Effects of Carbon Particles on the Structure and Properties of Immiscible Polymer Blends

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy (PhD) in the Faculty of Engineering and Physical Science

2013

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School of Materials
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LIST OF SYMBOLS

Ca    Capillary number
E'    Storage modulus
G'    Shear storage modulus
τ     Shear stress
λ     Spreading coefficient
γ     Interfacial tension
tan δ Loss tangent
σ     Surface tension
X_c   Degree of crystallinity
v/w   volume per weight
ΔH_f  Heat of fusion
X_p   Weight fraction of crystalline polymer
p     Particle loading
p_c   Critical percolation threshold
t     power constant
δ     Hildebrandt solubility parameter
X     Flory Huggins interaction parameter
ΔG_m Free energy change of mixing
ΔH_m Change in enthalpy of mixing
ΔS_m Change in entropy of mixing
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<tr>
<td>1D</td>
<td>One Dimension</td>
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<tr>
<td>3D</td>
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<tr>
<td>AC</td>
<td>Alternate Current</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered electrons</td>
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<tr>
<td>CB</td>
<td>Carbon Black</td>
</tr>
<tr>
<td>CL</td>
<td>Cathodoluminescence</td>
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<tr>
<td>cm(^{-1})</td>
<td>Wavenumber</td>
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<tr>
<td>cm(^{2})</td>
<td>Square centimetre</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
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<tr>
<td>DMTA</td>
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<td>FTIR</td>
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<tr>
<td>GPA</td>
<td>Giga Pascal</td>
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<td>g</td>
<td>Gramme</td>
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<td>h</td>
<td>Hour</td>
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<tr>
<td>KBr</td>
<td>Potassium bromide</td>
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<td>LVR</td>
<td>Linear viscoelastic region</td>
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<td>MWCNTf</td>
<td>Functionalised multiwall carbon nanotubes</td>
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<td>Optical microscope</td>
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<td>Pascal</td>
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<td>PP</td>
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<td>Poly(methyl methacrylate)</td>
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<tr>
<td>$T_m$</td>
<td>Crystalline melting temperature</td>
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<td>$T_g$</td>
<td>Glass transition temperature</td>
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<tr>
<td>WAXD</td>
<td>Wide angle x-ray diffraction</td>
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ABSTRACT

Effects of Carbon Particles on the Structure and Properties of Immiscible Polymer Blends

The University of Manchester
Muhammad Bilal Manzoor
Doctor of Philosophy
23 June 2013

Two types of binary immiscible polymer blend and composite systems, based on polypropylene (PP)/polystyrene (PS) and PP/Poly(methyl methacrylate) (PMMA), and a ternary polymer blend system of PP/PS/PMMA was prepared via melt compounding. Matrix/minor phase concentration was kept to 80/20 vol% for all the blends prepared. Structural changes upon the addition of minor phase were observed using SEM and TEM. Both of the PP/PS and PP/PMMA binary blends studied in this work show continuous-discontinuous (matrix-droplet) type morphologies. The coarse particle morphology of the dispersed phases suggested high interfacial tensions, and ease of pull-out of dispersed droplets indicates poor adhesion between the phases. Both of these proposals were supported by the results of DMTA and dynamic shear rheometry. The values of $T_g$ of the dispersed phase components remained the same in the blends, again indicative of immiscibility. Morphologies of the ternary polymer blends were predicted using the spreading coefficient model, which predicted encapsulation of PMMA by PS. SEM of solvent-etched surfaces and TEM results were in agreement with this prediction. The addition of CB to the blends caused micro-structural changes in the blends and produced electrically conductive composites. CB acted differently towards the PS and PMMA phases. Higher loadings of CB (10 wt.%) in the PP/PS blend increased its electrical conductivity and dynamic moduli more than in PP/PMMA blends due to the formation of a co-continuous morphology and to strong PS-CB interactions. Whereas at lower CB loadings (2 and 5 wt. % CB) the rise in mechanical moduli and electrical conductivities was comparable to that in PP/PMMA-CB. The less significant increase in electrical conductivity of PP/PMMA-CB composites compared to PP/PS-CB composites was due to the absence of a co-continuous morphology, which can impart a double percolation effect. Based on this behaviour, and the morphological results of the ternary polymer blends, a ternary polymer-CB composite was formulated which showed both higher mechanical and electrical properties than those of binary blend-CB composites and of the neat binary polymer blends. The concentration ratios of the dispersed phase were found to be very important in determining the structure and properties of the ternary blend-CB composites. Functionalised CNT behaved differently than CB towards these binary blend systems. Instead of PS, CNT preferred to reside in the PMMA phase of the binary blend composite systems, which led at higher CNT loadings to the formation of a co-continuous PMMA phase. This morphological change significantly improved the dynamic moduli and electrical conductivity of the PP/PMMA-CNT composites. GNP based binary blend composites exhibited morphological changes similar to the CB based composites but at lower GNP loadings than for CB and CNT. As with the CB and CNT based systems; GNP blend composites forming a co-continuous morphology (PP/PS-GNP) exhibited superior moduli and electrical conductivity. Binary GNP blend composites exhibited moduli and electrical conductivities superior to CB and CNT binary blend composites. A general trend of a rise in $T_g$ of PP was seen with addition of all of these carbon particles. WAXRD measurements confirmed the presence of smaller crystals in the composites as a result of fast crystallisation caused by the rise in PP matrix $T_c$. 
DECLARATION

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Chapter 1: Introduction

This chapter gives a brief background on immiscible polymer blends, followed by the aims of this project and the content of the thesis.

1.1 Background

Polymers exhibit a range of advantageous properties over metals and ceramics; for example, low density, ease of manufacturing, toughness and ductility. On the other hand there are also some disadvantageous properties; for example lower modulus and strength. As metal alloys are developed by mixing two or more metals, in the same way polymers are mixed together to form polymer blends. When polymers are mixed together the blend formed may be miscible or immiscible depending upon their molecular structure. Due to differences in chemical structure, higher molecular weights, polarities and low entropy of mixing most blends separate into phases [1], often with weak interfaces which fail easily under mechanical or thermal stresses. To enhance the interfacial adhesion between the phases of immiscible blends interfacial agents, known as compatibilisers, are used. Typically compatibilisers are block or graft copolymers [2] containing chemically identical (or similar) chain segments to the blend components, [3] which drives the copolymer to the interface of the blend. This results in reduced interfacial tension and improved adhesion between the phases. The reduction in interfacial tension also results in a finer and more stable morphological structure in immiscible blends [4]. Thus, in this way the blend become compatibilised and exhibits improved mechanical properties.
More recently, solid micro- and particularly nano-sized particles are being used to improve adhesion between the phases of immiscible polymer blends. These particulates have been shown to have compatibilisation effects in polymer blends [4]. In this work, a range of carbon particulates; namely carbon black (CB), multiwall carbon nanotubes (MWCNT) and graphite nanoplatelets (GNP) have been studied to assess their effects on the morphology and properties of model polymer blends. In addition to potentially improving mechanical properties, these conductive carbon particles have the potential to increase the electrical conductivity of polymer blends [5, 6] if they form a conductive network in the multiphase polymer matrix. In single-phase polymer matrices, the levels of conductive filler required to form a network can often reduce the mechanical properties of a polymer matrix [7]. Using multiphase polymer blends provides a potential route of using reduced amounts of fillers to achieve the same or higher conductivity levels [8], by positioning the filler in selected phase(s) and/or interface(s).

1.2 Scope of the Thesis

The first stage of this research was to investigate how morphology may be manipulated in blends of polypropylene (PP), polystyrene (PS) and poly (methyl methacrylate) (PMMA). Initial studies were of addition of varying levels of PS or PMMA as the dispersed phase in a PP matrix; followed by the formation of ternary blends of the three polymers to study the effect of changes in the concentration of the dispersed phase (PS/PMMA) on morphology and properties. The next stage progressed to the effects of the different carbon fillers on the morphologies of the immiscible polymer blends and of these morphological changes on their mechanical and electrical properties. Firstly, micro-composites of binary polymer blends were prepared with carbon black (CB) followed by a study of the effects of CNT and GNP nanoparticles on the structure
development of polymer. The mechanical and electrical properties of the resulting binary and ternary polymer composites were measured and correlated with morphology.

1.3 Objectives

The objectives of this PhD work were:

1. To study the structure development of PP/PS and PP/PMMA binary blends in the presence of CB, MWCNT or GNP as potential compatibilising particles.
2. To study the effects of any morphological changes on the mechanical and electrical properties of these binary blends.
3. To study the effects of a third polymer (PS or PMMA) on the properties of binary composites containing CB, MWCNT or GNP.

1.4 Thesis Structure

This thesis consists of seven chapters. Chapter 1 has introduced the background of the problem and the aims of the research. Chapter 2 presents a review of the literature on the preparation and characterisation of polymer blends and composites. The review provides the basis for the experimental methodology and analytical studies of this work. The need to synthesise polymer blends with good mechanical and electrical properties and their potential applications are also discussed in this chapter. Chapter 3 describes the raw materials used and methodology of the work. Accounts of sample preparation and specimen characterisation techniques are also given. In chapter 4 results of the characterisation of the polymer binary blends, and the properties and morphology development of the ternary polymer blends are presented and discussed. Chapters 5 and 6, respectively, present the results and discussion on the effects of micro-scale CB
particles, and of CNT and GNP nanoparticles, on the structure and properties of the polymers blends discussed in chapter 4. In addition, the formation of electrically conductive structures is discussed using results from impedance spectroscopy. Chapter 7 presents the conclusions and recommendations for the future work.

1.5 References


Chapter 2: Literature Review

In this chapter firstly a review of previous work on the structure and techniques used for preparing polymer blends is given, and in the latter sections the effects of nanoparticulates on the structure and properties of polymer blends is reviewed particularly in terms of mechanical and electrical properties.

2.1 Introduction to Multiphase Polymer Blends and their Composites

Polymer blends have been a major area of growth in the polymer industry for the last four decades. By using a suitable blending technique a combination of physical, mechanical properties can be achieved and tailored to an end-use application [1]. The mechanical properties of (immiscible) multiphase polymer blends may appear inherent from those of their parent polymers, to a large extent they are dependent on the adhesion between the phases[2]. For a multiphase blend to possess good mechanical properties, the applied stress should be transferred uniformly between the phases. For this to occur requires strong interfaces between the phase and for this there are two possibilities. Firstly, its phases may be inherently “compatible” with each other[3], i.e. sufficient interfacial mixing occurs between phases to create adhesion between the phases (interphase mixing will not occur as the blend is immiscible). Secondly, the interfaces in a blend may be modified, often using additives known as “compatibilisers” to increase interfacial mixing or provide interfacial bonding.

In this review we concentrate on immiscible blends, those that phase separate to form a multiphase polymer system, as these are the subject of the thesis. Polymers can be made conductive by adding conductive fillers. Proper dispersion and distribution of these
fillers is important for good conductive properties of polymers. The application of a conductive polymer composite depends on its volume resistivity [4]. A balance between the electrical and mechanical properties is also important from an application point of view [5] and morphological studies of polymer blends can tell much about the resulting properties of the material [6]. Electrically conducting polymers are needed for electromagnetic interface shielding (EMI) [7, 8], applications which are increasingly using conducting polymer composites [9]. Another application of conducting polymers is electrostatic dissipation (ESD) of static charge in order to avoid harmful arc discharge [9]. Levels of conductivity required for EMI are higher than for ESD, and volume resistivities of $10^2$-$10^6 \ \Omega \text{cm}$ are sufficient to bleed off the electrical charges [9]. For example, antistatic prevention is needed in parts in conveyor belts and weaving machine arms [9]. Addition of conductive fillers to a polymer can enhance the electrical properties but at the expense of mechanical properties. The use of multiphase polymer-filler composites has the potential to enhance the electrical conductivity of a composite at lower filler concentrations due to selective localisation of filler in one of the phases or at the interface(s). For example, PP/PS binary blend composites with 10 vol % of CB have been shown to give 70% higher shielding effects than PS-CB composites [7] due to selective localisation of CB with in the PS phase.

Electrically conductive polymers are also useful in electronics applications as adhesives in circuit elements. Conductive polymers having good thermal conductivities have also been used for self limiting heating electrical systems [10]. PE-CB composites have been used in fault current limiters in electrical systems [10]. The idea being that when a high electrical current passes through the semi-crystalline PE, it heats up and the volume expansion near the melting point disrupts the conductive network (Figure 2.1) Thus it behaves as a current limiting device.
The electrical resistivity of a polymer composite is dependent on the size of the filler. Larger size filler particles have been shown to result in lower electrical resistivity. For example, in PP, PE and Epoxy matrices filled with CB, TiB$_2$, Fe or Au. TiB$_2$ particle sizes of 100-200 $\mu m$ were found to give up to four times less volume resistivity than particles of 50 $\mu m$ [12]. Conductive polymer composites with smaller sized filler particles are also known to heat up more quickly as a greater number of particles are involved in completing the conductive network, hence giving more contact points in the conductive network and also a reduced distance between neighbouring filler particles [13].

The amount of filler required for the formation of a conductive network (i.e. the threshold concentration) is also dependent on the aspect ratio of the filler. Fillers with higher aspect ratios can form conductive networks at lower threshold concentration [14] as they efficiently form filler-filler contact points. Threshold concentration is also dependent on the morphology of the composites and type of matrix. A semi crystalline matrix aids by increasing excluded volume for the fillers (which are excluded from the
crystals) thereby reducing threshold concentrations [15]. Thus the formation of multiple phases in the matrix is another way to decrease threshold concentration within a composite and that is the approach explored in this thesis.

2.2 Morphology Development in Polymer Blends

Morphology development in polymer blends can be explained by the help of thermodynamics. In thermodynamic terms mixing or blending of two or more polymers is always facilitated by a decrease in free energy of mixing given by the following expression [16]

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

(2.1)

Where $\Delta G_m$ is the free energy change of mixing, $\Delta H_m$ is the change in enthalpy of mixing and $T\Delta S_m$ term represents the change in entropy of mixing. For a polymer blend to be miscible $\Delta G_m$ should $<0$ [16]. In polymer blends the entropy term is small and positive, therefore mixing of two polymers will be facilitated by a negative value of $\Delta H_m$ (exothermic process) to lower the $\Delta G_m$ term [16]. In the case of immiscible blends the latter term is absent and in order to improve mixing (i.e. dispersion), a third component (compatibiliser) having an exothermic interaction (-ve $\Delta H_m$ ) with the blend components or having a similar architecture as the blend components (zero enthalpy change in mixing) is added to achieve good dispersion [16]. The principles underlying particle filled polymeric compounds may be described in terms similar to this. In the case of filled polymer systems the entropy of mixing may depend on the flexibility of the polymer chains and the size of filler agglomerates [16]. Mixing of a polymer with fillers is facilitated if accompanied by small or negative change in $\Delta G_m$ (strong polymer-filler interaction)[16]. If the filler-particle interaction is poor, adding a third
component (coupling agents) which favourably interacts with both polymer and fillers will aid dispersion by achieving a negative change in $\Delta G_m$ [16].

Mutual solubility measurements of polymer blends based on the Hildebrandt solubility parameter ($\delta$) have been used in order to measure the miscibility of blends [16, 17]. The smaller the difference in $\delta$ of two components, the better is their mutual solubility (miscibility) or compatibility. It was suggested that $\delta$ has three components depending upon the type of intermolecular interactions; namely, dispersion, dipole-dipole interactions and hydrogen bonding [16]. The differences among the three have to be taken into account to predict mutual compatibility.

$$\Delta \delta = (\Delta \delta_d^2 + \Delta \delta_p^2 + \Delta \delta_h^2)^{1/2} \quad (2.2)$$

Flory-Huggins theory is the classical theory for calculating the free energy density of mixing of two homopolymers [17].

$$\frac{\Delta G_{mix}}{KT} = \left( \frac{\Phi_A}{V_A N_A} \right) \ln \Phi_A + \left( \frac{\Phi_B}{V_B N_B} \right) \ln \Phi_B + \frac{X \Phi_A \Phi_B}{v} \quad (2.3)$$

where $N_A$ is the number of repeat units in chain A and $V_A$ is the volume of each monomer in the chain, $X$ the Flory-Huggins interaction parameter, $\Delta G_{mix}$ the free energy change on mixing per unit volume, $K$ the Boltzmann constant and $T$ is absolute temperature [17]. Equation 2.3 can be used to predict phase diagrams for polymer blends. The onset of phase separation can be predicted from the values of the Flory Huggins interaction parameter ($X$) at the critical point ($X_c$) [18].

$$X_c = \frac{1}{2} \left( \frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}} \right)^2 \quad (2.4)$$

$X_c$ is the value of the Flory Huggins interaction parameter ($X$) at the critical point, which is the point below which a binary homogenous mixture can exist. Above the critical point the blend phases cannot form a homogenous (miscible) mixture. $X$, being a
measure of the interaction between chain segments A and B, can thus be measured from their solubility parameters as below [17, 18].

\[ X = \frac{V_n}{RT} (\delta_A - \delta_B)^2 \]  

(2.5)

Table 2.1 Molecular weights and solubility parameters values for PP, PS and PMMA obtained from literature.

<table>
<thead>
<tr>
<th></th>
<th>(M_w)</th>
<th>(N_i)</th>
<th>(\delta) (J/mL)^{1/2} [19]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>570,000 [20]</td>
<td>1345.6</td>
<td>16.6</td>
</tr>
<tr>
<td>PS</td>
<td>32700 [21]</td>
<td>314</td>
<td>18.5</td>
</tr>
<tr>
<td>PMMA</td>
<td>120,000 [22]</td>
<td>1198.6</td>
<td>19</td>
</tr>
</tbody>
</table>

For any polymer blend to be miscible the \(X\) value obtained by solubility parameters must be below the critical value of \(X_c\) [17]. This work focussed on blends of PP, PS and PMMA; therefore \(X\) values of different binary blend combinations of these polymers, based on \(\delta\) data available in the literature (Table 2.1) have been calculated in appendix 1 and the results are given in Table 2.2. For PP/PS binary blends the value of \(X_c\) is 0.0035 while the \(X\) value for the blend is 0.39 which is very much higher than \(X_c\) (\(X / X_c = 111\)), therefore the PP/PS blend is highly immiscible. The data in table 2.2 shows that similarly immiscibility is predicted from the tabulated values for PP/PMMA (\(X / X_c = 423\)) whereas PS/PMMA is a much less immiscible binary pair (\(X / X_c = 7.5\)).

Table 2.2 Flory Huggins interaction parameter values calculated for different binary blends of PP, PS and PMMA.

<table>
<thead>
<tr>
<th>Blend</th>
<th>(X_c) (from equation 2.4)</th>
<th>(X) (from equation 2.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/PS</td>
<td>0.0035</td>
<td>0.39</td>
</tr>
<tr>
<td>PP/PMMA</td>
<td>0.0015</td>
<td>0.635</td>
</tr>
<tr>
<td>PS/PMMA</td>
<td>0.0036</td>
<td>0.027</td>
</tr>
</tbody>
</table>
2.2.1 Polymer Processing Conditions

The properties of a multiphase blend are determined by the morphology formed during the mixing process [23]. This study utilises melt mixing, a process in which the main variables are mixing temperature, time and shear rate. Deciding on the processing temperature can be problematical when blending polymers with different processing temperatures and different structures (i.e. amorphous which must be processed above $T_g$ and semi-crystalline, which must be processed above $T_m$). Han [24] noted that at $T_g$ the viscosity of an amorphous thermoplastic polymer is very high and so it cannot be considered equivalent to the $T_m$ of a semi-crystalline polymer. It was shown that for plastication of amorphous polymers processing temperature should be $\geq 55 \, ^\circ C$ above $T_g$, termed the critical flow temperature, $T_{cf}$. Critical flow temperature can be used as the de facto melting temperature for amorphous polymers. A study of binary blends of amorphous and semi-crystalline polymers suggested that typically a co-continuous morphology was obtained the when processing temperature was near $T_g$ whereas a dispersed phase morphology was obtained when the processing temperature was near $T_{cf}$, at the same compositions.

The order of addition of the components to the mixer is also very important for morphology development specially when using a filler. The state at which the filler is added is also important from the filler distribution point of view. The typical procedure for melt mixing of blends is the simultaneous addition of all the polymers to the mixer. If a filler is subsequently added to the mixer with the polymers in the molten state then the distribution of filler is dependent on the nature of polymers involved, their viscosity ratios and interfacial tensions. On the other hand if the polymers and fillers are added simultaneously [25], if one of the polymer in the blend melts at a lower temperature the filler will distribute in that polymer and may not be able to travel to a preferred phase or
to the interface depending upon the mixing time. A third approach, that of first melt mixing with the polymer having a lesser affinity for the filler and subsequently adding the other polymer(s) to the mixer is also used in the melt mixing of multiphase polymer composites [25]. These techniques are used to tailor the morphology of the materials or to selectively localise the filler in a certain phase. For Example [26], Elias and co-workers, working on PP/PS composites with silica found the silica to have lower affinity for PP compared to PS. Thus, the silica was first mixed with PP and then PS was incorporated into the mixing chamber. Silica particles were seen in the PS phase by the end of mixing and showed that only a few minutes of mixing was sufficient for the silica to transfer from PP to PS.

