The mass density and melting temperature of this HDPE were 0.964 g/cm$^3$ and 133°C, respectively, and the particle size was measured to be 30–90 μm. Graphite (#4424) obtained from Asbury had a density of 2.24 g/cm$^3$ and an aggregate size of about 40 μm. Two types of polyacrylonitrile-derived CF identical in diameter (7.0 μm) and mass density (1.77-1.80 g/cm$^3$) but different in length (1.00 mm for CF$_1$ and 0.25 mm for CF$_2$) were obtained from Goodfellow. The volume resistivity of the CF was reported to be $1.5 \times 10^{-3}$ Ω-cm.
Figure 3.1. Optical micrographs of (a) G and (b) G+CF filler particles spread randomly on a glass slide. The total filler mass is equal in both figures. Addition of CF provides long conductive paths and improves the interparticle contacts within the network.

3.3.2 Preparation

The HDPE and fillers were first dry-mixed in a mechanical mixer to achieve a reasonably uniform dispersion, and then spread in a 40 × 120 mm² metal picture-frame mold with a thickness of either 0.2 or 0.5 mm. The mold was placed in a
Carver hydraulic press and heated to 170°C. A pressure of 7.2 MPa was applied and held for 3 min to completely melt the HDPE. The mold was then cooled by circulating cold water through the platens. Composite films with filler loading levels up to 75% G or 20% CF were obtained by this process. Composites containing more than 20 wt% CF were visibly heterogeneous and therefore excluded from further consideration in this study.

3.3.3 Characterization

The electrical resistivity of 40 × 40 mm² sections of the molded films was measured at ambient temperature using the four-point probe technique (Veeco 5000) and correcting for sample geometry. The average resistivity of each specimen was obtained from seven repeated measurements at different locations on the specimen. Thermal properties of the HDPE in the composite films (including crystallinity, melting and crystallization temperatures) were discerned by differential scanning calorimetry (DSC, Perkin-Elmer DSC-7) at heating and cooling rates of 20°C/min. The mechanical properties of the composite samples were investigated using dynamic mechanical analysis (DMA, TA Instruments DMA 983). The shear moduli and loss angle were measured at small strain amplitudes and a fixed frequency of 1.0 Hz in the linear viscoelastic regime. Composite samples measuring 13 × 40 × 0.5 mm³ were cut for DMA. Samples were annealed at 90°C for 1 h prior to DMA and DSC analyses to ensure removal of residual stresses arising from molding and quenching. Variable-pressure scanning electron microscopy (SEM, Hitachi S-3200N) was
used to ascertain the morphology of the composite films. Images were acquired from the sample surface in contact with the mold (after polishing) and from surfaces fractured in liquid nitrogen. To enhance the backscattered electron contrast between the HDPE matrix and the carbonaceous G, CF and G/CF fillers, specimens were stained with chlorosulfonic acid (HSO$_3$Cl), which selectively reacts with and stains the amorphous regions of HDPE [49,50]. An optical microscope (Olympus BH-2) equipped with a digital camera (Fuji HC-300Z) was used to discern the effects of composite film preparation on CF breakage in a limited number of HDPE/CF composites.

### 3.4 Results and Discussion

#### 3.4.1 Specimen Homogeneity and Process Reproducibility

Composite films of HDPE/G and HDPE/CF at relatively high filler concentrations (50 and 75 wt% G, 15 wt% CF) have been cut in half, stacked and subsequently re-molded to their original thickness to check on homogeneity and process reproducibility using electrical conductivity as the measure of merit. Conductivity data collected from four repeated cut-stack-mold cycles are presented in Figure 3.2 and reveal that the film with 50 wt% G exhibits very reproducible conductivity. Generally speaking, the HDPE/G composites visibly appear more homogeneous than those containing CF and is reflected in the size of the error bars included in Figure 3.2. Higher loading levels of filler than those provided in Figure 3.2 adversely affect film uniformity and process reproducibility, as discerned from both conductivity measurements and appearance. According
to the data shown in Figure 3.2, changes in conductivity over four mold cycles are tolerably small, in which case we conclude that composite films produced after the first molding cycle are sufficiently homogeneous for further analysis.

Figure 3.2. Composite homogeneity and process reproducibility measured on the basis of electrical conductivity. As seen in the schematic illustration, samples have been cut in half, stacked and remolded to their original thickness during each cycle. Carbon fibers measuring 1.00 mm long have been used in the HDPE/CF composites.
3.4.2 Mixing/Molding Conditions and Carbon Fibers

Mixing and molding of the HDPE/CF and HDPE/(G+CF) composites may have deleterious effects on the mechanical integrity of CF, often resulting in fiber breakage especially in high-aspect ratio CF. To discern the magnitude of fiber breakage due to the dry-mixing step in the protocol adopted here, the CF has been separated from the HDPE-CF powder by placing the powder in water. Upon sedimentation, the higher-density CF is dried on a microscope slide. Carbon fibers have also been extracted from molded films by (i) dissolving the HDPE in hot decalin, (ii) removing the fibers from the solvent and (iii) again drying them on a microscope slide. The lengths of the CF have been measured by optical microscopy and are compared with the as-received fibers in Table 3.1. The average length reported in this table corresponds to 200 individual fibers in each composite.

The average length of the CF measuring 1.00 mm in length (CF1) is found to be 24% less than the reported initial length. In marked contrast, the fibers measuring 0.25 mm in length (CF2) are very close to their reported initial length. Processing the fibers in a mechanical mixer expectedly causes fiber breakage, the extent of which depends on fiber length and polymer/fiber ratio (mixing time and speed remain constant). The length of CF1 decreases by 60% with respect to its original length after mixing, whereas the length of the shorter CF2 is only reduced by 12% of its original length. Addition of HDPE to the powder resulted in less fiber breakage upon mixing, with the 95/5 w/w HDPE/CF mixture displaying very little change in fiber length upon mixing. The molding process employed
here also promotes additional fiber breakage, which is more pronounced for the shorter fibers than for the longer fibers. This counter-intuitive observation is attributed to the mold thickness, which is larger than the CF$_2$ length of 0.24 mm but smaller than the CF$_1$ length of 0.76 mm. Thus, the CF$_2$ fibers have a greater tendency to align parallel to the thickness direction of the mold and subsequently fracture when pressure is applied. The longer CF$_1$ fibers, on the other hand, tend to align in the plane of the mold and are less likely to fracture when pressure is applied.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Average Length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-received</td>
</tr>
<tr>
<td>Pure CF$_1$ (1.00 mm)</td>
<td>0.76 ± 0.13</td>
</tr>
<tr>
<td>HDPE/CF$_1$ (95/5 w/w)</td>
<td>—</td>
</tr>
<tr>
<td>HDPE/CF$_1$ (90/10 w/w)</td>
<td>—</td>
</tr>
<tr>
<td>HDPE/CF$_1$ (85/15 w/w)</td>
<td>—</td>
</tr>
<tr>
<td>Pure CF$_2$ (0.25 mm)</td>
<td>0.24 ± 0.08</td>
</tr>
<tr>
<td>HDPE/CF$_2$ (85/15 w/w)</td>
<td>—</td>
</tr>
</tbody>
</table>

### 3.4.3 Electrical Conductivity

The variation of conductivity with respect to filler concentration is displayed in Figure 3.3 for HDPE composites containing G and the two CF lengths. A feature of interest in this figure is the minimum filler concentration (expressed in wt%)
that yields a measurable conductivity, which we designate as the threshold concentration. As anticipated, the composites containing the longest fibers (CF₁) exhibit the lowest threshold concentration at ~7.5 wt%, compared with ~12.5 wt% for the HDPE/CF₂ composites and ~50 wt% for the HDPE/G composites. High-aspect-ratio CF fillers possess the longest uninterrupted path for electrons, leading to higher conductivity at a given loading level. Graphite, however, consists of small primary particles that tend to aggregate into larger low-aspect-ratio clusters. It tends to disperse more evenly into the polymer matrix, thereby resulting in fewer particle-particle contacts at a given loading level and, consequently, a lower-conductivity polymer composite. As the filler concentration is increased beyond the threshold concentration, the conductivity of the all the HDPE composites is observed to increase rapidly. The maximum conductivity of a conductive composite containing randomly oriented fibers can be estimated [51] from

\[ \sigma_{\text{max}} = \frac{2}{3\pi} \phi \sigma_f \]  

(3.1)

where \( \phi \) and \( \sigma_f \) denote the volume fraction and conductivity, respectively, of the fiber. Using the volume resistivity quoted by the supplier for \( \sigma_f \), Eq. 3.1 yields the conductivity values identified by the dashed line in Figure 3.3.
Figure 3.3. Electrical conductivity of HDPE composites containing pure G or CF fillers. The first datum point in each data set represents zero (unmeasurable) conductivity, and the second datum point identifies the first measurable conductivity value. The dashed line represents predicted conductivities for randomly dispersed fibers according to Eq. 3.1.

The conductivities measured experimentally fall below this prediction, especially for the HDPE/CF\textsubscript{2} composites containing the shorter fibers. This disagreement is attributed to the presence of contact resistance between the CF, which is not considered in the derivation of Eq. 3.1. While the electron transport mechanism responsible for the conductivity of polymers filled with G or CF is still unclear, Dawson and Adkins [52] propose that the conductivity in CB-filled polymers (which are qualitatively similar to G-filled polymers) is regulated by
interparticle electron transfer at low filler loadings and intraparticle electron transfer at high filler loadings.

Figure 3.4 shows the conductivity of HDPE composites with various mixtures of G and CF at a constant total filler concentration (30 or 60 wt%). The conductivity of these HDPE/(G+CF) composites generally increases with (i) increasing filler concentration and (ii) increasing CF composition at a fixed total filler concentration. Composites without CF are good insulators, and composites with 30 wt% filler remain nonconductive until the CF content of the filler exceeds 30–50 wt%, depending on CF length. In contrast, the conductivity of composites containing 60 wt% filler (which is above the threshold concentration of HDPE/G composites) increases rapidly upon addition of small quantities of CF. The conductivity of the composite jumped from ~0.1 (Ω·cm)^{-1} at 50 wt% pure G and from ~5.0 (Ω·cm)^{-1} at 10 wt% pure CF, to ~18.0 (Ω·cm)^{-1} when these two fillers are combined in a 40/(50+10) HDPE/(G+CF) composite. This result demonstrates that the conductivity of a HDPE/G composite above its threshold concentration can be significantly improved upon addition of small amounts of CF. Composites prepared with high G or CF loading levels possess high electron densities and small gaps between filler particles, which tends to induce high conductivity. Unfortunately, this trend has a limit. Composite films containing more than 20 wt% CF overall are difficult to prepare and are visibly heterogeneous.
Figure 3.4. Electrical conductivity of HDPE composites containing mixtures of G and CF. Each data set represents a constant total filler concentration (in wt%): 30 (circles) and 60 (triangles). The CF₁ (1.00 mm) and CF₂ (0.25 mm) fillers are designated by open and filled symbols, respectively. Solid lines serve to connect the data.

Addition of CF to HDPE/G composites increases the electrical conductivity due to bridging of G particles by CF. This bridging phenomenon increases the uninterrupted length of the conductive paths and the strength of the percolated filler network and, hence, the level of conductivity. Another feature evident in Figure 3.4 is that, in all cases, improved conductivity is more pronounced for CF₁ than for CF₂. Jana [53] has performed Hall effect measurements and finds that an increase in CF aspect ratio is accompanied by an increase in mobile carrier concentration. Hence, the effects of high mobile carrier concentration in CF₁
taken together with a high degree of bridging between filler particles combine to explain the high conductivity achieved in the HDPE/(G+CF₁) composites.

