

# **DEVELOPMENT OF CARBON BLACK-LAYERED CLAY/EPOXY NANOCOMPOSITES**

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**by  
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# ABSTRACT

## DEVELOPMENT OF CARBON BLACK-LAYERED CLAY/EPOXY NANOCOMPOSITES

In this study, a novel epoxy nanocomposite with electrical conductivity and having improved mechanical and thermal properties was synthesized. Carbon black/epoxy composites and carbon black-layered clay/epoxy nanocomposites were prepared by mixing via 3-roll mill. The first type of the composite was produced to determine the percolation threshold concentration ( $V_c$ ). The second type with constant carbon black concentration, slightly over  $V_c$ , was synthesized to investigate the influence of clay content on the thermal, mechanical, electrical and structural properties of nanocomposites. Carbon black used in the study was extra conductive filler with 30 nm spherical particles. Layered clay was  $\text{Na}^+$  Montmorillonite treated with ditallow dimethylamine to assure better intercalation within the epoxy resin.  $V_c$  value was determined to be 0.2 vol% and 0.25 vol% carbon black was added together with varying clay contents to the epoxy system to produce nanocomposites. Only the nanocomposites with 0.5 vol. % clay loading showed electrical conductivity. However, the composites with higher clay loadings showed insulating behaviour due to hindrance of carbon black network by clay layers. According to the XRD results, nanocomposites exhibited some extent of exfoliation. It was found that tensile modulus values of the epoxy increased; however flexural modulus values remained constant, with increasing clay content. Elastic modulus of neat epoxy (3.7 GPa) was increased about 28 % with 0.5 vol% clay addition. Thermomechanical analysis results revealed that the storage modulus, glass transition temperature and initial degradation temperature of epoxy was slightly enhanced due to clay loading.

## ÖZET

### KARBON SİYAHİ-TABAKALI KİL/EPOKSİ NANOKOMPOZİTLERİN GELİŞTİRİLMESİ

Bu çalışmada, elektriksel iletkenliği olan ve gelişmiş termal ve mekanik özelliklere sahip yeni bir epoksi nanokompozit sentezlenmiştir. Karbon siyahı /epoksi kompozitler ve karbon siyahı-tabakalı kil/epoksi nanokompozitler 3-merdaneli kalender ile karıştırılarak hazırlanmıştır. İlk tip kompozit, perkolasyon eşik konsantrasyonunu ( $V_c$ ) belirlemek için üretilmiştir. İkinci tip, karbon siyahı konsantrasyonu  $V_c$  değerinin biraz üstünde sabit tutularak, kil miktarının nanokompozitlerin ısı, mekanik, elektriksel ve yapısal özelliklerine etkisini incelemek amacı ile sentezlenmiştir. Çalışmada kullanılan karbon siyahı 30 nm'lik küresel partiküllerden oluşmuş ekstra iletken bir dolgudur. Tabakalı kil olarak, epoksi reçine içerisinde iyi şekilde dağılımını sağlamak amacıyla ditallow dimethylamin modifiye edilmiş  $Na^+$  Montmorillonite kullanılmıştır.  $V_c$  değeri 0.2 hac.% olarak ölçülmüş ve 0.25 hac. % karbon siyahı ile değişken miktarlarda kil epoksi sistemine eklenerek nanokompozitlerin üretilmiştir. Sadece 0.5 hac.% kil eklenmiş olan nanokompozitler elektriksel iletkenlik göstermiştir. Bununla birlikte, daha yüksek miktarlarda kil içeren nanokompozitler ise karbon siyahı iletkenlik ağının kil tabakaları tarafından engellenmesinden dolayı yalıtkan davranış göstermiştir. XRD sonuçlarına göre, nanokompozitler kısmen dağılmış bir yapı sergilemiştir. Kil miktarının artmasıyla çekme modül değerleri artarken eğme modül değerleri sabit kaldığı bulunmuştur. Katkısız epoksinin elastic modül değeri (3.7 GPa) 0.5 hac.% oranında kil ilavesi sonucunda 28% oranında arttığı gözlenmiştir. Isıl-mekanik analiz sonuçları, kil eklenmesiyle storaj modülü, camı geçiş sıcaklığı ve bozunma sıcaklığının bir miktar arttığını ortaya çıkarmıştır.

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# CHAPTER 1

## INTRODUCTION

In the last decade nanocomposite materials, consisting of a polymeric matrix materials and nanofillers have attracted scientific and industrial interest due to their improved properties. At low filler contents as compared with the conventional micro- and macro- or neat counterparts they exhibit superior property enhancements. Numerous different types of polymer and fillers have been used so far to prepare nanocomposites. Nylon-6 (Okada and Usuki 2006), poly(propylene) (Marchant and Jayaraman 2002), poly(ethylene) (Wang, et al. 2003), rubber (Gatos and Kocsis 2005) and epoxy (Park and Jana 2003) have been used as polymers and reinforced by addition of silica, titanium dioxides, carbon nanotubes and layered clays. To produce more functional materials, different type of fillers can be used together to obtain diverse favourable properties from the nanocomposites.

Polymer clay nanocomposites have applications mainly in the automotive industry and beverage packaging due to their improved mechanical properties and barrier resistance, respectively (Gao 2004). The conductive composites (especially the ones reinforced with carbon black) having electrical conductivity of less than  $10^{-8} \text{ Scm}^{-1}$  are utilized in wide range of applications including electromagnetic radiation shielding, electrostatic discharge (ESD) protection and electro-packaging applications to avoid electrical charges and electrical magnetic field from disturbing the communications (Kupke, et al. 1998).

The most commonly studied nanofillers are modified layered clays, especially montmorillonite, due to its high cation exchange capacity (CEC). Modification of clays changes the hydrophilic nature of clay to hydrophobic and increases the interlayer distance between their layers. Therefore, it assures better dispersion in the organic polymer matrix with expanded interlayer spacing (Mohan, et al. 2006). Due to its nanoscale dispersion, increased mechanical, thermal, barrier properties are observed in the nanocomposites. In addition, incorporation of conductive nano-particles into a polymer matrix renders nanocomposite electrically conductive. Carbon black, a form of amorphous carbon, has been recently used as filler in antistatic or electrical conductive

modification of polymer systems (Degussa 2008). Due to higher surface area to volume ratio of carbon black, a low amount addition is sufficient to introduce electrical conductivity.

Epoxy resins are an important family of thermosets that find wide applications as matrices of the polymer nanocomposites due to their good mechanical properties. Moreover, the curing agents of epoxy systems, especially amine hardeners have affinities to integrate between the clay layers; hence they assist to reach exfoliation in nanocomposites (Tjong 2006).

Three main routes to prepare nanocomposites are described in the literature. These are in-situ polymerization, solution intercalation and the melt processing technique. In melt processing, mechanical mixing of thermoplastic polymers with the clay is performed in order to exfoliate the clay layers in the polymer, while the clay and the polymer are dissolved in an organic solvent in solution intercalation method. In in-situ polymerization, the clay layers are blended with the thermosetting resins. Exfoliation of clay is expected during the polymerization (Ahmadi, et al. 2004). Mechanical mixing and sonication are the general mixing methods involved in this method. Recently, shear mixing by a three roll mill with adjusted gap widths has been started to be used for nanocomposite preparation. With the help of this mill the gaps between the rolls can be adjusted to a min of 5  $\mu\text{m}$  which makes this novel technique one step ahead to reach the nanoscale exfoliated dispersion.

Depending on the nature of the layered clay and polymer matrix and the level of interactions between them a phase separated, intercalated and exfoliated types of nanocomposites can be obtained. Exfoliated nanocomposites have higher phase homogeneity as compared to the intercalated ones; therefore the exfoliated structure is more desired leading to enhanced properties of the nanocomposites (Alexandre and Dubois 2000). Apart from these morphologies, introduction of two different types of fillers e.g. carbon black in addition to layered clay shows different morphology named as “nano-unit morphology” (Konishi and Çakmak 2006).

To our knowledge, there is no study on the development of carbon black-layered clay/ epoxy nanocomposites and their characterization in terms of electrical, structural, thermal and mechanical properties. Due to lack of information in literature the objectives of this study are, 1) to produce carbon black layered clay epoxy nanocomposites by shear mixing via three roll mill with arranged gap width of  $7 \leq \mu\text{m}$ . 2) to investigate the effect of carbon black addition to electrical conductivity and

percolation behavior of carbon black epoxy composites. 3) to examine the effect of layered clay content on the electrical, thermal, mechanical and structural properties of carbon black layered clay/epoxy nano-composites.

Nanocomposites with various filler contents were prepared by three roll mill. Electrical properties were investigated in terms of direct current conductivity measured by four point probe method. Structural examinations were performed by XRD and SEM to evaluate the exfoliation of clay layers within the epoxy matrix. Tensile and flexural test were realized to reveal mechanical properties of nanocomposites. In terms thermal investigations, Tg measurements performed by DMA and DSC and thermal degradation behaviours are determined by TGA. Finally, all properties were interpreted according to structure property relationships.

## CHAPTER 2

### BACKGROUND

#### 2.1. Polymer Nanocomposites

Polymer nanocomposites are materials created by introducing nano-fillers into a polymer matrix in order to have improved properties compared with their neat polymer or micro and fibre reinforced ones. Polymer clay nanocomposites have attracted scientific and industrial interest starting with the Toyota's discovery of significant improvements on the mechanical and flame retardant properties of nylon-6/montmorillonite nanocomposites (Okada, et al. 1990).

Polymer materials have been filled with several different types of fillers to exhibit favourable properties in terms of elastic and flexural modulus, fire retardance, and gas permeability (Fischer 2003, Ray and Okamoto 2003). The fillers can be layered clay, carbon nanotubes silica etc. and polymers can be epoxy, nylon-6, polystyrene, polyurethane, rubber and etc. (Ray and Okamoto 2003).

Polymer nanocomposites have applications mainly in the automotive industry and beverage packaging. These include use of clay/nylon-6 nanocomposites as timing belt covers for Toyota cars and engine covers on Mitsubishi's GDI engines, clay/polypropylene nanocomposites as seat backs in the Honda Acura. In terms of beverage applications, Alcoa CSI uses clay/polymer nanocomposites as barrier liner materials for enclosure due to their improved barrier resistance (Gao 2004).

##### 2.1.1. Methods of Nanocomposite Production

Several methods have been developed to produce polymer nanocomposites according to the starting materials and processing techniques. However three main methods have been applied widely. These are: in situ polymerization, solution induced intercalation and melt processing methods.

In situ polymerization involves inserting a polymer precursor or monomer between clay layers followed by expanding and dispersing the clay layers into the

matrix by polymerization. The solution-induced intercalation method applies solvents to swell and disperse clays into a polymer solution in which the layered clays are first swollen in a solvent. Then mixed with the polymer causing polymer chains intercalate and displace the solvent within the interlayer of the clay. The melt processing method induces the intercalation of clays and polymers above the softening point of the polymer (Gao 2004, Ray and Okamoto 2003). Production methods for nanocomposites are summarized in Table 2.1.

Table 2.1. Methods of nanocomposite production

<b>Production Methods</b>	<b>Polymerization</b>	<b>Suitable Polymers</b>	<b>Advantages/Disadvantages</b>
In-situ polymerization	Monomer is introduced between clay layers then expand and disperse the clay layers in the matrix by polymerization.	Nylon-6 Epoxy Polyurethane Polystyrene	Leads to well- exfoliated morphology in nanocomposites
Solution intercalation	Solvent is mixed with the clay to swell and disperse then polymer is added to the system and displace the solvent	Polyimide PMMA	High costs of solvent and phase separation from solvent
Melt Processing	Melt polymers and clays are intercalated	Nylon-6 PET Polystyrene	Compatible with the industrial polymer processing techniques

### 2.1.2. Structure and Morphology of Nanocomposites

Depending on the nature of the layered clay and polymer matrix and the level of interactions between them, three different types of polymer nanocomposite morphology are observed. These are: intercalated, exfoliated and phase separated.



In intercalated nanocomposites polymer molecules penetrate into the galleries of clay and the interlayer spacing is increased, while clay layers form separate phases in phase separated structures. Exfoliated nanocomposites are obtained when the clay layers are completely delaminated by the polymer matrix and homogeneously dispersed in the polymer matrix. Due to this homogeneous distribution of the layers exfoliated nanocomposites exhibit superior properties compared to intercalated and phase separated ones. (Becker, et al. 2002). Moreover, partially intercalated and partially exfoliated nanocomposite morphology can be observed. In this commonly occurring case, the exfoliated layers and intercalated clusters are randomly distributed in the matrix.

X-ray diffraction measurements are used to characterize the morphology of nanocomposites. If there are reflections in the low angle region this indicates intercalated nanocomposite, However if the peaks are broad or disappeared completely, this signifies complete exfoliation. (Gilman 1999)

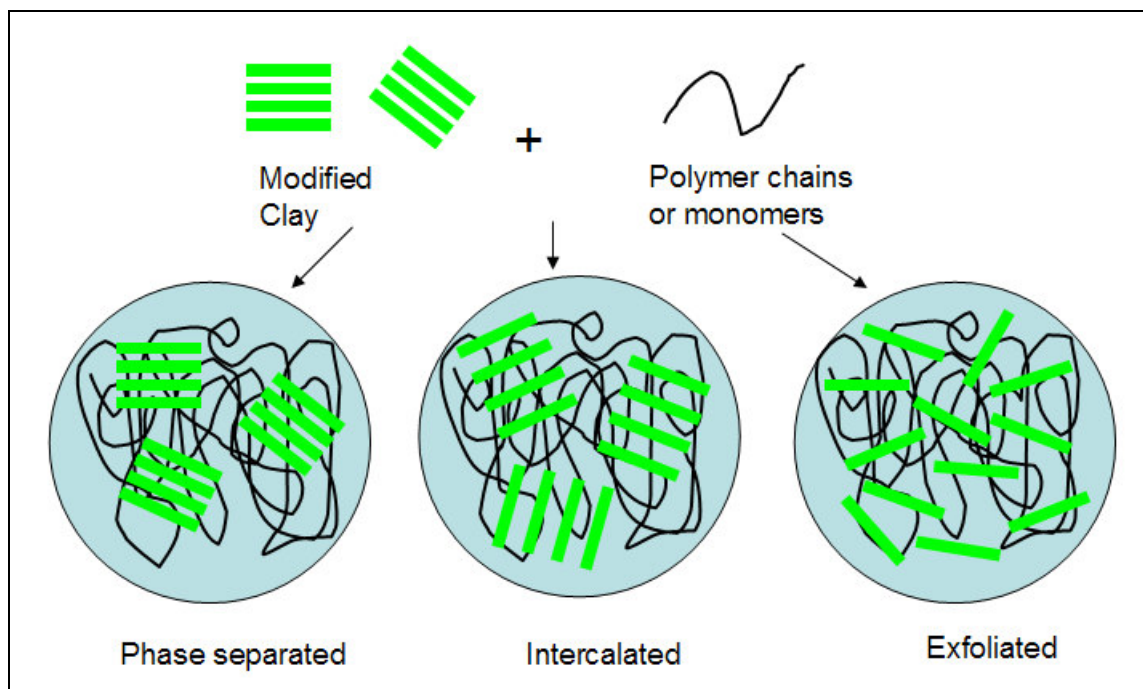


Figure 2.1. Morphology of layered clay polymer nanocomposites

However, these morphologies depend on the distribution of clay layers. Considering carbon black-layered clay/polymer nanocomposites morphology named as

“organoclay carbon black unit morphology” was proposed in literature (Konishi and Çakmak 2006).

## 2.2. Carbon Black

Carbon black (CB) is a material produced by the incomplete combustion or thermal cracking of a hydrocarbon raw material. CB is a form of amorphous carbon that has an extremely high surface area to volume ratio. It is one of the first nano-materials that find common use especially as a pigment for printing inks and reinforcing phase in automobile tires (Wikipedia 2008) and recently used in antistatic or electrical conductive modification of polymer systems (Degussa 2008). Carbon black particles tend to form agglomerates as seen in Figure 2.2.

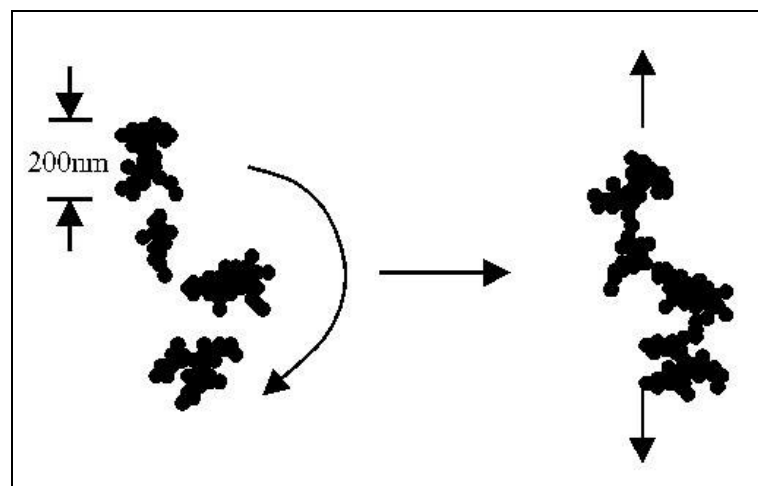


Figure 2.2. Carbon black aggregates

### 2.2.1. Structure and Properties of Carbon Black

Carbon black is composed of small crystallites which are made up of parallel graphitic layers with a spacing of approximately 0.35 to 0.38 nm in contrast to the graphite (0.35 nm). CB represents a structural form intermediate between graphite and truly amorphous material. This structure varies depending on the production process and differences in the particle size (Donnet, et al. 1993).

Particle size, size of structure and surface chemistry are the basic properties of carbon black. The diameter of spherical particles is the fundamental property affecting

blackness and dispersibility of carbon black when mixed with resins. In general, the smaller the particle size is, the higher the blackness of carbon black becomes. However, dispersion becomes difficult due to increasing in coagulation force. Like particle size, the size of the structure also affects the blackness and dispersibility of carbon black. Generally, the increase of structure size improves dispersibility but lowers blackness. Carbon black with a larger structure in particular shows an excellent conductive property. In terms of surface chemistry, various functional groups exist on carbon black's surface. The affinity of carbon black with inks or paint varnishes changes depending on the type and amount of the functional groups (Mitsubishi 2008).

### **2.3. Layered Clays**

Layered clays are minerals that assemble regularly with the unit crystalline layer, usually at the nanoscale. Minerals can be montmorillonite (MMT), kaolinite, saponite, illite etc. A layer of clay mineral is about 1 nm in thickness and consists of platelets of around 100 nm in width, representing filler with a significantly large aspect ratio.