A study on PS/PE composite with CB to study electrical percolation [27], showed the localisation of filler can affect the properties significantly. Four different CB composite systems were prepared over a range of CB concentrations with matrices of PS, PE, PS/PE (45/55 ratio) and PS/PE (45/55 ratio) but with CB localised at the interface, (achieved by melt mixing CB with PE followed by the addition of PS). In terms of conductivity, the PE matrix composite showed a lower percolation CB concentration than PS, attributed to its semi-crystalline structure. Whereas PE and PS polymers had percolation concentrations near 20 wt. % of CB, the in the PS/PE (45/55) blend composite percolation was achieved at 3 wt. %. This composite also showed a co-continuous morphology and a double percolation effect. The term double percolation describes the percolation of a blend phase extending throughout the material and conducting through the conductive network formed in this phase. It was suggested that a double percolation can also be created by the migration and interaction of filler with a preferred polymer phase, resulting in an increase in viscosity and ultimately formation of a co-continuous morphology at a lower concentration of dispersed phase. For the
fourth PE/PE composite with CB localised at the interface, percolation was achieved at 0.4 wt% of CB. However, the formation of a conductive network at the interface was dependent on the concentration of dispersed phase and the degree of crystallinity of the PE. If the concentration of the dispersed phase decreases, the co-continuous morphology will change to a droplet morphology, breaking up the conductive network.

### 2.2.2 Rheological Behaviour

In addition to the melt mixing process conditions, the morphology formed also depends on the rheological properties of the blend components, blend composition and interfacial tension between the phases[1]. The morphologies obtained from mixing of immiscible blends are the continuous-dispersed phase morphology and co-continuous morphology. It was proposed [28] that a co-continuous morphology can be transformed into droplet morphology by raising the mixing temperature and that the co-continuous morphology is transition morphology. It is normally observed that a co-continuous morphology is formed when the composition of the blend phases is approximately equal. Whereas when the compositions are very different a dispersed morphology is expected [6]. Dispersed phase morphology is normally formed when the minor phase has higher viscosity and the major phase, having a lower viscosity, forms the matrix. It has also been determined [28] that blend ratio governs the state of dispersion for asymmetric blends whereas viscosity ratio determines the state of dispersion for symmetric blends. Melt mixing of immiscible polymer blends is a complex process involving, melting of pellets, dispersive mixing, distributive mixing and droplet coalescence [29]. Pellet melting at high temperatures is followed by dispersive mixing in which the size of the dispersed phase is reduced (due to applied shear stresses). Initially a thin layer of molten dispersed phase is formed as pellets are
sheared against the internal surfaces of the mixer; this layer is unstable and due to interfacial instabilities develops holes and finally a lace like structure (Figure 2.3) which finally breaks up into droplets. Distributive mixing is the homogenisation of the dispersed phase within the matrix. In the presence of a compatibiliser a finer morphology is formed while the absence of compatibilisers results in the formation of a coarse morphology due to coalescence [29].

The droplet break up continues until the applied shear stresses ($\tau$) can no longer compete with the surface tension ($\sigma$) of the newly formed dispersed phase droplet of smaller radius ($R$).
These two stresses are related by a dimensionless number known as the capillary number (Ca), given by

\[ Ca = \frac{\tau}{\sigma} \]

Ca determines the stability of the droplet and whether it will disperse further or not. Droplet breakup (Figure 2.3) will occur if the value of Ca reaches a critical value, \( Ca_{\text{crit}} \), indicating that the value of \( \tau \) is high enough to compete with \( \sigma \). At \( Ca > Ca_{\text{crit}} \) the blend morphology is unstable as \( \tau \) is higher than \( \sigma \) and droplets are stretched into filaments by the shear fields. In the initial stages of the mixing \( Ca >> Ca_{\text{crit}} \), i.e. \( \tau \) values are much higher than \( \sigma \) values leading to the deformation of droplets into long filaments. As the mixing continues, Ca reduces due to the reduction in R with mixing time until at \( Ca \approx Ca_{\text{crit}} \) and \( \tau \) is of same order of magnitude as \( \sigma \). The rate of droplet deformation is dependent on the viscosity ratio of the blend components [29].

Han et al [28] studied the effects of viscosity ratios and processing time on the morphology development of immiscible blends. A schematic diagram of the

Figure 2.3 A schematic diagram of formation of PA6 droplet in PA6/PE binary blend showing Capillary instability growing in a molten PA6 thread in a PE matrix [22].
morphology development of a blend as a function of processing time is presented in Figure 2.4. The authors reported the diagram for two crystalline polymers. When using an amorphous polymer, $T_m$ has to be replaced by $T_{cf}$ of the amorphous polymer. Initially at temperatures high enough for melting of both the polymers a dispersed phase morphology is formed, if the viscosity of component B is lower and component B is not a major component in the blend. On the other hand, if the viscosity of the major component is less than the second polymer in the blend a transitional co-continuous morphology appears first and then changes to a dispersed phase morphology. If the mixing time is sufficiently short the co-continuous morphology can be retained.

![Figure 2.4 Schematic diagram of morphology development as a function of processing time, viscosity ratio and concentration ratios of blend phases in a binary polymer blend [21].](image)

2.3 Ternary polymer blends

Multiphase polymer blends may also exhibit a composite droplet morphology [1]. This term is used to describe a sub-inclusion within a droplet type morphology. For example, Figure 2.5 is an SEM of a HDPE/PS/PMMA 70/15/15 ternary polymer blend. The PS ‘shell’ around the PMMA dispersed phase has been removed by cyclohexane to enhance the contrast. Control of micro structure of multiphase blends is important as mechanical
properties are dictated by the morphology. Favis and co workers [31] working on HDPE/PS/PMMA ternary blends with HDPE as the matrix phase demonstrated that the morphology of the ternary blend can be controlled by altering the relative proportions of the dispersed phases (PS and PMMA). With 70% HDPE and 30% (PS+PMMA); PS was shown to reside at the interface of HDPE and PMMA and also resulted in a significant particle size reduction. It was suggested that increasing PS concentration reduced the interfacial tension and the matrix/dispersed phase viscosity ratio.

Figure 2.5 SEM of a HDPE/PS/PMMA 70/15/15 ternary polymer blend showing complex droplet morphology and encapsulation of PMMA by PS (PS has been removed by selective etching) [24].

Hobbs [32] studying a ternary blend of PMMA/PC/PBT, where PBT was the matrix and PMMA the main dispersed phase, found that PMMA was surrounded by PC. The same results were obtained when the PMMA/PC concentration was reversed emphasising that encapsulation is governed by interfacial tension and not by composition ratio.

The morphology development in a ternary polymer blend is influenced by the following factors: interfacial tension > viscosity ratio > shear stress [33]. Morphology can be predicted with the knowledge of interfacial tension [33, 34]. Hobbs and co workers while working on the effect of interfacial forces used spreading coefficients to predict
morphologies from rheological data [32]. They found that the morphologies predicted by the spreading coefficient equation (below) were in agreement with the experimental results.

\[
\lambda_{CB} = \gamma_{BA} - \gamma_{CA} - \gamma_{BC}
\]

Where: component A is the matrix and B and C are dispersed phases; \(\lambda_{CB}\) is the spreading coefficient of component C over B; \(\gamma_{BA}\) is the interfacial tension between B and A; \(\gamma_{CA}\) is the interfacial tension between C and A; and \(\gamma_{BC}\) is the interfacial tension between B and C. For the component C to spread over B (to encapsulate B) its spreading coefficient over B has to be positive (Figure 2.6). To obtain meaningful results from the equation it is suggested that the interfacial tensions of the polymer pairs be calculated with a great care. In addition, the interfacial tensions should measured/calculated at the processing temperature.

Hobbs et al. [32] tested their model successfully for several ternary and quaternary blends including PMMA, PS, PC, PBT and SAN. More recently Guo [35] and co-workers developed a new model for the prediction of morphology based on the interfacial tension data and called it the free energy model. For any type of morphology,

\[
G = \sum_i n_i u_i + \sum_{i\neq j} A_{ij} \alpha_{ij}
\]

where \(G\) is the Gibbs free energy, \(n\) is number of moles of component \(i\) and \(u\) is chemical potential of component \(i\), \(A\) is the interfacial area between \(i\) and \(j\), \(\alpha\) is the interfacial tension between the two phases. The first term is the same for all morphologies but the second term varies for different morphologies. The most stable morphology is the one with lowest free energy. It was found that viscosity and elasticity of the two minor phases also influence the morphology of ternary polymer blends [36]. It was later demonstrated [37] that the elasticity difference between the components under the condition of dynamic flow changes the interfacial tension and this interfacial
tension is different from that in the absence of flow. Reigner et al. modified the Guo [35] equation for free energy and introduced a term for dynamic interfacial tension.

\[ \lambda_{AB} > 0 \text{ or } \lambda_{AC} > 0 \]
\[ \lambda_{BC} < 0 \]
\[ \lambda_{CB} < 0 \]

**Figure 2.6** The schematic diagram of various possible morphologies of a ternary blend predicted by the spreading coefficient model.

In a study [33] on ternary blends of PMMA/PS/PP all the above models were tested. Polymers were blended in a matrix/ dispersed phase ratio of 80/20 wt. %. Having fixed the proportion of matrix the composition of the two dispersed phase components was varied and morphological predictions from the models were tested. Morphologies predicted by the surface tension model [33] were in agreement with experimental results for all the blends studied. While the dynamic model [33] could not explain the encapsulation of PP by PS when PMMA was the matrix and the free energy model failed to predict the encapsulation of PS by PMMA when PP was the matrix.

The high viscosities of polymers limit the number of methods available to determine the interfacial tension between the blend phases. In a comparative study [38] of different methods of measuring the interfacial tension it was concluded that rheological methods are less time consuming and have fewer experimental difficulties. Whilst investigating interfacial tension between polymer blends by rheology, Gramespacher and co-workers found that weighted relaxation spectra of polymer blends obtained by shear oscillations
of the blends show an additional peak which is characteristic of a relaxation time that can be correlated with the interfacial tension. The interfacial tensions obtained by this method were in good agreement with the values given in the literature [39].

2.4 Compatibilisation of polymer blends

The properties of immiscible polymer blends are dictated by their phase morphology and hence understanding and control of the morphology is vital. Typically, melt mixing of immiscible polymers results in blends which are mechanically weak, due to concentration of stress at the interface and weak coupling between the phases. This problem can be overcome by the addition of a third component known as a compatibiliser [40]. Typically, block and graft co-polymers are used as compatibilisers which behave as an emulsifier. These interfacial emulsifiers can also be generated in situ (reactive compatibilisation) during the blending process. The first method, physical compatibilisation, provides a better control over the compatibiliser but it is not always easy for a copolymer to reach the interface [41]. On the other hand in situ formation of compatibiliser by reactive compatibilisation is often difficult to control [42].

Due to the high interfacial tensions in immiscible blends, when they are removed from the mixer the dispersed domains will increase in size to decrease the interfacial area [40]. High interfacial tensions between the blend phases result in a coarse morphology. Generally these coarse morphologies are unstable and stress transfer between the phases is not uniform, resulting in mechanically weak material [36]. The final shape of the dispersed phase is the result of a dynamic equilibrium between the forces from the matrix (the shear stress and the elasticity of the matrix) and the resisting force (the elasticity of the droplet and the interfacial tension) [43]. Compatibilisers impart a finer morphology to an immiscible blend [41]. Finer morphologies are an indication of the lower interfacial tensions between the polymer phases [36]. Legros and co-workers [36]
reported *in situ* formation of a copolymer in Poly(butylene terephthalate) (PBT)/Polyethylene (PE) / Ethylene vinyl acetate (EVA) ternary blends and reported a finer morphology. Interfacial tension measurements confirmed a decrease in the tension between the phases. Scanning electron micrographs confirmed better adhesion between the phases.

![Figure 2.7 Compatibilisation effect of SBS addition on PP/PS 70/30 blend](image)

After compatibilisation with styrene-butadiene-styrene the mechanical properties of polystyrene (PS)/polypropylene (PP) blends were reported to be significantly increased [44]. Good adhesion between the phases can be seen in Figure 2.7.

Macosko et al [45] studied the evolution of the average diameter of (PMMA/PS/poly(S-b-MMA) diblock copolymer) blends as a function of the mixing residence time; 3 min. of mixing (at a maximum shear rate of ≈50 s⁻¹) was adequate to reach the final particle size. At shorter processing times coalescence occurred resulting in increased particle size. Addition of block co-polymers as compatibilisers resulted in stable morphology and prevented coalescence. When compatibilisers are added there is an increase in the energy required for coalescence due to steric interactions between the compatibiliser
and polymer [30]. Figure 2.8 is a schematic diagram of an immiscible polymer blend showing the presence of layers of copolymers at the interface. According to thermodynamic arguments, the block residing in the matrix phase is located outside the droplet as it is incompatible with the phase within the droplet, and can be imagined as the droplet enclosed in a shell of copolymer with the outer portion of shell consisting of matrix-compatible block segments [30]. The matrix fluid tries to drain out as the neighbouring droplets come close together to coalesce. The copolymer molecules do not allow this to occur due to steric repulsion between the matrix-compatible segments of copolymer coating the two droplets.

![Schematic diagram showing; segments of compatibiliser attached to both phases of immiscible polymer blend in the border region and inhibiting coalesces due to steric interactions][30]

The amount of copolymer is a governing factor, and should be sufficient to produce enough steric interactions in order to prevent coalescence [30].

Micro- and nano-sized solid particles have been shown to be effective in stabilising the morphology of immiscible emulsions [46]. These small particles diffuse to the interface of the immiscible polymers and inhibit coalescence [25]. In addition to stabilise the
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morphism these particles also reinforce the material [47]. There are many phenomena that can be involved in the morphology change due to compatibilisation of polymer blends by particles [25]. Firstly is the reduction in the interfacial energy resulting in formation of droplets of smaller size. The addition of filler creates another interface between the polymers and the filler and thus the resultant morphology is the balance of forces on all the interfaces [25]. Modifications or reduction in the interfacial tensions due to the presence of fillers changes the equilibrium and droplet breakup is favoured to achieve a new equilibrium state.

The presence of the filler particles around a dispersed phase droplet can inhibit coalescence by sterically restricting droplet-droplet interactions and hence can result in a finer and more stable morphology. This prevents the size increase of the droplet during melt mixing or subsequent moulding. A stable morphology is needed to ensure consistent properties of the material even if it is subjected to a subsequent processing step. For this purpose materials are sometimes annealed [25]. Annealing requires keeping the material at a higher temperature for several hours and cooling slowly. Gubbel et al studied the effect of annealing on a PS/PE 45/50 composite with CB [15]. It was reported that the morphology after annealing coarsened at 2 wt. % of CB but at 5 wt. % addition of CB there was no change in the domain sizes of the dispersed PS.

Introduction of carbon nanotubes (CNT) and other nanofillers have diversified this field of research. Polymer matrix based nanocomposites have become a very exciting field of research since nanofillers vary in their shape, structure, surface energy and their ability to exfoliate [48]. Recently the discovery of graphene has given a new direction to carbon reinforced nanomaterials [49]. When rigid fillers are added to a polymer, the modulus of the polymer is normally expected to rise. But the effect of compatibilisation
can be better understood by studying strength at break because it better reflects the adhesion between different phases. The effect of nanofillers on strength at break is seen to be opposite to that of the copolymers [50]. Normally a reduction in strength at break is reported in the literature at higher loadings of nanofillers [50]. The reason being that when copolymers are added to immiscible polymer blends they form covalent bonds between the phases, whereas addition of nanofillers does not result in covalent bond formation between filler and polymer and the adhesion between polymer and filler is not strong except if there is some strong interaction created between filler and polymers by surface modification of filler [50]. For example Young et al showed that the presence of a filler network resulted in a more toughened PP and its strength increased to 15 times that of pure PP but the elongation and stress at break decreased [50].

2.4.1 Electrically conductive polymer blends

In addition to compatibilisation, carbon particles like CB, CNT and GNP (graphite nanoplatelets) have excellent ability to conduct electricity and polymers containing these particles are used in many applications [9]. In comparison to a single polymer filled with carbon particles a multiphase polymer blend can potentially achieve percolation at lower concentration of carbon particles. In an ideal situation the carbon fillers reach the interface(s) of the immiscible polymers to lower the percolation threshold [46]. The affinity of carbon particles towards the dispersed phase sometimes result in the formation of a co-continuous structure for the dispersed phase polymer and a conductive network is formed within that co-continuous polymer phase.
This double percolation effect eases the formation of conductive network through the material [51] as shown in the Figure 2.9. CB, CNT and GNP are the carbon particles used in this research. A description of previous work using these particles follows.

**2.5 Carbon black polymer composites**

Carbon black (CB) is an amorphous form of carbon, formed by the incomplete combustion of aromatic hydrocarbons at high temperatures [52]. Carbon black can be prepared from aromatic oils such as coal tar or crude oil or natural gas, by processes of incomplete combustion and thermal degradation of hydrocarbons. Incomplete combustion of feedstock in the absence or limited amount of oxygen results in the formation of carbonaceous material. The common feedstock for CB production is oils rich in aromatics with high carbon to hydrogen ratio. Higher carbon to hydrogen ratio is desirable in the feed stock for the production of CB. CB formed by this process is
agglomerated and can have high or low structures. In order to control the aggregates formation potassium salt additives are added in the vapour state. The salt additives control the aggregation of CB. Primary particles formed fuse together to form aggregates [53] (Fig 2.10), which in turn form agglomerates due to van der Waals forces. The number of particles forming the aggregate and the size of the aggregate determine the structure of carbon black. If the primary aggregates are composed of many particles and there are considerable branches and chains the CB is referred to as a high structure carbon black, whereas CB with less particles in primary aggregates is called a low structure carbon black. Since the particles in high structure CB are closely packed their conductivity is higher compared to low.

Good distribution of the CB particles in the polymer matrix is important to form a conductive path [4]. During mixing the shearing forces act on the carbon black agglomerates to overcome the weak van der Waals forces and break them to smaller aggregates which are then distributed in the polymer matrix. But if carbon black is mixed for longer times the aggregates may separate, breaking the conductive path [54]. Thus, conductivity of CB filled composites increases during the initial stages of mixing up until a certain mixing time after which it drops [4, 55]. Cemberola [55] studied styrene butadiene rubber (SBR)/CB and reported that both the electrical and mechanical properties of the composites were influenced by mixing times; long mixing times also reduced the dynamic moduli of the composites and increased the electrical resistivity of the material due to loss of contacts between CB particles. However, even if moved apart, CB particles can still conduct by a tunnelling mechanism [56]. Increasing temperature in the composite can also increase the gap with in the CB particulates. Different grades of CB were studied by Sichel and co-workers [57] who reporting that the gap between the particulates increased due to thermal expansion of the polymer and when there was
no physical contact between the CB particles, they still conducted by tunnelling [57]. Percolation theory has been used to determine the critical filler content. The equation derived for the conductivity of the materials is as follows.

\[ \sigma(p) = \sigma_c (p - p_c)^t \text{ for } p > p_c \]

Where \( \sigma \) is the specific conductivity and \( \sigma_c \) is the proportionality constant, \( p \) is the filler loading (wt. %), and \( p_c \) is the filler loading at the onset of percolation threshold and is called the critical filler content (wt. %). The power constant \( t \) describes the dimensionality of the conductive network formed. It has been reported in the literature that a value of 1.33 depict the formation of a two dimensional conductive network whereas the value of \( t \) rises to 2.2 with the formation of a three dimensional conductive network [56]. Values of \( t \) deviated from the theoretical values for low structure CB whereas high structure CB composites showed values within the theoretical value range of 1.3-2.0. The deviation of the exponent \( t \) was due to the low structure of CB and the tunnelling mechanism for the electrical conductivity [56]. High structure CBs (Figure 2.10) have lower threshold concentrations [56].

![Transmission electron microscope image of CB showing agglomerates of high structure carbon black](image-url)

**Figure 2.10** Transmission electron microscope image of CB showing agglomerates of high structure carbon black [58].
In a work on interaction between polymer and CB, the effects of the addition of CB to a polypropylene (PP) matrix was studied [59]. Microscopic studies revealed good interaction between CB and PP which resulted in increased viscosity. Jean and co-workers [59] also observed increase in viscosity upon the addition of CB to ethylene co-ethylacrylate (EEA) and proposed that viscosity control is important for such systems as it determines the morphology and conductive structure.

Using CB to achieve conductive polymers usually needs large amounts of CB. This increased amount of filler reduces the mechanical properties. An alternative approach to obtain a conductive material with better mechanical properties is the use of immiscible polymer blends [60]. Tchoudakov and co-workers used Nylon and polypropylene (PP) with CB. CB was found to prefer the Nylon phase over PP and selective localisation of CB resulted in a lower amount of filler needed for the material to percolate giving less reduction in mechanical properties [60]. In the formation of the binary polymer blend-CB composites, CB may either have greater affinity for the dispersed phase or for the matrix. If the affinity for the dispersed phase is greater it can result in the elongation of dispersed phase domains as a result of viscosity increase due to polymer-CB interactions [61]. On the other hand if CB particles have higher affinity for the matrix phase, then the dispersed phase polymer acts like an excluded volume and a conductive network is formed at lower concentration [60]. In a semi-crystalline matrix CB particles will disperse in the amorphous phase only because during crystal growth the filler particles are excluded from the crystals. Hence an increase in degree of crystallinity is one of the ways to reduce the percolation concentration. A combination of these techniques can be used if ternary polymer-CB composites are prepared to further reduce the percolation threshold concentration.
The critical carbon content needed for percolation also depends on the surface tension between the polymer and the carbon particles. The effect of polymer structure on percolation concentration was studied by Miyasaka et al [62]. Linear polyethylene (LPE), branched polyethylene (BPE), isotactic polypropylene (iPP) and polystyrene (PS) were used in the study. The percolation concentration of CB increased with the increase in surface tension. In another study [62] on polypropylene (PP), Polycarbonate (PC) and co-polyamide 6/6-9, the percolation concentration was 2 and 4 phr for PP and PC, respectively, whereas for copolyamide 6/6-9 due to its higher surface tension it was 14 phr.