3.4.4 Morphological Characteristic

A series of SEM micrographs obtained from stained samples of HDPE/G and HDPE/CF₂ composites are presented in Figure 3.5. Recall that images are collected from sample surfaces in contact with the mold, as well as from cross-fracture surfaces. Micrographs of HDPE/G near the threshold concentration (Figures 3.5a,b) reveal the existence of G particles exhibiting both short- and long-range connectivity in the plane and through the thickness of the composite film. Analogous images acquired from the HDPE/CF₂ samples (Figures 3.5c-d) show that the fibers are primarily aligned in the plane of the sample throughout the thickness of the sample. Fracture surfaces of composites containing both G and CF exhibit the cleaved appearance typical of brittle failure. Higher resolution images of fractured HDPE/CF composites provides evidence for fiber pullout during fracture, indicating weak HDPE-CF interfacial bonding.
3.4.5 Dynamic Mechanical Properties

The dynamic storage modulus ($G'$) has been measured from 25 to 120°C for all the composites examined here and does not show the existence of any thermal transitions over this range (recall that, according to the manufacturer, the
melting point of the HDPE is 133°C). Variation in the dynamic loss modulus ($G''$) is insignificant among the various samples, in which case these data are not presented. Values of $G'$ consistently lie in the range of $10^8$–$10^9$ Pa and decrease at different rates as the melting temperature of HDPE is approached. The magnitude of $G'$ obtained for neat HDPE at 25°C ($7 \times 10^8$ Pa) agrees well with the findings of Takayanagi and Sinnott [54], who report a value of $G'$ on the order of $10^9$ Pa for HDPE at ambient temperature. Figure 3.6a displays the temperature dependence of $G'$ for HDPE/G and HDPE/CF composites with 15 wt% filler. All the fillers promote a small increase in $G'$ near ambient temperature, but their primary effect is to improve the stiffness of the composites at higher temperatures. The temperature at which $G'$ begins to decrease significantly occurs in the vicinity of 60°C for pure HDPE, 100°C for HDPE/G, and 120°C for HDPE/CF$_2$. Surprisingly, the modulus for HDPE/CF$_1$ remains high throughout the entire temperature range investigated. The mechanical reinforcing behavior of these samples corresponds well with their threshold filler concentrations as deduced from Figure 3.3. At 15 wt% loading, the composite filled with CF$_1$ is well above its threshold concentration, whereas the sample filled with CF$_2$ is just above its threshold concentration, and the sample filled with G is well below its threshold concentration. Thus, the polymer composite possessing the most complete percolated filler network appears to exhibit the best high-temperature mechanical properties.
Figure 3.6. The dynamic storage modulus ($G'$) as a function of temperature for pure HDPE ($\triangle$), as well as HDPE/G ($\bullet$), HDPE/CF$_1$ (O) and HDPE/CF$_2$ (■) composites measured according to two different concentration criteria: (a) 15 wt% filler and (b) threshold concentrations (50 wt% G, 7.5 wt% CF$_1$, 12.5 wt% CF$_2$).
To discern the effect of filler percolation on mechanical property development in these HDPE composites, we next examine the composites at their threshold concentrations. According to the data provided in Figure 3.6b, all three fillers yield remarkably similar mechanical properties at this condition (50 wt% G, 7.5 wt% CF₁, 12.5 wt% CF₂). In this case, the sample containing G has a slightly higher $G'$ than either of the CF composites, presumably due to its substantially higher filler concentration. The results presented in this figure suggest that the magnitude and temperature (T) dependence of $G'$ for these HDPE composites depends primarily on the proximity of the filler loading level to the threshold concentration, rather than on the type or absolute concentration of the filler present. This conclusion is further supported by the data displayed in Figure 3.7, which shows the variation of $G'$ with respect to temperature for HDPE/CF composites containing 5, 10 and 15 wt% CF. This concentration range spans the threshold concentrations for both CF₁ and CF₂. The composites with 5 and 10 wt% CF₂ in Figure 3.7a are below their threshold concentrations of 12.5 wt% CF₂, and they exhibit indistinguishable values of $G'$ over the entire temperature range. The sample with 15 wt% CF₂ is above the threshold concentration and exhibits a slightly higher value of $G'$ at low temperatures, but a markedly higher $G'$ as the melting point is approached. Similar behavior is observed for the HDPE/CF₁ composites in Figure 3.7b. In this case, the specimens with 10 and 15 wt% CF₁ lie above the threshold concentration of 7.5 wt% CF₁ and exhibit virtually identical and enhanced $G'(T)$ behavior relative to the HDPE/CF₁.
composite with 5 wt% CF$_1$. Without exception, the HDPE/CF composites are much stiffer than pure HDPE over the entire temperature range investigated.

Figure 3.7. Temperature and composition dependence of $G'$ for (a) HDPE/CF$_2$ and (b) HDPE/CF$_1$ composites at four different filler concentrations (in wt%): 0 ($\triangle$), 5 (◆), 10 (○) and 15 (■).
Values of $G'$ measured at 30 and 100°C for HDPE/(G+CF) composites are displayed in Figures 3.8a and 3.8b, respectively. To permit comparison, the sample compositions are identical to those in Figure 3.4, and the total filler content for each data set is constant. At 30°C, $G'$ is significantly improved by increasing the overall filler concentration from 30 to 60 wt%, while increasing the length or concentration of CF in the filler has a less profound effect. In the composites with 30 wt% total filler concentration, $G'$ ranges from $1.4 \times 10^9$ Pa to $2.2 \times 10^9$ Pa when the CF content of the filler increases from 0 to 50 wt%. Similarly, $G'$ ranges from $2.9 \times 10^9$ Pa to $3.8 \times 10^9$ Pa when the CF content of the filler increases from 0 to 25 wt% at 60 wt% total filler concentration. In this case, an increase in CF composition at constant total filler content is accompanied by a reduction in the composition of G from above its threshold concentration to below its threshold concentration. Concurrently, the CF concentration increases from below to above its threshold concentration. These offsetting effects may explain the weak dependence of $G'$ on CF content evident in Figure 3.8a. At 100°C (Figure 3.8b), $G'$ behaves in similar fashion with regard to CF composition, except that a marginally more pronounced reinforcing effect is apparent for the longer fibers relative to the shorter fibers at the same total filler concentration.
Figure 3.8. Variation of $G'$ with respect to filler composition and fiber length for HDPE/(G+CF) composites containing 30 and 60 wt% filler (circles and triangles, respectively) at (a) 30°C and (b) 100°C. The CF$_1$ (1.00 mm) and CF$_2$ (0.25 mm) fillers are designated by open and filled symbols, respectively. Solid lines serve to connect the data.
3.4.6 Thermal Properties

While the G, CF and G/CF fillers serve to reinforce HDPE at elevated temperatures (see Figures 6-8), the thermal properties of the HDPE matrix — e.g., the heat of fusion and melting and crystallization temperatures — are not affected significantly by their presence. Thus, a detailed description of the corresponding DSC data is not presented. The specific heat of fusion for all the filler types (including mixtures) and at all loading levels has been found to vary by less than 10% from the value for pure HDPE (210 J/g). We therefore conclude that the improved thermal resistance of our filled HDPE composites at elevated temperatures is not due to filler-induced changes in HDPE crystallinity. The largest effect on the transition temperatures occurs in the 85/15 w/w HDPE/CF₁ composite, which exhibits a mere 4°C increase in melting temperature, as well as a 4°C reduction in crystallization temperature, relative to pure HDPE. Transition temperatures do not change appreciably for HDPE/G or HDPE/(G+CF) composites containing up to 50 wt% total filler.

3.5 Conclusions

This study has demonstrated that the addition of a second carbonaceous filler, such as CF, to HDPE/G composites improves their electrical conductivity and high-temperature mechanical integrity (as measured by \( G' \)). The observed increase in conductivity is more pronounced if the concentration of G is already above its threshold concentration. In this case, the conductivity of the composite has been found to jump from \( \sim 0.1 \, (\Omega \cdot \text{cm})^{-1} \) at 50 wt% pure G and \( \sim 5.0 \, (\Omega \cdot \text{cm})^{-1} \)
at 10 wt% pure CF to ~18.0 (Ω-cm)^{-1} when these two fillers are combined in a 40/(50+10) w/w HDPE/(G+CF) composite. This result confirms that the conductivity of a HDPE/G composite already loaded above its threshold concentration can be significantly improved upon addition of a reasonably small amount of CF. Optical and electron micrographs reveal that the G particles exhibit short- and long-range connectivity in the HDPE matrix, whereas CF may exhibit preferential alignment, depending on its length relative to the composite film thickness. The magnitude and temperature dependence of $G'$ measured for HDPE/CF and HDPE/G composites are more sensitive to the proximity of the filler loading level to the threshold concentration than on the filler type or concentration. Addition of these fillers, as well as their mixtures, does not significantly alter the thermal properties of HDPE, in which case the observations reported herein can be attributed solely to the fillers employed. The reinforcing effect of long carbon fibers is more pronounced at elevated temperatures below the melting point of the HDPE matrix.

3.6 Acknowledgments

The authors thank Mr. A. Rieves (National Power Inc.) for providing the HDPE and graphite powder; Drs. R. F. Davis, T. Hare and D. M. Maher (NCSU) for technical assistance; and Mr. J. J. Semler for his suggestion of using carbon fiber/graphite mixtures.
3.7 References


4. VOLUME-EXCLUSION EFFECTS IN POLYETHYLENE BLENDS FILLED WITH CARBON BLACK, GRAPHITE OR CARBON FIBER

Wiriya Thongruang¹, C. Maurice Balik¹ and Richard J. Spontak¹,²*

¹Departments of ¹Materials Science and Engineering and ²Chemical Engineering
North Carolina State University
Raleigh, NC 27695, USA

Running Header: Volume Exclusion in Filled Polyethylene Blends
Keywords: HDPE, UHMWPE, polymer composite, percolation threshold, conductivity, viscoelasticity


4.1 Abstract

Conductive polymer composites possessing a low percolation threshold concentration due to double percolation of a conductive filler and its host phase in an immiscible polymer blend afford a desirable alternative to conventional composites. In this work, blends of high-density polyethylene (HDPE) and ultrahigh molecular weight polyethylene (UHMWPE) are used to produce ternary composites containing either carbon black (CB), graphite (G) or carbon fiber (CF). Blend composition is found to have a synergistic effect on electrical conductivity, with pronounced conductivity maxima observed at about 70-80 wt% UHMWPE in the CB and G composites. A much broader maximum occurs at

* To whom correspondence should be addressed (E-mail: Rich_Spontak@ncsu.edu).
about 25 wt% UHMWPE in composites prepared with CF. Optical and electron microscopies are employed to ascertain the extent to which the polymers, and hence filler particles, are segregated. Differential scanning calorimetry of the composites confirms that the constituent polymers are (i) indistinguishable in terms of their thermal signatures and (ii) virtually unaffected by the presence of any of the fillers examined here. Dynamic mechanical analysis reveals that CF imparts the greatest stiffness and thermal stability to the composites.

4.2 Introduction

Conductive polymer composites containing carbonaceous fillers such as carbon black (CB), graphite (G) or carbon fiber (CF) are commonly employed in a wide variety of industrial applications, including battery electrodes, fuel cells, antistatic media and corrosion-resistant materials. While the electrical conductivity of such composites generally increases with increasing filler content, high filler loading levels can be accompanied by a reduction in mechanical properties if the filler particles are insufficiently wetted. Difficulties associated with filler dispersion encountered during composite processing also become more pronounced at high filler concentrations. To retain desirable properties, processing ease and low cost, recent efforts have sought to produce conductive polymer composites with a low percolation threshold concentration (PTC). The PTC of a conductive polymer composite is sensitive to such material factors as the structure, aggregation, size and size distribution of filler particles, and can likewise be affected by the viscoelasticity of the polymer matrix [1] and the
processing route used to fabricate the composite [2,3]. One of the most exciting developments in the design of low-PTC composites involves the use of immiscible polymer blends in which the conductive particles selectively reside in one of the polymer phases or along the interface [4-6].

Over the past decade, several studies have investigated polymer blends filled with CB [7-11]. As far as we are aware, Asai et al. [12] have reported the first use of a polyethylene blend as the matrix of a conductive polymer composite. Their analysis of an immiscible blend composed of high-density polyethylene (HDPE) and polypropylene (PP) clearly demonstrates that CB particles predominantly distribute in the HDPE phase of the blend. Moreover, localization of CB in HDPE phase induces a much lower PTC than that exhibited by either of the constituent polymers [13]. Due to the localization of CB particles within the HDPE phase of an immiscible blend composed of HDPE and poly(vinylidene fluoride) (PVDF), the conductivity of the composite depends on both CB content and blend composition. In similar fashion, the CB particles in composites prepared by adding ultrahigh molecular weight polyethylene (UHMWPE) to mixtures of low molecular weight polyethylene (LMWPE) and CB disperse only in the LMWPE phase [15]. Scenarios explaining the segregation of CB in polymer blends have been proposed by Mamunya [16], who addresses CB particles that are randomly distributed within the polymer matrix, initially contained in one of the blend constituents, and localized along the polymer-polymer interface.

As Yi et al. [17] point out, factors such as the intrinsic mechanical properties of the constituent polymers, the fabrication route by which polymer blend/CB
composites are produced and the ultimate application conditions must also be carefully considered in the rational design of such composites. In the case of blends composed of UHMWPE and polystyrene (PS), Breure et al. [10] have shown that the UHMWPE can be crosslinked with gamma radiation to enhance the mechanical properties of UHMWPE/PS/CB composites. Several different polymer blends composed of HDPE filled with CF have been recently examined by Zhang et al. [18-20]. Their results reveal that composite conductivity depends on the existence of double percolation, which refers to the percolation of CF in the HDPE phase and the continuity of the HDPE phase in the blends. The dispersion of CF is sensitive to the volume fraction of filler, as well as processing parameters such as temperature and time. As demonstrated by Chan et al. [21], double percolation as described by Zhang et al. [18-20] is not, however, required if the filler locates along the polymer-polymer interface rather than in one of the phases comprising the polymer blend. Such localization of CB is evident from the micrographs displayed in Figure 4.1 and results in increased conductivity due to the creation of continuous CB channels.

In the present study, we investigate HDPE/UHMWPE blends filled with CB, G or CF to ascertain, in systematic fashion, the effects of filler concentration/type and blend composition on electrical conductivity, composite morphology and thermo-mechanical properties. In accord with the results of Chan et al. [21], the high viscosity of UHMWPE is anticipated to promote filler localization at the HDPE/UHMWPE interface, whereas the low viscosity of HDPE may help to connect CB channels throughout the entire composite volume. Thus,
combination of the distinctly different melt-flow properties of these two chemically identical polymers may synergistically achieve high conductivity at a low PTC of added filler.

