Study of the conductivity of Nylon 6/ABS blends.

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STUDY OF THE CONDUCTIVITY OF NYLON 6/ABS BLENDS

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A thesis submitted in partial fulfilment of the requirements of
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PREFACE

This thesis is submitted in partial fulfilment of the requirements of Sheffield Hallam University for the degree of Master of Philosophy. It contains an account of research carried out between October 1996 and March 1999 in the School of Engineering, Sheffield Hallam University, under the supervision of Dr. Syed T. Hassan, Dr. David W. Clegg and Prof. Asim K. Ray. The work reported in this thesis was not carried out in collaboration with other workers and the contents of the dissertation are original, except where references are made to other work. No part of this dissertation has been submitted to other university for a degree.

Mansor Mohamad Saman
September 1999

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ABSTRACT

In this research project the study was conducted on conductivity of acrylonitrile butadiene styrene (ABS)/Nylon 6 blend with carbon black as conductive filler. Three different blends of ABS/carbon black, Nylon 6/carbon black and ABS/ Nylon 6/carbon black with various compositions were prepared by mixing together by using a single screw extruder. Each compound was reblended to achieve homogeneous mixture and the effect of processing was studied.

Conductivity of the low resistance of blends were obtained by measuring sheet resistance using four-point probe as according to ASTM F 1529. The sheet resistance could only be detected for ABS/carbon black 20 wt % and above, and ABS/Nylon 6 with 80:20 ratio with 10 wt % of carbon black. Whereas, for Nylon 6/carbon black blends and the others high resistance of blends, their resistances were measured by Teraohmeter according to ASTM D 257 method.

Percolation threshold (critical volume fraction) of the blends was studied to find actual conductive filler contents to avoid deterioration of mechanical properties. In this case, tensile tests were conducted according to ASTM D 638 to establish their mechanical properties. Meanwhile, scanning electron microscopy (SEM) was used to study the morphology of blended polymers, interface of polymer/carbon black and aggregation phenomenon between carbon black and polymers. The correlation between conductivity, mechanical properties and morphological characterisation of all the blends was studied.

The results show that, the addition of carbon black up to 10%, increases conductivity and tensile strength of ABS/carbon black and Nylon 6/carbon black blends. Conductivity continues to increase with further addition of carbon black, but at the expense of tensile strength reduction due to the effect of brittle nature of carbon black.

By adding ABS in ABS/Nylon 6/carbon black blends, conductivity increases, whereas tensile strength decreases. However, tensile strength of ABS/Nylon 6/carbon black blends were too low to compare with individual polymer blended with carbon black, due to immiscibility between ABS and Nylon 6.

Reblending the compound for the third time increases conductivity and mechanical properties due to increase in homogeneity and uniform distribution of carbon black dispersion. Both ABS and conductive carbon black absorb moisture that can effect the properties of compound. Drying of the compound will remove moisture which will result in improvements in conductivity and tensile strength.

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NOMENCLATURE AND ABBREVIATIONS

σ	Conductivity
φ	Filler density
ρ	Resistivity or specific resistance
ν	Specific void space (DBP value)
ϖ	Weight fraction of filler
ωa	Wetting coefficient
τ_c	Tensile strength of composite
$\varnothing_c$	Percolation threshold (critical volume fraction)
δ_f	Theoretical density of filler powder
ϕ_F	Volume fraction of the filler
δG	Interfacial free energy at the interface
Δg_c	Critical interfacial excess energy
$\gamma_{i\text{-}j}$	Surface tension of i/j interface
ϕ_p	Packing fraction
τ_p	Tensile strength of unfilled polymer
ρ_s	Surface resistivity
ρ_v	Volume resistivity

A	The effective area of the measurement electrode
ABS	Acrylonitrile Butadiene Styrene
$A_{i\text{-}j}$	Area of i/j interface
C	Co-ordination Number
C_c	Critical mean contact number
C.F.	Correction Factor
CB	Carbon Black
d	Diameter
DBP	Dibutyl Phthalate
$dG(\mathrm{mix})$	Free energy of mixing

dH(mix)	Enthalpy of mixing
dS(mix)	Entropy of mixing
DSC	Differential Scanning Calorimetry
EMI	Electromagnetic Interference
EPDM	Ethylene-Propylene-Diene Rubber
ESD	Electrostatic Discharge
EVA	Ethylene Vinylacetate
g	Gap (distance) between measurement electrode and guard ring of Teraohmeter
HIPS	High Impact Polystyrene
I	dc current (amperes)
l	Length
LDPE	Low Density Polyethylene
NBR	Nitrile-Butadiene Rubber
p	Concentration of conductive components
P	Effective perimeter of the guard ring of Teraohmeter
PA	Polyacetylene
PAN	Polyacryonitrile
PAn	Polyaniline
PAR	Polyarylate
PBT	Polybutylene Terephthalate
p_C	Percolation threshold concentration
PC	Polycarbonate
PE	Polyethylene
PEEK	Polyetheretherketone
PET	Polyethylene Terephthalate
PMMA	Polymethylmethacrylate
PP	Polypropylene
PPE	Polyphenylene ether
PPO	Polyphenylene oxide
PPP	Polyparaphenylene

PPS	Polyphenylene Sulphide
PPy	Polypyrrole
PS	Polystyrene
PTC	Positive Temperature Coefficient
PTh	Polythiopene
PU	Polyurethane
PVC	Polyvinyl Chloride
R	Resistance, (Ω)
r	Radius
RFI	Radio Frequency Interference
R_h	Sheet resistance
R_s	Surface resistance
R_v	Volume resistance
s	Probe spacing.
S	Specific surface area
S_0	Surface area of carbon particle
SAN	Styrene Acrylonitrile
SEM	Scanning Electron Microscopy
T	Temperature
t	Thickness of the sample
t	Universal exponent or critical exponent which related to the dimensionality of the system
T_g	Glass transition temperature
TGA	Thermal Gravimetric Analysis
TNF	Trinitrofluorenone
TPUR	Thermoplastic Polyurethane Rubber
TTF-TCNQ	Tetrathiofulvalene-tetracyanoquinodimethane
UV	Ultraviolet
V	dc voltage
V_0	Volume of carbon particle
V_t	Volume of tapped powder

w	Width
W_f	Measured weight of powder sample (filler)

Sample Identification

ABS01CB	ABS with 1 wt. % Carbon Black Blend
ABS05CB	ABS with 5 wt. % Carbon Black Blend
ABS10CB	ABS with 10 wt. % Carbon Black Blend
ABS20CB	ABS with 20 wt. % Carbon Black Blend
ABS30CB	ABS with 30 wt. % Carbon Black Blend
NCB5	Nylon 6 with 5 wt % Carbon Black Blend
NCB10	Nylon 6 with 10 wt % Carbon Black Blend
NCB20	Nylon 6 with 20 wt % Carbon Black Blend
NCB25	Nylon 6 with 25 wt % Carbon Black Blend
ABS2/N8/CB10	ABS/Nylon 6 blend with composition ratio of 20:80 (ABS:Nylon 6) and 10 wt % of Carbon Black content
ABS4/N6/CB10	ABS/Nylon 6 blend with composition ratio of 40:60 (ABS:Nylon 6) and 10 wt % of Carbon Black content
ABS6/N4/CB10	ABS/Nylon 6 blend with composition ratio of 60:40 (ABS:Nylon 6) and 10 wt % of Carbon Black content
ABS8/N2/CB10	ABS/Nylon 6 blend with composition ratio of 80:20 (ABS:Nylon 6) and 10 wt % of Carbon Black content
ABS5/N5	ABS/Nylon 6 blend with composition ratio of 50:50
ABS5/N5 - 2C	ABS/Nylon 6 blend with composition ratio of 50:50 - recycled two times
ABS5/N5/CB2	ABS/Nylon 6 blend with composition ratio of 50:50 and 2 wt % of Carbon Black content
ABS5/N5/CB5	ABS/Nylon 6 blend with composition ratio of 50:50 and 5 wt % of Carbon Black content

ABS5/N5/CB10	ABS/Nylon 6 blend with composition ratio of 50:50 and 10 wt % of Carbon Black content
ABS5/N5/CB20	ABS/Nylon 6 blend with composition ratio of 50:50 and 20 wt % of Carbon Black content
ABS5/N5/CB20-2C	ABS/Nylon 6 blend with composition ratio of 50:50 and 20 wt % of Carbon Black content - recycled two times

CHAPTER 1

INTRODUCTION

Polymers with their high resistivities of 10^{13} - 10^{18} Ωcm and good dielectric performances are normally used in electrical and electronic applications as insulators. However in the last thirty years[1-7], great interest in conductive polymers has been prompted by their advantageous properties, including mechanical strength, flexibility, dimensional and chemical stability, low cost and ease of processing.

The electrical resistivity of the polymer can be reduced with the addition of electrically conductive filler which can produce conductive polymer composites. Conductive plastic composites have a wide variety of applications, example includes electrostatic discharge (ESD) products, conductive packaging for static-sensitive electronic components (anti static), conductive shield compounds for cables (semi-conductive) and highly conductive materials conducting discs for information storage and EMI/RFI shielding.

The conductive fillers normally used are metal, carbon black, graphite and intrinsically conductive polymers in the form of fibres, flakes, powders, spheres and platelets. However, carbon black was the earliest filler[8] which is used widely because it is cheap and light. The distribution and amount of filler are very important in the production of conductive composites.

An excess amount of filler can cause deterioration of mechanical and other properties of base material. To avoid this, a percolation threshold, referred to as the critical amount of filler necessary to build up a continuous conductive network, has to be optimised. It depends on filler particle form, spatial distribution, processing conditions, filler porosity and the use of additives.

The orientation of a conductive composite during processing affects the distribution of the carbon black aggregates and results in greater conductivity in the direction of orientation rather than perpendicular to it. To maintain the original structures of particles, extrusion is the more practical process because of the economical and environmental considerations.

Nylon, a semi-crystalline polymer, has excellent dimensional stability at elevated temperature, heat resistance and low resistivity (10^{12} S m^{-1}) polymer. Previous research[7] shows that nylon 6 gives high conductivity compared to other polymers due to the amide group. ABS is an amorphous polymer with an excellent balance of properties including good toughness, rigidity, appearance and good chemical resistance. The unique combination of these amorphous and crystalline materials provide an excellent balance of properties of materials[9-14], such as good appearance, impact resistance, chemical and heat resistance, dimensional stability and better flow.

Besides these good properties, the blend of these two different phases of polymers is interesting in investigating conductive behaviour. Previous research[15] showed that carbon black was found to be preferentially located in the amorphous phase of semi-crystalline polymers. Rejection of conductive filler occurs from the crystalline phase and segregates in the amorphous regions. This is an interesting effect as there are implications for the percolation threshold at which conducting networks are generated in the polymer and/or polymer phase.

1.1 Objective of Study

The principle aim of the research is

i) to study the effect of amorphous/crystalline phase of ABS/Nylon 6 blends and the location of carbon black in both phases on conductivity of the composite

ii) to show how the composition (ABS/ Nylon 6/ Carbon black) affects conductivity and to find a suitable ratio that can reduce the amount of conductive filler required.

iii) to create new material with mechanical properties tailored to a particular application. Therefore the mechanical properties of the blend will be studied, since addition of fillers modifies the mechanical properties of polymers.

This is a complex problem because the nylon has two phases and ABS contains amorphous phase of various types e.g. Styrene Acrylonitrile and Butadiene Styrene copolymer.

The research programme will include the following:

1. Blend ABS with various amounts of carbon black.
2. Blend Nylon 6 with various amounts of carbon black.
3. Blend of Nylon 6 with ABS with different composition than followed by different amount of carbon black

   Percolation point will be detected for every blend of different composition.
4. Evaluation of the following properties:
   - i) Resistivity/Conductivity
   - ii) Morphology by SEM
   - iii) T_g by DSC
   - iv) Mechanical Properties - Tensile Strength

The conductivity performance is determined by sheet resistivity measurement using a four-point probe technique.

In this project, scanning electron microscopy (SEM) was used to study the morphology of blended polymers; the interface of polymers/fillers and adhesion between them, and the random dispersion of the filler within the system. Also, the basic shapes of the filler particles and the aggregation or agglomeration phenomenon usually associated with the particles will be observed.

1.2 Outline of Thesis Structure

The Introduction (Chapter 1) provides an outline of an introduction to polymer resistivity and the addition of electrical conductive filler to produce conductive polymer composites. The chapter refers to conductive filler used and its distribution. The advantages of ABS/Nylon 6 blends as conductive composites are also explained. Objectives of the study are presented and the research programme is outlined.

The Literature Review (Chapter 2) covers the historical background of conductive polymers, follows the definition of conductivity, composites and conductive polymers. Three types of conductive polymers are described. Conductive composites are explained in more detail that include polymer, conductive fillers used and percolation threshold. The classifications of polymer blends are elaborated.

Materials and Processing of Experimental Materials (Chapter 3) covers data of ABS, Nylon 6, carbon black and conductive polyamide compounds. Single screw extruder was used for blending. The blends were compressed by hydraulic hot press into a sheet form.

Theoretical Analysis (Chapter 4) includes theories of conductivities, mechanical properties and morphological characteristics. The measurement of resistance and tensile strength are derived. The distribution of carbon black is explained.

Experimental Techniques (Chapter 5) explains the experimental technique to measure conductivity, mechanical and morphological analysis. Sample preparations of each experiment are described. Surface and volume resistances were measured by Teraohmeter, while sheet resistance was measured by a four point probe. Instron Testing Machine was used to measure tensile strength. Carbon black distribution was analysed by SEM.

Results and Analysis (Chapter 6) reports the result and analysis of conductivity, mechanical and morphology of blends. Resistance measurements of ABS/carbon black, Nylon 6/ carbon black and ABS/Nylon 6/carbon black blends are summarised in tables. Tensile strengths of the blends are also included in tables. SEM photomicrographs illustrate distribution of carbon black in ABS and Nylon 6 phases.

Discussion (Chapter 7) deals with the effect of carbon black on conductivity and mechanical properties of ABS/Nylon 6/carbon black blends. The effect of reblending and polymer composition on conductivity and mechanical properties are also discussed. Morphologies of the blends with different methods of sample preparation are explained.

The Summary and Conclusions (Chapter 8) summarises and concludes the effect of carbon black, reblending and polymer composition on the properties of ABS/Nylon 6/carbon black blends.

Future Work (Chapter 9) suggests further research in the area of conducting polymers.

CHAPTER 2

LITERATURE REVIEW

2.1 Historical Background

There are different ways to make conducting polymers, by pyrolysis, doping and producing inherently conductive polymer structure by incorporating a transition metal atom into the polymer backbone[16].

Investigations into piezoelectric polymers extend as far back as the 1920s, when it was discovered that certain organic polymers such as rubber and celluloid could be rendered piezoelectric by cooling in an electric field[17]. Research was continued with biological polymers in 1941 by Martin[18], who found a small piezoelectric effect in the protein keratin (a constituent of hair and finger nails). This area was further investigated by Fukuda in the 1950s and 60s[19,20]. He found detectable piezoelectricity in wood, bone and tendon, DNA, polysaccharides and the polypeptide poly-γ-methyl-L-glutamate.

Research and development activities on intrinsically conductive polymers have been pursued over the last ten to fifteen years but have yet to bear any significant result[1]. In addition these polymers are mechanically weak and are impossible to process by normal melting or solution techniques. They can be utilised as light weight batteries, low cost photovoltaic cells, photoresists for integrated circuits, light weight wires and cables, sensors and EMI shielding.

The other method to make polymers electrically conducting[16] is by the incorporation of conductive fillers which are not related to the chemistry of the polymer. Conductive polymers are used instead of metallic conductors, because of:

i) Ease of shaping
ii) Low density
iii) Wide range of electrical conductivities
iv) Low thermal conductivity
v) Corrosion Resistance

Conductive rubber has been known since the late nineteenth century. It was a major interest and patented in 1930, when it was used for prevention of corona discharge in cables[21]. Interest in the use of non-insulating rubber for antistatic purposes was developed in the late 1930s. The effective development of antistatic rubber goods to medical use was after 1945. Conductive material has been used for heating purposes since 1940.

Plastics have become antistatic and conductive recently. In the late 1950s and early 1960s, metals were added to plastics to produce conductive materials. The method of processing and the properties of the conductive epoxy compound containing silver was outlined by Delmonte[22], Miller[23], and Kilduff and Bendery[24]. Gold, silver and nickel have been used in conductive paints.

Carbon black has been used as a reinforcing ingredient in polymer composites for the last 50 years[25]. In the rubber tyre industries it was used to enhance wear resistance. At present carbon black is also used in plastics for three purposes: colouring, UV light absorption and conductivity[26]. For the first two purposes only 2 phr are used, but for antistatic more than 5 phr is used.

Research was undertaken in early 1970s to minimise use of conductive filler in conducting composites. Critical volume fraction, also called percolation threshold, is a critical volume amount where a transition of insulative-conductive occurred. The theory of percolation began with Kirkpatrick[27] in 1973. In 1975 Janzen related the theory with a continuous conductive network in polymeric matrix built by carbon black[28] which depended to the filler's structure.

Miyasaka in 1982 also agreed that critical volume fraction is related to carbon black properties[7]. It not only depends on density, surface area and filler volume, but also interfacial energy with polymer phases. The conductive path in the polymer phase was studied in depth by Ruschau and Newnham[29] in 1992. They believed that packing behaviour of conductive filler that produces conductive skeleton in polymer, varies with the variation of filler's morphology.

Research to minimise the use of conductive filler in polymer blends still being carried forward by researchers. One of the ways is to introduced the fillers in polymer blends. Although first commercial thermoplastics blend developed in 1942[30] but the use of conductive filler in the blended polymers started around 1990s. In polymer blends, conductive fillers are distributed in different phases and interfaces of polymers. However distribution stages are different with the types of polymer blends.

The advantage of a polymer blend is, the ratio of blend at which the structural connectivity of a filler-rich phase is formed, is also a factor in reducing percolation threshold. Previous research[15,31-35] found the highest conductivity point at a certain blend ratio. Gubbels found that at PE/PS blend of 45/55 weight composition the percolation threshold was 0.4 wt % of carbon black or volume fraction of 0.002[33]. In conductive polymer blends double percolation are found, one for the polymer phase and one for the filler[36].

2.2 Conductivity

Electric current is a flow or directed motion of electric charges. The conductivity σ ($\Omega^{-1}\,m^{-1}$) is the ability of ions to migrate through the solid[1]. It also means the ratio of the current density in a conductor to the electric field cause the current to flow. That is the inverse of resistivity ρ (Ωm).

The materials in which the electrons are completely free to move are called ideal conductors, and those in which they are restricted, are called ideal insulators. Most metals are quite good conductors whereas ceramic and plastics are generally good insulators. The range of conductivities of materials is shown in Figure 2.1[37]. To determine how good a conductor is, a potential difference (a voltage) is applied across a sample of the material and the current flow is measured.

2.3 Composite

A composite is a solid material containing two or more constituents, in which the individual components retain their separate identities. It has properties different from those of its own components. There are different types of composites which consist of polymer composites, metal composites, concrete composites, ceramic composites and so on.

Polymer composites are categorised into combinations of: polymer-polymer (polymer blends), polymer-gas (foamed polymer) and polymer-filler (e.g.: glassfibre reinforced plastics)

2.3.1 Matrix

The matrix is the component of a composite material in which the fibres or filler materials are embedded. For polymer composites, the matrix is a homogenous polymer that may be thermoplastics or thermosetting polymer. Thermoplastics are polymers that soften when heated and harden when cooled. Thermosetting polymers are polymers in which chemical reaction (cross-linking) happens while the resins are being moulded.

2.3.2 Fillers and Reinforcements

Fillers may be defined as additives in solid form added to a polymer either for economy or to modify its properties. They are important in functional roles such as improving the stiffness or surface finish of the final product. Fillers are generally inorganic materials such as calcium carbonate, silica, talc and glass. Organic fillers are wood flour, cellulose fibre and so on. Fillers do not exist as discrete particles, but as aggregates and agglomerates.

2.4 Conductive Polymers

As shown in Figure 2.1, polymers are electrical insulators with conductivities in the range of 10^{-13} - 10^{-18} Ω^{-1} cm^{-1}. Electroactive or conductive polymers are divided into three groups according to the way they are processed. There are intrinsically conductive polymers, filled polymers, and piezoelectric and pyroelectric polymers.

2.4.1 Intrinsically Conductive Polymers

Intrinsic polymers, also called doped polymers, are prepared by the introduction of specific functional groups or atoms containing free electrons into polymers[38]. The three methods involved are chemical (vapour and immersed), electrochemical (can produce p-doped and n-doped) and photo-chemical (irradiation). Examples of this group of polymers are polyacetylene (PA), polyphenylene sulphide (PPS), Polypyrrole (PPy), Polythiophene (PTh), Polyparaphenylene (PPP), Polyaniline (PAn), tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) and trinitrofluorenone (TNF). The conductivities of this class of polymers are around $10^{2}\,\Omega^{-1}\,cm^{-1}$.

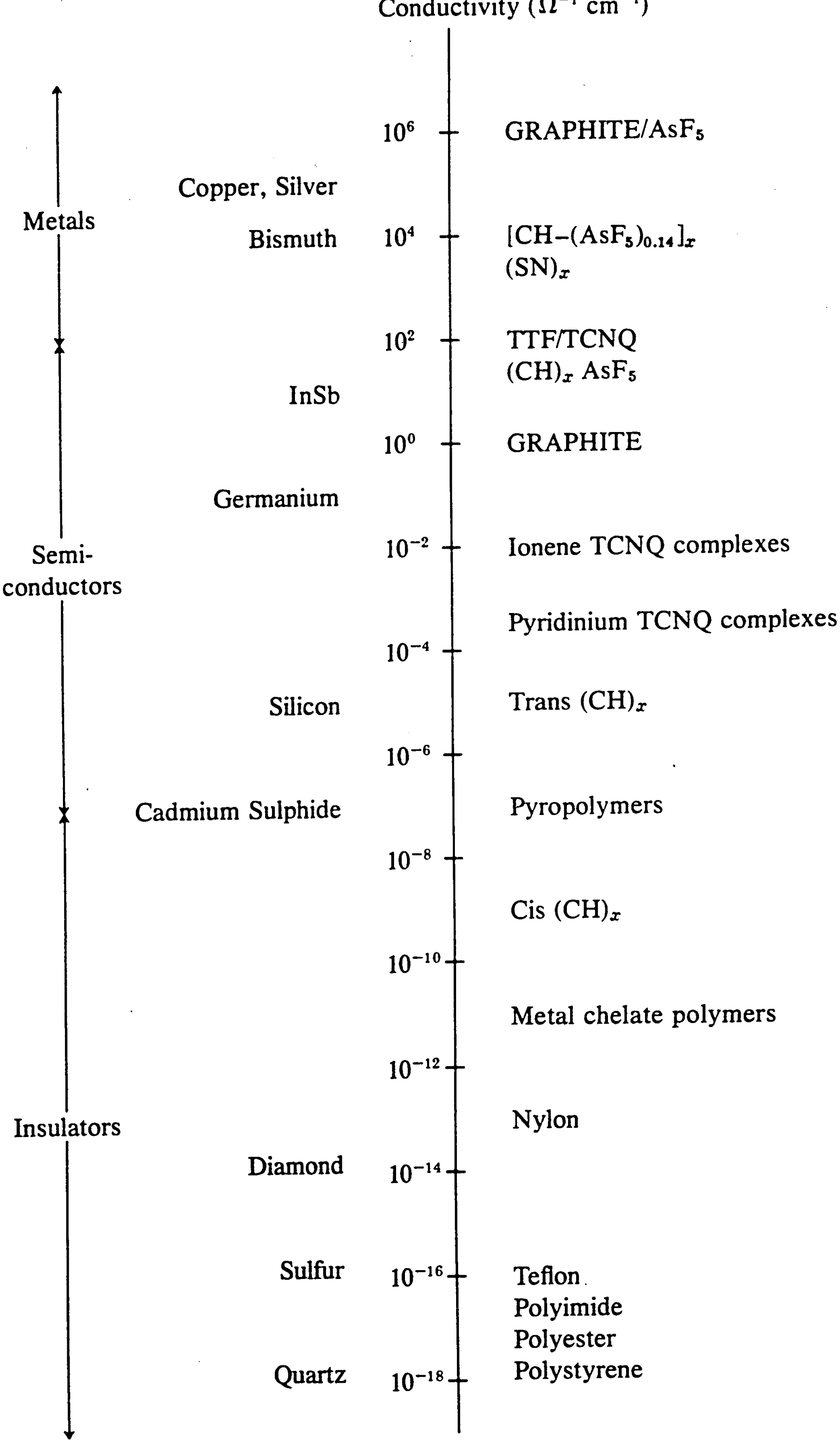

Fig. 2.1: The Conductivity of Materials [37]

2.4.2 Filled Polymers or Conductive Composites

Meanwhile, filled polymers or conductive composites consist of polymers and conductive fillers. Polymers normally used for such applications are polycarbonate (PC), polyolefin, acrylonitrile butadiene styrene (ABS), polyamide, PPS, polyurethane (PU) and ethylene vinylacetate (EVA). Conductive fillers are carbon black, carbon/graphite fibres, metal fibres, metal flakes and powders, and metallised fibres, spheres and platelets[8], and intrinsically conductive polymers. Carbon black is widely used as conductive filler because it is cheaper and does not have much effect on the physical properties of polymers.

Conductive composites can be classified into three categories: anti-static, semi-conductive and conductive according to the filler contents. Conductive plastic composites are used in a wide variety of end use applications; from less conductive electrostatic discharge (ESD) products to highly conductive materials for EMI/RFI shielding.

2.4.3 Piezoelectric and Pyroelectric Polymers

The crystalline materials with the lack of centrosymmetry, can allow movement of the positive and negative ions when mechanically stressed to produce a dipole. These materials are termed as piezoelectric. The piezoelectric materials also possess pyroelectric properties, i.e., electric polarisation is generated at temperature change. These classes can be subdivided further into ferroelectric crystals, in which the dipole moments of the individual crystalline units can be reversed by the application of an electric field[16].

2.5 Conductivity Factors

The conductivity of a material depends on many factors. One of the factors is crystallinity[8]. Crystalline and semi-crystalline polymers attain conductivity at lower loading of conductive filler compared to amorphous polymers, since higher effective filler loading is obtained in the amorphous phase due to rejection from the crystalline phase. Highly crystalline resins tend to impart slightly higher conductivity. Cross-linking of a conductive composite tends to reduce conductivity as a result of lower density and less crystallinity.

Previous research has found that electrical conductivity of a compound increases with increasing crystallinity and decreasing polarity or surface tension of the matrix polymer[5-7,39]. Higher polarity and surface tension of polymer give a larger critical content of filler[7].

In conductive composites, the distribution of conductive fillers aggregates affects its level of conductivity. The distribution of fillers is varied by the method of processing. The orientation of a conductive composite during processing affects the distribution of the carbon black aggregates and results in greater conductivity in the direction of orientation rather than perpendicular to it. Mechanical flexing which pulls the carbon black aggregate apart slightly, results in lower conductivity. However, if the flexed composite relaxes to its original shapes, conductivity returns to near its original value[40].

Mixing time in relation to shear optimisation is very important to obtain maximum conductivity. As shown in Figure 2.2[40], when mixing time increases, conductivity increases as a result of improved dispersion until a conductivity plateau is reached. Mixing times above this point mean that the viscosity becomes higher which can degrade the filler and break down its aggregates. As a result, it lowers the conductivity. Shear input is influenced by resin type, filler type and loading, and type and condition of mixing equipment.