2.6 Polymer –nanotube composites

2.6.1 Introduction to carbon nanotubes

After the discovery of carbon nanotubes (CNTs) by Ijmia [63] a large volume of work on the structure and properties of CNT has been performed by researchers in various fields like materials, physics, electrical and mechanical engineering due to their remarkable physical and mechanical properties [63, 64]. A CNT with a single molecular layer is called a single walled carbon nanotube (SWCNT) and one consisting of multiple concentric layers is called a multi wall carbon nanotube (MWCNT). The adjacent layers of carbon atoms have intermediate distance of 0.34nm [63]. The cylindrical layers are joined by weak van der Waal forces. The carbon atoms in CNT are joined by covalent bonds due to which they have very high strength to weight ratio. This makes CNTs the ultimate carbon fibre [65]. Due to van der Waal interactions between nanotubes they normally form bundles.
2.6.2 Synthesis of CNT

CNTs are normally prepared by arc discharge, laser ablation or chemical vapour deposition (CVD) methods. In the arc discharge method an electric potential is applied across two graphite electrodes in an inert atmosphere, normally argon [63]. When the electrodes are brought closer, the anode starts to vaporise with a discharge [66] this results in the deposition of CNT on the cathode. In arc discharge method CNT production and structure are controlled by the potential difference applied across the electrodes. The thickness of tubes can be controlled by the addition of metal powder in the apparatus; this is normally done by drilling a hole in the anode and then filling it with metal. Usually Fe, Ni, Co, Pt, or binary combinations of these are used [66].

Laser ablation is a method of removing material from a solid using high intensity laser beams. Graphite is heated to high temperatures and is targeted by high energy laser beam in an inert atmosphere. 1200 °C temperature has been reported as the optimum temperature for the production of 300 nm length MWCNT with a thickness of 4-24 layers [67]. Argon is injected in the direction of laser beam in order to facilitate the collection of CNT by a collector towards the end of the laser chamber. Just like the arc discharge method, CNT produced by the laser ablation method are entangled. A graphite target is used for the preparation of MWCNT, and metal-graphite composite is used to prepare SWNT [67].

CVD is a method to produce high performance materials by vapour deposition. In a typical CVD method a substrate is exposed to a volatile material which deposits on the substrate to form the desired material [68]. In the CVD method the catalyst materials are heated to higher temperatures (500 °C-1200 °C). Hydrocarbon or carbon monoxide is passed through the catalyst in a furnace. The reaction time determines the length of
CNT formed. For all the CVD methods a catalyst is needed, as proposed by Baker [69] hydrocarbon is decomposed on the surface of the catalyst to give carbon and hydrogen. Carbon atoms diffuse through the catalyst and form tubes at the other end.

2.6.3 Structure of CNT

CNT behave differently when their hexagonal structure is oriented differently [70]. Three structures form on the base of orientation of the hexagonal carbon ring. Figure 2.11 is a plane graphene layer with dots representing carbon atoms. It can be seen from the image that if the green dot is rolled towards any of the red or blue a new structural arrangement of the atoms is formed although the original structure of the CNT remains cylindrical. Rolling towards red dots produces zigzag structure whereas rolling towards blue dots produces armchair structure.

![Figure 2.11 Different chiral structures of SWCNT formed by rolling graphene sheet in different ways [71].](image)

Rolling of graphene sheet towards any intermediate angles produces chiral structure of CNT. Different chiral forms of CNT show different behaviour, in particular chirality
influences the electrical properties. Graphite is considered as a semi metal but CNT have proven to behave like metals and semi conductors depending upon chirality [70].

2.6.4 Surface modification of CNT

The seamless arrangement of carbon atoms makes the surface of CNT quite unreactive, although different functional groups can be added to the surface of CNT to increase reactivity [72]. Normally these modifications are done on the tips to keep the structure of CNT unaffected [72]. Early work on CNT was on the oxidation of CNT at 700 °C in the presence of air for 10 min to produce hemispherical edges. These hemispherical caps are more reactive [73] than the walls of CNT. Later studies on the oxidations of CNT were performed in the presence of NO, NO₂, N₂O, O₃ and ClO₂ [74]. The presence of these gasses does not affect CNT but amorphous carbon impurities are susceptible to gas phase oxidation. Solution oxidation of CNT was performed by HNO₃ in 1994 [74], after which oxidising solutions mixtures such as HNO₃+H₂SO₄, HClO₄, H₂SO₄+K₂Cr₂O₇, H₂SO₄+KMnO₄ [75, 76] have been used. The degree of oxidation depends on the strength of the oxidising agent. Following oxidation by these solutions, groups like COOH, -CO, and OH become attached to the CNT. Solution oxidation is better than other oxidation methods [77]. Oxidation reaction of CNT with HNO₃+H₂SO₄ mixture is shown in Figure 2.12. Oxidation of CNT begins from the tips of CNT and the defect sites on the CNT. The reaction then moves gradually towards the inner graphitic layers, causing removal of outside layers and hence can result in thinner CNT. Once the COOH and OH groups are attached further functionalisation of CNT can be done as desired. Functional groups on the CNT can interact better with polymers and among themselves. Ring formation of CNT has been reported due to esterification reaction between COOH and OH groups present on the opposite ends of CNT [77]. Ultrasonication can enhance the oxidation reaction of CNT significantly by creating more defect sites on the surface of the CNT. These defect sites are further attacked by the oxidation chemicals resulting
in more functional groups attached to CNT than without ultra-sonication. Techniques like microwave irradiation and ball milling of CNT in the presence of acids have been reported to result in smaller length CNTs [77]. Acid treatment of CNT can also serve as a pre-processing technique in order to remove any impurity attached to the surface of CNT. These impurities can be amorphous carbon or catalyst attached to the surface during the process of removal of CNT from the furnace [78]. The presence of functional group on the surface of CNT also helps in distribution of CNT within solutions or polymer matrices [78].

2.6.5 Polymer-CNT nanocomposites processing

CNT can be melt mixed with polymers using conventional techniques. CNT when subject to melt mixing break less compared to carbon fibres [79]. Mixing at high shear helps in distribution of CNT within the matrix. Potschke et.al [80] reported an increase in the melt viscosity of MWCNT-polycarbonate (PC) composite during processing. This increase in viscosity was higher than that for CB due to the higher aspect ratio of CNT [80].

The strength of a CNT composite depends on good dispersion and efficient load transfer between CNT-polymer. When the interface is weak CNT behave as flaws in the material resulting in the stress concentration at that point and failure of material at lower
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stress [81]. Kuzmani et al [82] working on functionalisation of CNT found that functional groups attach to CNT by covalent bonds and that these functional groups modify the behaviour of CNT. $\pi - \pi$ interactions between the CNT and molecules of polymer have been reported to result in overlapping of CNT by the polymers matrix[72]. These attachments between CNT and matrix were found to be even stronger than conventional attachments by covalent bond [83]. Potschke et al. [84] used binary blends of PE/PC in order to form a conductive blend at lower concentration of MWCNT. Microscopy revealed the presence of MWNT at the interface between the blend. The percolation concentration of CNT decreased due to the formation of co-continuous dispersed phase giving a double percolation effect.

2.7 Polymer GNP composite

Graphite nanoplatelets (GNP) (also known as graphite nano sheets, graphite nanoflakes or exfoliated graphite) is a two dimensional graphitic material [85]. The stacked layers are bonded to each other by van der Waals forces with an interlayer distance of 0.34 nm [86], and a specific surface area of 2630-2965 m$^2$/g) [85]. The thickness and diameter of the GNP can be tuned by a variety of techniques, such as intercalation, oxidation, heat treatment, microwave irradiation and ultrasonic treatment [85].

The graphite crystal lattice consists of two dimensional single carbon atom graphene sheets with sp$^2$ hybridised carbon atoms bonded in a hexagonal ring. The adjacent graphene sheets are held together by weak van der Waals forces. Thus the graphene sheets can easily slide giving graphite a soft nature [87]. The ground state orbital configuration of carbon is 1s$^2$, 2s$^2$, 2p$^2$. The energy level gap between 2s and 2p orbitals lead electron to a vacant energy 2p orbital [87]. This energy promotion allows sp, sp$^2$, sp$^3$ configurations leading to different molecular structure formation. sp bonding
gives rise to chain structure, sp2 bonding represents planer structure and sp3 type of bonding is representative of tetrahedral structure [87]. Compared to other 2D fillers such as nanoclays, GNP s have superior thermal and electrical conductivity and lower density. Sp2 hybridised sheets of graphene have modulus of 1100 GPa [88]. Natural graphite is composed of layered sheets of carbon atoms attached by covalent bonds. These layers are joined by weak van der Waal forces [89].

2.7.1 Synthesis of GNP

Unlike other graphitic fillers like nanotubes which involve expensive apparatus and high energy consumption methods (chemical vapour deposition, arc discharge, laser ablation) [90] for their production, GNP s can be easily derived from any graphitic rich resource, making GNP a cost effective filler [85]. GNP can be synthesised by CVD and arc discharge method [91], but mechanical milling and graphite intercalation chemical approaches are preferred [92]. Mechanical milling breaks up the bulk graphite. The resulting GNP s are larger in size. The large sized particles are subjected to chemicals for graphite intercalation, typically H2SO4. Graphite layers are dipped in H2SO4 solution containing oxidisers such as nitric acid HNO3, H2O2, KMnO4, or O3 [93]. These graphite intercalate compounds are then heated to higher temperature (1000 °C) for 20-30 s, the heat produces large amount of gases like SO2 and H2O. These gases result in further expansion of the graphite [94]. The heat expansion can be performed in air or nitrogen atmosphere. Nitrogen atmosphere reduces the graphite oxide formation during acid intercalation [94]. Large volume materials of high exfoliation ratio have been obtained by microwave irradiation instead of heating [95]. Ultrasonication breaks down expanded graphite to GNP [94].
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The alkali metals are second choice to intercalate graphite, and potassium is usually used for this purpose [85] although caesium and sodium-potassium compounds are also sometimes used. Graphite intercalated compounds containing potassium are treated with aqueous exfoliating agents like water or alcohol [96] resulting in the generation of $\text{H}_2$ gas, which breaks down the van der Waals forces of graphite layers and separates them apart. In order to neutralise the pH, GNP are washed with water several times. Acid treated GNP can be further treated with alkali metals in order to get lower thickness of GNP by double intercalation and exfoliation [97].

2.7.2 Polymer-GNP composites

GNP polymer composites can be prepared by intercalation of monomers in graphite followed by *in situ* polymerisation. Due to limited spacing between graphene layers (0.335nm), and lack of functional groups on graphene surface and edges, pristine graphite has not been suitable for intercalation by *in situ* polymerisation [98]. Graphene oxide has been reported to be suitable for *in situ* polymerisation due to the presence of functional groups on the graphene sheet and higher interlayer spacing (0.61- 1.1nm) [99].

Solution mixing is another approach used to prepare polymers-GNP composites. But in both solution mixing and *in situ* polymerisation, GNP have been reported to be chemically or electrochemically reduced to graphite [99] before or after polymer addition. Separate preparation of GNP and melt mixing into polymers has been used to avoid such issues [99].

Electrical conductivity of GNP-PS composites has been reported to improve and the material behaves as an electrical semiconductor on addition of GNPs. A percolation
threshold value of 1.8 wt. % of GNP was reported [100]. Addition of GNPs to PP has been reported to impart better mechanical, thermal and electrical properties [101]. GNPs are also reported to give lower electrical resistivity compared to other carbon materials like carbon fibre and carbon black [102]. These properties combined with low cost, make GNPs useful in electromagnetic interference shields and thermal conductor applications [100]. Graphite is known for its excellent thermal and electrical conductivity [100], properties absent in clay-polymer nanocomposite materials, and as a result GNP based composites with epoxy resin showed improvements in these properties compared to clay based composites [103].
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2.8 References


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CHAPTER 3: Experimental

This chapter is divided into three main sections; i.e. materials, processing and characterisation. The first section describes the types of polymers and carbon particles used in this work: In the second section the processing methods employed for material preparation are described. The last section describes the techniques used for the characterisation of the materials: electron microscopy, differential scanning calorimetry, dynamic mechanical thermal analysis and electrical impedance testing being the main techniques used in this work. A brief account of the working principles and the purpose of using these techniques is also presented.

3.1 Materials

3.1.1 Polymers

Polypropylene (PP), polystyrene (PS) and poly(methyl methacrylate) (PMMA) were the polymers used in this work. For all the polymer blends Polypropylene (PP) was used as the matrix phase and two types of binary polymer blends were prepared with either PS or PMMA as the dispersed phase. Ternary polymer blends were composed of all three polymers. Blends with different volume ratios of these polymers were prepared and characterised. The grades of the polymers used in this study along with their supplier and melt flow indices are given in Table 3.1.
3.1.2 Carbon Black (CB)

The carbon black (CB) used was a high structure grade furnace black, Printex L, supplied by Degussa. The BET surface area for the CB particles was 150m$^2$/g. and the single particle diameter was 25 nm. Dibutyl phthalate absorption number (DBP) is used in the industry to measure the structure of CB by determining the amount of DBP a given mass of carbon black can absorb before reaching a specified viscous paste. The DBP structure measuring value of Printex L was 109-123ml / 100g.

3.1.3 Multiwall Carbon Nanotubes (MWCNT)

The grade of MWCNT used in this study was Nanocyl NC7000 grown via the catalytic carbon vapour deposition process (CVD). The primary use of NC7000 is in applications requiring low percolation threshold such as high performance electrostatic dissipative plastics. The average diameter of these MWCNT was 9.5 nm with an average length of 1.5 µm. Carbon purity of these CNT was 90 %, with the remaining 10% being metal oxides from the CVD process. The surface area of NC7000 was given as 250-300 m$^2$/g.

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**Table 3.1 Grades, suppliers and Properties of the polymers used in this study.**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Supplier</th>
<th>Grade</th>
<th>Melt Flow Index (g/10 min)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>Borealis</td>
<td>HD 601 CF</td>
<td>8 (230°C / 2.16 kg)</td>
<td>0.910</td>
</tr>
<tr>
<td>Poly(methyl Methacrylate)</td>
<td>Lucite</td>
<td>CP 75</td>
<td>3.4 (230°C / 3.5kg)</td>
<td>1.19</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Total Petrochemicals</td>
<td>PS 1540</td>
<td>12 (200°C / 5kg)</td>
<td>1.05</td>
</tr>
</tbody>
</table>
3.1.4 Graphite Nano platelets (GNP)

XG Sciences GNPs (also termed Graphene nanoplatelets, XGNP®) consist of thin stacks of graphene sheets. The GNP grade M particles are quoted by the manufacturer as having an average thickness of 6 nm and typical surface area of 120-150 m²/g, with the GNP-15 used in this work having an average particle diameter of 15 µm.

3.2 Processing

Polymers were melt mixed in a Haake Polydrive Torque Rheometer (Figure 3.1), which is a small batch-type internal mixer. It has a ram which can seal the material in the mixing chamber once the batch is loaded. Two roller rotors (Figure 3.1b) were used for melt mixing the materials.

All the materials were dried at 80°C for 24 hours in vacuum oven prior to melt blending to remove moisture. Polymers were pre mixed mechanically before loading into the mixer. The mixing chamber was heated to 200 °C and the roller speed was adjusted to 100 rpm before loading the batch. The mixing time was 10 minutes for all samples.

Figure 3.1 Haake Polydrive Torque Rheometer used in this work a) mixing chamber b) Roller rotors c) rotors fitted in the mixer.
3.2.1 Polymer Blends

Binary blends of PP/PS and PP/PMMA were prepared at 5, 10, 15 and 20 vol. % of the dispersed phase (based on the density data in Table 3.1). Ternary polymer blends of PP/PS/PMMA were prepared at 80/5/15, 80/10/10 and 80/15/05 vol. %.

3.2.2 Polymer Blend-CB Composites

PP/PS–CB and PP/PMMA-CB 80/20 vol % binary blend composite were prepared at 2, 5, 7 and 10 wt. % CB. For the ternary PP/PS/PMMA–CB blends the PP matrix phase was 80 vol % and the dispersed phase (PS+PMMA) was kept at 20 vol %. The ratio of PS and PMMA in the dispersed phases was varied. Ternary polymer blend composites of PP/PS/PMMA were prepared at 80/5/15, 80/10/10 and 80/15/05 vol % with 10 wt. % of CB.

3.2.3 Polymer Blend Carbon Nanocomposites

CNT and GNP were the two nano sized fillers used in this work. For the preparation of CNT composites the CNT were first functionalised and then subject to processing. CNT were refluxed in a 3:1 mixture of concentrated H₂SO₄ (Fisher Scientific) and HNO₃ (Fisher Scientific) at 120 °C for 3 hours, followed by a thorough wash with distilled water through 0.1 μm pore size filter paper (Anodisc 47, Whatman cat. No 6809-5012) until neutral pH of the filtrate was obtained. In order to mix acid treated CNT with PP, p-xylene (Sigma Aldrich) was used as a solvent to dissolve PP. 3g of PP was dissolved in 150 ml of xylene under reflux at 140 °C. In order to form a solution blend of PP-CNT, 3 mg of treated CNT were first stirred in 25ml of xylene at 140 °C for 2 hours by magnetic stirring. This xylene-CNT dispersion was then mixed with the refluxed PP solution at 140 °C with magnetic stirring for 1 hr. The PP-CNT blend was then
precipitated by drop-wise addition into excess (500 ml) of acetone. The sample powder were filtered out and washed thoroughly with acetone, and left overnight to dry in an oven at 80 °C.

The master batch of PP-CNT prepared by solution mixing was melt mixed with PS and PMMA using the Haake. Binary composites of PP/PS and PP/PMMA (both 80/20 vol %) with 0.5, 1, 2, and 5 wt % of CNT were prepared. PP/PS/PMMA 80/05/15, 80/10/10 and 80/15/05 (vol. %) ternary blend-CNT composites at 5wt % of CNT were also prepared.

Polymer-GNP composites were also prepared by melt mixing in the Haake. PP/PS and PP/PMMA 80/20 binary composites were prepared with 0.5,1,2 and 5 wt% of GNP.

The resultant blends and composites were subsequently compression moulded at 200 °C and 13 MPa pressure for 5 minutes to form 1.5mm thick sheets.

3.3 Methods of Characterisation

3.3.1 Microscopy

Microscopy is widely used to visualise the structure of materials. Micro- structural and nano-structural features can be visualised using high power microscopes. In this work optical microscopy (OM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) have been used. A brief account of each technique follows.

3.3.1.1 Optical Microscopy (OM)

An optical microscope uses visible light to magnify the images of samples. OM can be operated in reflective or transmission mode, and polarized light can be used to examine
specimens which exhibit optical anisotropy. This optical anisotropy arises when a material transmits or reflects light with different velocities in different directions [2]. The differences in the resultant light can be detected by a filter called an analyser. Both the analyser and polariser are at a different orientation to each other and allow only plane-polarised light to be transmitted [3]. An isotropic material cannot change the plane orientation of the polarizing light so when polarised light leaves the material and enters the analyser in a cross position it is cancelled out.

The effects of addition of the amorphous dispersed phases (PS, PMMA) on the crystal size of PP were studied using OM under polarised light. Both reflective and transmission OM was performed using an Olympus TH\textsubscript{3} and an Olympus PX41 microscope respectively. In transmission OM; samples were analysed using both normal and polarized light. Plane polarized light was used to observe PP spherulites in the polymer blends.

Samples for transmission optical microscopy were prepared by embedding a strip of a polymer blends, cut from a compression moulded sheet (1.5mm thickness), in beam capsule moulds filled with epoxy resin. 10 ml of epoxy resin was mixed with 6 drops of hardener for 5 minutes. The mixture was then poured in the beam capsule moulds containing sample strips and allowed to cure at room temperature for 24 hours. Epoxy was only used as a support to facilitate the mounting of samples on a Leica Ultracut E microtome and hence facilitate the cutting process. Small sections of thickness greater than 1 micron were cut using a glass knife on the microtome. The cut sample was then placed on glass slide and covered with a borosilicate glass cover slip of 0.85mm thickness. Parmount solution (Agar Scientific) was used to attach the slide and cover slip, which was left at room temperature for 30 min to allow the solution to dry. For
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Reflective mode OM, samples were prepared by cryogenic fracture under liquid nitrogen and then supported on the glass slide by double sided tape to be viewed under the microscope.

3.3.1.2 Scanning Electron Microscopy (SEM)

SEM is a technique that produces an image of a specimen by scanning an electron beam over its surface. The high power electron beam interacts with the specimen and penetrates to a certain depth, dependent on the accelerating voltage and the specimen nature. These interactions between the beam and the specimen generate secondary electrons (SE), backscattered electrons (BSE), X-rays and cathodoluminescence (CL). BSE are incident electrons which are scattered by the atoms in the specimen whereas SE are the electrons ejected from atoms within the specimen [2]. BSE retain 60-80% of the energy of the incident electrons and are deflected to higher angles whereas SE are low energy electrons and are scattered to lower angles [4]. SE are useful in getting surface topographic contrast whereas BSE are useful in getting elemental composition contrast. X-rays, which are produced by the interaction of electrons with the specimen, may also be detected in an SEM equipped with a X-ray detector. Cathodoluminescence (CL) is the emission of light when atoms excited by high-energy electrons return to their ground state [5]. In the SEM, CL detectors either collect all light emitted by the specimen or can analyse the wavelengths emitted by the specimen and display an image. SE imaging mode was used in this work.

Samples of polymer blends and blend composites were cryogenically fractured from liquid nitrogen. To improve contrast, the samples were etched with either cyclohexane (Fisher Scientific) or acetic acid (Fisher Scientific) for selective extraction of PS or PMMA, respectively. The samples were mounted on 0.5” pin stubs (Agar Scientific)
using carbon adhesive tape (Agar Scientific). Their surface was then coated with gold using an Edward S150B sputter coater, to prevent charging during SEM.

