CONDUCTIVE COATING MATERIALS

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ABSTRACT

CONDUCTIVE COATING MATERIALS

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In this study, electrically conductive coating materials composed of epoxy resin and carbon black (CB) were prepared by applying two different mixing techniques (Grinding and Mechanical Mixing). The effect of carbon black addition, ultrasonication, mixing type and surface modification of carbon black on the morphologies, electrical and mechanical properties of the composites were investigated.

According to test results, Grinding Method is much more efficient and for this method, percolation concentration was found as 2 vol %. The electrical resistivity value obtained at this composition is around 10^7 ohm.cm. Also, for the samples prepared by Grinding Method, the hardness increased by adding conductive filler, but the impact energy and adhesive strength decreased with increasing carbon black content.

Ultrasonication was applied to the samples containing 2 vol % CB obtained by Grinding Method to reduce the electrical resistivity further. Three different ultrasonic mixing times were tried, however, no positive effect was observed on electrical and mechanical properties.

Since the addition of carbon black has a negative effect on the processability of the mixture, it was aimed to obtain desired conductivity value at lower percolation concentration by modifying carbon black surface with different silane coupling agents and formamide. The best result in terms of electrical conductivity was obtained for the materials produced with formamide treated carbon black by Grinding Method. At 1 vol % concentration, the electrical resistivity was found as approximately 10^6 ohm.cm which is three orders smaller than the resistivity of materials prepared with untreated carbon black.

Keywords: epoxy, carbon black, electrical conductivity, mechanical properties

ÖZ

İLETKEN KAPLAMA MALZEMELERİ

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Yüksek Lisans, Kimya Mühendisliği
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Bu çalışmada, iki değişik karıştırma yöntemi (öğütme ve mekanik karıştırma) uygulanarak epoksi reçine ve karbon siyahından oluşan iletken kaplama malzemeleri hazırlanmıştır. Karbon siyahı ilavesinin, ultrasonik karıştırma zamanının, kullanılan iki değişik karıştırma yönteminin ve karbon siyahının yüzey değişikliğinin yapısal, elektriksel ve mekanik özellikler üzerine olan etkileri incelenmiştir.

Deney sonuçlarına göre, öğütme yönteminin çok daha verimli olduğu anlaşılmıştır ve bu yöntem uygulanılarak elde edilen malzemede kritik karışım değeri hacimce % 2 olarak bulunmuştur. Bu karışımla elde edilen malzemenin elektriksel direnci yaklaşık 10^7 ohm.cm'dir. Ayrıca, yine öğütme yöntemi ile elde edilen örneklerde karbon siyahı miktarının artışıyla, sertlik değerleri artmış fakat çarpma enerjisi ve yapışma kuvveti azalmıştır.

Elektriksel direnci daha fazla miktarda azaltmak için öğütme yöntemi ile hazırlanan hacimce % 2 karbon siyahı içeren örneklere ultrasonik karıştırma uygulanmıştır. Üç farklı ultrasonik karıştırma zamanı denenmiş, fakat elektriksel özellikler üzerinde olumlu bir etki gözlenmemiştir.

Karbon siyahı katılması malzemenin işlenebilirliğini zorlaştırdığı için, karbon siyahının yüzeyini değişik silan bağlayıcıları ve formamid ile değiştirerek istenen elektriksel iletkenliği daha düşük kritik bileşimlerde elde etmek amaçlanmıştır. Eletriksel iletkenlik açısından en iyi sonuç, öğütme yöntemi kullanılarak hazırlanan ve formamid ile yüzeyi değiştirilen karbon siyahı ile üretilen malzemede elde edilmiştir. Hacimce % 1 karbon siyahı derişiminde elektriksel direnç yaklaşık 10^6 ohm.cm olarak bulunmuştur, bu değer yüzeyi modifiye edilmemiş karbon siyahı ile üretilen malzemenin elektriksel direncinden 1000 kat daha küçüktür.

Anahtar Sözcükler: epoksi, karbon siyahı, elektriksel iletkenlik, mekanik özellikler

To my family

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INTRODUCTION

During the past two decades, the application of electrically conductive coatings has gained an accelerated reputation. One of the main applications is to provide shielding for all types of electronics equipment in order to prevent radiofrequency (RFI) and electromagnetic (EMI) interference. Almost all electrical and electronics devices are vulnerable to this type of interference which can result in various equipment fault. Electrically conductive coatings also offer antistatic protection. Anti-static coatings are increasingly applied in the coating of oil-storing or transporting facilities, floor coating of semiconductor manufacturing factory, computer room, hospitals etc. where static electricity can be a cause of problems such as fire and explosions.

Although there are numbers of coating methods which are suitable for several applications, especially paint coatings have hold a prominent position in this market. This has been due to the excellent performance of these coatings as well as the simplicity and versatility of the techniques that are used to apply them.

Electrically conductive materials used for coating applications are generally produced by incorporating electrically conductive fillers into the polymer resin. Epoxy is widely used among polymeric resins because of its outstanding mechanical and thermal properties. It has excellent adhesion properties, low shrinkage and good chemical resistance.

Carbon black is mostly used as conductive filler because of its metallic conductivity character to enhance the electrical conductivity of the materials. It is composed of spherical primary particles fused in aggregates like graphite structure.

Electrical conductivity of polymer composites increases by several orders of magnitude when the critical value of conductive filler is added to the polymer matrix. This is known as percolation threshold phenomena and the minimum critical amount of filler which must be added to the system is called as percolation concentration. At percolation threshold concentration, conductive filler can form chain structure in the polymer matrix. Electrical properties of conductive polymer composites strongly depend on electrical resistivity of composite constituents, filler composition, filler size and dispersion, and process parameters at which the composites are prepared.

In the literature, there have been several studies about electrically conductive polymer composites produced with epoxy matrix and different conductive filler [1, 2]; however, there is a lack of use of mixing technique called Grinding Method to prepare the electrically conductive composites for coating applications. In addition, different chemicals are chosen to modify the surface of carbon black to improve the final properties of the composites.

The objective of the study is to produce electrically conductive coating materials which have a volume resistivity of between 10^6 – 10^{10} ohm.cm suitable for antistatic applications at low filler concentrations. It is also aimed to improve electrical and mechanical properties of the composites by chemical treatment of the carbon black surfaces.

In this study, carbon black/epoxy composites were prepared by using “Grinding Method”. In order to investigate the effect of carbon black concentration, epoxy resin was filled with carbon black at different concentrations while keeping processing parameters constant. Then, the effects of ultrasonic mixing were studied at constant carbon black concentration and other process parameters. In addition, another mixing method called as “Mechanical Mixing Method” was applied to compare the two preparation methods. Finally, carbon black surfaces were modified by using four different coupling agents and also formamide. The effects of surface treatment on final properties of the materials were also studied by producing composites having same amount of carbon black at constant process conditions of the Grinding Method.

The morphology of the fracture surfaces of the samples were observed by Scanning Electron Microscope (SEM). X-Ray Photoelectron Spectroscopy (XPS) was used to determine the surface chemistry of the neat and treated carbon black. Mechanical properties of the materials including tensile strength, tensile modulus, elongation at break, impact energy, hardness and adhesion strength were also evaluated.

CHAPTER 2

BACKGROUND

2.1 Composites

A composite is a material system consisting of two or more components that are insoluble in each other on a macro-scale, with two or more distinct phases having recognizable interfaces between them. Composite materials show the superior mechanical performance that can not be achieved by any of the components acting alone, as a result of the principle of combined action [3, 4]. Composites are combination of at least two materials in which one of the materials, called reinforcing phase, is in the form of fibers, sheets or particles and is incorporated in the other materials called the matrix phase. The reinforcing materials are stiffer, stronger and harder than the matrix materials in most cases. If the composite is designed correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve a combination of desirable properties not available in any single conventional material [5].

The properties of composites depend primarily on the properties of the each phase, ratio of reinforcing materials to matrix and also the geometry and orientation of the reinforcing components [3]. Characteristic high strength and stiffness to weight ratios make composite structures ideal for many applications especially where movement is involved, such as automobiles, ships, and aerospace crafts [6].

According to the matrix material used, composites can be categorized as metal-matrix composites (MMC), ceramic-matrix composites (CMC), polymer-matrix composites (PMC), carbon-carbon composites (CCC), intermetallic composites (IMC) or hybrid composites [7].

2.2 Polymer Matrix Composites

The mostly used matrix materials for composites are polymers due to the versatility of their mechanical performance and also advantages of processing that does not require high pressures and high temperatures [3].

The polymer matrices can be divided into two main groups, thermosets and thermoplastics. The two alternatives differ profoundly in terms of manufacture, processing, physical and mechanical properties of the final product and the environmental resistance of the resultant composite [8].

Thermoset polymers (epoxy, polyester, polyimides, etc.) have individual chains which are chemically linked by covalent bonds during curing by subsequent chemical or thermal treatment [9]. Thermoset materials can be formed only one time as the chemical reaction is irreversible. This stability gives these materials good strength and heat resistance at a relatively low cost.