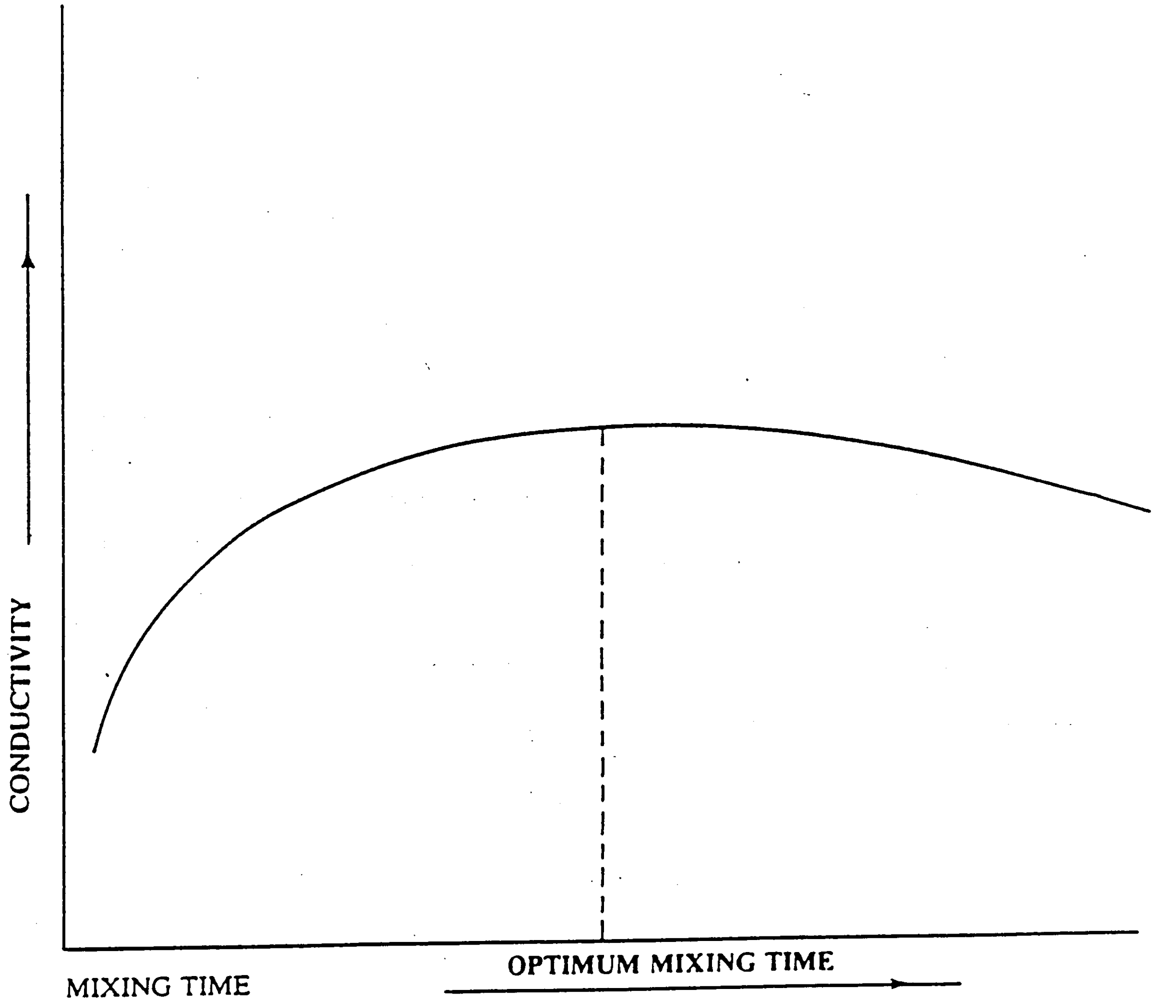

Fig 2.2: Conductivity Vs Mixing Time [40]

The other factor is temperature. In some types of semi-crystalline polymers, the volume resistivity of a carbon black composite changes with temperature. Generally, below the polymer's melting point, volume resistivity increases as temperature increases. This phenomenon is referred to as a positive temperature coefficient (PTC)[41]. This happens because the temperature increase expands the polymer structure which increases inter-aggregate distances. The degree of PTC is inversely related to type, surface area, structure and loading of fillers.

2.6 Conductive Composite

Polymers which have resistivities in the range of $10^{12}\ \Omega^{-1}\ m^{-1}$ to $10^{18}\ \Omega^{-1}\ m^{-1}$, are mixed with conductive fillers in various types and forms. The addition of electrically conductive filler to a nonconducting polymer matrix can reduce electrical resistivity of the polymer due to the formation of chain-like or network-like conductive paths by the filler.

2.6.1 Polymers

Materials or resins with linear, branched or crosslinked structures are classed as polymers whose degree of polymerisation exceeds 50 to 70[30]. They can be classified by their morphologies: amorphous, crystalline or elastomeric.

Crystalline polymers exhibit excellent chemical resistance, ease of processing and significant property improvement with the addition of fibrous reinforcements. However they are tough and stiff and the examples of this type of polymers are Polyethylene (PE), Polypropylene (PP), Polyacetal, Nylon (Polyamide, PA) and Polybutylene Terephthalate (PBT).

Amorphous polymers have good dimensional stability, rigid and hard, but poor chemical resistance and are difficult to process. Many of them are transparent and more brittle than crystalline polymer. Such polymers are Polycarbonate (PC), Polyarylate (PAR), Polystyrene (PS) and Polymethylmethacrylate (PMMA). Elastomers provide good resilience and excellent impact strength, but lack stiffness and tensile strength. Polymers in this group are ethylene-propylene-diene rubber (EPDM), butadiene rubber and thermoplastic polyurethane (TPUR).

2.6.2 Conductive Fillers

Polymer composites can be rendered insulating, antistatic or conductive depending on filler concentrations[15]. Less filler is used when it is in fibre form rather than powder[38]. In addition, fibres can improve the mechanical properties of composites. Mixtures of powder and fibres can also reduce volume resistivity[42].

2.6.2.1 Carbon/Graphite Fibre

Fillers in the form of fibre or flakes can enhance compound performance and reduce its concentration[38]. Carbon/graphite fibres are amongst the newer materials produced. They are made from polyacryonitrile (PAN) or petroleum pitch. PAN based fibres give better physical and conductivity properties compared to pitch based fibres.

With their good properties such as very high strength and stiffness, low density, low mould shrinkage, low coefficient of friction, excellent chemical and environmental resistance, they are used in advanced aerospace structural components, sports goods and automotive industries.

The thermoplastic materials which are commercially used with carbon/graphite fibres are nylon (polyamide), polycarbonate/graphite (PC), polystyrene (PS), PP, thermoplastic polyester, polysulfone, polyphenylene sulphide (PPS), polyamide-imide and polyetheretherketone (PEEK). Within the range of 20 to 40% by weight of chopped carbon/graphite fibre, these compounds can be used for EMI shielding applications.

The brittle characteristic of the fibres gives disadvantages to the filled compounds, where they can easily break during processing, consequently reducing shielding effectiveness and limits in application. It was reported that conductive plastics materials with volume resistivity as low as 0.3Ω-cm can be fabricated from mixtures of carbon black and graphite fibre[43].

2.6.2.2 Carbon Black

One of the earliest fillers to be used was carbon black which was found to provide antistatic properties[8]. Nowadays it is still used widely because it is cheaper and lighter than metallic particles[31,38]. The carbon black particles are in powder or pellet form, may be as small as 140 Å in diameter or as large as 3000 Å[44].

Typical carbon blacks are composed of nearly pure carbon in colloidal entities of spheroidal particles which may be individually dispersed or agglomerated (fused together) in micron sized clusters of branched, irregular shape of aciniform (grape like) morphology[45]. The entities are generally called aggregates. As carbon black was one of the first materials examined after the development of the electron microscope in 1932, the aggregates of the entities can be seen as shown in Figure 2.3[45].

The degree of electrical conductivity imparted (by specific grade) depends on the type of carbon black used which is related to its physical and chemical properties. These properties are dependent on the method by which the carbon black is produced, raw material used and temperature applied. The physical properties are characterised by surface area and structure.

The total surface area of carbon black is determined by the adsorption of nitrogen gas[46] or iodine adsorption in the liquid phase. Higher surface area has more aggregates per unit weight, which are more electrically conductive at a given loading. Porosity which gives more surface area for wetting, can reduce interaggregate separation resulting in increased conductivity.

For nonporous spheres the specific surface area is inversely proportional to particle diameter[45].

$$S = \frac{6000}{\varphi d} = \frac{3225.8}{d}$$

where S is the specific surface area (m^2/g); φ the true density of carbon black, taken as 1.86; and d the particle diameter (nm). The aggregation (aciniform morphology) of carbon black particles, prevents accurate measurement of their diameter.

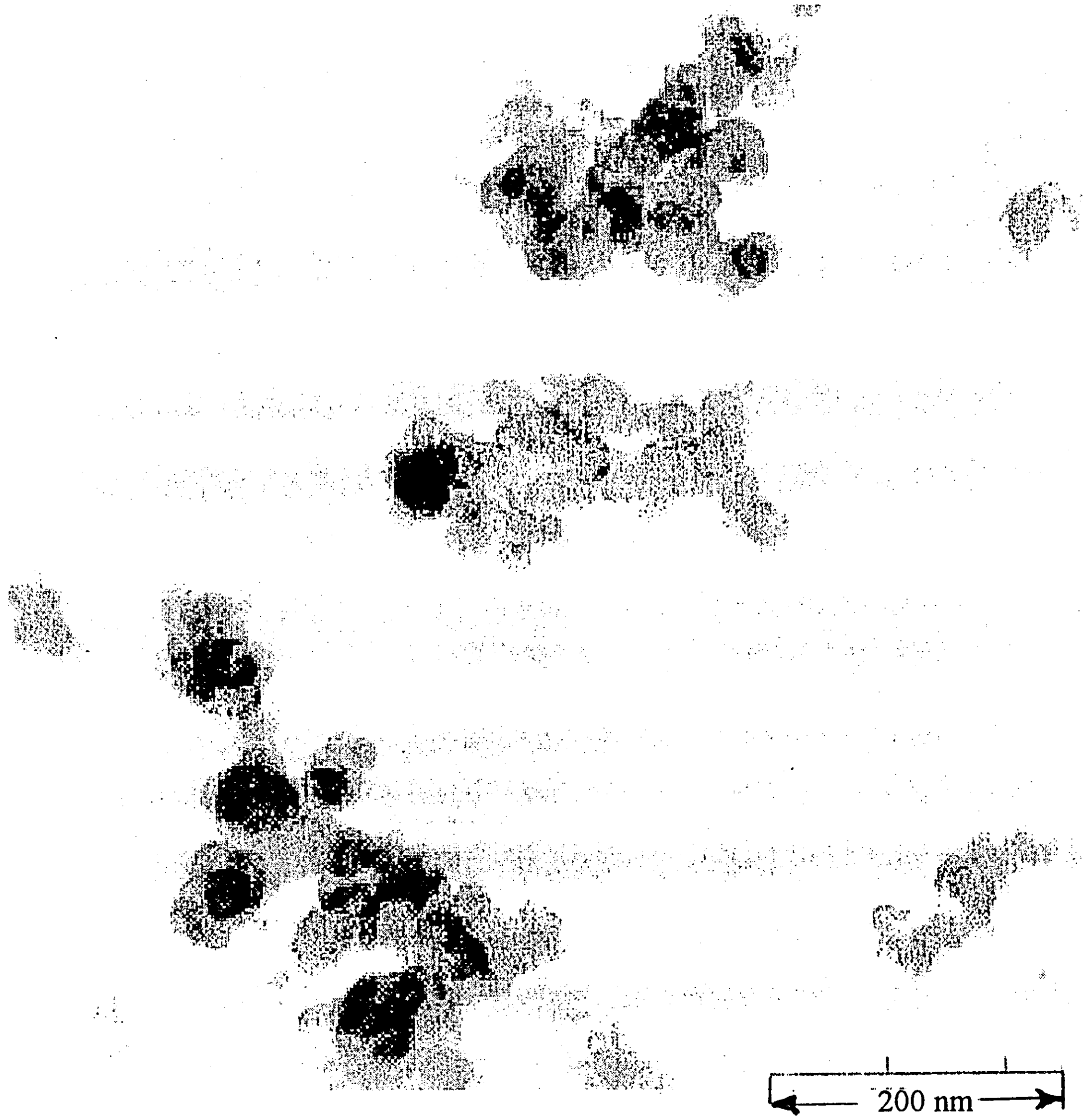

Fig. 2.3:'Graphited' reinforcing black (N 220), illustrating capsular morphology (45)

Carbon black has essentially the same microstructure as graphite but less ordering of the carbon layers in carbon black. The carbon atoms in the layer bonded in hexagonal rings, that are free to flow and carry a conductive current. This structure formed by carbon black when dispersed in a polymer matrix influences the electrical properties of composites[47].

Carbon black 'high structure' is associated with a large number of particles per aggregate, say 100 to 300, whereas 'low structure' may have 30 to 100 particles[45]. Higher structure aggregate means inter-aggregate contact increases, which gives higher conductivity. The formation of long chainlike aggregates of carbon black produces the highest-conductivity composites.

Structure, defined by the Dibutyl Phthalate Absorption Test, characterises the number of particles or the aggregation of carbon black particles (bulkiness)[48]. The test is done by adding *n*-dibutyl phthalate (DBP) until the void spaces in the carbon blacks are filled.

The chemical properties of carbon black affect the conductivity of composite, for example lower volatile contents, gives good conductivity. The rate of absorption also depends on type and loading of carbon black, where if the compound is exposed to high humidity and moisture, it can absorb more moisture compared to the base resin. The compound with high moisture content will show low conductivity.

The carbon blacks are crystallographically related to graphite and, as such, are intrinsic semiconductors, which show resistivity of 0.01 - 0.1 Ω-cm[30]. They will produce different levels of conductivity when mixed with polymers. The conductivity levels are anti-static, semi-conductive and conductive, which are shown in Figure 2.4[40]. They are made by varying the amounts of different grade of carbon black (indicated as X, Y and Z), as shown in Table 2.1[40].

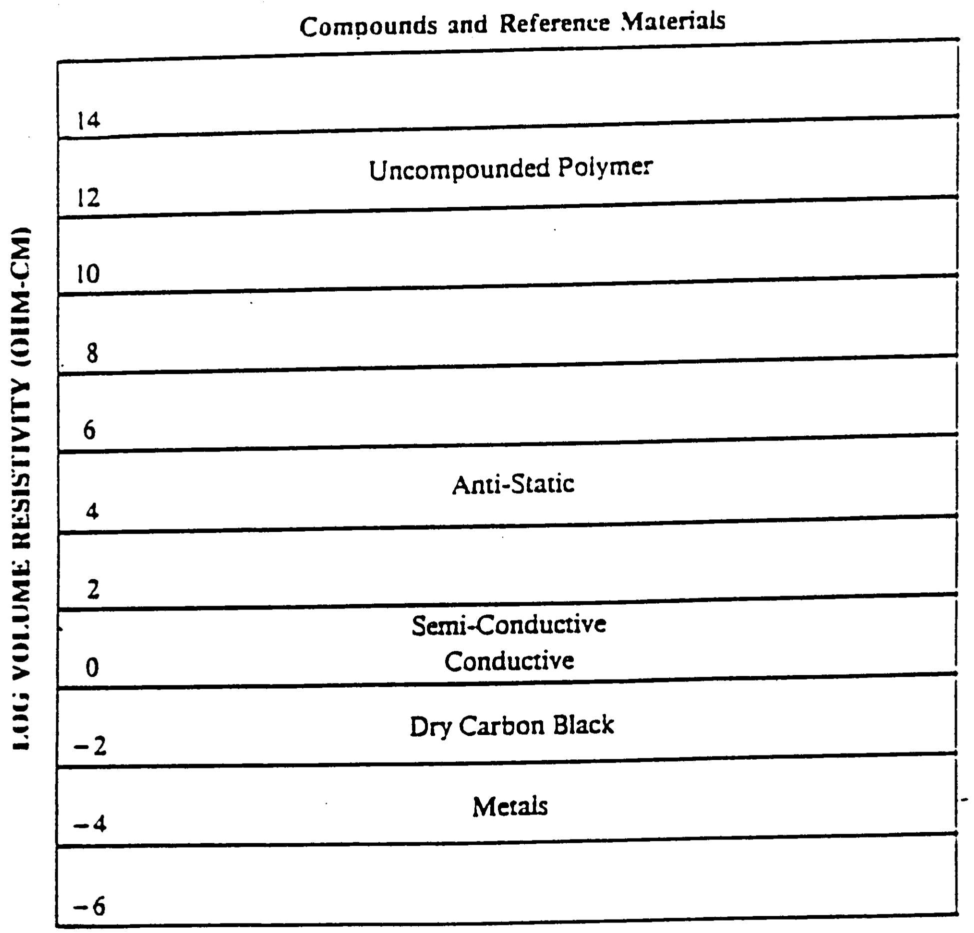

Fig 2.4: Volume Resistivity of Polymer [40]

Table 2.1: Carbon Black Concentrations for Typical Conductive Applications [40]

	Conductive Carbon (weight fraction)		
CB Grade	X	Y	Z
Anti-static	18-25%	15-20%	5-8%
Semi-conductive	25-38%	20-35%	8-18%
Conductive	over 35%	over 33%	over 18%

The shape of the conductivity versus carbon black loading curve is important when selecting a carbon black loading for an anti-static composite. It is similar to a semi-conductive composite, but with higher loading requirement. Figure 2.5[40] shows the curves of volume resistivity versus carbon black (different grade) concentration in EVA.

A critical level is a sharp fall in resistivity occurred when carbon black is increased (around 10 wt %.). If the amount of carbon black increases more than 35 wt %, the composite is very brittle and with more than 40 wt %, it is difficult to mix since the resultant compound is in the form of a powder that will not flow[42].

Ketjenblack is an effective filler which has a higher conductivity value per unit weight compared to other carbon blacks[47,49]. It has been introduced within the last few years. It consists of hollow highly structured graphitic spheres which tend to fracture, interpenetrate and form chains and aggregates when dispersed in a polymer matrix.

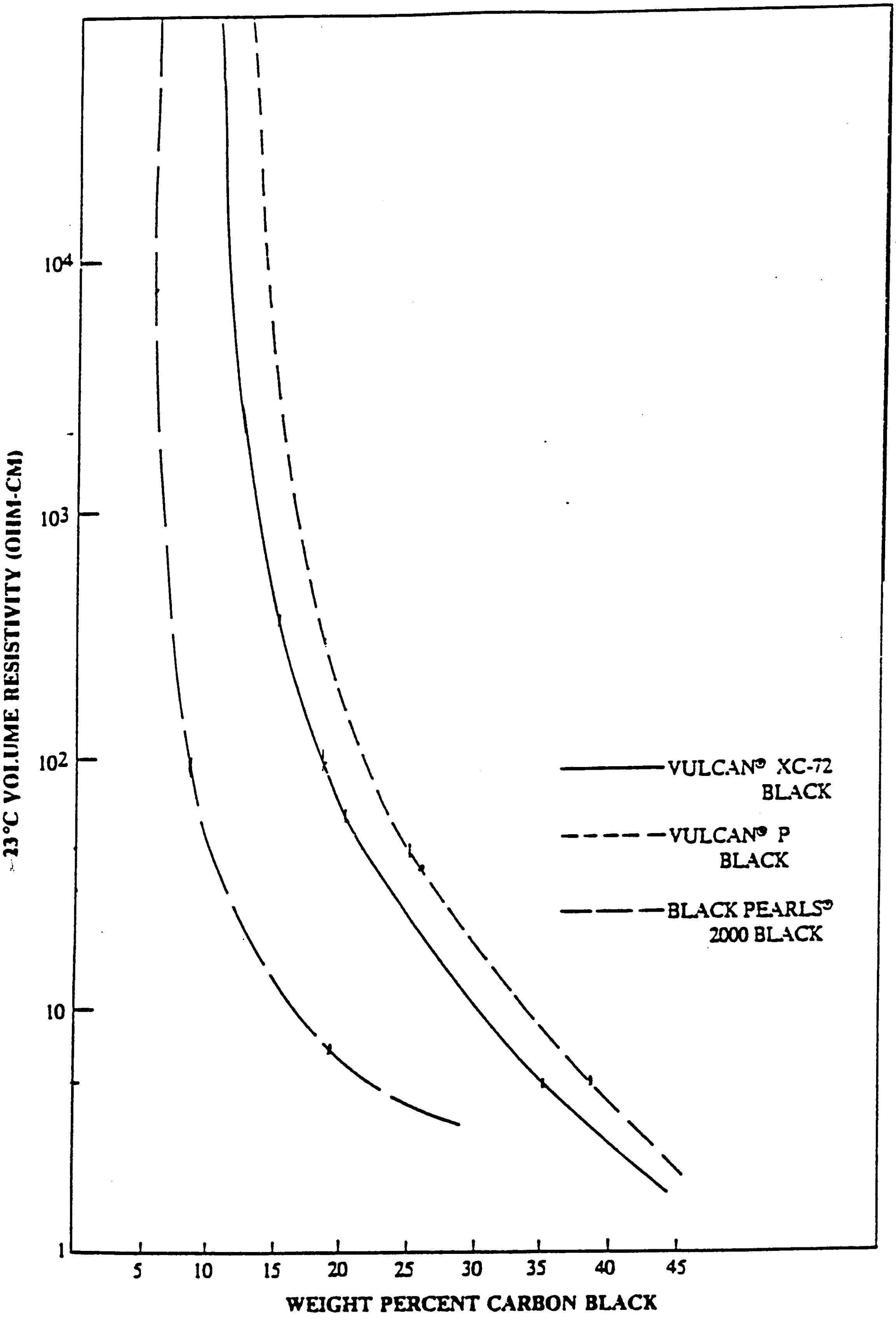

Fig 2.5: Volume Resistivity Vs Carbon Black Concentration in EVA [40]

2.6.3 Carbon Black in Polymer Matrix

Aggregation occurs due to van der Waals forces. Aggregates can be broken up during processing. Carbon black, which is a colloidal particle size pigment, needs a substantial amount of shear to disperse properly in plastics. As mentioned earlier in section 2.5 shear input affects conductivity. To obtain optimum shear input, some factors should be considered such as type of resin, grade of carbon black, loading and mixing equipment[40].

The dispersion of carbon black particles will affect the properties of conductive composites. There are two types of filler distribution in polymer blends; (1) homogeneously distributed in one phase of the blend matrix, (2) heterogeneously distributed at interface of two polymers[31]. Proper dispersion is essential because initially, in the dry state, carbon black aggregates are in direct contact with each other and always agglomerate or associate with many others aggregates. Mixing pulls them apart which consequently increases electrical resistivity. However, repeated crushing of carbon black causes extensive reduction in DBP value[49] (void spaces in carbon black), that increases percolation threshold.

There are three steps of dispersion of carbon black in a polymer[50]. The first step is to force the molten polymer into the interstices of agglomerates and aggregates, where it can eliminate voids and air pockets. The second stage is deagglomeration, in which the agglomerates are pulled apart by shear or extensional flow. In the third stage the individual aggregates are distributed throughout the polymer by the random pattern of mechanical mixing.

The type and amount of conductive carbon black not only influences the conductivity level, but also effects physical and mechanical properties, surface appearance, processability and cost of the composite. This is demonstrated by the relationship of mechanical properties of materials and resistivity of conductive EVA composites with different grades of carbon black as shown in Figure 2.6[40].

The graph plotted in the figure shows that, when volume resistivity decreases, tensile yield strength increases. This means the addition of carbon black causes the tensile strength of conductive composite to increase, while conductivity also increases.

All carbon-polymer composites depend on the conductivity of carbon, whether as graphite fibres, sheets, or black for their desirable electrical properties[47]. Conducting carbon-polymer composites can be used as conductive packaging for static-sensitive electronic components (anti static), conductor shield compounds for cables (semi-conductive), conducting discs for information storage and EMI shielding materials (conductive).

There is a special bond between carbon filler and polymeric material which is considered to give mechanical reinforcement to polymer[51]. Therefore it has been used as a reinforcing ingredient in polymer composites[52]. Carbon-rubber composites give enhanced wear resistance in rubber tyres. More recently there has been a demand for mouldable conducting materials which can be mass produced, are light-weight, corrosion resistant, and are less expensive than metal parts.

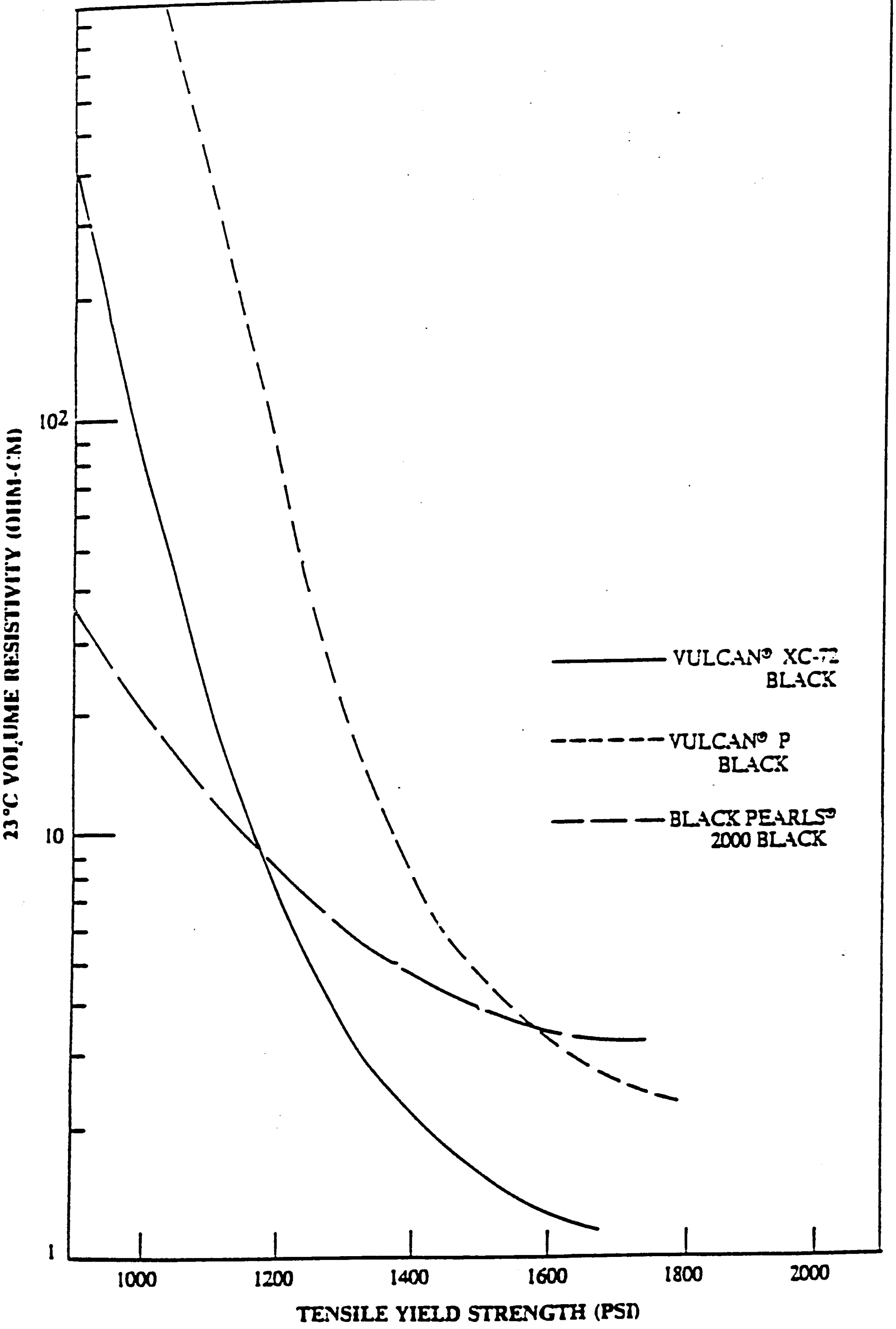

Fig 2.6: Volume Resistivity Vs Tensile Strength of Conductive EVA Composites [40]

2.6.4 Percolation Threshold

Electron flow through a carbon black/polymer composite is achieved when the carbon black forms a conductive network within the polymer. The flow occurs when the carbon black aggregates are in contact or separated by very small distances (electron tunnel). The more aggregates in contact or close for tunnelling, the greater the composite's electrical conductivity.

According to the tunnelling model for conduction, an electron may travel along a continuous carbon pathway and must tunnel across any gap it encounters to reach the next conducting pathway[47]. Some researchers[53,54] believe that the electrical conductivity is due to the "tunnel effect" in the thin layer of polymer sandwiched by conducting particles. The conductive particles within the chain need not necessarily be touching, but small gaps between them may allow current to flow.

The tunnelling charge, that is the conduction mechanism involved, depends on: (1) carbon black resistivity, (2) temperature, (3) non-linear I-V characteristics of the composites, (4) electron micrographs of composites, and (5) the pressure dependence of the resistivity.

Miyasaka and his research team[7] agreed with Janzen[28] that the electrical conduction through the composite occurred when the coagulation of filler particles, which form a conductive network, exist. The critical amount of filler necessary to build up a continuous conductive network and hence accordingly to make the material conductive is referred to as the percolation threshold[33].

This continuation of particles chains is responsible for a sharp break or sudden change in the relationship between the filler content and the conductivity of composite[7,28]. In an insulating matrix containing randomly dispersed conductive particles, a sharp change in conductance when the volume of the conductive particles reaches a critical value is called the percolation threshold[47]. The phenomenon of percolation is illustrated in Figure 2.7.

The increasing of conductive filler produces better conductive paths (continuous) that will increase conductivity. However, after the production of conductive paths, further addition of the filler only gives a small increase of conductivity. The theoretical value of a percolation threshold depends on the hypothetical shape and distribution of particles. The sharp change of conductivity is more obvious in polymer filled[47] with metallic powder compared to carbon black-filled powder.