Samples were viewed using a Carl Zeiss EV060 variable pressure SEM (VPSEM) using a 5 KV accelerating voltage for polymer blends and 20 KV for polymer blend composites. A VPSEM is like a conventional SEM but it has an advantage that pressure in the chamber can be adjusted which is useful in removing the "electron charging" artefact from images. These charging artefacts are the result of electrons from the electron beam building up on a nonconductive sample. The extra electrons then jump from the sample unpredictably, causing lines and streaks on the image. Alternatively the unpredictable electron discharge repels the beam, causing jumps in the image or the appearance of black patches [5]. Quantitative analysis of the images was performed using Image J software.

3.3.1.3 Transmission Electron Microscopy

A transmission electron microscope generates images with much higher magnification and resolution than OM or SEM. TEM was used as a complementary technique to SEM to observe the morphologies of the polymer blends and composites. The dispersion of the particulates, and their preference of a particular phase over another, were both established by TEM. The optics of TEM are approximately same as those of a light microscope i.e. light source, condenser lens, specimen stage, objective lens and projector lens (Figure 3.2). In a TEM an electron beam is used instead of visible light and glass lenses which are used for visible light are replaced by electromagnetic lenses.
TEM was performed using a Philips CM200 at a 200 kV accelerating voltage. In the CM200 the electron beam is produced by a field emission gun. An accelerating voltage is applied across the microscope to direct the electrons towards the specimen. The lenses are electromagnets, and by varying the current to these the strength of the magnetic field changes which acts as a lens with varying focusing power. The beam of electrons makes its path following right hand rule passing through the field. Condenser lenses (figure 3.2) are used to vary the strength of illumination in the image. In high resolution microscopes two condenser lenses are used. A single condenser lens illuminates a greater area of the sample, when required. Two condenser lenses control the beam very well and the diameter of the focused beam is reduced thus helping in preventing damage to the specimen [1]. The specimen holder containing a specimen grid is mounted into the stage, which supports the specimen grid. Following the stage

Figure 3.2 Schematic diagram of a TEM optics showing lens arrangements [1].
are the magnifying lenses (objective lens, intermediate lens, projector lens). The projector lenses are used to enhance the magnification of the image [2, 6].

Strips of polymer blends and blend composites embedded in epoxy resin were prepared in the same manner as described in the OM section. A glass knife was used to expose a sample strip by removing the cured epoxy from the sample surface using a Leica Ultracut E microtome at room temperature. A diamond knife was then used to cut sections of approximately 70 nm thickness which were collected on 300 mesh copper grids.

3.3.2 Differential Scanning Calorimetry (DSC)

DSC is a technique which measures the difference in heat flow to a sample and to an inert reference whilst they are subjected to a controlled temperature programme in a controlled environment. The two common types of DSC are power-compensation (PC) and heat-flux (HF) [7, 8]. In PC- DSC there are separate chambers for the sample and the reference pan, and both has its own heating elements to control the temperature [2]. When a temperature difference occurs between the two chambers during the thermal programme the amount of power needed to compensate for that difference also changes, which is equal to the amount of heat flow needed to maintain the same temperature in the two chambers [9]. HF-DSC was used in this work, and this technique measures the temperature difference between the sample and reference placed in the same heating chamber. Both the sample and reference are heated or cooled at a constant rate. When the sample undergoes any exothermic or endothermic transition the temperature difference is converted to equivalent heat flow.
For the homopolymers, polymer blends and blend composites DSC was used to study the crystalline melting and crystallisation transitions of the PP matrix. DSC was carried out under a nitrogen atmosphere on a TA Instruments DSC Q100 fitted with a RCS cooling system. Hermetic aluminium pans and lids were used to seal the samples (approximately 7-10mg) and a sealed empty pan was used as the reference. A heat/cool/heat programme was used to give data for two heating runs and one cooling run. For the first heating run samples were first cooled to -25 °C and then heated to 180 °C at a heating rate of 10 °C /min. To erase their thermal history samples were kept at 180 °C for 5 minutes and then cooled to -25 °C at 3 °C /min for the cooling run. Finally the second heating run was recorded during heating the sample from -25 °C to 180 °C at 10 °C /min.

3.3.3 Dynamic Mechanical Thermal Analysis (DMTA)

As polymers are viscoelastic materials their mechanical behaviour exhibits both solid and liquid-like properties, which are readily studied using DMTA [9]. In DMTA a controlled cyclic strain is imposed on a specimen and its stress response is measured, or vice-versa. In DMTA, when an oscillatory sinusoidal stress is applied to a perfectly elastic material the resulting strain is also sinusoidal and is in-phase and proportional to the stress. On the other hand when stress is applied to viscoelastic materials, like polymers, the resulting strain is out-of-phase. This phase lag is due to the time needed for molecular chains to rearrange and is associated with relaxation phenomena. Thus DMTA is used to study molecular relaxations as well as the inherent thermo-mechanical properties of polymers [9].

The ratio of stress to strain is known as the modulus (E). In DMTA data is sometimes represented in terms of complex modulus (E*) given by
\[ E^* = E' + iE'' \]

Where \( E' \) is the storage modulus, a measure of the elastic characteristic or solid nature of the material; \( E'' \) is the loss modulus, a measure of the liquid-like or viscous characteristic of a material. The larger the value of \( E' \) relative to \( E'' \) means that more of the energy required to deform a sample is elastically recoverable (stored) rather than viscously dissipated as heat. Physically the storage modulus is related to the stiffness of a material whereas the loss modulus is its damping capacity [9].

The ratio of loss modulus to storage modulus is known as the material loss factor, loss tangent or \( \tan \delta \) and represents the energy dissipated in the sample during one cycle of deformation.

The dynamic mechanical properties of the polymer blends and composites were studied using a TA Instruments Q800 DMA, in single cantilever beam mode (Figure 3.3). Samples were tested over a temperature range of -25 °C to 180 °C at a heating rate of 3 °C/min and 1 Hz frequency. A single cantilever clamp with a clamping distance of 10 mm was used which was calibrated with a steel bar before testing. The specimens were
cut from 2mm thick compression moulded sheets of the materials with dimensions of 20 x 10 x 2 mm (L x W x T). The sides of the specimens were ground using grade 600 silicon carbide grinding paper on a Buehler Metaser Universal polisher in order to keep the sample width uniform.

3.3.4 Wide-Angle X-ray diffraction (WAXD)

WAXD is a non-destructive analytical technique used to obtain information about the crystallographic structure of materials by analysing information from the intensity of an X-ray beam scattered from a sample. The X-ray beam is produced by an X-ray tube and passes through a slit which collimates the X-ray beam. The diverging beam then strikes the sample and is diffracted from the crystal planes of the specimen and enters the detector.

Polymers often undergo changes in their crystal phases due to the effects of filler addition [10, 11], and WAXD can identify these changes. In this work WAXD was used to identify any effects of the addition of CB, CNT and GNP on the crystal structure of PP in the blend composites.

Specimens for XRD were obtained by cutting a square sample of 25 x 25 mm from compression moulded sheets. XRD patterns were obtained using a Philips X’Pert MPD X-ray generator using Cu- Kα (λ = 0.1541 nm) anode and X-ray tube working at 40 mA and 50kV. In order to record diffracted beam from a wide range of angles, the sensor was rotated through angles from 5° to 85°. The data were collected in θ – 2θ mode using a step size of 0.05° and a counting time of 4.5 s
3.3.5 Electrical Impedance Spectroscopy

Electrical impedance spectroscopy (EIS) is a powerful tool in characterising the electrical properties of materials. In EIS an electrical stimulus (current or voltage) is applied to the material and its response (current or voltage) is measured. When electrical current is applied to a material it leads to an overall response which involves the flow of electric charge throughout the material, the rate of which depends on the electrical resistances within the material [12]. In this work conductive fillers (CB, CNT and GNP) are used to make the insulating polymer materials more conductive. The strength of the measured electrical response depends upon the conductivity of these fillers and the phase boundaries present within the material.

There are three common methods for measuring the impedance of the material: Firstly a step signal of voltage is applied and the time varying current is measured; secondly a voltage signal composed of random noise is applied and the resulting current is measured; thirdly a single frequency signal of current or voltage is applied and the phase shift and difference in amplitude of the real and imaginary parts of the current are measured. Of all these methods, the third approach is most common and was used in this work [12].

Electrical impedance measurements were made using a Numetriq PSM1735 Transimpedance Amplifier. Square plates of 25 mm and 1mm thickness were cut from compression moulded sheets, polished and then coated with silver paint. Silver loaded epoxy adhesive (RS components) was used to attach the copper wires to the samples. a shunt resistance of 5 Ω (OHM) was applied in parallel to the circuit. For all the composite materials, the response to the voltage signal was tested over a frequency range of 1 Hz to 1 MHz.
3.3.6 Fourier Transform Infrared Spectroscopy (FTIR)

A Nicolet 5700 FTIR spectrometer was used to identify the functional groups attached to the CNT following the acid treatment (described in section 3.3.3). When the material is subjected to infrared (IR) radiation, some of the radiation is absorbed and some is transmitted through the sample. The resultant spectrum—the ‘fingerprint’ of the sample and represents the molecular absorption and transmission of IR. Samples for FTIR were prepared by mixing dried functionalised-CNT (f-CNT) with dried (130 °C for 3 hrs) KBr in a 5/95 wt % ratio. FTIR spectra were taken from 600-2200 cm\(^{-1}\) wave number.

3.3.7 Rheological measurements

A Rheometric Scientific RMS800 dynamic rheometer was used for rheological measurements of the materials. In order to determine the linear viscoelastic regions of the materials, strain sweeps were performed at 200 °C and 1 Hz frequency over a range of 1-1000% strain. A 25mm diameter parallel plate configuration with a constant gap of 0.25mm at 200 °C was used. Dynamic frequency sweeps were carried out at a constant amplitude of 5 % strain. The dynamic shear moduli of the materials as a function of frequency, ranging from 0.1-10 rad./s for the blends were studied.
Chapter 3: Experimental

3.4 References


Chapter 4: Results and Discussion -

Homopolymers, Binary and Ternary Polymer Blends

4.1 Introduction

This chapter deals with the characterisation of the homopolymers and the binary and ternary polymer blends. DSC, DMTA, optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were the main techniques used to characterise the blends.

4.2 Characterisation of Homopolymers

DSC and DMTA were used to characterise the homopolymers to determine glass transition temperatures (T_g) and crystalline melting temperatures (T_m). The data are given in Table 4.1 and plotted in Figures 4.1 and 4.2. It was noted that T_g values obtained from DSC and DMTA are different. Generally values obtained by DSC are slightly lower than those obtained by DMTA due to differences in the measurement methods of both the instruments [1].

The most popular method to determine values of T_g is DMTA which also identifies other relaxations associated with polymer chains and side groups [1]. For example, the beta transition associated with PMMA was seen using DMTA whereas nothing was observed using DSC. Figure 4.2 shows tan delta data for the homopolymers; the peaks seen are the glass transitions of PS and PMMA.
Figure 4.1 DSC curves for homopolymers; a) heating cycle showing peaks at \( T_g \), \( T_m \) b) crystallisation exotherm peak at \( T_c \) of PP.

Figure 4.2b shows the damping behaviour of the homopolymers over the temperature range -25 to +55 °C. This beta transition is responsible for the toughness of PMMA [2]. A peak for the \( T_g \) of PP was also shown by DMTA due to its semi-crystalline nature whereas in DSC no glass transition was observed.
Figure 4.2 Tan delta measurements for homopolymers; a) full scale showing $T_g$ peaks for PS and PMMA b) data for temperature range -25 to +55 °C to show $T_g$ peak for PP.
Han and co-workers [3] proposed that at $T_g$ the viscosity of an amorphous polymer is very high, such that the melt processing temperature should be at least 55 °C above their $T_g$. Thus, using the $T_g$ values obtained by DMTA and following the guidance given by Han et.al [3] the blending temperature for the Haake was determined to be 200 °C.

4.3 Characterisation of Binary Polymer Blends

4.3.1 Optical Microscopy (OM)

Transmission OM has been used widely by researchers [4] to study the crystallisation of PP. As the matrix phase of all the blends in this study is PP the crystal structure of PP in the binary and ternary blends was studied using transmission OM under both normal and cross-polarised light. Figure 4.3a show an image of the binary PP/PS blend under normal light, showing the dispersed PS droplet type morphology. When the same sample is observed under crossed polarisers (Figure 4.3b), crystallites are observed in the semi-crystalline PP matrix.
Chapter 4: Homopolymers, Binary and Ternary Polymer Blends

Figure 4.3 Transmission optical microscopy image of PP/PS 80/20 blend under a) normal light and b) polarised light showing spherulites of PP.

As is obvious from these images, the polymers forming the dispersed phase structure are not easily identified in transmission OM images, for detailed study of the morphology SEM and TEM were performed.

4.3.2 Scanning Electron Microscopy (SEM)

The morphologies of the binary and ternary blends were studied using electron microscopy. To increase the contrast between the phases the binary blends were etched with selective solvents. Acetic acid and cyclohexane have been used by many researchers to selectively etch PMMA and PS, respectively [5-7]. Binary blends of PP/PS 80/20 and PMMA/PS 80/20 were etched with both solvents to study their effects on all of the polymers used in the blends. From Figure 4.4 it is obvious that cyclohexane only removed PS whereas acetic acid only etched PMMA.
Figure 4.4 SEM images of selective etching by different solvents: i) PP/PMMA 80/20 blend; a) unetched b) cyclohexane etched c) acetic acid etched. ii) PP/PS 80/20 blend; d) unetched e) cyclohexane etched f) acetic acid etched.

In the images in Figure 4.4 the spherical particles of the dispersed phase can be seen to be lying loose on the surface; evidence of poor interfacial bonding in both types of blends [8]. It has been shown in many studies that the dispersed phase droplet size reduces and that particles are bonded more strongly after compatibilisation between the different phases (e.g. see [9, 10]). The coarse morphologies exhibited by uncompatibilised blends also result in reduced mechanical properties due to poor interfacial adhesion [11]. The average domain diameter as measured by Image J

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software for PP/PS 80/20 blends is $3.69 \mu m$ and that of PP/PMMA 80/20 droplets is $10 \mu m$. During melt blending the dispersive mixing of immiscible polymers will continue until the shear forces deforming the larger dispersed phase droplets to form smaller droplets can no longer overcome the surface tensions of newly formed smaller droplet [12]. The dispersed phase domains tend to reduce their surface area to volume ratio by adopting spherical shapes. Thus bigger spherical domains are indicative of higher surface tensions in the PP/PMMA blends than in the PP/PS blends.

4.3.3 DMTA of Binary Blends

Figure 4.5 shows the dynamic storage modulus of the binary blends. The storage moduli of the binary blends decrease with the increase in the fraction of dispersed phase. Markku and co-workers [13] working on PP blends reported the same decrease in the modulus of blends which then changed to an increase with the addition of compatibilising agents. Stricker and co-workers [11] reported similar results with uncompatibilised and compatibilised blends. The $T_g$ for the dispersed phases of PMMA and PS can be seen at 130 °C and 112 °C respectively. These transitions can be seen more clearly in the tan delta curves in Figure 4.6. The first peak at $\approx 7 °C$ is the $T_g$ of PP. The intensity of this peak increases with the level of PP. The presence of a second peak in both Figures 4.6 a) and b) confirms the presence of a second immiscible phase in these binary blends. Peaks at temperatures 130 °C and 112 °C correspond to $T_g$ for PMMA and PS respectively. The width and height of these $T_g$ peaks increase with the increase in concentration of the dispersed phase. For ease in distinguishing the peaks in ternary blends a level of 20 % of the dispersed phase was selected to be used in ternary blends and composites.
Figure 4.5 Dynamic storage modulus of; a) PP/PMMA b) PP/PS binary blends at various compositions of dispersed phase showing a decrease in dynamic moduli by increase in the dispersed phase vol %. 
Figure 4.6 Tan delta versus temperature for a) PP/PMMA b) PP/PS binary blends at various compositions of the dispersed phase. Blends being immiscible show individual $T_g$ peak for each polymer phase.
4.4 Ternary Polymer Blends

4.4.1 Morphology Development

More complex morphologies can be formed in ternary blends and these morphologies can be predicted using the spreading coefficient model [14-16] discussed in chapter 2. Using interfacial tension data for PS/PP, PP/PMMA and PS/PMMA blends from Zhang et al [17] and that for PP/PS, PMMA/PP and PMMA/PS from Valera et al [7], the phase morphology was predicted by the spreading coefficient model. Interfacial tensions and spreading coefficients calculated are given in table 4.2. Spreading coefficient calculations are given in Appendix-1.

Table 4.2 Interfacial tension data and spreading coefficients of binary polymer blends.

<table>
<thead>
<tr>
<th>Polymer blends</th>
<th>Interfacial Tension $\gamma$ (mN/m)</th>
<th>Spreading coefficient $\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/PS</td>
<td>5</td>
<td>-6.52</td>
</tr>
<tr>
<td>PS/PP</td>
<td>3.61</td>
<td>-2.78</td>
</tr>
<tr>
<td>PP/PMMA</td>
<td>4.31</td>
<td>-11.6</td>
</tr>
<tr>
<td>PMMA/PP</td>
<td>7.7</td>
<td>-0.32</td>
</tr>
<tr>
<td>PMMA/PS</td>
<td>1.01</td>
<td>-2.79</td>
</tr>
<tr>
<td>PS/PMMA</td>
<td>2.09</td>
<td>3.08</td>
</tr>
</tbody>
</table>

The value of spreading coefficient was positive only for the PS/PMMA binary blend. This positive value suggests the spreading of a PS shell over a core of PMMA. The values of spreading coefficient for all the other binary phases were negative; hence there is only predicted a tendency for PS to encapsulate the PMMA phase.
The $\delta$ values given in table 2.1 can also give an idea of complex morphology e.g. in the ternary blend of PP/PS/PMMA it may be suggested that the binary pairs of PS/PMMA and PP/PS are more likely to have a common interface between them and that an interface between PP/PMMA is less likely to form as the $\delta$ value difference between PP and PMMA is more than that between PS/PMMA and PP/PS. This suggests a composite droplet morphology in PP/PS/PMMA blends with PS encapsulating PMMA. These prediction were checked by both SEM (Figure 4.7) and TEM (Figure 4.8) imaging of the ternary blends. Figure 4.7 shows SEM micrographs of unetched and cyclohexane-etched ternary polymer blends. Voids around the PMMA phase are seen after etching the ternary blend with cyclohexane. Cyclohexane etching removes the PS (Figure 4.4) and exposes the PMMA core sitting in the void. This strongly suggests the encapsulation of PMMA by PS in agreement with the prediction from the spreading coefficient model. Similar agreements have been reported by Valera et.al [7] working on ternary blends of PP/PS/PMMA with varying PS/PMMA ratios in a 20% (PS+PMMA) dispersed phase. At higher volume (10, 15 %) of PS in the ternary blends all the PMMA droplets were encapsulated by PS [7] and similar results are presented in Figure 4.7 (a,b). At 10 vol % of PMMA, multiple droplet encapsulation occurs (Figure 4.7 b) due to the increased amount of PMMA to be encapsulated by PS. The TEM image in Figure 4.8 confirms the formation of a composite (core-shell) droplet morphology. Identification of the different phases in Figure 4.8 was done on the basis of spreading coefficient model predictions and SEM micrographs of the cyclohexane etched ternary blends in Figure 4.7.

When the PMMA is 75% of the dispersed phase (Figure 4.7c) PS still encapsulated the PMMA, but due to smaller amount of PS the voids representing etched PS are smaller than those for higher PS concentrations (Figure 4.7 a, b) and due to insufficient amount
Chapter 4: Homopolymers, Binary and Ternary Polymer Blends

Figure 4.7 SEM images of PP/PS/PMMA: a) 80/15/05 b) 80/10/10 c) 80/05/15 ternary blend showing encapsulation of PMMA by PS in a complex droplet type morphology.
of PS available to encapsulate PMMA some non-encapsulated PMMA droplets were reported [17]. This shows that the encapsulation of PMMA by PS is governed by the interfacial tension between the PS and PMMA and not by the composition of the dispersed phase [17]. More images of ternary polymer blends at different magnifications are presented in Appendix-2.
4.4.2 DMTA

Dynamic storage moduli of the binary and ternary polymer blends of PP/PS/PMMA at 25 °C are plotted in Figure 4.9. At 20 vol% of PS (i.e. with no PMMA) the elastic modulus of the materials is lowest of all the blends presented (Figure 4.9) indicating highly immiscible behaviour in these blends. The higher elastic modulus of the PP/PMMA 80/20 blends is an indication of lower immiscibility than in the PP/PS blends. These moduli (Figure 4.9) as a ratio against the dynamic modulus of PP at 25 °C are given in Table 4.3. The PP/PMMA 80/20 blend shows a decrease of 25 % compared to the modulus of pure PP matrix, while the modulus of PP/PS is 60% of that of PP. Ternary blends show improved moduli as shown in Figure 4.9 with the addition of PMMA and thus we can say the properties are governed by the concentration of dispersed phases in the ternary blends. Tan delta analysis (Figure 4.10) of the blends revealed multiple peaks, corresponding to the $T_g$ values of the components; the agreement with values for the homopolymers shows the immiscibility of the blends.

![Figure 4.9 Dynamic storage moduli of PP 80/(PS + PMMA)20 ternary blends at various concentrations of PS; moduli decreases at higher concentration of PS.](image-url)
With the addition of a third component to the binary blends a shift in the higher temperature $T_g$ peaks for the dispersed phase is observed (data given in Table 4.3). Thus, when PMMA was added to the binary blend of PP/PS 80/20, PS encapsulated the PMMA in these ternary blends which resulted in a shift in the peak for the $T_g$ of PS towards that of PMMA. The width of the tan $\delta$ peaks also increased due to the presence of core-shell phases in the blend. The increase in width of the peak at 5 and 10 wt% of PMMA is very small as compared to 15 wt% PMMA. At 15 % there was less encapsulation of PMMA by PS and PMMA was also present in a discrete dispersed form.