Thermoplastic polymers (polyolefins, polystyrene, polyamides, etc.) are formed by changing their physical state. In processing, they are softened by heat until they melt, formed into the desired shape, and resolidified by cooling them until they "freeze". Thermoplastics can be repeatedly remelted and reformed [10].

2.3 Conductive Polymer Composites

Conductive polymer composites have a great importance among all engineering materials. However, for a long time, polymer materials were excluded from a number of applications that required electrical conductivity. This situation altered radically when it was observed that the introduction of some kind of carbon black into elastomer produced a new property, electrical conductivity [11].

The study of this phenomenon has shown that insulating polymer matrices become electrically conductive when certain amount of conductive filler such as carbon black, graphite, metallic powder etc. is added [11].

The theory behind this phenomenon has been of both theoretical and experimental interest for a long time. Concerning the interpretation of the results, the most useful model is the percolation theory which is applied to describe the insulator-to-conductor transitions in composites made of conductive filler and insulating matrix [12].

In percolation theory, the most important parameter is the percolation threshold concentration which is defined as the minimum amount of conductive filler that must be added to insulating matrix to cause the onset of electrical conductivity [13].

The most significant parameter that affects the electrical conductivity of the composite is the filler distribution within the matrix, which results from processing conditions, particle and particle/macromolecule interaction and special parameters such as shape of conductive filler [14].

While considering the mechanism of the electrical conductivity of the composite, two main mechanisms should be clarified;

1- current passing through continuous chains of carrier (direct contact)
2- overcoming by charge carriers of the barrier caused by thin polymer and other layers between filler particles (tunneling)

If the filler content is not enough for the formation of continuous current conductive paths, tunneling mechanism proceeds through the polymer matrix between the conductive filler particles. It was stated that, electrons can be carried by tunneling directly from one electrode to another at insulator film thicknesses below 3-5 nm. Starting from the certain concentration of the filler that is called percolation threshold, the distribution of the electrically conductive filler particles forms the continuous current conductive paths due to the direct contact of the filler with each other [11].

From the analysis of the electrically conductive polymer composites containing carbon black as conductive filler, it was shown that, chemical linkages between filler and polymer has a critical role in the mechanism of conductivity.

The investigations done by ESR have shown that there are covalent bonds between carbon black particles and polymer molecules. Consequently, these bonds might allow free motion of charge carriers along the chains formed [11].

The particle size and the agglomeration structure of the carbon black are also important for electrical conductivity of the composites. Small size of particle is a required criterion for carbon black particles to grow a conductive path at lower concentrations. Since, it is difficult to provide well distribution of filler, conductive composite requires a large amount of filler particles to build the conductive chains in polymer matrix.

The applications of electrically conductive polymer composites are based on the analysis of both advantages and shortcomings. Besides the electrical conductivity, the advantages of electrically conductive polymer composites are their low specific weight, high stability against the chemicals (such as acids, alkali, etc.) and simplicity of the processing into the articles. For example, electrically conductive polymer composite processing demands lower energy consumption than metal processing [11].

Electrically conductive polymer composites are used in many applications, because these materials combine electrical conductivity with the ability to be formed into complex shapes [15]. An electrically conductive composite can be used in static dissipative, slightly electrically conductive (e.g., fuel gauges, etc.), or EMI (Electromagnetic Interference)/RFI (Radio Frequency Interference) shielding applications (computer and cellular phone housings, etc) and also in conductive coating applications.

Electromagnetic radiation shielding, which is the process of limiting the coupling of an electromagnetic field between two locations, becomes more important with global spreading of devices, machines and apparatus which are exposed to electromagnetic radiation. Investigation of new materials have shown that promising shielding performance could be achieved with composites containing an electrically non-conducting polymer matrix filled with conductive fillers, such as metal powders or carbon based materials [16].

Static electricity is another problem for the articles and it directly depends on the surface resistance of the materials. It should be noticed that “static” in this case does not mean “no movement”, rather it means “charge imbalance” because electrons move away from where they are, so that one becomes more negatively charged, and another more positively charged. If the materials are not grounded, they consequently will accumulate an adequate electrical charge capable of producing a static spark which can ignite flammable gases and dusts. Finally, it can cause fire and explosion especially in tanks, aircraft and petrochemical plant [17].

The generation of static electricity cannot be prevented because of its origin; however, the accumulation and discharging without control can be prevented by using electrically conductive composites. Especially, conductive coatings are becoming increasingly popular for the control of static electric discharging [18].

2.3.1 Self-Conductive Polymers

Electrically conductive polymers can be classified as, [11]

a) Filled (mentioned above)
b) Self-conducting ones that conduct electric current due to their structure

The characteristic of self-conductive polymers which makes them conductive is the presence of conjugated π-bonds where delocalization occurs and their conductivity can be changed by several orders of magnitude by doping. The process of introducing charge carriers is called as “doping” [9]. There are two types of doping process; p-type and n-type (see Figure 2.1). p-type doping is the partial oxidation of the polymer by a chemical oxidant and results in decreasing of the number of electrons. These missing electrons form “holes” into which another electron can move [19].

On the other hand, n-type doping is the partial reduction of the polymer by a chemical reducing agent with the injection of “electrons”. Since the required ionization energy is so small, these extra electrons can easily move and become conduction electrons [19].

Consequently, in the undoped state, these conjugated polymers are typically semiconducting, the doping process incorporates charge carriers (either electrons or holes), and if these are stable, the polymer becomes electrically conducting to a level that is proportional to its doping level [11].

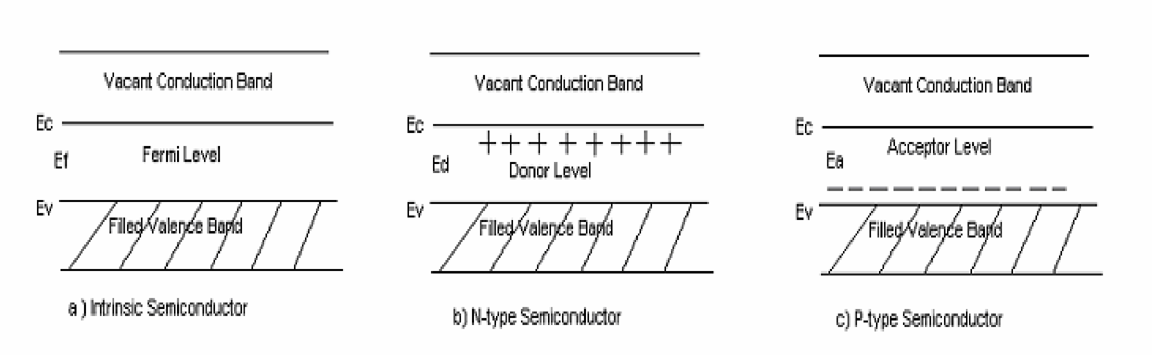


Figure 2.1 Energy Band Sheme for a) Intrinsic Semiconductor, b) N-type Semiconductor and c) P-type Semiconductor [19].

2.4 Polymeric Resins

2.4.1 Epoxy Resin

Epoxy resins are the one of the major thermosetting industrial plastics that were synthesized by Pierre Castan in Switzerland late in 1930s [20]. The epoxy group also known as oxirane contains an oxygen atom bonded with two carbon atoms as seen in Figure 2.2.

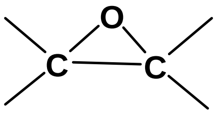


Figure 2.2 Chemical structure of simple oxirane

The most outstanding property of the epoxy resins is their excellent adhesion which is because of the secondary hydroxyl group placed along the molecular chain. Moreover, cured epoxy resins have good mechanical properties, superior dimensional stability, and good resistance to heat and chemical attack. Since epoxy resins give off no by-product, such as water, during the curing, they exhibit unusually low shrinkage [21].

Epoxy resins are formed from a long chain molecular structure similar to vinylester with reactive sites at either end. However, in the epoxy resin, these reactive sites are derived by epoxy groups instead of ester groups. The absence of ester groups means that the epoxy resin has particularly good water resistance. The epoxy molecule also contains two ring groups at its centre which are able to absorb both mechanical and thermal stresses better than linear groups and therefore give the epoxy resin very good stiffness, toughness and heat resistant properties [22].

Because of these unusually valuable properties, epoxy resins are mostly used in various of industrial applications such as adhesives, construction materials (flooring, paving and aggregates), composites, casting compounds, sealants, varnishes and paints, as well as laminating resins.

Epoxy resins can be characterized in terms of epoxide equivalent, hydroxyl equivalent, softening point, average molecular weight and heat distortion temperature [23].

The major part of these resins is derived from bisphenol-acetone and epichlorohydrin [24].

Epichlorohydrin is a colorless, mobile liquid with a characteristic chloroform-like, irritating odor. It is extremely reactive and usually combines through the epoxy group with a substance containing an active hydrogen atom [20]. The structural formula of epichlorohydrin is given in Figure 2.3.