The most important reason for layered silicates to be a candidate in preparing nanocomposites is their unit layer structure. This structure helps to form a nanophase in situ in a polymer matrix during its compounding or polymerization. Most layered silicates have strong dispersion and cation exchange properties. There is also a requirement that the layers be expandable and easily exfoliated during formation of the nanocomposite. Layered clay can be classified due to their unit crystal types; 1:1 type. Its unit crystal is composed of one crystal sheet of silica tetrahedron (Figure 2.3) combined with one-crystal sheet of alumina octahedron (Figure 2.4). Ex. Kaolinite, illite. 2:1 type. Its unit crystal is composed of two crystal sheets of silica tetrahedron combined with one crystal sheet of alumina octahedron between them. Ex. Saponite, montmorillonite. 2:2 type. Its unit lamellar crystal is composed of four crystal sheets, in which crystal sheets of silica tetrahedron and alumina or magnesium octahedron are alternately arranged. Ex. Chlorite (Ke and Stroeve 2005).

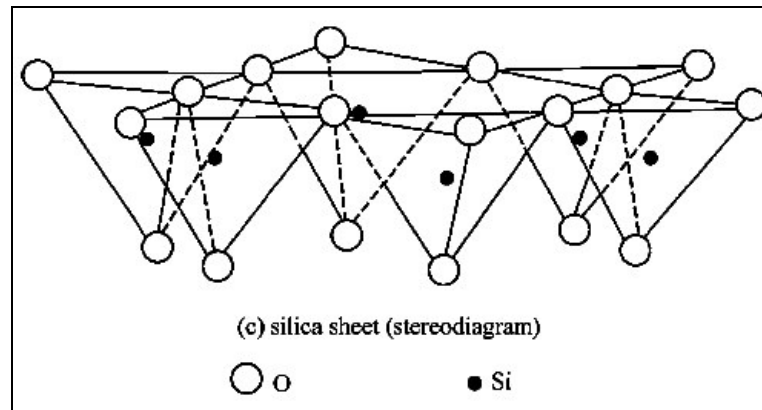


Figure 2.3. Sketch map of silica sheet  
(Source: Ke and Stroeve 2005)

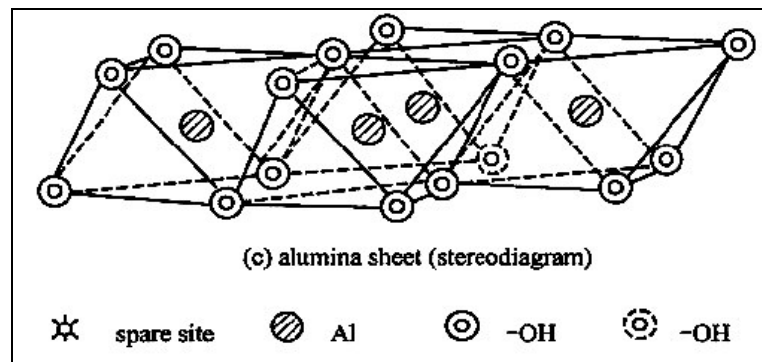


Figure 2.4. Sketch map of alumina sheet  
(Source: Ke and Stroeve 2005)

### 2.3.1. Organically Modified Layered Clays

Hydrophilic nature of clays hinders their good interaction with organic polymers. Therefore, surface modifications of clay are necessary to render clay hydrophobic in order to promote exfoliation. Surface modifications have been commonly used to achieve a better interaction of clay surface with the polymer matrix.

Ion exchange of the gallery cations in the pristine mineral by alkylammonium ions is a common method to modify the clay interlayer from hydrophilic to hydrophobic (Zilg, et al. 2000). The swelling of clay in an aqueous alkylammonium ion solution leads to an extension of the interlayer galleries due to the hydration of inorganic cations ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) contained in these galleries, allowing the alkylammonium ions to intercalate between the platelets. (Le Pluart, et al. 2001).

Organoclays obtained by cation exchange offer a great diversity of interlayer structures. The interplatelets' structure depends on the alkyl chain length and on the cation exchange capacity, which is the maximum number of monovalent cations exchangeable per 100 grams of clay (Le Pluart, et al. 2001). Vaia et al. (1994) reported four types of idealized organizations of individual long-chain alkylammonium ions in the galleries of layered clays as monolayer, bilayer, paraffin-like monolayer, paraffin-like bilayer.

### **2.3.2. Structure and Properties of Organically Modified Montmorillonite**

Montmorillonite ( $A_{14}[\text{Si}_4\text{O}_{10}](\text{OH})_2$ ) has a 2:1 layer structure consisting of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of alumina, as shown in Figure 2.5. Montmorillonite has layer charges due to isomorphic substitution. Isomorphic substitution occurs when some atoms in the crystal structure are replaced with other atoms with different valence electrons. When there is an isomorphic substitution of  $\text{Mg}^{2-}$  for  $\text{Al}^{3-}$  in the octahedral lattice, a negative charge of minus one (-1) is generated, which is normally counterbalanced by cations ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) adsorbed from the ambient solution (Ke and Strove 2005)

Among the different types of clays, montmorillonite presents a high swelling capacity. Gallery cations ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) are small and easily hydrated, and that is why montmorillonite is the smectite clay with the highest swelling capacity compared to illites and kaolinites, which do not have expandable galleries due to strong interlayer interactions. The type of cations present in the galleries governs the swelling capacity of the smectite clays (Le Pluart, et al. 2001).

The intercalation of organic cations, such as alkylammonium ions in the galleries, gives montmorillonite hydrophobic behavior and makes it compatible with a polymer matrix. Moreover, the use of long-chain organic cations (18 carbon atoms) leads to extended galleries, which assists the introduction of monomers or polymer within the clay galleries in the of nanocomposite synthesis step.

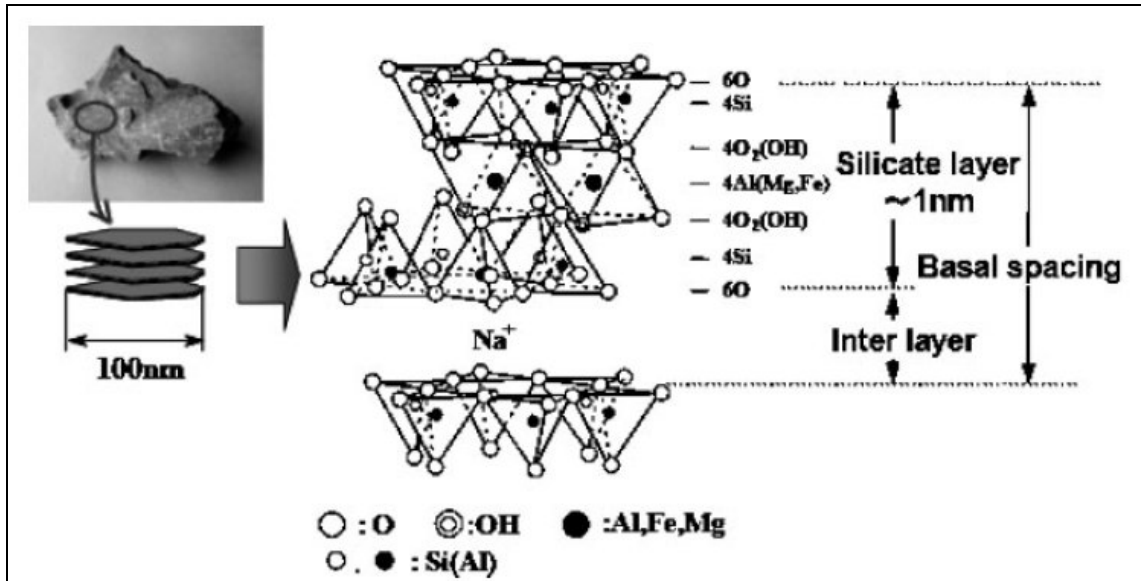


Figure 2.5. Structure of Montmorillonite

(Source: Okada and Usuki 2006)

## 2.4. Epoxy Resins

Epoxy resins are of widely different structures characterized by the presence of a 1,2-epoxide group. This group is a 3-member cyclic ether which is reactive with a wide variety of reagents. The epoxide group is usually presented as a glycidyl amine or ether as part of an aliphatic ring system.

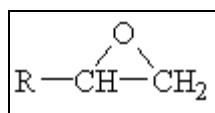


Figure 2.6. Structure of epoxide group

Epoxy resins are characterized by good mechanical strength and chemical resistance. The largest use for epoxies is in coatings, composites, casting and adhesives. Main commercial epoxy resins are:

- Diglycidyl ether of bisphenol A, DGEBA
- Diglycidyl ether of bisphenol F, DGEBF
- Epoxy novolac, EN
- Triglycidyl ether of tris (hydroxyphenyl) methane

- N,N-diglycidylaniline, DGA
- Triglycidylparaaminophenol, TGPAP
- N,N,N',N'-tetraglycidyl-4,4'-methylene dianiline (TGMDA)
- 3,4-epoxycyclohexyl methyl 3',4'-epoxy cyclohexane carboxylate (Bader, et al. 1990)

### 2.4.1. Structure and Properties of Diglycediyl Ethers of Bisphenol A (DGEBA)

DGEBA are the most widely used epoxy type, accounting for about 90 % of all epoxies. They are synthesized from reaction between epichlorohydrin and bisphenol A under the presence of sodium hydroxide.

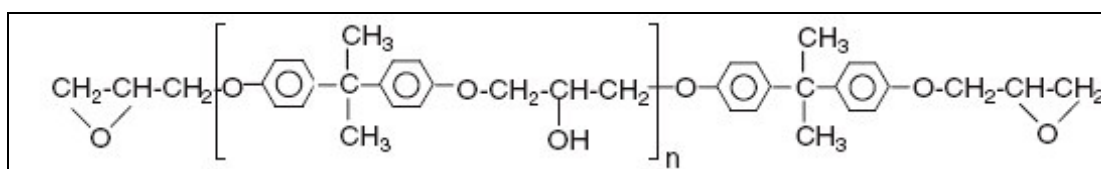


Figure 2.7. Structure of typical DGEBA resin  
(Source: Pascault, et al. 2002)

The properties of the DGEBA resins depend on the value of  $n$ , which is the number of repeating units commonly known as degree of polymerisation. This number depends on the stoichiometry of synthesis reaction. In general,  $n$  ranges from 0 to 25 in many commercial products.

### 2.5. Curing Agents

Epoxy resins undergo a quick transformation from the liquid state to hard thermoset solids at different temperatures with the addition of a chemically active compound known as a curing agent. Although the epoxide group reacts with wide variety of groups, only three types are mainly used in curing epoxy resins. These are amines and amine derivatives, acid anhydrides, catalytic curing agents. Amines are the most commonly used curing agents for epoxy. Primary and secondary amines are highly reactive with epoxy. Tertiary amines are generally used as catalysts, known as accelerators for curing reactions.

## 2.5.1. Structure and Properties of Aliphatic Amines

Aliphatic amines are relatively strong bases and are so much more reactive compared to aromatic amines towards epoxy. They introduce excellent chemical and solvent resistance to cured resin. Aliphatic amines have short pot lives, offering fast curing at ambient temperatures (Bader, et al. 1990). Figure 2.8. shows molecular formulas of some aliphatic amine curing agents.

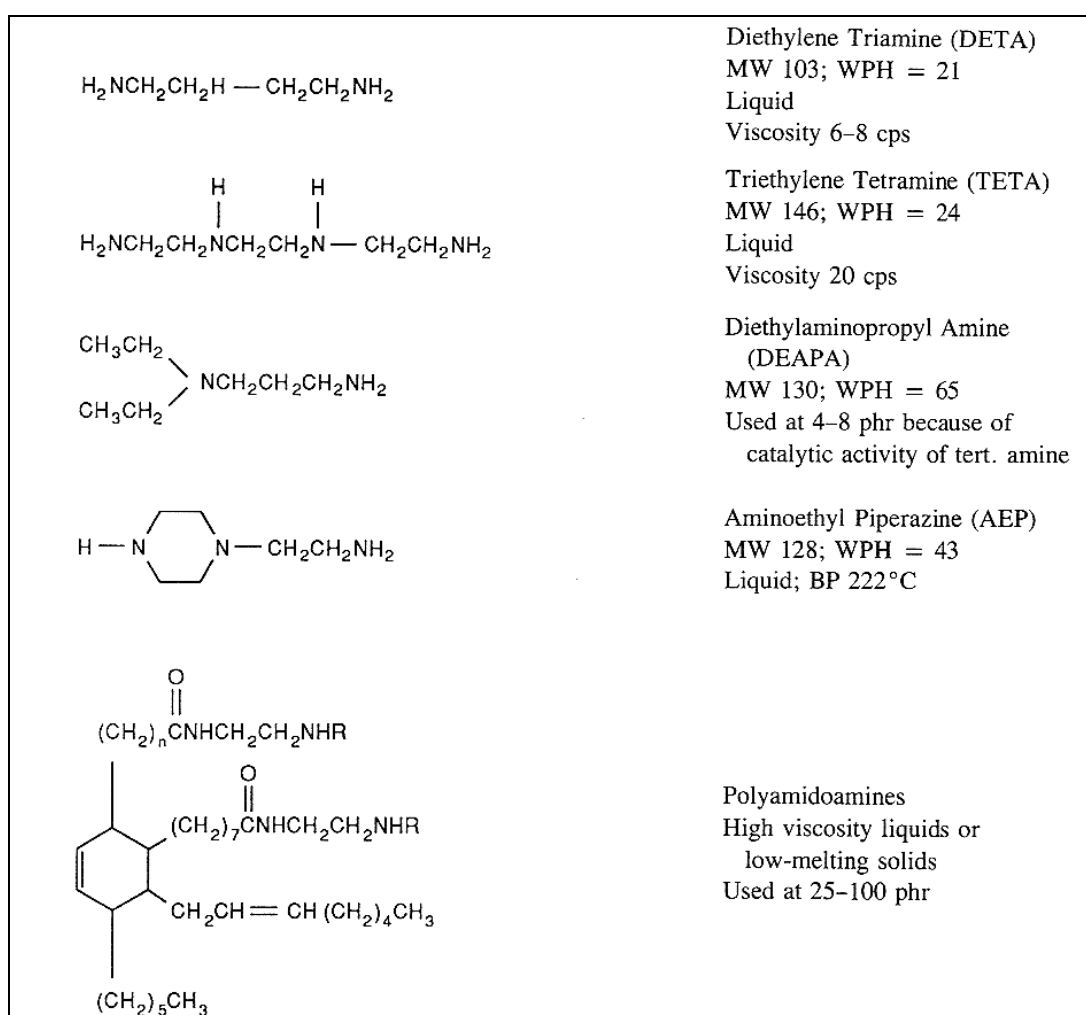


Figure 2.8. Aliphatic amine curing agents

(Source: Bader, et. al 1990)

A thermosetting resin is said to be cured when a crosslinked network of polymer chains is formed. The only significant reaction occurring between aliphatic amines and the epoxy group is the amine-hydrogen-epoxide ring reaction shown in Figure 2.9. for



aliphatic amines, addition of the first amine hydrogen is followed closely by addition of the second hydrogen without heating so that room temperature cure occurs.

## 2.6. Studies on the Structure and Properties of Nanocomposites

Depending on the filler type, it was reported in the literature that incorporation of fillers causes some improvements in different properties of nanocomposites. Layered clays have been known to improve mechanical, thermal and barrier properties on the polymer system they are added (Ray and Okamoto 2003). Carbon black particles create a conductive network in the polymer it is introduced (Flandin, et al. 1999). In this section, literature survey on the effect of carbon black and clay addition to electrical property and influence of clay content to the structural, mechanical and thermal property of nanocomposites are given

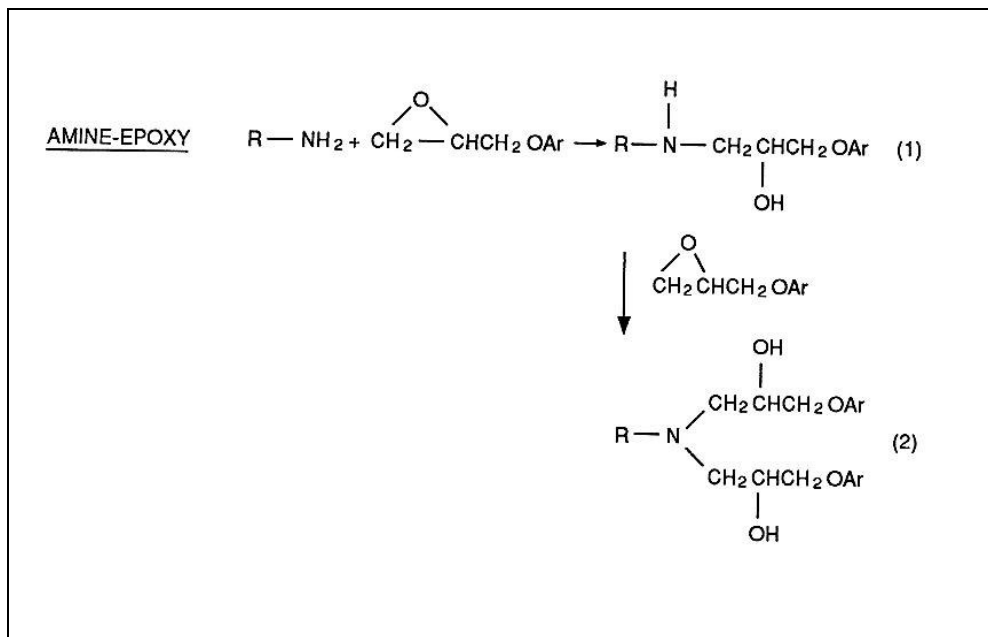


Figure 2.9. Curing of reaction epoxy with amine hardeners

(Source: Bader, et al. 1990)

### 2.6.1. Studies on the Electrical Properties of Nanocomposites

Conductive polymer nanocomposites were produced with the intercalation of conductive fillers and insulating polymer matrix. They had, in general an electrical

resistivity less than  $10^8 \Omega \cdot \text{cm}$ , due to very low filler content of conductive fillers (Kupte, et al. 1998). In literature, there are some studies on electrical conductivity behaviors of some hybrid nanocomposites with the introduction of carbon black and nonconductive filler effect on the carbon black conductivity network.

Konishi and Cakmak (2006) studied the effect of modified clay and carbon black content on the conductivity and percolation behaviour of carbon black / polyamide 6-based nanocomposites (Figure 2.10). They found that percolation threshold substantially shifts to lower carbon black volume fractions in the presence of optimum concentration of modified clay. In other words, conductivity was increased with the addition of clay and maintained within static dissipative  $10^{-6}$ – $10^{-9} \text{ S} \cdot \text{cm}^{-1}$  range. Thus, they stated that clay can be used as a dispersion control agent in these polymer–carbon systems to induce self assembly of CB network at low CB content.