Thus, above the threshold the material will be conductive and below it, the material is still insulating. Addition of conductive particles will give conductive paths that will increase conductivity. However, it is important to use the lowest possible filler content, because high contents of filler deteriorate the mechanical properties of composite.

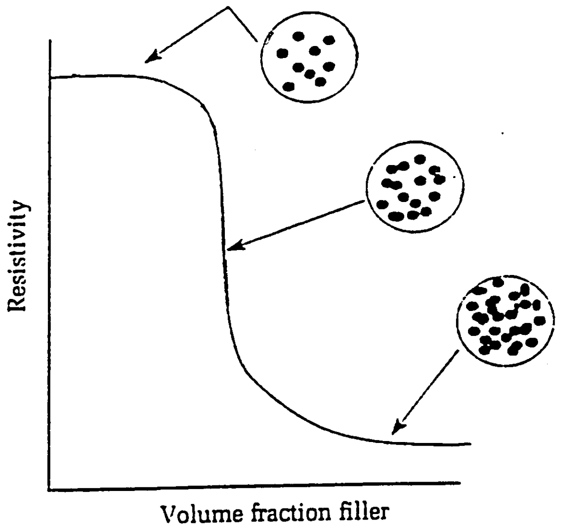

Figure 2.7: The phenomena of percolation from the existence of continuous conductive path

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Figure 2.7: The phenomena of percolation from the existence of continuous conductive path

The theory of percolation was developed by Kirkpatrick[27] which is given by

$$\varnothing_c = [1 + (C/C_c)\varphi\nu]^{-1}$$

where $\varnothing_c$ = Percolation threshold
C = Co-ordination Number
C_c = Critical mean contact number
φ = filler density
ν = specific void space (DBP value)[55]

Janzen proposed that the critical volume fraction for carbon black-filled polymer used as anti-static material must be related to the specific void space for a pure filler material, that is, the ability (or inability) of a filler to pack to a certain density[28].

He also proposed that the relation of percolation threshold with specific void space and structure of carbon black in carbon black composite is given by equation:

$$\varnothing_C = (1 + 4\varphi\nu)^{-1}$$

Janzen[28] found that value of $\varnothing_C$ is between the range of 0.07 to 0.30. The critical point ($\varnothing_C$) depend on filler particle form, spatial distribution, processing conditions, filler porosity and the use of additives[33].

The conductive composite can be thought of as a conductive skeleton with its packing geometry determined by the conductive filler alone[29]. Critical volume fractions can be predicted based on packing behaviour (known packing density) of the filler, provided the filler is well dispersed in the polymer; generally ~ 0.05 below specific packing fraction of the filler.

Packing density varies with the variation of the filler's morphology. Hence, critical volume fraction is given by:

$$\varnothing_c \approx \phi_p - 0.05$$

where ϕ_p = packing fraction given by:

$$\phi_p = (W_f/V_t)/\ \delta_f$$

where W_f = measured weight of powder sample

V_t = volume of tapped powder

δ_f = theoretical density of filler powder

Fine powders do not pack as densely due to the greater significance of short range attractive/repulsive forces, so $\varnothing_c$ increases with increasing particle size. The more spherical the powder, the less interparticle friction and the higher the $\varnothing_c$.

The critical volume fraction is also given by[7]:

$$\varnothing_c = [1 + (k/\Delta g_c)(S_0/V_0)]^{-1}$$

where Δg_c = critical interfacial excess energy

S_0 = surface area of carbon particle

V_0 = volume of carbon particle

k = interfacial energy per unit area of the interface

Near the transition, resistivity[27] is given by:

$$\rho = (p - p_C)^{-t}$$

where, ρ = bulk resistivity

p = concentration of conductive components

p_C = percolation threshold concentration

t = universal exponent

The relation between dc conductivity (σ) and percolation threshold (ρ_c) of the conductive composite is shown by equation[33]:

$$\sigma \approx \sigma_0 (\rho - \rho_c)^t$$

where ϖ = weight fraction of filler

t = critical exponent which related to the dimensionality of the system

Double percolation refers to two percolations, one for the polymer phase and one for the filler in this phase or interface[36]. The filler rich phase becomes conductive at the percolation threshold, the polymer blend becomes conductive at a phase ratio where structural continuity is achieved.

2.7 Polymer Blends

A polymer blend is a mixture of at least two different polymers or copolymers to widen the possible structure of polymers which can combine the properties of both polymers[30]. For example a blend of rigid and soft materials may give an intermediate modulus level product.

In 1942, the first commercial thermoplastic blend was PVC with nitrile-butadiene rubber (NBR). Amorphous-crystalline blends are the most commercially successful blend and alloy groups, because they have two different combination phases that result in balance properties of blend.

There are four reasons why polymer blends are needed:

a. to reduce cost by diluting with low cost polymer

b. to develop desired combination of properties

c. to develop high performance blends

d. for recycling

Compatibility of polymers is determined by the size and distribution of the different phases. In thermodynamics, compatibility is miscibility or mixing on a molecular scale. It can give desired physical properties. It is also defined as one which does not exhibit phase separation after blending. Polymers with greater affinity for one another are mutually soluble and act as one polymer which shows a single glass transition peak. However, in some cases, small affinity can give partial miscibility.

Good mixing is concerned with the magnitude of the interfacial tension between two components. It can be shown by mechanical behaviour that is dependent on the adhesion of interfaces, where the stress can transfer efficiently between the component phases. However, mechanical properties show that, most polymers do not adhere to each other well. From thermodynamics, physical and phase separation behaviour, it is assume that blends which do not exhibit phase separation and having some of the desired properties will at least have some mixing on molecular scale.

The relationship between blends and alloys is shown in Figure 2.8. Generally, there are three groups of blend. The first group which has good affinity for one another and are therefore compatible (miscible) are homogeneous and show properties of single phase material. The second group which is incompatible (immiscible) is heterogeneous, that exhibit miscibility and immiscibility under certain conditions. The third group are a group of blends which exhibit both miscibility and immiscibility depending on the conditions.

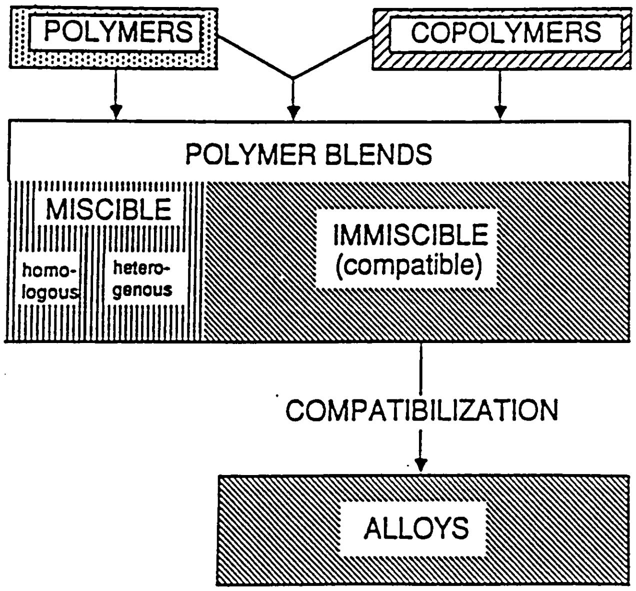


Fig. 2.8: Interrelation in Polymer Blend Nomenclature (30)

2.7.1 Miscible Blends

Three types of miscible blends are as follows:

1. Both components are amorphous:
   example PPO (high thermal stability, difficult to process) blended with PS (easily processed, poorer thermal resistance) produces a blend that can be easily processed but thermal resistance is lower than pure PPO, depending on PS amount which reduces cost (PS cheaper)
   others example are: PMMA + SAN, PPE/PS
2. One is a crystalline polymer: e.g.: PC + PET (crystalline)
3. One is a plasticizer: e.g.: PVC/PBT

2.7.2 Immiscible Blends

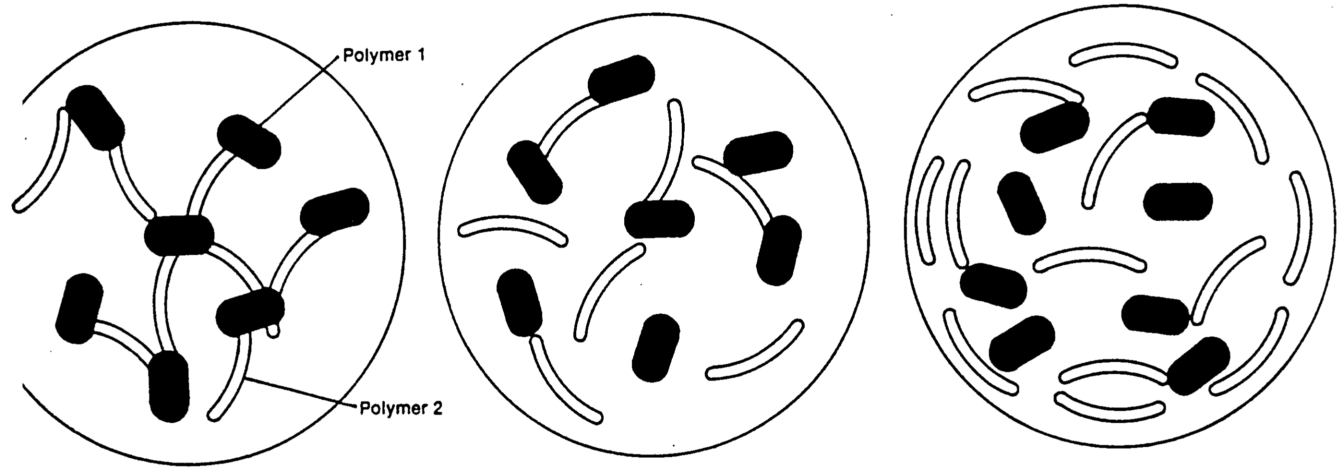
Most blends are immiscible, because the components' different molecular weights have a tendency to separate into their own phases when mixed[56]. This cause immiscible blend systems with poor mechanical properties. However, proper control of phase morphology during processing and addition of compatibilizer, can improve the interfacial properties.

Four types of immiscible blends are:

1. Rubber: Elastomer/Elastomer blend e.g.: automobile tyres
2. Fibre: polyester and cotton in textile technology
3. Thermoplastics Elastomer - phase-separated block copolymer
   - e.g.: ethylene-propylene based Elastomer blend with LDPE
4. Plastics
   a) plastics-Elastomer blends:
      for example: rubber toughening of brittle plastics for impact modification such as HIPS
   b) plastics-plastics blends:
      ABS can be blended with different polymers like PVC, PU and PC to give a variety of properties.

A polymer alloy is an immiscible polymer blend having a modified interface and/or morphology.

Polymer-polymer mixtures can be divided into three possible morphologies: 'miscible', 'partially miscible' and 'immiscible' as shown in Figure 2.9[57]. 'Partially miscible' like 50/50 ratio of blends, will improve adhesion of the interface of two polymers and results in generally good physical and mechanical properties.



Miscible
- Single phase
- Single T_g

Partially miscible
- Phases separate as ratio progresses toward 50/50
- The two T_gs are between the T_gs of constituent polymers

Immiscible
- Two phases
- Two T_gs are similar to constituent polymers

Fig. 2.9: Miscible, partially miscible and immiscible polymer blends on a microscopic scale (57)

Polyolefins prepared in a common solvent may show miscibility, whereas those prepared by mechanical mixing are immiscible. However most polyolefins are compatible.

2.7.3 Polymer Blends as Conductive Polymers

Multicomponent polymer matrices are more suitable for the preparation of electrically conductive polymers compared with single polymer systems[38] because they may form particular morphologies suitable for conductive polymer composites[15].

The high loading of fillers which may reduce the mechanical properties, also increases the melt viscosity of the compound giving difficulty in processing. This high amount can be controlled by the formation of a conductive pathway through multicomponent polymer or polymer blend.

Shaw[58] described a number of methods to achieve dispersion, aided by application of heat, solvents & shearing. In these multicomponent polymer matrices, the conductive filler is distributed in more than one phase of polymer and the interface between different polymers. The distribution of filler which is called 'hetero-distribution' of conductive fillers may give additional advantages, such as decrease of concentration required to obtain an electrically conductive composite[38].

The other advantage of a polymer blend which is the ratio of the blend at which the structural connectivity of a filler-rich phase is formed, is also a factor in reducing percolation threshold. Previous research[15,28,31-35] found the highest conductivity point at a certain blend ratio. Gubbels found that at PE/PS blend of 45/55 weight composition the percolation threshold was 0.4 wt % of carbon black or volume fraction of 0.002[33].

The electrical conductivity of carbon black filled polymer blends is determined by two factors, carbon black concentration in the filler-rich phase and the phase continuity[31]. The combined factors are referred to as the double percolation threshold[31,38] (one for polymer phase & one for the filler in this phase or interface).

CHAPTER 3

MATERIALS AND PROCESSING OF EXPERIMENTAL MATERIALS

3.1 Introduction

Selection of resin, filler and method of processing is very important in compounding of polymeric materials. These factors influence shear optimisation that is needed in filler distribution.

In this project, carbon black was chosen as conductive filler because it is cheaper and lighter than metallic particles[31,38]. The type, amount and distribution of conductive carbon black are very important in controlling physical and mechanical properties, surface appearance, processability, cost of the composite and conductivity level.

ABS is an amorphous polymer that has a resistivity of 10^{14} S m^{-1}. It has an excellent balance of properties including good toughness, rigidity, appearance and good chemical resistance. However it is dimensionally unstable at temperatures greater than T_g of the poly-SAN rigid phase (105°C) and attacked by a number of organic compounds[9].

Nylon, on the other hand, has excellent dimensional stability at elevated temperature, heat resistance and outstanding chemical resistance to moderately polar and non-polar organic species[10]. It is a semi-crystalline polymer which has been selected for study because of its attractive mechanical properties, in spite of the fact that it has very low resistivity (10^{12} S m^{-1}) compared to other semi-crystalline polymers. Previous research[7] shows that nylon 6 gives high conductivity compared to other polymers due to the amide group. However nylons are notch sensitive and are softened by aqueous and highly polar organic materials.

ABS and Nylon 6 are normally mixed with conductive fillers separately to produce conductive composites[7,11]. However in this project, these different phases of polymer were mixed and blended with conductive carbon black. Polymer blends, which are mixtures of different polymers to widen the possible structure of the polymers, can give combined properties of the constituent polymers.

The alloy of modified ABS with nylon introduced by Borg-Warner Chemical Inc., (trade name: Elemid$^{\text{TM}}$)[12], Stapron N[10] and Monsanto (Triax$^{\text{TM}}$) shows a unique marriage of amorphous and crystalline materials and provides an excellent balance of properties[9-14], such as good appearance, impact, chemical and heat resistance, dimensional stability and better flow.

Multicomponent polymer matrices are also more suitable for the preparation of electrically conductive polymer than single polymer systems[38] because they may form particular morphologies suitable for conductive polymer composites[15]. In these multicomponent polymer matrices, the conductive filler is distributed in more than one phase of polymer and the interface between the different polymers. The distribution of filler, which forms conductive pathways through a multicomponent polymer, is called hetero-distribution of conductive filler.

The ratio of the blend at which the structural connectivity of a filler-rich phase is formed, is also a factor in reducing percolation[15,28,31-35]. Gubbels found that at a PE/PS blend of 45/55 weight % composition the percolation threshold was 0.4 wt % of carbon black or a volume fraction of 0.002[33].

3.2 Materials

The materials' specification used for this project are:

3.2.1 Acrylonitrile Butadiene Styrene (ABS)

The ABS used was HANALAC ABS 780 from Hannam Chemical Corporation, Korea with properties:

Melt Index: 70 g/10 min (MFI 200/21.6)
Specific Gravity: 1.04 g/cm^3
Tensile Strength at Yield: 50 N/mm^2
Modulus of elasticity : 2400 N/mm^2
Flexural Strength: 67 N/mm^2

3.2.2 Nylon 6

The nylon 6 used was Grilon R50S from Grilon, Switzerland with properties:

Melting Point: 220°C (dry)
Tensile Strength at Yield: 80 N/mm^2 (dry), 40 N/mm^2 (condition)
Modulus of elasticity : 2800 N/mm^2 (dry),650 N/mm^2 (condition)

3.2.3 Carbon Black

The carbon black used was Conductex 975 Ultra "Conductive Furnace Black" supplied by Selvaco Ltd, with properties:

Volume Resistivity: 10 Ω.cm (for 27% wt)
Bulk density: 150-160 kg/m^3
Specific gravity: 1.8
Diameter: 21 nm
pH: 7

3.2.4 Conductive Polyamide Compound

The conductive compound used was Black "Conductive Compound - Nylon N54/CON2" produced and supplied by Colloids Ltd, with properties:

Form: 3 mm cylindrical pellets
Surface Resistance: 1 x 10^3 Ω.cm
Density: 1.1-1.4 g/cm^3
Melting Point: Over 200°C

3.3 Processing

In addition to the type of resin and carbon black, the processing method affects the conductivity of polymer composites. Polymer processing is the forming of polymer compounds into desired shapes and fixing the shapes by cooling or crosslinking. Compounding the polymer refers to combining a base polymeric material with additives, colours, modifiers, reinforcements, fillers or other polymers (blending) to modify the base material so that it performs better, has good appearance and processes easily.

As mentioned earlier, the conductivity of a conductive composite will increase with the addition of conductive filler. However a high content of filler may increase the melt viscosity of the compound that can present difficulty in processing. If the amount of carbon black increases more than 40% wt, it is difficult to mix and will not flow[42].

The other way to achieve the desired level of conductivity and shielding is to produce a good distribution of filler. The orientation of a conductive composite during processing affects the distribution of carbon black aggregates and results in greater conductivity in the direction of orientation rather than perpendicular to it. Therefore, careful handling is required in order to achieve the desired level of conductivity and shielding. Interfacial energy is found to be one of the most important factors affecting the distribution of carbon black particles in polymer blends.

For maximum conductivity, the colloidal particles of carbon black require optimum shear to disperse properly in plastics. Shear optimisation is related with mixing time. As shown in Figure 2.2[40], when mixing time increases, conductivity increases as a result of improved dispersion until a conductivity plateau is reached.

Mixing polymers is an endothermic process. The process can be divided by its mechanism into extensive and intensive mixing. 'Extensive' means that the minor component is deformed and rearranged spatially, while in 'intensive' mixing the minor component is eroded and ruptured under certain stress levels. In order to preserve particle structures, intensive mixing should be reduced.

3.3.1 Mixing

The resin and conductive carbon black powder, 500g in total, was mixed in a plastic container. They were tumbled in the mixer for 10 minutes. Three batches of compound were prepared. The compounds with different ratios of polymers and carbon black are shown as follows:

i) Acrylonitrile Butadiene Styrene/ Carbon Black Mixture
The different amounts of carbon black used were: 1%, 5%,10%, 20% and 30% of weight.

ii) Nylon 6 / Carbon Black Mixture
The different amounts of carbon black used were: 5%,10%, and 20% of weight.

iii) Acrylonitrile Butadiene Styrene/Nylon 6/Carbon Black Mixture

ABS and Nylon 6 were blended with the following composition ratio of (ABS: Nylon 6): 80:20, 60:40, 50:50, 40:60 and 20:80. Each of these blends were mixed with 10 weight % of carbon black. For the blend of 50:50, it was mixed with 2, 5 and 10 weight % of carbon black.

3.3.2 Blending

Dispersion of molecules in processing will be achieved by different methods such as application of heat, solvents and shearing. Some applications require processing to maintain the original structure of particles. In the solvent casting method it is possible to control mixing quality and particle structures, but it is not economical[52] and environmental problems, due to solvent disposal, are present.

Melt mixing is simple and fast, no additives are added, but it causes degradation at high temperatures. Different methods of processing used for polymeric compounding are the internal mixer[15], single screw extruder, twin screw extruder and two roll mill[40]. The internal mixer, in which compounding is in an enclosed temperature controlled machine chambers, is a clean method and the most effective in making a uniform mixture.

Meanwhile for two roll mill machines, a longer time is taken to make the mixture uniform, although polymer degradation may occur[7,32]. It is the oldest and most common method used for blending rubber and thermoplastics. For economic and environmental considerations, extrusion is the most practical process[52]. It also maintains the original structures of materials particles.

In the single and twin screw extruder method, to produce a uniform mixture, blending should be carried out two or three times. The single screw extruder is less popular because it is relatively inefficient. The twin screw extruder is the most popular method because it mixes efficiently, highly versatile and continuous. It is economical for higher line-rate requirements..

It was found that the sizes of particles were very sensitive to screw types, screw speeds and die geometry[52]. The higher the stress level generated, the smaller the particle size. Twin screw extrusion is more flexible in terms of screw configuration and better feeding capability. The particles which were broken into smaller pieces were well mixed. Studies by Chicheng Wang and co-researcher found that larger particles sizes were observed in the films from single screw extrusion compared with twin screw extrusion[52]

Before all the mixtures were blended through the extruder, they were preheated in 60°C in an oven for 24 hours to remove moisture. This is because the compounds which were exposed to high humidity and moisture, could absorb moisture that could result in low conductivity. The rate of absorption depends on type and loading of carbon black.

3.3.2.1 Single Screw Extruder

The blending was carried out by using a BETOL single screw extruder general purposes machine with the specification of:

Screw diameter: 25.4 mm
Die diameter: 3-mm
Screw rotation range: 0 - 60 rotation per minute (rpm)
Three zones at barrel and two zones at die section.

The photo of the extruder screw and BETOL extruder machine are shown in Figure 3.1 and Figure 3.2.

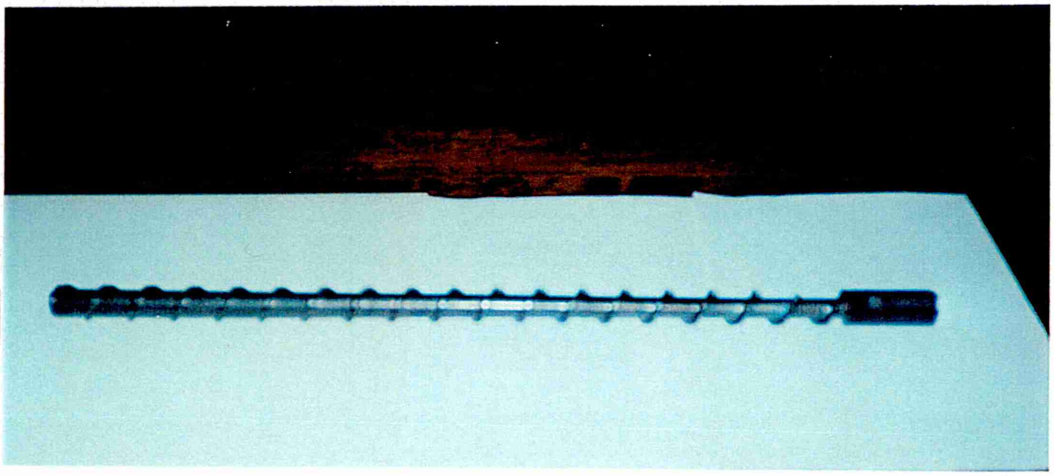


Fig. 3.1: Photo of Screw for General Purpose Extruder Machine

Fig. 3.2: Photo of BETOL Single Screw Extruder Machine

The conditions of the extruder for each blend are as follows:

3.3.2.2 Acrylonitrile Butadiene Styrene/ Carbon Black Blend

Barrel Temperature:
Zone 1: 180°C
Zone 2: 200°C
Zone 3: 220°C
Die Temperature:
Zone 2: 225°C

The compound was mixed and extruded with a screw rotation of 10 rpm. It was extruded for a second and third time with a barrel temperature of 170°C (zone 1), 180°C (zone 2), 190°C (zone 3), 190°C (die temperature) and screw rotation of 20 rpm.

3.3.2.3 Nylon 6/Carbon Black Blend

Barrel Temperature:
Zone 1: 220 - 230°C
Zone 2: 230 - 240°C
Zone 3: 240 - 250°C
Die Temperature:
Zone 2: 250°C

The compound was mixed and extruded with a screw rotation of 20 rpm. . It was extruded for second and third time with the same condition.

3.3.2.4 Acrylonitrile Butadiene Styrene/Nylon 6/Carbon Black Blend

Two steps involved in blending of ABS, Nylon 6 and carbon black.

First step:

i) Blending ABS with Nylon 6

Barrel Temperature:

Zone 1: 210°C
Zone 2: 220°C
Zone 3: 230°C

Die Temperature:

Zone 2: 240°C

Then followed by,

ii) Blending ABS/Nylon 6 with carbon black

Barrel Temperature:

Zone 1: 220°C
Zone 2: 230°C
Zone 3: 240°C

Die Temperature:

Zone 2: 240 - 250°C

The compound was mixed and extruded with a screw rotation of 20 rpm. It was reblended for a second and third time with the same condition.

3.3.3 Granulating/Recycling

After cooling at room temperature the compound was granulated. In order to get a homogeneous mixture, the granules were reblended, after tumbling in the mixer for 10 minutes. Then again the compound was regranulated. The effect of reblending was studied by repeating the process of compounding and granulating for a third time.

3.3.4 Preparation of Sheets

The compression moulding machine used for preparing sheets is a Moore hydraulic hot press. The sheets of all materials and compounds were prepared as follows:

3.3.4.1 Acrylonitrile Butadiene Styrene

The top and bottom platens of the compression moulding machine were heated to a temperature of 180°C. About 80g granules of ABS was placed in the 160 mm x 160 mm mould. When the temperature met the setting temperature, the mould was put between the compression platens. With a pressure of 1 to 2 tons (on 4 in. dia. ram) applied, the mould was left in compressed form for 10 to 15 minutes.

When the mould temperature met the platen temperature and all the granules turned molten, the heaters of the compression moulds were switched off. Then the mould was cooled by running cooling water through the compression platens, while the pressure was increased gradually to 6 tons (70 - 90 kg/cm^2). When the temperature dropped to 40°C the pressure was released.

3.3.4.2 Acrylonitrile Butadiene Styrene/ Carbon Black Blend

The same procedure was repeated for ABS/carbon black blends with the following conditions:

Granules weight: 80-90 g
Temperature: 180 - 190°C (Top and Bottom)
Pressure: 5 - 8 tons (on 4 in. dia. ram)
(60 - 100 kg/cm^2)

3.3.4.3 Nylon 6

The following conditions were applied:

Granules weight: 80 g
Temperature: 250°C (Top and Bottom)
Pressure: 15 tons (on 4 in. dia. ram)
(190 kg/cm^2)

3.3.4.4 Nylon 6/Carbon Black Blends

The following conditions were applied:

Granules weight: 85 - 90 g
Temperature: 240 - 250°C (Top and Bottom)
Pressure: 10 - 15 tons (on 4 in. dia. ram)
(120 - 190 kg/cm^2)

3.3.4.5 Acrylonitrile Butadiene Styrene/Nylon 6/Carbon Black Blend

The following conditions were applied:

Granules weight: 85-90 g
Temperature: 240 - 250°C (Top and Bottom)
Pressure: 10 - 12 tons (on 4 in. dia. ram)
(120 - 150 kg/cm^2)

3.3.4.6 Conductive Polyamide Compound

The following conditions were applied:

Granules weight: 85-90 g
Temperature: 250°C (Top and Bottom)
Pressure: 12 - 14 tons (on 4 in. dia. ram)
(150 - 170 kg/cm^2)

The 3 mm thick sheets prepared by compression moulding were used for mechanical testing, electrical resistivity measurement and scanning electron microscopy morphology study.

CHAPTER 4

THEORETICAL ANALYSIS

4.1 Introduction

In polymer blends, thermodynamics mixing, the free energy of mixing is given by:

$$dG(\text{mix}) = dH(\text{mix}) - TdS(\text{mix})^{59} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4.1)$$

where $dG(\text{mix})$ = Free Energy of Mixing
$dH(\text{mix})$ = Enthalpy of Mixing
$dS(\text{mix})$ = Entropy of Mixing
T = Temperature

$dS(\text{mix})$ is usually low or negligible for long chain molecules. $dH(\text{mix})$ is positive for non-polar systems. $dG(\text{mix})$ may be obtained using Flory-Huggins lattice theory. The theory show that how mixing depend on temperature and concentration.

4.2. Conductivity Properties

Unlike conductive polymer which has inherently conductive backbone to make polymer inherently conductive, conductive plastics are inherently nonconductive materials that are made conductive by incorporating a conductive additive. As mentioned in Chapter Two, the addition of electrically conductive filler to a nonconducting polymer matrix, form a chain-like or network-like conductive path. This will reduce electrical resistivity of the polymer.