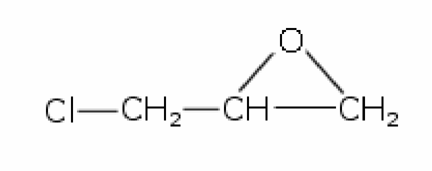


Figure 2.3 Chemical structure of epichlorohydrin molecule

Bisphenol A or bis (4-hydroxyphenyl) is an organic compound composed of two phenol rings connected by a methyl bridge, with two methyl functional groups attached to the bridge. The hydroxyl functional group on each phenol is *para-* to the connecting methyl bridge (see Figure 2.4).

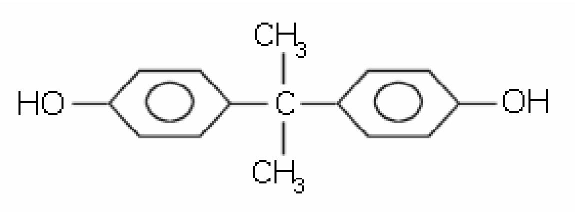


Figure 2.4 Chemical structure of Bisphenol A

A general synthesis for making Bisphenol A is a condensation reaction of acetone and phenol together with hydrochloric acid, which acts as a catalyst as illustrated in Figure 2.5 [25].

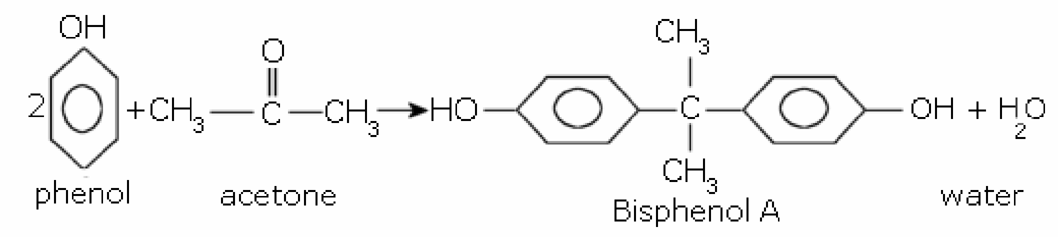


Figure 2.5 Formation of Bisphenol A [20]

Diglycidyl Ether of Bisphenol A (DGEBA), which is the widely used epoxy resin, is synthesized by reacting excess epichlorohydrin with bisphenol A in the presence of an alkaline catalyst (see Figure 2.6). The whole structure of DGEBA is also given in Figure 2.7

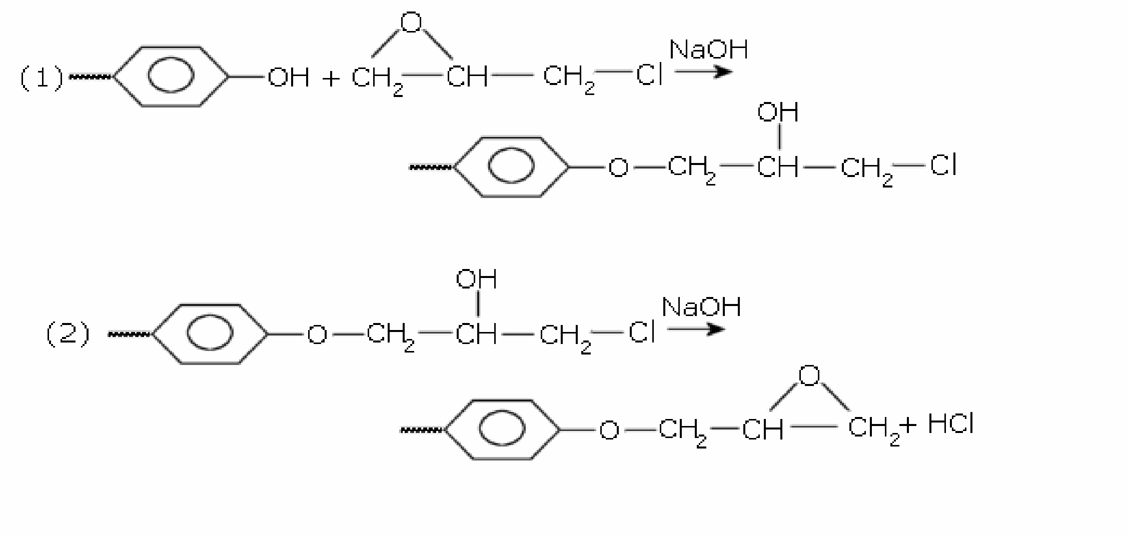


Figure 2.6 Two-step reaction of DGEBA formation [20].

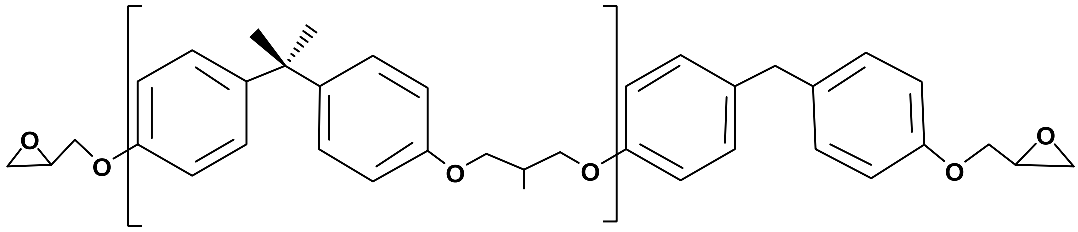


Figure 2.7 Idealized chemical structure of DGEBA

Epoxy resins differ from polyester resins in that they are cured by a 'hardener' rather than a catalyst. The hardener, often an amine, is used to cure the epoxy by an “addition reaction” where both materials take place in the chemical reaction. The chemistry of this reaction means that there are usually two epoxy sites binding to each amine site. This forms a complex three-dimensional molecular structure.

2.4.2 Curing Agents

The one of the valuable properties of epoxy resins is their ability to react with the epoxy end-groups to generate three dimensional networks providing the final material with rigidity, hardness and the inability to reflow. This curing reaction occurs by addition of a chemically active reagent known as curing agent or hardener which has active hydrogen attached to nitrogen, oxygen or sulphur [20].

The curing reactions take place by means of three reactions;

1. Direct linkage between epoxy groups
2. Linkage of epoxy groups with aromatic or aliphatic hydroxyls
3. Crosslinkage with the curing agent through various radicals.

The curing reactions determine the percentage of the curing agent that is needed. If the curing agent is of crosslinking type, it will be noticed that there is a calculated stoichiometric ratio which theoretically gives the exact amount of curing agent required for complete consumption of the reactive groups in the resin.

The widely used curing agents are usually amine based hardeners and they can be aliphatic, aromatic and cycloaliphatic.

Aliphatic amines give fast cure at ambient temperature and provide satisfactory properties for a variety of commercial applications. They are relatively moisture insensitive and resistance to chemicals. The mostly used aliphatic amine is diethylene triamine (DETA). Its chemical structure is given in Figure 2.8.

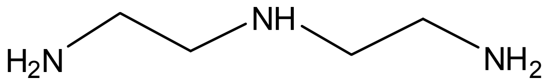
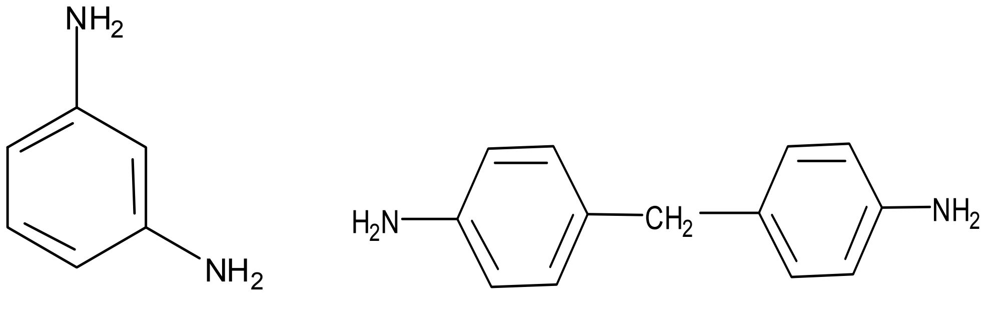


Figure 2.8 Chemical structure of DETA

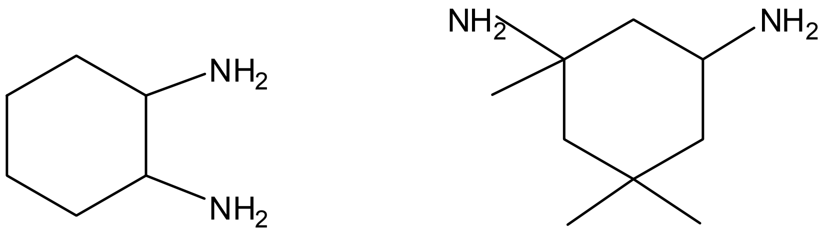
Aromatic amines have an advantage over the aliphatic ones; they provide a significant increase in heat-distortion temperature of the cured resin system. Widely used aromatic amines are Meta-phenylenediamine (MPDA) and Methylene diamine dianilene (MDA) and their chemical structures can be seen in Figure 2.9.