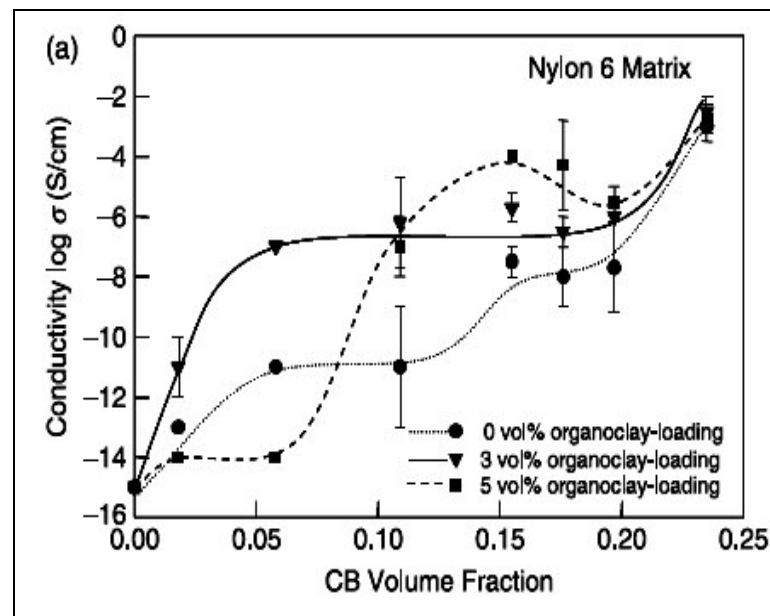


Figure 2.10. Plots of log conductivity versus CB volume fraction at room temperature for various nylon 6/CB systems (Source: Konishi and Çakmak 2006)

Zhang et al. (2007) studied the effect of silica concentration on electrical conductivity of carbon black–silica/epoxy nanocomposites. They found that with increasing content of silica, CB particles were optimally dispersed, contributing to the generation of a conductive network. Compared with the nanocomposite containing no silica, the conductivity of the nanocomposites containing CB increased with increasing volume fraction of silica to reach a maximum value at a ratio of 0.6:1.0 (SiO<sub>2</sub>:CB) as

shown in Figure 2.11. Then conductivity decreased with further increases in the silica network content. Excessive silica prevented electron flow and gave rise to lower conductivity.

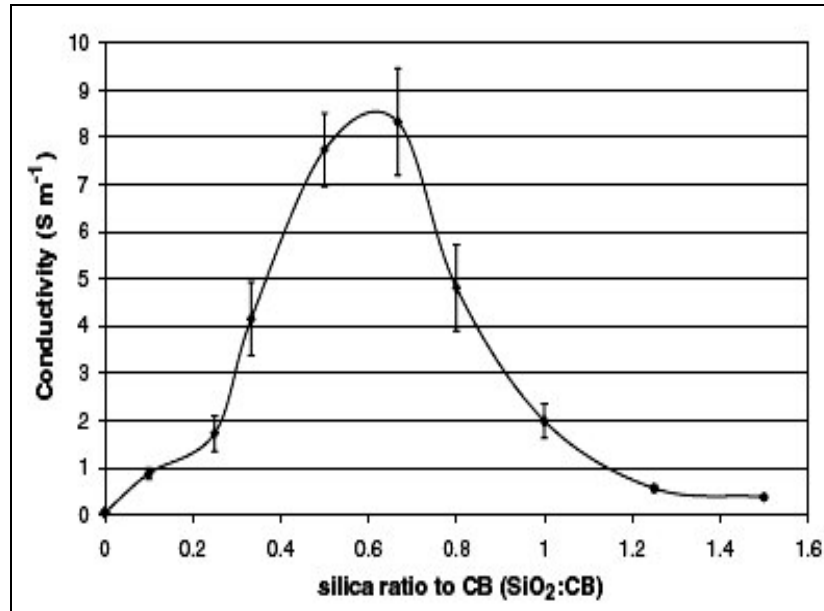


Figure 2.11. Variation of conductivity of silica–CB–polymer resin nanocomposites with varying ratio of silica (SiO<sub>2</sub>) to carbon black (CB) (Source: Zhang, et al. 2007)

The influence of melt dispersion of intercalated montmorillonite nanofiller (MT) content on electrical properties of three conductive polymer composites; poly(ethylene)-carbon black (PE-CB), poly(propylene)-carbon black (PP-CB) and poly(ethylene-coethyl acrylate)-carbon black (EEA-CB) was investigated by Feller et al. (2004). As seen in Figure 2.12 even at very low content (less than 1.25% v/v), MT had an important effect on the percolation threshold. They found that composites showed rather different electrical behaviours. Increasing MT content decreased EEA-CB resistivity of about 0.25 % over 0.6% MT v/v, whereas for PP-CB and PE-CB, a large resistivity increase was observed up to 0.06% MT w/w of 0.3 and 0.15% respectively. Over 0.6% MT, PP-CB resistivity slightly increased and PE-CB resistivity decreased by 0.15% .

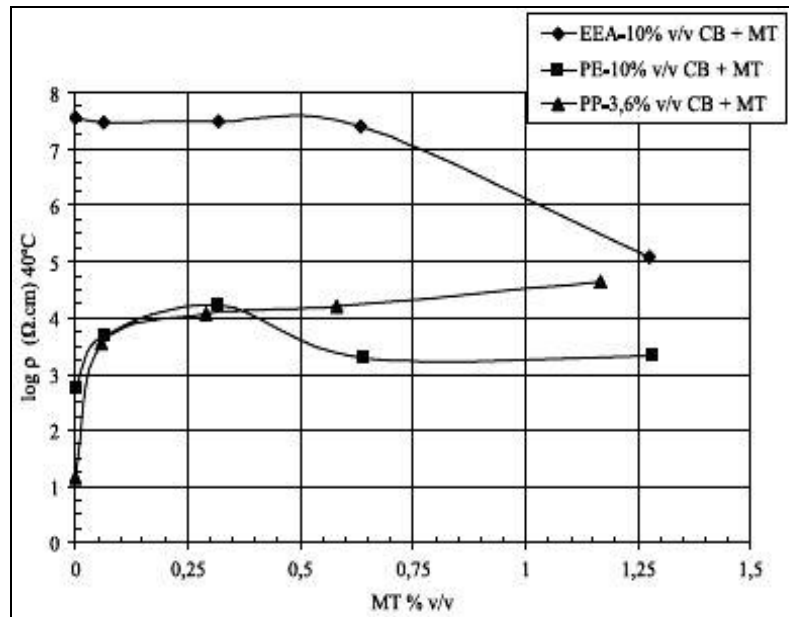


Figure 2.12. Influence of MT content on conductive polymer composites  
(Source: Feller, et al. 2004)

## 2.6.2. Studies on the Structure and Morphology of Nanocomposites

It is known that structure and morphology has a significant influence on the final properties of nanocomposites. The structure of the polymer-layered clay nanocomposites has been investigated by X-ray diffraction to determine the interlayer spacing. Morphology was interpreted according to observations on the characteristic peaks of clays in the final composites. If the characteristic peak was replaced by a broad hump or lost this indicates exfoliated morphology is observed. However, if the peak is still definite intercalated morphology is observed (Ahmadi, et al. 2004).

In this part, X-ray diffraction analysis of clay/ epoxy nanocomposites, SEM micrographs of fracture surfaces of clay epoxy nanocomposites and proposed surface morphologies of carbon black- clay / polymer nanocomposites are summarized.

Yasmin et al. (2003) studied modified clay/epoxy nanocomposites with concentrations of 1–10 wt.%. Nanocomposites were prepared by shear mixing by a tree roll mill. Two types of clay nanoparticles were used as the reinforcement. One of them was octadecyl trimethyl ammonium (ODTMA) modified Nanomer I.28E (Yasmin, et al. 2003), and the second was methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium (MT2EtOH) modified the Cloisite 30B (Yasmin, et al. 2003). The degree of intercalation /exfoliation and the d-spacing between clay platelets were investigated by

XRD. Nanomer I.28E/epoxy showed an intercalated structure with an average d-spacing of 3.6 nm, whereas the Cloisite 30B/epoxy showed an exfoliated structure (d-spacing >8 nm confirmed by TEM). According to these results, they revealed that these two surface modification treatment of montmorillonite clay was more effective with the MT2EtOH quaternary ammonium type organic modifier than with the ODTMA. They concluded that the degree of intercalation/exfoliation depends on the type of the surface modification treatment.

SEM fractographs for both Nanomer I.28E/epoxy and Cloisite 30B/epoxy nanocomposites was shown in Figure 2.13. Nanomer I.28E/epoxy showed a rougher fracture surfaces as compared to the Cloisite 30B/epoxy. This was related to the intercalated structure of Nanomer 1.28E/epoxy.

Feller et al. (2004) also studied morphology of montmorillonite nanofiller and three conductive polymer composites: poly(ethylene)-carbon black (PE-CB), poly(propylene)-carbon black (PP-CB) and poly(ethylene-coethyl acrylate)-carbon black (EEA-CB). They revealed that there were interactions of MT with either CB or the polymer chains. Also interactions of MT clay platelets with CB or polymer chains through the functional amino-alkyl ammonium short chain was considered and they proposed nanoscale morphology as seen in Figure 2.14

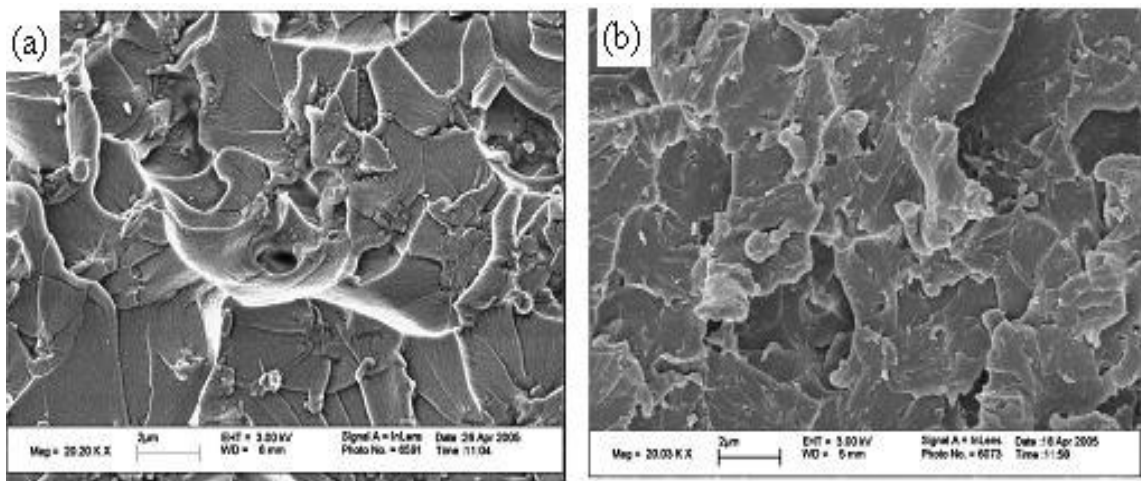


Figure 2.13. SEM fractographs of 1 wt.% clay nanocomposites: (a) Nanomer 1.28E/epoxy (b) Cloisite 30B/epoxy (Source: Feller, et al. 2004)

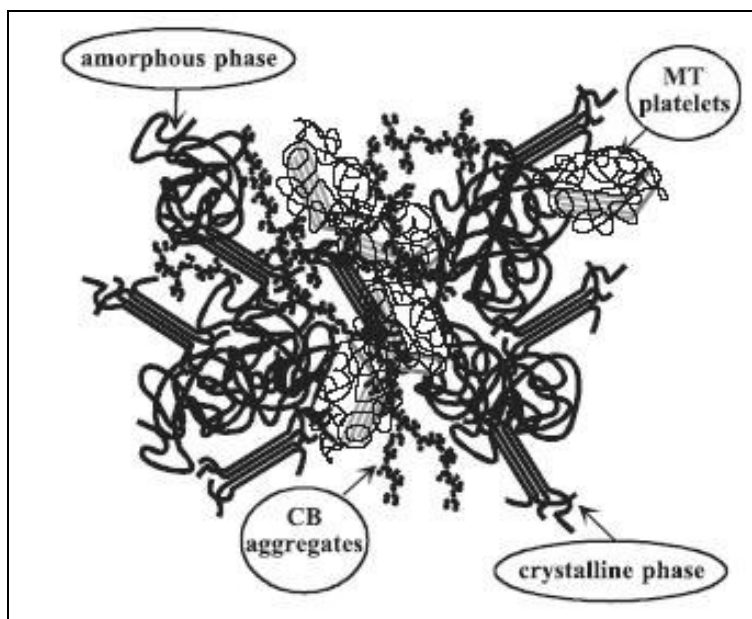


Figure 2.14. Schematic representation of the conductive polymer composites organization at nanometric scale (Source: Feller, et al. 2004)

Konishi and Cakmak (2006) examined the morphology of organoclay/carbon black (CB) nylon-6 nanocomposites. They defined organoclay/CB ‘nano-unit’ morphology as seen in Figure 2.15. It was composed of stacked organo-montmorillonite platelets that deform to surround partially around one or two primary CB aggregates. This elementary nano-unit structure induced CB network within polyamide 6 matrices (Konishi and Cakmak 2006).

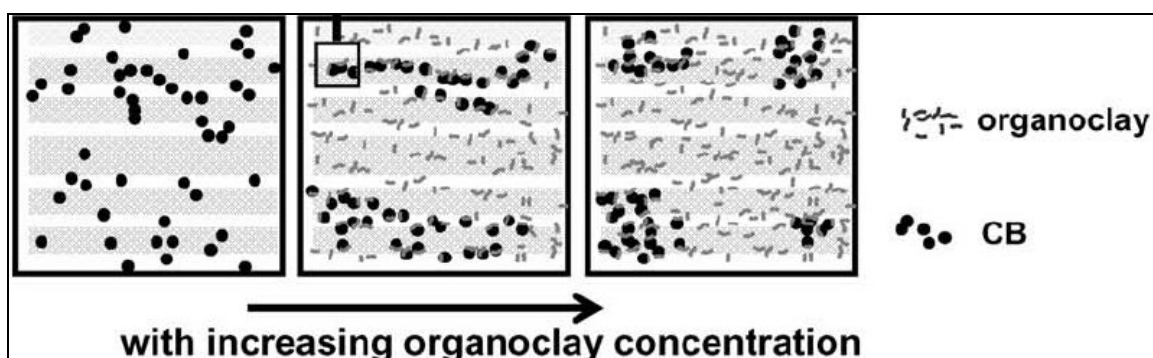


Figure 2.15. Schematic of the proposed organoclay/CB ‘nano-unit’ morphology (Source: Konishi and Çakmak 2006)

### 2.6.3. Studies on the Mechanical Properties of Nanocomposites

In this part, studies performed to determine effect of clay content on the tensile and flexural properties of layered clay/ epoxy nanocomposites were reviewed. In general, increase in modulus however decrease in strength was observed and all explanations to these behaviours were related to nanocomposite morphology.

Yasmin et al. (2006) investigated the mechanical properties of modified clay/epoxy nanocomposites with concentrations of 1–10 wt.% prepared by shear mixing. They revealed that the addition of clay particles improved both the elastic modulus and storage modulus of pure epoxy significantly. Furthermore, with increasing clay content, modulus increased gradually. This was attributed to intercalation/exfoliation of Cloisite 30B in epoxy matrix. They concluded that their results also confirmed the direct relation between the degree of exfoliation and the mechanical properties of these nanocomposites.

Basara et al. (2005) studied the influence of clay content and type on the structure and mechanical properties of epoxy-clay nanocomposites. Epoxy was reinforced by 0.5–11 wt. % natural (Cloisite Na<sup>+</sup>) and organically modified (Cloisite 30B) types of montmorillonite. They found that tensile modulus values increased with increasing clay loading due to the stiffening effect of clay in both types of nanocomposites. Whereas tensile strength values of Cloisite 30B and Cloisite Na<sup>+</sup> nanocomposites showed a maximum at 1 and 0.5 wt % of clay, respectively. They related the decrease in tensile strength values at higher clay contents to the stress concentration effect of the agglomerated clay particles, lower filler surface area and lower polymer-clay surface interactions.

Kotsilkova (2005) studied the flexural properties of clay/epoxy nanocomposites. The nanocomposites produced by two different method; direct (without solvent) and solvent processing techniques. He also used three different types of organic modifiers to modify clay. These are SAN (Hexadecyl octadecyl ammonium chloride), STN (Trioctane methyl ammonium chloride), SPN (Oligo(oxypropylene) diethyl methyl ammonium chloride). He found that the mechanical properties are found to significantly dependent on the type of nanocomposite structure and the use of solvent. The nanocomposites produced by the direct processing technique showed increased flexural modulus depending on the type of the organic modifier. As seen in Figure 2.16 (a) The

modulus of the nanocomposites at 5 vol % clay content enhanced significantly in the following order: SPN (0%), SAN (20%), and STN (64%). In contrast, as shown in Figure 2.16 (b) the modulus values of nanocomposites produced by solvent processing technique were not affected. However, flexural strength of nanocomposites were increased as compared to the ones processed by the direct processing method. He related this behavior to the strength and the effect of solvent, which obviously act as a plasticizer for the epoxy resin and alters the interfacial interactions.

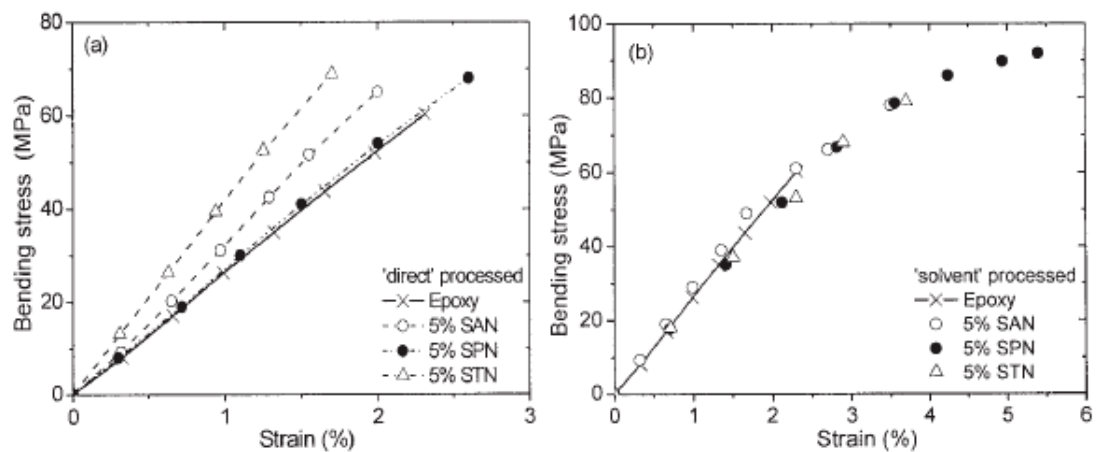


Figure 2.16. Bending stress–strain curves of epoxy resin and 5 vol % nanocomposites of SAN, STN, and SPN prepared by (a) direct processing and (b) solvent processing (Source: Kotsilkova 2005)

Isik et al. (2003) investigated the effect of clay loading on the tensile properties of modified clay/epoxy the nanocomposites. It was observed that tensile strength decreased with increasing amount of clay. They related this to the influence of clay agglomerates which causes stress concentration and to the decreased polymer clay interactions. They also found that the tensile modulus of the nanocomposite increased with increasing amount of clay.