Conductivity and resistivity are very important characteristics of material. Conductivity,σ ($\Omega^{-1}m^{-1}$ or S m^{-1}), is the ratio of the current density in a conductor to the electric field causing the current to flow[60]. Meanwhile, resistivity ρ (Ωcm), is an intristic property of a conductor, which gives the resistance in terms of its dimensions[60]. It is reciprocal of conductivity.

The most important useful resistivities are volume and surface resistivity. As a general guide, a volume resistivity in a range 10^{0}-$10^{-3}\Omega$cm is required in conductive plastic materials in order to achieve the desired level of effective shielding[8].

At low carbon black concentrations, the resistivity of the composite is close to that of the polymer matrix, 10^{11} to $10^{16}\Omega$.cm. Increasing carbon blacks contents can change resistivity level of materials from antistatic materials to EMI shielding materials, as shown in Figure 4.1. The figure shows that surface resistivity for polymers are in the range of 10^{13} to $10^{18}\Omega$/sq. The figure also shows carbon black, metals and other materials surface resistivity. Beside the effect of conductive filler's concentration, the resistance of plastics also depends on many factors, including temperature and moisture content.

The performance of conductive composites depends on the range of their surface conductivities. For the composites where surface resistivity lies between the range of[61]:

10^{-1}-10^{2} Ω/sq. - can perform well as EMI/RFI shielding materials
10^{2}-10^{6} Ω/sq. - as ESD (Electrostatic Discharge Protection)
10^{9}-10^{13} Ω/sq. - as antistatic composite

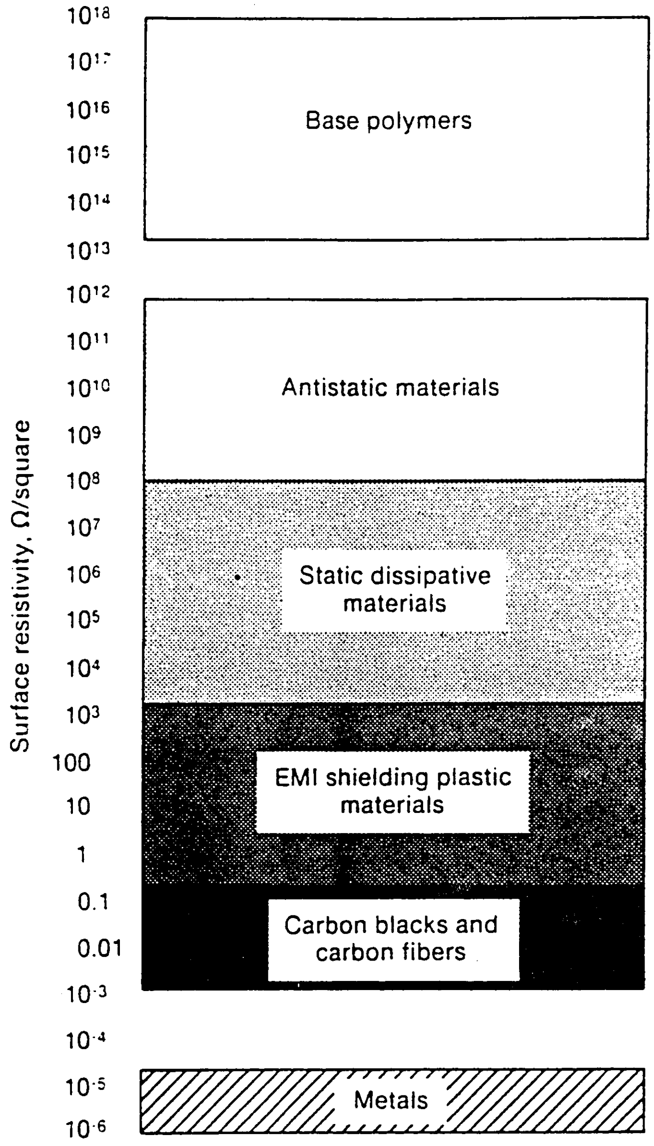


Fig. 4.1: Surface Resistivity ranges for polymers, conductive plastics, and other materials (62)

4.2.1 Resistance Measurement

Since electrical conductivity, σ, is the reverse of resistivity, that is $1/\rho$ ($\Omega^{-1}cm^{-1}$), resistance measurement is a method to measure conductivity of the materials.

Resistance, R (Ω), is given by,

$R = V/I$

where, V = Voltage

I = Ampere

or

$R = \rho l/A$

where, ρ = specific resistance ((Ωcm)

l = Length (cm)

A = cross sectional area (cm^2)

Specific resistance, also known as resistivity, written as:

$\rho = Rwt/l$

where, w, t and l are width, thickness and length of the sample in cm

There were three types of resistivities measured volume, surface and sheet. Volume resistivity (Ωcm) is the ratio of the potential gradient parallel to the current in the material to the current density[62]. It is determined by placing two electrodes in intimate contact with the surface of the specimen and measuring the current and potential difference across the electrodes.

The volume resistivity is given by equation:

$\rho_v = R_v A/t$ ....(4.2)[63]

where R_v = volume resistance between the electrodes

A = the effective area of the measurement electrode

t = thickness of the sample

Surface resistivity (Ω/sq.) is resistivity between opposite sides of a unit square inscribed on the surface[60]. It is determined by the measurement of the current flowing when a voltage is applied to electrodes on the surface of the specimen.

The surface resistivity is given by equation:

$$\rho_s = R_s P/g \quad \text{.......................}(4.3)^{63}$$

where R_s = surface resistance

P = the effective perimeter of the guard ring of the instrument

g = gap (distance) between measurement electrode and guard ring of the instrument

In semiconductor industries, the resistivity measurement is usually taken using the four-point probe method. The reason for making electrical measurement by this technique is to prevent resistance from the sample/electrode contacts. The four-point probe is often referred as “dual configuration” or “configuration switched” measurement. This method is non-destructive, although it may damage certain semiconductors when excessive probe pressure is applied. The probes are in lines with equal spacing.

The sheet resistance (also called the sheet resistivity) can be measured by a four-point probe technique and is given by

$$R_h = (V/I)\ \text{C.F.}^{64} \quad \text{........................}(4.4)$$

where; R_h = sheet resistance (Ω/ □) or (Ω/ sq.)

V = dc voltage (volts)

I = dc current (amperes)

C.F. = correction factor

Correction factor depends on the d/s ratio, where d is the diameter of a circular sample or the side of a rectangular sample that is perpendicular to the probe line[64], and s is the probe spacing. For a large d/s ratio (more than 40), C.F. = 4.53.

From sheet resistance equation, resistivity, ρ (Ωcm), is given by

$$\rho = R_h t \text{ ....(4.5)}$$

where; t is thickness of sample

For the thickness of sample greater than the probe spacing (s), resistivity is given by,

$$\rho = 2\pi s(V/I)^{65} \text{ ....(4.6)}$$

The resistance measurement is one of the methods to determine the shielding effectiveness of materials[8], because there is a correlation between shielding effectiveness and electrical conductivities. Surface resistivity of 1Ω/sq. corresponds to about 30-35dB shielding effectiveness.

4.3 Mechanical Properties

Composites are increasingly used for mechanical applications, although in this work we are studying the conductivity of polymer blends containing conductive filler. Mechanical properties are clearly very important and the experimental materials were tested to assess their mechanical response.

The basic characterisation of mechanical properties involves the determination of modulus of elasticity, ultimate tensile strength, impact resistance, flexural resistance, etc. Shear modulus is a measure of the stiffness of a material subjected to shear loading. Impact tests that indicate a materials toughness, can be used to compare the responses of different materials[66].

Rosato DV explained that mechanical properties of heterogeneous polymer-polymer blends depend on the mechanical properties of the polymers, the morphology of the system and the degree of mechanical contact between the phases[66]. Mechanical properties depend on composition, properties of each components, geometrical configuration and shapes of structural elements. Some components considered chemically homogeneous but physically heterogeneous.

Increasing the filler content produces an increase in the mechanical strength and a decrease in elongation at break. The brittleness caused by high loading of filler can often be balanced by adding a flexible component such as EVA[67]

4.3.1 Tensile Strength

The tensile test is among the most widely employed methods used to characterise the mechanical properties of composites. It can give important information regarding the material's elastic properties, deformation characteristics, yield, tensile strength and toughness.

Filler in fibre form can normally improve the tensile strength of a composite because fibres are able to support stress that is transferred from the polymer matrix. Irregular particulate fillers decrease the composites' tensile strength due to their inability to support stress. The drop in tensile strength in many thermoplastic composites filled with particulate fillers has been observed by researchers[68-70].

No adhesion between particulate filler and polymer matrix means that the filler cannot carry the proportion of load applied to the composite. This phenomenon also allows air to be trapped between matrix and fillers that gives porosity to the composite. As a result, stress which is concentrated on the porosity around the particle will reduce tensile strength.

Nicolais and Nicodemo[70] estimated the lower bound of tensile strength of filled polymer in which there is no adhesion between spherical fillers and the polymer matrix. They described tensile strength using the equation below:

$$\tau_c = \tau_p (1 - 1.21\, \phi_f^{2/3}) \quad \text{...} (4.7)$$

where τ_c and τ_p refer to the tensile strength of composite and unfilled polymer respectively, ϕ_f is volume fraction of the filler, the constant, 1.21, is a stress concentration factor and 2/3 is a geometrical factor for the filler.

4.4 Morphology

Morphology is a description of the shapes of microstructural units in materials, such as spherulites in polymers[60]. It is one of the methods used to study the compatibility of the mixture.

4.4.1 Morphology of Polymer Blend

Macroscopic electrical resistivity of a filled polyblend strongly depends on the distribution of the filler. Ph Leclère and his research team have studied the localisation of carbon black in different phases of polymers[36]. The polymers they used were Polyethylene and Polystyrene. The two types of carbon black used as conductive fillers were Degussa Printex XE-2 and Cabot Black Pearls BP-100. The morphology of the blend was characterised using Lateral Force Microscopy (or Friction Force Microscopy). The differences of friction coefficient among the particles of PE, PS and carbon black, could be distinguished by this type of microscopy. The carbon black particles could be found in the phases of PE and PS and the interface of both polymers.

Marek Kozlowski and Anna Kozlowska in their research had found that carbon black was preferentially located in an amorphous phase of semi-crystalline polymers[15]. The situation is shown in Figure 4.2. Conductive filler is rejected from the crystalline phase and segregates in the amorphous regions. This is an interesting effect as there are implications for the percolation threshold at which conducting networks are generated in the polymer and/or polymer phase.

Selective localisation of CB at an interface can reduce percolation threshold to 0.5 wt. % and retain mechanical properties. High filler contents can present poor mechanical properties, making difficult in the processing and produce high final cost. The dispersion of CB as a function of blend composition & CB loading.

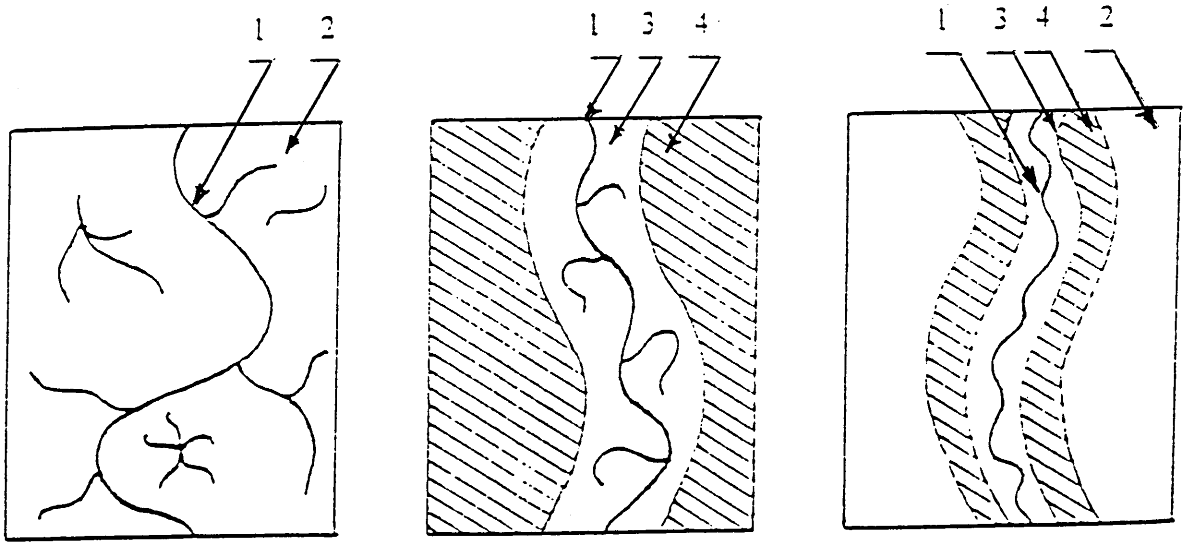


Fig 4.2: The location of carbon black in the amorphous polymer (left), semi-crystalline polymer (centre) and the blend of both (right)
1 - Carbon Black; 2 - amorphous polymer;
3 - amorphous phase of crystalline/amorphous polymer;
4 - crystalline phase of crystalline polymer (15)

The dispersion or localisation of filler in polymer phases differs with the types of polymer blends. It is explained by wetting behaviour of filler in powder form at two liquid phases that is shown in Figure 4.3:

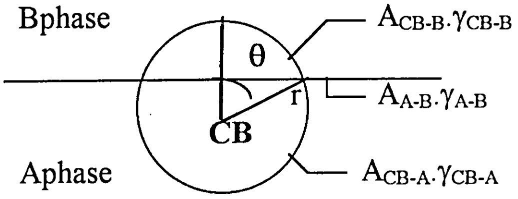


Fig. 4.3: Schematic Interpretation of Carbon Black at The A/B Interface (31)

The attraction of carbon black to polymer phases depends on interfacial free energy at the interface which is given by:

$$\delta G = \gamma_{CB\text{-}A}.\ \delta A_{CB\text{-}A} + \gamma_{CB\text{-}B}.\ \delta A_{CB\text{-}B} + \gamma_{A\text{-}B}.\ \delta A_{A\text{-}B} \quad \text{................(4.8)}$$

$$= \gamma_{CB\text{-}A}.(2\pi r \sin\theta\ r\ \delta\theta) - \gamma_{CB\text{-}B}.(2\pi r \sin\theta\ r\ \delta\theta)$$

$$+ \gamma_{A\text{-}B}.(2\pi r \sin\theta\ r\ \delta\theta)\cos\theta$$

where, r = radius of powder

$\gamma_{i\text{-}j}$ = surface tension of i/j interface

$A_{i\text{-}j}$ = area of i/j interface

at equilibrium state: $\delta G = 0$,

so, $$\frac{\gamma_{CB\text{-}A} - \gamma_{CB\text{-}B}}{\gamma_{A\text{-}B}} = \cos\theta = \omega a \quad \text{...(4.9)}$$

ωa is called 'wetting coefficient'

when $\omega a > 1$ Carbon black distributes within the A phase

$-1 < \omega a < 1$ Carbon black distributes at the interface

$\omega a < -1$ Carbon black distributes within the B phase

So, interfacial energy is an important factor effecting the distribution of carbon black particles in polymer blends. Viscosity of a matrix polymer affects the aggregation of fillers.

CHAPTER 5

EXPERIMENTAL TECHNIQUES

5.1 Conductive Properties

5.1.1 Sample Preparation

For surface and volume resistivity measurements, the specimens with the size of 150 mm X 150 mm were prepared by using a compression moulder. For the sheet resistivity test, the four point probe, the compressed sheet was cut into 75 mm width specimen. Three specimens were prepared for each batch of compounds.

5.1.2 Electrical Resistance Measurement

Electrical resistance measurements were carried out on ABS/carbon black, Nylon 6/carbon black and ABS/ Nylon 6/ carbon black blends with different compositions of polymers and fillers as shown in Table 5.1, 5.2 and 5.3.

Table 5.1: ABS/carbon black blends with different composition of carbon black are marked as follows:

Sample Mark	Carbon Black Content (wt. %)
ABS	0
ABS01CB	1
ABS05CB	5
ABS10CB	10
ABS20CB	20
ABS30CB	30

Table 5.2: Nylon 6/carbon black blends with different composition of carbon black are marked as follows:

Sample Mark	Carbon Black Content (wt. %)
Nylon 6	0
NCB5	5
NCB10	10
NCB20	20
NCB25	25

Table 5.3: ABS/Nylon 6/carbon black blends with different composition of polymers and carbon black are marked as follows:

Sample Mark	Composition of ABS: Nylon 6 in Blend	Carbon Black Content (wt. %)
ABS2/N8/CB10	2:8	10
ABS4/N6/CB10	4:6	10
ABS5/N5 - 2C*	5:5	0
ABS5/N5	5:5	0
ABS5/N5/CB2	5:5	2
ABS5/N5/CB5	5:5	5
ABS5/N5/CB10	5:5	10
ABS5/N5/CB20	5:5	20
ABS5/N5/CB20-2C*	5:5	20
ABS6/N4/CB10	6:4	10
ABS8/N2/CB10	8:2	10

Note: *2C - two cycles of blending
The rest of the blends were reblended for three cycles.

Electrical resistance measurement also was carried out on the conductive polyamide compound which was marked as 'N54/CON2'

5.1.2.1 Surface and Volume Resistivity Measurement

The surface and volume resistance were carried out using a CEAST Teraohmeter Model 6138/000 with the following condition:

Applied Voltage: 500 V
Time of electrification of measurement: 60 s
Room Temperature: 20 - 23°C
Humidity: 55%
Test Method: ASTM D 257-92[63]

The Figure 5.1 shows the electrode of the instrument for measuring volume and surface resistance.

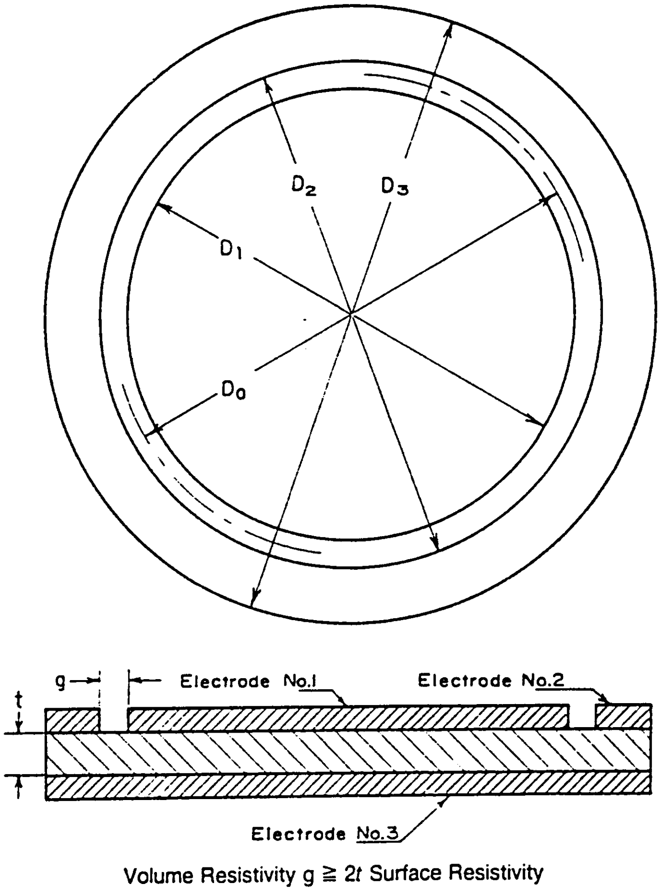


Fig. 5.1: Measuring Volume and Surface Resistance on Flat Specimen (63)

The volume resistivity (Ω cm) was calculated using the equation 4.2 as,

$$\rho_v = R_v A/t$$

where R_v = measured resistance value (Ω)

$A = 58.85\ \text{cm}^2$

t = average thickness of the sample (cm.)

The surface resistivity (Ω/sq.) was calculated using the equation 4.3 as,

$$\rho_s = R_s P/g$$

where R_s = measured resistance value (Ω)

$P = 25.38$ cm

$g = 0.578$ cm

5.1.2.2 Sheet Resistivity Measurement

The sheet resistance was carried out by measuring voltage and current of sample using four point probe model K&S. The test was performed at room temperature (18 - 20°C) according to ASTM F 1529[71] method. The Figure 5.2 shows the diagram of four point probe method.

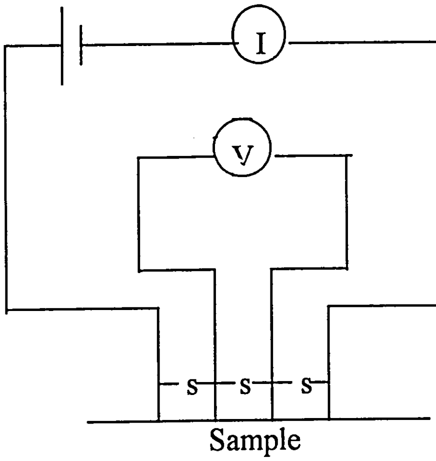


Fig 5.2: Four Point Probe Method Diagram

The sheet resistance was calculated using the equation 4.4 by putting C.F. = 4.53,

$$R_h = 4.53\ V/I$$

Since the thicknesses of the samples are 3 to 4 mm. which are greater than probe spacing (s), resistivity was calculated using equation 4.6 as,

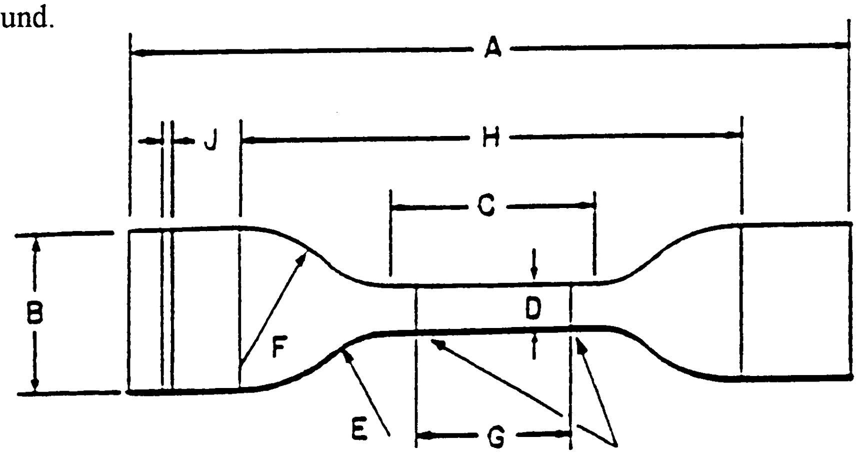
$$\rho = 2\pi s(V/I)^{65}$$

where $s = 1$ mm

5.2 Mechanical Properties

5.2.1 Tensile Test Specimen Preparation

The compressed sheets were machined into dumbbell shape test specimens for tensile testing according to ASTM D 638 Type IV[72]. The type IV dumbbell shape is shown in figure 5.3 below. Five specimens were prepared from each batch of compound.



position of reference lines

Fig. 5.3: Dumbbell shaped specimen type IV (72)

Dimension are in millimetres

A	Overall length, minimum	115
B	Width at ends	25±1
C	Length of narrow parallel portion	33±2
D	Width of narrow parallel portion	6+0.4,-0
E	Small radius	14±1
F	Large radius	25±2
G	Distance between reference lines	25±1
H	Initial distance between grips	80±5
J	Thickness, minimum	1
	maximum	3
	preferred	2

5.2.2 Tensile Strength Tests

Tensile tests were carried out using a Tensile Testing Machine, JJ Instruments Model T20K, with a load cell of 20 kN. The tests were performed at room temperature as specified in ASTM D 638 with a gauge length of 25 mm and a crosshead speed of 50 mm/min. Five specimens were tested for each compound of ABS/carbon black, Nylon 6/carbon black and ABS/Nylon/carbon black. The graphs of force versus extension were plotted from which tensile strength was calculated for each of the blends. There was no extensometer attached to the machine. In addition the extensions of most specimens were small (between 1 to 2 mm), therefore accurate elongation could not be measured. Hence, elastic Modulus (E_m) cannot be calculated accurately.

5.3. Morphology Structure Characterisation

Microscopy is the name given to a group of experimental methods that permit magnification of morphological structures to make details visible. The group consists of Optical Microscopy (OM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

The discovery of the optical microscope was made in 1590 by the Dutch optician, Zacharias Jensen, whose microscope consisted of a 45 cm long tube with two lenses (objective and eyepiece)[73]. The first recognised modern SEM was described by Zworykin et al.[74]. Oatley and his student who began the development of SEM in 1948, could commercialise their first machine of the Cambridge Scientific Instruments Mark 1 'Stereoscan' in 1965[75].

Electron microscopy can reveal the fine structures of many different types of material[76]. The Scanning Electron Microscopy (SEM) is the most popular microscopic technique[77]. This is due to the 'user friendliness' of the apparatus, the simplicity of interpretation of most images and the ease of specimen preparation.

It is a uniquely versatile and powerful tool for the characterisation and visualisation of materials. It combines high spatial resolution with the ability to look at samples of a practical size and offer a wide range of imaging modes.

SEM is a mapping and not imaging device. The sample is probed by a beam of electrons scanned across the surface. Radiation from the specimen, stimulated by the incident beam, is detected, amplified, and used to modulate the brightness of a second beam of electrons scanned, synchronously with the first beam, across a cathode ray tube display. By using multiple detectors, several signals can be collected simultaneously and then be displayed individually or combined in perfect register with each other. This makes SEM a useful tool since multiple views of a sample in different imaging modes can be collected and compared in a single pass of the beam.

SEM is mainly used to reveal surface topography (the external shape of a specimen) at magnifications in the range of 10 times to about 50,000 times. It can also be used for compositional analysis by detecting the characteristic x-rays emitted from the specimen. The technique is sometimes called microprobe analysis[76].

The other reason why SEM is the most widely used of all electron beam instruments not only because it is easy to interpret micrographs but also its capability to complement instruments such as the scanning tunnelling microscope (STM) or atomic force microscope (AFM)[77].

The basic components of SEM are shown in Figure 5.4. They can be divided into two main categories, the electron-optical and detector systems, and the scanning, processing, and display systems.

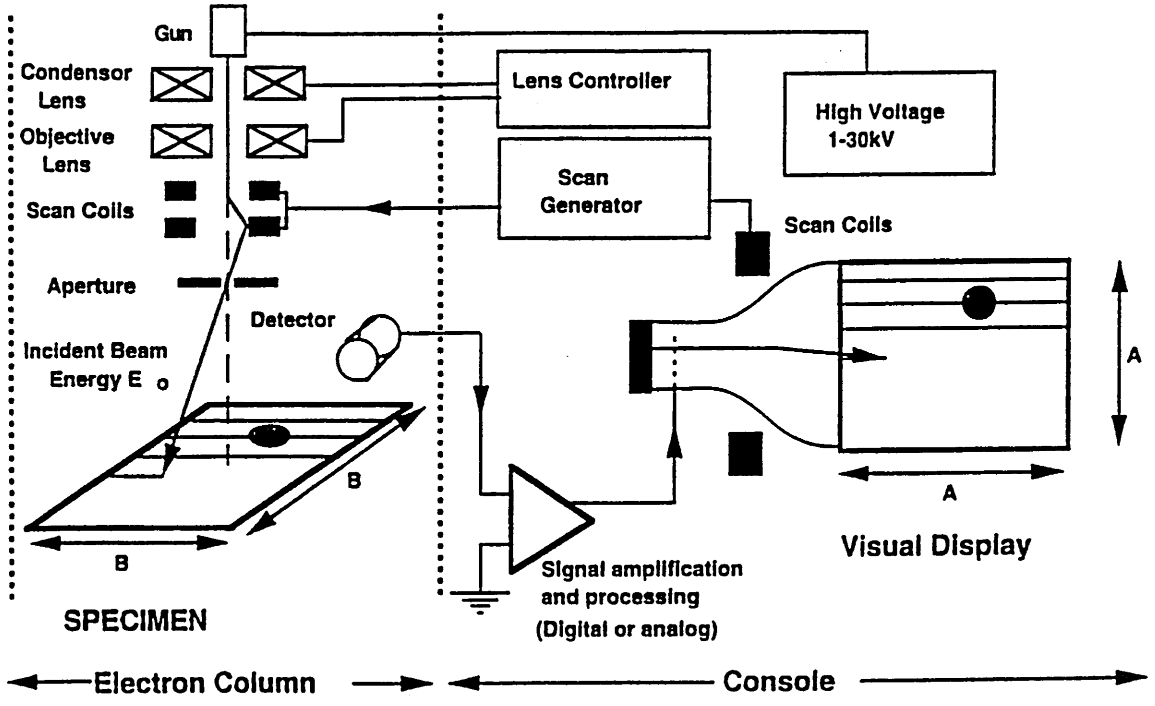


Figure 5.4: Basic components of the scanning electron microscope (77)

In this project, scanning electron microscopy (SEM) was used to study the morphology of blended polymers. This includes study of the interface of polymers/fillers, the adhesion between them, the random dispersion of the filler within the system[29], and also to observe the basic shapes of the filler particles and the aggregation or agglomeration phenomenon usually associated with the particles.