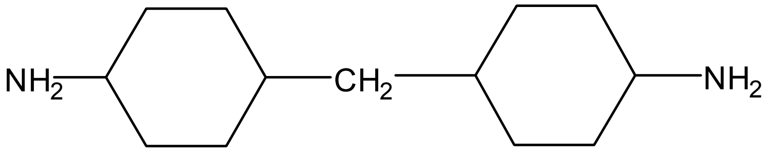
(MPDA) (MDA)

Figure 2.9 Chemical structures of MPDA and MDA

Cycloaliphatic amines cure at low temperature and show good film properties (e.g. excellent gloss). They are resistance to chemicals and water spotting. 1,2, diaminocyclohexane (DACH), Methylenebiscyclohexanamine (4,4'-PACM) and isophoronediamine (IPDA) can be given as examples of cycloaliphatic amines. Their chemical structures are seen in Figure 2.10.



(DACH) (IPDA)



(4,4-PACM)

Figure 2.10 Chemical structures of DACH, IPDA and 4,4-PACM

2.4.3 Polyurethane Resins

Polyurethanes (PUs) are formed by reaction of a polyol (an alcohol with more than two reactive hydroxyl groups per molecule) with a diisocyanate or a polymeric isocyanate in the presence of suitable catalysts and additives by addition polymerization. Its structural formula is represented in Figure 2.11.

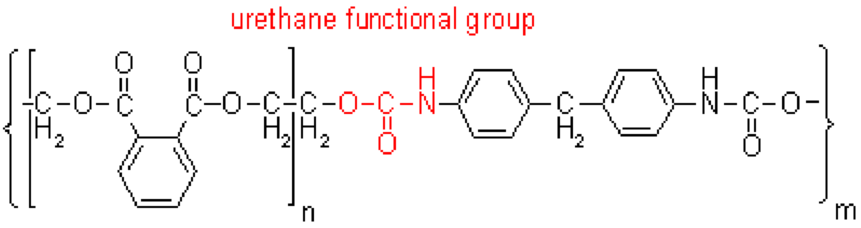


Figure 2.11 Chemical structure of polyurethane

By using additives, catalysts or a blowing agent, PUs can be formulated as a padding, binder, coating, sealant or filler. Since polyurethanes are fully controllable, they can be dispensed as a flexible foam, froth, elastomer, rigid forms, spray, pour or injected material. PU resins are used in many industrial applications such as, adhesives, construction materials, composites, insulation materials, coating, etc. [23].

2.4.4 Acrylic Resins

The polyacrylates, from which acrylic emulsions are made, are a group of polymers obtained by the polymerization of derivatives of acrylic acid and of α-methyl acrylic acid. High quality acrylic resin is a necessary component of high quality acrylic polymer emulsion. Among the acrylic resins, polymethyl methacrylate (PMMA) was first marketed by Rohm and Haas in Germany in 1927. Chemical structure of PMMA can be seen in Figure 2.12.

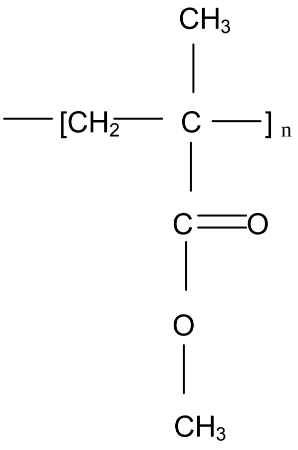


Figure 2.12 Chemical Structure of PMMA

The hardness, flexibility and other mechanical properties of polymers are largely dependent on the chain length and degree of branching of the R-group.

Acrylics are widely used in lighting fixtures because they are slow burning or may be made self-extinguishing, and do not produce harmful smoke or gases in the presence of flame. They are also an essential part of decorative, automotive, car refinish and wood coatings. Other applications of acrylic resins include adhesives and toner resins.

2.5 Fillers

Fillers are ingredients, which are added to the system in order to improve the properties of the composite material such as strength, thermal conductivity, adhesion properties and electrical conductivity for special applications [26]. They can be organic or inorganic, metallic or non-metallic.

2.5.1 Carbon Black

Carbon black is the generic name for the family of materials involving essentially of carbon in the form of spheroidal colloidal particles and it is manufactured industrially by the incomplete combustion or the thermal decomposition of aromatic hydrocarbons. Carbon is the essential component element and its actual content changes from 80-99 % by wt, depending on the manufacturing process and aftertreatment [27].

Carbon black has been produced for over 2000 years. Commercial production began in the 1860s and was promoted by the discovery of its reinforcing effect for rubber in the beginning of twentieth century [28]. It has been used as a pigment and as reinforcing filler in rubber. Besides functioning in rubber, carbon black is also used as a UV stabilizer, antistatic and electromagnetic shielding agent, colorant, ink pigment, thermal antioxidant and conductive filler in plastics [29].

In the manufacturing process of carbon black, natural gas, acetylene oils from coal or petroleum consisting aromatic hydrocarbons can be used as raw materials. Production methods of carbon black are classified according to type of chemical reaction into thermal-oxidation decomposition (furnace, lamp, and channel black) and thermal processes. The main distinction between these two methods is the presence or absence of oxygen [28]. The most widely employed process for carbon black production is the furnace process.

2.5.1.1 Furnace Process

The furnace process is commercially the most important one. This method was introduced in 1922 to produce larger particle sizes. The smaller particle size carbon blacks have been produced in the oil furnace process since 1942. Mainly, the furnace process is based on the thermal-oxidative decomposition of oils [30].

In the oil furnace process (Figure 2.13), feedstock that contains an aromatic liquid hydrocarbon is heated and injected continuously into a high-temperature and high-energy combustion zone of a natural gas-fired furnace, where it is decomposed to form carbon black. In the flame, temperatures reach from 1200 to 1600°C depending on the produced carbon black type. The oxygen in air is not sufficient for the complete combustion of the feedstock; therefore it is partially pyrolyzed to form carbon black. Then, primary quenching is applied by using water to reduce the temperature to 650°C to stop the cracking.

The exhaust gases entraining the carbon particles are further cooled to about 230°C by passage through heat exchangers and direct water sprays. The fabric filter is used to separate carbon black from the gas stream.

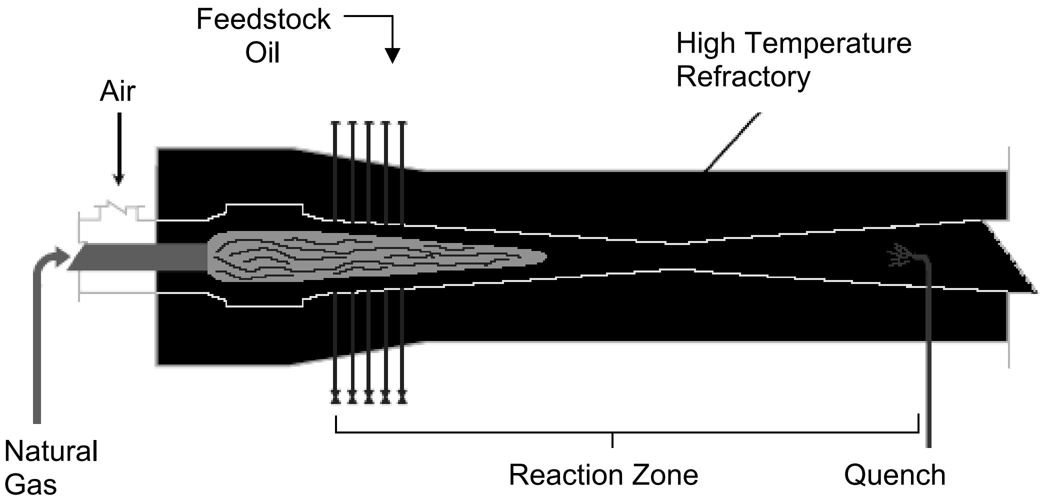


Figure 2.13 Schematic view of Furnace Process

Usually six furnaces are joined to a single collection system and the carbon stream first passes through electrostatic precipitators, then goes to primary, secondary and tertiary cyclone collectors. Thereafter, it is pulverized in a micropulverizer in order to remove grit [30].

According to the feed composition and grade of the carbon black produced, process yields range from 35 to 65 percent. Design of furnace and operating conditions determine the particle size and the other physical and chemical properties of the carbon black. Generally, yields are highest for large particle blacks and lowest for small particle blacks [31].

2.5.1.2 Thermal Process

The thermal process is a cyclic operation in which the feedstock, predominantly natural gas is thermally decomposed into carbon particles and hydrogen at about 1300 °C. The process is carried out in two cylindrical furnaces [30]. The effluent gas from the first reactor is cooled by water sprays to about 125°C, and the carbon black is removed from the hydrogen gas by a fabric filter. The filtered gas (90 percent hydrogen, 6 percent methane, and 4 percent higher hydrocarbons) is cooled, dehumidified, compressed and used as a fuel to heat a second reactor. When the first reactor becomes too cool to crack the natural gas feed, the positions of the reactors are reversed, and the second reactor is used to crack the gas while the first is heated [31].