Figure 4.1. Optical micrographs illustrating the segregation of CB particles in UHMWPE at two filler concentrations (in wt%): (a) 3 and (b) 20 (reproduced from ref. 21 with permission of the Society of Plastics Engineers).

4.3 Experimental

4.3.1 Materials

As-received powders of HDPE and UHMWPE obtained from Celanese were used to prepare composites at different blend compositions with three carbonaceous fillers: CB, G and CF. The $M_w$ of the HDPE was <200 kg/mol, and its mass density, melting temperature and particle size range were 0.964 g/cm$^3$, 
133°C and 30-90 µm, respectively. The $M_w$ of the UHMWPE ranged from 3,000 to 5,000 kg/mol. Its mass density, melting temperature and particle size range were 0.930 g/cm$^3$, 133°C and 100-150 µm, respectively. The mass density of the CB (V-XC 72, Cabot) was 1.92 g/cm$^3$ (measured as dense pellets). Its primary particle and aggregate sizes were about 20 nm and 1 µm, respectively. The mass density of the G (4424, Asbury) was 2.24 g/cm$^3$, and its aggregate size was about 40 µm. Chopped CF derived from poly(acrylonitrile) (34-700, Goodfellow) and initially measuring 760 µm long [22] was used in this study. Its reported diameter and volume resistivity were 7.0 µm and $1.5 \times 10^{-3}$ Ω-cm, respectively.

### 4.3.2 Preparation

Powders of as-received HDPE and UHMWPE were first dry-mixed in a mechanical mixer, after which CB, G or CF was added and further dry-mixed to achieve reasonably uniform dispersion. Mixed polymer/filler powders were subsequently spread in a rectangular metal mold measuring 40 × 120 mm$^2$. The mold and its contents were quiescently heated to 190°C (at about 10°C/min) in a Carver press (Model-C). A pressure of 7.2 MPa was then applied for 3 min at this temperature to ensure complete melting of both polymers. The mold was then cooled at about −20°C/min by circulating cold water through the platens to inhibit polymer migration. Composite films measuring 0.2 or 0.5 mm thick were obtained after molding.
4.3.3 Characterization

The electrical resistivity of composite films cut to $40 \times 40 \text{ mm}^2$ was measured at ambient temperature using the four-point probe method (Veeco-5000). After accounting for specimen thickness and geometry, an average resistivity was deduced from seven repeated measurements at different locations on each composite. The average resistivity was then converted to an average conductivity for reporting purposes. The distribution of CB particles in several polymer blends was determined by energy-filtered transmission electron microscopy (TEM). Specimens were cryoultramicrotomed at $-140^\circ\text{C}$ (Ultracut S, Reichert-Jung), and images were collected on a microscope (EM902, Zeiss) operated at 80 kV and an energy loss ($\Delta E$) setting of 50 eV. A reflection optical microscope (BH-2, Olympus), equipped with a digital camera (HC-300Z, Fuji), was used to acquire images of HDPE/UHMWPE blends filled with G. In this case, composite specimens were lightly polished to ensure smooth surfaces.

The effects of added fillers on melting and crystallization temperatures ($T_m$ and $T_c$, respectively), as well as on the heat of fusion ($\Delta h_f$), were ascertained from differential scanning calorimetry (DSC). The calorimeter (DSC-7, Perkin-Elmer) was typically operated at heating and cooling rates of 20°C/min, respectively. The mechanical properties of composite specimens measuring $13 \times 40 \times 0.5 \text{ mm}^3$ were investigated by dynamic mechanical analysis (DMA). Shear moduli and the loss angle were measured (DMA 983, TA Instruments) as a function of temperature at small strain amplitudes and a fixed frequency of 1.0 Hz in the linear viscoelastic limit. Specimens were routinely annealed at 90°C for
1 h prior to DMA and DSC to ensure removal of residual stresses arising from molding and quenching.

4.4 Results and Discussion

4.4.1 Electrical Conductivity

Throughout this study, the PTC is regarded as the first point at which a non-zero electrical conductivity is measured. In HDPE composites filled with CB, G and CF, values of the PTC are found [22] to be 15, 50 and 7.5 wt%, respectively. As anticipated and confirmed by the data displayed in Figure 4.2, the conductivity of these composites increases with increasing filler concentration. Ternary composites have been prepared by blending UHMWPE and HDPE at different compositions with each of the carbonaceous fillers at the PTC levels listed above. According to the data presented in Figure 4.3, the conductivities measured from these composites are sensitive to blend composition. The first noteworthy feature of this figure is that the conductivity of neat UHMWPE filled with CB (Fig. 4.3a) or G (Fig. 4.3b) is higher (by as much as 550% in Fig. 4.3b) than that of neat HDPE at the same filler loading. This observation is in agreement with the findings of Chan et al. [21]. In contrast, the conductivity of CF-filled HDPE is higher than that of CF-filled UHMWPE (Fig. 4.3c).
Figure 4.2. Variation of conductivity with filler concentration in HDPE composites containing CB (●), G (○) or CF (▲). The first point in each series signifies zero conductivity, while the second point identifies the lowest filler concentration at which a non-zero conductivity could be measured. The solid lines serve as guides for the eye.

At intermediate blend compositions, the measured conductivity initially increases non-linearly with respect to increasing UHMWPE concentration in composites filled with either CB or G. In both cases, the conductivity exhibits a maximum in the vicinity of 70-80 wt% UHMWPE and then decreases as the concentration of UHMWPE is increased further. It is intriguing that, despite a significant difference in filler concentration, these maxima occur at virtually the same blend composition. To put the magnitude of this maximum in perspective, the conductivity of the HDPE/UHMWPE composites filled with CB increases by
Conductivity ($\Omega$-cm)$^{-1}$ vs. UHMWPE content (wt%).

(a) Conductivity ($\Omega$-cm)$^{-1}$ vs. UHMWPE content (wt%).

(b) Conductivity ($\Omega$-cm)$^{-1}$ vs. UHMWPE content (wt%).
Figure 4.3. Conductivity presented as a function of HDPE/UHMWPE blend composition for composites with three different fillers at their PTC in HDPE: (a) 15 wt% CB, (b) 50 wt% G and (c) 7.5 wt% CF. The error bars denote the standard error in the data.

slightly more than an order of magnitude, from 0.03 to 0.8 $(\Omega\text{-cm})^{-1}$, as the concentration of UHMWPE increases from 0 to 80 wt%. The same change in blend composition promotes a $60\times$ increase in conductivity, from 0.1 to 6.0 $(\Omega\text{-cm})^{-1}$, in composites filled with G. Analogous blends filled with CF do not, however, show the same variation of conductivity with respect to blend composition. In these composites, the conductivity increases slightly up to about 25 wt% UHMWPE and then decreases. This observed difference in conductivity dependence can most likely be attributed to filler length (relative to the polymer particle sizes) and concentration.
The CB and G particles employed here range in (aggregate) size from 1 to 40 µm and are either smaller than or comparable in size to the polymer particles. In this case, the blend composition is expected to have a more profound impact on the ability of particles to form conductive channels. It immediately follows that the conductivity of the composites containing CB or G would be more sensitive to the composition of the polymer matrix. The pronounced maximum in these composites strongly suggests that the filler particles reside within one of the polymers comprising the composite or along an internal interface. Relative to a random mixture of filler particles within a unary polymer matrix (either HDPE or UHMWPE in the present study), the PTC of a HDPE/UHMWPE composite exhibiting a morphology-directed arrangement of filler particles should be lower. The CF filler, on the other hand, is about 5X longer than the as-received UHMWPE particles (a reduction in CF length is expected [22] during mechanical mixing). Due to its larger size, it is anticipated to be less sensitive to blend composition, which is confirmed by the data provided in Figure 4.3c. We note, however, that the conductivity of HDPE/UHMWPE composites filled with CF decreases measurably at high UHMWPE concentrations.

The degree to which the polymer blend is segregated must therefore be considered in an attempt to explain the spatial distribution of filler particles in a ternary polymer/polymer/filler composite. In a poorly mixed HDPE/UHMWPE blend, the filler particles could possibly localize (randomly) within the HDPE phase or along the HDPE-UHMWPE interface. The first scenario is illustrated for three different blend compositions at constant filler concentration in Figure 4.4. In
blends with a low UHMWPE content (Fig. 4.4a), UHMWPE-rich regions are dispersed within a continuous HDPE-rich matrix. Since the melt viscosity of

![Schematic illustration of volume-exclusion effects ternary composites of HDPE/UHMWPE/filler at a constant filler loading level. In composites with little UHMWPE (a), the filler particles (shown as speckles) are excluded from high-viscosity UHMWPE-rich dispersions (shaded) and reside mainly within the lower-viscosity HDPE-rich matrix. As the UHMWPE content is increased (b), the volume of accessible HDPE-rich regions decreases and the relative concentration of filler particles residing in continuous HDPE-rich channels increases, resulting in double percolation of the filler particles and HDPE. As the composition of UHMWPE in the blend is increased further to almost 100 wt% (c), the filled HDPE-rich channels become increasingly discontinuous, in which case the net conductivity of the composite decreases. This scenario is consistent with the conductivity maxima evident in Figures 4.3a and 4.3b.](image)

UHMWPE is higher than that of HDPE, the filler particles are expected to reside almost exclusively in the continuous HDPE-rich matrix. As the concentration of UHMWPE is increased (Fig. 4.4b), the volume of HDPE-rich matrix available for filler particles to occupy decreases, resulting in a greater concentration of
conductive elements within continuous HDPE-rich channels. As the composition of UHMWPE is increased further (Fig. 4.4c), the filled HDPE-rich regions become increasingly discontinuous due to volume exclusion, resulting in a net loss in composite conductivity. The scenario depicted in Figure 4.4, as well as one wherein filler particles localize along the interface between HDPE- and UHMWPE-rich regions, can induce double percolation [18-21] within the composite and increase the conductive pathway as morphology-directed filler channels are established.

Volume-exclusion effects such as these occur in composites prepared with immiscible polymer blends [23,24]. While most polymer blends are intrinsically immiscible due to endothermic mixing and a vanishingly small entropy of mixing, blends of chemically identical species (e.g., HDPE and UHMWPE) may exhibit transient phase segregation due to substantial differences in their melt viscosity [25]. During melt processing, the two polymer species may simply not have sufficient time to homogenize. If blend miscibility is achieved, however, filler particles are believed to distribute randomly throughout the homogeneous polymer matrix. Interfacial energy constitutes one of the most important factors in determining the nonrandom distribution of filler particles in an immiscible polymer blend [26]. It should be noted, however, that the presence of inorganic filler particles might likewise affect the inherent interfacial energy, and consequently alter the native interfacial structure, of such a blend [27,28]. Thus, the HDPE/ UHMWPE composite morphology may reflect not only the difference
in melt viscosity between HDPE and UHMWPE but also hindered homogenization due to the presence of filler particles.

4.4.2 Morphological Characteristics

Micrographs of HDPE/UHMWPE composites filled with CB and G are presented in Figures 4.5 and 4.6, respectively, and show that these fillers segregate on the basis of blend composition. Within the neat HDPE and HDPE-rich blends, the distribution of these particles is relatively uniform and random. As the concentration of UHMWPE is increased, the filler particles localize, presumably within a HDPE-rich phase. Such localization is attributed to the low melt viscosity of HDPE relative to UHMWPE. Both factors contribute to selective wetting of filler particles, as reported by Feng and Chan [29] in their studies of HDPE/PVDF/CB and PP/UHMWPE/CB composites. The HDPE and PP, respectively, constitute the low surface tension/viscosity blend components into which CB selectively disperses. Due to double percolation, the conductivities of these filled blends are higher than those of the constituent polymers at the same filler loading level. Calberg et al. [30] have shown that the extents to which (i) the phases in an immiscible blend are co-continuous and (ii) the CB particles localize along a polymer-polymer interface strongly influence conductivity and can substantially decrease the PTC. Another consideration is that the low-viscosity component may promote the migration of filler particles to the polymer-polymer interface [16] during melt flow. In this case, a high melt viscosity results in a highly branched filler morphology due to poor surface wetting, whereas a
relatively uniform dispersion is obtained when a low-viscosity polymer can more fully wet the filler particles.

Figure 4.5. Energy-filtered transmission electron micrographs of HDPE/UHMWPE blends containing 15 wt% CB at four blend compositions (in wt% UHMWPE): (a) 0, (b) 50, (c) 60, (d) 70, (e) 80 and (f) 100. Note the existence of CB-rich channels in (c)-(e).
Figure 4.6. Optical micrographs of HDPE/UHMWPE blends containing 50 wt% G at four blend compositions (in wt% UHMWPE): (a) 0, (b) 25, (c) 50 and (d) 100. These images have been acquired from polished specimen surfaces.