5.3.1 Sample Preparation

Before characterisation is carried out by SEM, sample preparation is most important to get a clear photomicrograph. Sample preparation steps are as follows:

5.3.1.1. Sample Mounting

Two method were used in preparation of sample mounting

a) Conductive Bakelite Mould

The compressed sheet made by hot-press compression mould was cut into 1 cm^2 which was put into a ram. Conductive bakelite powder was placed on top of sample, and the ram was lowered and screwed. They were placed under pressure and heated to approximately 130°C. After cooling and releasing pressure, the sample was removed.

b) Cold Setting Mould

The same size of sample as above was put in 30 mm diameter of circular plastic mould. Epoxy resin (EPOFIX) was mixed with hardener 7:1 ratio, then was poured into the plastic mould. The mould was put in vacuum desiccator to remove excess air bubbles. The casting was hardened within 10 minutes at room temperature.

5.3.1.2 Grinding/Polishing of Sample

The mounted sample was then ground on emery paper, beginning with 80 grit, 120, 240, 320, 400, 600 and finally 1200 grit. The sample was washed, dried and a final polish was achieved by the use of 6μ and 1μ diamond paste used on mapped cloths. Two specimens (different axis) were prepared for each batch of compounds.

To get a smooth surface, the sample was polished with 0.5μ of polish using silicon solution. For sensitive and softer polymer, the sample was polished with 0.25μ diamond paste used on mapped cloths.

5.3.1.3 Carbon Coating

The sample was mounted on an Aluminium stub, then was coated with carbon particles using Edward E306A Carbon Coater. To make electrical current pass through the sample, a line of conducting silver paint was applied from sample to aluminium stub as shown in Figure 5.5.

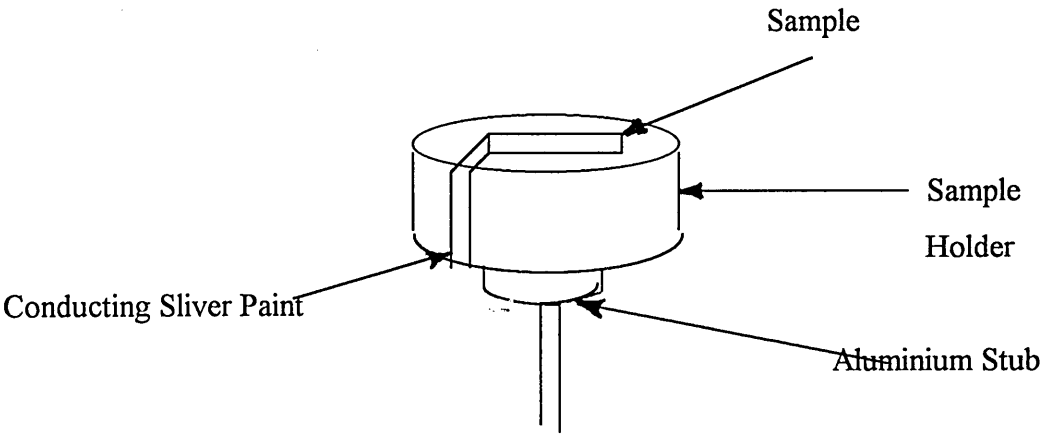


Fig 5.5: Mounted Sample on Aluminium Stub for SEM Analysis

5.3.2 Characterisation by Scanning Electron Microscopy

The SEM equipment used to analyse the sample was a Philips XL40 ASEM with EDAX EDX X-Ray Analyser. Three batches of blends' samples were analysed, ABS/Carbon Black blends, Nylon 6/ Carbon Black blends and ABS/ Nylon 6/Carbon Black blends. The microstructures of the samples studied from photomicrographs are shown in the next chapter.

CHAPTER 6

RESULTS AND ANALYSIS

6.1 Resistance Measurement

From sheet, surface and volume resistances measured by using methods described in Chapter 5, all ABS/carbon black, Nylon 6/carbon black and ABS/Nylon 6/carbon black blends resistivities were calculated and summarised as shown in Table 6.1 to Table 6.7. Sample identifications have been explained in Chapter 5. Errors shown in tables show the values of standard deviation calculation from 10 readings for each specimen.

6.1.1 ABS/Carbon Black Blends

Current readings could not be taken by using four probe point technique for ABS/carbon black blends with carbon black content up to 10 wt %, because the resistances of the blends are too high to be measured by the equipment. Therefore sheet resistance and resistivity for these blends cannot be calculated. Summary of sheet resistance and resistivity values of all ABS/carbon black blends with different amount of carbon black contents are shown in Table 6.1.

The result in Table 6.1 shows that sheet resistance and resistivity of ABS/carbon black blends decrease with the addition of carbon black from 20 to 30 wt %. Sheet resistance and resistivity of ABS/carbon black blends for two cycles of blending were calculated and are shown in Table 6.1.

Table 6.1: Sheet resistance and resistivity of ABS with different contents of carbon black

Sample	CB Content (%) [Wt - Vol.]	Sheet Resistance, Rs (Ω/□)[◊]	Resistivity ρ (Ωcm)[◊]	Sheet Resistance, Rs (Ω/□)*	Resistivity, ρ (Ωcm)*
ABS	0	-	-	-	-
ABS01CB	1 - 0.6	-	-	-	-
ABS05CB	5 - 3.0	-	-	-	-
ABS10CB	10 - 6.0	-	-	-	-
ABS20CB	20 - 12.6	242.4 ± 0.4	33.6 ± 0.1	229.7 ± 21.0	31.9 ± 2.9
ABS30CB	30 - 19.8	25.8 ± 2.2	3.6 ± 0.3	20.0 ± 0.6	2.8 ± 0.1

Note: [◊] - two cycles of blending
* - three cycles of blending

To show that reblending cycles affect resistivity of the blend, sheet resistance was measured in ABS with 30 wt. % carbon black blends for four cycles of blending as shown in Table 6.2.

Table 6.2: Sheet resistance and resistivity of ABS/ 30 wt. % carbon black blend with different cycles of blending

Blending Cycles	Sheet Resistance, Rs (Ω/□)	Resistivity, ρ (Ωcm)
2	25.8 ± 2.2	3.6 ± 0.3
3	20.0 ± 0.6	2.8 ± 0.1
4	$(2.03 \pm 1.59) \times 10^{-1}$	$(2.83 \pm 2.20) \times 10^{-2}$

Table 6.1 and Table 6.2 show that resistivity of ABS/carbon black blends decreases when blend cycles increase from two to three times.

The graph of sheet resistivity of ABS/ 30 wt % carbon black blend versus blending cycle is plotted on a log scale shown in Figure 6.1. The graph shows that resistivity drops rapidly when the ABS/carbon black blend was recycled four times.

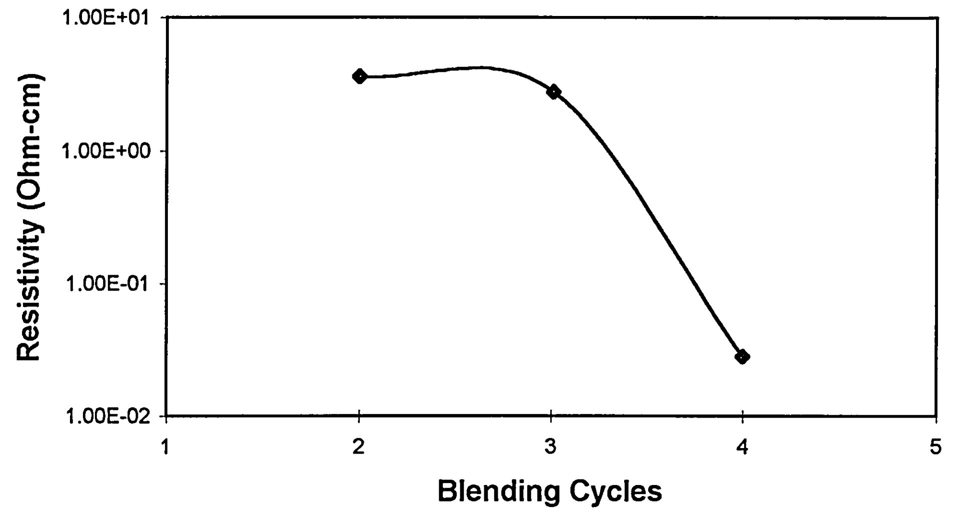


Fig. 6.1: Resistivity versus Blending Cycle of ABS/ Carbon Black (30 wt. %) blends

Since sheet resistance cannot be measured on ABS and ABS/carbon black blends with less than 10 wt. % of carbon black, Teraohmeter equipment was used to measure surface and volume resistance of these samples. However, this equipment can only measure resistance as low as 10^6 Ω. Therefore surface and volume resistances of ABS/10 wt. % carbon black blends cannot be measured. Surface and volume resistivity of ABS and ABS blended with 5 wt.% carbon black are shown in Table 6.3.

Table 6.3: Surface and volume resistivities of ABS and ABS blend with 5 wt % of carbon black

Sample	Carbon Black Content (wt. %)	Surface Resistivity (Ω per square)	Volume Resistivity (Ω-cm)
ABS	0	>1 X 10^{16}	3.11X 10^{15}
ABS05CB	5	2.2 X 10^{12}	6.59 X 10^{15}

Table 6.3 shows that surface resistivity of ABS decreases when blended with 5 wt. % of carbon black. Very little increase of volume resistivity was observed with the addition of same amount of carbon black.

6.1.2 Nylon 6/Carbon Black Blends

As with the ABS/carbon black blends behaviour, sheet resistance could not be measured on all Nylon 6/carbon black blends with up to 25 wt. % of carbon black, because their resistance are too high to be measured by four point probe method. Therefore the surface and volume resistivity of Nylon 6 and Nylon 6 blended with different amounts of carbon black are shown in the Table 6.4.

Table 6.4: Surface and volume resistivities of Nylon 6 and Nylon 6 blends with different amounts of carbon black

Sample	Carbon Black Content (wt %)	Surface Resistivity (Ω per square)	Volume Resistivity (Ω-cm)
Nylon 6 (resin)	0	8.8 X 10^{15}	2.5 X 10^{15}
Nylon 6 (extruded)	0	>1X10^{16}	1.3 X 10^{15}
NCB5	5	4.4 X 10^{11}	1.5 X 10^{14}
NCB10	10	1.3 X 10^{11}	3.4 X 10^{13}
NCB25	25	6.6 X 10^{10}	1.1 X 10^{13}

The graph of surface and volume resistivities of Nylon 6/carbon black blends versus percentage of carbon black content are plotted in log scale as shown in Figure 6.2.

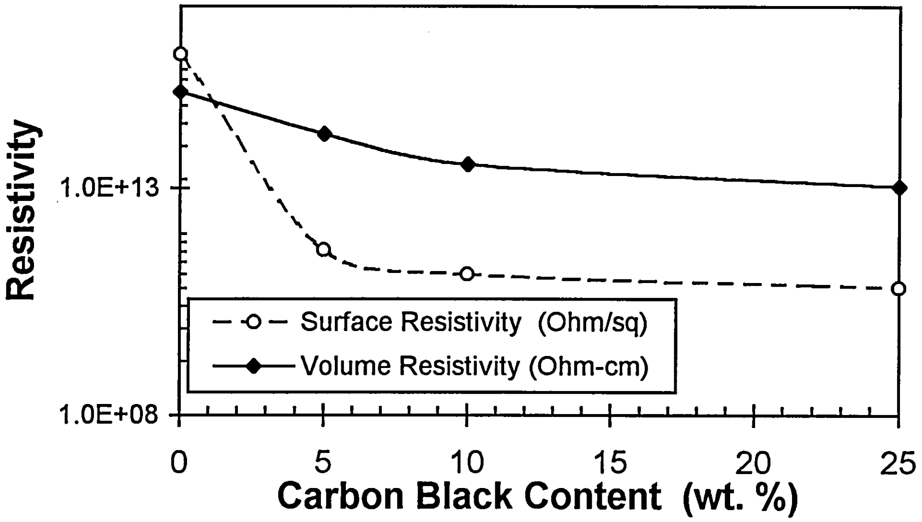


Fig. 6.2: Surface and Volume Resistivity versus Carbon Black content (wt. %) of Nylon 6/Carbon Black blends

The graph shows that surface and volume resistivities of Nylon 6/carbon black blends decrease with the addition of a carbon black content of 5 wt %. Above this amount, both resistivities show almost no change up to 25 wt. %.

6.1.3 ABS/Nylon 6/Carbon Black Blends

To study the effect of ABS/Nylon 6 composition ratio on the resistivity of the blends, surface and volume resistances were measured on ABS/Nylon 6/carbon black blends with varied ratios of ABS:Nylon 6 and fixed content of carbon black (10 wt. %). Surface and volume resistivities of all these blends were calculated and summarised in Table 6.5.

Table 6.5: Surface and volume resistivities of ABS/Nylon 6/Carbon Black with different composition ratio of polymers

Sample	ABS: Nylon 6 ratio	Surface Resistivity (Ω per square)	Volume Resistivity (Ω-cm)
ABS2/N8/CB10	20:80	1.94×10^{10}	4.54×10^{14}
ABS4/N6/CB10	40:60	1.76×10^{12}	6.34×10^{13}
ABS5/N5/CB10	50:50	1.33×10^{12}	1.82×10^{13}
ABS6/N4/CB10	60:40	8.78×10^{10}	4.70×10^{10}
ABS8/N2/CB10	80:20	$< 1 \times 10^{7}$	$< 1 \times 10^{8}$

The graph of surface and volume resistivities of ABS/Nylon 6/carbon black blends versus percentage of ABS content in the blends are plotted in Figure 6.3 and 6.4 respectively. The graph in Figure 6.3 shows a surface resistivity drop when the composition ratio of ABS:Nylon 6 is 20:80. The resistivity increases again with further addition of ABS until the composition ratio above 40:60 (approximately 44% of total weight of ABS/Nylon 6 blends). The resistivity achieved a lowest value at ABS: Nylon 6 composition ratio of 80:20.

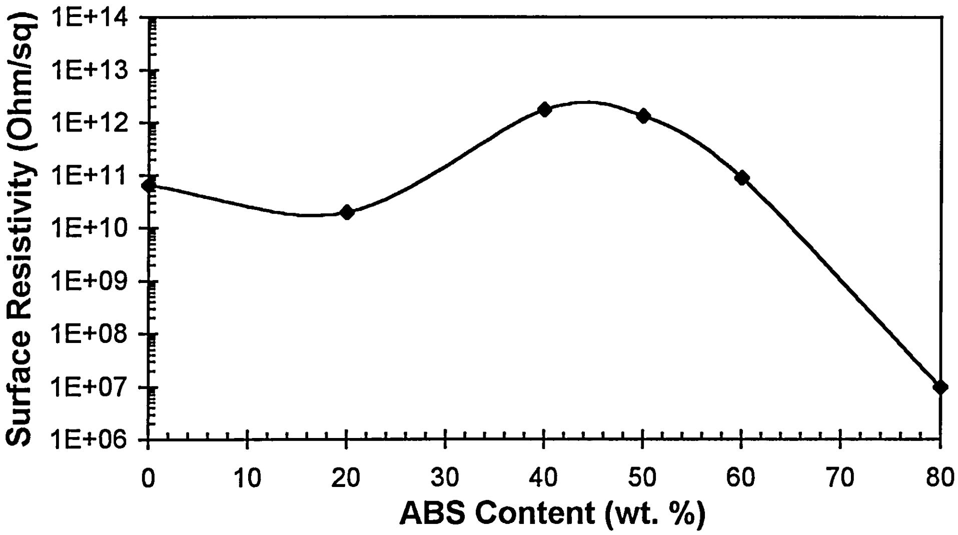


Fig. 6.3: Surface Resistivity versus ABS content (wt %) of ABS/Nylon 6/Carbon Black blends

The graph in Figure 6.4 shows that volume resistivity was little affected at the early stage of ABS addition. The resistivity decreases faster when the composition ratio of ABS: Nylon 6 was above 50:50, and achieved a lowest value at a composition ratio of 80:20.

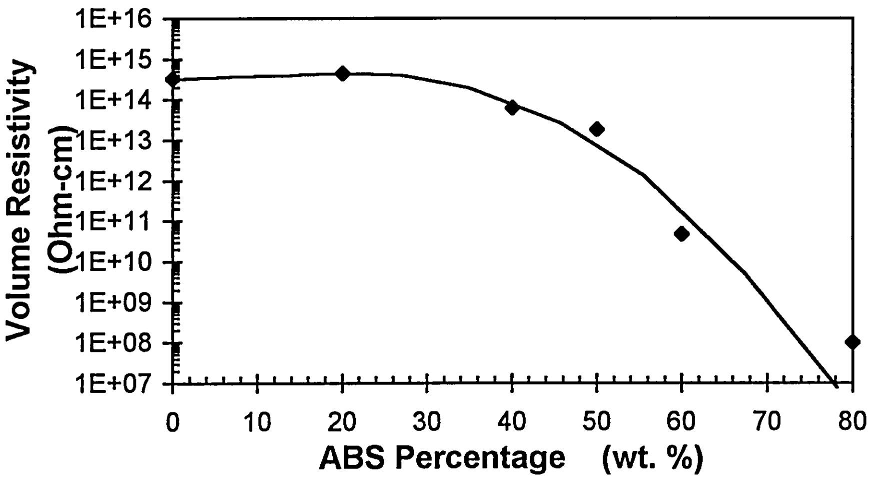


Fig. 6.4: Volume Resistivity versus ABS content (wt. %) of ABS/Nylon 6/Carbon Black blends

To study the effect of carbon black content on ABS/Nylon 6/carbon black blends, surface and volume resistances were measured on ABS/Nylon 6/carbon black blends with an ABS:Nylon 6 composition ratio of 50:50 and varied content of carbon black. Surface and volume resistivities of all these blends were calculated and summarised in Table 6.6.

Table 6.6: Surface and volume resistivities of ABS/Nylon 6/Carbon Black with different contents of carbon black

Sample	Carbon Black Content (wt.%)	Surface Resistivity (Ω per square)	Volume Resistivity (Ω-cm)
ABS5/N5 - 2C*	0	$> 1 \times 10^{16}$	1.56×10^{15}
ABS5/N5	0	$> 1 \times 10^{16}$	2.31×10^{15}
ABS5/N5/CB2	2	2.20×10^{13}	3.01×10^{14}
ABS5/N5/CB5	5	1.98×10^{13}	2.62×10^{14}
ABS5/N5/CB10	10	1.33×10^{12}	1.82×10^{13}
ABS5/N5/CB20	20	6.72×10^{5}	7.30×10^{6}
ABS5/N5/CB20-2C*	20	3.86×10^{5}	8.14×10^{5}

Note:* 2C - two cycles of blending

The graph of surface and volume resistivity of ABS/Nylon 6/carbon black blends (with ABS/Nylon 6 composition ratio of 50:50) versus percentage of carbon black content (weight) is plotted in Figure 6.5. The graph shows that both surface and volume resistivities decrease with the addition of carbon black content. The resistivities decrease more quickly above 10 wt % of carbon black content.

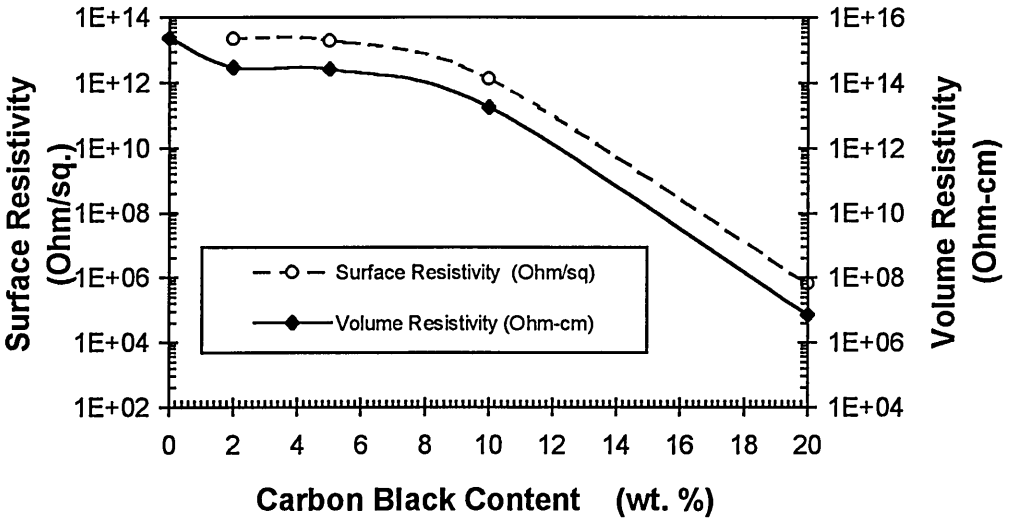


Fig. 6.5: Surface and Volume Resistivity of ABS/Nylon 6 (50:50) with Carbon Black blends versus weight percentage of Carbon Black content

Meanwhile, sheet resistances were measured for the blends with surface and volume resistance less than 10^6 Ω. Sheet resistance and resistivity for these blends are shown in Table 6.7.

Table 6.7: Sheet resistance and resistivity of ABS/ Nylon 6/carbon black blends and Conductive Polyamide Compound

Sample	CB Content (wt. %)	Sheet Resistance, Rs (Ω/□)	Resistivity ρ (Ωcm)
ABS8/N2/CB10	10	234.4 ± 124.7	32.5 ± 17.3
ABS5/N5/CB20	20	2.7 ± 1.2	$(3.8 \pm 1.7) \times 10^{-1}$
N54/CON2	22	2.9 ± 1.1	$(4.1 \pm 1.6) \times 10^{-1}$

Table 6.7 shows that sheet resistance and resistivity of ABS/Nylon 6 with composition ratio of 50:50 blended with 20 wt % of carbon black are quite similar to Conductive Polyamide Compound - N54/CON2.

6.2 Tensile Strength Tests

Tensile strengths of ABS/carbon black, Nylon 6/carbon black and ABS/ Nylon 6/carbon black blends were calculated and summarised as shown in tables 6.8 to 6.13. Errors shown in tables show the values of standard deviation calculation from tensile strength of five specimens.

6.2.1 Acrylonitrile Butadiene Styrene/ Carbon Black Blend

Tensile strengths of ABS blended with different amount of carbon black are shown in Table 6.8. The graph of tensile strength versus carbon black content is plotted, as shown in Figure 6.6.

Table 6.8: Tensile Strength of ABS with different carbon black content

Sample	CB content (wt. %)	Tensile Strength (N/mm^2)*	Tensile Strength (N/mm^2)$^\Diamond$
ABS	0	39.7 ± 1.2	-
ABS01CB	1	40.0 ± 1.0	40.4 ± 0.5
ABS05CB	5	41.7 ± 0.8	40.7 ± 2.0
ABS10CB	10	42.2 ± 0.6	42.4 ± 0.7
ABS20CB	20	37.5 ± 1.5	28.0 ± 5.4
ABS30CB	30	22.3 ± 1.8	21.7 ± 5.1
ABS01CB$^+$	1	42.5 ± 0.2	-

* The compound was reblended for second cycle

$^\Diamond$ The compound was reblended for third cycle

$^+$ Sample was dried in oven with temperature 90°C for 2 hours

For comparison, the tensile strength of all ABS/carbon black blends were calculated using the equation of tensile strength for filled polymers as described by Nicolai & Nicodemo[70] (Eq. 4.7). By taking the specific gravity of ABS and carbon black as 1.04 and 1.8 respectively, the volume fraction of filler for each blend can be calculated. The calculated tensile strengths of all ABS/carbon black blends are shown in Table 6.9

Table 6.9: Calculated Tensile Strength* of ABS with different carbon black contents by using equation 4.7

Sample	CB content (% vol.)	Tensile Strength (N/mm^2)	Tensile Strength (N/mm^2)*
ABS01CB	0.6	40.0 ± 1.0	38.1
ABS05CB	3.0	41.7 ± 0.9	35.1
ABS10CB	6.0	42.2 ± 0.6	32.3
ABS20CB	12.6	37.5 ± 1.9	27.6
ABS30CB	19.8	22.3 ± 2.0	23.4

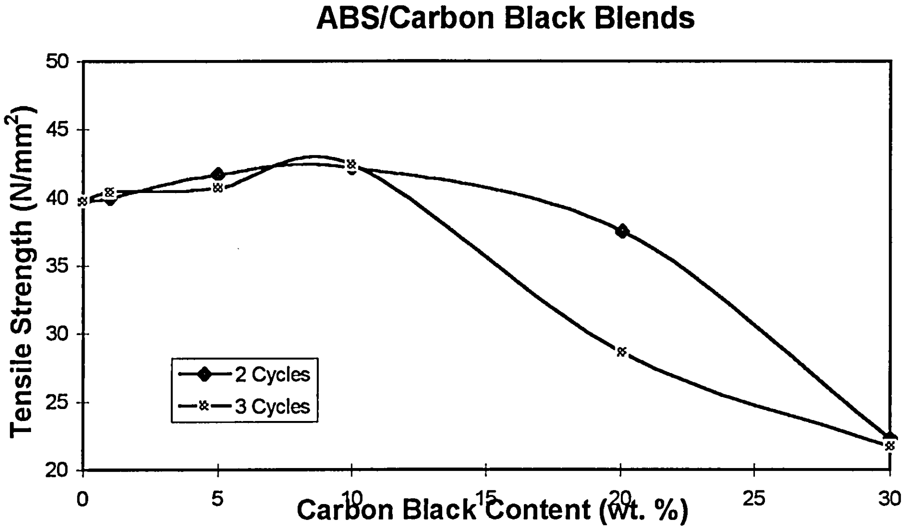


Fig 6.6: Tensile Strength versus Carbon Black Content of ABS/Carbon Black Blends

The graph in Figure 6.6 shows that tensile strength of ABS/carbon black blends increases with the addition of carbon black content up to 10 wt. %. The tensile strengths of two and three cycles of blending are quite similar at this early stage. Above 10 wt. %, tensile strength decreases rapidly, whereas three cycles show lower tensile strength compared to two cycles of blending.

6.2.2 Nylon 6/Carbon Black Blend

Tensile Strengths of Nylon 6 blended with different amounts of carbon black are shown in Table 6.10.

Table 6.10: Tensile Strength of Nylon 6 with different percentage of Carbon Black

Sample	CB Contents (wt %)	Tensile Strength$^{\iota}$ (N/mm^2)	Tensile Strength$^{\kappa}$ (N/mm^2)
Nylon5CB	5	60.6 ± 1.3	54.8 ± 6.8
Nylon10CB	10	50.6 ± 3.9	67.4 ± 2.0
Nylon20CB	20	37.4 ± 5.4	58.0 ± 5.2
N54/CON2*	22$^{\#}$	43.9 ± 2.5	-

Note:

* - Conductive Polyamide Compound
\# - measured by TGA
ι - two cycles, κ - three cycles

By taking the specific gravity and tensile strength of Nylon 6 as 1.126 and 69.9 N/mm^2 respectively, the volume fraction of carbon black was calculated. Using the equation 4.7, calculated tensile strengths of all Nylon 6/carbon black blends are shown in Table 6.11

Table 6.11: Calculated Tensile Strengths* of Nylon 6 with different carbon black contents using equation 4.7

Sample	CB content (% vol.)	Tensile Strength (N/mm^2)	Tensile Strength (N/mm^2)*
Nylon 6	0	69.9 ± 1.7	69.9
Nylon5CB	3.2	54.8 ± 6.8	61.5
Nylon10CB	6.6	67.4 ± 2.0	56.2
Nylon20CB	13.7	58.0 ± 5.2	47.5
N54/CON2	15.0	43.9 ± 2.5	46.0

Note: * - σ_p = Tensile Strength of Nylon 6
= 69.9 N/mm^2 (from experimental)

The graph of tensile strength of Nylon 6/carbon black blends with two and three cycles of blending and calculated tensile strength versus carbon black content are plotted as shown in Figure 6.7.