The mechanical properties of epoxy/montmorillonite nanocomposites under flexural loadings were studied by Akbari and Bagheri (2007). They observed a reduction in flexural strength with increasing the amount of organoclay and related this to intercalated structures of nanocomposites.

Kaya (2005) studied tensile and flexural properties of epoxy/clay nanocomposites. Modified and unmodified montmorillonite were added to the epoxy matrix



with varying contents (1-10 wt.%). In her thesis, she reported that both tensile and flexural modulus values tend to increase with the increasing fraction of unmodified and modified clay. At high clay loadings, modified clay exhibited slightly higher elastic modulus values as compared to those of unmodified montmorillonite. This was related to effect of modification causing better penetration of the matrix resin into the clay galleries. However, it was found that the flexural and tensile strength values decreases for the nanocomposites prepared with both types of clay as compared to neat epoxy. This was related to the formation of voids, weak adhesion points along the particle/matrix interface formed during nanocomposite processing.

The effect of the organoclay nanoparticles on the morphology and properties for epoxy/organoclay nanocomposites was examined by Dean et al. (2005). Intercalated morphologies with varying degrees of interlayer expansion were observed mechanical properties of the samples were correlated with the morphological study. As the clay loading increased, the modulus increased by 35% for the 2% sample, 15% for the 4% sample, and 30% for the 6% sample, respectively. The strength values decreased with clay loading.

Velmurugan and Mohan (2004) examined the effect of clay content on the tensile properties of quaternary ammonium modified clay/epoxy nanocomposites. They observed that the modulus of the nanocomposites enhanced about three times as compared to neat epoxy with the addition of 10 wt% clay. The improvement of elastic modulus was explained due to the exfoliation of clay layers and interfacial adhesion between the clay and the epoxy matrix. However, the tensile strength reduced regardless of the clay content as compared to neat epoxy.

#### **2.6.4. Studies on the Thermal Properties of Nanocomposites**

In general, the incorporation of clay into the polymer matrix was found to enhance glass transition temperature and thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition (Ray and Okamoto 2003).

Basara et al. (2005) also studied the effect of clay type and content on the glass transition temperatures of nanocomposites. They found that the glass transition temperature of neat epoxy was increased from 73°C to 83.5°C with 9 wt % organically

modified MMT (Cloisite 30B) and to 75°C with 9 wt % natural clay (Cloisite Na<sup>+</sup>) addition. They explained these increases due to the hindered mobility of polymer chains with clay addition.

Thermal degradation behaviour of epoxy/montmorillonite nanocomposites containing 2wt % (EpClay-2) and 10wt% (EpClay-10) organic montmorillonite and pure epoxy were investigated in detail by Gu and Liang (2003). They showed that thermal behaviour of nanocomposites were depend on the clay loading and structure of nanocomposites. EpClay-10 had the lowest initial degradation temperature, while EpClay-2 had the highest values.

Velmurugan and Mohan (2004) also investigated thermal properties of layered clay/ epoxy nanocomposites. They reported a thermal stability improvement in epoxy nanocomposites containing 10 wt. % modified clay. The initial degradation temperature of this nanocomposite was about 60 °C higher than that of neat epoxy.

Park et al. (2002) studied the thermal properties of epoxy/clay nanocomposites. According to their results, the thermal stability of the nanocomposites was improved due to the exfoliated clay layers within the epoxy matrix.

Yasmin et al. (2006) also investigated the mechanical and viscoelastic behavior of clay/ epoxy nanocomposites by DMA (Figure 2.18). They found that the addition of both types of clay particles improved storage modulus of pure epoxy significantly. They also revealed that the higher the clay content, the higher the modulus of the nanocomposite. In addition to that Yasmin et al. (2006) observed continuous drop in T<sub>g</sub> with increasing clay content for both nanocomposites and related that to clay aggregates, interphase regions, adhesion problems at the clay– matrix interface.

Ratna and his colleagues (Ratna, et al. 2003) studied dynamic mechanical behaviours of epoxy/clay nanocomposites. They revealed that incorporation of clay led to a promising increase in storage modulus and a modest increase in T<sub>g</sub> of the nanocomposites. The increase in storage modulus values was explained in terms of the nanocomposite morphology.

Isık et al. (2003) also investigated the thermal properties of the nanocomposites of layered clay/ epoxy nanocomposites. They determined the glass transition temperatures of nanocomposites by DSC. As a result, T<sub>g</sub> was increased with increasing clay content. They explained this behaviour interms of restricted mobility of polymer chains due to the clay and polymer interaction.

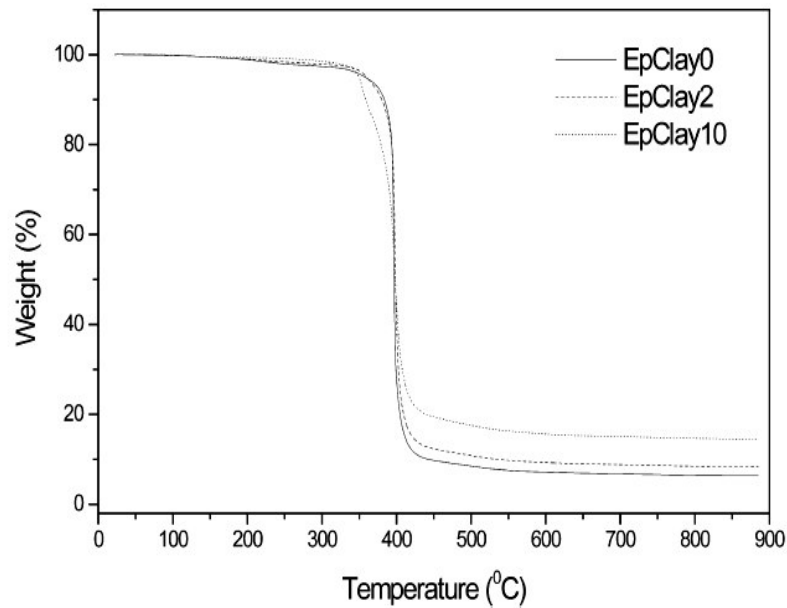


Figure 2.17. TGA plots of EpClay-0, EpClay-2 and EpClay-10 nanocomposites  
(Source: Gu and Liang 2003)

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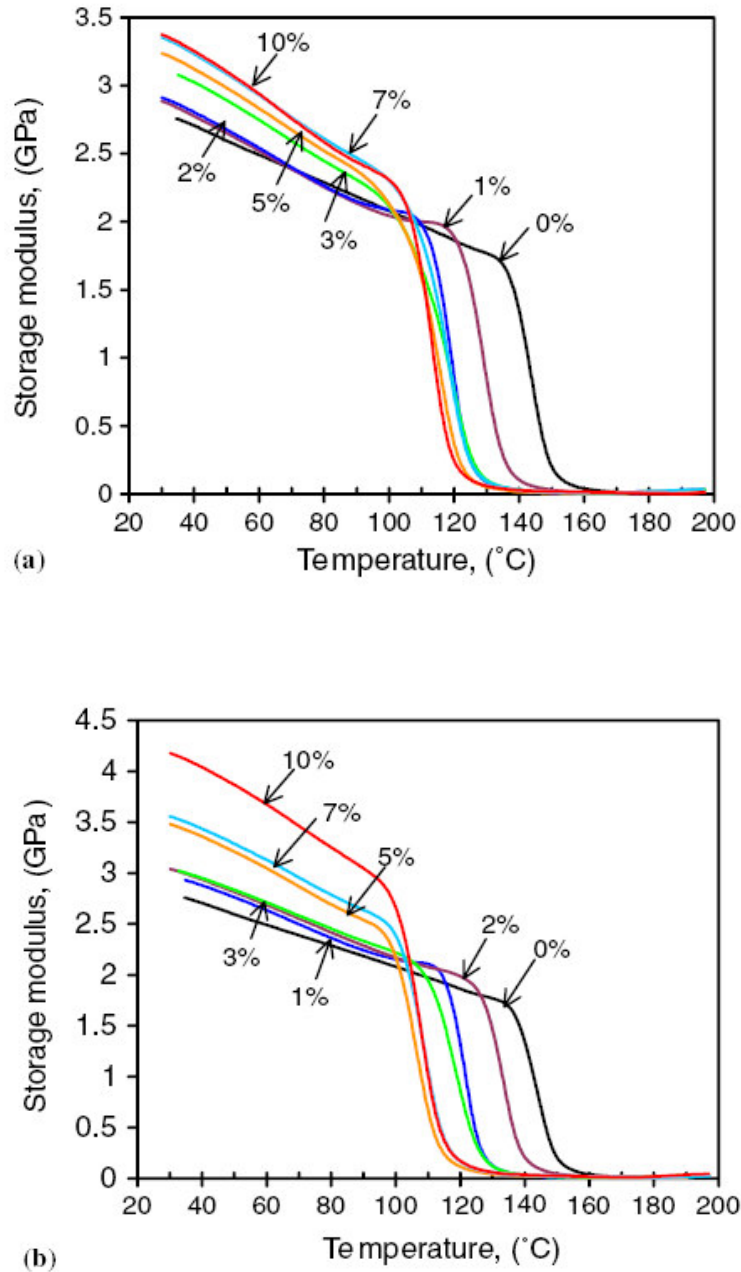


Figure 2.18. Variation of storage modulus with temperature: (a) Nanomer I.28E/epoxy; (b) Cloisite 30B/epoxy (Source: Yasmin, et al. 2006)

Wang and Qin (2007) processed clay/ epoxy nanocomposites by ultrasonic stirring and performed thermal characterization of these composites. The experimental results of thermogravimetric analysis showed that thermal decomposition temperatures

increased with the increase in the duration of ultrasonic stirring independent of clay content. However, both the glass transition temperature and the storage modulus of the composites decreased as measured from the dynamic mechanical analysis.

## CHAPTER 3

### EXPERIMENTAL

#### 3.1. Materials

Nanocomposites were prepared by using epoxy as matrix and modified layered clay and carbon black particulates as fillers. Epoxy system used in this study was a diglyceryl ether of bisphenol A (DGEBA) resin hardened with aliphatic amines. The epoxy and the hardener were purchased from Résoltech Company (Eugilles, France) under the commercial names of Résoltech 1040 and Résoltech 1048 respectively. Modified clay was a ditallow dimethylamine (quaternary amine) (~65% C18, ~30% C16, ~5% C14) treated Reşadiye clay ( $\text{Na}^+$ -Montmorillonite) having a cation exchange capacity of 100 meq/100g. Carbon black employed in this study was Printex XE 2-B supplied by Evonik Degussa Company (Frankfurt, Germany).

#### 3.2. Preparation of Nanocomposites

At the first stage, carbon black /epoxy nanocomposites with different carbon black contents were synthesized to find out the percolation threshold concentration. It is the concentration where the insulating nanocomposite becomes electrically conductive. In the second stage, carbon black concentration was kept constant above percolation threshold concentration and hybrid nanocomposites with varying clay contents of 0.5, 1, 1.5, 2.5, 4 vol. % were synthesized via in-situ polymerization method.

Figure 3.1 shows the illustration of nanocomposite preparation. The clay fillers were dried in a Memmert VO 200 vacuum drying oven at 80°C for 2 hours in order to remove the moisture. The epoxy resin with the desired amount was mixed with filler at room temperature for 30 minutes using a Heidolph RZR mechanical stirrer (Figure 3.2). The blend was poured into the Exackt 80 S three roll mill (Figure 3.3) to further intercalate the clay layers with epoxy. The blend was kept in the mill for 2 hours and it was collected in a cup using a metal blade. Then, a stoichiometric amount of curing agent was added to the blend (22 parts curing agent: 100 parts epoxy by weight).

Finally, the mixture was casted into silicon molds. The nanocomposites were cured at room temperature for 40 minutes and post cured at 60°C for 8 hours in a furnace (Memmert -600).

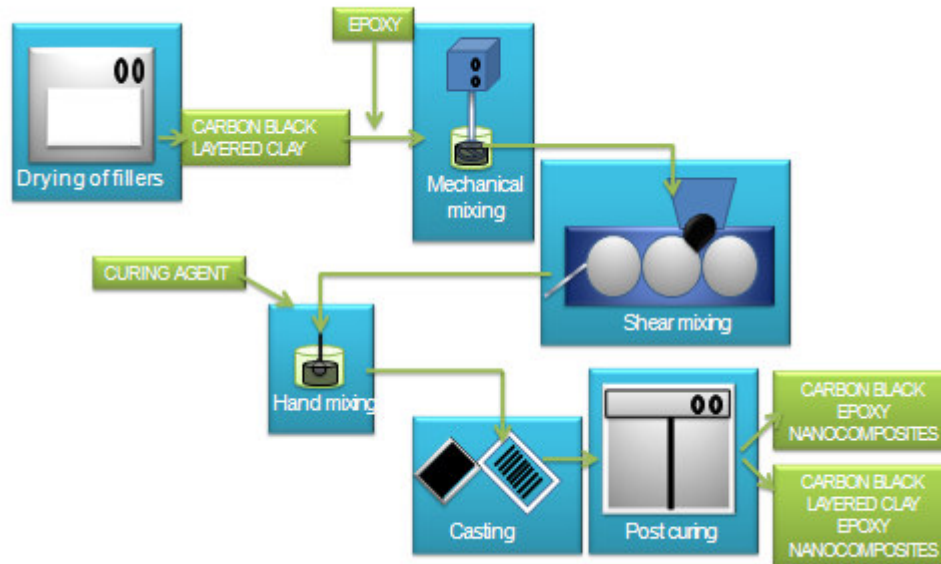


Figure 3.2. Schematic illustration of nanocomposite preparation



Figure 3.2. Mechanical Stirrer



Figure 3.3. Three roll mill

### **3.3. Characterization of Nanocomposites**

In this part, nanocomposite characterization techniques used in the study are described. Characterization has a crucial role in interpreting the structure and property relationship between nanocomposites. The techniques used are; X-ray diffraction (XRD) and scanning electron microscopy (SEM) for microstructural characterization, tensile and flexural tests for mechanical property characterization, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) for thermal property characterization and electrical resistivity measurements for electrical property characterization.

#### **3.3.1. Electrical Property Characterization**

Electrical conductivity measurements of carbon black/epoxy nanocomposites were performed firstly in order to determine the percolation threshold concentration. Once the threshold concentration was determined, the hybrid nanocomposites were produced by keeping the carbon black concentration constant and varying the clay contents. To find out the effects of clay addition on the electrical properties of nanocomposites, electrical resistivity measurements were carried out.

##### **3.3.1.1. Electrical Resistivity Measurements**

In order to determine direct current electrical conductivity and to evaluate related percolation phenomena in nanocomposites four-point probe method was used. With this method, a wire was contacted on samples with silver paint at four locations named probes as seen in Figure 3.4. The current passes from the two outer probes, while the two inner probes connected to a voltmeter reads the resulting voltage drop across the sample.



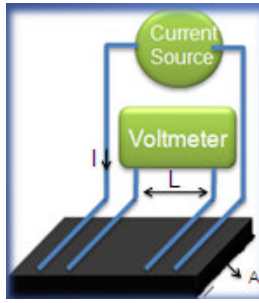


Figure 3.4. Four-point probe method for electrical measurements

For this purpose, specimens with dimensions of  $10(L) \times 10(W) \times 1(T) \text{ mm}^3$  were used. The measurements were performed at room temperature and at least five specimens were measured to have precise results. First, the resistances of nanocomposites were determined using the current and voltage values, and then conductivity was calculated from the equations:

$$\frac{1}{\rho} = \frac{(R \times A)}{l} \quad (3.1)$$

$$R = \frac{V}{I} \quad (3.2)$$

In the equations,  $\rho$  is the electrical resistivity ( $\Omega \cdot \text{m}$ ),  $1/\rho$  is the conductivity ( $\text{S/m}$ ),  $R$  is the resistance ( $\Omega$ ),  $V$  is the potential difference (Volt),  $I$  is the current (Amperes),  $l$  is the distance between two inner probes (mm).

### 3.3.2. Structural Characterization

#### 3.3.2.1. X-Ray Diffraction Analysis

X-ray diffraction analysis was performed on both nanocomposites and fillers in order to determine the degree of exfoliation and change of d-spacing between the clay layers intercalation. Analyses were performed by a Bruker AXS X-ray Diffractometer using  $\text{Cu-K}\alpha$  ( $\lambda = 0.15406 \text{ nm}$ ) radiation source operating under a voltage of 40 kV and a current of 40 mA. The diffraction angle ( $2\theta$ ) was varied from  $1.2^\circ$  to  $12^\circ$ . The samples

of nanocomposites of 2 mm thickness and clay particulates in powder form were scanned at a rate of 1°/min and step size was 0.02 °.

### **3.3.2.2. Scanning Electron Microscopy**

Scanning electron microscope (SEM) was used to investigate the fracture surfaces of neat epoxy and carbon black-layered clay/epoxy nanocomposites. Backscattered electron images from the surfaces of tensile tests specimens were obtained. Samples were deposited with gold to avoid charging. Micrographs were obtained at magnifications of 1000X and 5000X.

### **3.3.3. Mechanical Property Characterization**

There exists no special standards for nanocomposites. Hence the mechanical tests and measurements are usually related to existing standards. The mechanical properties were obtained by using the standardized techniques for pure polymer matrix.