Coupled with previous results, the images displayed in Figures 4.5 and 4.6 indicate that CB and G particles, respectively, randomly distribute in the low-viscosity HDPE, as well as in miscible blends of HDPE with UHMWPE, and promote relatively low conductivity. At high concentrations of UHMWPE, (meta)stable immiscible blends may form due to (i) differences in melt viscosity or (ii) localization of filler particles within the HDPE or along the HDPE-UHMWPE interface. As the concentration of UHMWPE is increased in the present HDPE/UHMWPE blends, the interfacial area initially enlarges, resulting in a greater
propensity for filler particles to localize along the interface. This expectation, coupled with the formation of submicron-size HDPE channels filled with CB (see Figs. 4.5c-e), is presumed to be responsible for double percolation and the corresponding increase in conductivity evident in Figure 4.3a. In similar fashion, the speckled texture apparent in Figure 4.6c is consistent with G particles separated by channels of HDPE, which could likewise induce double percolation and enhance conductivity (see Fig. 4.3b). At very high UHMWPE concentrations, however, the UHMWPE particles most likely become more connected, thereby reducing the extent to which filler particles are able to form continuous pathways (see Figs. 4.4c and 4.6d) and, consequently, the conductivity of the composite.

In addition to viscosity and phase-segregation considerations, thermal history and process route may also have a significant impact on the electrical properties of composites derived from polymer blends [31]. For instance, quiescent melt pressing tends to yield a lower value of the PTC than melt mixing during extrusion due to low shear forces [32]. The filler particles employed in this study have not been subjected to extensive shear forces, in which case they retain much of their primary morphology, as evidenced by the images in Figures 4.5 and 4.6 in conjunction with prior results [22]. As a result, we expect that the smaller CB and G particles initially disperse within the low-viscosity HDPE and along on the HDPE/UHMWPE polymer interface, resulting in an increased conductivity and a reduced PTC. This result is most pronounced at the conductivity maxima evident in Figures 4.3a and 4.3b. For this reason, attention is focused on composites prepared from a 25/75 (w/w) HDPE/UHMWPE blend
throughout the remainder of this work. The dependence of conductivity on filler loading level is provided in Figure 4.7 for this blend and reveals that the conductivity of the 25/75 HDPE/UHMWPE composite is consistently higher than that of the parent HDPE composite at the same filler concentration. Moreover, the PTC decreases from 15 to 5 wt% for CB and from 50 to 35 wt% for G relative to neat HDPE. As expected from previous discussion, however, the conductivity and PTC of 25/75 HDPE/UHMWPE composites filled with CF are virtually identical to those measured in HDPE composites.

![Conductivity vs. Filler Concentration](image)

**Figure 4.7.** Dependence of conductivity on filler loading level in a 25/75 w/w HDPE/UHMWPE blend containing CB (●), G (○) or CF (▲). The error bars represent the standard error in the data, and the solid lines serve as guides for the eye.
4.4.3 Thermal Properties

To ascertain the roles of phase miscibility, polymer co-crystallization and filler concentration/ type on the thermal behavior of 25/75 HDPE/UHMWPE composites, DSC has been performed to identify $T_m$, $T_c$ and $\Delta h_f$. Thermograms acquired from the neat HDPE and UHMWPE, as well as from the HDPE/UHMWPE blend, are presented in Figure 4.8a and confirm the existence of a single melting/crystallization peak in each system. Values of $T_m$, $T_c$ and $\Delta h_f$ deduced from these data, listed in Table 4.1, indicate that these three systems exhibit the same melting and crystallization peak temperatures at ca. 133 and 107°C, respectively. The corresponding crystallinity of HDPE (85.0%) is much larger than that of UHMWPE (45.4%). The measured crystallinity of the 25/75 HDPE/UHMWPE blend (56.4%) compares favorably with that calculated from the

**Table 4.1.** Thermal properties of HDPE, UHMWPE and a 25/75 w/w HDPE/UHMWPE blend.\(^a\)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta h_f$ (J/g)</th>
<th>Crystallinity(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>133</td>
<td>107</td>
<td>209</td>
<td>85.0</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>133</td>
<td>107</td>
<td>111</td>
<td>45.4</td>
</tr>
<tr>
<td>HDPE/UHMWPE blend</td>
<td>132</td>
<td>107</td>
<td>138</td>
<td>56.4</td>
</tr>
</tbody>
</table>

\(^a\) Determined from DSC performed at heating and cooling rates of 20 and –20°C/min, respectively. \(^b\) Calculated from the ratio of the measured $\Delta h_f$ to that of a 100% crystalline polyethylene (245.3 J/g).
linear rule of mixtures (54.6%). On the exclusive basis of this one result, it remains unclear, however, whether or not the HDPE and UHMWPE are completely miscible at this blend composition. While Near-Edge X-ray Absorption Fine Structure (NEXAFS) microscopy has been successfully used [33] to distinguish HDPE from low-density polyethylene in immiscible polyolefin blends, no conventional methods are readily available to differentiate HDPE from UHMWPE due to their identical chemical attributes. Careful examination of the full width of the crystallization peak at half maximum, combined with small-angle light scattering, may be used to study the formation of co-crystals in HDPE/UHMWPE blends [34,35], but are clearly beyond the scope of the present study.
<table>
<thead>
<tr>
<th>Filler content (wt%)</th>
<th>CB</th>
<th>G</th>
<th>CF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m$</td>
<td>$T_c$</td>
<td>$\Delta h_f$</td>
</tr>
<tr>
<td></td>
<td>(°C)</td>
<td>(°C)</td>
<td>(J/g)</td>
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<td>107</td>
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<td>15</td>
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<td>—</td>
</tr>
<tr>
<td>50</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*Detected from DSC performed at heating and cooling rates of 20 and –20°C/min, respectively.*
Figure 4.8. Thermograms acquired from HDPE, UHMWPE, a 25/75 HDPE/UHMWPE blend and conductive polymer composites derived therefrom. In (a), heating and cooling curves are shown for HDPE (thin solid line), UHMWPE (thick solid line) and their blend (dashed line). In (b), analogous curves are displayed for the blend with G (thin solid line), CB (thick solid line) or CF (dashed line) at 15 wt% filler.
Addition of 15 wt% filler to the systems shown in Figure 4.8a results in the thermograms displayed in Figure 4.8b and the data provided in Table 4.2. According to this figure, CF promotes a marginal depression in T_m relative to the CB and G fillers. All three composites filled with CB, G and CF exhibit nearly identical peak melting and crystallization temperatures within 2°C at 15 wt% filler and 5°C overall, in good agreement with the findings of Xu et al. [36] in their study of UHMWPE composites containing CB. They also report that the crystallinity of UHMWPE is unaffected by the presence of CB and infer from these results that the polymer crystal size is independent of filler loading level. Similar behavior is observed in the present HDPE/UHMWPE blends, in which the crystallinity varies by less than 5%.

### 4.4.4 Mechanical Properties

The temperature dependence of the dynamic storage modulus (G’) over the range from 25 to 120°C is shown in Figure 4.9 for HDPE, UHMWPE and the 25/75 HDPE/UHMWPE blend. In all cases, G’ initially decreases gradually with increasing temperature and then abruptly drops as the material becomes sufficiently softened. The corresponding dynamic loss modulus (G”) does not exhibit any noteworthy variation over the temperature range examined and is not included here for that reason. Likewise, the loss factor (tan δ=G”/G’) simply mirrors G’ and is excluded from further discussion. According to the data included in Figure 4.9, HDPE exhibits the highest value of G’ of the three
systems up to about 68°C due to its high crystallinity (85.0% from DSC analysis). Over this temperature range, values of $G'$ measured from the 25/75 HDPE/UHMWPE blend consistently lie between those of HDPE and UHMWPE, but do not precisely follow the rule of mixtures. The catastrophic temperature, defined as the temperature at which $G'$ abruptly drops, is about 90°C for neat HDPE, 98°C for the 25/75 HDPE/UHMWPE blend and 118°C for UHMWPE.

![Figure 4.9. The dynamic storage modulus ($G'$) presented as a function of temperature for HDPE (●), UHMWPE (▲) and a 25/75 HDPE/UHMWPE blend (◇). The solid lines serve to connect the data.](image)

Note that these catastrophic temperatures are substantially lower (by at least 14°C) than the peak melting temperatures discerned from DSC. Two possible
scenarios may explain this apparent disparity. The first is that the catastrophic temperature may identify the onset of crystal melting, which is reflected by an increase in heat flow in DSC thermograms (see Fig. 4.8a) and occurs at temperatures substantially lower than the peak melting temperature. The DSC results do not, however, show the same strong composition dependence as $G'$. Another possibility is that the polymer specimens start to flow at the catastrophic temperature, in which case they may no longer be firmly fixed during analysis. Either way, the results shown in Figure 4.9 confirm that UHMWPE exhibits the highest thermal stability relative to HDPE and the 25/75 HDPE/UHMWPE blend due to its extensive chain entanglement, which effectively serves to hinder chain slippage.

Values of $G'$ measured from the 25/75 HDPE/UHMWPE blend filled with CB, G and CF at a constant loading level of 15 wt% are presented for comparison in Figure 4.10. The filler most capable of improving the thermal stability of the blend (and both parent polymers), as assessed from a temperature-invariant $G'$ with no abrupt drop-off, is CF. As the temperature is increased from 25 to 120°C, $G'$ decreases from $1.52 \times 10^9$ to $4.02 \times 10^8$ Pa, but remains measurable over the entire temperature range. This observation, combined with the conductivity measurements provided in Figure 4.7, indicates that the CF is well above its PTC at a concentration of 15 wt%. In contrast, the $G'$ values of the blend filled with CB and G appear remarkably similar in Figure 4.10. As with the unfilled blend, the values of $G'$ measured from these composites initially decrease with
increasing temperature and then catastrophically decrease at a temperature in the vicinity of 110°C, which is measurably higher than the 98°C for the unfilled blend. This behavior is consistent with our previously reported finding [22] that $G'$ for CB and G composites exhibits similar temperature dependence at filler concentrations below their respective percolation thresholds.

![Graph](image.png)

Figure 4.10. The variation of $G'$ with respect to temperature for a 25/75 HDPE/UHMWPE blend (◇) and its composites filled with 15 wt% CB (●), G (○) or CF (▲). The solid lines serve to connect the data.

The variation of $G'$ with respect to filler concentration at 30°C in the 25/75 HDPE/UHMWPE blend filled with CB, G and CF is displayed in Figure 4.11, which reveals that $G'$ increases substantially, as expected from stiffness
considerations [37], with increasing G and CF content. This trend is not, however, observed for the composite filled with CB. In this case, $G'$ increases marginally (nearly within experimental uncertainty) with increasing CB concentration over the range of concentrations explored. [Composites prepared at higher CB loading levels yield irreproducible results and are not included here for that reason.] An increase in $G'$ reflects the inherent stiffness of the CB, as well as good adhesion between HDPE and CB particles. In the event that a strong HDPE-CB interface forms, the composite is anticipated [38] to resist deformation, resulting in a higher $G'$.

![Graph showing the dependence of $G'$ on filler concentration at 30°C in composites derived from a 25/75 HDPE/UHMWPE blend filled with CB (●), G (○) or CF (▲). The solid lines serve as guides for the eye.](image_url)
The nearly linear increases in $G'$ with regard to G and CF concentration closely follow the series form of the rule of mixtures, which can be expressed [39] by $X_c=X_f\Phi_f+X_m\Phi_m$, where $X$ represents a property of interest, $\Phi$ denotes the volume fraction and the subscripts c, f and m refer to the composite, filler and matrix, respectively. This expression is derived for uniform strain conditions and assumes that the filler particles and matrix are isotropic and well bonded to each other. Ishigure et al. [40] suggest that the modulus for a composite containing a spherical filler can be more accurately predicted from the parallel form of the rule of mixtures: $X_c=(\Phi_f/X_f+\Phi_m/X_m)^{-1}$. An increase in the aspect ratio of the filler eventually leads to recovery of the series form. While these mixing rules provide useful estimates of composite properties, it must be remembered that the properties of most composites are often a complex function of many parameters, including filler size, size distribution, shape and surface chemistry.

**4.5 Conclusions**

The conductive polymer composites investigated during the course of this study demonstrate that double percolation of small inorganic fillers (e.g., CB and G) in a segregated polymer phase can be achieved in blends of HDPE and UHMWPE. At blend compositions in the vicinity of 70-80 wt% UHMWPE, the conductivity can increased by more than an order of magnitude at constant filler concentration. Similar, but less pronounced, results are realized in CF composites, which exhibit a relatively broad conductivity maximum closer to 25 wt% UHMWPE. This difference is attributed to the characteristic sizes of the filler
particles (and their aggregates) relative to the sizes of the as-received polymer particles. Transmission electron micrographs of these ternary composites reveal that the distribution of CB particles in blends with a high UHMWPE content is nonrandom, suggesting that the particles, as well as the HDPE in which they reside, are at least partially segregated from the UHMWPE fraction. Comparable results are visible in optical micrographs acquired from composites filled with G.