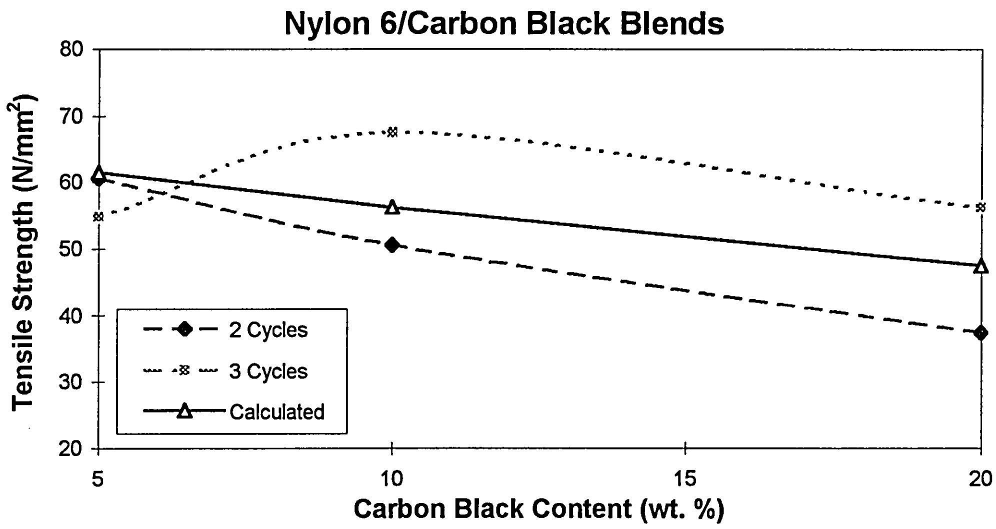


Fig.6.7: Tensile Strength versus Carbon Black Content of Nylon 6/Carbon Black Blends

The graph on Figure 6.7 shows that the tensile strength of Nylon 6/carbon black blends for two cycles of blending and calculated tensile strength decreases with the addition of carbon black content. However tensile strength for three cycles of blending increases with the addition of carbon black content up to 10 wt %, before it decreases with further addition of carbon black. Unlike three cycles, the graph also shows that tensile strength of two cycles of blending is always lower than the calculated tensile strength.

6.2.3 Acrylonitrile Butadiene Styrene/Nylon 6/Carbon Black Blend

For the tensile strength of ABS/Nylon 6/carbon black blends, two variables were investigated. Firstly, tensile strengths of varied composition ABS/Nylon 6 blends with fixed content of 10 wt. % carbon black were studied. The results are shown in Table 6.12. Secondly, tensile strength of ABS/Nylon 6 (50:50 of composition ratio) with varied amount of carbon black were studied. The results are shown in Table 6.13.

Table 6.12: Tensile Strength of ABS/Nylon 6/Carbon Black blends with different composition of polymers

Sample	Composition of ABS: Nylon 6	Tensile Strength$^{\iota}$ (N/mm^2)	Tensile Strength$^{\kappa}$ (N/mm^2)
Nylon10CB	0:100	67.43± 2.05	50.65 ± 3.88
ABS2/N8/CB10	20:80	5.49 ± 0.12	-
ABS4/N6/CB10	40:60	4.14 ± 0.78	-
ABS5/N5/CB10	50:50	3.25 ± 0.24	2.34 ± 0.16
ABS6/N4/CB10	60:40	2.72 ± 0.67	-
ABS8/N2/CB10	80:20	2.68 ± 0.46	-
ABS10CB	100:0	42.42 ± 0.68	42.20 ± 0.62

ι - three cycles, κ - two cycles

Table 6.12 shows that the tensile strength of ABS/Nylon 6/carbon black blends are too low compared with ABS/carbon black and Nylon 6/carbon black blends.

Table 6.13: Tensile Strength of ABS/Nylon 6 (50:50) blends with different carbon black contents

Sample	Carbon Black Content (wt. %)	Tensile Strength$^{\iota}$ (N/mm^2)	Tensile Strength$^{\kappa}$ (N/mm^2)
ABS5/N5	0	2.11 ± 0.41	(2.07 ± 0.14)
ABS5/N5/CB2	2	3.54 ± 0.18	-
ABS5/N5/CB5	5	3.48 ± 0.25	-
ABS5/N5/CB10	10	3.25 ± 0.24	2.34 ± 0.18

ι - three cycles, κ - two cycles

The graph of tensile strength versus ABS content (carbon black content of 10 wt. %) is plotted as shown in Figure 6.8, whereas the graph plotted in Figure 6.9, shows tensile strengths at a 50:50 ratio of ABS/Nylon 6 blends versus different carbon black contents.

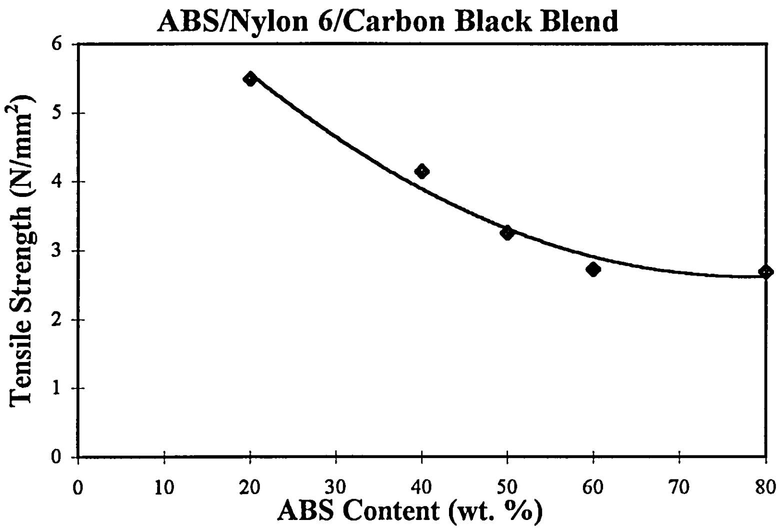


Fig. 6.8: Tensile Strength versus ABS Content of ABS/Nylon 6 /Carbon Black Blends (Carbon Black content of 10 wt %)

The graph in Figure 6.8 shows that tensile strength of ABS/Nylon 6/carbon black blends decreases when ABS content in the blends increases.

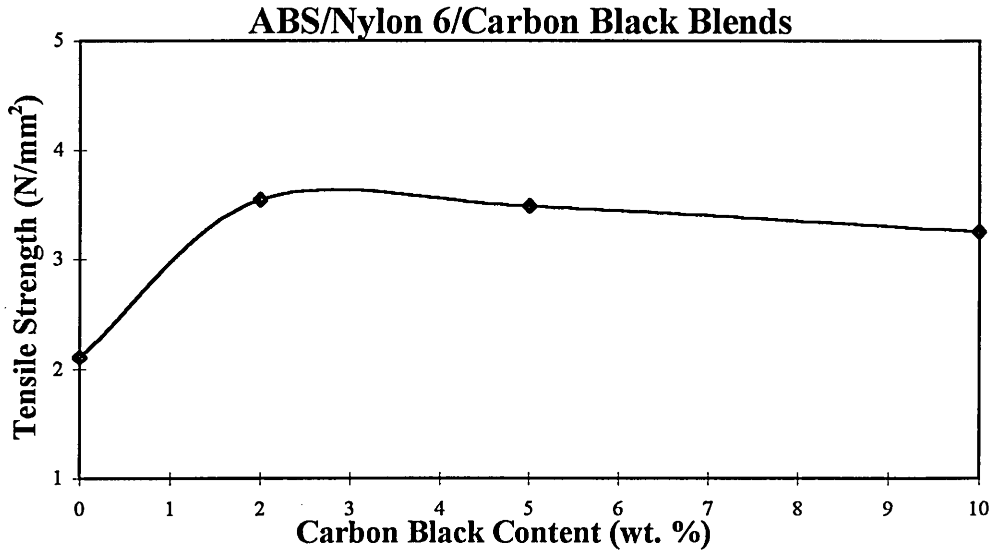


Fig. 6.9: Tensile Strength versus Carbon Black Content of ABS/Nylon 6 /Carbon Black Blends (for ABS/Nylon 6 with 50:50 composition)

The graph in Figure 6.9 shows that the addition of carbon black to ABS/Nylon 6 blend increases the tensile strength of the blend. However, further addition of carbon black more than 2 wt. %, decreases tensile strength of ABS/Nylon 6/carbon black blends, although still higher than the tensile strength of ABS/Nylon blend itself.

6.3. Morphology Characterisation by Scanning Electron Microscopy

Three types of SEM photomicrograph were taken from morphological characterisation of ABS, Nylon 6 and carbon black individually or blended. Photomicrograph samples mounted in conductive bakelite mould, samples mounted in cold setting mould and samples coated with gold were used. All samples were marked as described in Chapter 5.

6.3.1 Sample Mounting in Conductive Bakelite Mould

Only three SEM photographs were taken from samples mounted in conductive bakelite which were marked as ABS1CB, ABS10CB and ABS30CB. The photomicrographs are shown in Figure 6.10 (ABS1CB), Figure 6.11 (ABS10CB) and Figure 6.12 (ABS30CB).

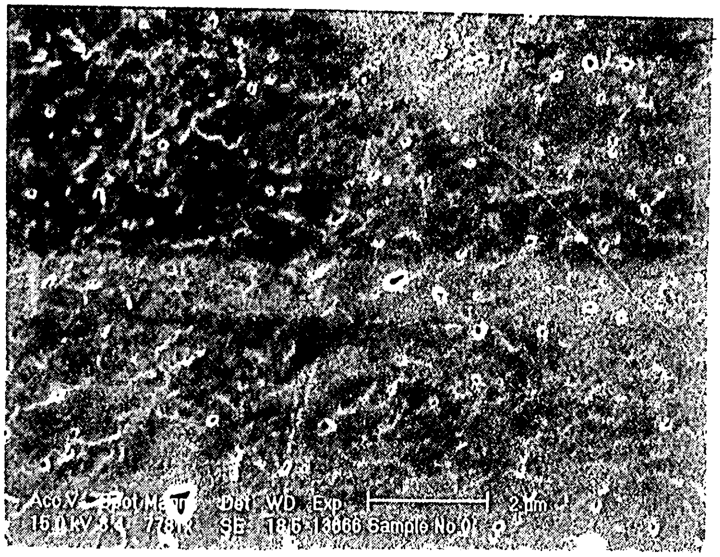


Figure 6.10: SEM Photomicrograph of ABS/Carbon Black (1 wt. %.) Blend

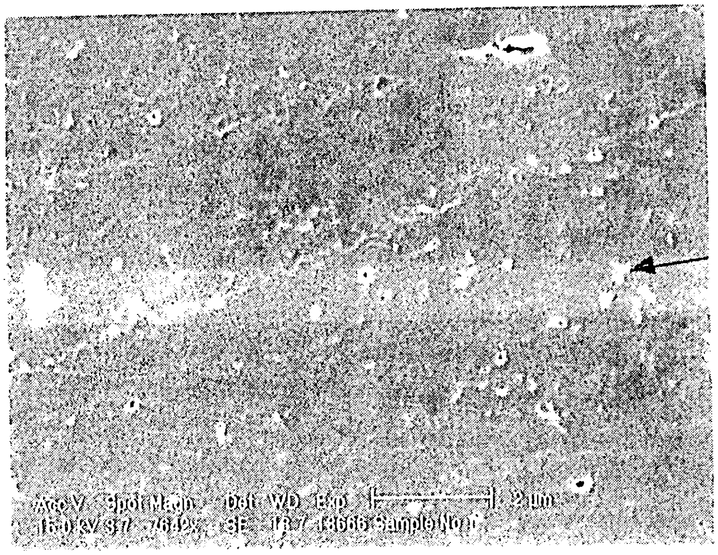


Figure 6.11: SEM Photomicrograph of ABS/Carbon Black (10 wt. %.) Blend

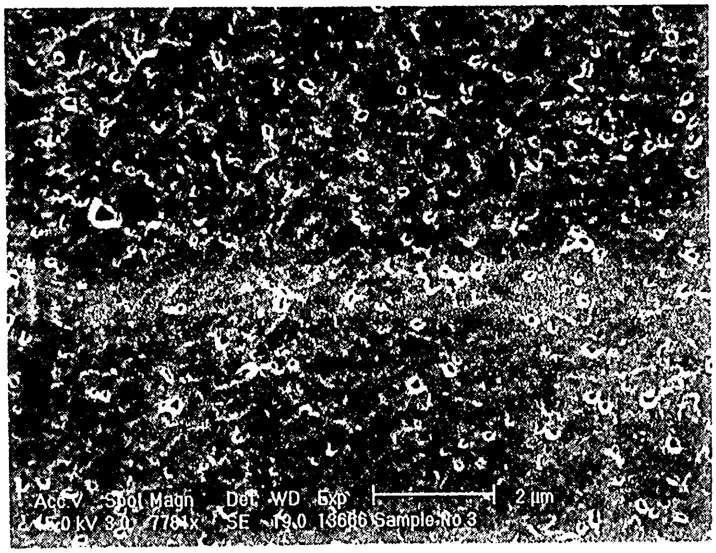


Figure 6.12: SEM Photomicrograph of ABS/Carbon Black (30 wt. %.) Blend

Figure 6.10, 6.11 and 6.12 show that little difference can be observed from SEM photomicrographs, although ABS/carbon black blend with 30 wt. % in Figure 6.12 shows more carbon black particles in the ABS phase. Consequently morphologies of ABS/carbon black blends cannot be studied. Figure 6.10 shows that carbon particles are surrounded by ABS matrix. The size of carbon black is about 0.1-0.2 μm.

Carbon black is found to a lesser extent in Figure 6.11 compare to Figure 6.10, although carbon black content in both is 10 wt. %. This is because the sample was taken from part of the blend which contain less carbon black because of unequal distribution of carbon black. Markings observed on the photomicrograph are scratches from the grinding and polishing operation. Figure 6.12 shows that ABS blend with 30 wt % of carbon black has more carbon black with bigger size aggregate, 0.2-0.3 μm.

6.3.2 Sample Mounting in Cold Setting Mould

SEM photomicrograph of ABS/carbon black and Nylon 6/carbon black blend samples mounted in Cold Setting Mould are shown in Figure 6.13 (ABS20CB), 6.14 (ABS30CB), 6.15 (NY5CB-2C) and 6.16 (NY20CB). Figure 6.13 and 6.14 do not show a good and clear photomicrograph. Therefore, the distribution of carbon black particles in ABS matrix cannot be observed.

Meanwhile photomicrographs of Nylon 6 with 5 and 20 wt. % of carbon black content in Figure 6.15 and 6.16 respectively, did not clearly show carbon black particles. There is not much difference between both Nylon 6/carbon black blends shown in the photomicrographs. However. more carbon black particles are found in Nylon 6/carbon black blends compared to ABS/carbon black blends, although in Nylon 6 phases, carbon black particles are separated and smaller than in ABS phases.

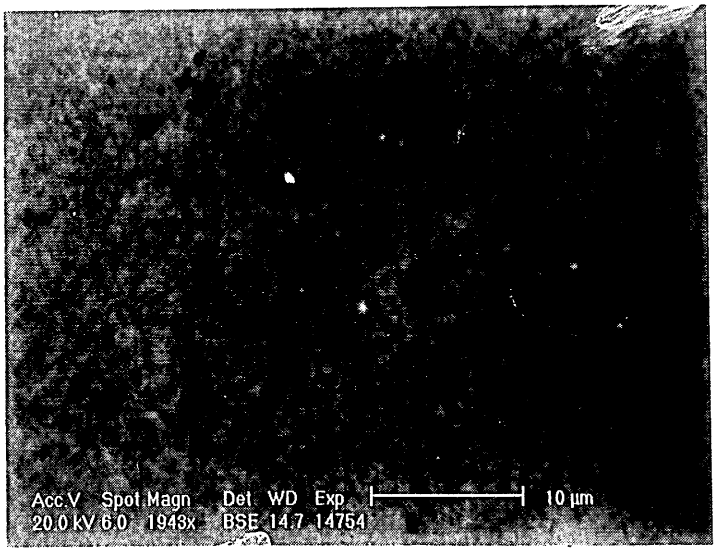


Figure 6.13: SEM Photomicrograph of ABS/Carbon Black (20 wt. %.) Blend

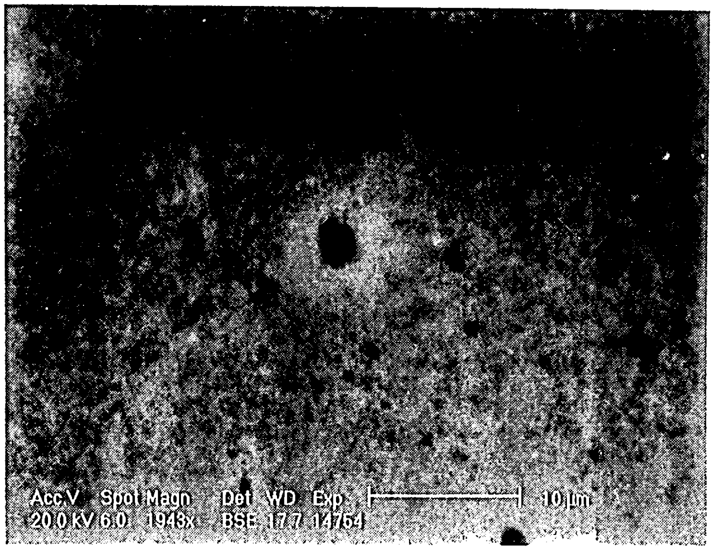


Figure 6.14: SEM Photomicrograph of ABS/Carbon Black (30 wt. %.) Blend

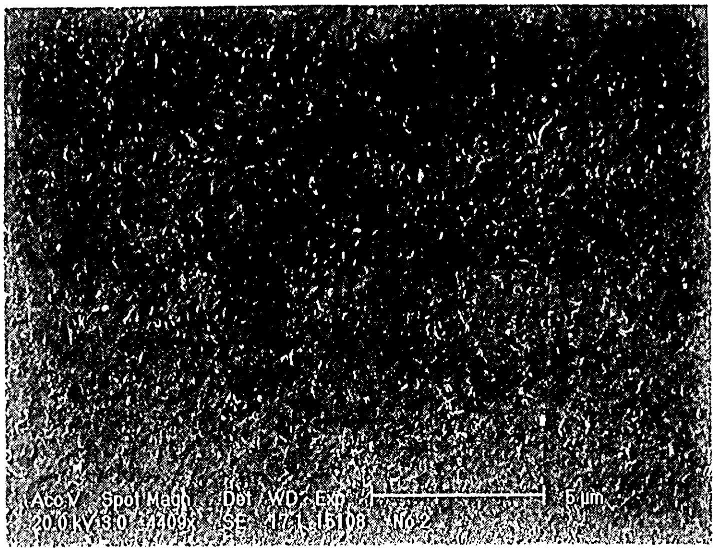


Figure 6.15: SEM Photomicrograph of Nylon 6/Carbon Black (5 wt. %.) - Blend

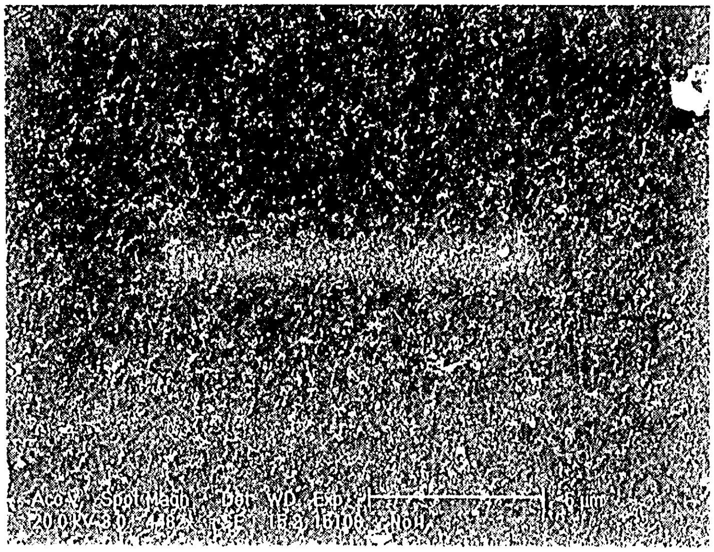


Figure 6.16: SEM Photomicrograph of Nylon 6/Carbon Black (20 wt. %.) Blend

6.3.3 Sample Coated with Gold

Because of the unclear images found, carbon coating was changed to gold coating. SEM photomicrograph of samples coated with gold are shown in Figure 6.17 to Figure 6.34. The sample shown in Figure 6.17 (ABS20CB) is the only sample mounted in bakelite, the rest were mounted in cold setting compound.

6.3.3.1 ABS/Carbon Black and Nylon 6/Carbon Black Blends

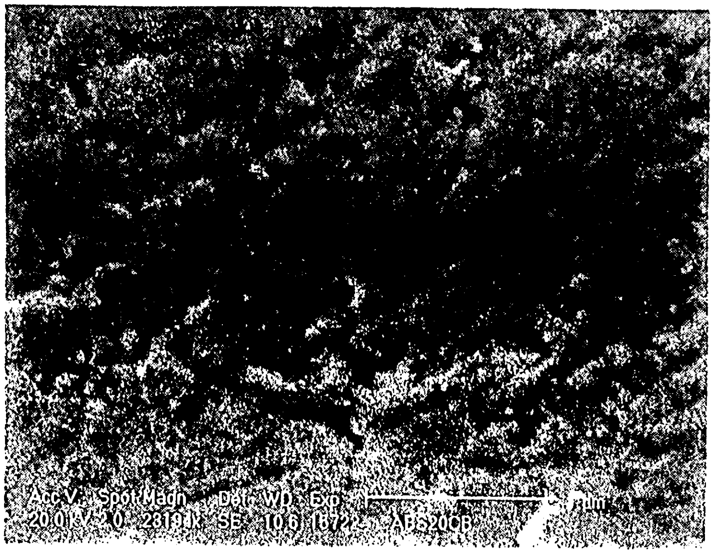


Figure 6.17: SEM Photomicrograph of ABS/Carbon Black (20 wt. %.) - Blend in Conductive Bakelite Mould

The photomicrograph in Figure 6.17 shows that the ABS/carbon black (20 wt. %) blend mounted in conductive bakelite presents a blurred structure. However, carbon black particles can be observed in this photomicrograph which was magnified 23,000 times. The rest of the samples which were mounted in cold setting moulds and coated with gold show clear images.

Figure 6.18 shows an SEM photomicrograph of Nylon 6 with 20 wt. % of carbon black content. To get a clear image of carbon black particles in Nylon 6 matrix, an SEM photomicrograph at 23,000 times magnification was taken which is shown in Figure 6.19.

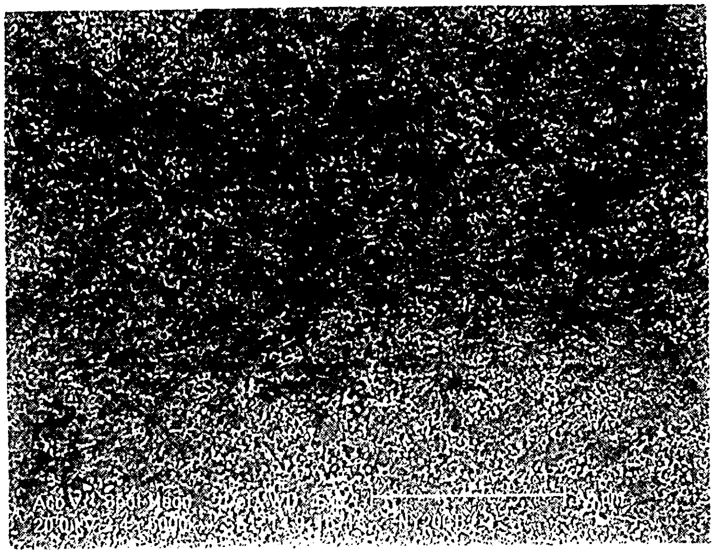


Figure 6.18: SEM Photomicrograph of Nylon 6/Carbon Black (20 wt. %.) Blend

SEM Photomicrograph of Nylon 6/carbon black blend in Figure 6.18 is of the same blend used in Figure 6.16, but it is clearer due to being coated with gold. Scratches and holes are shown clearly in Figure 6.18. They might be due to grinding and polishing of the sample. Carbon black particles might move out from the surface while polishing which leaves holes on the sample's surface.

The hole and carbon black particles distribution can be seen clearly in SEM photomicrograph at 23000X magnification as shown in Figure 6.19. Carbon black particles of size about 0.1 μm diameter, can be seen clearly in the Nylon 6 matrix. In comparison with the size of carbon black in Nylon 6 matrix, an SEM photomicrograph of carbon black particles themselves was taken and shown in Figure 6.20.

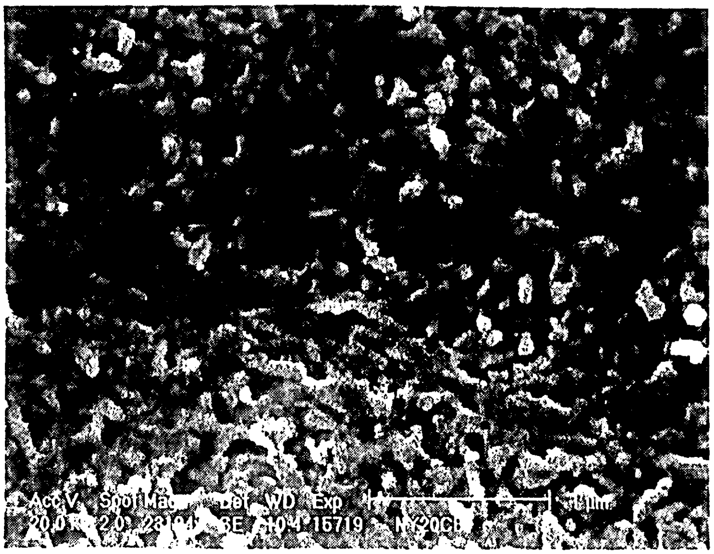


Figure 6.19: SEM Photomicrograph of Nylon 6/Carbon Black (20 wt. %.) Blend at 23,000X magnification

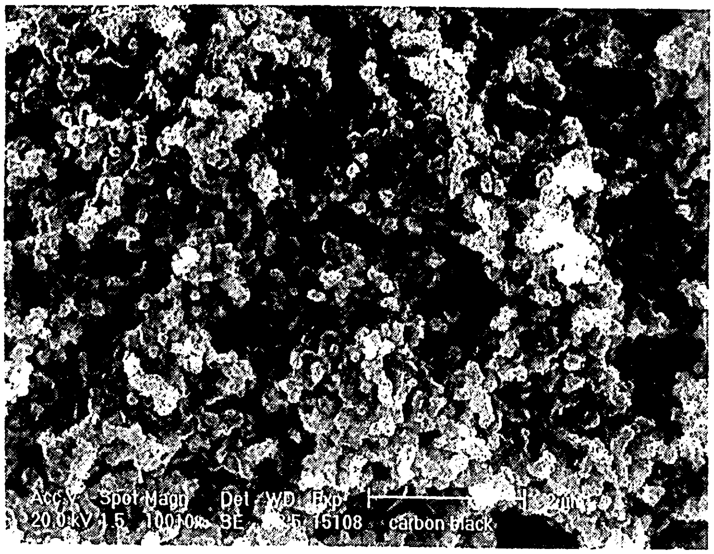


Figure 6.20: SEM Photomicrograph of Carbon Black

At a magnification of 10,000 times, Figure 6.20 shows aggregations of irregular form of carbon black particles with size 0.1 to 0.2 µm.

To study the effect of carbon black on the blends' structure and mechanical properties of Nylon 6, SEM photomicrographs of Nylon 6 and Nylon 6/carbon black blends were compared. An SEM photomicrograph of Nylon 6 is shown in Figure 6.21, while Nylon 6/carbon black (10 wt %) blend is shown in Figure 6.22.