The collected thermal black is pulverized by fabric filter and pelletized to a final product. In the thermal process, the relatively coarse particles (180 to 470 nm) are produced and very high yields (35 to 60 percent) are obtained, however, they do not have the strong reinforcing properties required for rubber products.

2.5.1.3 Physical Properties of Carbon Black

Carbon black can be defined as very fine spherical elementary particles. Measuring the particle size of carbon black is very difficult and for this purpose electron microscope has been very important to investigate the morphology of the carbon black [24]. In most cases, carbon black particles exist as aggregates, fused particles. The aggregates, however, have a tendency to agglomerate in dispersion into larger units. Aggregates differ in size and shape; therefore different techniques are used to characterize them. Electron microscopy again provides the most reliable results [30].

Surface area is an important parameter for carbon blacks since they interact with other substances by means of their surfaces. The measurements of surface area give an indirect characterization of carbon black particle size. The widely used methods for surface area determination are adsorption methods that use iodine and nitrogen mainly. The adsorption tests (mg/g of carbon) measures the amount of iodine (or nitrogen) which can be adsorbed on the surface for a given mass of carbon black [24].

The analysis of structure or morphology of carbon black is a more difficult task. The structure is determined by shape and degree of aggregate branching. Increasing effective surface area typically increases modulus, hardness and electrical conductivity. Oil absorption (using dibutylphthalate absorption, DBPA) is the measurement method of structure. A high number of DBPA represents higher structure. Dibutylphthalate (DBP) absorption measures the relative structure of carbon black by determining the amount of DBP in a given mass of carbon black [24].

Carbon black has metallic conductivity character with the conductivity value in the range of 0.1 – 10^2 S/cm and has a huge number of free charge carriers. The electrical properties of the carbon blacks depend on graphitization degree, surface cleanliness, porosity and particle diameter [32].

Carbon black has graphite like bulk structure (Figure 2.14) that has been investigated by X-ray diffraction. Each particle consists of parallel orientated graphitic planes [11]. The inter-planer distance values are in the range of 0.35-0.38 nm that is higher than the space between graphite layers.

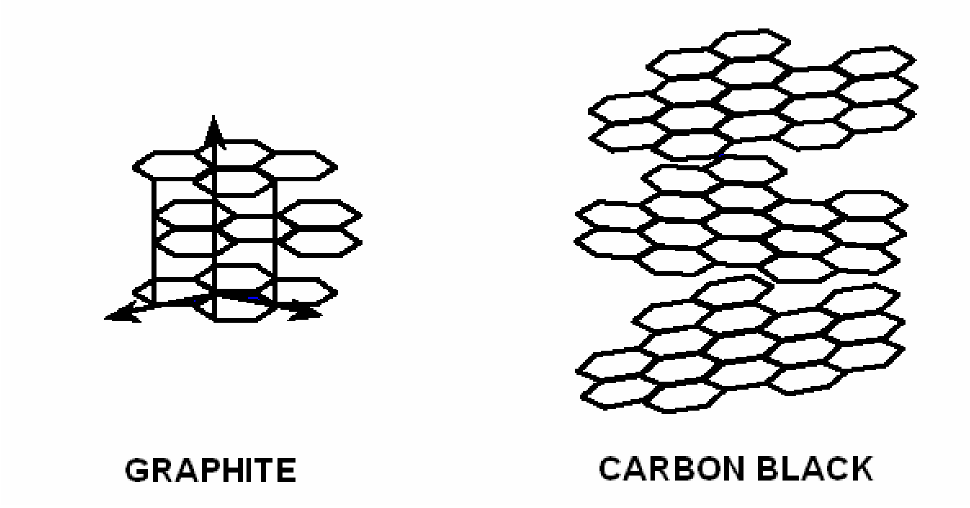


Figure 2.14 Atomic structural models of graphite and carbon black

2.5.1.4 Chemical Properties of Carbon Black

Carbon is the major element in carbon black; however, number of other elements is always found in small amounts that significantly influence the properties of the carbon black [24]. Hydrogen is always present because of the hydrocarbons that are raw materials of the black. Oxygen comes from the particle formation in the flame. Sulphur is mainly introduced by feedstock [30]. According to elemental analysis, the chemical composition is in the following limits [34] :

Carbon	80.0-99.5 wt %
Hydrogen	0.3-1.3 wt %
Oxygen	0.5-15.0 wt %
Nitrogen	0.1-0.7 wt %
Sulfur	0.1-0.7 wt %

The surface chemistry, however, is very different from the bulk content of the carbon black. The surface activity of carbon black depends on the degree of heterogeneity of the surface and the amount of chemical functional groups on the edges of the graphitic layers [27]. Especially the oxygen is much richer on the surface that forms different functional groups which play an important role in the carbon black properties such as electrical conductivity. It was reported in the literature that the electrical conductivity of the carbon black is strongly influenced by surface chemistry [33]. Probable functional groups on carbon black particles are given in Figure 2.15.

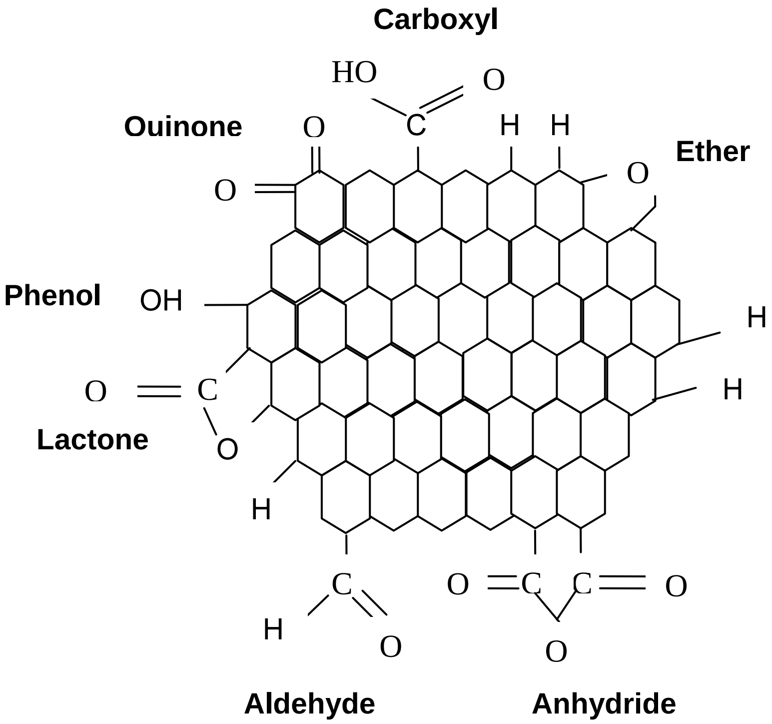


Figure 2.15 Aromatic layer plane of carbon black with functional side groups

The hydrogen is present as CH groups at the edge of the carbon layers. Nitrogen can be integrated into aromatic layer system as heteroatoms. Oxygen which has greatest importance bounds to the surface of the carbon black in the form of acidic or basic functional groups. They are called as “surface oxide” and their compositions on the surface differ according to production processes [34].

The present functional groups on the carbon black surface can be determined by using different techniques such as acid-base titration, electron spin resonance (ESR) and X-ray photoelectron spectroscopy (XPS) [24].

2.5.2 Graphite

Graphite derives its name from the Greek word "graphein". Depending upon the purity, its specific gravity is 2.2 to 2.3. It is flexible but not elastic. It is chemically inert and has high thermal and electrical conductivity.

Since it shows both metal and non-metal properties, it is a unique material. The unusual combination of properties is because of its crystal structure that can be seen in Figure 2.16. In graphite, each carbon atom is covalently bonded to three others in the same plane and form hexagonally six-membered planar ring system. The layers are stacked parallel to each other. Only relatively weak van der Waals forces of attraction hold the layers together [27].

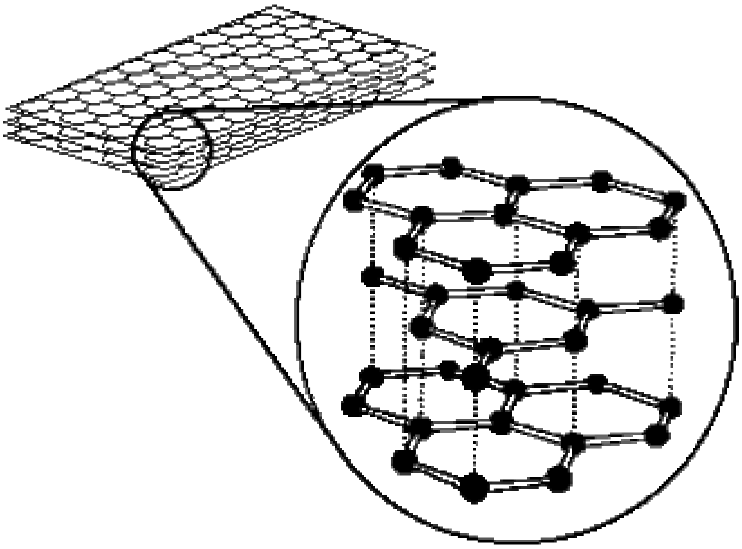


Figure 2.16 Structure of graphite

Final properties of graphite depend on the selection of raw materials and the graphitization step in which temperature rises between 2500 and 3000 °C.