Thermal analysis of the neat polymers, their blends and their composites (including a 25/75 w/w HDPE/UHMWPE blend) with either CB, G or CF confirms that the thermal characteristics of these systems remain essentially unchanged. This observation indicates that the composite matrix is, for the most part, unaffected by the presence of these inorganic fillers. Dynamic mechanical analysis, on the other hand, demonstrates that the stiffness of the composites is sensitive to both filler type and concentration. Composites containing CF are found to be the most resistant to applied deformation and increasing temperature up to the melting point of UHMWPE. Significant improvement in both conductivity and mechanical properties is achieved here by adding a filler to a polymer blend. We have previously shown [22] that comparable synergistic results can be obtained by incorporating two fillers into the matrix of a single polymer (HDPE). In a forthcoming report, we shall exploit these two sets of complementary results by examining the properties of quaternary composites consisting of HDPE, UHMWPE and mixtures of fillers.
4.6 Acknowledgements

The authors thank Mr. A. Rieves (National Power Inc.) for providing the HDPE and graphite powder, Drs. R. F. Davis, T. Hare, D. M. Maher (NCSU) and K. C. Caster (Lord Corp.) for technical assistance.

4.7 References


5. BRIDGED DOUBLE PERCOLATION IN CONDUCTIVE POLYMER COMPOSITES: AN ELECTRICAL CONDUCTIVITY, MORPHOLOGY AND MECHANICAL PROPERTY STUDY

Wiriya Thongruang,1 Richard J. Spontak1,2 and C. Maurice Balik1*
Departments of 1Materials Science & Engineering and 2Chemical Engineering
North Carolina State University
Raleigh, NC 27695, USA

Running title: Graphite-Filled Polyethylene Blends
Keywords: polyethylene, conductive polymer composites, graphite, carbon fiber, percolation

(submitted to Polymer)

5.1 Abstract

Conductive polymer composites are ubiquitous in technological applications and constitute an ongoing topic of tremendous commercial interest. Strategies developed to improve the level of electrical conductivity achieved at a given filler concentration have relied on double-percolated networks induced by immiscible polymer blends, as well as mixtures of fillers in a single polymer matrix, to enhance interparticle connectivity. In this work, we combine these two strategies by examining quaternary composites consisting of high-density polyethylene (HDPE), ultrahigh molecular weight polyethylene (UHMWPE), graphite (G) and carbon fiber (CF). On the basis of our previous findings, we examine the

*To whom correspondence should be addressed (E-mail: balik@ncsu.edu).
electrical conductivity, morphology, thermal signature and mechanical properties of HDPE/UHMWPE/G systems that show evidence of double percolation. Upon addition of CF, tremendous increases in conductivity are realized. The mechanism by which this increase occurs is termed \textit{bridged double percolation} to reflect the role of CF in spanning non-conductive regions and enhancing the continuity of conductive pathways. At CF concentrations above the percolation threshold concentration, addition of G promotes increases in conductivity and dynamic storage modulus in which the conductivity increases exponentially with increasing modulus.

\textbf{5.2 Introduction}

Conductive polymer composites (CPCs) typically consist of a polymeric matrix into which a carbonaceous filler is incorporated. These multifunctional materials are routinely employed in various commercial applications due to their good electrical conductivity, light weight, corrosion resistance and enhanced mechanical properties. Examples of applications that use CPCs include battery and fuel cell electrodes, as well as anti-static and corrosion-resistant materials. Common conductive fillers of current technological relevance include carbon black (CB), graphite (G) and carbon fiber (CF). While the utility of CPCs is well-established, a new generation of efficient CPCs composed of different polymers/fillers and possessing (i) a low percolation threshold concentration (PTC) and (ii) high electrical conductivity continues to be sought. The principal objective of efforts in this vein is to optimize application properties with regard to
processability and cost. Processing and associated economic challenges arising from the addition of large quantities of solid fillers to polymeric media have, however, thwarted the development of CPCs. Factors such as the size, shape, chemistry and aggregation behavior of filler particles [1] must be considered in conjunction with the thermodynamic and rheological properties of the polymer matrix [2] and the processing conditions employed [3,4]. Ongoing attempts to localize filler particles at the interface or within one of the phases of an immiscible polymer blend have demonstrated [5-7] that the PTC can be substantially reduced in this manner for a given filler.

While several previous studies [8-12] have used this strategy to reduce the PTC of CB in a variety of polymer blends, we turn our attention here to those blends in which one of the components is high-density polyethylene (HDPE). Due to melt-viscosity considerations, CB particles tend to reside predominantly within the HDPE phase, which consequently promotes a considerable reduction in the PTC of CB relative to comparable CPCs produced from either constituent polymer [13-16]. Ultrahigh molecular weight polyethylene (UHMWPE) has been examined by Chan et al. [17] as a unique matrix polymer for CPCs. The high melt viscosity of UHMWPE effectively forces CB particles to locate almost exclusively along the interface that develops when individual polymer particles are sintered together in the melt state. As in immiscible polymer blends, this method of incorporating CB into a polymeric medium results in a reduced PTC. In similar fashion, CB particles have been added to blends of UHMWPE and low-molecular-weight polyethylene (LMWPE) prepared by the gelation/crystallization
process to generate ternary CPCs wherein the CB particles dispersed only in the low-viscosity LMWPE phase [18]. Mamunya [19] has proposed that CB, as well as other conductive particles, can be forced to segregate in polymer blends if the particles either reside (as a random distribution) within one of the blend components prior to mixing or migrate to the polymer-polymer interface after mixing.

Previous studies of immiscible polymer blends filled with CB have not only focused on improving electrical conductivity, but have also investigated the corresponding variations that arise in mechanical property development and fabrication [16,20-22]. Other fillers, such as G and CF, have likewise received similar attention in the ongoing development of CPCs. Several different polymer blends composed of HDPE filled with CF have been examined by Zhang et al. [23-25]. They have shown that the conductivity of such ternary CPCs can be enhanced through double percolation, which refers to the percolation of CF in the HDPE phase and the continuity of the CF-filled HDPE phase in the polymer blend. They also report that the dispersion of CF depends on the volume fraction of filler and process parameters such as time and temperature. We have recently observed [16] double-percolation behavior in immiscible HDPE/UHMWPE blends filled with either CB or G. In the case of each filler, the electrical conductivity and dynamic mechanical properties improve markedly as the concentration of UHMWPE in the blends increases (up to about 80 wt%). On the basis of morphological evidence, these results are interpreted to indicate that continuous HDPE channels filled with percolated filler particles form in
UHMWPE-rich blends. More modest increases in electrical conductivity and mechanical properties are observed in HDPE/UHMWPE blends filled with CF due to the large size of the CF particles relative to that of the phase domains comprising the blends.

In a separate study [26], we have also found that mixtures of conductive fillers (e.g., G and CF) in a single polymer matrix can be used to enhance the electrical conductivity and dynamic mechanical properties of CPCs. This observation reflects an overall improvement in the conductive pathway established by particles differing in size and shape. Thus far, we are unaware of any reports that combine, in synergistic fashion, the approaches of blend-induced double percolation and mixture-induced interparticle bridging in the rational design of quaternary CPCs. The present study investigates the electrical conductivity, morphology, thermal signature and mechanical properties of HDPE/UHMWPE blends filled with mixtures of G and CF. These components have been selected to permit direct comparison with our previous reports of CPCs prepared with either (i) HDPE and filler mixtures or (ii) HDPE/UHMWPE blends containing a single filler. While comparable CPCs modified with CB are of equal interest in this vein, they are excluded here due to processing difficulties.

5.3 Experimental

5.3.1 Materials

The HDPE and UHMWPE polymers used here were received as powders from Celanese. The weight-average molecular weight, mass density, melting
temperature and particle size range of the HDPE were <200 kg/mol, 0.964 g/cm$^3$, 133°C and 30-90 μm, respectively. The corresponding characteristics of the UHMWPE (GUR-4130) were 3,000-5,000 kg/mol, 0.930 g/cm$^3$, 133°C and 100-150 μm, respectively. Graphite (#4424) with a density of 2.24 g/cm$^3$ and an aggregate size of about 40 μm was obtained from Asbury. Chopped CF (#34-700) derived from poly(acrylonitrile) was purchased from Goodfellow. It had a diameter of 7.0 μm, a density of 1.77-1.80 g/cm$^3$ and a length of 760 μm [26]. Its volume resistivity was reported as $1.5 \times 10^{-3} \ \Omega{-}\text{cm}$.

5.3.2 Preparation

Powders of as-received HDPE and UHMWPE were first dry-mixed in a mechanical mixer prior to the addition of G, CF or G/CF mixtures. Upon addition of these fillers, each polymer/ filler mixture was further dry-mixed to achieve a reasonably uniform dispersion. This mixture was then uniformly spread in a 40 × 120 mm$^2$ rectangular metal mold, which was subsequently placed in a Carver hydraulic press (Model-C) and heated at ~10°C/min to temperatures between 160 and 190°C. At these temperatures, 7.2 MPa of pressure was applied to the mixture for 3 min to ensure complete melting of both polymers. The mold was then cooled at ~20°C/min by circulating cold water through the platens to inhibit polymer migration. Composite films measuring 0.2-0.8 mm thick and having a maximum filler-mixture loading level of 60 wt% G and 15 wt% CF were obtained by this process. Composite films containing higher concentrations of filler mixture were not uniform and consequently excluded from this study.
The electrical resistivity of CPC films cut to 40 × 40 mm$^2$ was measured at ambient temperature by the four-point probe technique (Veeco 5000). The output was subsequently corrected for sample geometry. The average resistivity of each sample was obtained from seven repeated measurements at different locations on the sample, and was then converted to an average conductivity for reporting purposes. The spatial distribution of the G/CF mixture in several HDPE/UHMWPE blends was determined by reflection optical microscopy (BX-60, Olympus). Images of polished sample surfaces (in contact with the metal mold) were acquired with a digital camera (Spot RT, Diagnostic Instrument). The effects of G/CF mixture on the thermal characteristics of the polymer blend — e.g., melting and crystallization temperatures ($T_m$ and $T_c$, respectively), specific heat of fusion ($\Delta h_f$) and overall crystallinity — were measured by differential scanning calorimetry (DSC). The calorimeter (DSC-7, Perkin-Elmer) was operated at heating and cooling rates of 20°C/min. Crystallinities were ascertained from the ratio of the measured $\Delta h_f$ to $\Delta h_f$ corresponding to 100% crystalline polyethylene (245.3 J/g [27]). The mechanical properties of these quaternary CPCs were investigated by dynamic mechanical analysis (DMA) performed on a DMA 983 (TA Instruments). In these tests, the dynamic storage and loss shear moduli ($G'$ and $G''$, respectively), as well as tan$\delta$ (= $G''/G'$), were evaluated as functions of temperature at small strain amplitudes and a fixed frequency of 1.0 Hz in the linear viscoelastic limit. Specimens measuring 13 × 40
\times 0.5 \text{ mm}^3 \text{ were annealed at } 90^\circ \text{C for 60 min prior to DMA and DSC analyses to ensure removal of residual stresses arising from molding.}

5.4 Results and Discussion

Since the CPCs of interest here are composed of four different components, namely, HDPE, UHMWPE, G and CF, a small subset of the total specimen matrix must be identified for feasibility purposes. Part of the subset is mandated on the basis of CPC processability (as discussed in the previous section). Additional insight into specimen choice can be gleaned from prior experimental findings. Ternary CPCs based on HDPE/UHMWPE blends containing either CB or G exhibit conductivity maxima at blend compositions near 80 wt% UHMWPE. Therefore, it is sensible to select one of the HDPE/UHMWPE blends near this composition for investigation in the present study. In addition to examining CPCs composed of HDPE as the reference material (in which G and CF distribute uniformly), we also elect to choose an intermediate blend composition to facilitate comparison. Composite films consisting of HDPE, 50/50 and 25/75 w/w HDPE/UHMWPE blends and filled with mixtures of G and CF are reproducible (within acceptable experimental error) in terms of their measured properties and are selected here for detailed analysis. For the sake of brevity, the 50/50 w/w HDPE/UHMWPE blend is hereafter referred to as PE_{bl}^{(1)}, whereas the 25/75 w/w HDPE/UHMWPE blend is denoted PE_{bl}^{(2)}. In addition to CPC composition, variation in process conditions must also be considered to achieve CPC reproducibility. Molding temperatures ranging from 160 to 190°C have been
used to prepare CPCs filled with G/CF mixtures. According to the electrical conductivity data presented in Figure 5.1 for $\text{PE}_{\text{bl}}^{(2)}$, this process variable significantly affects CPC property development and reproducibility. In contrast, the molding time at 190°C has little effect on conductivity (data not shown). Thus, molding is conducted at 190°C for 3 min throughout the remainder of this study.