![Figure 4.10 Tan delta data for binary and ternary immiscible polymer blends; in ternary blends $T_g$ of the dispersed phase shifts towards that of the higher concentration dispersed phase (PS+PMMA).](image-url)
4.4.3 Rheometry

The rheological behaviour of polymer blends helps provide an understanding about structure development in polymer blends. The dynamic shear moduli for the binary and ternary blends were measured by dynamic shear rheometry. Initially strain sweep tests were performed in order to determine the linear viscoelastic region (LVR) for the binary and ternary blends (Figure 4.11). All the binary and ternary blends exhibit two regions (Figure 4.11). Firstly, a region at lower strain where shear modulus (G’) is independent of strain, known as linear (Newtonian) viscoelastic region (LVR); and secondly a region where G’ is dependent on the strain, i.e. a non-linear (non-Newtonian) region. From the Figure 4.11 it is obvious that addition of PS and PMMA dispersed phases does not have any effect on the LVR of the PP matrix. While the shear modulus of the blends is lower than pure PP.

### Table 4.3 Dynamic moduli and $T_g$ of binary and ternary polymer blends.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Modulus / Modulus of PP at 25 °C</th>
<th>$T_g$ of dispersed phase (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP80PMMA20</td>
<td>0.76 ± 0.19</td>
<td>111.6 ± 0.5</td>
</tr>
<tr>
<td>PP80PS05PMMA15</td>
<td>0.73 ± 0.11</td>
<td>113.7 ± 0.9</td>
</tr>
<tr>
<td>PP80PS10PMMA10</td>
<td>0.66 ± 0.10</td>
<td>115.8 ± 0.6</td>
</tr>
<tr>
<td>PP80PS15PMMA05</td>
<td>0.63 ± 0.09</td>
<td>123.1 ± 0.7</td>
</tr>
<tr>
<td>PP80PS20</td>
<td>0.60 ± 0.15</td>
<td>130.4 ± 0.3</td>
</tr>
</tbody>
</table>
Figure 4.11 Dynamic shear storage moduli as a function of strain at 200 °C for binary and ternary polymer blends; Neat polymers have higher moduli than their blends.

Figure 4.12 Frequency sweep data for homopolymers and ternary polymer blends; polymer blends have lower moduli than neat polymer due to immiscibility in polymer blends.
The storage modulus in Figure 4.12 of all materials increased with increasing frequency. These frequency scans are useful in investigating time-dependent shear behaviour of polymers. The storage moduli of the dispersed phase components i.e. PS and PMMA were found to be higher than that of the PP matrix. Thus as a result of blending PS and PMMA with PP, the modulus of the resulting blend should be higher than that of PP, whereas a decrease was observed (Figure 4.12). The modulus of the binary PP/PS 80/20 blend is lower than that for the PP/PMMA 80/20 blend. This behaviour is suggestive of highly immiscible polymers with thin, weak interfaces. A study [18] of the compatibilisation of PP/PS blend suggested that the incompatibility and higher interfacial tensions were the major cause of decreased storage modulus observed in their polymer blends. This was supported by the fact that higher moduli were observed with the addition of a compatibiliser.

For the ternary blends containing both PS and PMMA as dispersed phase, the modulus values are lower than the homopolymer but are between the range of moduli for binary polymer blends of PS and PMMA. Therefore in the ternary blends the composition of the dispersed phase governs the properties of the blend; e.g. for PP/PS/PMMA 80/15/05 the modulus is close to the modulus of the PP/PS 80/20 blend but for PP/PS/PMMA 80/05/15 blend it is close to the modulus of the PP/PMMA 80/20 binary blend.
4.5 Summery and Conclusions

Both of the PP/PS and PP/PMMA binary blends studied in this work show continuous-discontinuous (matrix-droplet) type morphologies. The coarse particle morphology of the dispersed phases suggested high interfacial tensions, and ease of pull-out of dispersed droplets indicates poor adhesion between the phases. Both of which were supported by the results of DMTA and dynamic shear rheometry. The values of T_g of the dispersed phase components remained the same in the blends, again indicative of immiscibility. Morphologies of the ternary polymer blends were predicted using the spreading coefficient model, which predicted encapsulation of a PMMA by PS. SEM of solvent-etched surfaces and TEM results were in agreement with this prediction.
4.6 References


Chapter 5: Results and Discussions-

Carbon Black Based Composites

5.1 Introduction

In this chapter the effects of adding carbon black (CB) on the morphology development and the resulting properties of selected blends is presented. The binary-blend and ternary-blend carbon black (CB) composites were prepared by melt mixing. For all the composites polypropylene (PP) was the matrix at 80 vol. % with 20 vol. % dispersed phase (based on the density data in Table 3.1). Two types of binary blend composites, one with polystyrene (PS) as the dispersed phase and the other with polymethylmethacrylate (PMMA) as the dispersed phase with different wt.% of CB were prepared and examined by SEM, TEM, DSC, DMTA and impedance spectroscopy. Following on from the results of the binary-blend composites, ternary blend–CB composites composed of all three polymers (PP/PS/PMMA) with CB were prepared and characterised.

5.2 Binary Blend-CB Composites

5.2.1 Morphology

When a filler is added to a polymer blend the blend morphology may change due to interactions of the filler with the polymer phases [1]. During melt blending the carbon black particles will tend to prefer the phase with lower viscosity [2]. Torque rheometry in the Haake mixer showed that in our system the melt viscosities decrease in the order PMMA>PP>PS in the ratio 3.1:1.6:1.0.
Figure 5.1 SEM of PP/PS 80/20 binary blend CB composite at a) 2 wt.% b) 5 wt.% c) 10 wt.% of CB; dispersed phase morphology changes from droplet type to co-continues.
Figure 5.2 TEM of PP/PS 80/20 binary blend CB composite at a) 2 wt. % b) 5 wt. % c) 10 wt.% of CB; showing CB particles localised in dispersed phase and morphology changes from droplet type to co-continuous morphology
From SEM (Figure 5.1) and TEM (Figure 5.2) images of 80/20 binary PP/PS-CB composites at 2, 5 and 10 wt. % of CB it can be seen that the droplet size of PS increases with the increase in CB loading. This increase in the size of PS domains is the result of the preferential interaction between CB and PS. The change in domain size after the addition of carbon black is due to the changes in melt viscosities of the polymers. The viscosity of the polymer phase preferred by CB is known to increase with the addition of CB [2-4]. As a result the domain size of the polymer phase preferred by CB (in this case PS) composites increases [3]. The TEM images in Figure 5.2 confirm that the CB particles are distributed in the PS droplets. The original spherical droplets of PS in PP/PS blends (see Figure 4.5 in Chapter 4) change to more elongated structures upon the addition of CB (Figure 5.1 a, b and Figure 5.2 a, b) due to increased viscosity of the PS. On a further increase in CB to 10 wt % the PS phase shows signs of being close to forming a co-continuous phase (Figure 5.1c and Figure 5.2c).

In contrast, with the increase in concentration of CB a decrease in the droplet size of PMMA is obvious from the SEM (Figure 5.3) and TEM (Figure 5.4) images. In this case, the CB particles can clearly be seen in the matrix phase in Figure 5. 4; hence in this system CB prefers the PP phase over PMMA. This is in agreement with viscosity arguments. Chan et al [4], working on dispersion of CB in polymer blends of different viscosities, found that in a PP/PMMA blend where the viscosities of PP and PMMA were comparable the CB would disperse in PMMA. With an increase in viscosity of the PMMA, CB was found to be present at the interface between PP and PMMA, and with a further increase in viscosity of the PMMA the CB was found to be dispersed in the PP phase. As stated previously, the viscosity of the PMMA in this study is higher than PP. In Figure 5.4 CB can be seen located at the interface as well as within the PP matrix phase.
Figure 5.3 SEM of PP/PMMA 80/20 binary blend-CB composite at a) 2 wt. %
b) 5 wt. % c) 10 wt. % of CB; droplet size of PMMA dispersed phase decrease with rise in CB concentration
Figure 5.4 TEM of PP/PMMA 80/20 binary blend-CB composite at a) 2 wt. % b) 5 wt. % c) 10 wt. % of CB; CB particles present at the interface of PP and PMMA.
With an increase in CB concentration from 2 to 5 then 10 wt %, due to PP-CB interactions, the viscosity of the PP phase rises and PMMA droplet size decreases (Figure 5.3). Gueskens et al. working on immiscible blends of a random ethylene-propylene copolymer (EPM) and PS with CB, observed a decrease in size of PS droplets with an increase in CB concentration [5, 6].

5.2.2 Crystallisation and Melting

The effect of CB addition on the crystallinity and melting behaviour of binary blend–CB composites was determined using DSC. The DSC curves in Figure 5.5 show the crystallisation peaks for PP/PS-CB and PP/PMMA-CB binary blend composites. PP is well known to readily exhibit nucleation effects upon filler incorporation; therefore it is not surprising that increases in the crystallisation temperature \( T_c \) of PP have been reported upon addition of CB. For example, Bhatacharia and co-workers [7] reported a rise of 5 °C in \( T_c \) due to nucleation effects, in which with the filler particles in the PP act as nucleation sites for crystal formation. In Figure 5.5 at the \( T_c \) values rise gradually with the addition of CB in PP/PS-CB composites shifting to 117 °C at 10 wt. % CB.

Whereas in PMMA composites, at 2 wt.% CB, PP \( T_c \) rises to 122 °C but further addition of CB has no effect on \( T_c \) for this system. This behaviour can be explained using the TEM images in Figures 5.2 and 5.4. In the PS composites most of the CB is seen to reside in the PS phase with only a small proportion in the PP; as the number of CB particles in the PP phase increase with increasing CB wt. % more nucleation sites are created. Whereas in the PMMA composites, the CB prefers to reside in the PP matrix over PMMA, therefore on addition of 2 wt. % CB most of the CB resides in the PP and creates many nucleation sites. Further addition of CB does not affect the \( T_c \) of
the composites, indicating that significant numbers of further active nucleation sites are not created.

![Diagram](image)

**Figure 5.5** DSC Crystallisation peaks for a) PP/PS-CB; b) PP/PMMA-CB composites at CB loadings of 2-10 wt.%; showing an increase in $T_c$ with increase in CB concentration.

From the DSC melting behaviour in Figure 5.6 it is evident that melting peaks for the PS based composites shift towards lower temperatures (from 164.9°C for PP down to
159.5 °C for 10 wt. % CB) and the width of the peaks decreases. Values of degree of crystallinity (DoC) were calculated from the areas under these melting peaks using:

\[ X_c = \frac{\Delta H_f(T_m)}{X_p \Delta H_f^o(T_m^o)} \]

Where \( X_c \) is the degree of crystallinity, \( \Delta H_f \) is the heat of fusion at \( T_m \) and \( \Delta H_f^o \) is the heat of fusion of PP with 100% crystallinity (209 J/g [8, 9]). Due to the presence of other (amorphous) polymers and fillers \( \Delta H_f^o \) has been multiplied by the weight fraction, \( X_p \), of the PP.

Previous studies [9, 10] also reported a reduction in the width of the crystallisation and melting peaks in PP and suggest that it is due to the formation of a narrower crystal distribution. The rise in \( T_c \) and decrease in \( T_m \) for the composites suggest a reduced time for crystallisation and hence thinner crystals are formed [10]. The decrease in the width of the melting peaks for both binary composites implies a decrease in the degree of crystallinity. The degree of crystallinity values are shown in Table 5.1 and do show a decease as the wt.% of CB increases, indicating that interactions with the surface of the CB particles restricts the segmental mobility of PP and hinders crystallisation. It is has also been proposed that the presence of filler may cause defects in the crystal structure which reduces the melting to lower temperatures.[11], indicating that the crystallisation process and the final crystal structure of PP can both be affected by CB addition [12].
Figure 5.6 DSC Melting peaks for a) PP/PS-CB; b) PP/PMMA-CB composite at CB loadings of 2-10 wt.% showing a decrease in $T_m$ with addition of CB.
In order to observe any change in the crystal form, materials were analysed using x-ray diffraction (Figure 5.7). Alpha and beta type crystallite structures have been reported in PP-CB composites [12]. The $\theta^2$ values labelled on the peaks are those for the more common alpha form crystal structure of PP [12]. Beta form crystals have been reported to show a peak between the peaks at 14.1 and 16.9 $\theta^2$ values [12]. Formation of beta crystals has been proposed to be responsible for reductions in $T_m$ of PP composites [12]. However, Figure 5.7 shows no indication of beta crystal formation. The reduced intensity of the peaks reflects the smaller PP fraction, lower DoC and smaller crystal size in the composites. Peaks for the PP/PS-CB composite indicate smaller crystal size than the PP/PMMA composite; an effect also prominent in the melting behaviour of PP/PS-CB composites where, at 10wt% of CB, $T_m$ dropped to 160 °C which is 2 °C less than the PP/PMMA composite. As no beta crystallites are detected in the binary blend composites of PP/PS and PP/PMMA composites (Figure 5.7) the decreased $T_m$ of the composites (Figure 5.6) appears to be due to the formation of smaller size crystals during the fast crystallisation caused by an increase in $T_c$.

<table>
<thead>
<tr>
<th>CB /wt.%</th>
<th>PP % crystallinity in PS composites</th>
<th>PP % crystallinity in PMMA composites</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>30.2 ± 1.0</td>
<td>32.5 ± 1.2</td>
</tr>
<tr>
<td>5</td>
<td>28.2 ± 1.5</td>
<td>31.2 ± 1.1</td>
</tr>
<tr>
<td>10</td>
<td>24.9 ± 0.7</td>
<td>27.3 ± 1.6</td>
</tr>
</tbody>
</table>

Table 5.1 Degree of crystallinity, DoC, (%) of PP matrix in binary PP/PS and PP/PMMA blend-CB composites at various CB loadings.
5.2.3 DMTA

The dynamic thermo-mechanical behaviour of the binary blend-CB composites is discussed in this section. The properties of polymer composites are strongly dependent on morphological changes in the matrix due to the addition of filler particles and on the levels of dispersion and distribution of the filler particles. Figure 5.8 shows data for the dynamic storage (elastic) modulus of the binary blend-CB composites over a temperature range of -25 to +150 °C. It can be seen that the composites have higher moduli than the neat binary-blend matrices due to the reinforcing effect of CB, an effect which increases with the amount of CB in the composite. In order to emphasise the improvement in modulus by the addition of CB, the ratio of the moduli of the blend composites to that of pure PP at 25 °C is given in Table 5.2. All the PP/PS CB

![Figure 5.7 XRD of the PP/PS and PP/PMMA binary blend- CB composites with 10 wt.% of CB; showing no change in the crystalline form of PP.](image-url)
composites show an increase in modulus compared to that of PP but in case of PP/PMMA the modulus at 2, 5 wt. % CB is even lesser than that of pure PP. Reason for this being, on addition of either of the dispersed phases (PS or PMMA) to the PP matrix, the modulus of the binary blends dropped (section 4.2.3 of Chapter 4) due to poor adhesion between the phases. Addition of CB to the blends caused morphological changes. Strong PS-CB interactions resulting in co-continuous morphology are responsible for higher moduli in that system.

Interactions with fillers are known to influence the $T_g$ of the polymers [13]. and have been reported to decrease [14, 15] or to increase [16]. In the PP/PS-CB composites as the CB amounts, the $T_g$ of the PP phase does not change significantly (Figure 5.9). There is only 2 °C rise in $T_g$ of PP while the PS $T_g$ rise by 5 °C at 10 wt. % CB (Table 5.2). The reason for this being the preference of CB towards PS over PP (Figure 5.2) resulting in a filled co-continuous PS phase. In contrast, the $T_g$ of PS increases, and due to the restriction in segmental movements in PS caused by CB-PS interactions. The area of the tan delta peak for the $T_g$ of PS also increases, particularly at higher temperatures (above the peak value) resulting from the increase in the volume of the PS phase (due to incorporation of the CB) and strong PS-CB interactions.

The loss tangent graphs (Figure 5.9) for the PP/PMMA binary composites, the small peak at around 7 °C is the $T_g$ of PP whereas the other peak at 130 °C corresponds to the $T_g$ of PMMA. Figure 5.9 shows a shift ($\approx 6$ °C) in the $T_g$ of PP (Table 5.2) towards higher temperature. The TEM images in Figure 5.4 showed that the CB is localized predominantly in the vicinity of the PP/PMMA interface in PP/PMMA-CB composites. Even this limited presence of CB in the PP phase imposes restrictions on the chain conformation of PP hence restricting the segmental motion of the chain.
Similarly an increase in $T_g$ of PMMA can be seen in Figure 5.9 together with a decrease in tan delta peak intensity and broadening of the peak as CB wt.% increases. Tan $\delta$ is increased particularly at temperatures above the $T_g$. As tan delta is the ratio of the viscous and elastic moduli, higher values of tan delta correspond to more viscous behaviour of the polymer [17]. As the peak shifts are quite small and are accompanied
by significant peak broadening at higher temperature, this is indicative of increased interfacial mixing in a blend or, in this case, the development of a reinforced interface due to the presence of CB.

Figure 5.9 Tan delta for a) PP/PS-CB b) PP/PMMA-CB composites at various CB loadings; peaks showing $T_g$ for the polymer components of the composites.
5.2.4 Electrical Impedance

The critical level of addition of conductive filler needed to form a continuous conducting path, and thus make the polymer conductive, is called the percolation threshold. It is characterized by a sudden drop in polymer resistivity followed by relative independence from further filler addition [18]. PP is the matrix in the blend composites and unfilled is an insulator with volume resistivity of $10^{13}$ to $10^{16} \, \Omega \cdot cm$ [19]. Lower percolation levels are required to achieve better mechanical properties, which can be obtained by efficient arrangement of the filler within a polymer matrix. Polymer-polymer and polymer-filler interactions play a vital role in obtaining these arrangements. Formation of an immiscible blend can be a way to reduce the percolation

<table>
<thead>
<tr>
<th>Materials</th>
<th>DMTA Modulus Ratio Composite/PP at 25 °C</th>
<th>DMTA $T_g$ of PP °C</th>
<th>DSC $T_c$ of PP °C</th>
<th>DSC $T_m$ °C</th>
<th>DMTA $T_g$ of dispersed phase °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS20CB02</td>
<td>1.28 ± 0.8</td>
<td>7.8 ± 1.8</td>
<td>114.4 ± 0.9</td>
<td>162.8 ± 1.5</td>
<td>114.1 ± 1.5</td>
</tr>
<tr>
<td>PS20CB05</td>
<td>1.33 ± 1.3</td>
<td>7.9 ± 0.5</td>
<td>115.8 ± 1.2</td>
<td>161.2 ± 0.3</td>
<td>115.8 ± 1.3</td>
</tr>
<tr>
<td>PS20CB10</td>
<td>1.64 ± 0.3</td>
<td>9.1 ± 1.5</td>
<td>117.9 ± 1.2</td>
<td>160.0 ± 1.1</td>
<td>117.8 ± 0.6</td>
</tr>
<tr>
<td>PMMA20CB02</td>
<td>0.83 ± 0.9</td>
<td>7.2 ± 0.4</td>
<td>121.1 ± 0.9</td>
<td>164.2 ± 0.9</td>
<td>130.7 ± 1.4</td>
</tr>
<tr>
<td>PMMA20CB05</td>
<td>0.88 ± 0.5</td>
<td>10.8 ± 1.7</td>
<td>121.2 ± 1.1</td>
<td>164.1 ± 0.4</td>
<td>130.8 ± 0.3</td>
</tr>
<tr>
<td>PMMA20CB10</td>
<td>1.06 ± 0.8</td>
<td>12.5 ± 1.6</td>
<td>121.9 ± 0.9</td>
<td>164.6 ± 0.8</td>
<td>133.5 ± 1.2</td>
</tr>
</tbody>
</table>
concentration. Filler particles can sometimes selectively localise in one of the phases or at the interface of the polymers reducing the amount of filler needed to achieve percolation [20]. Filler localization can also lead to the formation of a co-continuous blend. If a continuous phase is preferred by the filler this can produce the double percolation effect and further reduce the percolation concentration [1, 2].

Figure 5.10 Electrical conductivity of a) PP/PS-CB; b) PP/PMMA-CB composites as a function of frequency; conductive network formation is complete at higher loadings (7, 10 wt%) of CB.
Impedance spectroscopy performed on binary composites of PP/PS and PP/PMMA at lower CB concentrations (Figure 5.10) showed the insulating behaviour of these blends. CB, being conductive filler, can form a conductive network within the composite and impedance spectroscopy was used to detect the formation of such a network within the blends as CB level was increased. Specific electrical conductivity at various frequency of the AC current is presented in Figure 5.10. It is evident that at CB concentrations of 2 and 5 wt % electrical conductivity is dependent on the frequency, whereas at higher loadings electrical conductivity is much higher and independent of frequency, which is an indication of the formation of a stable conductive network within the composite.

Figure 5.11 is a comparison of conductivity values of both types of binary blend composites. It can be seen that for PS based composites conductivity values remain unchanged upon increasing CB content from 2 to 5 wt. % which indicates no conductive network formation at this concentration. The conductivity value of the 5 wt. % CB PMMA-based composites is an order of magnitude higher than the equivalent PS based system. This is due to the difference in morphology of the systems, as in the PMMA-based system CB forms a conductive network at the interface of PP/PMMA, while in the PS-based composites it is the PS phase which percolates and aids in the formation of a conductive CB network. The conductivity values increase five orders of magnitude from 5 wt. % to 7 wt. % addition of CB in both the binary composites. Further addition of CB does not increase the conductivity significantly. At 10 wt. % of CB the conductivity of the PS based composite is 0.34 S/m which is greater than that of the PMMA-based composite (0.14 S/m). This rise in the electrical conductivity of PS based composites can be attributed to the formation of a conductive network within a co-continuous PS dispersed phase thus exhibiting the double percolation effect.
5.2.4.1 Percolation Theory

As the density of conductive filler particles increases within a polymer, they start to interact and form a conductive network. At a critical point the network becomes complete, the resistance to electric flow reaches a minimum and the composite starts to conduct electricity. Further addition of filler beyond this level does not increase the conductivity significantly. Percolation theory has been used to determine the critical filler content [21, 22]. The equation derived for the conductivity of composite materials is as follows.

\[ \sigma(p) = \sigma_c (p - p_c)^t \quad \text{for } p > p_c \]

Where \( \sigma \) is the specific conductivity and \( \sigma_c \) is the proportionality constant, \( p \) is the filler loading (wt. %), and \( p_c \) is the filler loading at the percolation threshold (often called the critical filler content). The power constant, \( t \), describes the dimensionality of the conductive network formed. It has been reported [22] that a value of 1.33 indicates
the formation of a two-dimensional conductive network whereas the value of $t$ rises to 2.2 with the formation of a three-dimensional conductive network.