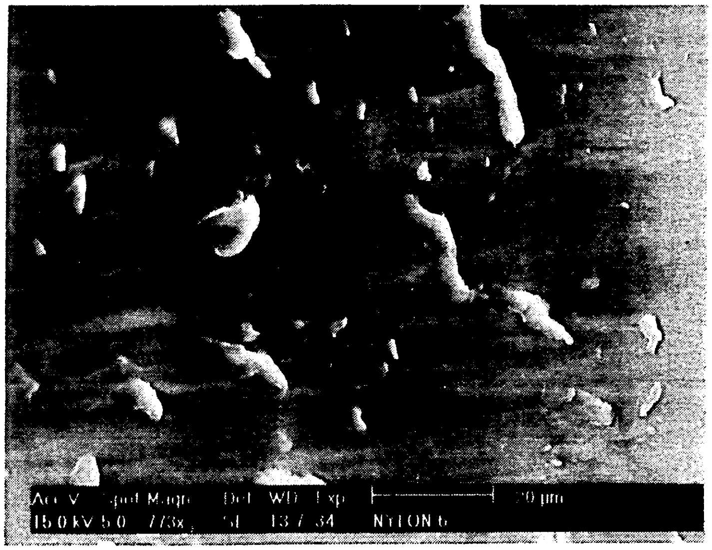


Figure 6.21: SEM Photomicrograph of Nylon 6

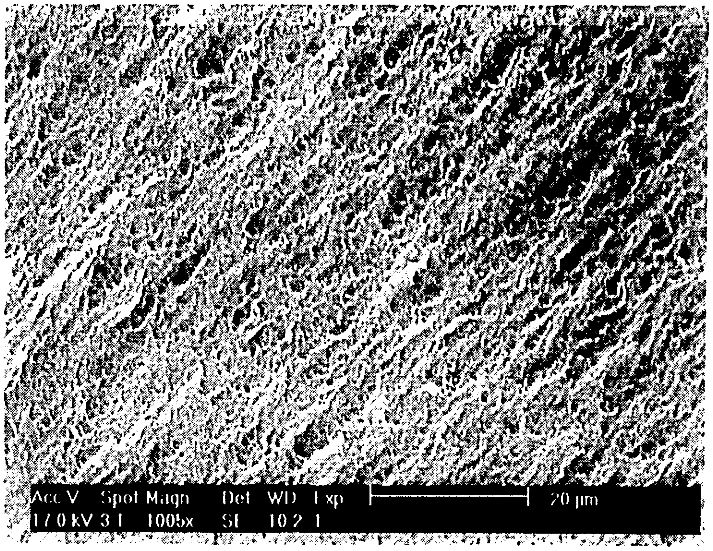


Figure 6.22: SEM Photomicrograph of Nylon 6/Carbon Black (10 wt. %.) Blend

Two different phases were found in Nylon 6 as shown in Figure 6.21. The structure of Nylon 6 changes with the addition of 10 wt % of carbon black in the matrix, which can be seen clearly in Figure 6.22. However, carbon black cannot be seen clearly.

The difference of Nylon 6/carbon black blend with Conductive Compound-Nylon N54/CON2 was studied by taking an SEM photomicrograph of the conductive Nylon compound which is shown in Figure 6.23.

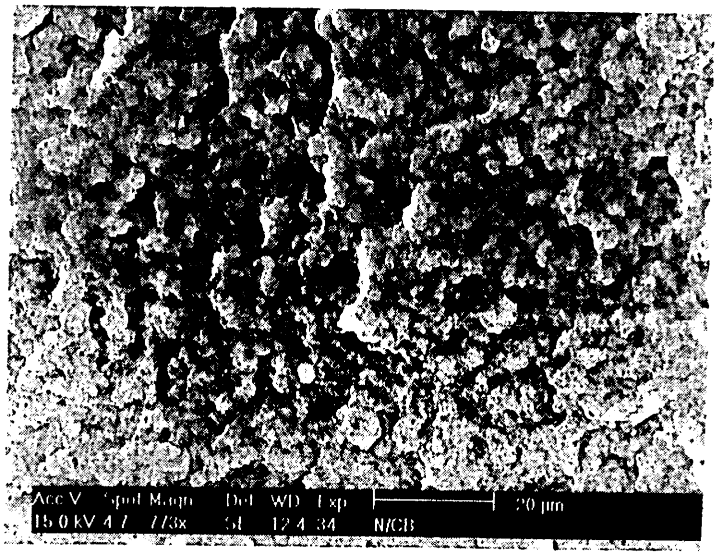


Figure 6.23: SEM Photomicrograph of Conductive Compound - Nylon N54/CON2

Figure 6.23 of Conductive Compound-Nylon N54/CON2 shows bigger particles than Nylon 6 with 10 wt % in Figure 6.22. The surface of the conductive compound is rougher than Nylon 6/carbon black (10 wt. %) blend.

6.3.3.2 ABS/Nylon 6/Carbon Black Blends

SEM photomicrographs of ABS/Nylon 6 (50:50) blends are shown in Figure 6.24 and 6.25. Figure 6.24 shows SEM photomicrograph at 25 times magnification, while Figure 6.25 at 1,000 times magnification.

Figure 6.24: SEM Photomicrograph of ABS/Nylon 6 (50:50) Blend at 25X magnificent

SEM photomicrograph in Figure 6.24 shows that ABS and Nylon 6 did not mix well for the first cycle of blending. This is shown by the separation of two different phases and striping of these two polymers at a magnification of 25X. Magnification at 1,000 times as shown in Figure 6.25 shows immiscible mix between ABS and Nylon 6. The rough surface of the sample can be seen on the photomicrograph.

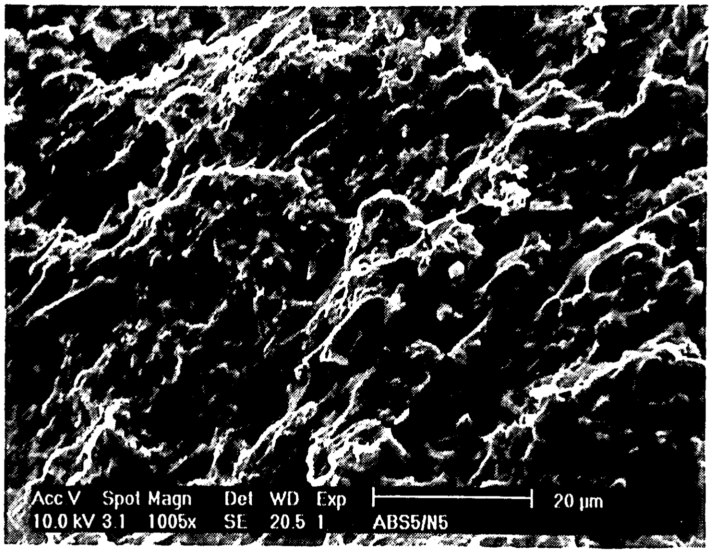


Figure 6.25: SEM Photomicrograph of ABS/Nylon 6 (50:50) Blend

The effect of carbon black on the morphologies of ABS/Nylon 6 blends was studied from the SEM photomicrograph shown in Figure 6.26 and 6.27. Additions of 2 wt % and 5 wt % of carbon black in ABS/Nylon 6 (50:50) are shown in Figure 6.26 and 6.27 respectively.

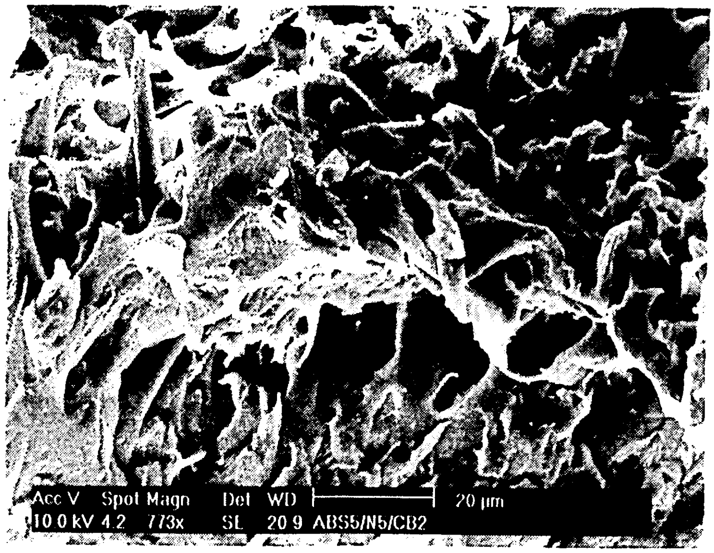


Figure 6.26: SEM Photomicrograph of ABS/Nylon 6 (50:50) with 2% Carbon Black (wt.) Blend

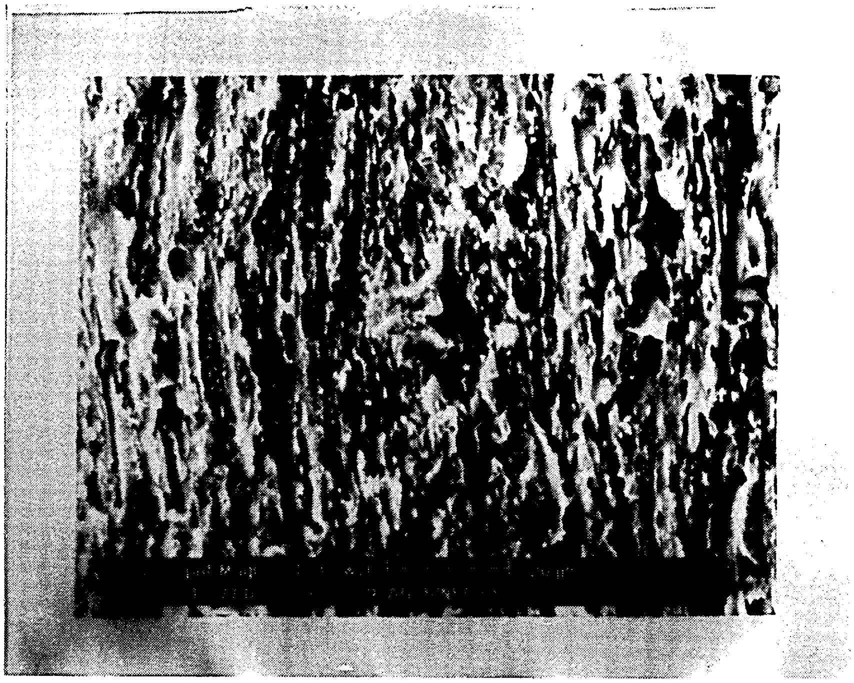


Figure 6.27: SEM Photomicrograph of ABS/Nylon 6 (50:50)
with 5% Carbon Black (wt.) Blend

Addition of 2 wt % of carbon black to ABS/Nylon 6 blends reduce the rough surface of the specimen as shown in Figure 6.26. However, with a further addition of carbon black content up to 5 wt %, the surface of the specimen becomes rough again. This is shown by the roughness of microstructure in Figure 6.27 compare to Figure 6.26.

To study the changes in morphology in ABS/Nylon 6/carbon black blends with varied polymers ratio composition, SEM photomicrographs of the blends of different ABS:Nylon 6 compositions were taken. SEM photomicrographs of different composition of ABS/Nylon 6 with 10 wt % of carbon black blends are shown in Figure 6.28 [ABS/Nylon 6 (20:80)], 6.29 [ABS/Nylon 6 (40:60)], 6.30 [ABS/Nylon 6 (60:40)] and 6.31 [ABS/Nylon 6 (80:20)].

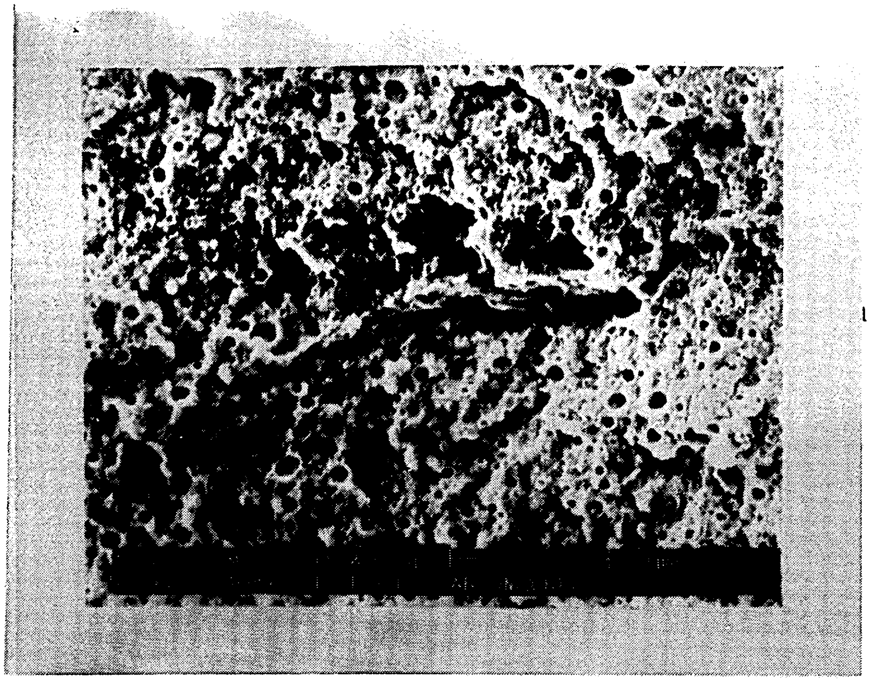


Figure 6.28: SEM Photomicrograph of ABS/Nylon 6 (20:80) with 10% Carbon Black (wt.) Blend

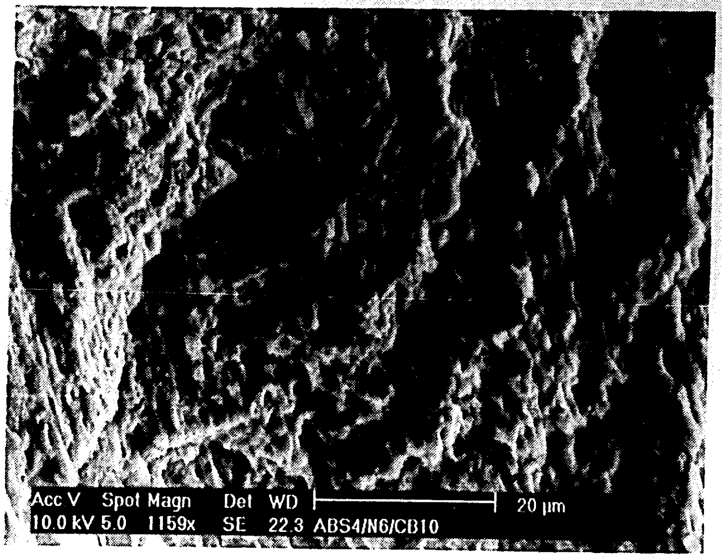


Figure 6.29: SEM Photomicrograph of ABS/Nylon 6 (40:60) with 10% Carbon Black (wt.) Blend

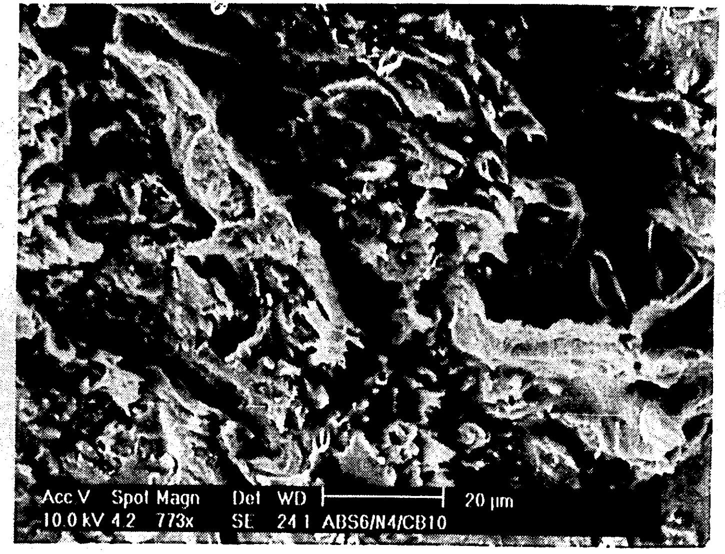


Figure 6.30: SEM Photomicrograph of ABS/Nylon 6 (60:40) with 10% Carbon Black (wt.) Blend

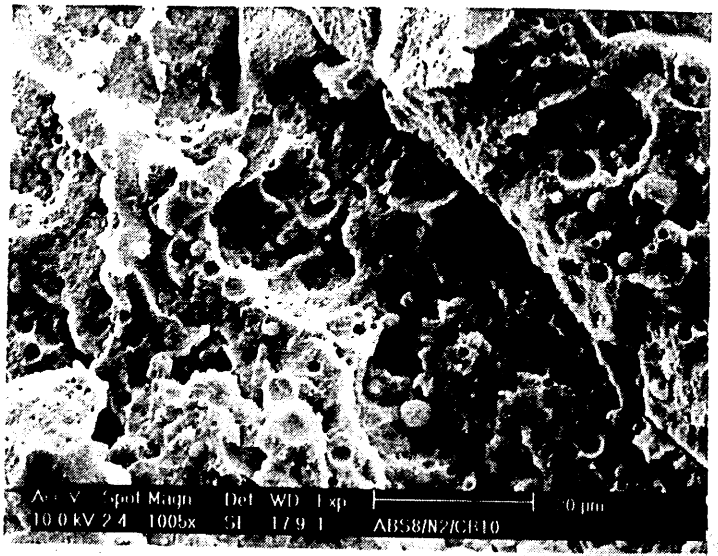


Figure 6.31: SEM Photomicrograph of ABS/Nylon 6 (80:20) with 10% Carbon Black (wt.) Blend

Figure 6.28 shows many holes and carbon black particles on the surface of the samples. The holes on the Nylon 6 surface shows that carbon black pulled out during polishing/grinding of the samples. However holes and carbon black particles decrease when composition of ABS in the blends increase as shown in Figure 6.29 to 6.31. Carbon black and Nylon 6 particles can be seen in ABS/Nylon 6 (80:20) as shown in Figure 6.31.

To see the changes of microstructure with the addition of ABS content, an SEM photomicrograph of ABS/carbon black (10 wt %) was studied as shown in Figure 6.32.

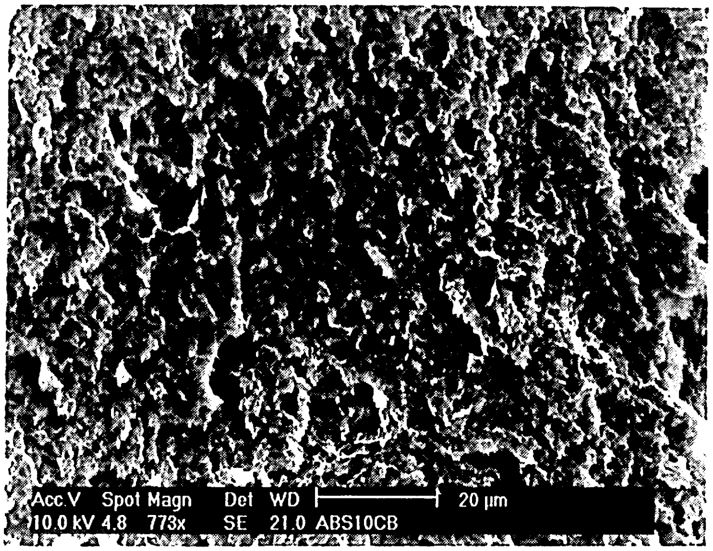


Figure 6.32: SEM Photomicrograph of ABS/Carbon Black (10 wt. %.) Blend

To look at the distribution of carbon black particles in the blend, photomicrographs were taken at a magnification of 23,000 times and shown in Figure 6.33 and 6.34.

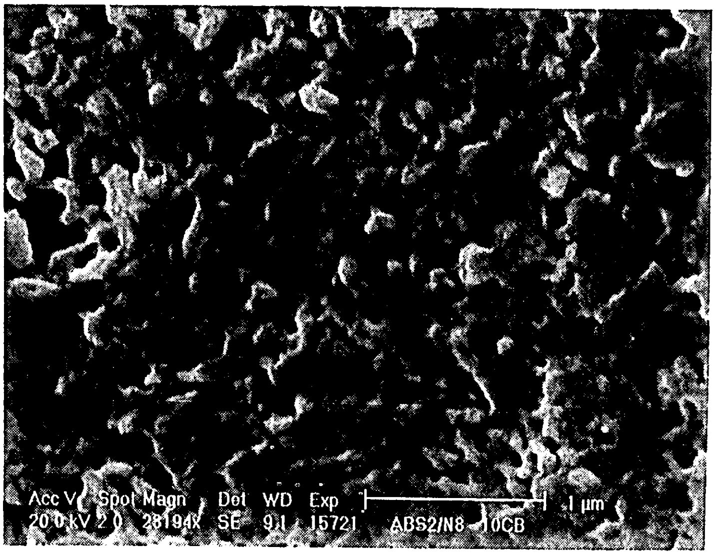


Figure 6.33: SEM Photomicrograph of ABS/Nylon 6 (20:80)
with 10% Carbon Black (wt.) Blend

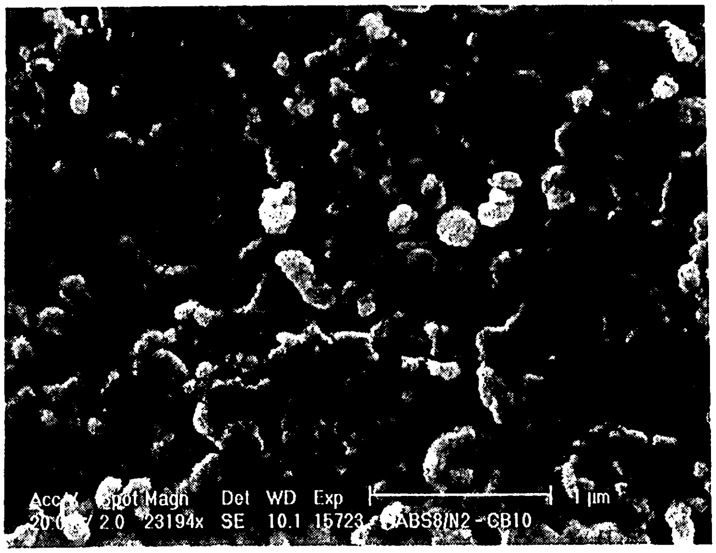


Figure 6.34: SEM Photomicrograph of ABS/Nylon 6 (80:20)
with 10% Carbon Black (wt.) Blend

Magnification of 23,000 times shows that carbon black particles distribution can be seen better in ABS/Nylon 6 (80:20) with 10 wt % carbon black blend (Figure 6.34) compared with ABS/Nylon 6 (20:80) containing 10 wt % carbon black (Figure 6.33).

CHAPTER 7

DISCUSSION

7.1 Conducting Behaviour of Polymer Blends

7.1.1 Effect of Carbon Black Content on Conductivity

7.1.1.1 Acrylonitrile Butadiene Styrene /Carbon Black Blends

The results in Table 6.1 shows that sheet resistance of ABS/carbon black blends could not be measured if carbon black content is 10 wt. % and below. This is because the resistance is more than 10^3 Ω, and could not be measured using a four-point-probe technique. The sheet resistance could be detected for the composite with 20 wt. % carbon black and above. The resistance decreased with the addition of carbon black content, which means conductivity increased. Table 2.1 in Chapter 2 shows that the conductivity of the compound improves by the addition of carbon black[40].

As a comparison with other research on conductivity of polymer blends, the amount of carbon black in the blend is converted from weight fraction to volume fraction. As shown in Table 6.1, 10% by weight fraction of carbon black is equal to 6% by volume. Previous work by J C Dawson[78] found that the resistivity of polycarbonate with 6% by volume of carbon black composite was 2.4 x 10^4 Ωm. Using the resistivity equation 4.5 [$\rho = 2\pi s(V/I)$], resistance (V/I) is calculated as 3.8 X 10^6Ω. From the sheet resistance equation 4.3 ($R_h = 4.53V/I$), sheet resistance of polycarbonate with 6% by volume of Carbon Black is calculated as 1.7 x 10^7 Ω/sq.

By using this value of resistivity for ABS with 10 wt % of carbon black blends, 3.8 MV of voltage was needed to give 1A of current. However, the voltmeter attached to four point probe could not read voltage higher than 1 kV. On the other hand, the ammeter could not read current in μA unit and below if the voltage is reduced to 3.8 V to give 1 μA.

Since a four point probe technique can only measure resistance up to 10^2 Ω, a Teraohmeter was used to measure surface and volume resistance of samples with high resistance. Table 6.3 shows that surface resistivity of ABS decreases when carbon black was added. However 5% of carbon black was not high enough to decrease the volume resistance of ABS, which was almost unaffected by this amount. This suggests that carbon black tends to move to the surface of the ABS phase compared with the internal phase. That is why surface resistance decreases faster compared to volume resistance.

7.1.1.2 Nylon 6/Carbon Black Blends

Sheet resistance could not be measured for Nylon/carbon black blend up to 25 wt. %. This shows that carbon black does not have an affect on the conductivity of Nylon 6 with up to 25 wt % of carbon black. However, the resistance could be detected on Conductive Polyamide Compound - N54/CON2, which is shown in Table 6.6. Analysis by TGA - Mettler-Toledo TA8000 shows that this conductive compound contains 22 wt. % of carbon black. The conductive carbon black filler used is known as "super conductive black".

Research by R. Tchoudakov and co-researcher on PP/Copolyamide (Nylon 6/ 6-9)/ CB blends[79], found that carbon black did affect resistivity of PP at 2 wt. %. But for copolyamide, more than 25 wt % of carbon black was needed to reduce its resistivity. These results emphasise that Nylon alone blended with carbon black does not give a high conductivity.

Table 6.4 and Figure 6.2 shows that surface and volume resistivity of Nylon 6/ carbon black blends decrease with the addition of carbon black. The graph shows that the surface resistivity curve is irregular at an early stage as compared to the volume resistivity curve. Similar to ABS/carbon black blends, at low content of carbon black in Nylon 6/carbon black blends, surface resistivity drops faster than volume resistivity. The surface resistivity curve becomes the same shape as the volume resistivity curve when carbon black content is more than 10 wt. %.

This phenomenon shows that carbon black inclines to move to or exist on the surface of Nylon at an earlier stage. When more than 10 wt % of the filler was added, it moved to the all amorphous phase of Nylon.

7.1.1.3 Acrylonitrile Butadiene Styrene/Nylon 6/Carbon Black Blend

To analyse the effect of carbon black content on ABS/Nylon 6 blends, the blends with 50:50 composition were mixed with 2, 5, 10 and 20 wt. % of carbon black. Table 6.6 and Figure 6.5 show that both surface and volume resistivities decrease when carbon black content increases. Both resistivities decrease faster after 10 wt % of carbon black content.

The graph in Figure 6.5 shows a better behaviour of resistivity changing with the addition of carbon black content, compared to Nylon/carbon black blends as shown in Figure 6.2. Figure 6.5 shows a similar shape of curve for both surface and volume resistivity. The similar shape of curve means that uniform blending made the polymer and carbon black distribute equally whether on the surface or bulk of the blend.

7.1.2 Effect of Reblending on Conductivity

Table 6.1 also shows that, sheet resistance of ABS20CB and ABS30CB blends decreases when the blend is recycled for a third time. This means that conductivity increases when the compound is reblended for the third time. To emphasise this point, Table 6.2 shows that blending for the fourth time decreases resistivity almost 100 times as compared to blends recycled three times. The graph in Figure 6.1 shows the trend of reblending on the resistivity of ABS blends with 30 wt. % carbon black.

This is due to the improvement in linking of carbon black particles in the compound after reblending. The reblending process might develop conductive network paths of carbon black particles through the polymer matrix. Also this process means mixing time was extended, and research by CCM Ma and his team have found that when mixing time was increased resistivity decreased[11]. This was supported by the graph plotted in Figure 2.2 in Chapter 2 that shows the increase of conductivity with mixing time until optimum mixing time is achieved[40].

However, the resistivities of ABS/carbon black blends (30 wt %) were measured on the surface of the sample, so it does not represent the complete resistivities of the blends. Unfortunately, surface and volume resistances could not be read by the Teraohmeter because they were too low. The lowest resistance which can be measured by the Teraohmeter is 10^6 Ω.

In addition, this process does not effect ABS/Nylon blends. Reblending of these blends did not improve their conductivity. This is shown by the surface and volume resistivity of ABS5/N5 and ABS5/N5/CB20 in Table 6.6 which were blended two and three cycles. On the contrary, three cycles of blend increase resistivity although it was small. This is because blending carbon black in a polymer-polymer blend not only distributes the filler in the phases of polymeric matrix, but also transports the filler from one phase to another phase (crystalline or amorphous) or interfaces of polymers.

M. Kozlowski[15] and R. Tchoudakov's research group[79], found that carbon black prefers to locate in an amorphous phase of semi-crystalline polymers. In these ABS/Nylon 6 blends, carbon black prefers to locate in amorphous phases of Nylon 6. Reblending ABS/Nylon 6/carbon black blends will move carbon black more to the Nylon phases and reduces the fillers content in the ABS phases. The lower content of carbon black in ABS will increase resistivity of the blends, because as discussed before carbon black content has lesser effects on Nylon compared with ABS.

7.1.3 Effect of Polymer Composition on Conductivity

Table 6.5 and the graph in Figure 6.3 show that, surface resistivity decreases when the content of ABS in ABS/Nylon 6/carbon black (10 wt %) increases. However, the resistivity increases again when the amount of ABS is more than 20%. The resistivity achieves a resistivity peak at approximately 44% of ABS content. After this point, the resistivity decreases again to the lowest resistivity at 80% of ABS content. The lowest value that can be measured by Teraohmeter is 10^6 Ω. Therefore, the lowest surface resistivity is 10^7 Ω/sq. can be calculated.