#### **3.3.3.1. Tensile Tests**

The tensile tests were performed using Shimadzu AG-I mechanical testing machine with a load cell of 5 kN. Dog-bone shaped tensile specimens were prepared according to DIN EN ISO 527.1 measurements, 5 mm in wide and 2.5 mm in thickness with a gauge length of 30 mm. The overall length of the specimen was 75 mm. Tests were conducted at room temperature. The cross-head speed was 1 mm/min. The tests were repeated for at least five samples of each concentration. The measured stroke values versus load data were used to calculate the stress and strain according to the equations:

$$\sigma = \frac{F}{A} \quad (3.3)$$

$$\varepsilon = \frac{(L - L_0)}{L_0} \quad (3.4)$$

In the equations,  $\sigma$  is the stress,  $F$  is the applied load (N),  $A$  is the cross sectional area of the specimen ( $\text{mm}^2$ ),  $\varepsilon$  is the strain,  $L_o$  is the initial distance between gauge tapes (mm),  $L$  is the distance between gage marks at any time (mm). Video extensometer was used to determine the strain during the test. The slope of initial linear part of stress strain plot was used to obtain modulus ( $E$ ) values:

$$E = \frac{\sigma}{\varepsilon} \quad (3.5)$$

### 3.3.3.2. Flexural Test

Flexural tests were conducted by using AGSC-J Shimadzu according to ASTM D 790. Rectangular flexural specimens were prepared as specified and loaded under 3-point bending configuration. The specimen dimension was  $80(L) \times 10(W) \times 4(T)$  mm. The cross-head speed of 1.7 mm/min and span width of 64 mm was set. The flexural strength and strain were calculated according to equations below:

$$\sigma = \frac{(3 \times F \times L)}{2 \times b \times d^2} \quad (3.6)$$

$$r = \frac{(6 \times D \times d)}{L^2} \quad (3.7)$$

In the equations;  $\sigma$  is the stress in the outer fibers at midpoint (MPa);  $F$  is the load at a given point on the load-deflection curve (N),  $L$  is the support span (mm),  $b$  is the width (mm),  $d$  is the depth (mm),  $r$  is the strain,  $D$  is the deflection of the centre of the beam (mm). Flexural modulus were determined same as the tensile one, by taking the slope of linear part of stress vs. strain curve.

### **3.3.4. Thermal Property Characterization**

#### **3.3.4.1. Differential Scanning Calorimetry**

The glass transition temperature of nanocomposites ( $T_g$ ) were determined by using TA Instruments Q10 DSC. The samples were heated from 25 to 200 °C with a heating scan of 10 °C/min.

#### **3.3.4.2. Thermogravimetric Analysis**

In order to determine the thermal decomposition temperatures, thermogravimetric analysis (TGA) was performed on nanocomposites with a Perkin–Elmer TG/ DTA under nitrogen atmosphere. Samples of 8-9 mg were heated from room temperature to 550 °C at a heating rate of 10°C/min.

#### **3.3.4.3. Dynamic Mechanical Analysis**

Storage modulus and glass transition ( $T_g$ ) measurements of nanocomposites were performed on Netzsch DMA-242C through three point bending mode. Experiments were carried out in the temperature range of 25 to 200 °C under nitrogen flow. Heating rate was 3 °C/min. Scans were conducted at a frequency of 1 Hz. The specimen dimension was 50(L) × 2.5(W) × 10(T) mm.

# CHAPTER 4

## RESULTS AND DISCUSSION

In this study, electrical, structural, mechanical and thermal characterizations of the nanocomposites were performed in order to determine the effect of clay content on these properties. Based on the electrical measurements, carbon black concentration was kept constant at 0.25 vol. % for all nanocomposites whereas clay content of the nanocomposites was varied. The experimental results were compared with the properties of the neat epoxy.

### 4.1. Electrical Properties

The electrical properties of carbon black/epoxy composites were characterized in terms of electrical conductivity and related percolation theory. The dependence of direct current (dc) conductivity at room temperature on carbon black concentration is seen in Figure 4.1.

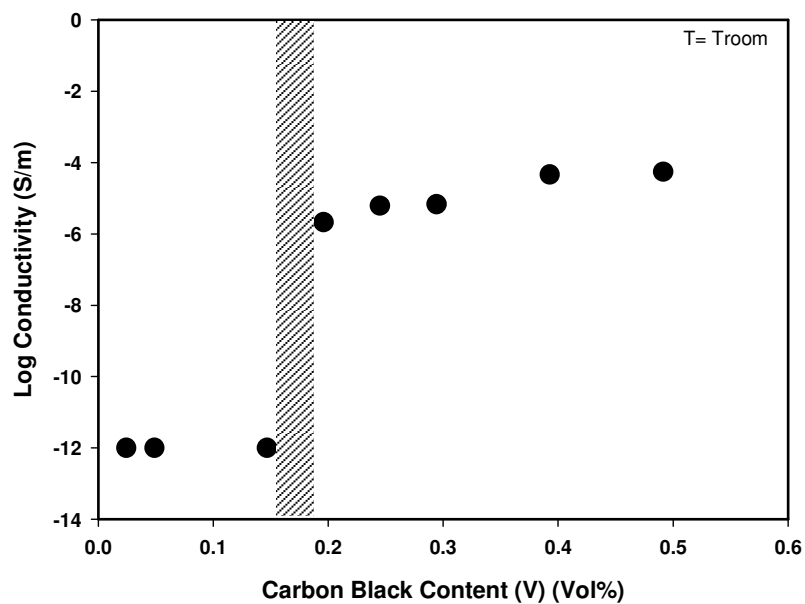


Figure 4.1. Influence of carbon black content on the conductivity of carbon black / epoxy composites. Hatched part shows the percolation threshold.

The behaviour of conductivity can be described in terms of percolation phenomena. At a critical filler concentration the characteristic percolation threshold transition occurs. Percolation threshold concentration is defined as the critical carbon black volume fraction ( $V_c$ ) where the conducting network is formed and the electrical conductivity is within static dissipative range of  $10^{-6}$ – $10^{-4}$  S.cm<sup>-1</sup>. In this study, the percolation threshold concentration was measured to be about 0.2 vol. % (0.4 wt %) carbon black loading. Hence for concentrations of 0.2 vol. % (0.4 wt %) and above, the composite is called electrically conductive.

The  $V_c$  value measured in this study was found to be relatively lower compared with the similar works reported in the literature. As an example, Zois et al. (1999) determined  $V_c = 6.2$  wt.% for polypropylene/carbon black (PP/CB) composite systems. Low values of  $V_c$  are related to highly structured carbon black network formation in the corresponding polymers, The electrical percolation in polymer–CB composites is greatly influenced by the type of polymers and CB, preparation temperature and mixing methods and time. (Konishi, et al. 2006).

The dc conductivity of such insulator-conductor composites near percolation threshold follows universal scaling laws given below;

$$\sigma_{dc} \propto (V - V_c)^t, \text{ for } V > V_c \quad (3.8)$$

where;  $\sigma_{dc}$  is the direct current electrical conductivity,  $V$  is the carbon black concentration (vol. %),  $V_c$  is the percolation threshold concentration (vol. %) and  $t$  is the critical exponent for three-dimensional structures. Values of  $t$  should be in the range of [1.7-2.0] (Zois, et al. 1999 and Flandin, et al. 1999). “ $t$ ” is determined from the slope of the best fitting of  $\sigma_{dc}$  versus  $(V - V_c)$  as shown in Figure 4.2. For the system studied  $t = 1.93$  was found. The critical exponent “ $t$ ” was in the range stated, between 1.7 and 2. This means, carbon black/ epoxy composites follow power-law behaviour. Zhang et al. (2007) observed low critical exponent “ $t$ ” which was out of range with carbon black/ polypropylene composites and related this result to poorly constructed carbon black network in polypropylene.

Based on the results in Figure 4.1, carbon black concentration of 0.25 vol % (0.5 wt. %) which was slightly above the  $V_c$  was chosen and kept constant for the production of carbon black- layered clay nanocomposites.

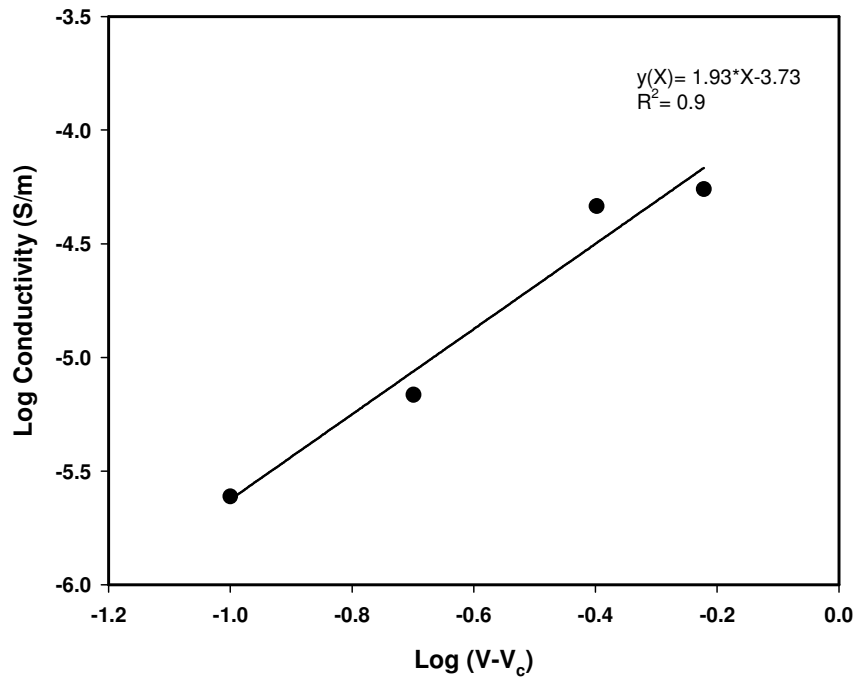


Figure 4.2. Log conductivity versus Log (V-V<sub>c</sub>) for carbon black/ epoxy composites

The effect of clay content on conductivity of nanocomposites is shown in Figure 4.3. The neat epoxy exhibited a conductivity value of about  $10^{-12}$  S/m. In other words it was an insulator. By the addition of 0.25 vol. % carbon black the conductivity of the epoxy rised to  $10^{-5}$  S/m. It was found that the conductivity of the carbon black/epoxy system decreased with clay addition. However, nanocomposites with 0.5 vol. % of clay loading exhibited conductivity. Clay layers acted as barriers and broke the conductivity network of carbon black particles. The results reported in Figure 4.3. are in agreement with the study of Zhang et al. (2007) who examined the effect of clay content on the conductivity of silica-epoxy nanocomposites. They first observed the increased conductivity of the nanocomposites containing carbon black as compared with the nanocomposite containing no silica up to a maximum value at a ratio of 0.6:1.0 (SiO<sub>2</sub>:CB) They also observed that with further increase of volume fraction of silica the conductivity was reduced. They related this decrease in conductivity to the hindered conductive path in the nanocomposite by the highly concentrated silica networks.

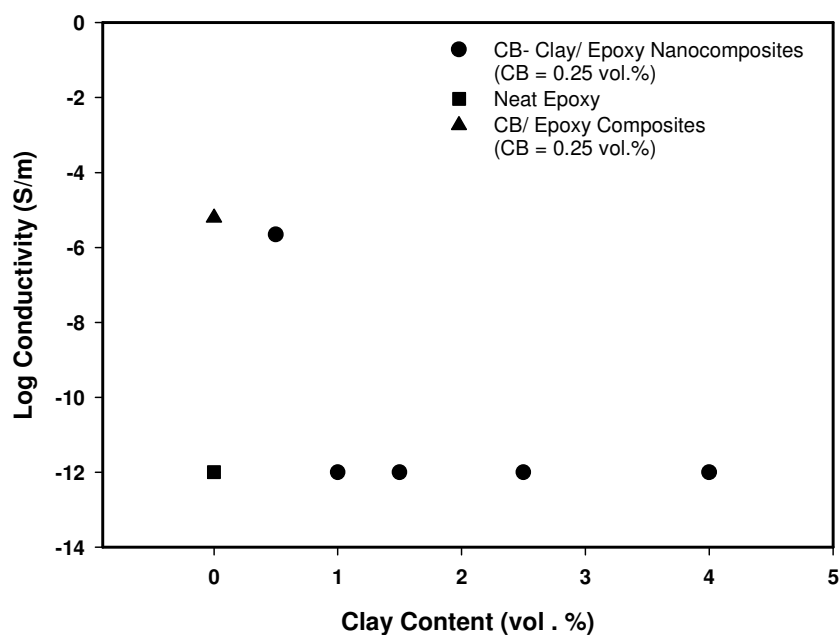


Figure 4.3. Effect of clay content on conductivity of carbon black-layered clay/ epoxy nanocomposites.

Nevertheless, conductivity value compared with conductive carbon black epoxy composite is lower than that of carbon black-layer clay epoxy nanocomposites. On the other hand, Konishi et al. (2006) observed that even with 5 vol % clay loading carbon black-layered clay/ nylon-6 nanocomposites' conductivity maintained in static dissipative range. Consequently, the results obtained indicate that the dispersion morphology of CB in the cross-linked epoxy matrix changes with the addition of clay layers. The change of conductivity with clay additions above 0.5 vol. % was found to be quite insignificant.

## 4.2. Structure and Morphology of Nanocomposites

X-ray diffraction analyses were performed to investigate the change of basal-spacing between the modified and unmodified clay and, and the intercalation amount of epoxy within the clay galleries.

The XRD patterns of the modified and the unmodified clay are shown in Figure 4.4. It was observed that the basal spacing for the unmodified clay was 1.2 nm. However with modification of clay by a quaternary amine surfactant (ditallow-



dimethylamine), the interlayer spacing increased from 1.2 nm to 1.8 and 3.7 nm. Observing two peaks after modification indicates two different gallery heights. This is because of the different orientations of the surfactant chains adsorbed into the clay galleries. Depending on the chain length of surfactants, cation exchange capacity (CEC) of the clay, and temperature the surfactant chains show different type of molecular arrangements. These are; mono- or bi-layers and paraffin types of mono- or bi-layer molecular arrangements as reported by Vaia et al. (1994) and seen in Figure 4.5. In addition, the low intensity broad peak around  $2\theta=6^{\circ}$ - $8^{\circ}$  indicates that there was still unexpanded layers in the modified clay.

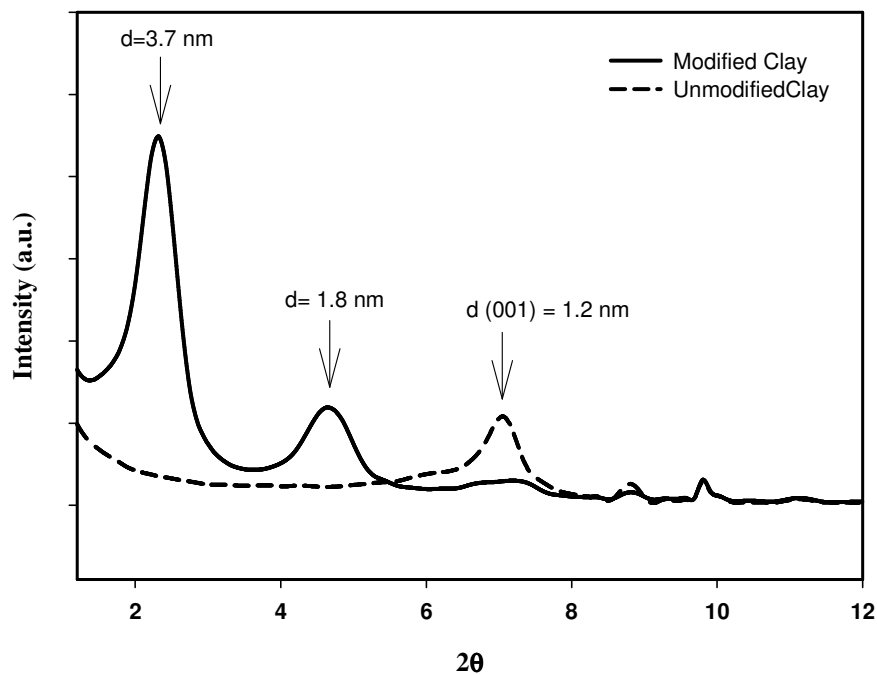


Figure 4.4. X-ray diffraction patterns of modified and unmodified Reşadiye clay ( $\text{Na}^+$ Montmorillonite)

The XRD patterns of the nanocomposites with varying clay contents are shown in Figure 4.6. The diffraction pattern for neat epoxy, modified clay and carbon black is also shown in the same figure. Carbon black has amorphous structure (Donnet, et al. 1993) therefore, it does not exhibit characteristic basal reflections. Hence, the morphology interpretation here is limited to the distribution of clay layers within nanocomposites.