In order to determine $p_c$, a value for $p_c$ was first estimated from the point where $\sigma$ starts to show a steep rise (Figure 5.12). The values of sigma beyond this point were then plotted against $p - p_c$ and fitted to a power function (using Origin Pro 8.0 software). The value of $R^2$ indicates the fitting error, and $R^2$ values were minimized by using different values of $p_c$. Figure 5.12 shows the percolation limits fitted to the experimental data. PP/PS composites percolate at 5.2 wt. % CB while PP/PMMA –CB composites percolate at 5 wt. %. The slightly higher value of percolation threshold in the PP/PS composites is due to agglomeration of CB in PS. CB-PS interactions, as seen in the Figure 5.2, result in a little higher concentrations of CB needed to percolate. Once the percolated network is formed (7 wt %) the conductivity values of PP/PS-CB composites at 10 wt % CB are higher compared to the equivalent PP/PMMA composite (Figure 5.11). As discussed earlier, the values of 1.33 and 2.2 for the power constant $t$ describe the 2D and 3D conductive network formation within a material. Higher values of $t$ result when more complex networks are formed [22]. In PP/PS CB composites a double percolated network forms a complex conductive structure resulting in a $t$ value of 4.2. In the PP/PMMA CB blend composites a conductive network is formed in the PP phase resulting in less complex structure than PP/PS composites and thus results in a $t$ value of 3.2 which is still higher than the theoretical value for the formation of 3D structure can be attributed to the multiphase nature of the polymer matrix.
Figure 5.12 Percolation limit fits to data for a) PP/PS-CB b) PP/PMMA-CB at various CB loadings.
5.3 Ternary Polymer Blend-CB Composites

Blending more than two immiscible polymer components can result in different types of morphologies depending upon the interfacial tensions between the phases [23]. For example, the blend may simply exhibit discreet multiple dispersed phases or exhibit a composite (or core-shell) droplet morphology; formed when one dispersed phase component encapsulates another dispersed phase.

Figure 5.13 PP/PS/PMMA 80/10/10-CB composite at 10 wt.% loading of CB. showing PMMA encapsulated by PS and CB particles selectively localised in PS phase outside PMMA.
Studies of ternary polymer blends [23, 24] have shown that the morphology can be controlled by altering the relative proportion of the dispersed phase. The spreading coefficient model has been used extensively to predict the morphology of polymer blends [25, 26] and, as discussed in Chapter 4, for ternary polymer blends of PP/PS/PMMA this model predicts a composite-droplet morphology. From the morphological studies of binary composites of both PS and PMMA presented in this chapter it was established that CB prefers to reside in the PS phase over PMMA.

![CB particles aggregated in PS](image1)

![PMMA](image2)

![CB particles aggregated in PS](image3)

![PMMA](image4)

Figure 5.14 PP/PS/PMMA 80/05/15-CB composite at 10 wt. % loading of CB; PS encapsulates PMMA and CB is present in PS outside PMMA.
In the TEM images in Figure 5.13 the white areas are identified as PMMA and it can be seen that with an increase in the concentration of PMMA (Figure 5.14) the white areas increase in size. No CB is seen in the PMMA phase. From the morphology study in Chapter 4, and the behaviour of CB towards binary composites presented in this chapter, it can be established that PP/PS/PMMA –CB composites exhibit composite droplet morphology with CB being present in the PS phase. The effects of this type of morphology on the resulting properties are discussed in the following sections. More TEM images are given in Appendix-2.

**5.3.1 Electrical and Mechanical Properties**

There are many ways of reducing the percolation threshold level of conducting filler needed for an insulating polymer to start to conduct electricity. Formation of ternary immiscible polymer blends may help to reduce the percolation level further. From the morphology of ternary blends the presence of PMMA inside PS will restrict the free pathway for the CB and will increase the excluded volume, hence the blend has the potential to be more conductive as compared to the binary PP/PS-CB10 composite.

Different fractions of PMMA and PS within the 20% dispersed phase were tried, all with a loading of 10 wt.% CB (Figure 5.15) and their electrical conductivity measured. It can be seen that the electrical conductivity is independent of frequency, but that it does change with the change in dispersed phase morphology.

Figure 5.16 shows the electrical conductivity and DMTA storage modulus data at 25 °C for the ternary blend composites. The highest modulus and electric conductivity were both exhibited by the PP/PS/PMMA 80/10/10 CB10 composite. The modulus obtained from this material is 2.5 times the modulus of the PP/PMMA 80/20 blend and 1.3 times
that of the PP/PS 80/20 blend. Similarly, the electrical conductivity obtained is 1.9 times that of the PP/PMMA-CB10 and is comparable with that of PP/PS-CB10. The improved properties of the PP/PS/PMMA 80/10/10 CB10 material are attributed to morphological changes upon the addition of CB.

![Graph showing the electrical conductivity of PP/PS/PMMA ternary composites at 10 wt.% CB.](image)

**Figure 5.15** Electrical conductivity of PP/PS/PMMA ternary composites at 10 wt.% CB.

![Graph showing the dynamic storage moduli and electrical conductivity of various PP/PS/PMMA-CB 10 composites.](image)

**Figure 5.16** Dynamic storage moduli and electrical conductivity of various PP/PS/PMMA-CB 10 composites; graph shows the dependence of modulus and electrical conductivity on the concentration of dispersed phase (PS+PMMA).
5.4 Summery and Conclusions

Addition of CB causes microstructural changes in the blends, but CB acts differently towards the PS and PMMA phases. Higher loadings of CB in the PP/PS blend increases its electrical conductivity and dynamic moduli due to the formation of a co-continuous morphology and to strong PS-CB interactions. Whereas in PP/PMMA–CB composites the increase in mechanical moduli and electrical conductivities at lower CB loadings (2 and 5 wt.% CB) is comparable to that in PP/PS-CB composites but an increase in CB concentration to 10 wt. % CB does not improve the dynamic mechanical modulus and electrical conductivity compared to PP/PS-CB composites. The less significant increase in electrical conductivity in these blends compared to PP/PS-CB composites is due to the absence of a co-continuous morphology which can impart a double percolation effect. Based on this behaviour, and the morphological results of the ternary polymer blends, a ternary polymer-CB composite was formulated which showed both higher mechanical and electrical properties than those of binary blend-CB composites, as well as the neat binary polymer blends. In addition, changes in the concentration ratios of the dispersed phase were found to be very important in governing the properties of the ternary blend-CB composites.
5.5 References


Chapter 5: Carbon Black Based Composites


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Chapter 6: Results and Discussion-

Carbon Nanocomposites

6.1 Introduction

This chapter deals with the polymer blend-composites based on nano sized fillers and is divided into two sections. The first part presents the results of the binary and ternary polymer-blend composites with multiwall carbon nanotubes (MWCNT), and the second section the polymer blend-composites based on graphite nanoplatelets (GNP). All the composites were prepared at 0.5, 1, 2 and 5 wt.% of the fillers. Two types of binary composite systems were studied, consisting of PP as matrix comprising of 80 vol% with the remaining 20 vol % comprising the dispersed phase of either PS or PMMA. In the ternary polymer blend-composites the matrix phase was kept to 80 vol% while the dispersed phase ratio was varied between PS and PMMA. All the composites were characterised using SEM, TEM, DSC, XRD, DMTA and electrical impedance spectroscopy.

6.2 Binary Blend –CNT Composites

6.2.1 Acid treatment of CNT

Prior to processing with polymers, CNT were refluxed with a H$_2$SO$_4$ and HNO$_3$ mixture in the ratio of 3:1 at 120 °C for 3hrs. This treatment has been used by many researchers to purify CNT and add functional groups to CNT [1-4]. CNT following the acid treatments are reported to have outer surfaces free of contamination as these treatments remove the amorphous carbon and contaminating metals adhered to the CNT following their preparation [2]. These treatments are known to reduce diameter and length of
CNTs [5]. Due to strong interaction between CNTs, they are not easily dispersed. Following the acid treatment they are known to disperse very well in water and can be subjected to further functionalisation [5]. FTIR has been used to qualitatively identify the functional groups attached to CNT as a result of this process. Figure 6.1 is the FTIR spectra of both the acid treated and as-received CNT.. The intensities are different and can not be compared due to difficulties in sample preparation. According to literature [2], at wavenumbers below 2000 cm\(^{-1}\) the most obvious features can be seen at 1400 and 1090 cm\(^{-1}\) and are attributed to CO-H and C-OH stretching respectively [2]. The peak at 1730 cm\(^{-1}\) is reported to be due to C=O stretching [6]. Jin et al showed that this peak originates at 1737 cm\(^{-1}\) and then shifts towards 1720 cm\(^{-1}\) depending upon the time for CNT treatment [7]. This peak has been observed by other researchers and is attributed to the vibration of the C=O group in COOH [2, 6]. It was suggested that as the time for CNT treatment increases the more COOH groups are attached to the CNT [8]. Peaks around 1090 and 850 are most likely due to sulphates and nitrate ions [2, 8].

![Figure 6.1 FTIR spectra of MWCNT before and after acid treatment (MWCNTf) showing presence of carboxyl functional groups on CNT following acid treatment.](image_url)
It was suggested [7] that when a strong acid attacks CNT, the outer -CH₂ and =CH groups are attacked first. The acid not only attacks lattice defects but also attacks the graphene structure, thus creating new defect sites [7]. Under strong acid conditions the graphene structure around the defect site is broken and tube is cut. The oxidation of CNT begins at their ends, resulting in open-ended CNT. The side walls of the CNT are also under attack which results in a decrease in the mean diameter and length of the CNT. Figure 6.2 shows the CNTs before and after acid treatment. Quantitative analysis using Image J software [6] revealed that the average diameter of the CNTs before acid treatment was 50nm ± 3nm and the size ranged from 35 to 64 nm. After acid treatment, the average diameter of the CNTs was reduced to 34 nm ± 2 nm with sizes ranging from 6 nm to 40 nm. A total of 100 measurements of each set of images were taken. One of the consequences of acid treatment is that shorter and thinner CNTs are reported to be more reactive than longer and thicker tubes [6].

![Figure 6.2 TEM images of MWCNT; a) before and b) after acid treatment.](image)

Following acid treatment the CNT were dried and dispersed in xylene using magnetic stirring for 2 hours. PP was also refluxed in xylene for 1 hour at 140 °C to form a solution and later this solution and the CNT dispersion were mixed under magnetic stirring for 1 hour at 140 °C. PP-CNT was precipitated using acetone followed by vacuum filtration and drying. Polymer blend-composites were prepared by mixing...
solution blended PP-CNT in the Haake Rheocord as described in section 3.2.3 of Chapter 3.

6.2.2 Characterisation of Binary Blend-CNT Composites

6.2.2.1 Morphology

Morphological development of the binary polymer blend-CNT composites was studied using SEM (Figure 6.4) and TEM (Figure 6.6) at various loadings of CNT. Figure 6.3 shows a decrease in dispersed phase droplet size with increasing amount of CNT in PP/PS binary blend composites. The domain sizes were measured using Image J software and are reported in Table 6.1. During melt mixing, the CNT tend to migrate towards polyolefins (PP in this case) [9]. TEM image (Figure 6.6a) shows no evidence of presence of CNT in PS phase and aggregates of CNT in PP (Figure 6.6b) confirm the preference of PP phase over PS. As the CNT are several microns in length, which is generally higher or at least comparable with the droplet size of the dispersed phase in immiscible polymer blends. During melt mixing when the dispersed phase droplets come into contact with CNT they are cut into smaller droplets as represented by the schematic diagram in Figure 6.3 [5]

![Schematic diagram](image)

Figure 6.3 Schematic representation of dispersed particle breakup by CNT during melt mixing [5].
On the other hand, in the PP/PMMA-CNT composites it is evident from Figure 6.4 and Table 6.1 that the domain size of PMMA increases with increasing concentration of CNT. It was confirmed by FTIR that carboxylic acid groups were attached to the CNT following acid treatment. Due to the polar nature of PMMA and the induced polarity on the CNT (due to attachment of polar groups), the CNT would prefer to reside in the PMMA phase in the PP/PMMA-CNT composites.

![SEM images of PP/PS-CNT composites](image)

Figure 6.4 SEM images of PP/PS-CNT composites; at a) 1 wt.% b) 2wt.% c) 5wt.% showing finer droplet morphology on CNT addition, and PP/PMMA composites; at d) 1 wt.% e) 2 wt.% f) 5 wt.% of CNT; showing elongated PMMA dispersed phase on CNT addition.
The elongation of PMMA domains, as shown in the SEM micrographs of Figure 6.4, is due to the increase in its viscosity because of its interaction with CNTs (Figure 6.6). In the TEM micrographs of Figure 6.6 CNTs can be seen to be present in the PMMA phase. Zhong et al showed that CNT can extend from one phase to another owing to their length [5] (as shown in Figure 6.5). In Figure 6.6 CNT are present at the interface of PMMA and PP indicating CNT to have affinity for both the PP and PMMA and thus forcing them to align at the interface of the PP/PMMA blend composite.

Figure 6.5 SEM of PC/PE-CNT blend composites, showing CNT extending between the phases [5].
Figure 6.6 TEM images of i)PP/PS-CNT composites a) droplet of PS b) CNT agglomerated in PP and ii)PP/PMMA-CNT composites c) CNT aligned at the PP/PMMA interface and d) CNT present in co-continuous PMMA.

6.2.2.2 Crystallisation and Melting

A change in the crystallisation behaviour of PP similar to that resulting from the addition of CB (section 5.2.2) is noted on the addition of CNT (Figure 6.7). The $T_c$ of the PP in both the blends show an increase upon CNT addition (Table 6.1) because, as with CB, the CNT give nucleation of PP crystals [11]. The $T_c$ for the pure PP used in this study is $110 \pm 1.2$ °C. In the PP/PS-CNT composites $T_c$ shifts from 110 °C to 120 °C upon addition of 0.5 wt. % CNT (Table 6.1). This rise can be attributed to the affinity of CNT towards PP, which is well-known for its nucleating behaviour [12]. In the PP/PS-CNT blend composites CNT would prefer to reside in the PP phase, owing to
their higher affinity for PP. Thus, even a small amount of CNT (0.5 wt%) have created enough nucleating sites for the $T_c$ to rise by 10°C. Further addition of CNT does not create nucleating effects which is evident by only a 4 °C rise in the $T_c$ upon adding additional CNT up to 5 wt. % to the blends. In the PP/PMMA-CNT composites, the shift in $T_c$ is steady but less significant at lower concentration of CNT, in contrast to the PP/PS composites. Figure 6.6 shows the CNT to reside in both the PP and PMMA phases in the PMMA blend composites. Due to interactions of CNT with both the PMMA and PP, a reduced percentage of CNT will interact with PP compared to that in PP/PS-CNT blend composites thus resulting in less nucleating sites for PP crystallites. This results in a steady but slower increase in the $T_c$ of PP in the PP/PMMA –CNT blend composites. At 5 wt. % CNT both the composites exhibit values of $T_c$ ≈124 °C, which is 12 °C higher than pure PP.

Table 6.1: Dispersed phase average diameter measured by Image J and Thermal Properties of binary polymer blend-CNT composites obtained from DSC and DMTA.

<table>
<thead>
<tr>
<th>Materials</th>
<th>SEM Average diameter of dispersed phase (µm)</th>
<th>DMTA Composite Modulus / Modulus of PP at 25°C</th>
<th>DSC $T_c$ of PP (°C)</th>
<th>DSC $T_m$ of PP (°C)</th>
<th>PP Xc (%)</th>
<th>DMTA Tg of dispersed phase (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS20CNT0.5</td>
<td>1.61</td>
<td>1.06 ± 0.18</td>
<td>120.8± 1.2</td>
<td>164.3±1.2</td>
<td>33.4 ± 1.3</td>
<td>111.8±1.5</td>
</tr>
<tr>
<td>PS05CNT01</td>
<td>1.52</td>
<td>1.13 ± 0.36</td>
<td>121.7± 0.9</td>
<td>164.4±1.5</td>
<td>31.08±1.8</td>
<td>112.5±0.8</td>
</tr>
<tr>
<td>PS20CNT02</td>
<td>1.21</td>
<td>1.30 ± 0.16</td>
<td>123.3± 1.4</td>
<td>164.3±1.3</td>
<td>31.08±1.8</td>
<td>114.6±1.1</td>
</tr>
<tr>
<td>PS20CNT5</td>
<td>0.98</td>
<td>1.52 ± 0.27</td>
<td>124.1± 1.2</td>
<td>164.7±0.9</td>
<td>29.71±1.3</td>
<td>115.1±0.5</td>
</tr>
<tr>
<td>PMMA20CNT0.5</td>
<td>0.91</td>
<td>1.43 ± 0.09</td>
<td>116.8± 1.3</td>
<td>164.2±1.7</td>
<td>33.79±0.9</td>
<td>129.4±1.4</td>
</tr>
<tr>
<td>PMMA20CNT01</td>
<td>1.24</td>
<td>1.52 ± 0.45</td>
<td>119.1± 1.2</td>
<td>164.2±1.3</td>
<td>32.55±1.1</td>
<td>129.8±0.8</td>
</tr>
<tr>
<td>PMMA20CNT02</td>
<td>1.65</td>
<td>1.60 ± 0.36</td>
<td>120.2± 1.4</td>
<td>164.4±0.9</td>
<td>31.95±1.8</td>
<td>130.2±0.9</td>
</tr>
<tr>
<td>PMMA20CNT05</td>
<td>2.12</td>
<td>1.72 ± 0.45</td>
<td>124.2± 0.8</td>
<td>164.6±2.8</td>
<td>29.44±1.2</td>
<td>131.6±1.2</td>
</tr>
</tbody>
</table>
Figure 6.7 PP crystallisation peaks for a) PP/PS-CNT and b) PP/PMMA-CNT composite at various CNT loadings showing rise in $T_c$. 
The melting behaviours of both the PP/PS and PP/PMMA binary composites at different loadings of CNT are shown in Figure 6.8, in which no noticeable change in the melting temperature is seen.

Figure 6.8 PP crystalline melting endotherms for a) PP/PS-CNT and b) PP/PMMA-CNT composite at various CNT loadings.
Manchando et al used the supercooling temperature, $T_s$, (the difference between the melting temperature ($T_m$) and crystallisation temperature ($T_c$)) to estimate the induction time for PP crystallisation [11]. The induction time reduces with a reduction in $T_s$ [11].

As the $T_c$ in both type of blends increases but the $T_m$ remains the same (Table 6.1) this can cause a reduction in $T_s$, indicating a reduction in the induction time for crystals to grow [14]. These lower induction times for crystallization indicate that CNT increased rate of crystallisation [15]. Degrees of crystallinity measured for these composites from DSC are given in Table 6.1. As the degree of crystallinity and induction time both decrease for both composites at higher loadings of CNT. Thus, adding CNT creates more nucleating sites resulting in rises in $T_c$ but a reduction in the induction time leads to rapid crystallisation. Hence smaller size crystals are formed indicating that interaction with the surface of the CNT restricts the segmental mobility of PP which hinders crystallisation and therefore the degree of crystallinity decreases [15]. All these changes may result in the change in crystal structure of PP [15] and it has been reported that addition of CNT can change the crystal form from alpha to beta crystal type [15].

Figure 6.9 shows XRD data for pure PP and CNT filled composites at 5 wt. % loadings of CNT. The $2\theta$ values labelled on the peaks are those for the more common alpha crystal form of PP [16]. As in the XRD results of CB based composites (Figure 5.7) no evidence of beta type crystal formation is visible in Figure 6.9. The reduced peak intensities reflect the lower DoC in the blend-CNT composites and the narrower peaks the presence of smaller sized crystals attributed to the lower induction times.
6.2.2.3 DMTA

Figure 6.10 is the dynamic storage modulus ($E'$) of both the PS and PMMA based binary blend composites at varying CNT loading. A general trend of a rise in $E'$ with the amount of CNT added is observed in the curves. Chih and co-workers, working on PP/MWCNT composites reported the stiffness and aggregation of CNT as two competing factors responsible for changes in modulus [17], and decreases in modulus at high concentrations of CNT has been reported due to agglomeration [11]. $E'$ as a ratio of $E'$ of pure PP at 25 °C for both the PS and PMMA binary blend CNT composites is given in Table 6.1. All the ratios are >1 indicating the $E'$ of the blend-CNT composites is higher than that of the PP matrix due to stiffening of these materials upon addition of CNT. The rise in $E'$ is greatest in PP/PMMA blend composites at 5 wt% CNT and can be attributed to the polar interactions between PMMA-CNT resulting in the co-continuous morphology of the blend (Figure 6.6). Similar results were seen (Table 5.2).
in the PP/PS-CB10 composites where the co-continuous morphology of the PP/PS-
CB10 blend composites have resulted in 1.5 times higher $E'$ than the equivalent
PMMA-based blend composites, which have a dispersed phase morphology.