Meanwhile, volume resistivity had almost no affect at the early stage of ABS addition. The volume resistivity reached the turning point at about 50% of ABS content. The resistivity decreased when the content of ABS increased to the lowest resistivity at 80% of ABS. This phenomenon is shown in Figure 6.4. From the reading of resistance measured by Teraohmeter that was below 10^6 Ω, volume resistivity is calculated as below 10^8 Ωcm.

Therefore, the addition of ABS at an early stage had two different effects on surface and volume resistivity. While the existence of ABS causes drastic change to surface resistivity at the content of 20 to 40 wt %, there is almost no affection volume resistivity at the same amount of ABS. Both of the resistivities obviously decrease when the content of ABS increases more than 50% by weight, until they meet the lowest value at 80 wt %.

Introduction of ABS in the blends cause carbon black migrates to ABS phases, instead of Nylon 6 (Nylon/carbon black blends). Again in these blends, surface resistivity drops more than volume resistivity at an early stage of addition of ABS. As explained before, carbon black inclines to move to the surface of ABS and Nylon rather than internal phases of both polymers. The same phenomenon happened in ABS/Nylon/carbon black blends. Because the existing carbon black in ABS gives more affect on conductivity compared to in Nylon 6, a small content of ABS can cause surface resistivity to drop more than volume resistivity.

However, when the amount of ABS increases to 40%, the surface resistivity increases. This is because, at the same content of carbon black in the blends (10 wt. %), increasing ABS content (from 20 to 40%) causes the weight percentage of carbon black to ABS to reduce almost twice (10:20 to 10:40). Volume resistivity, that is the resistivity of whole blends, does not show much difference with the increasing of ABS content, until ABS content is more than Nylon content, that is 60 wt. %.

As carbon black particles prefer to locate in amorphous phases of semi-crystalline polymer, reducing Nylon to 40% means the amount of carbon black per unit weight of Nylon is increased. The same amount of carbon black (10%) in 40% of Nylon will give almost 25% of this filler in the Nylon phase. According to R. Tchoudakov and co-researcher[79], the conductivity of Nylon was affected when the carbon black content was more than 25 wt %. This made surface and volume resistivities decrease at this stage. The resistivities continue to decrease until the content of Nylon 6 become 20% by weight.

To study the effect of ABS content on the conductivity of ABS/Nylon 6/carbon black blends, the content of ABS was increased to 90% by weight, that produced ABS/Nylon 6 blend in ratio of 9:1 with 10 wt % of carbon black. The sheet resistance was measured on this blend and also ABS with 10 wt % carbon black. It was found that their resistances were too high and could not be read on the measuring meter.

This phenomenon shows that, the conductivity of ABS/Nylon 6/carbon black blends does not depend on the content of ABS only, but also on the location of carbon black filler in the polymer phases. Although carbon black prefers to locate in the amorphous phase of Nylon 6, addition of ABS shows increased conductivity that means the filler also locates in the ABS phase.

However until a certain point, further addition of ABS reduces conductivity of the blends. This shows the location of carbon black not only in Nylon 6 and ABS phases only, but also in the interface of ABS/Nylon. Therefore the existence of ABS in the blend, creates another phase (interface and amorphous phase of ABS) besides the crystalline and amorphous phases of Nylon 6 that give more possibilities for the location of carbon black. Increasing ABS will cramp the conductive carbon black path in the amorphous phase of Nylon 6 and that will increase contact between the filler aggregates. This will increase conductivity.

At a certain point, which is called the percolation threshold, conductivity stops increasing and starts to reduce. In ABS/Nylon 6/carbon black blend, the turning point was found to be the blend containing 80%/20% by weight ratio blended with 10 wt % carbon black.

7.1.4 Comparison between Conductive Polyamide Compound and ABS/Nylon 6/Carbon Black Blends

Because surface and volume resistance is lower than 10^6 Ω which could not be measured by Teraohmeter, sheet resistance and resistivity were measured using four point probe. The results shown in Table 6.7 are sheet resistance and resistivity of ABS/Nylon 6 (80:20 composition ratio) with 10 wt. % carbon black, ABS/Nylon 6 (50:50 composition ratio) with 20 wt % carbon black and N54/CON2 blends. All the blends show good conductive properties that are between 10^1 to 10^{-1} $\Omega^{-1}cm^{-1}$, which is within the semi-conductive group of compounds as shown in Figure 2.4.

Table 6.7 shows that the sheet resistance and resistivity of ABS5/N5/CB20, which contains 50:50 ratio of ABS/Nylon blend with 20 wt % carbon black, is almost the same as the Conductive Polyamide Compound - N54/CON2 produced by Colloid Ltd. This shows that ABS/Nylon 6/carbon black blends can meet the required level of conductivity with a lesser quantity of filler. Therefore conductive blends can reduce the cost of the compound by adding cheaper polymer such as ABS and using less conductive filler.

7.1.5 Comparison between Sheet Resistance and Surface/Volume Resistance Measurement

Results in Table 6.2 and 6.7 show that sheet resistance and resistivity give large errors that are almost 50% of mean value. This is because of uneven distributions on the surface of the samples, which give large deviations between all readings taken. As explained in Chapter 4, the uneven distribution is due to different affinities of carbon black particles to each polymer and the interface of two polymers.

To get an accurate reading, the thickness of the sample must be less than probe spacing, that is 1mm. Because the probe spacing is too small, resistivities measured by this equipment only show resistivity at a certain point of the surface but do not represent the whole resistivity of the sample.

Therefore, surface resistivity measured by Teraohmeter is a more accurate resistivity of the whole surface area, because it measures the surface area of 58.85 cm^2, compared to sheet resistivity for 1mm radius area. However surface resistivity is not considered a true resistivity of the blends or other composites.

Previous research had found that heterogeneous composite materials always exhibit a resin rich surface[8]. This makes conductivity low at the surface which is not a true resistivity. Therefore volume resistivity was measured to find the average resistivity of the whole composite.

7.2 Mechanical Properties of Polymer Blends

7.2.1 Effect of Carbon Black on the Tensile Strength of Conductive Composites

7.2.1.1 Acrylonitrile Butadiene Styrene/ Carbon Black Blend

Fillers normally improve the tensile strength of composites, although it depends on the shape of the fillers. However an excess filler content can reduce mechanical properties (not only the tensile strength). This can be observed in ABS/carbon black composites. This is shown by the results in Table 6.8 and the graph on Figure 6.6, where tensile strength increases with the addition of carbon black content up to 10 wt. %. Above 10 wt. %, the tensile strength decreases drastically, because the grouping of carbon black particulates increases the brittleness of the composite.

7.2.1.2 Nylon 6/Carbon Black Blend

The results in Table 6.10 and the graph in Figure 6.7 show that, for second cycle nylon/carbon black reblending, tensile strengths decrease when carbon black content is increased. However like ABS/carbon black blends, the third cycles of nylon/carbon black blends increase with the addition of carbon black content up to 10 wt. %. Above 10 wt. %, the tensile strength decrease.

7.2.1.3 Acrylonitrile Butadiene Styrene/Nylon 6/Carbon Black Blend

The results in Table 6.13 and the graph in Figure 6.9 show that added carbon black in ABS/Nylon 6 blends increases tensile strength. Table 6.13 show that tensile strength of all ABS/Nylon 6 (50:50 composition)/carbon black blends are higher than ABS/Nylon 6 blend without carbon black. This shows that carbon black filler caused interfacial adhesion between ABS and Nylon 6 matrix to be stronger. Therefore putting carbon black fillers in the blend strengthen the blends.

However increasing carbon black above 2 wt %, tensile strength was decreased. As explained in section 4.3[67], the increase of carbon black filler increases the brittleness of the blend, consequently decreasing the tensile strength of the blends. The drop in tensile strength is a common phenomenon for many thermoplastics composites filled with particulate fillers[68-70].

7.2.2 Effects of Reblending on the Tensile Strength of Conductive Composites

Reblending of a composite can affect its mechanical properties. The graph in Figure 6.6 shows that there is no difference in tensile properties of ABS/carbon black composite for second and third cycles of blending for carbon black contents of 10 wt % and below. However the tensile strength of ABS/carbon black third cycle drops more compared to the second cycle for carbon black contents above 10 wt. %.

For Nylon 6/carbon black blends, reblending can improve their mechanical properties. The graph of Figure 6.7 shows that the tensile strength of Nylon 6/carbon black third cycle blends is higher compared to second cycle reblending amounts of carbon black above 10 wt. %. These results show that reblending for the third time distributes carbon black fillers uniformly.

Reblending also improves the mechanical properties of ABS/Nylon/carbon black blends. Table 6.13 shows that the tensile strength of ABS/Nylon with composition 50:50, blended with carbon black for third cycle is higher than for the second cycle of reblending. Again, this shows that recycling for the third time distributes carbon black fillers equally in the two phases of the polymer.

7.2.3 Effect of Moisture on the Tensile Strength of Conductive Composites

Drying the compound also improves its tensile strength. Both ABS and conductive carbon black absorb moisture and this can affect the properties of the compound. High contents of moisture inside the material can reduce its mechanical properties. This was confirmed by drying ABS/carbon black composite in an oven at temperatures of 90°C for two hours, before shaping it into dumbbell-shapes. The results in Table 6.8 show that tensile strength is increased by performing such an operation.

As mentioned in the Chapter 1, without adhesion between filler and polymer matrix, the filler cannot support any stress applied to the composite. This means that the stress is only carried by the matrix material. The moisture prevents particles of filler adhering to the polymer matrix. As a result tensile strength will be reduced.

7.2.4 Effect of Polymer Composition on the Tensile Strength Properties of Conductive Composites

As shown in the graph Figure 6.8, tensile strength also decreases when ABS content increases. This is because, reducing Nylon 6 which is a semi-crystalline polymer, means the crystallinity of the composite will drop. ABS which is amorphous, increases the brittleness of the blend as its content increases and that will decrease the tensile strength of the composite. As explained by Rosato[66], E. Martuscelli and R. Palumbo[80], mechanical properties of heterogeneous polymer blends depend on the mechanical properties and composition of its components, and degree of the mechanical contact between the phases. Because ABS has low tensile strength compared with Nylon 6, if more ABS is present in the ABS/Nylon 6 blend, the tensile strength of the blend will decrease.

However the tensile strengths of ABS/Nylon/carbon black blends are low compared to the tensile strengths of both ABS/carbon black and Nylon/carbon black blends. This phenomenon shows that the blends are not miscible or homogeneous. To make the blends miscible, a coupling agent has to be added. The adhesion of carbon black to the polymer matrix is also poor without a coupling agent, and as a result can reduce the tensile strength of polymer composites.

7.2.5 Comparison between the Experimental and Theoretical Tensile Strength of Conductive Composite

Equation 4.7 was used to compare the tensile strength obtained from experimental work with the estimated lower bound tensile strength of filled polymer from Nicolais and Nicodemo theory[70]. Table 6.9 shows that the tensile strength calculated/estimated from equation 4.7 is lower than the actual tensile strength. Because the estimated value is for spherical fillers which do not adhere to the polymer matrix, the higher results show that carbon black particles are not precisely spherical. The irregular shapes of carbon black particulate give better physical adhesion to the ABS matrix which can support higher stress. Therefore tensile strength is higher than theoretically calculated.

Table 6.9 shows that, with carbon black contents less than 10 wt %, tensile strength of both ABS/carbon black blends for second and third cycle of blending are higher than the theoretical value. However, above 20% of carbon black content, tensile strengths for the third cycle blends are quite close to theoretical. When carbon black contents of 30 wt %, both the tensile strengths of ABS/Nylon 6 blends and the theoretical value closer to each other.

Table 6.11 shows that the theoretical tensile strength of Nylon with 5 wt % of carbon black composite is quite close to the experimental value of second reblend (Nylon 5% carbon black). The experimental tensile strength of second reblend

Nylon filled carbon black gradually lowers compare to theoretical when the carbon black content is increased. However, recycling the blends for the third time raised the adhesion of carbon black particles to Nylon matrix, therefore increasing tensile strength compared to the theoretical value. The difference of the second and third cycles tensile strength blend with calculated tensile strength is shown in Figure 6.7.

7.3 Morphological Properties of Polymer Blends

7.3.1 The difficulty in SEM characterisation

Different methods of sample preparation can produce different images in photomicrographs. Grinding and polishing of plastics surfaces should be carried out carefully to prevent any scratches. Unlike metals or ceramics materials, the softness of plastics, makes difficult to get smooth or unscratched surfaces.

Scratches can be seen in SEM photomicrograph of ABS/carbon black blends in Figure 6.10 and 6.11, and Nylon 6/carbon black blends in Figure 6.15, 6.16 and 6.18. Carbon black can be differentiated from other materials by its colour. Unfortunately, carbon black particulates were pulled out while polishing and grinding the surface, especially in Nylon 6/carbon black blends, which show holes on their surfaces as shown in Figure 6.18, 6.19 and 6.22.

In this project, two methods of sample mounting were tried, that were mounting in conductive bakelite and in cold setting compound. Meanwhile, two types of conductive coating were also tried, carbon and gold coating. Figure 6.10, 6.11 and 6.12 show that mounting in bakelite is not suitable for polymers for the study of morphology of blend structure. The problem is that the temperature used to heat conductive bakelite might have degraded the polymer i.e. ABS. A different method of sample preparation was tried by changing conductive bakelite to cold setting compound to achieve a good image of the sample for subsequent SEM analysis.

Figure 6.13 and 6.14 show that a good image still could not be found after changing conductive bakelite to cold setting compound for ABS/carbon black blends. The photomicrograph is poorer than Figure 6.10 to 6.12. Nylon 6 with 5% and 20% of carbon black in Figure 6.15 and 6.16 respectively also did not show clearly the carbon black particles. This means that carbon coating on samples mounted in cold setting compound is not suitable in order to get a good image of blends structure.

Because unclear images of microstructure were found, carbon coating was changed to gold coating. While carbon coating was used to find the composition of the composite, gold coating was used to get clear images of the structure. However, gold coating on samples mounted in bakelite is also unsuitable as shown in Figure 6.17 which shows a blurred structure of ABS/carbon black (20 wt. %) blend. Therefore the rest of the samples were mounted in cold setting compound and coated with gold to get a clear image of the microstructure.

Although the image can be seen clearly, the distribution of carbon black in the polymeric phases and interfaces are quite difficult to differentiate. Therefore conductive paths are difficult to find. These phenomena show that grinding and polishing sequences for SEM sample preparation are not suitable for plastics or it might be that samples in film form are more suitable for such study.

7.3.2 ABS/Carbon Black Blends

The different carbon black contents and its distribution in the ABS matrix is difficult to compare as shown in Figure 6.10 to 6.14. This is due to sample preparation not suitable for polymer or uneven distribution of carbon black in the ABS matrix. SEM photomicrographs in Figure 6.13 and 6.14 are worse compared to others of ABS/carbon black blends. Carbon black is shown by black spots in the figures. Big spots mean aggregation or agglomeration occurred in the blends. However, Figure 6.12 shows that ABS blend with 30 wt % of carbon black has more carbon black with bigger size aggregation, 0.2-0.3 μm.

The microstructure of the ABS/ carbon black blend in Figure 6.17 shows an uneven surface which means that there is no miscibility between ABS and carbon black. Magnification more than 23,000X, as shown in Figure 6.17, shows distribution of carbon black particles with 30-40 nm average size in the ABS matrix.

7.3.3 Nylon 6/Carbon Black Blends

Unlike ABS/carbon black blends, carbon black particles can be seen more in Nylon 6/carbon black blends. The SEM photomicrographs in Figure 6.15 and 6.16 shows that carbon black distribute discrete and uniformly in Nylon 6. The size of carbon black is smaller compare to these in ABS blends. This means that no carbon black aggregation occurs in the Nylon matrix. Nylon with 20 wt % of carbon black in Figure 6.16 shows more and clear carbon black distribution.

The sample in Figure 6.16 coated with gold, gives better and a clear SEM photomicrograph of the Nylon 6/carbon black blend as shown in Figure 6.18. Scratches and holes can be seen clearly in the figure. It is believed that carbon black particles might be pulled out from the surface while polishing and grinding the sample, due to poor adhesion (attraction) between carbon black and the Nylon 6 matrix. In contrast to the ABS phase, carbon black is 'covered' by the ABS matrix, so fewer scratches or holes can be seen in ABS/carbon black blends. These proved the ability of carbon black to attract amorphous phases of polymer matrix.

The SEM photomicrograph magnified at 23000X in Figure 6.19 shows a distribution of carbon black particles with size 0.1 μm diameter in the Nylon 6 matrix. The size of carbon black was compared with original size as shown in Figure 6.20. Carbon black particles are in irregular shapes, its size being about 0.1 to 0.2 μm diameter. Figure 6.20 shows that carbon black particles originally aggregate among themselves. However, in the Nylon 6 matrix, they are not aggregated, this is because Nylon 6 is semi-crystalline.

However, addition of carbon black in Nylon 6 gives high impact resistance to structure of the polymer. The difference between original Nylon 6 and Nylon containing carbon black can be seen from the SEM photomicrograph shown in Figure 6.21 and 6.22. Two phases can be seen in Nylon 6 as shown in Figure 6.21, that are crystalline and amorphous. Addition of 10 wt. % of carbon black makes the structure of Nylon rough as shown in Figure 6.22. This effect also changes mechanical and conductivity properties of Nylon 6.

On the other hand, SEM photomicrograph of Conductive Polyamide Compound-N54/CON2 in Figure 6.23 shows an obviously different structure with Nylon 6/carbon black blends. It shows bigger particle sizes of carbon black, about 1 to 2 μm. The surface of the conductive compound is also more rough. These certainly give different mechanical and conductivity properties that will be discussed in the next section.

7.3.4 ABS/Nylon 6/Carbon Black Blends

Two variables were studied in ABS/Nylon 6/carbon black blends. Firstly, ABS/Nylon 6 with 50:50 ratio composition blended with different weight. % of carbon black. Secondly, ABS/Nylon 6 blends with different compositions, that were 20:80, 40:60, 60:40 and 80:20, which were blended with 10 wt % of carbon black. SEM photomicrographs of the first batch of blends (ABS/Nylon 6; 50:50, and blended with varied carbon black) are shown in Figure 6.24 to 6.27. Meanwhile, SEM photomicrographs of the second batch of blends (ABS/Nylon 6 different composition with 10 wt % carbon black) are shown in Figure 6.28 to 6.34.

Figures 6.24 and 6.25 show that ABS and Nylon 6 did not mix well. However, addition of carbon black to ABS/Nylon 6 blends reduce the miscibility of both polymers. This is shown by Figure 6.26 which shows the roughness of samples surface was reduced. However, increasing the amount of carbon black in the ABS/Nylon 6 (50:50) from 2 wt % to 5 wt % increases the brittleness of the blend, that reduces the affinity between these two polymers. This is shown by the roughness of microstructure in Figure 6.27 compare to Figure 6.26. This effect also changes the mechanical and conductivity properties.

The SEM photomicrographs in Figure 6.28 to 6.31 show the change in morphology of the ABS/Nylon 6/carbon black blend with the addition of ABS from 20 wt % to 80 wt % of the blends. At less percentage of ABS content in the blend, more holes and a crack were found instead of carbon black (Figure 6.28). Increasing ABS content in ABS/Nylon 6/carbon black blend helped to find carbon black particles in polymer phases, although carbon black still cannot be seen in ABS/Nylon 6 (40:60) with 10 wt % carbon black (Figure 6.29). ABS/Nylon 6 (80:20) in Figure 6.31 shows carbon black particles and Nylon particles. However, the ABS/carbon black 10 wt % blend, in Figure 6.32, does not show carbon black particles.

Carbon black particles can be seen clearly when magnified 23,000X in ABS/Nylon 6 blend (80:20) with 10% carbon black. The SEM photomicrograph in Figure 6.34 shows the carbon black particles distribution, whereas magnified ABS/Nylon 6 (20:80) photomicrograph does not show carbon black distribution (Figure 6.33).

7.4 Correlation of Conductivity, Tensile Strength and Morphologies of ABS/Nylon 6/Carbon Black Blends

From conductivity, mechanical properties and morphology characterisation, there is no doubt that carbon black is most important in changing the properties of ABS/Nylon 6/carbon black blends. Content, distribution and size of carbon black are important factors that influence all these properties of the blends. E. Martuscelli and R. Palumbo[80] explained in their work that mechanical properties of heterogeneous polymer-polymer blend also depend on the morphology of the system, geometrical configuration and the shapes of structural elements.

ABS with 10 wt % of carbon black, gives the highest tensile strength compared to other content. SEM photomicrographs of ABS/carbon black at 10 wt % do not show clearly carbon black particles compared to ABS with 1 and 30 wt % of carbon black. It seems carbon black particles are 'absorbed' by the ABS matrix at this stage. However, the resistivity of ABS/carbon black blends are still high at 10 wt % content. The addition of carbon black, more than 10% by weight, in ABS/carbon black composite caused the tensile strength to drop, but the conductivity of the composite increased after this point.

On the other hand, increasing the carbon content in Nylon 6/carbon black blends do not improve their conductivity or even mechanical properties. Although it achieved maximum tensile strength at 10 wt % of carbon black, the value is yet lower than Nylon 6 itself. SEM photomicrographs show that carbon black distributed individually in Nylon 6 which means no aggregation occurred. Without carbon black aggregation, electrical conductivity cannot exist in the blends.

More carbon black aggregation in ABS with 30 wt % gives the blend higher conductivity compared to other ABS/carbon black blends. The smaller carbon black particles which are not as aggregated in Nylon 6 as ABS, causes ABS to be more conductive than Nylon 6 at the same amount of carbon black.

Sizes of carbon black aggregates in Conductive Polyamide Compound-N54/CON2, as shown in Figure 6.23, are bigger than Nylon 6 with 10 wt % carbon black (Figure 6.22). This makes N54/CON2 far more conductive than Nylon 6/carbon black blends. However the tensile strength of N54/CON2 is lower than Nylon 6/carbon black 20 wt % carbon black. By using carbon black content of 22 wt. % (measured by thermal gravimetric analysis) in N54/CON2 and calculated by equation 4.7, the tensile strength of the compound is less than the theoretical value.

The carbon black distribution plays an important role in conductive polymer blends. Changing the ratio of ABS/Nylon 6 will change the conductivity of the blends. By increasing ABS content in the ABS/Nylon 6 blend the distribution of carbon black can be seen clearly, consequently the conductivity increases. Conductivity achieved the maximum peak at 80 wt % of ABS content in ABS/Nylon 6 blend, at the same stage where carbon black forms an effective network to achieve the same level of conductivity . However, the tensile strength meets the lowest value at this stage as shown in Table 6.12.

Introducing carbon black in ABS/Nylon 6 blends improve their structure, as well as their mechanical properties and conducting behaviour. Figure 6.24 and 6.25 show two phases of ABS and Nylon 6. However, the addition of 2 wt % of carbon black in ABS/Nylon 6 blend (50:50), as shown in Figure 6.26, does not show separated phases of ABS and Nylon 6. The miscibility of the blends is improved by the filler. This causes an increase in tensile strength of ABS/Nylon 6 blends. Increased carbon black content to 5 wt %, causes the morphology of the blends rough, as shown in Figure 6.27. This caused tensile strength decrease but still higher than ABS/Nylon 6 blend without filler.

Although further addition of carbon black makes the blends more brittle, as shown by roughness of surface in the SEM photomicrograph, the conductivity still improve. By increasing the carbon black content to 20 wt % in ABS/Nylon 6 (50:50) the conductivity increases to the maximum value of 38 $\Omega^{-1}cm^{-1}$, approaching the conductivity of N54/CON2 (41 $\Omega^{-1}cm^{-1}$). However its tensile strength is low compared with the latter (almost ten times lower, as shown in Table 6.11 and 6.13).

7.5 ABS/Nylon 6/Carbon Black Blends as Conductive Compound

Although ABS/Nylon 6/Carbon Black blends can be conductive polymer, its tensile strength is low compared with the conductive polyamide compound N54/CON2. ABS/Nylon 6/carbon black with ABS:Nylon 6 ratio of 80:20 is the best composition. Although it conductivity is less than ABS5/N5/CB20 and N54/CON2 as shown in Table 6.7.

Generally conductive polymers do not have good mechanical properties but it is believed that either some additive may be added to N54/CON2 beside 22 wt % of carbon black to improve it tensile strength, or different size and type of carbon black is used to give better distribution of the filler.

CHAPTER 8

SUMMARY AND CONCLUSIONS

8.1 Conductivity Properties

The improvement of conductivity of ABS/carbon black blends can be detected when carbon black content increases to more than 20 wt % in the blends. In Nylon 6/carbon black blends, the conductivity can be detected when carbon black content increased more than 25 wt %. The conductivity of ABS/Nylon 6/carbon black blends increase when ABS contents increase because carbon black particles prefer to locate in amorphous phases of both polymers in the blends. ABS/carbon black and Nylon 6/carbon black blends do not make a good conductor compound compare to ABS/Nylon 6/carbon black blends.

Reblending improves the conductivity, due to increase of mixing time. This is true for ABS/carbon black blends, but not ABS/Nylon 6/carbon black blends. Volume resistivity represents the true resistivity of the material, instead of surface resistivity. Sheet resistivity measured by four point probe is only suitable for thin sheet or film with even distribution of conductivity.

The conductivity of the composite will be increased by improving conductive paths by:

1. increasing carbon black
2. choosing a suitable composition of polymer-polymer blends and conductive fillers
3. reblending or extending processing time

From experimental work, the percolation threshold for each conductive blend is:

i) 20 wt % carbon black in ABS/carbon black blend

ii) 25 wt % carbon black in Nylon 6/carbon black blend

iii) 10 wt % carbon black in ABS/Nylon 6 blend with 80:20 weight ratio.

8.2 Mechanical Properties

The results show that the addition of carbon black content up to 10 wt. % in a single polymer (ABS/carbon black and Nylon 6/carbon black) increases the tensile strength. On the contrary, for multiphase heterogeneous polymers, the addition of carbon black fillers more than 10 wt % decreases tensile strength.

Reblending of semi-crystalline polymer (Nylon 6) with filler for a third cycle, increases its tensile strength, due to the improvement of fillers distribution and adherence to polymer matrix. Reducing the moisture inside the material or blends can increase adhesion between filler and polymer and this can increase tensile strength.

By increasing ABS content in blends decreases the mechanical properties. The irregular shape of carbon black fillers can improve the mechanical properties of a filled composite if it is distributed evenly in the matrix material and with good adhesion with the matrix. Theoretical tensile strengths of ABS/carbon black and Nylon 6/carbon black are more than experimental results.

8.3 Morphologies Characterisation

Sample preparation is vital to get clear image of microstructure of polymers and distributed filler phase. Different methods of sample preparation cause different images of microstructure. Gold coating is the best to reveal clear images of the structure.

It is important to relate morphologies characterisation with conductivity and mechanical properties of conductive polymer blends. Carbon black distributes in aggregated form in ABS phases, while in the Nylon 6 phase carbon black distributes in discrete manner with no aggregation. Therefore ABS/carbon black is more conductive than Nylon 6/carbon black blends with the same amount of carbon black contents. Holes can be found on Nylon 6/carbon black blends which show that carbon black pulled out while polishing the sample's surface. This means that poor adhesion between Nylon 6 and carbon black phases.

ABS/Nylon 6 forms immiscible blends which show separate phases. Addition of a small amount of carbon black adheres to both phases and reduces the separation. This improves mechanical properties of the blend. Addition of more carbon black, increases roughness of blend which has an adverse effect on mechanical properties of the blend.

CHAPTER 9

FUTURE WORK

As a new compound, there are still more analysis needed to improve the properties of ABS/Nylon 6/carbon black blends, although the blends show good conducting behaviour, for example ABS/Nylon 6 of 80:20 composition blended with 10% carbon black and ABS/Nylon 6 of 50:50 composition blended with 20% carbon black. The morphology characterisation could not be analysed thoroughly due to the difficulty to establish a best method for sample preparation.

For future work, some recommendations have to be taken in order to improve ABS/Nylon 6/carbon black blends properties:

1) To upgrade conductivity level of the blends, super conductive carbon black should be added. Different grades of carbon black should be tried to find the best conductive filler. Carbon fibres are also a good alternative as conductive filler which becomes oriented during processing as a result the composite will exhibit anisotropic conductivity. Thin sheet of sample is suggested to be used to get better conductive response.

2) Processing method needs to be improved to get a good distribution of carbon black particles in polymers matrix. Twin screw extruder is suggested where less time is taken in blending and consequently reblending can be avoided. Internal mixer can produce good compound, as it is a clean method and uses small amount of materials.

3) Mechanical properties can be upgraded when twin screw extruder is used, because recycling can deteriorate mechanical properties. Addition of coupling

agents in the blends can adhere filler with polymer matrix. Injection moulding can produce anisotropic sample which can improve mechanical properties. As a conductive filler, carbon fibre can also act as reinforcement that can improve mechanical properties of the blends.

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