2.5.3 Carbon nanotubes

Carbon nanotubes are long, thin, cylindrical carbon molecules that were discovered in 1991 by S. Iijima. They are unique materials due to their size, shape, and remarkable physical properties. They can be defined as graphite sheet rolled into a cylinder. Carbon nanotubes offer extraordinary mechanical and electrical properties in such a way that they have over 1 Tera Pascal Young's modulus [35].

There are two main types of carbon nanotubes; single-walled nanotubes and multi-walled nanotubes.

Single-walled structure is the fundamental type that has three basic geometries; armchair, zigzag, and chiral. The schematic models of these geometries can be seen in Figure 2.17 [36].

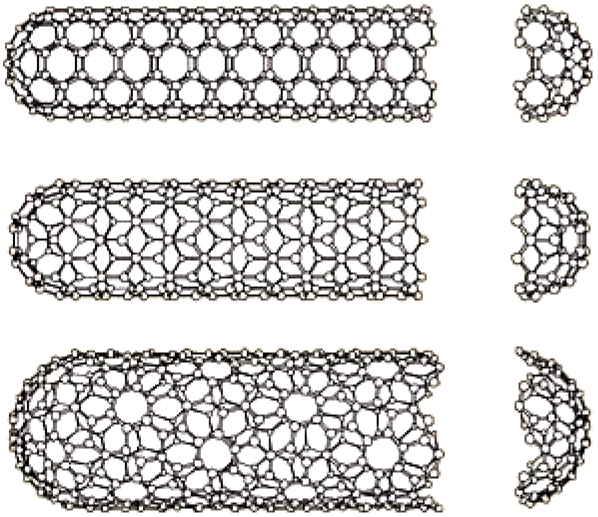


Figure 2.17 Models of single-walled nanotubes; armchair (top), zigzag (middle), chiral (bottom).

Multi-walled carbon nanotubes (MWCNT) can similarly be thought as coaxial cylinders of single-walled carbon nanotubes, one within another (See in Figure 2.18).

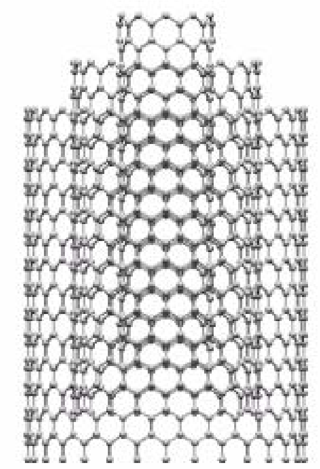


Figure 2.18 Multi-wall Carbonnanotube (MWCT)

Different methods are employed in order to produce nanotubes, such as arc discharge, laser ablation and chemical vapor deposition (CVD). Compared to the other methods, the CVD method is the most promising method that offers larger production capacity at lower cost. In CVD method (Figure 2.19), carbon-containing gas (such as acetylene, ethylene, ethanol, etc.) reacts with a metal catalyst particle (usually cobalt, nickel, iron or a combination of these as cobalt/iron or cobalt/molybdenium) at temperatures above 600°C [30].

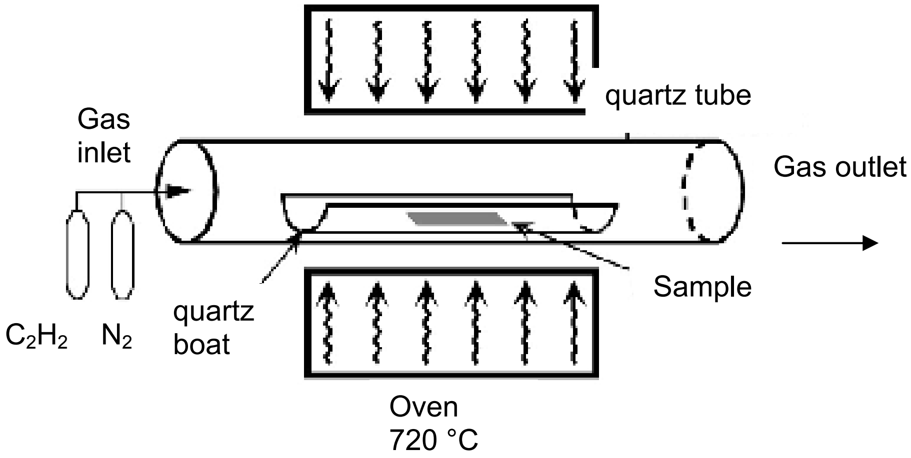


Figure 2.19 Basic schematic of CVD method

2.6 Surface Modification

In recent years, new techniques are investigated in order to obtain low percolation concentration in electrically conductive composites. It is well known that the conductivity of the composites strongly depends on the filler concentration, dispersion of filler in the matrix, conductivity of the filler and matrix and surface area of the filler; however very few studies have been done to determine the relation between surface chemistry and electrical conductivity of the filler. Surface modification methods have attracted much attention recently in order to lower the resistivity of the composites by changing the surface chemistry of the fillers.

Two distinct types of surface modifier can be described; non-coupling and coupling. The non-coupling ones attach to the filler surface with a chemical bond but not to the polymer matrix with a strong bonding [37]. The coupling types, usually known as coupling agents, have two different functional groups, one that is attracted to the surface of the filler and the other that is attracted to the polymer [2]. This interaction with the polymer is generally due to some chemical functionality, however, in some cases, it is due to long enough chains to entangle with the matrix [37].

Coupling agents are generally used for inorganic filler containing composites to improve the adhesion between fillers and polymer, preferably by chemical bonds. Their use improves the performance of reinforcements. Mostly used coupling agents are silanes that have general formula $(X)_3$-Si-$(CH_2)_3$-Y in which X (hydrolyzable group) reacts with fiber surface, while Y (organofunctional group) reacts with polymer matrix [38]. Figure 2.20 shows the structure of different functional organosilanes.

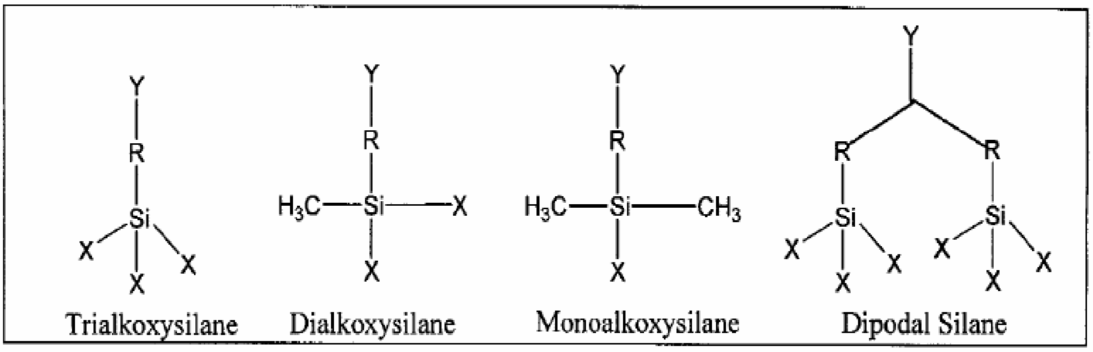


Figure 2.20 Generic structures of functional organosilanes with varying numbers of hydrolyzable substituents on silicon.

Two reactions can be recognized for the Si-X group with surface hydroxyls. One is the direct reaction with the surface which forms siloxane bond and eliminate HX (Figure 2.21.a), the other is prehydrolysis with surface moisture followed by condensation of silanol (Figure 2.21b-c) [39].

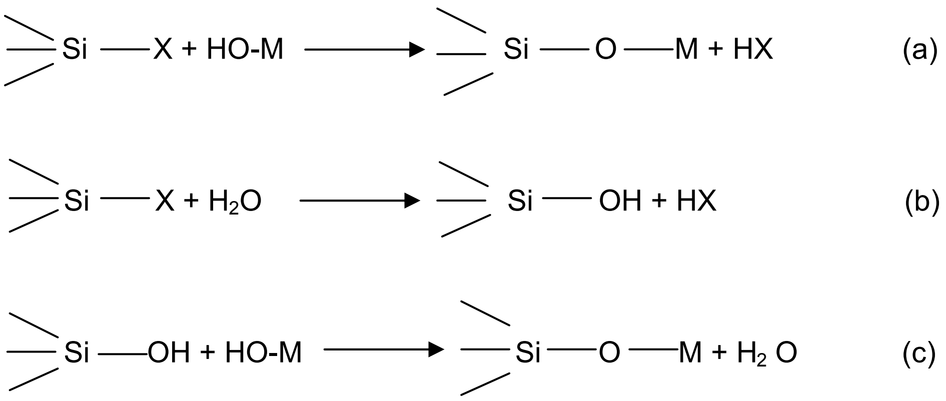


Figure 2.21 Reactions of Si-X groups with surface hydroxyls [39]

Surface chemistry of the fillers should be analyzed via different techniques such as X-Ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS) in order to predict which reactions can take place on the surface of the filler by coupling agent treatment.