According to the results in Figure 4.6, the nanocomposites showed no sharp diffraction peaks. The absence of basal reflection suggests good dispersion of the clay

layers in the epoxy matrix indicating some extent of exfoliation. The shear mixing process may be appropriate to obtain exfoliation of clay layers. During 3-roll milling, clay addition increased the viscosity of the resins and caused to increase in extra shear forces. These high intensive shear forces separate the clay layers, increase the basal spacing, thereby provide good dispersion of clay layers, and morphologically favor the formation of nanocomposites with some extent of exfoliation. On the other hand, a broad hump with low intensity is observed on the X-ray diffraction patterns in the range of  $2\theta=1.5^\circ-3.5^\circ$  with higher clay loadings. This implies partial exfoliation of the clays at higher loading

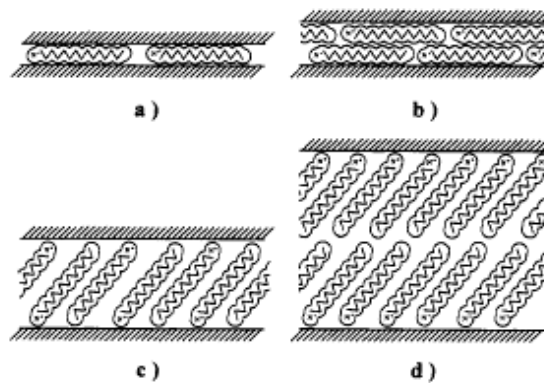


Figure 4.5. Alkyl chain aggregation in clays: (a) lateral monolayer; (b) lateral bilayer; (c) paraffin-type monolayer; (d) paraffin-type bilayer (Source: Vaia, et al.1994)

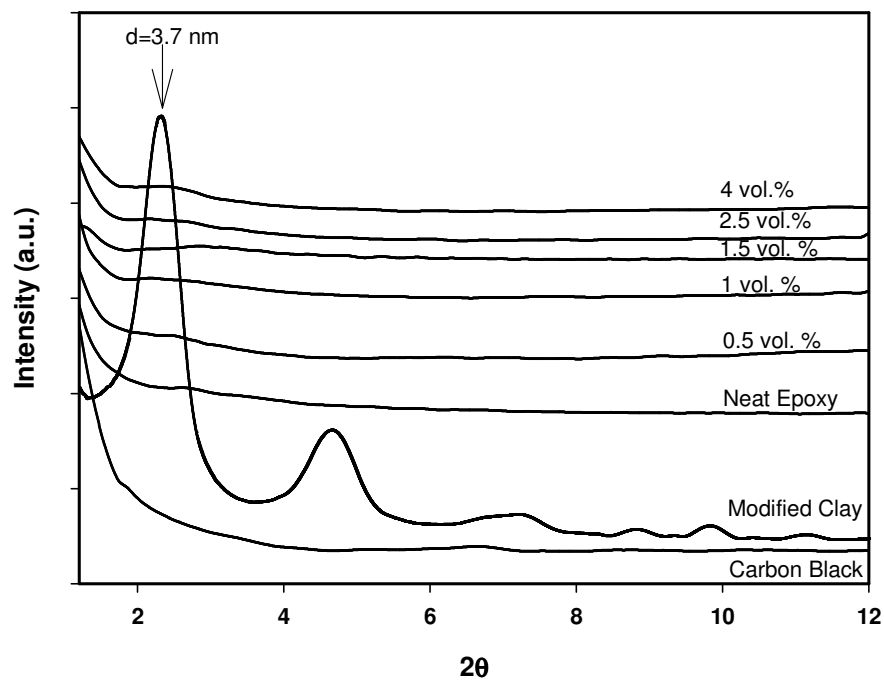
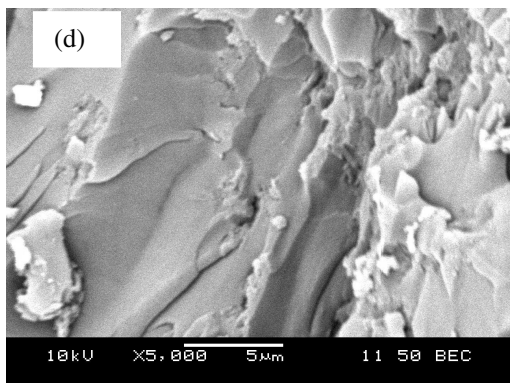
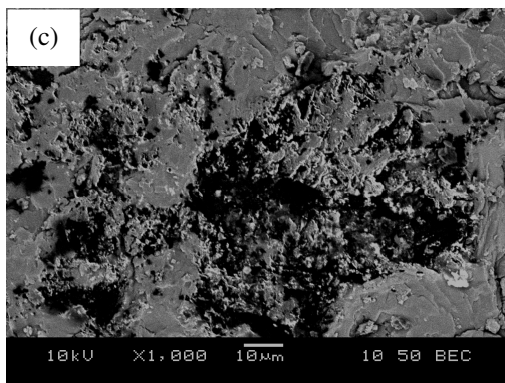
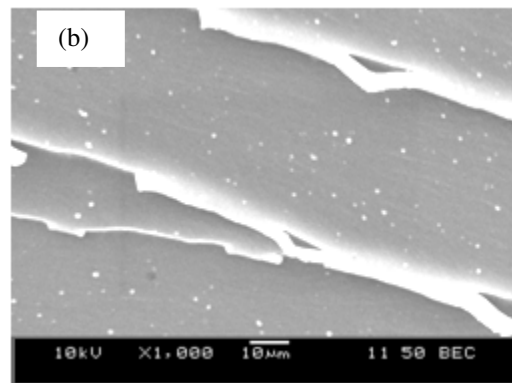
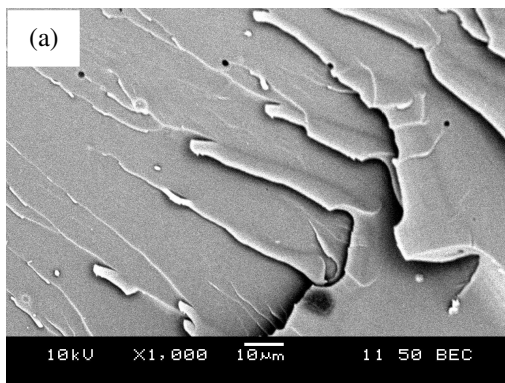


Figure 4.6. X-ray diffraction patterns for neat epoxy, carbon black and modified clay and the nanocomposites

Figures 4.7 from (a) to (l) shows the fracture surfaces of backscattered images of the neat epoxy and 0.5, 1, 1.5, 2.5, 4 vol.% clay containing nanocomposites (0.25 vol.% CB) respectively at 1000X and 5000X magnifications. As seen from the images, neat epoxy exhibits relatively more brittle fracture mode as compared to the nanocomposites. The nanocomposites with carbon black and clay additions show altered fracture surfaces. Surfaces exhibit more deformations. This is due to the branching of the progressing cracks due to the presence of carbon black and clay particles. However, the same particles may act as stress concentrations points and therefore the failure may initiate at lower stress and strain values. This results associate with the mechanical test results. In addition, the dispersion of clay particles are appropriate within the matrix. No significant agglomerates were observed on the examined surfaces. Only the samples with 0.5 vol% clay indicates the possible carbon black agglomeration. On the other hand, by the addition of clay and with increasing clay content carbon agglomerations were observed to disperse. This may be related with the contribution of the clay particles on the carbon black dispersion within the polymer matrix. This results associates well with the electrical conductivity values.



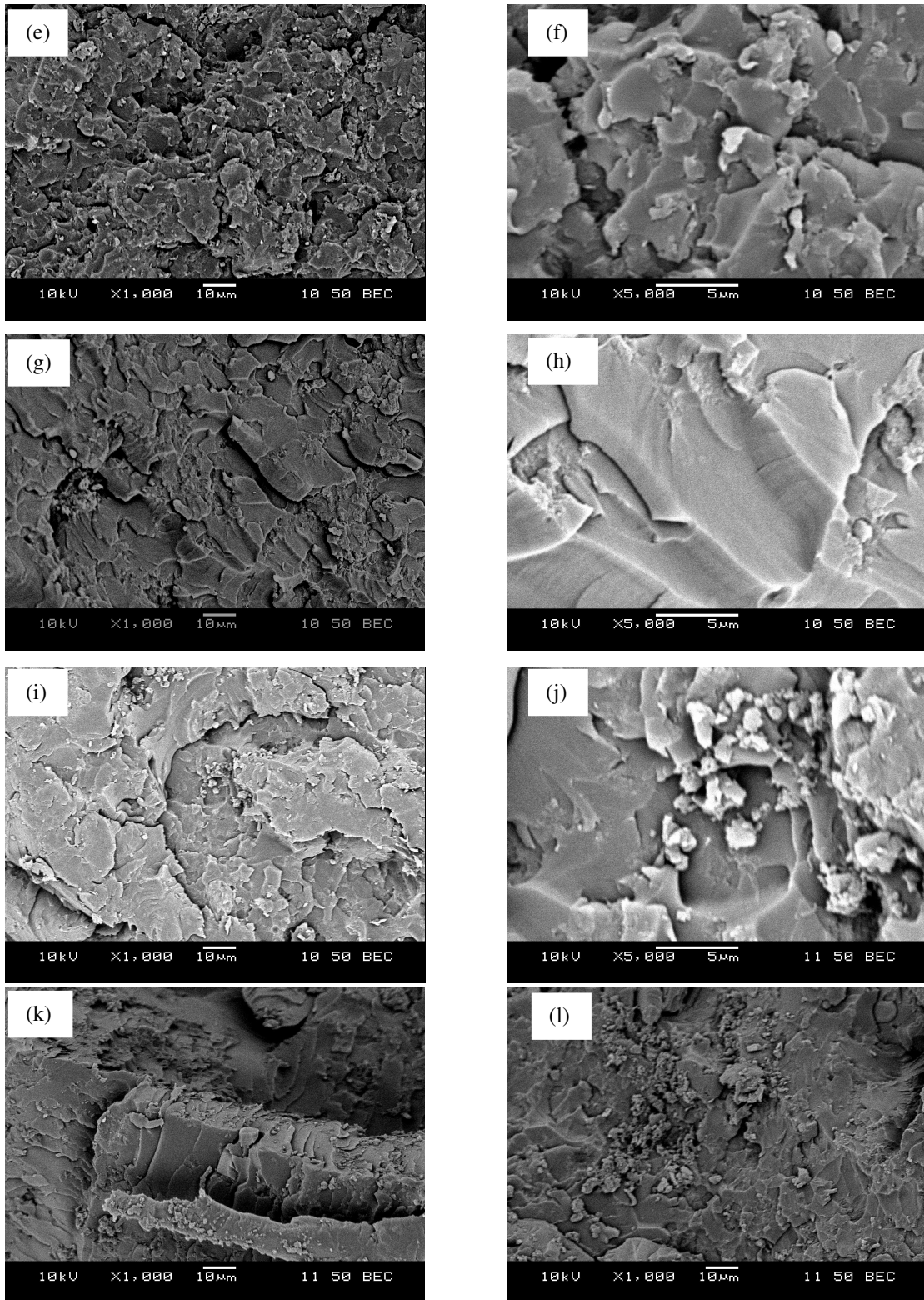


Figure 4.7. (a) Neat Epoxy (1000X) (b) Neat Epoxy (5000X) (c) 0.5 vol.% (1000X) (d) 0.5 vol.% (5000X) (e) 1 vol.% (1000X) (f) 1 vol.% (5000X) (g) 1.5 vol.% (1000X) (h) 1.5 vol.% (5000X) (i) 2.5 vol.% (1000X) (j) 2.5 vol.% (5000X) (k) 4 vol.% (1000X) (l) 4 vol.% (5000X) clay containing carbon black-layered clay/ epoxy nanocomposites (CB =0.25 vol.%)

### 4.3. Mechanical Properties

Tensile and flexural tests were performed for investigating the mechanical properties of nanocomposites. The discussions were made throughout the effect of clay content. Tensile stress–strain behaviour of the nanocomposites and the neat epoxy is shown in Figure 4.8 with the addition of fillers the strain to failure values decreases and nanocomposites show more brittle behaviour compared to neat epoxy. This was due to the hard and rigid fillers that restrict the elongation and hence reduce the deformation

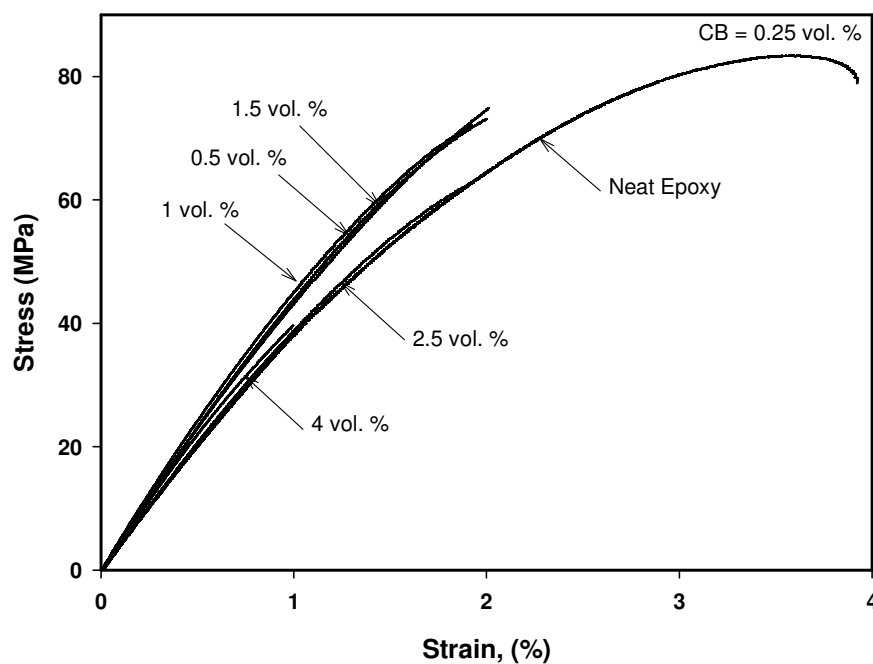


Figure 4.8. Stress-strain behavior of neat epoxy and carbon black-layered clay-epoxy/nanocomposite

The variation of elastic modulus values with respect to filler content is shown in Figure 4.9 The elastic modulus value for neat epoxy was measured to be about 3.7 GPa. It was observed that the modulus values exhibit a remarkable increase at rather low clay additions. The modulus values up to 1.5 vol.% clay contents remain almost constant at about 4.8 GPa. An improvement of about 28 % is observed with an addition of up to 1.5 vol.% of clay, At higher concentrations above 1.5 vol. % clay loadings, modulus values decreased slightly. In the study of Wang et al. (2006) 13% enhancement was achieved with 3 wt.% filler loading into epoxy polymer matrix. Moreover Nigam et al. (2007)

found that addition of the 6 wt. % clay to the epoxy matrix resulted with a 100% increase in the tensile modulus.

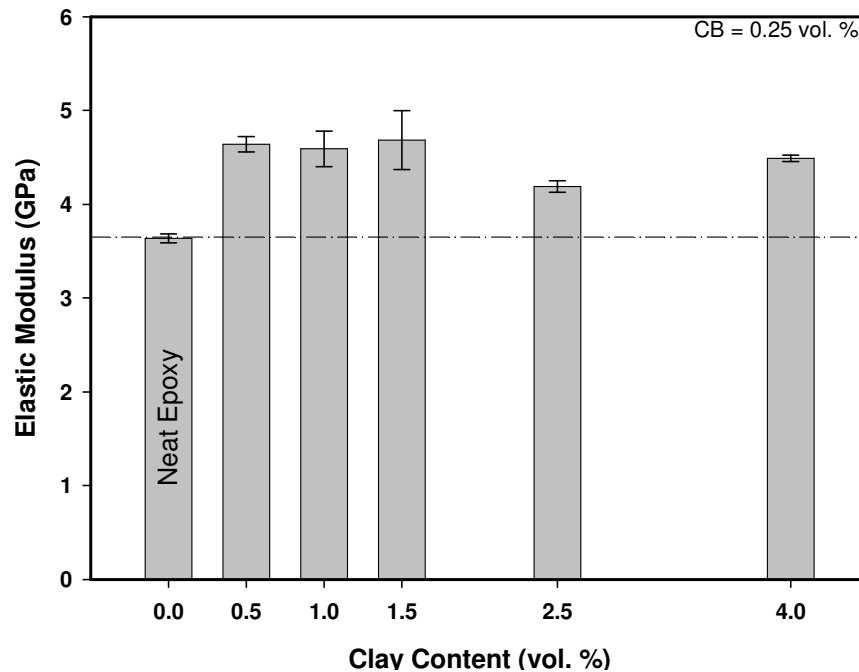


Figure 4.9. Influence of clay content on elastic modulus of carbon black -layered clay/ epoxy nanocomposites.

The improvement in elastic modulus can be ascribed to the strong interaction between the fillers and matrix, the good dispersion and exfoliation of clay layers (Yasmin, et al. 2006). Moreover, the enhanced modulus can be directly related to the stiffening effect of the fillers since the clay possesses much higher modulus than epoxy (Qi, et al. 2006, Fu, et al. 2008 and Wang, et al. 2006). When nanocomposite is under loading, the clay whose elastic modulus is higher than the epoxy resists the applied force and restrains the mobility of polymer chains. As a result, the deformation of nanocomposite is hindered (Yasmin, et al. 2006). This cause to lower failure strain and strength values due to microcrack initiation at early strain levels.

Figure 4.10 shows the average tensile strength of neat epoxy and nano-composites. The ultimate tensile strength value of neat epoxy was measured to be about 80 MPa. However, 0.5 vol.% clay addition decreased the tensile strength to 73 Mpa, which corresponds to a 9 % reduction relative to neat epoxy. This trend remained constant up to 1.5 vol.% clay contents. However, with clay contents higher than 1.5vol.%, the strength values decreased dramatically, such that, with 4 vol. % clay

loading, about 50 % decrease in the strength value was observed compared to that of neat epoxy. This implies that the increasing amount of clay agglomerates in the nanocomposites is governed by the clay content. These agglomerates hinders the intercalation of epoxy within the clay layers. Therefore, inferior dispersion of clay is observed due to lower filler epoxy interactions. With increasing clay loads, these effects gain significance and decrease the tensile strength values of the nanocomposites. Besides, the lower strength values obtained may also associate with the incomplete degassing of the air entrapped during production of nanocomposites. While processing, the filler epoxy mixture becomes highly viscous due to shear mixing and this restrains degassing.

The tensile strength reduction due to the incorporation of clay was also observed in the study of Basara et al. (2005) with layered clay /epoxy nanocomposites. They related this decrease to the weak interactions between layered clay and polymer. On the other hand, Nigam et al. (2004) reported increased strength values with increasing clay contents.

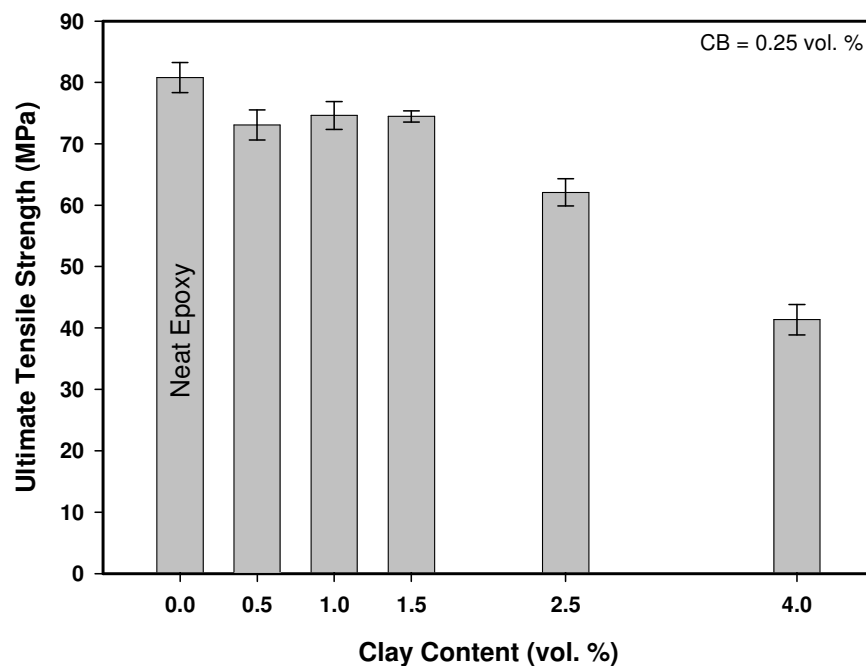


Figure 4.10. Influence of clay content on the tensile strength of nanocomposites

Figure 4.11 shows the flexural stress-strain behaviours of the neat epoxy and nanocomposites. Similar to the tensile behaviors, strain to failure values decreased and ductility reduced with increasing filler content. This reduced deformation was a result of

rigid clay layers restraining elongation compared to epoxy matrix. Moreover, the stress concentrations around them lead to brittle nanocomposites.