![Conductivity vs Temperature](image)

**Figure 5.1.** Conductivity presented as a function of molding temperature for three composites prepared with 35 wt% $\text{PE}_{\text{bl}}^{(2)}$, 50 wt% G and 15 wt% CF. In all cases, the molding time is 3 min. The solid line serves as a guide for the eye, and the error bars denote one standard error in the data.
5.4.1 Electrical Conductivity

Figure 5.2 provides the electrical conductivity of CPCs based on PE_{bl}^{(2)} as a function of either G or CF loading level. The first datum point in each data set identifies no conductivity, whereas the second point corresponds to non-zero conductivity near the PTC. These data clearly show that the PTC of the CPCs containing CF is substantially lower than that of the CPCs with G. Moreover, conductivity is observed to be more strongly dependent on filler concentration in the CF-based CPCs than in the G-based materials. This composition sensitivity is attributed to the size of the CF particles, which are considerably longer than

![Graph showing electrical conductivity vs. filler concentration](image)

Figure 5.2. Dependence of conductivity on filler concentration for composites derived from PE_{bl}^{(2)} and containing either G (○) or CF (●). The solid lines serve as guides for the eye, and the error bars denote one standard error in the data.
the G particles and which are more likely to form continuous conductive pathways within the polymer blend. Conductivity measurements acquired from the quaternary CPCs of principal interest in the present work are displayed as a function of filler content in Figure 5.3 for HDPE, PE\textsubscript{bl}\textsuperscript{(1)} and PE\textsubscript{bl}\textsuperscript{(2)} containing 15 wt% CF and varying concentrations of G. Note that CPCs composed of neat UHMWPE are excluded from this comparison due to their typically low conductivity [16]. Since the convention by which we designate composition in

![Figure 5.3](image_url)

**Figure 5.3.** Variation of conductivity with total filler concentration for HDPE (●), PE\textsubscript{bl}\textsuperscript{(1)} (○) and PE\textsubscript{bl}\textsuperscript{(2)} (△) composites containing mixtures of G and CF. In all cases, the concentration of CF accounts for 15 wt% of the composite. The solid lines serve to connect the data, and the error bars denote one standard error in the data.
these quaternary CPCs is important, we provide an example of how to analyze the data shown in this figure. Consider the CPC composed of PE\textsubscript{bl}(2) with 60 wt% filler. This system consists of 15 wt% CF, 45 wt% G and 40 wt% polymer, the latter of which can be further divided into its blend components — 10 wt% HDPE and 30 wt% UHMWPE.

As anticipated from Figure 5.2, an increase in filler concentration is generally accompanied by an increase in electrical conductivity due to greater interparticle contact. Comparison of the data in Figures 5.2 and 5.3 reveals that CPCs prepared from neat HDPE and mixtures of G and CF exhibit significantly higher conductivity than CPCs derived from PE\textsubscript{bl}(2) in the presence of only G. At 75 wt% filler, for instance, the conductivity of the PE\textsubscript{bl}(2)/G composite is about 18 (\Omega\text{-cm})\textsuperscript{-1}, whereas that of the HDPE/G/CF composite is about 37 (\Omega\text{-cm})\textsuperscript{-1}. Addition of 15 wt% CF to 60 wt% G therefore accounts for more than a 100% increase in conductivity. By incorporating UHMWPE into these CPCs, the conductivity can be further improved, as evidenced by the data obtained from the PE\textsubscript{bl}(1)- and PE\textsubscript{bl}(2)-based CPCs in Figure 5.3. If we again consider the CPCs with 75 wt% filler, we see that the conductivity increases from 37 to 64 to 69 (\Omega\text{-cm})\textsuperscript{-1} as the UHMWPE content increases from 0 to 50 to 75 wt%. Over this composition interval under constant filler conditions, the electrical conductivity increases by 1.5-2.2× over the entire range of filler concentrations examined. The results provided in Figures 5.2 and 5.3 also indicate that substitution of 15 wt% CF for G in the PE\textsubscript{bl}(2)/G composite promotes a considerable increase in electrical conductivity (by about 280% at 75 wt% filler content).
It is interesting to note that the conductivity increases evident in Figure 5.3 become more pronounced at mixed filler concentrations above 50 wt%. At this concentration, the CPCs consist of 35 wt% G and 15 wt% CF. According to the conductivity measurements provided in Figure 5.2 and detailed elsewhere [16], the PTC of G in PE_{bl}^{(2)} is approximately 35 wt%. In neat HDPE, this PTC occurs at closer to 50 wt% G [26]. Thus, the PTC of G can be controllably lowered through judicious choice of blend components and composition in a CPC. In marked contrast, the PTC of CF is relatively independent of composition in the HDPE/UHMWPE system, varying from about 5.0 wt% in neat HDPE to 7.5 wt% in PE_{bl}^{(2)}. At 15 wt%, CF is above its PTC in all the CPCs discussed with regard to the conductivity measurements in Figure 5.3. Two issues must therefore be addressed to elucidate the mechanism by which conductivity is improved in these systems. The first is the role of the UHMWPE in the polymer blends, and the second is the CF loading level. Addition of UHMWPE to HDPE results in transient phase segregation due to a substantial difference in melt viscosity [28]. An increase in UHMWPE content therefore promotes the formation of UHMWPE- and HDPE-rich regions, as schematically depicted in Figure 5.4a. If the matrix consists of HDPE, both G and CF at a given filler concentration are anticipated to remain isotropically distributed within the low-viscosity HDPE phase. In this case, the purpose of the CF is to bridge distant and unconnected G particles, thereby increasing the net conductivity of the composite.

As the composition of UHMWPE increases, however, the HDPE is arranged into continuous channels that remain filled with G particles. This leads to the
formation of a double-percolated network [8,16,23-25,29,30], which is illustrated in Figure 5.4b. Such localization of filler particles induces an enormous increase in filler connectivity. If one phase (A, gray) of an immiscible blend possesses a higher melt viscosity than the other (B), G and CF particles will locate in B (a). As the fraction of A increases (b), the G/CF mixture becomes constrained within channels of B, eventually forming a bridged double-percolated network. In this case, discrete G-rich channels of B are connected by CF particles.
in conductivity. As alluded to earlier, double percolation occurs up to about 80 wt% in the HDPE/UHMWPE blend system. At this blend composition, a conductivity maximum is observed [16] in the case of CB and G fillers. At higher UHMWPE concentrations, conductive pathways are obstructed and CPC conductivity decreases as the HDPE-rich regions eventually become isolated.

This model explains how the composition of the polymer blend comprising a CPC impacts conductivity, but does not address how the mixed G/CF filler promotes the tremendous conductivity increases evident in Figure 5.3. Since the CF particles are substantially longer than the particle sizes of HDPE and UHMWPE, we anticipate that, at high UHMWPE concentrations, the CF can span UHMWPE-rich domains and connect G-rich HDPE domains that may not be otherwise connected. This postulated scenario is shown in Figure 5.4b and suggests that the CF particles not only bridge G particles within single HDPE channels, but also bridge G particles residing in neighboring channels, thereby promoting more conductive pathways through the composite medium. We therefore refer to this mechanism as bridged double percolation to reflect the requirements of (i) double percolation and (ii) interchannel connectivity.

Since double percolation (and, by logical inference, bridged double percolation) is most pronounced in CPCs derived from PE_{bi}^{(2)}, we focus our attention on this system for the remainder of this study. Another consideration in the design of CPCs based on bridged double percolation is the role of CF concentration. As mentioned earlier, CF at 15 wt% is above its PTC and promotes electrical conductivity and mechanical stability [26]. Figure 5.5 displays
conductivity data acquired from PE$_{bl}^{(2)}$ filled with 5 and 15 wt% CF and varying levels of G. At low mixed filler concentrations, the conductivity level of the CPCs with 5 wt% CF is not far removed from the PTC of the system (i.e., near zero conductivity). Beyond 50 wt% filler, however, the conductivities of the CPCs with 5 and 15 wt% CF are both found to increase sharply. Over the entire filler concentration range examined here, the conductivities of the CPCs with 5 wt% CF are generally less than those of the composites with 15 wt% CF.

Figure 5.5. Conductivity presented as a function of total filler concentration for PE$_{bl}^{(2)}$-based composites containing mixtures of G and CF at two different loading levels of CF (expressed as wt% of the composite): 5 (▲) and 15 (△). The solid lines serve to connect the data, and the error bars denote one standard error in the data.
This observation is consistent with the bridged double-percolation model depicted in Figure 5.4. In the event that no CF is added to PE_{bl}^{(2)} (see Figure 5.2), the maximum conductivity achieved at any given filler loading level directly reflects the conductive pathways established solely by contacted filler particles in continuous HDPE channels. To achieve greater conductivity, CF particles must be present to ensure that the G particles in neighboring channels are physically connected even though the channels are not.

5.4.2 Morphological Characteristics

Since the fillers employed here are relatively large, we expect that the bridged double-percolation model proposed here can be corroborated by examining the morphologies of the quaternary CPCs discussed with regard to Figure 5.3. Optical micrographs acquired in reflection mode of polished CPCs composed of 35 wt% polymer and 65 wt% filler (50 wt% G and 15 wt% CF) are displayed for different blend compositions in Figure 5.6. If the polymer matrix is neat HDPE (Figures 5.6a-b), the G and CF particles, which appear as bright features set against a dark polymer-rich background, are observed to be uniformly and isotropically distributed. Note, however, the existence of relatively large gaps between some of the particles. These gaps, most likely due to the presence of HDPE spherulites, reduce the degree of contact between neighboring particles and, hence, the net conductivity of the HDPE/G/CF composite. Once UHMWPE is introduced into these CPCs, the particles adopt a more selective, anisotropic spatial arrangement. In the CPCs derived from PE_{bl}^{(1)} (Figures 5.6c-d), the G
particles localize within continuous regions that are presumably HDPE-rich, since low-viscosity HDPE can efficiently wet the carbonaceous filler particles and flow

Figure 5.6. Low- and high-magnification optical micrographs obtained from composites produced with 50 wt% G, 15 wt% CF and 35 wt% of the following polymeric constituents: (a,b) HDPE, (c,d) PE$_{bl}^{(1)}$ or (e,f) PE$_{bl}^{(2)}$. These images have been acquired in reflection mode from polished specimen surfaces.
around high-viscosity obstacles. While many of the CF particles tend to orient within these regions, some span across polymer-rich (dark) regions that measure on the order of 100-200 μm across. This size scale is consistent with the particle size of the as-received UHMWPE, in which case it is reasonable to designate these regions as UHMWPE-rich. As expected, the G particles do not disperse within these regions due to the high-viscosity of UHMWPE. Figures 5.6c-d confirm that HDPE/UHMWPE blends can undergo transient phase-segregation, which agrees with the previous findings of Vadhar and Kyu [28]. These images also demonstrate that (i) the filler particles selectively localize within the HDPE phase, and (ii) the CF serves to connect G particles residing in the same, as well as in adjacent, channels.

If the UHMWPE content is further increased to 75 wt% of the HDPE/UHMWPE blend (as in Figures 5.6e-f), the HDPE-rich regions become narrower due to greater volumetric constraints, thereby forcing the G and CF particles to pack together more efficiently at constant filler concentration. The presence of CF-induced interchannel connections is clearly visible in these micrographs and further supports the bridged double-percolation mechanism introduced earlier. Another interesting point to recognize in this image pair is that the area fraction of UHMWPE-rich regions increases with increasing UHMWPE composition. This observation, which is to be expected for fully immiscible polymer blends, implies that these two polymers, while chemically identical, do not co-crystallize under the conditions employed here, as explained by Sumita et al. [31]. It is important to remember that the highly constrained particles evident
Figure 5.7. Optical micrographs of PE_{bl}^{(2)} filled with 15 wt% CF and different concentrations of G (in wt%): (a) 0, (b) 10 and (c) 35. These images have been collected under the same conditions as those shown in Figure 5.6.

In Figures 5.6e-f reflect a CPC at high filler loading. A series of optical micrographs obtained at lower filler concentrations is provided in Figure 5.7. In this series, all the CPCs possess 15 wt% CF and levels of G ranging from 0 wt%
in Figure 5.7a to 35 wt% in Figure 5.7c. In Figure 5.7a, the CF particles are randomly oriented in a continuous polymer matrix. While no evidence of phase segregation is discernible in this CPC (which is to be expected since the CF particles are longer than, and less affected by, the high-viscosity UHMWPE domains), large gaps are seen to exist between the CF particles. Addition of 10 wt% G (Figure 5.7b) is accompanied by the onset of particle localization. As in Figure 5.7a, however, the dispersion of CF particles does not appear to be strongly affected. Note that some of the CF particles reside in close proximity to the G particles. Increasing the G concentration to 35 wt% (Figure 5.7c) clearly reveals that (i) the G particles localize within the HDPE-rich channels and (ii) CF particles span UHMWPE-rich regions to connect G particles in adjacent HDPE-rich regions.

5.4.3 Thermal Properties

As mentioned earlier, an important consideration in the development of CPCs derived from a semicrystalline polymer blend is the influence of polymer crystals on filler particle dispersion. The converse is likewise true. A solid filler incorporated into the matrix of a semicrystalline polymer may behave as a heterogeneous nucleating agent. To determine if G, CF or G/CF mixtures have any influence on HDPE or UHMWPE crystallization, we next examine the thermal signatures of the polymer blends and CPCs prepared during the course of this study. Table 5.1 is a compilation of the thermal properties measured from HDPE, UHMWPE and select HDPE/UHMWPE blends in the absence of filler.
Within experimental uncertainty, $T_m$ and $T_c$ are virtually independent of blend composition in this series. The crystallinity of the neat HDPE is determined from the measured value of $\Delta h_f$ to be 85.0%, which is much higher than that of the UHMWPE (45.4%). The crystallinities of the 50/50 and 25/75 w/w HDPE/UHMWPE blends are 65.0 and 56.4%, respectively. It is reassuring that these experimental values are in agreement with crystallinities predicted from the linear rule of mixtures (65.5 and 54.6%, respectively).