2.7. Characterization Techniques

2.7.1 X-Ray Spectroscopy (XPS)

X-Ray Spectroscopy (XPS) also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a surface analysis technique. It is used in order to obtain chemical information about the surfaces of the materials. This method is based on the induced emission of photoelectrons by using X-Ray beam. X-ray excites the electrons of the sample atoms and if their binding energy is lower than the X-ray energy, they are emitted as photoelectrons. All elements, except hydrogen can be detected by XPS [40].

XPS analysis not only provides elemental information, because the technique is detecting the binding energy of emitted electrons, it can also provide some chemical bonding information.

2.7.2 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope (SEM) is the instrument that is used for the examination and analysis of the structural characteristics of materials. The main objective of SEM analysis is magnification and focus for clarity. It is limited to a surface view only, it does not give information about the interior of the specimen.

In SEM, the surface of the materials is scanned with the accelerated electrons beam. The electrons which reflected from the surface are collected and the analysis of the scanned surface can be done on screen at that different magnification [41].

If the material is not a good conductor, it is coated with a thin layer of conducting material such as gold, silver and aluminum.

2.7.3 Tensile Test

In tensile test, a dog bone shape specimen is pulled at a constant rate of elongation with application of a known force and the required force to break the specimen is measured simultaneously.

In discussing tensile properties, some important terms should be clear which are shown in Figure 2.22

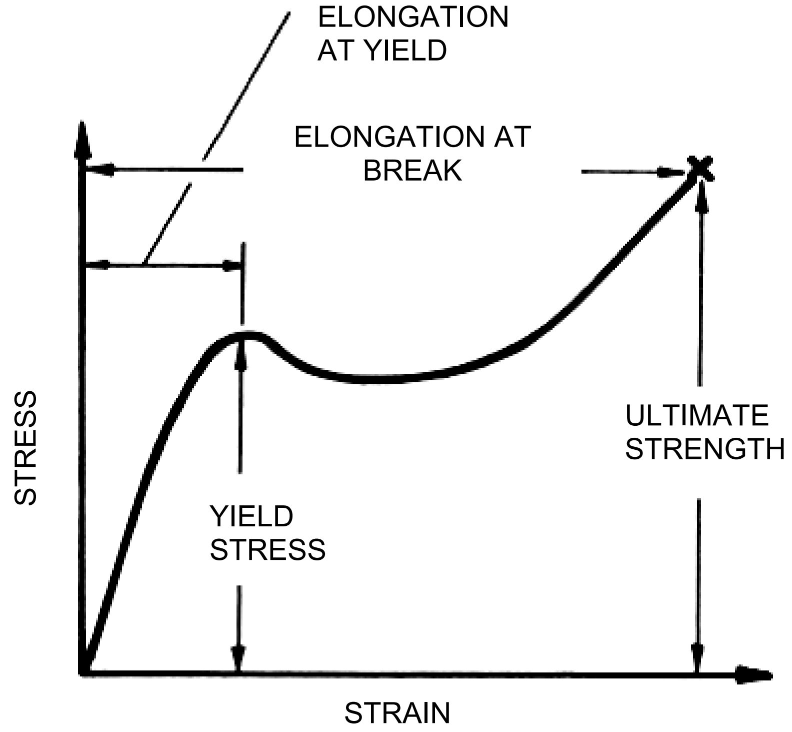


Figure 2.22 Generalized tensile stress-strain curve for polymeric materials.

Tensile stress, σ, is defined as the force per unit area perpendicular or normal to a force,

$$\sigma = F / A_o \qquad (2.1)$$

Tensile strain, ε, is defined as the ratio of change in gauge length of the specimen in the direction of applied load stress to its original gage length,

$$\varepsilon = (\Delta L) / L_o \quad (2.2)$$

where; L_o = Original gauge length

ΔL= the change in gauge length due to deformation

Ultimate Strength is calculated by dividing the maximum load in Newtons by the original cross-sectional area of the specimen (mm^2). The result is expressed in terms of Mega Pascal (MPa)[42].

$$\text{Ultimate Strength} = \frac{\text{Force (Load) (N)}}{\text{Cross Section Area (mm}^2\text{)}} \quad (2.3)$$

The initial slope of stress-strain curve provides a value for Young's modulus (or the modulus of elasticity) which is a measure of stiffness [43]. The result is expressed in MPa unit.

$$\text{Tensile Modulus} = \frac{\text{Difference in Stress}}{\text{Difference in Corresponding Strain}} \quad (2.4)$$

2.7.4 Electrical Properties

Two point probe method and four point probe method are used to measure the electrical resistivity of the samples according to standards [44]. For the samples whose resistivity values are lower, four point probe method is more suitable and two point probe method is used for the samples with higher resistivity values. Two probe method measures total resistance between two probes. These resistances consist of the probe resistance, the contact resistance between metal probe and semiconductor surface, the spreading resistance under each probe and the composite resistance. Therefore, the four point probe technique has an advantage over two point probe method by measuring only the composite resistance at a high accuracy.

A constant current is supplied to the samples and the resistances are calculated from voltage drop across the samples. The volume resistivity, ρ is calculated by using the following formula:

$$\rho = [(V) / (I)] * [(S) / (L)] \qquad (2.5)$$

in which
V = the voltage drop,
I = the current,
L = is the length
S = the cross sectional area of the samples [44].

2.8 Previous Studies

Novak et al. [45] investigated the electrical conductivity, impact strength and adhesion strength of epoxy and polyurethane resins, filled with two different graphite (KS15 and KS6) having different particle size. In all investigated cases, the percolation concentration was determined to be 22 vol %. It was found that, the grade of graphite had no significant effect on electrical conductivity. It was also observed that, the impact strength decreased with increasing conductive filler content and the highest values were obtained for polyurethane/graphite KS6 system. Moreover, a decrease in the adhesion strength of filled resin to aluminum with increasing filler content was determined. The highest adhesion strength was found for the epoxy/graphite KS6 system.

Novak et al. [46] studied the analysis of correlation between percolation concentration and elongation at break in filled electroconductive epoxy-based adhesives. In order to determine the effect of filler type on percolation concentration and electrical conductivity, four different conductive fillers; carbon black, graphite, silver coated basalt particles and fibers were used. Percolation concentrations were found as 14 vol % for epoxy/carbon black, 22 vol % for epoxy/graphite, 28-29 vol % for both epoxy/silver coated basalt particles and fibers. In addition, it was seen that elongation at break of filled resins decreased with an increase in the filler content in all cases.

Johnson et al. [47] focused on a novel dispersion technique which involves the exfoliation of an aklylamine hectorite clay in the presence of nanofiber agglomerates. Poly (butyl methacrylate-co-methyl methacrylate) and poly (butyl methacrylate) were used as the polymeric matrix and carbon nanofiber was used as the conductive filler. It was hypothesized that clay platelets penetrate the pores of the nanofiber agglomerates and provides well dispersion without sacrificing nanofiber properties. By utilizing this novel dispersion technique, the percolation concentration was found to be 4 vol %. It was also observed that electrical conductivity increases as a power law function of fiber concentration.

Novak et al. [1] prepared electro conductive adhesives based on epoxy and polyurethane resins. To make the adhesives electrically conductive, silver-coated particles and short fibers were used as conductive filler. The percolation concentrations were obtained as follows; 28 vol % for epoxy/Ag-coated particles and 29 vol % for epoxy/Ag-coated fibers and 29 vol % for PU/Ag-coated particles and fibers. Mechanical properties were also investigated. The highest impact strength and adhesion strength values were obtained for epoxy/silver-coated short fibers composites.

El-Tantawy et al. [48] investigated the effects of different concentration of carbon black and sintering on the electrical conductivity of epoxy composites as a function of temperature during heating and cooling cycles. It was seen that electrical conductivity increased with increasing carbon black content. It was also found that temperature dependence of electrical conductivity depends on carbon black concentration and can be improved by sintering process. Moreover, it was concluded that epoxy-carbon black composites show good thermal stability.

Schueler et al. [49] studied the agglomeration and electrical percolation behavior of carbon black dispersed in epoxy resin. Percolation concentration was affected by manufacturing process. Two main forces in carbon black can be considered; London-van der Waals and repulsive coulombic force which occurs when the surface of the particles dispersed in matrix becomes charged. It was hypothesized that this repulsive force causes a potential energy barrier that prevent the particles to come close enough to form conductive network. It was proven that, this potential barrier can be exceeded by applying external shear forces or increasing the ionic concentration. In this study, extra conductive carbon black was used as conductive filler and $CuCl_2$ solution was added to the system to increase the ionic concentration. It was shown by experimental results that, agglomeration can be induced by shear forces or increasing ionic concentration and a percolation threshold as low as 0.06 vol % was achieved.