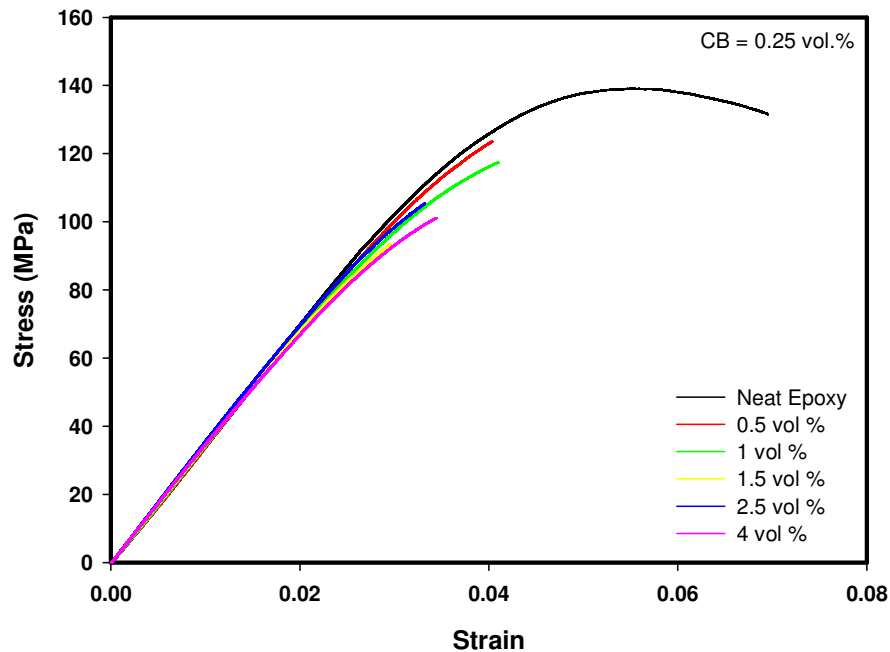


Figure 4.11. Flexural stress-strain behavior of neat epoxy and nanocomposites

The effect of clay content on the flexural modulus of nanocomposites is provided in Figure 4.12. The modulus strength value of neat epoxy was measured as 3.5 GPa. It was found that the flexural modulus values were not affected by clay addition as seen in the literature. In general, nano-filler additions such as clay results in improved flexural modulus as compared to neat epoxy (Ratna, et al. 2003, Mohan, et al. 2006 and Becker, et al. 2002). The interaction quality between the fillers and matrix is a prominent parameter affecting this property. The adhesive strength and the interfacial stiffness of the composite also play a critical role in stress transfer from matrix to fillers. If the interface between filler and matrix is not strong enough, stress can not be effectively transferred through. Therefore, the effectiveness of the filler to carry the load decreases and results in less modulus values (Mohan, et al. 2006).



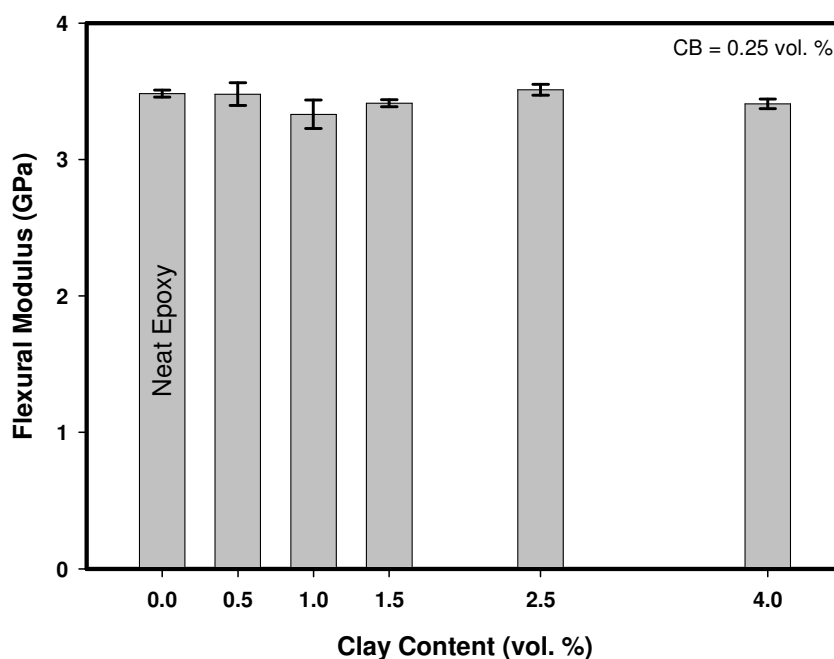


Figure 4.12. Influence of clay content on the flexural modulus of nanocomposites

Figure 4.13 exhibits the flexural strength of the neat epoxy and carbon black-layered clay/ epoxy nanocomposites. It was observed that the flexural strength values decreases for the nanocomposites compared to neat epoxy. Flexural strength of neat epoxy is found as 137 MPa. Maximum reduction was observed with 1.5 vol.% clay addition in which flexural strength value decreased to 90 MPa. A reduction about 35 % was seen compared to neat epoxy. Low strength values can be ascribed to the worse distribution of the fillers in the matrix, voids introduced during processing, and weak interactions between filler and matrix. These fasten the crack propagation which in turn causes failure at low stresses (Mohan, et al. 2006). In the study of Dean et al. (2005) the flexural strength of the nanocomposites was decreased with increasing clay content. They observed maximum decrease of 40% with 4 vol.% loading. They related this decrease to the variations in crosslink topology. On contrary, Zhou et al. (2005) and Lu et al. (2004) have reported increased flexural strength with increasing filler content.

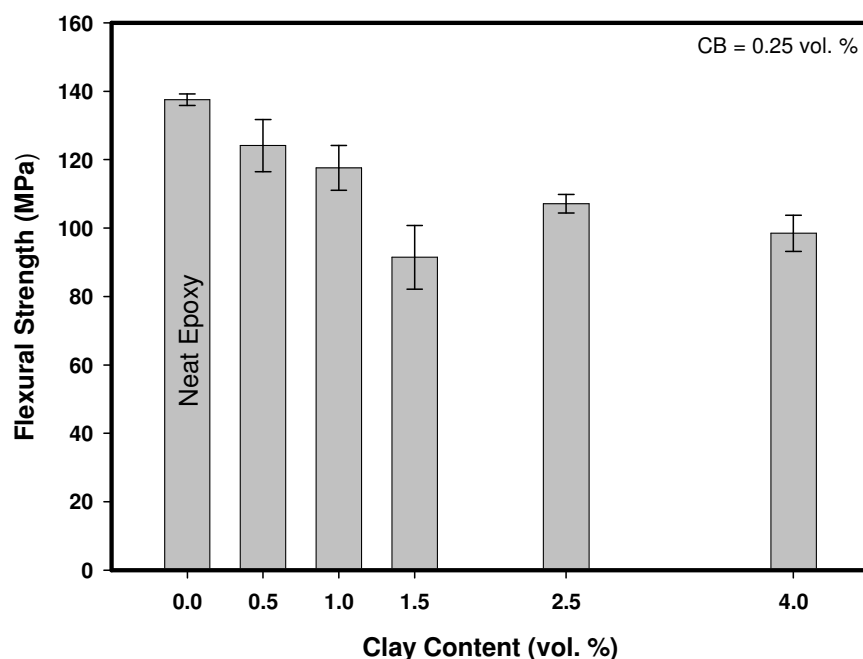


Figure 4.13. Influence of clay content on the flexural strength of nanocomposites.

#### 4.4. Thermal Properties

Thermal degradation and stability of the nanocomposites were studied by conducting thermogravimetric analysis. Figure. 4.14 shows the thermograms of neat epoxy and nanocomposites. The remaining weight after degradation due to the formation of volatile products is plotted as a function of temperature. In all composites, the thermal degradation was one-stage process regardless of the clay content and occurs due to the crosslinking degradation. Similar results were reported by Wang and his friends (Wang, et al. 2007).

Some important temperatures of TGA analysis are listed as follows:  $T_5$ ,  $T_{50}$  and  $T_{95}$ . They are defined as temperature at which 5, 50 and 95% of the mass is volatilized. Initial degradation temperature at which 5% degradation takes place is the characteristic temperature for evaluating the thermal stability. Because of the high mineral content of clay and char formation in consequence of degradation under nitrogen atmosphere, it was not possible to evaluate  $T_{95}$  for the nanocomposites. Temperatures related to the thermal stability, and char yield obtained from TGA data are seen in Table 4.1.

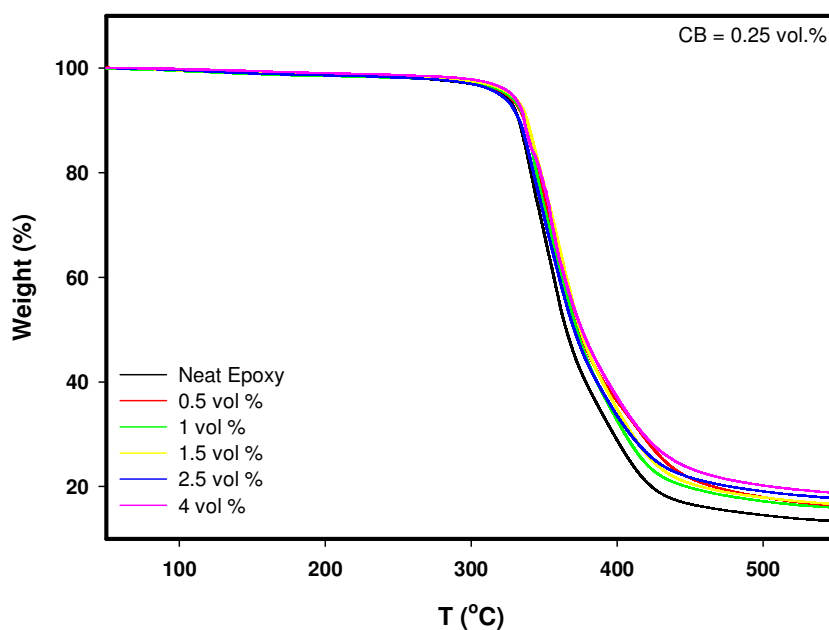


Figure 4.14. The TGA thermograms of neat epoxy and carbon black-layered clay/epoxy nanocomposites

Table 4.1 TGA values of neat epoxy and carbon black-layered clay/epoxy nanocomposites \*.

Clay Content (vol. %)	T <sub>5</sub> (°C)	T <sub>50</sub> (°C)	Char Yield (%) at 550 °C
0	320.45	364.66	13.37
0.5	323.61	373.88	16.36
1	324.68	371.95	15.92
1.5	326.63	374.58	16.66
2.5	319.01	370.18	17.78
4	327.40	375.53	18.78

\*Constant CB concentration = 0.25 vol%

On the basis of T<sub>5</sub> values obtained, the thermal stability of the pure epoxy was found to slightly increase with the increasing clay content, except with 2.5 vol. % filler loading. The thermal degradation of this nanocomposite began at lower temperatures than that of other nanocomposites and neat epoxy. The incorporation of 4 vol. % clay in neat epoxy increased the 5% and 50% decomposition temperatures by 7°C and 11°C, respectively. Even though the T<sub>50</sub> differences were not significant among nanocomposites, a noticeable increase was apparent relative to neat epoxy.

Nevertheless, the nanocomposites show higher char content or reduced weight loss at 550°C with increasing filler content. This also indicates that the thermal stability of neat resin was improved with the addition of fillers. The corresponding enhancement is attributed to the exfoliated morphology of nanocomposites and to the barrier effect of clay layers (Wang, et al. 2007). Clays have good barrier resistance to nitrogen and they act as insulators thus, slowing down the degradation rate. In addition to that, exfoliated nanocomposites are known to have better barrier properties and thermal stability compared to intercalated nanocomposites (Gu, et al. 2003). Considering the X-ray diffraction results in this study, the exfoliated nanocomposites morphology was in accordance with enhanced thermal stability. The improvement of thermal stability due to the addition of clay has also been reported in different studies (Gu, et al. 2003 and Park, et al. 2002).

The variation of storage modulus with temperature and the effect of clay content on storage modulus are seen in Figure 4.15 and Figure 4.16 respectively, for neat epoxy and nanocomposites.

At room temperature, nanocomposites show slightly higher storage modulus with the addition of clay compared to neat epoxy. The storage modulus value of neat epoxy was measured as 3.8 GPa. with the addition of 0.5 vol. % clay the storage modulus increased to 4.1 GPa, an increase about 7 % was observed. The improvement was related to the some extent of exfoliation of clay layers within the epoxy matrix. Moreover, the enhancement by clay addition is also related to the increased stiffness leading the confinement of mobility of chain molecules. The modulus improvement observed in this study (max. 10%) was modest compared to results of Yasmin et al. (2006) and Zhang et al. (2004) 50% and 42.86 % of maximum increase respectively compared to neat epoxy.

The glass transition temperatures ( $T_g$ ) are determined from the peak position of  $\tan \delta$ .  $T_g$  values with varying clay content are seen Table 4.2 and plotted in Figure 4.16.

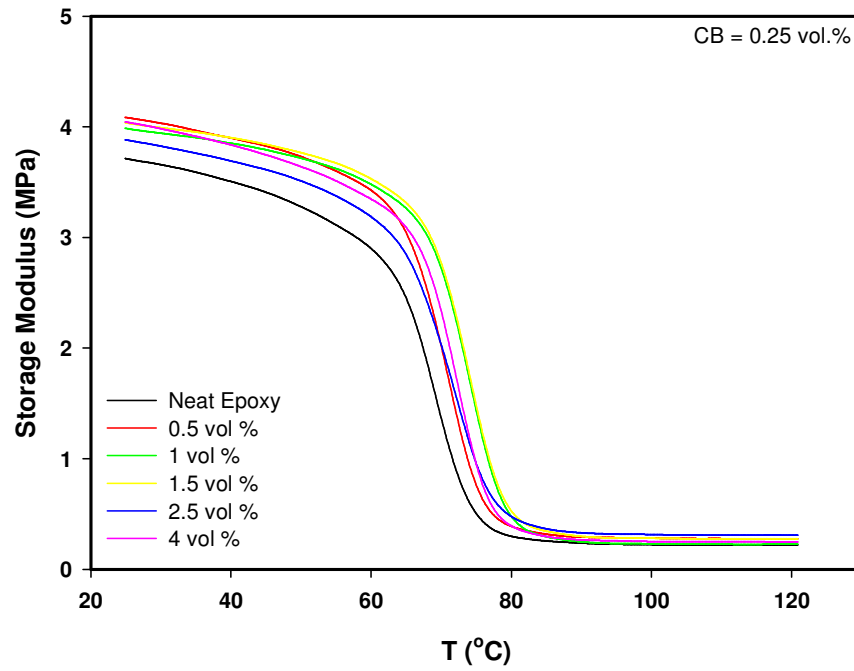


Figure 4.15. Storage modulus versus temperature plots of neat epoxy and nanocomposites

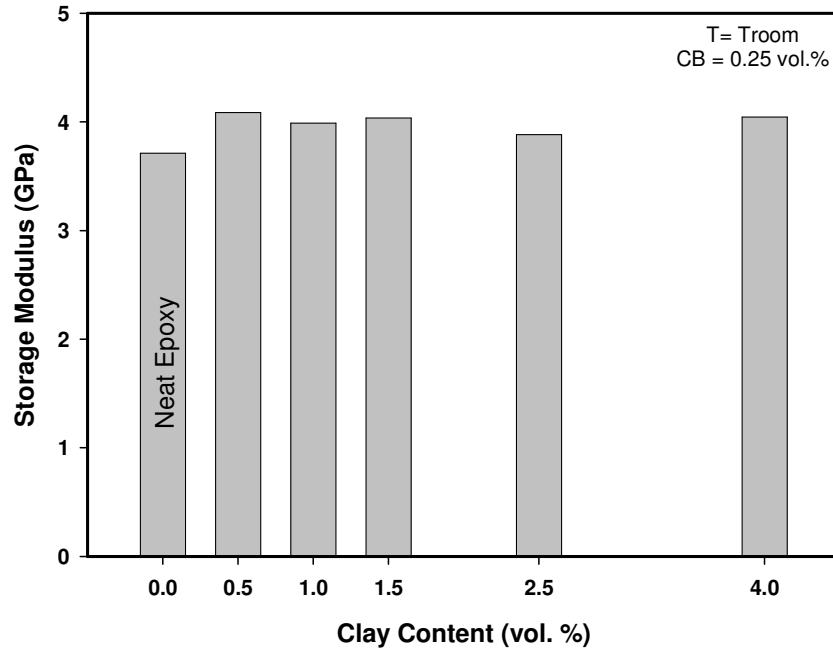


Figure 4.16. Influence of clay content on storage modulus of nanocomposites

Table 4.2. T<sub>g</sub> values of carbon black-layered clay/ epoxy nanocomposites measured by DMA

Clay Content (vol. %)	T <sub>g</sub> (°C)
0	74.3
0.5	75.5
1	79.9
1.5	83.9
2.5	76.4
4	76.5

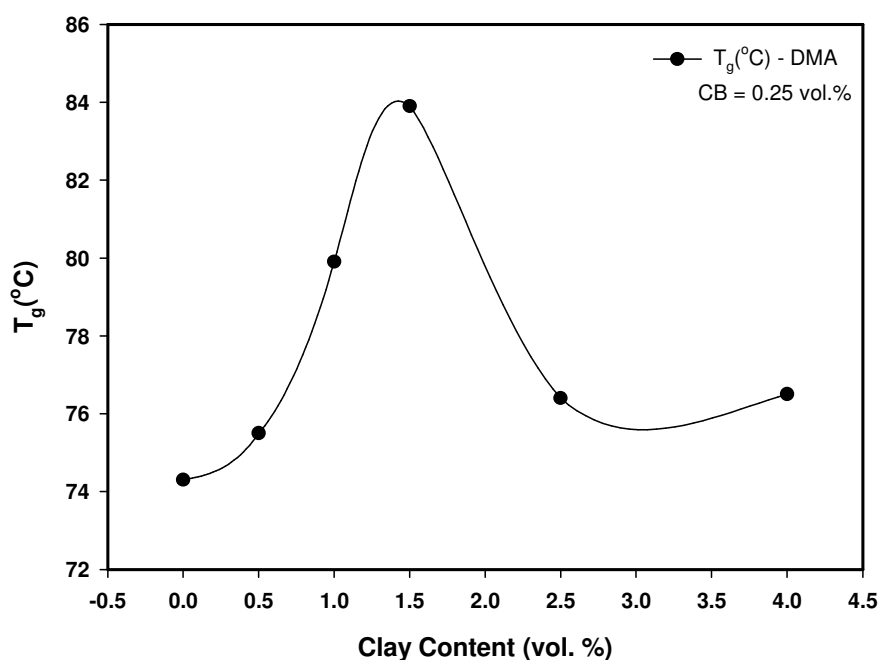


Figure 4.17. Influence of clay content on the glass transition temperature of nanocomposites measured by DMA.