Since the melting temperatures of the two polymers are almost identical, it cannot be ascertained from these data alone if HDPE and UHMWPE co-crystallize. While an in-depth analysis of DSC thermograms and light scattering patterns may reveal whether these polymers are capable of co-crystallization [32,33], such analysis is beyond the scope of the present study. According to the

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta h_f$ (J/g)</th>
<th>Crystallinityb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>133</td>
<td>107</td>
<td>209</td>
<td>85.0</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>133</td>
<td>107</td>
<td>111</td>
<td>45.4</td>
</tr>
<tr>
<td>50/50 w/w HDPE/UHMWPE</td>
<td>135</td>
<td>107</td>
<td>160</td>
<td>65.0</td>
</tr>
<tr>
<td>25/75 w/w HDPE/UHMWPE</td>
<td>132</td>
<td>107</td>
<td>138</td>
<td>56.4</td>
</tr>
</tbody>
</table>

\[^a\] Determined from DSC performed at heating and cooling rates of 20°C/min.

\[^b\] Calculated from the ratio of the measured $\Delta h_f$ to $\Delta h_f$ of a 100% crystalline polyethylene (245.3 J/g [27]).
data provided in Table 5.2, addition of a mixed filler composed of 50 wt% G and 15 wt% CF to the three polymer systems listed in Table 5.1 has almost no effect on the thermal properties of the resultant CPCs. These findings, which are consistent with previous results acquired from CPCs consisting of (i) HDPE with mixtures of G and CF [26] and (ii) PE_{bl}^{(2)} with either G or CF [16], demonstrate that the carbonaceous fillers examined here do not alter the thermal properties of the parent polymers and their blends. Moreover, these fillers do not induce heterogeneous nucleation in these polyethylene-based CPCs. In similar fashion, Xu et al. [34] have also reported that CB does not affect the thermal behavior of UHMWPE on the basis that the polymer crystal size is independent of the filler loading level.

Table 5.2. Thermal properties for CPCs composed of HDPE and UHMWPE/HDPE blends.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Specimen\textsuperscript{b}</th>
<th>T\textsubscript{m} (°C)</th>
<th>T\textsubscript{c} (°C)</th>
<th>Δh\textsubscript{f} (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE/(G+CF)</td>
<td>135</td>
<td>108</td>
<td>199</td>
<td>81.1</td>
</tr>
<tr>
<td>PE_{bl}^{(1)}/(G+CF)</td>
<td>133</td>
<td>110</td>
<td>159</td>
<td>64.8</td>
</tr>
<tr>
<td>PE_{bl}^{(2)}/(G+CF)</td>
<td>132</td>
<td>105</td>
<td>132</td>
<td>53.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Specimens consisted of 35 wt% polymer, 50 wt% G and 15 wt% CF, and were characterized as in Table 1.

\textsuperscript{b}PE_{bl}^{(1)} and PE_{bl}^{(2)} refer to the 50/50 and 25/75 w/w HDPE/UHMWPE blends, respectively.
5.4.4 Mechanical Properties

The dynamic shear moduli ($G'$ and $G''$) of all the polymer blends and CPCs investigated here have been measured from 25 to 120°C. Since the storage modulus directly relates to specimen stiffness and mechanical stability, we only discuss the temperature ($T$) dependence of $G'$ in this section. [The corresponding temperature dependence of $G''$ does not reveal any notable features and is not included here.] The effect of temperature on $G'$ measured from the neat HDPE and UHMWPE, as well as from PE$_{bl}$\(^{(1)}\) and PE$_{bl}$\(^{(2)}\), is shown in Figure 5.8. In all cases, $G'$ is observed to decrease monotonically with increasing temperature until it reaches a temperature at which it drops precipitously. This temperature, which is associated with the onset of crystal melting or polymer flow, is material-dependent: about 90°C for HDPE and PE$_{bl}$\(^{(1)}\), 98°C for PE$_{bl}$\(^{(2)}\) and 117°C for UHMWPE. Note that these temperatures are significantly lower than the $T_m$ values reported in Table 5.1. As expected from the previous DSC results, the $G'(T)$ data provided in Figure 5.8 do not exhibit any other thermal transitions, in which case we now turn our attention to the magnitude of $G'$. Up to ca. 70°C, $G'$ measured from the four systems discussed above lies the highest $G'$. While the values of $G'$ obtained from the two blends fall between those of neat HDPE and UHMWPE, they do not obey the rule of mixtures, which most likely reflects poor mixing [35]. At temperatures just above 70°C, the relative order in which $G'$ continues to decrease with increasing temperature changes. For instance, $G'(T)$ corresponding to the neat HDPE becomes more sensitive to temperature and decreases more sharply than that of
the other systems as it approaches its catastrophic-failure temperature. The data displayed in Figure 5.8 reveal that UHMWPE exhibits the greatest thermal stability relative to HDPE and the two blends due to its high degree of chain entanglement (which hinders polymer motion at elevated temperatures).

Figure 5.8. The dynamic storage modulus ($G'$) displayed as a function of temperature for unfilled HDPE (●), UHMWPE (▲) and PEbl(2) (○). Values of $G'$ measured from PEbl(1) lie very close to those of neat HDPE and are not included here for that reason. The solid lines serve to connect the data.

Upon addition of 50 wt% G and 15 wt% CF to HDPE and the two polymer blends discussed with regard to Figure 5.8, the magnitude of $G'$ increases by at least 6×, as is evident in Figure 5.9. The CPC composed of HDPE exhibits the highest $G'$, followed closely by the CPC derived from PEbl(1). This order is
consistent with the DSC results listed in Table 5.2, which confirm that polymer crystallinity is unaffected by the addition of the G/CF mixture. Although these filler-induced increases in the magnitude of $G'$ are certainly attractive, the most striking feature of the $G'(T)$ data in Figure 5.9 is the absence of a temperature at which a steep reduction in $G'$ occurs (as in Figure 5.8). Incorporation of the G/CF mixed filler into HDPE and the two HDPE/ UHMWPE blends promotes a substantial improvement in the thermal stability of the CPCs to temperatures beyond 120°C. While this improvement is achieved at a relatively high loading of mixed filler (50 wt% G and 15 wt% CF), it is important to identify the CPC

![Figure 5.9](image_url)

Figure 5.9. Temperature dependence of $G'$ for composites containing 50 wt% G, 15 wt% CF and 35 wt% of the following polymeric constituents: HDPE (●), PE_{bl}^{(1)} (○) or PE_{bl}^{(2)} (△). The solid lines serve to connect the data.
features responsible for such improvement. Figure 5.10 shows $G'(T)$ for the PE$_{bl}^{(2)}$ blend and its CPCs with varying levels of G and CF. As in Figure 5.8, the unfilled blend exhibits a temperature at which $G'$ decreases dramatically.

Figure 5.10. Variation of $G'$ with respect to temperature for PE$_{bl}^{(2)}$ filled with mixtures of G and CF at different concentrations (in w/w G/CF): 0/0 (■), 0/15 (○), 35/0 (△), 35/15 (▲) and 60/15 (○). The solid lines serve to connect the data.

Addition of either G or CF to the blend at a loading level near or above the PTC (35 wt% for G and 5 wt% for CF) yields a ternary CPC that remains thermally stable at much higher temperatures. Mixtures of these fillers (i) maintain thermal stability at temperatures beyond 120°C and (ii) increase the magnitude of $G'$ over the temperature range explored. Consider, for example, the properties of the
CPCs at 30°C. The value of $G'$ for the unfilled PE$_{bl}^{(2)}$ blend at this temperature is about 0.45 GPa. The corresponding values of $G'$ for the ternary CPCs with 35 wt% G or 15 wt% CF are 1.14 and 1.41 GPa, respectively. By combining both fillers at these concentrations to form a quaternary CPC, $G'$ increases to 2.31 GPa, which is surprisingly close to the sum of the $G'$ values (2.55 GPa) obtained from the two ternary systems.

![Graph showing conductivity and $G'$ vs. G concentration](image)

Figure 5.11. Dependence of conductivity (○) and $G'$ (●) on G loading in PE$_{bl}^{(2)}$ filled with 15 wt% CF. The solid lines connect the data. Error bars on the conductivity data denote one standard error, while those on the $G'$ data represent ±10% uncertainty.

Thus, the mechanical, as well as conductive, properties of quaternary CPCs can be finely tuned by judicious choices of blend and filler composition. While
the experimental matrix for quaternary systems precludes systematic variation of all the CPC components employed here, we now focus on establishing the effect of G concentration on the electrical conductivity and mechanical properties of CPCs composed of PE_{bl}^{(2)} with 15 wt% CF. These data are presented in Figure 5.11. On the basis of the previous findings reported in this work, an increase in the loading level of G is expected to increase both the conductivity and $G'$, which is apparent in this figure. It is interesting to note that the conductivity displays an abrupt increase at the PTC of G (35 wt%). Whereas the G-induced increase in conductivity is significant as it increases by an order of magnitude from $6.9 \, (\Omega \cdot \text{cm})^{-1}$ at 0 wt% G to $69 \, (\Omega \cdot \text{cm})^{-1}$ at 60 wt% G, the corresponding increase in $G'$ is relatively modest. These measurements reveal that once a filler is percolated in a CPC (recall that, at 15 wt%, CF is above its PTC), incorporation of additional filler material strongly impacts the conductivity by establishing more conductive pathways. Since a reinforcing network is already in place, however, the additional filler has less effect on the mechanical properties of the CPC. The data provided in Figure 5.11 can be cross-plotted, as in Figure 5.12, to yield conductivity as an explicit function of $G'$. This relationship reveals an unexpected result, namely, that the conductivity increases exponentially (denoted by the solid line in Figure 5.12) with respect to $G'$ in the quaternary CPCs used to generate Figure 5.11. Thus, a small increase in $G'$ can result in a rather significant increase in electrical conductivity.
Figure 5.12. Conductivity shown as a function of $G'$ for the same systems displayed in Figure 5.11. The concentrations of $G$ (in wt%) are 0 (○), 10 (●), 35 (△), 50 (▲) and 60 (◇). The solid line is an exponential fit to the data. The error bars are described in the caption of Figure 5.11.

5.5 Conclusions

Conductive polymer composites remain an important topic in the development of new and efficient multifunctional materials. Numerous studies have previously established the importance of polymer-polymer miscibility in the presence of a single carbonaceous filler, as well as the utility of using mixed fillers in the presence of a single polymer. In this work, we have combined these two design strategies — a phase-segregated polymer blend and a mixture of fillers — to develop novel quaternary composite materials composed of HDPE, UHMWPE, graphite and carbon fiber. On the basis of electrical conductivity measurements,
we have proposed the concept of a bridged double-percolation network. In this model, one filler (e.g., graphite) is selectively located and percolated within a polymer phase that forms continuous channels and is itself percolated throughout the blend. The purpose of the second filler (e.g., carbon fiber) is to span across insulating regions and further connect existing conductive pathways. In this manner, the second filler serves to bridge the double-percolated network and enhance the net conductivity of the composite. This model is consistent with optical micrographs obtained from composites differing in blend and filler composition. These factors also affect the mechanical properties of such composites. Once the percolation threshold concentration of either filler is reached, the dynamic storage modulus of these quaternary composites becomes less temperature-dependent and remains stable up to 120°C, which is about 30°C higher than the temperature at which the modulus of HDPE drops precipitously (due to the onset of crystal melting or polymer flow). At these filler concentrations, further addition of filler results in a substantial increase in electrical conductivity, but a modest increase in modulus. Under the conditions examined here, we find that conductivity increases exponentially with increasing modulus. The mechanisms and relationships identified in this work are anticipated to expedite the rational design of multicomponent conductive polymer composites, as well as promote an improved understanding of how the properties of commodity materials can be best utilized to achieve application requirements.
5.6 Acknowledgements

We thank Mr. A. Rieves (National Power American Technology, Inc.) for providing the HDPE and graphite powder, and Drs. R. F. Davis, T. Hare, D. M. Maher (NCSU) and K. C. Caster (Lord Corporation) for technical assistance.

5.7 References


6. CONCLUSIONS

This study clearly demonstrates that the electrical conductivity of multicomponent conductive polymer composites (CPCs) depends sensitively on filler type, composition and concentration, as well as on the composition and morphology of the polymer matrix. The percolation threshold concentration (defined here as the minimum filler concentration that yields a measurable conductivity at the conductor-insulator transition) of graphite-filled HDPE is found to be ~50 wt%, compared to 7.5 wt% for long carbon fibers (L=1.0mm) and 12.5 wt% for short carbon fibers (L=0.25mm). At the same filler concentration, composites of HDPE containing only graphite particles exhibit a low conductivity relative to those with carbon fiber.