In Figure 6.11, the first peak at $\approx 7 \, ^\circ C$ in both the PP/PS and PP/PMMA tan $\delta$ curves is
the $T_g$ of PP. The $T_g$ of PP in the PS based CNT composites has increased to $\approx 9.8 \, ^\circ C$
whilst for the PMMA based composites $T_g$ of PP at 5 wt % loading of CNT is $\approx 8.2 \, ^\circ C$.
An increase in $T_g$ of PP in the PP/PS-CNT blend composites is due to PP-CNT
interactions resulting in finer PS morphology (as explained in section 6.2.2.1). These
PP-CNT interactions restrict the PP segmental mobility causing $T_g$ to rise. The $T_g$ of the
PS dispersed phase almost remains the same (Table 6.1) as there is much less PS-CNT
interaction and the CNT are aggregated in the PP phase (Figure 6.6). In PP/PMMA-
CNT composites a change in $T_g$ of both the PP and PMMA phases is observed (Table
6.1) due to CNT interactions with both PP and PMMA.

In both type of composites the tan delta values for the materials containing higher
amount of CNTs is lower. As tan delta is the ratio of loss to storage modulus of the
material, a decrease in tan delta can be inferred as a rise in the elastic behaviour of the
material. As the DoC decreases at higher CNT loadings the lower tan delta values can
be attributed to increased polymer-CNT interactions.
Figure 6.10 Dynamic storage modulus for a) PP/PS-CNT b) PP/PMMA-CNT composites at various CNT loadings; dynamic moduli increase with increase in CNT wt. % in the composite.
6.2.2.5 Electrical Impedance

MWCNTs are effective conductive fillers for imparting electrical conductivity to normally insulating polymers. It is known from previous studies that CNT can give...
significant improvements in the electrical properties of the composites [5, 21]. The effectiveness of the conductive reinforcement can be assessed by electrical impedance analysis of the composites. Electrical impedance data for CNT composites based on PP/PS and PP/PMMA binary blends are given in Figure 6.12. In both types of composite, electrical conductivity increases with an increase in CNT content. The change in conductivity in the PP/PMMA is more pronounced than in the PP/PS composites. At 5 wt. % CNT the PP/PMMA composite exhibits a conductivity level 4 orders of magnitude higher than the equivalent PP/PS composite. This difference in conductivity at the same loading of CNT can be related to the differences in morphology between the composites [9, 22]. In the PP/PMMA composites, TEM images (Figure 6.6) showed CNT to be aligned at the interface of PP and PMMA, owing to the affinity of CNT for both PP and PMMA. Whereas in the PP/PS composites, CNT were seen in to be present in the form of agglomerates in the PP phase, indicating that the CNT having a higher affinity for themselves than for PP. Due to the formation of these agglomerates, a conductive network does not form at 2 wt.% CNT. Even at 5 wt. % of CNT, in the PP/PS composites frequency dependence of specific conductivity occurs at higher frequencies, indicating an unstable/incomplete conductive network. In the PP/PMMA composites, due to their different morphology a stable conductive network forms at 2wt. % of CNT and the conductivity is invariant at higher frequencies.
Figure 6.12 Specific conductivity of a) PP/PS-CNT b) PP/PMMA-CNT composites at various frequencies.
6.2.2.5.1 Percolation Theory

Percolation theory has been widely used to describe network formation of conducting fillers in polymer composites [24, 25]. As the density of conductive filler particles increases within a polymer, they start to interact and form a conductive network. At a critical point the network becomes complete, the resistance to electric flow reaches a minimum, and the composite starts to conduct electricity. Further addition of filler beyond this level does not increase the conductivity significantly. Percolation theory has been used to determine the critical filler content. Electrical conductivity data were plotted as described in section 5.2.4.1 of chapter 5. Figure 6.13 shows the fitting curves to pass through most of the data points. The critical values obtained for the binary composites of PP/PS and PP/PMMA with CNT are 1.2 and 0.49 wt.%, respectively. The \( t \) values obtained by applying percolation theory to the experimental data are 3.3 for PP/PS and 3.9 for PP/PMMA composites, which are much higher than the values of 1.33 and 2.2 for two- and three-dimensional network formation. In the literature a wide range values of \( t \) have been reported [24]. Wolfgang et al. in a review reported \( t \) values ranging from 1 to 4 for CNT composites [25]. It has been suggested that high values of \( t \) an increasing tunnelling barrier for CNT. For example, Kilbridge et al. [24] determined a \( t \) value of 1.36, greater than the expected theoretical value for the formation of a two-dimensional network, but it was suggested that there existed a thick layer of polymer between the clusters of CNT and that electrons would have to travel by a hopping mechanism across the clusters. Values of 2.7 for \( t \) have also been reported [21] it was again suggested that this deviation is due to polymer layers between the CNT. Based on these observations [21, 24] it can be suggested that relatively thick polymer layers are present in between the CNT in the binary blend composites.
Figure 6.13 Percolation limit fits to experimental data for a) PP/PS-CNT b) PP/PMMA-CNT at various CNT loadings.
The specific conductivity values for the PP/PMMA composites are higher than the PP/PS composites at the same loading, which suggests the formation of a more efficient conductive three dimensional conductive network in the PP/PMMA composites. In such a situation the $t$ values should have been greater for PP/PS composites. But this is not the case. Wolfgang and co-workers [25] suggest that it is very difficult to obtain CNT geometrical network information from the value of $t$, their reasons being that the percolation theory is derived for ideal systems containing homogenous dispersions and spherical particles (due to the spherical particle shape assumption linked to the derivation of the percolation theory). Due to entanglements, diameter/length variations and the waviness of CNT, CNT-polymer composites are far from ideal systems [25]. Thus determination of geometrical network information would require the introduction of a particle shape correction factor to the percolation theory, which may bring the values of $t$ down to the theoretical values of 1.3 and 2.2 for 2D and 3D network formation. To our knowledge no such particle shape correction factors have been introduced to the basic percolation theory and experimentally tested. Secondly according to percolation theory the values of $t$ are limited to the concentration range near percolation threshold. Thus, one of the reasons for the higher $t$ value of the PP/PMMA composites is that the conductivity of the analysed samples is far above the threshold limit whereas in PP/PS composites it is two orders of magnitude less than for the PP/PMMA composites. In a recent work it has been suggested that higher values for $t$ indicate the formation of more complex networks [26], which may well describe the current situation, where conductive networks are forming within specific regions of a multiphase material

The percolation threshold for PP-CNT composites has been reported as 2 wt.% [27]. The percolation values for our case are lower for both the PP/PS and PP/PMMA
composites at 1.2 and 0.49 wt.% respectively. This is due to the excluded volume created by the presence of PS in the PP/PS composites, as most of the CNT reside in the PP phase. In the PP/PMMA composites, segregation of the CNT at the PP/PMMA interface is the reason (where both PP and PMMA act to exclude volume).

6.2.3 Ternary Blend-CNT composites

Based on the morphological behaviour of ternary polymer blends and ternary polymer blend-CB composites (sections 4.3.1 and 5.3) it has already been established that in the ternary polymer composites a PS ‘shell’ encapsulates a PMMA ‘core’ phase. To confirm this prediction, morphological studies of ternary polymer blend-CNT composites were performed using SEM. The samples were etched with cyclohexane for 4 hours to remove PS. The SEM images in Figure 6.14 show cavities around the PMMA droplets from where PS has been removed by cyclohexane. Some fibrous structure can be seen residing in these cavities created by extraction of PS phase. It may be proposed that these are CNT as no such fibrous structures were noted in any of the SEM images of ternary polymer blends (Figure 4.10). As seen in the binary PP/PS-CNT blend composites (Figure 6.6 a,b) CNT prefers PP phase over PS and therefore presence of CNT in PS cavity is unlikely thermodynamically, on the other hand this may be regarded as the fibre pulled out by cryogenic fracture during sample preparation causing CNT to land on the PS.

The PMMA phase elongates on addition of CNT to the binary PP/PMMA-CNT composites (see Figure 6.4 and Figure 6.6). Increasing the amount of PMMA promotes the formation of more elongated PMMA structures as seen in Figure 6.12b. The cavities around the elongated PMMA phases are spaces left by the removal of PS by cyclohexane. There are two polymer interfaces present in the ternary polymer blend-CNT composites (i.e. PMMA - PS and PP-PS).
It was established earlier that in the PP/PMMA-CNT binary blend composites (Figure 6.6), the CNTs align themselves along the PP/PMMA interface owing to their affinity for both of the polymers, but no such alignment was seen in the PP/PS-CNT binary.

Figure 6.14 SEM images of PP/PS/PMMA-5 wt.% CNT composites at a) 5 vol% b) 15 vol% of PMMA in the dispersed phase, showing composite droplet morphology and encapsulation of PMMA by PS.

It was established earlier that in the PP/PMMA-CNT binary blend composites (Figure 6.6), the CNTs align themselves along the PP/PMMA interface owing to their affinity for both of the polymers, but no such alignment was seen in the PP/PS-CNT binary.
blend composites (Figure 6.6) as CNT has very less affinity for PS. In the ternary blends, as there is no common interface between PP and PMMA the CNT cannot align at the PMMA-PS interface but rather they may prefer to reside in both the PP and PMMA phase due to their higher affinity towards PP and PMMA as compared to PS.

### 6.2.3.1 Electrical and Mechanical Properties

Dynamic storage modulus data for the ternary polymer–CNT blend composites at 5wt% of CNT are plotted in Figure 6.15. The modulus of the composites remains approximately the same, whereas the conductivity drops with increasing PS content in the dispersed phase of the blend. This can be explained by the morphology of the ternary polymer blend composites (Figure 6.14). When both the PS and PMMA present in the dispersed phase, the PS encapsulates the PMMA and CNT present in the PMMA and PP phases act as reinforcement in the ternary composites and maintain the modulus essentially constant. A slight drop in modulus at higher vol.% (15%) of PS can be due to the increase in thickness of the PS phase [26], as the CNT are incompatible with the PS phase hence increase in the thickness of the PS phase reduces modulus of the material. Due to the same reason, electrical conductivity of the ternary polymer blend-CNT composites increases with a decrease in the PS content (Figure 6.15).
Graphite nanoplatelets (GNP) are a type of graphitic nanofillers consisting of 2D graphene sheets stacked together. These nano particles are reported to have outstanding electrical, thermal and mechanical properties [27, 28]. SEM, TEM, DSC, DMTA, XRD, and electrical impedance spectroscopy has been used to characterise the polymer blend-GNP composites.

Figure 6.15 Storage modulus and electrical conductivity of ternary composites (5 wt.% CNT) at various PS loadings; showing dependence of conductivity and moduli on the concentration of individual polymers in the dispersed phase (PMMA+PS).

6.3 Polymer Blend-GNP Composites
6.3.1 Characterisation of Polymer-GNP Composites

6.3.1.1 Morphology

The GNP-15 used in this work is reported to have an average diameter of 15 µm and thickness of < 10 nm [29]. The TEM image in Figure 6.17c shows a GNP platelet in the PP/PS composites. The thickness of this flake measured using Image J software is 25 nm, indicating that during melt processing some of the GNP may have agglomerated. A rise in the average thickness of GNP (30-80 nm) due to agglomeration during melt mixing was reported by Guohua Chen and co-workers [30]. Similarly, during mixing GNP have been reported to lose their layered structure and form agglomerates which can be 200-300 µm in size [29].

Figure 6.16 shows SEM micrographs of binary polymer blend-GNP composites. The domains of the dispersed phase show micro-structural changes in both the PP/PS and PP/PMMA blend-GNP composites similar to those in CB and CNT composites. At lower concentrations of GNP (0.5 wt.%) both the blend composites show droplet type morphologies. 1 wt.% addition of GNP to the blends results in different structural changes in both the PS (Figure 6.16 b) and PMMA (Figure 6.16f) based blend composites. In the PP/PS blend composites at 1 wt% GNP the dispersed domains of PS have become elongated (Figure 6.16 b). Indicating the presence of GNP in the PS phase, as the viscosity of the PS would increase with the addition of GNP [31]. The rise in viscosity is related to the formation of a GNP network and the degree of delamination and exfoliation of GNP during mixing [32, 33], which results in the formation of GNP sheets of higher aspect ratio. Higher aspect ratio GNP can form a network at lower loadings compared to micro particles like CB and Graphite [33]. This would result in a significant increase in melt viscosity even at low loadings of GNP, and due to this rise
in viscosity, the structure of the PS phase elongates. These elongations have already been seen in PP/PS-CB composites (section 5.2.1) due to preference of PS phase over PP by CB. SEM images of PP/PS-GNP binary blend composites at higher concentrations (2 and 5 wt.%) of GNP (Figure 6.16 c,d) show all the surface of the blend is covered with GNP particles suggesting the presence of GNP in both the PP and PS phases, which is indicative of compatibility of GNP with both PP and PS. TEM (Figure 6.17b) confirms the presence of GNP near the interface of PP and PS. This may be due to an affinity for both PS and PP and GNP are attracted towards the interface. In this scenario the PS phase also elongates as in Figure 6.17b; suggestive of good PS-GNP interactions causing PS viscosity to rise.

In the PP/PMMA blend composites the domain size decreases at 0.5 and 1 wt % addition of GNP (Figure 6.16 e,f,) and a finer morphology is obtained (Image J software measurements are given in Table 6.2). The decrease in the PMMA domain size is suggestive of a higher affinity of GNP towards the PP matrix phase in PP/PMMA binary blend composites, resulting in increase in the viscosity of the PP matrix surrounding PMMA dispersed phase; forcing the PMMA droplets to a smaller size in order to balance the viscous forces. At higher loading of GNP, SEM images (Figure 6.16g,h) also show all the surface covered with GNP suggesting a dense loading of GNP in the PP matrix. TEM (Figure 6.17a,) is in agreement with the SEM images (Figure 6.16 g, h) showing that the GNP are present mostly in the PP matrix in the PP/PMMA composites, which causes the droplets of the PMMA phase to decrease in size due to the viscosity rise of the PP. Thus we can say in both PS and PMMA basedblend composites with GNP; The GNP compatibilise both the dispersed phase of PS and PMMA due to its presence in the PP matrix.
Figure 6.16 SEM images showing morphological changes in i) PP/PS-GNP composite at a) 0.5 wt.% b) 1 wt.% c) 2 wt.% d) 5 wt.% . ii) PP/PMMA composites at e) 0.5 wt.% f) 1 wt.% g) 2 wt.% h) 5 wt.% of GNP.
Figure 6.17 TEM images of a) PP/PMMA-GNP b) PP/PS-GNP composites at 5 wt.% GNP showing GNP present near the PP/PS interface c) GNP platelet.
Figure 6.18 DSC crystallisation peaks for a) PP/PS-GNP b) PP/PMMA-GNP composites at various GNP loadings; showing an increase in $T_c$ of PP in both the blends with the addition of GNP. Peak values tabulated in table 6.2.
Figure 6.19 DSC crystalline melting peaks for a) PP/PS-GNP b) PP/PMMA-GNP composites at various GNP loadings. Peak values tabulated in table 6.2
6.3.1.2 Crystallisation and Melting

The PP crystallisation behaviour during DSC (Figure 6.18) of both the PS and PMMA based composites with GNP show a shift towards higher temperatures at higher loading of GNP. The T_c value for the PP used in this work is 110 °C. At 0.5 wt% of GNP the T_c of the binary PP/PS and PP/PMMA blend composites are 124 and 123 °C (Table 6.2) respectively. At 5 wt% the T_c of PP in PP/PS is ~126 °C and for the PMMA based blend composite is ~127 °C. In PP/PS composites the GNP prefers the PS phase over PP and thus the rise in T_c is ~1 °C less than that for PP/PMMA blend composites due to preference of PP over PMMA (Figure 6.16, 6.17); causing more nucleation and hindrance to segmental mobility due to PP-GNP interaction. In binary blend-CNT composites (Table 6.1) the maximum T_c achieved at 5 w.t% is ~124 °C. This shows that the GNP is a better nucleating agent than CNT. The major change in T_c of PP (10 °C) is in the PP/PMMA composites at 0.5 wt. % . This can be explained with the help of Figure 6.16 and Figure 6.17, showing the presence of GNP in PP and not in PMMA. Thus, in PP/PMMA blend composites the GNPs create more nucleating sites than in PP/PS composites (in which PS is preferred phase). Further addition of GNP to the blends does not cause significant changes to T_c. Possibly due to saturation of nucleating sites at lower wt. % of GNP or increased GNP-GNP interactions giving little increase in PP-GNP interfacial area.

The crystalline melting peaks (Figure 6.19) show little change in the melting behaviour of the composites with increasing concentration of GNP. Xiang and co-workers [34], working on the thermal properties of GNP-Paraffin composites, also reported no change in their melting behaviour. The melting temperature of the GNP composites is comparable to that of pure PP although the melting peaks narrow at higher loadings of GNP, which may be attributed to the fact that when the filler wt. fraction in the
composite is increased by the total wt. fraction of decreases [34]. No change in $T_m$ and the increase in $T_c$ of PP in the binary blend composites of PS and PMMA suggest a decrease in super cooling ($T_s$) temperature for the composites. As was discussed earlier in this chapter (section 6.2.2.2), this decrease in $T_s$ means less time available for crystallisation or fast crystallisation. The data in table 6.2 show a decrease in degree of crystallinity for the composites. Disruption of the crystal structure by incorporation of GNP has been suggested by authors [15, 17, 35]. However, XRD analysis (Figure 6.20) of the binary blend GNP composites showed that the peaks generated are the same as those for the neat PP although smaller crystallite formation is suggested by the low intensity and narrowing of the peaks for the composites. There is an additional peak seen at 26.5 degrees. This peak is not present in either the CB (Figure 5.7) or CNT (Figure 6.9) based blend composites. Ramanathan et al, working on PMMA-GNP composites, have reported that this peak indicates the presence of GNP crystallites [36].

![Figure 6.20 XRD peaks for GNP binary composites and PP showing no change in crystalline form of PP in the blends filled with GNP.](image-url)
6.3.1.3 DMTA

Gupta and co-workers have reported superior enhancement of dynamic storage modulus by GNP compared to clay nanoparticles [37]. The PP/PS and PP/PMMA binary blend GNP composites also show an increase in storage modulus with increasing GNP content (Figure 6.21). Modulus enhancement is also reported in table 6.2 as a ratio of the composite modulus to the modulus of pure PP at 25 °C.

The dynamic modulus at 25 °C in CNT based binary blends at 5wt % CNT (Table 6.1) was ~1.52 times that of pure PP for PP/PS and 1.72 for PP/PMMA. For the GNP binary blend composites these values have risen to ~2.08 and ~2.23 (Table 6.2) showing improved mechanical behaviour of the composites with GNP. For all the PP/PS and PP/PMMA GNP blend composites tan delta (Figure 6.22) shows two peaks for the $T_g$ of both the polymers in the blend showing their immiscibility. Thus we can say the rise in storage modulus (Table 6.2) is due to the reinforcing effect of the nanofillers aided by good adhesion between the GNP and the polymers. The first peak in Figure 6.20 at ~ 7 °C is for the $T_g$ of PP and the second one at ~115 °C to ~125 °C is the $T_g$ of PS and the peak from 130 °C to 142 °C range is the $T_g$ of PMMA. The $T_g$ of both the PS and PMMA shift to the higher temperatures at higher loading of GNP (Table 6.2) due to GNP-polymer interactions which restrict segmental movement. The $T_g$ of PS shifts by 13 °C in PP/PS GNP composites (Table 6.2) at 5 wt % GNP. Similarly, the rise in the $T_g$ for PMMA in the PP/PMMA-GNP composites is 12 °C. The $T_g$ rise due to GNP is 10 °C for PS and 9 °C more for PMMA based materials as compared to CNT based composites of the similar blends at 5 wt% filler loading. This indicates greater resistance to segmental mobility imposed by GNP as compared to CNT and may be due to the surface roughness of GNP particles [36].
Figure 6.21 Dynamic storage modulus for a) PP/PS-GNP b) PP/PMMA-GNP composite at various GNP loadings; showing increase in dynamic moduli with increase in GNP wt%.
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The tan δ peaks for the T_g of PS are more pronounced than those for PMMA, this is due to the presence of GNP particles in the PS phase as shown by the TEM images (Figure 6.17). In nanocomposites these mobility effects have been found to propagate away from the polymer-filler interface and gradually taper off with distance [38], thus creating an

Figure 6.22 Tan delta for a) PP/PS-GNP b) PP/PMMA-GNP composites at various GNP loadings; Peaks show the T_g of individual polymer phases in the binary blends.

The tan δ peaks for the T_g of PS are more pronounced than those for PMMA, this is due to the presence of GNP particles in the PS phase as shown by the TEM images (Figure 6.17). In nanocomposites these mobility effects have been found to propagate away from the polymer-filler interface and gradually taper off with distance [38], thus creating an
enormous volume of polymer with significantly altered viscoelastic behaviour causing the $T_g$ of nanocomposites to rise significantly [39].

Table 6.2: Dispersed phase average diameter measured by Image J and Thermal Properties of binary polymer blend-GNP composites obtained from DSC and DMTA.