The nanocomposites show higher T<sub>g</sub> compared to that of neat epoxy (74.3 °C). The T<sub>g</sub> values are increased up to 2.5 vol % clay loading with increasing clay content. Maximum increase in T<sub>g</sub> (9.6 °C) is observed by the incorporation of 1.5 vol. % clay. This increase is related to the barrier effect of exfoliated clay layers that hinder the benzene ring mobility of epoxy. However further addition of clay into the nanocomposites causes a decline in the glass temperature, also related to the intercalated zones present in the exfoliated nanocomposites with 2.5 vol. % and 4 vol.% clay loading.

Variation of T<sub>g</sub> values measured by DSC was dissimilar to the ones measured by DMA as seen in Table 4.3 and Figure 4.18 According to DSC measurements,

incorporation of clay increased the  $T_g$  regardless of clay content. The  $T_g$  values of the nanocomposites did not show noticeable change among each other compared with their increase over neat epoxy. Isik et al. (2003) also observed that the glass transition temperatures of nanocomposites were increased with increasing clay content. The authors explained this behaviour in terms of restricted mobility of polymer chains due to the clay and polymer interaction. Figure 4.19 shows the DSC thermograms of neat epoxy and carbon black-layered clay/epoxy nanocomposites. According to this figure a broad hump was formed with increasing clay content shifting the  $T_g$  values higher.

Table 4.3.  $T_g$  values of carbon black-layered clay/ epoxy nanocomposites measured by DSC

Clay Content (vol. %)	$T_g$ ( $^{\circ}\text{C}$ )
0	73.1
0.5	79.9
1	80.9
1.5	81.4
2.5	80.8
4	80.3

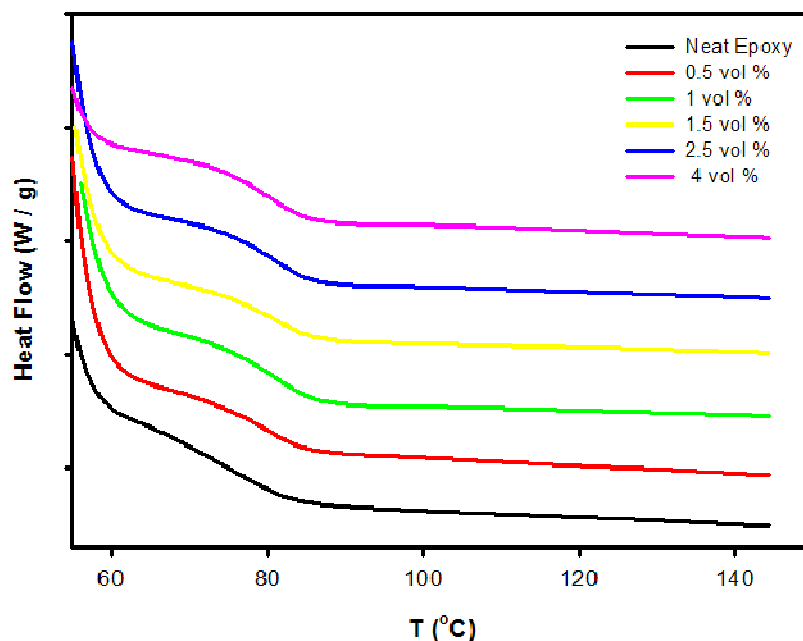


Figure 4.18. DSC Thermograms of carbon black-layered clay /epoxy nanocomposites

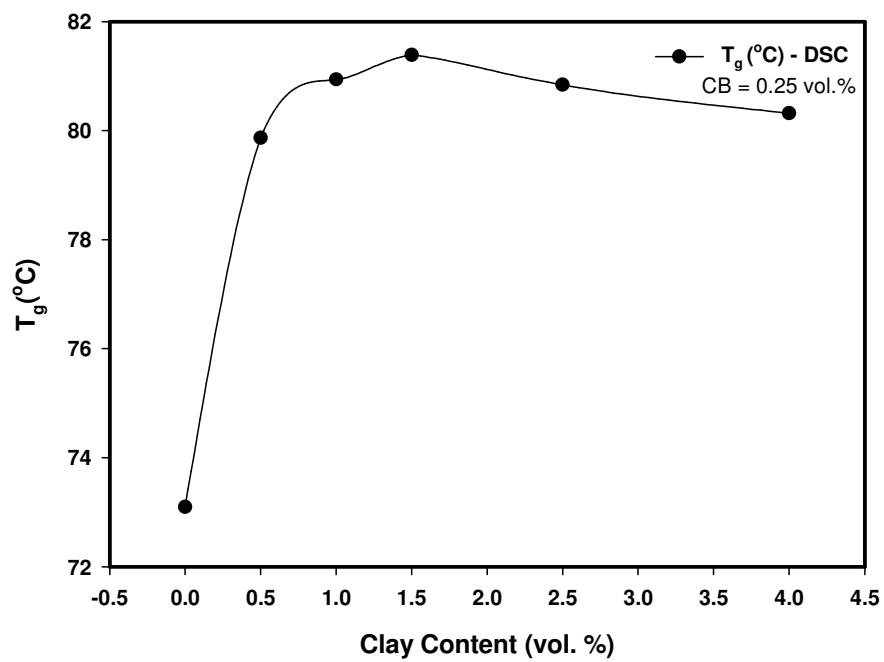


Figure 4.19. Influence of clay content on the glass transition temperature of nanocomposites measured by DSC



## CHAPTER 5

### CONCLUSIONS

In this study carbon black (CB)-layered clay/epoxy nanocomposites were developed. The layered clay content varied from 0.5 vol. % to 4 vol%, whereas the CB concentration was kept constant slightly above the percolation threshold concentration (0.25 vol. %) to introduce electrical conductivity to nanocomposites. The percolation threshold concentration (0.2 vol. %) was determined by synthesizing CB / epoxy composites with varying clay content then measuring the resistivities by four point probe method at room temperature.

Electrical conductivity results revealed that direct current conductivity decreases with clay addition into CB/ epoxy composites. Nanocomposite with only 0.5 vol. % of clay content was electrically conductive ( $\log(\sigma_{dc})=10^{-5}$ ), whereas the other concentrations above it was not conductive. From XRD patterns of modified and unmodified clay, it was observed that modification of clay by ditallow-dimethylamine increased the interlayer spacing from 1.2 nm to 1.8 and 3.7 nm. The X-ray diffraction profiles of the nanocomposites showed no sharp diffraction peaks that implied some extent of exfoliation in the morphology. Tensile modulus values for the nanocomposites up to 1.5 vol.% clay content remained almost constant at about 4.8 GPa. An improvement of about 28 % was observed with an addition of 1.5 vol.% of clay as compared to neat epoxy (3.7 GPa), At higher concentrations, modulus values decreased slightly. The tensile strength values decreased with increasing clay content. With 0.5 vol.% clay addition tensile strength decreased to 73 MPa, which corresponds to a reduction of 9 % relative to the value for neat epoxy (80 Mpa). It was found that the flexural modulus values were not affected by the clay addition. However, flexural strength values, of the nanocomposites decreased as compared to neat epoxy. Maximum reduction was observed with 1.5 vol.% clay addition in which flexural strength value decreased to 90 MPa. A reduction about 35 % was observed relative to neat epoxy (137 MPa). Thermogravimetric analysis results revealed that, on the basis of initial degradation temperatures ( $T_5$ ), the thermal stability of the pure epoxy was found to slightly increase with the increasing clay content, except with 2.5 vol. % filler loading.

The incorporation of 4 vol. % clay in neat epoxy increased the 5% decomposition temperatures by 7°C. In addition to these results the nanocomposites showed higher char content at 550°C with increasing filler content. In terms of dynamic mechanical analysis, storage modulus of nanocomposites slightly improved with clay addition as compared to neat epoxy. However, storage modulus values remained almost constant with further clay loading. The modulus enhancement was around 10% with the addition of fillers relative to neat epoxy. DMA analysis revealed that nanocomposites show higher T<sub>g</sub> compared to that of neat epoxy (74.3 °C). Maximum increase in T<sub>g</sub> (by 9.6 °C) was observed by the incorporation of 1.5 vol. % clay. However, further addition of clay (2.5 vol. % and 4 vol.% clay loading) into the nanocomposites decreased the T<sub>g</sub> of nanocomposites.

Consequently, the attempt of producing more functional nanocomposite both electrically conductive and having enhanced thermal and mechanical properties have resulted in success only with 0.5 vol.% clay loaded nanocomposites. Other compositions also showed some increase on mechanical and thermal properties. However they were not electrically conductive and their increase in terms of mechanical and thermal properties did not show noticeable change among each other. Therefore, 0.5 vol% clay loading was regarded as the optimum concentration for producing electrically conductive carbon black (0.25 vol. %)- layered clay/ epoxy nanocomposite with enhanced thermal and mechanical properties.

## REFERENCES

- Ahmadi, S. J., Y. D. Huang and W. Li. 2004. Review: Synthetic Routes, Properties and Future Applications of Polymer-layered Silicate Nanocomposites. *Journal of Materials Science* 39:1919-1925.
- Alexandre M. And P. Dubois. 2000. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Materials Science and Engineering* 28:1-63.
- Akbari, B. and R. Bagheri. 2007. Deformation mechanism of epoxy/clay nanocomposite. *European Polymer Journal* 43:782-788.
- Basara C., U. Yilmazer and G. Bayram. 2005. Synthesis and characterization of epoxy based nanocomposites. *Journal of Applied Polymer Science* .98:1081-1086.
- Bader, M. G., W. Smith, A. B. Isham, J. A. Rolston, A. B. Metzner, eds. 1990. *Processing and Fabrication Technology*. Basel: Technomic Publishing.
- Becker, O., R. Varley and G. Simon. 2002. Morphology, thermal relaxations and mechanical properties of layered silicate nanocomposites based upon high-functionality epoxy resins. *Polymer* 43: 4365-4373.
- Dean, D., R. Walker, M. Theodore, E. Hampton and E. Nyairo. 2005. Chemorheology and properties of epoxy/layered silicate nanocomposites. *Polymer* 46:3014-3021.
- Donnet, J. B., R. C. Bansol, and M. J. Wang, eds. 1993. *Carbon Black*. New York: CRC Press.
- Evonik Industries Degussa. 2008. Pigment blacks <http://www.degussafp.com/> (Accessed April 5, 2008).
- Flandin, L., Y. Bréchet, G. R. Canova and J. Y. Cavaillé. 1999. AC electrical properties as a sensor of the microstructural evolution in nanocomposite materials: experiment and simulation. *Modelling Simulation. Materials Science. Engineering* 7: 865-874
- Feller, J. F., S. Bruzard and Y. Grohens. 2004. Influence of clay nanofiller on electrical and rheological properties of conductive polymer composite. *Materials Letters* 58: 739-745.
- Fu, S. Y., X. Q. Feng, B. Lauke and Y. W. Mai. 2008. Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites. *Composites: Part B* 39:933-961.

- Gao, F., 2004. Clay polymer composites; The story *Materials Today* 7(11):50-55.
- Gatos, K.G. and J. Karger-Kocsis. 2005. Effects of primary and quaternary amine intercalants on the organoclay dispersion in a sulfur-cured EPDM rubber. *Polymer* 46:3069-3076.
- Gilman, J. W. 1999. Flammability and Thermal Stability Studies of Polymer Layered Silicate Clay/ Nanocomposites. *Applied Clay Science* 15: 31-49.
- Gu, A. and G. Liang. 2003. Thermal degradation behaviour and kinetic analysis of epoxy/montmorillonite nanocomposites. *Polymer Degradation and Stability* 80: 383-391.
- Isik, I., U. Yilmazer and G. Bayram. 2003. Impact Modified Epoxy/ Montmorillonite Nanocomposites: Synthesis and Characterization. *Polymer* 44: 6371-6377.
- Kaya, E. D. 2006. Development of epoxy/clay nanocomposites. *İYTE Thesis of Master of Science*
- Ke, Y.C. and P. Stroeve, eds. 2005. *Polymer-Layered Silicate and Silica Nanocomposites*. New York: ELSEVIER Books.
- Kotsilkova R. 2005. Processing–Structure–Properties Relationships of Mechanically and Thermally Enhanced Smectite/Epoxy Nanocomposites. *Journal of Applied Polymer Science* 97(6):2499–2510.
- Konishi, Y. and M. Cakmak. 2006. Nanoparticle induced network self-assembly in polymer–carbon black composites. *Polymer* 47: 5371-5391.
- Kupke M., H. P. Wentzel and K. Schulte. 1998. Electrically conductive glass fibre reinforced epoxy resin. *Materials Research Innovations* 2:164-169.
- Le Pluart, L., J. Duchet, H. Sautereau, P. Halley and J. F. Gerard. 2003. Rheological properties of organoclay suspensions in epoxy network precursors. *Applied Clay Science* 25(3-4): 207-219.
- Lu, H. J., G. Z. Liang, X. Ma, B. Y. Zhang and X. B. Chen. 2004. Epoxy/clay nanocomposites: further exfoliation of newly modified clay induced by shearing force of ball milling. *Polymer International* 53: 1545-1553.
- Marchant, D. and K. Jayaraman. 2002. Strategies for Optimizing Polypropylene-Clay Nanocomposite Structure. *Industrial & Engineering Chemistry Research* 41: 6402-6408.

- Mitsubishi Chemical. 2008. Three Main Properties of Carbon Black <http://www.carbonblack.jp> (Accessed May 5, 2008).
- Mohan, T. P., M. R. Kumar and R. Velmurugan. 2006. Mechanical and barrier properties of epoxy polymer filled with nanolayered silicate clay particles. *Journal of Materials Science* 41: 2929-2937.
- Nigam, V., D. K. Setua, G.N. Mathur and K.K. Kar. 2004. Epoxy-Montmorillonite Clay Nanocomposites: Synthesis and Characterization. *Journal of Applied Polymer Science* 93:2201-2210.
- Okada, A., M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi, O. Kamigato. 1990. Nylon 6 –clay hybrid. *Materials Research Society Proceedings* 171:45-54.
- Okada, A. and A. Usuki. 2006. Twenty Years of Polymer-Clay Nanocomposites. *Macromolecular Materials & Engineering* 291 :1449-1476.
- Park, J. H. and S.C. Jana. 2003. Mechanism of Exfoliation of Nanoclay Particles in Epoxy-Clay Nanocomposites. *Macromolecules* 36:2758-2768.
- Park, S. J., D. I. Seo and J. R. Lee. 2002. Surface Modification of Montmorillonite on Surface Acid–Base Characteristics of Clay and Thermal Stability of Epoxy/Clay Nanocomposites. *Journal of Colloid and Interface Science* 251 :160-165.
- Pascualt, J. P., H. Sautereau and J. Verdu, eds. 2002. *Thermosetting Polymers*. New york: Marcel Dekker.
- Qi, B., Q.X. Zhang, M. Bannister and Y. W. Mai. 2006. Investigation of the mechanical properties of DGEBA-based epoxy resin with nanoclay additives. *Composite Structures*. 75: 514-519.
- Ratna, D., N. R. Manoj, R. Varley, S. Raman and G. P. Simon. 2003. Clay-reinforced epoxy nanocomposites. *Polymer International* 52: 1403-1407.
- Ray, S.S. and M. Okamoto. 2003. Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in Polymer Science* 28: 1539-1641.
- Tjong, S.C. 2006. Materials Science and Engineering. *Structural and Mechanical Properties of Polymer Nanocomposites* 53(3-4) : 73-197.
- Vaia, R.A., R.K. Teukolsky and E.P. Giannelis. 1994. Interlayer Structure and Molecular Environment of Alkylammonium Layered Silicates. *Chemistry of Materials* 6: 1017-1022.

- Velmurugan R. and T. P. Mohan. 2004. Room Temperature Processing of Epoxy-Clay Nanocomposites. *Journal of Materials Science*. 39: 7333-7339.
- Wang, K., L. Chen, M. Kotaki and C. He. 2007. Preparation, microstructure and thermal mechanical properties of epoxy/crude clay nanocomposites. *Composites: Part A*. 38: 192-197.
- Wang, S., Y. Hua, Q. Zhongkaic, Z. Wang, Z. Chen and W. Fan. 2003. Preparation and flammability properties of polyethylene/clay nanocomposites by melt intercalation method from Na<sup>+</sup> montmorillonite. *Materials Letters* 57 : 2675-2678.
- Wang, L., K. Wang, L. Chen, Y. Zhang and C. He. 2006. Preparation, morphology and thermal/ mechanical properties of epoxy/nanoclay composite. *Composites: Part A* 37: 1890-1896.
- Wang, J. and S. Qin. 2007. Study on the thermal and mechanical properties of epoxy–nanoclay composites: The effect of ultrasonic stirring time: *Materials Letters* 61: 4222-4224.
- Wikipedia Encyclopaedia. 2008. Carbon black. <http://en.wikipedia.org/> (Accessed April 3, 2008).
- Yasmin, A., J. L. Abot and I. M. Daniel. 2003. Processing of clay/epoxy nanocomposites with a three-roll mill machine. *Materials Research Society Symposium Proceedings* 740:75-83.
- Yasmin, A., J. L. Abot and I. M. Daniel 2003. Processing of clay/epoxy nanocomposites by shear mixing. *Scripta Materialia* 49: 81-86.
- Yasmin, A., J. Luo, J. L. Abot and I. M. Daniel, 2006. Mechanical and thermal behavior of clay/epoxy nanocomposites. *Composites Science and Technology* 66: 2415-2422.
- Zhang, W., R.S. Blackburna, and A.A. Dehghani-Sanijb, 2007. Effect of silica concentration on electrical conductivity of epoxy resin–carbon black–silica nanocomposites. *Scripta Materialia*. 56:581-584.
- Zilg, C., R. Thomann, J. Finter and R. Mulhaupt. 2000. The influence of silicate modification and compatibilizers on mechanical properties and morphology of anhydride-cured epoxy nanocomposites. *Macromolecular Materials & Engineering*. 280(81):41-46.
- Zhou, Y., F. Pervin, M.A. Biswas, V.K. Rangari and S. Jeelani, 2006. Fabrication and characterization of montmorillonite clay-filled SC-15 epoxy. *Materials Letters*. 60:869-873

Zois, H., L. Apekis, and M. Omasova, 1999. Electrical Properties and Percolation Phenomena in Carbon Black Filled Polymer Composites. 10<sup>th</sup> International Symposium on Electrets 529-532.