Double percolation can be achieved with filled blends of HDPE and UHMWPE and can increase the conductivity of the composite relative to that of composites derived from either of the parent polymers. The composite conductivity at constant filler concentration in CPCs composed of HDPE, UHMWPE and either carbon black or graphite is found to increase by more than an order of magnitude in the vicinity of 70-80 wt% UHMWPE, whereas similar (albeit less pronounced) behavior for carbon fiber occurs at about 25 wt% UHMWPE. The percolation threshold concentrations of graphite-, carbon black- and carbon fiber-filled HDPE and a 25/75 w/w HDPE/UHMWPE blend are listed for comparison in Table 6.1 and clearly indicate that the use of a polymer blend successfully reduces the threshold loading level of these fillers due, most likely, to double percolation.
Due to their size and shape, carbon black and carbon fiber possess lower percolation threshold concentrations than graphite. A pronounced increase in conductivity can be achieved in composites consisting of HDPE or HDPE/UHMWPE blends with mixtures of graphite and carbon fiber, even at relatively low concentrations of carbon fiber. The long-range connectivity of graphite above its threshold concentration and the continuity of carbon fiber both contribute to the increased conductivity of the composite, as explained by our bridged double percolation model.

**Table 6.1.** Threshold concentrations for CPCs composed of HDPE and a 25/75 HDPE/UHMWPE blend.

<table>
<thead>
<tr>
<th>Composite</th>
<th>G (wt%)</th>
<th>CB (wt%)</th>
<th>CF (L=1mm) (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>50</td>
<td>15</td>
<td>7.5</td>
</tr>
<tr>
<td>HDPE/UHMWPE</td>
<td>35</td>
<td>5.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Table 6.2 compares the electrical conductivities of binary, ternary and quaternary CPCs produced during the course of the present study. Composites containing carbon black are excluded from this comparison due to processing difficulties. At the same filler concentration (50 wt%), the conductivities of HDPE and the HDPE/UHMWPE blend composites containing both graphite and carbon fiber are 100 and 200x, respectively, higher than the conductivity of the base
Composites possessing the same filler mixture at a loading level of 65 wt%, the conductivity of the HDPE/UHMWPE composite is about 50% higher than the conductivity of the HDPE analog. A bridged double-percolation network forms in the quaternary composite of HDPE/UHMWPE filled with graphite and carbon fiber. In these composites, the carbon fiber serves as the bridge spanning insulating regions and leads to a rather substantial increase in composite conductivity.

Table 6.2. Conductivity comparison for composites of binary, ternary and quaternary systems. The 25/75 HDPE/UHMWPE blend with CF (L=1mm) are used in this comparison.

<table>
<thead>
<tr>
<th>Composition (wt%)</th>
<th>Conductivity (Ω-cm)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HDPE</td>
</tr>
<tr>
<td>Polymer/(G+CF)</td>
<td></td>
</tr>
<tr>
<td>50/(50+0)</td>
<td>0.1</td>
</tr>
<tr>
<td>85/(0+15)</td>
<td>7.8</td>
</tr>
<tr>
<td>35/(50+15)</td>
<td>25.6</td>
</tr>
<tr>
<td>50/(35+15)</td>
<td>10</td>
</tr>
</tbody>
</table>

Micrographs obtained from composites of the polymer blends with high UHMWPE content reveal that the distribution of both carbon black and graphite particles is certainly nonrandom. The filler particles in these composites preferentially reside in the low-viscosity HDPE phase, which occupies the volume excluded by the high-viscosity UHMWPE. Such volume exclusion is deemed
responsible for the creation of long, uninterrupted conductive paths of a filler-rich phase. This double-percolated morphology yields a highly conductive composite. In addition, carbon fiber is able to span insulating polymer regions in quaternary composites, thereby forming a bridged double-percolated network.

Significant improvement in mechanical properties is achieved by adding any of the carbonaceous fillers examined here to the polymer matrix. Composites containing carbon fiber (especially the long fiber) are the most resistant to applied deformation and increasing temperature as the temperature approaches the polymer melting point, as evidenced by the dynamic storage modulus. The magnitude and temperature dependence of this modulus from HDPE/CF and HDPE/G composites are more sensitive to the proximity of the filler loading level to the percolation threshold concentration than on filler type or concentration. However, dynamic mechanical analysis of composites prepared with a 25/75 HDPE/UHMWPE blend matrix demonstrates that the stiffness of these composites is sensitive to both filler type and concentration.

Differential scanning calorimetry is ineffective in analyzing the miscibility of HDPE/UHMWPE blends due to the similarity of their melting temperatures. Thermal analysis of the neat polymers, their blends and their composites (including a 25/75 w/w HDPE/UHMWPE blend) with either carbon black, graphite or carbon fiber, as well as graphite/carbon fiber mixtures, confirms that the thermal characteristics of these systems remain essentially unchanged. This observation indicates that the composite matrix is virtually unaffected by the presence of these inorganic fillers.
7. FUTURE WORK

The following issues are recommended for further analysis of quaternary conductive polymer composites such as those studied herein:

- For certain applications (such as electrodes for large-scale stationary batteries or capacitors), thicker conductive composite films (>0.8 mm) are needed. Thicker samples of the quaternary composites studied here should be prepared and their properties compared to their thinner analogs to ascertain the possible effects of nonrandom filler orientation.

- Preliminary measurements of 25/75 HDPE/UHMWPE composites filled with mixtures of carbon black and carbon fiber (L=1mm) yield conductivities about three times higher than the corresponding composites prepared from a corresponding mixture of graphite and carbon fiber (see Figure 7.1). However, it is difficult to prepare carbon black-filled blends containing more than 35% carbon black using the dry mixing and molding process developed here. This problem reflects the tremendous volume expansion of carbon black particles that occurs as the densified pellets are dispersed during mixing with the polymer. The actual volume fraction of CB in the ground powder may be significantly higher than that predicted from the weight and density of the carbon black pellets added to the mixer, as previously described in Chapter 2. The increased volume of filler can cause incomplete wetting by the polymer and poor dispersion. Graphite, however, does not expand significantly during mixing, and composites prepared with
graphite retain good mechanical properties at high loading levels (up to 75 wt% graphite). It would be desirable to investigate samples with higher carbon black content, prepared by more energetic (high shear) mixing methods that are capable of distributing the carbon black particles more uniformly in the polymer. Such mixing could, for example, be achieved in Banbury or Brabender mixers. The degree of carbon fiber breakage during these more energetic mixing methods must, however, be carefully monitored.

![Graph showing electrical conductivity vs filler concentration](image)

Figure 7.1 Electrical conductivity of quaternary composites containing CB/CF and G/CF mixtures. The 25/75 HDPE/UHMWPE blend with 5 wt% CF are used to prepare all the samples.
Graphite fibrils have been reported [1] to lower the threshold concentration for composites of nylon 6 and polycarbonate relative to PAN-based carbon fiber. Graphite fibril-based composites exhibit the same conductivity as PAN-based composites containing twice the concentration of filler, and reached higher ultimate conductivities. Graphite fibrils are recommended for future conductive HDPE and HDPE/UHMWPE composite studies. However, a careful cost-benefit analysis should also be performed.

The miscibility and co-crystallization behavior of HDPE and UHMWPE could not be ascertained here from thermal calorimetry since their melting and crystallization peaks overlap. In addition, it is difficult to differentiate HDPE from UHMWPE morphologically due to their identical chemical attributes. Analysis of the width of the DSC crystallization peak, coupled with small-angle light scattering, has been used [2] to support the conclusion that co-crystallization occurs in HDPE/UHMWPE blends. While evidence of HDPE and UHMWPE co-crystallization and phase segregation would be useful in designing composites, inspection of the DSC results in Chapter 4 shows that the crystallization peak widths of these polymers and their blends are too similar, thereby precluding such determination. Use of polymers with different thermal signatures is recommended to alleviate this shortcoming.

7.1 References

8. APPENDIX

A. Calorimetric comparison of solvent blending and dry mixing/molding in HDPE/UHMWPE blends

Solvent blending is often used to prepare polymer blends with greater (nonequilibrium) miscibility than is thermodynamically expected and can, depending on lattice matching, produce crystals containing both polymer constituents (co-crystals). Here, we turn our attention specifically to blends composed of HDPE and UHMWPE. The thermal properties of 50/50 HDPE/UHMWPE blends prepared by solvent blending are compared here with blends produced by the dry mixing/molding method detailed in Chapter 3 to discern whether HDPE and UHMWPE form separate crystals or co-crystallize. The solvent blending procedure has been previously described in Chapter 2. Samples weighing ca. 8 mg from both blending methods have been analyzed by differential scanning calorimetry (DSC) in the same manner used throughout this study (i.e., heated and cooled in the calorimeter at a rate of 20°C/min). Data derived from the first scan cycle are provided in Table A1. Thermograms reveal single melting and crystallization peak temperatures, and an example of thermograms showing melting endotherms is presented in Figure A1. The heat of fusion is higher for the solvent-blended blend, but the heat of crystallization obtained when the same sample is cooled is similar to that obtained from the sample produced by dry mixing/molding. As expected, the solution-crystallized sample possesses a higher crystallinity than samples crystallized from the melt.
Figure A1. DSC thermograms obtained upon heating 50/50 HDPE/UHMWPE blends prepared by solvent blending and dry mixing/molding.
Table A1. Thermal properties of 50/50 HDPE/UHMWPE blends prepared by dry mixing/molding and solvent blending.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Thermal Properties</th>
<th>Mixing-molding</th>
<th>Solvent-blending</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting onset temperature (\textdegree C)</td>
<td>130.6</td>
<td>127.1</td>
</tr>
<tr>
<td>Melting peak temperature (\textdegree C)</td>
<td>140.0</td>
<td>140.5</td>
</tr>
<tr>
<td>Crystallization onset temperature (\textdegree C)</td>
<td>121.2</td>
<td>120.1</td>
</tr>
<tr>
<td>Crystallization peak temperature (\textdegree C)</td>
<td>117.2</td>
<td>116.9</td>
</tr>
<tr>
<td>Heat of fusion $\Delta h_f$ (cal/g)</td>
<td>43.3</td>
<td>53.8</td>
</tr>
<tr>
<td>Heat of crystallization $\Delta h_c$ (cal/g)</td>
<td>43.0</td>
<td>45.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Determined from DSC-910 (DuPont) performed at heating and cooling rates of 20\textdegree C/min.

B. The effect of molding and DSC scan cycle on thermal properties

Unfilled 25/75 w/w HDPE/UHMWPE blends are chosen for this analysis. The cutting/stacking/molding process is described in Chapter 3, and films have been characterized by DSC to ascertain process reproducibility and the effect of thermal history on thermal properties. Results of this analysis are displayed in Tables B1 and B2. Note that there is no significant difference in (i) the peak melting and crystallization temperatures (Table B1) or (ii) the heats of fusion and crystallization (Table B2) for any of the systems studied. We therefore conclude that the blend produced after the first molding cycle is identical, in terms of thermal properties, to blends generated after subsequent molding cycles. In similar fashion, the thermal properties obtained from the first DSC scanning cycle are expected to be representative of all subsequent cycles.
Table B1. Peak melting and crystallization temperatures for 25/75 w/w HDPE/UHMWPE blends.\textsuperscript{b}

<table>
<thead>
<tr>
<th>Mold cycle number</th>
<th>Melting temperature (\textdegree C)</th>
<th>Crystallization temperature (\textdegree C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1\textsuperscript{st} scan</td>
<td>2\textsuperscript{nd} scan</td>
</tr>
<tr>
<td>1</td>
<td>135.4</td>
<td>136.7</td>
</tr>
<tr>
<td>2</td>
<td>136.3</td>
<td>137.9</td>
</tr>
<tr>
<td>3</td>
<td>135.3</td>
<td>137.3</td>
</tr>
</tbody>
</table>

\textsuperscript{b}Determined from DSC-4 (Perkin-Elmer) performed at heating and cooling rates of 20\textdegree C/min.

Table B2. Fusion and crystallization enthalpies for 25/75 w/w HDPE/UHMWPE blends.\textsuperscript{b}

<table>
<thead>
<tr>
<th>Mold cycle number</th>
<th>Heat of fusion (cal/g)</th>
<th>Heat of crystallization (cal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1\textsuperscript{st} scan</td>
<td>2\textsuperscript{nd} scan</td>
</tr>
<tr>
<td>1</td>
<td>42.5</td>
<td>47.0</td>
</tr>
<tr>
<td>2</td>
<td>44.3</td>
<td>46.8</td>
</tr>
<tr>
<td>3</td>
<td>44.4</td>
<td>44.4</td>
</tr>
</tbody>
</table>

C. Reproducibility of HDPE/G/CF films

The reproducibility of the mixing/molding process is examined by producing two series of HDPE/G/CF composites and measuring their electrical conductivities. All samples contain 60 wt% total filler, and the CF content is varied from 10 to 35 wt%. Results from this analysis are displayed in Figure C1.
The process yields composites with very reproducible conductivities at all CF loading levels.

Figure C1. Electrical conductivities of two series of HDPE/G/CF (L=1mm) composites.
9. BIBLIOGRAPHY