<table>
<thead>
<tr>
<th>Materials</th>
<th>SEM Average diameter of dispersed phase polymer (µm)</th>
<th>DMTA Modulus Ratio Composite/PP at 25 °C</th>
<th>DSC $T_c$ (°C) of PP</th>
<th>DSC $T_m$ (°C)</th>
<th>DSC $X_c$ %</th>
<th>DMTA $T_g$ (°C) of dispersed phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS20GNP0.5</td>
<td>0.65</td>
<td>1.49 ± 0.63</td>
<td>124.27 ± 1.2</td>
<td>164.68 ± 1.6</td>
<td>34.13 ± 1.1</td>
<td>115.93 ± 0.4</td>
</tr>
<tr>
<td>PS20GNP 01</td>
<td>0.92</td>
<td>1.75 ± 0.36</td>
<td>125.4 ± 1.3</td>
<td>164.93 ± 1.2</td>
<td>32.21 ± 1.4</td>
<td>116.63 ± 1.5</td>
</tr>
<tr>
<td>PS20GNP02</td>
<td>1.02</td>
<td>2.03 ± 0.45</td>
<td>125.86 ± 0.9</td>
<td>164.94 ± 1.4</td>
<td>31.80 ± 0.9</td>
<td>123.85 ± 0.9</td>
</tr>
<tr>
<td>PS20GNP 5</td>
<td>-</td>
<td>2.08 ± 0.19</td>
<td>126.62 ± 0.9</td>
<td>165.1 ± 0.9</td>
<td>29.82 ± 0.7</td>
<td>125.66 ± 1.1</td>
</tr>
<tr>
<td>PMMA20GNP0.5</td>
<td>0.82</td>
<td>1.49 ± 0.36</td>
<td>122.43 ± 1.2</td>
<td>164.68 ± 1.5</td>
<td>33.48 ± 1.2</td>
<td>132.71 ± 0.9</td>
</tr>
<tr>
<td>PMMA20GNP01</td>
<td>0.77</td>
<td>1.82 ± 0.54</td>
<td>123.68 ± 1.4</td>
<td>164.79 ± 1.3</td>
<td>32.48 ± 0.6</td>
<td>135.75 ± 1.2</td>
</tr>
<tr>
<td>PMMA20GNP02</td>
<td>0.68</td>
<td>2.04 ± 0.27</td>
<td>124.8 ± 1.5</td>
<td>164.81 ± 1.5</td>
<td>31.20 ± 0.8</td>
<td>141.64 ± 0.6</td>
</tr>
<tr>
<td>PMMA20GNP05</td>
<td>-</td>
<td>2.23 ± 0.38</td>
<td>127.64 ± 0.9</td>
<td>164.76 ± 0.9</td>
<td>27.22 ± 0.9</td>
<td>142.15 ± 0.9</td>
</tr>
</tbody>
</table>

In the PP/PMMA-GNP blend composites, as most of the GPNs are present in the PP phase (Figure 6.17) and PP segmental mobility is hindered resulting in rise in tan delta value. Owing to the selective localisation of GNP the $T_g$ of PS increases gradually with the addition of GNP while in the PP/PMMA blend composites a noticeable rise in the $T_g$ of PMMA is seen after 2 wt.% addition. An increase in $T_g$ in GNP nanocomposites has been attributed to the higher surface roughness of GNP [36] and that the particles strongly attract polymer molecules. This strong interaction between polymer and GNP reduces the polymer chain segmental mobility and facilitates good dispersion at all filler loadings. Consequently, the amount of interfacial area between polymer and GNP increases with filler content, causing an increase in $T_g$ as well as an increases in modulus [36]. As the $T_g$ of PMMA also increases we can say there appears to be a good interaction between PMMA and GNPs.
6.3.1.4 Electrical Impedance

Electrical conductivity as a function of frequency for PP/PMMA and PP/PS composites at various loadings of GNP is plotted in figure 6.23. In both the PMMA and PS based composites specific conductivity is dependent on the frequency at lower loadings (0.5 and 1 wt. %) of GNP. In the PMMA based composites at 2 wt % GNP loading three distinct regions are present i.e. two straight and one transit region at approximately 15000 Hz. In the first region the specific conductivity values are independent of frequency below 15,000 Hz. These transitions are reported when the capacitive elements dominate the resistive element in the system [24]. The third region is frequency dependent and the specific conductivity increases with the frequency. No such regions are present in PS based composites at 2 wt % of GNP, which are three orders of magnitude more conductive than the PMMA based composites. Phase elongation of PS resulting in the formation of a co-continuous phase is the reason for this rise in the electrical conductivity. Selective localisation of GNP in the co-continuous PS phase (double percolation) eases the formation of a conductive network in the PP/PS blend composites. In PP/PMMA blend composites no such co-continuous morphology is formed and that is why they are less conductive at the same wt.% of GNP. In the PP/PS composites the formation of a conductive network is complete at 2 wt.%, and further addition of GNPs does not increase conductivity. Whereas in PMMA based materials the specific conductivity does not increase appreciably at 0.5 and 1 wt.% of GNP and at 5 wt.% the increase in electrical conductivity is over three orders of magnitude, indicating that the conductive network formation is not complete at 2 wt.% of GNPs unlike the PP/PS blend composites.
6.3.1.4.1 Percolation Theory
As the density of the conductive filler increases within a polymer matrix, the particles start to form a conductive network. Eventually, a point is reached where the network is complete; at this point the resistance to electric flow is a minimum and the material starts to conduct electricity. Further addition of filler beyond this point does not increase the conductivity significantly. As discussed earlier, percolation theory has been used to determine the critical filler content [40]. Electrical conductivity data fitted by percolation theory (using the power law function in Origin Pro software, as described in section 6.2.2.5) is shown in figure 6.24. The critical GNP contents determined using the percolation equation are 0.67 and 1.02 wt.% for the PS and PMMA based binary blend GNP composites, respectively.

The lower percolation value for the PP/PS-GNP blend composites is due to the double percolation effect. In fact the very steep rise in conductivity values between 1 wt.% and 2 wt.% in the PP/PS composites could not be fitted accurately by the percolation equation, hence the $R^2$ values of PP/PS GNP are less than those for the PP/PMMA composites. Measured values of $t$ applying percolation theory to the experimental data are 2.9 for PS based composites and 3.8 for PMMA composites. The values for the PP/PS-GNP blend composites are a higher than the value of 2.2 reported in the literature for the formation of a three-dimensional conductive network [24]. From the percolation theory results of CNT (section 6.2.2.5) and GNP based composites it can be suggested that blends forming a co-continuous morphology result in higher $t$ values than for those exhibiting droplet morphologies. Higher values of $t$ indicate the formation of more complex networks [24, 41]. Thus in the current situation, where percolated network is formed wit in a specific phase of a multiphase blend, higher $t$ values can be expected.
Figure 6.23 Specific conductivity of a) PP/PMMA-GNP b) PP/PS-GNP composites at various frequencies
Figure 6.24 Percolation limits fits to experimental data for a) PP/PMMA-GNP b) PP/PS-GNP at various GNP loadings.

\[ \sigma = 1.6E - 6(\rho - 1.02)^{2.9}, R^2 = 0.92 \]

\[ \sigma = 0.38(\rho - 0.67)^{3.8}, R^2 = 0.91 \]
6.4 Summery and Conclusions

From the results obtained by from the different characterisation techniques, it is obvious that composites containing either CNT or GNP exhibit superior mechanical and electrical properties to the neat blends. Morphological changes in the blends due to the presence of these nano-scale fillers have played an important role in improving the mechanical behaviour and making the insulating blend conductive at lower CNT or GNP concentrations. In both the CNT and GNP filled composites, the formation of a co-continuous dispersed phase imparts superior electrical and mechanical properties compared to blends which retain droplet type morphologies. Co-continuous morphology resulted in lower percolation threshold concentrations in the binary blend CNT and GNP composites. Similarly, in the ternary CNT composites one of the dispersed phases forming a co-continuous morphology resulted in improved mechanical behaviour, higher electrical conductivity and a lower percolation limit.
6.5 References


CHAPTER 7:

Conclusions and Recommendations for Future work

7.1 Conclusions

PS (a non-polar thermoplastic) and PMMA (a polar, amorphous thermoplastic) were used in this work to form immiscible binary and ternary blends with PP (a semi-crystalline thermoplastic) as the matrix. Two types of binary blends based on PS or PMMA as the dispersed phase with PP (PP/dispersed phase 80/20 volume ratio) generally resulted in the formation of a dispersed phase (droplet type) morphology. Poor adhesion and a high degree of immiscibility in the binary blends resulted in lower elastic and shear moduli than the homopolymers. Ternary polymer blends with dispersed phases of both PS and PMMA formed a composite droplet (core-shell) morphology with PMMA droplets encapsulated by PS. Dynamic and shear moduli values for ternary blends were between those of the binary blends of both the PS and PMMA and were controlled by manipulating the concentrations of dispersed phase.

The effects of CB particles on the morphology of the binary and ternary blends were studied. Carbon particles imparted electrical conductivity to the insulating polymer blends and varying the concentration of CB in the blends caused micro-structural changes. CB interacted differently in binary blend composites of PP/PS and PP/PMMA due to preferential localisation of the CB in different polymer phases. At 2 wt % CB, PS domain sizes started to increase in size resulting in elongated morphological structures of PS at 5 wt % CB and eventually forming a co-continuous PS phase at 10 wt% CB. In contrast, PMMA droplet sizes decreased as the CB concentration was increased and a
finer dispersed phase morphology was obtained at 10 wt% CB in the PMMA based blend composites. A general trend of increasing elastic moduli and $T_c$ with CB content was observed in both types of blend composites by DMTA and DSC. Impedance spectroscopy revealed that the formation of a percolated network was aided in binary CB composites by the formation of a co-continuous morphology, due to double percolation effects. Thus, PP/PS-CB10 binary blend composites showed higher conductivity values than equivalent PP/PMMA-CB blend composites. In the ternary blends, electrical conductivity and elastic moduli of the CB composites were found to be a function of concentration of individual dispersed phase polymers (PS+PMMA) and tended to exhibit properties similar to the binary blend composites of the dominant dispersed phase.

Carboxylic acid functionalised MWCNT interacted differently with the dispersed phases in the binary polymer blend composites than CB. CNT showed greater affinity towards PMMA, due to the polar nature of PMMA and the polarity induced on CNT due to functionalisation. This resulted in elongation of PMMA domains owing to strong CNT-PMMA interactions and eventually resulted in the formation of a co-continuous phase. Functionalised CNT were found to align at the interface of PP/PMMA by TEM. Eventually as CNT content increased, the PP/PMMA–CNT composites developed superior electrical and mechanical properties over the PP/PS-CNT composites. For example, PP/PMMA-CNT composites showed electrical conductivity 4 orders of magnitude higher than the PP/PS-CNT composites. Dynamic moduli of the PP/PMMA-CNT blends composites were higher than for PP/PS-CNT composites owing to the co-continuous morphology of the PMMA based composites. Ternary polymer blend-CNT blend composites, similar to the CB composites and neat ternary polymer blends, tended
to exhibit properties similar to the binary blends of the dominant dispersed phase (PS or PMMA).

GNP interacted in a similar way to CB towards both the PP/PS and PP/PMMA binary polymer systems. Thus, PS phase was preferred over PP in the PP/PS composites; but GNP had affinity for PP as well, whilst in PP/PMMA composites neither dispersed phase was preferred and GNP resided in the PP matrix. Preferential distribution of GNP in PS led eventually at 2wt% GNP to the formation of a co-continuous PS phase, resulting in superior moduli and electrical conductivities for the PP/PS composites. The percolation threshold was achieved at lower concentration of GNP in the PP/PS-GNP composites, and the ease of formation of a conductive network and higher values of electrical conductivity were due to the co-continuous morphology of the PP/PS-GNP composites and to double percolation effects.

With all the filler particles used in this work (CB, CNT, GNP) a general trend of rise in PP $T_c$ was observed due to the nucleating effects of all the filler particles. The greatest rise in $T_c$ was 15 °C in the PP/PMMA-GNP 5wt% blend composites. The rise in $T_c$ was found to be dependent on the preferential interaction of the filler particles, e.g. in the CB based composites the preferred phase is PS and thus there was less PP-CB interaction causing a $T_c$ rise of ~5 °C at 10 wt% CB, whilst for the same concentration of CB the $T_c$ of the PP/PMMA binary increased by ~9°C. The nucleating effect of CNT caused a rise of ~12 °C in PP/PS based composites while for PP/PMMA only ~8 °C rise was observed due to preferential localisation of CNT in the PMMA.

Similarly, the effect of filler addition on reinforcement was different for both the PP/PS and PP/PMMA blend systems due to differences in the preferred phase of the filler
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particles. In PP/PS polymer blend composites the dynamic storage moduli was ~1.6 times that of pure PP at 10 wt% CB whereas increases of ~1.52 and 2.08 times were achieved at 5 wt% of CNT and GNP respectively. Similarly, addition of CB, CNT and GNP to PP/PMMA blends reinforced the blends, giving modulus increases of ~0.83, 1.72 and 2.23 times, respectively. The rise in the dynamic storage moduli at lower concentrations of nanofillers (CNT and GNP), compared to micro sized fillers (CB), were due to both the large surface area of nanofillers available to interact with the polymers and to strong polymer-filler interactions.

As the morphological changes caused by the addition of CB, CNT, and GNP to PP/PS and PP/PMMA resulted in different $T_c$ and dynamic behaviour for the same blend, likewise the changes in $T_g$ of the dispersed phase of the polymer blends were found to be dependent on the morphological changes caused by selective localisation of fillers. In the PP/PS blend–composites the $T_g$ of PS increased by ~5 °C at 10 wt% CB whilst the increase in $T_g$ was ~3 and 13°C at 5 wt% of CNT and GNP, respectively. Again, due to preferential interaction causing better polymer-filler adhesion, filler particles impart resistance to segmental movements of dispersed phase polymer chains causing $T_g$ to rise. Consequently, the maximum rise (~12 °C) in $T_g$ of PMMA in PP/PMMA based composites was observed with GNP

Carbon fillers created a conductive network within the blends, and selective localisation of the fillers helped to decrease the critical percolation threshold concentration due to formation of a double percolated network. For example, with GNP a co-continuous morphology (PP/PS-GNP composites) resulted in a percolation threshold concentration of 0.61 wt% GNP; while for the droplet morphology of the PP/PMMA –GNP composites the value was 1.02 wt%. Similar results were observed with CB and CNT
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particles. The values of dimensionality constant, $t$, obtained by percolation theory fitting to the experimental data were 3.8, 3.3 and 4.2 for CB, CNT and GNP particles, respectively. Values of 2.9, 3.9 and 3.2 for CB, CNT and GNP in PP/PMMA based blend composites were obtained. These values are very high compared to theoretical value of $t = 2.2$ for the formation of a 3D network. Moreover the highest $R^2$ values obtained for the electrical percolation plots were for CB composites (0.97, 0.95 for PP/PS-CB and PP/PMMA-CB blend composites) compared to 0.92 and 0.91 for the CNT and GNP based PP/PS systems, and 0.97 and 0.92 for the CNT and GNP base PP/PMMA systems, respectively. The reasons for these variations in $t$ and $R^2$ are not clear and different explanations are presented in the literature. For example, the variation in $t$ is often ascribed to the limitations of percolation theory, or to tunnelling effects, or to the formation of “complex structure” which in this case can be the presence of conductive network within one phase of a co-continuous blend.

7.2 Recommendations for future work

The results reported in this thesis suggest that the end use properties of the blend-carbon particle composites are dependent on the morphologies of the composites. It has also been concluded that these morphologies are dependent on the phase preference of the carbon particles in binary and ternary blend composites. Acid-functionalised CNT resided in the PMMA while both the CB and GNP preferred the PS in the dispersed phase. If the composition of the dispersed phase is changed from 80/20 to 70/30, it may help in forming elongated dispersed phases resulting in formation of a co-continuous morphology at lower filler loadings, and hence electrical percolation may be achieved at lower concentrations due to a more pronounced double percolation effect.
A further study can focus on use of combinations of carbon fillers, particularly when preparing ternary polymer blends. Binary and ternary filler combinations can give superior properties in epoxy composites [1]. Using combinations of CB/GNP electrical percolations were achieved at lower values than GNP alone [1]. Similar results were reported for CNT/GNP-epoxy composites [1]. A schematic diagram of carbon particle arrangements when used in combination was proposed (Figure 7.1) and confirmed by SEM images [1].

![Schematic diagram of carbon particle arrangement when used in combination](image)

*Figure 7.1: Schematic diagram of carbon particle arrangement when used in combination [1]*

When GNP filler is used alone, the conductive network is formed solely due to contact between the GNP particles. When CB is added with GNP, the CB particles act as spacers which can both decrease the agglomeration of the GNP and effectively link the GNP resulting in the formation of additional conductive paths [1]. The introduction of long CNT together with GNP/CB can further bridge the gaps between graphite sheets, resulting in a remarkable improvement in bulk conductivity [1].

If these combinations are applied to polymer blends containing higher volumes (30 vol %) of dispersed phase. More excluded volume can be created due to preferential distribution of filler in the dispersed phase or interface resulting in a decrease in percolation threshold concentration. On the basis of results presented in this thesis,
addition of combinations of fillers (CB/GNP/CNT) to PP/PS may result in CB and GNP to residing in the PS phase and to CNT forming a conductive network within the PP matrix. The PS dispersed phase would elongate to form a co-continuous phase due to the presence of GNP and CB. CB particles would act as spacers in between GNP particles and hence may result in higher values of electrical conductivity. Using these CB/CNT/GNP combinations in a PP/PMMA binary blend may result in alignment of CNT at the PP-PMMA interface while CB and GNP would be distributed in the PP matrix. In this case the crystallinity of the PP would restrict the free volume available to CB and GNP resulting in percolation through both the PP and PMMA phases.

In ternary blend (CB/GNP/CNT) composites of PP/PS/PMMA, PS would encapsulate the PMMA dispersed phase and CNT would percolate through the PMMA. In contrast, the PS phase would form a co-continuous morphology filled with CB and GNP particles to achieve a lower percolation threshold.

7.3 References

Appendix-1

Prediction of Polymer blend immiscibility by Flory Huggins interaction parameter.

From the table 2.1

\[ N_{PS} = 314 \]
\[ N_{PMMA} = 1198.68 \]
\[ N_{PP} = 1345.63 \]

For PP/PS blends equation 2.4 can be written as:

\[ X_c = \frac{1}{2} \left( \frac{1}{\sqrt{N_{PP}}} + \frac{1}{\sqrt{N_{PS}}} \right)^2 \]

\[ X_c = 0.0035 \]

Equation 2.5 for this polymer blend can be written as

\[ X = \frac{V_r}{RT} (\delta_{PP} - \delta_{PS})^2 \]

Assuming \( V_r = 250 \)

\[ X = 0.39 \]

As \( X \gg X_c \) it suggests the immiscibility in PP/PS blends.

Similarly for PP/PMMA blends

\[ X_c = 0.0015 \]
\[ X = 0.635 \]

For PS/PMMA blends

\[ X_c = 0.0036 \]
\[ X = 0.027 \]

For all the above polymer blend systems \( X \gg X_c \), which is an indication of immiscible polymer blend systems.
Appendix-1

Prediction of morphology by spreading coefficient model

In order to calculate the spreading coefficient of PP/PS/PMMA ternary blend let us assume that:

A= PP
B= PMMA
C= PS

According to spreading coefficient model

\[ \lambda_{CB} = \gamma_{BA} - \gamma_{CA} - \gamma_{BC} \]

Where as component A is matrix and B and C are dispersed phases. \( \lambda_{CB} \) is the spreading coefficient of component C over B. \( \gamma_{BA} \) is the interfacial tension between B and A. \( \gamma_{CA} \) is the interfacial tension between C and A. and \( \gamma_{BC} \) is the interfacial tension between B and C. For the component C to spread over B (to encapsulate B) its spreading coefficient over B has to be positive.

Interfacial tension data from literature (as mentioned in chapter 4)

\( \gamma_{AC} = 5 \)

\( \gamma_{CA} = 3.61 \)

\( \gamma_{AB} = 4.31 \)
\( \gamma_{BA} = 7.7 \)
\( \gamma_{BC} = 1.01 \)
\( \gamma_{CB} = 2.09 \)

Spreading coefficient for all the possible binary combinations of ABC ternary blend can be calculated as.

\[
\lambda_{AB} = \gamma_{BC} - \gamma_{AC} - \gamma_{BA} = 1.01 - 5.0 - 7.7 = -11.69
\]
\[
\lambda_{BA} = \gamma_{AC} - \gamma_{BA} - \gamma_{AB} = 5 - 1.01 - 4.31 = -0.32
\]
\[
\lambda_{AC} = \gamma_{CB} - \gamma_{AB} - \gamma_{CA} = 2.09 - 5 - 3.61 = -6.52
\]
\[
\lambda_{CA} = \gamma_{AB} - \gamma_{CB} - \gamma_{AC} = 4.31 - 2.09 - 5.0 = -2.78
\]
\[
\lambda_{BC} = \gamma_{CA} - \gamma_{BA} - \gamma_{CB} = 3.61 - 7.7 - 2.09 = -2.79
\]
\[
\lambda_{CB} = \gamma_{BA} - \gamma_{CA} - \gamma_{BC} = 7.7 - 3.61 - 1.01 = 3.08
\]

As all the values are negative except \( \lambda_{CB} \) and that
\( \lambda_{CB} > 0 \)
\( \lambda_{BC} < 0 \)

This satisfies the condition for polymer C (PS) to encapsulate polymer B (PMMA).
Appendix-2

SEM and TEM images of blends

Figure A.1 SEM of a) cyclohexane etched b) un etched PP/PS/PMMA 80/5/15 ternary polymer blend; PMMA encapsulated by PS
Figure A.2 SEM of PP/PS/PMMA 80/10/10 Ternary polymer blend at different magnifications etched with cyclohexane showing PMMA droplet encapsulation by PS.
Figure A.3 SEM of PP/PS/PMMA 80/15/05 Ternary polymer blend at different magnifications etched with cyclohexane showing PMMA droplet encapsulation by PS.
Figure A.4 TEM of PP/PS/PMMA 80/10/10 Ternary polymer blend at different magnifications showing PMMA encapsulation by PS.
Figure A.5 TEM of PP/PS-CB 5wt% blend composites at different magnifications showing CB residing in PS phase.
Figure A.6 TEM of PP/PS/PMMA 80/10/10 -CB (10wt.% ) blend composites at different magnifications showing PMMA encapsulated by PS phase densely filled with CB.
Figure A.7 TEM of PP/PS/PMMA 80/10/10 -CB (10wt.% ) blend composites at different magnifications showing PMMA encapsulated by PS phase densely filled with CB.