Li et al. [50] proposed a new surface treatment method that covers the UV/ozone treatment of graphite and investigated its effects on the properties of graphite nanoplatelet/epoxy nanocomposites. It was found that the UV/ozone treatment enhanced the electrical conductivity and mechanical properties of the composites by increasing the interfacial adhesion of graphite-epoxy composites. In addition to surface treatment, ultrasonic effect was also studied. It was shown that ultrasonication had a negative effect on electrical conductivity but improved the mechanical properties of the composites.

Sandler et al. [51] searched the effects of carbon nanotube concentration dispersed in an epoxy matrix on the electrical properties. In this study, untreated catalytically-grown carbon nanotubes were dispersed in an epoxy matrix and the percolation threshold was found as low as 0.1 vol % without compromising the mechanical properties of the composites.

Yoon et al. [52] introduced a different way to reduce the percolation concentration of carbon black in the matrix by applying surface treatment using amine-terminated coupling agent. It was obtained that the electrical conductivity of carbon black/polymer composites was significantly affected by surface treatment, because the amine group of coupling agent reacts with carboxyl groups that exist on the carbon black surfaces to form amine salts and these salts decrease the energy required for hopping mechanism of the electrons. By using this method, percolation threshold concentration for the high density polyethylene (HDPE)/ γ-aminopropyltrimethoxysilane (APS) treated carbon black composites, was reached at 0.4 vol % filler.

In our study, it was aimed to obtain composites having electrical resistivity in the semiconductive range at low percolation threshold concentration for the carbon black filled epoxy systems by applying different mixing processes and also by modifying carbon black surfaces with different chemicals. Ultrasonication was also added to the mixing process to see its effect on electrical conductivity of the samples. In addition the electrical properties, it was also aimed to improve mechanical properties of the composites.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

3.1.1 Epoxy

Epoxy resin produced from bisphenol A and epichlorohydrin was used as polymer matrix because of its mechanical performance, chemical resistance and excellent adhesion. It was purchased from GEMA Dis. Tic. Ltd. Sti, İstanbul. The trade name of the epoxy used is EPIKOTE 816 MV and it is sold in the form of liquid in a 18 kg barrel. Properties of the epoxy obtained from the company are given in Table 3.1.

Table 3.1 Properties of the epoxy

Property	Unit	Value
Density, 25 °C	kg/l	1.12
Viscosity, 25 °C	Pa.s	0.9-1.1
Epoxy group content	mmol/kg	5000-5300
Flash Point	°C	145

3.1.2 Curing Agent

Low viscosity, modified cycloaliphatic amine was used as curing agent. It was purchased from GEMA Dis. Tic. Ltd. ŞTİ, İstanbul, Turkey. The commercial name of curing agent is EPIKURE^{TM} CURING AGENT F205. It is a mixture of cycloaliphatic amines and benzyl alcohol and is used in the formulation of room temperature curing compositions such as industrial floorings. The composition of the EPIKURE^{TM} CURİNG AGENT F205 can be seen in Table 3.2.

Table 3.2 Composition of the curing agent (EPIKURE^{TM} CURİNG AGENT F205)

Chemical Name	Weight %
Benzyl alcohol	35-40
Isophoronediamine (IPDA)	30-35
Bisphenol A polymer with a 5-amino-1,3,3-trimethylcyclohexanemethanamine and chloromethyl	25-30

Properties of the curing agent obtained from the company are listed in Table 3.3.

Table 3.3 Properties of curing agent

Property	Unit	Value
Density, 25 °C	kg/l	1.04
Viscosity, 25 °C	Pa.s	0.5-0.7
Recommended proportion with EPIKOTE 816	phr*	54

*parts weight per 100 parts weight of resin

3.1.3 Carbon Black

Carbon black used as electrically conductive filler in this study was obtained from Turkish Petroleum Refinery (TUPRAS), Turkey. Table 3.4 summarizes the physical properties of the carbon black.

Table 3.4 Physical properties of the carbon black

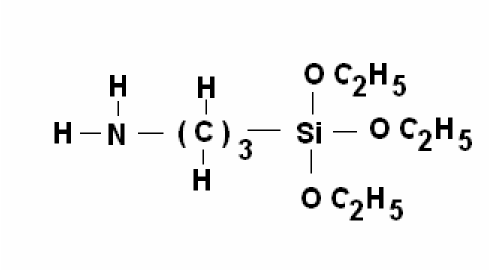
Product Type	ISAF N-220
Iodine Number (mg/g)	119
Dibutylphthalate Abs. (ml/100 g)	114.2
+325 Mesh total grit (44 micron)	0.0016 (wt.%)

3.1.4 Chemicals for Surface Modification

In order to decrease the electrical resistivity of the composites, the surface of the carbon black was treated by using different silane type coupling agents and formamide. Four different types of coupling agents, 3-Aminopropyltriethoxysilane (Ameo), 3-Aminopropylmethyldiethoxysilane (1505), N-(n-Butyl)-3-aminopropyltrimethoxysilane (1189) and 3-Glycidyloxypropyltrimethoxysilane (Glymo) were used in this study. They are supplied from CAM Elyaf, Gebze. Physical properties of these coupling agents and formamide are listed in Tables 3.5-3.9. Also, chemical structures of these chemicals are given in Figures 3.1-3.5.

Table 3.5 Properties of 3-Aminopropyltriethoxysilane (Ameo) type of silane coupling agent

Property	Value	Unit	Method
Density (20 ºC)	0.95	g/cm^3	DIN 51757
Refractive index, n	1.422		DIN 51423
Viscosity (20 ºC)	1.85	mPa.s	DIN 53015
Boiling point	≥68 ºC	ºC	DIN 51356
Flash point	93/199	ºC/ºF	DIN 51758

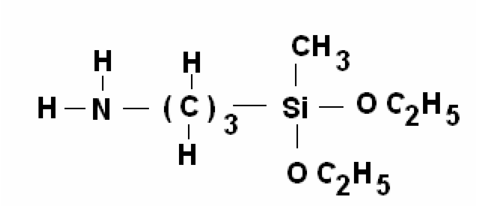


$$\mathrm{H-\overset{H}{N}-(\overset{H}{\underset{H}{C}})_3-\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}-OC_2H_5}$$

Figure 3.1 Chemical structure of Ameo type of silane

Table 3.6. Properties of 3-Aminopropylmethyldiethoxysilane (1505) type of silane coupling agent

Property	Value	Unit	Method
Density (20 ºC)	0.92	g/cm^3	DIN 51757
Refractive index, n	1.427		DIN 51423
Viscosity (20 ºC)	2	mPa.s	DIN 53015
Boiling point	202	ºC	DIN 51751
Flash point	85	ºC	DIN 51758



$$\mathrm{H-\overset{H}{N}-(\overset{H}{\underset{H}{C}})_3-\overset{CH_3}{\underset{OC_2H_5}{Si}}-OC_2H_5}$$

Figure 3.2 Chemical structure of 1505 type of silane

Table 3.7. Properties of N-(n-Butyl)-3-aminopropyltrimethoxysilane (1189) type of silane coupling agent

Property	Value	Unit	Method
Density (20 ºC)	0.95	g/cm^3	DIN 51757
Viscosity (20 ºC)	2.5	mPa.s	DIN 53015
Boiling point	238	ºC	DIN 51751
Flash point	110	ºC	DIN 51755

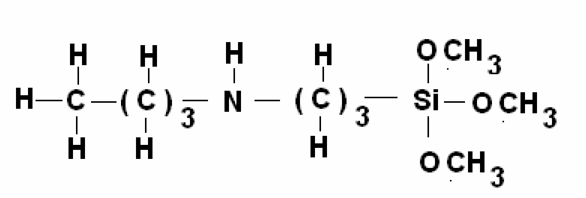


Figure 3.3 Chemical structure of 1189 type of silane

Table 3.8 Properties of 3-Glycidyloxypropyltrimethoxysilane (Glymo) type of silane coupling agent

Property	Value	Unit	Method
Density (20 ºC)	1.07	g/cm^3	DIN 51757
Refractive index, n	1.429		DIN 51423
Viscosity (20 ºC)	3.7	mPa.s	DIN 53015
Boiling point	90	ºC	DIN 51356
Flash point	122	ºC	DIN 51758

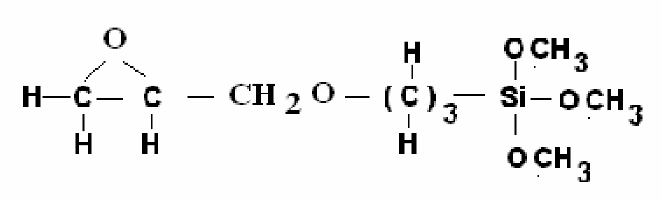


Figure 3.4 Chemical structure of Glymo type of silane

Table 3.9 Properties of formamide

Property	Value	Unit
Density (20 ºC)	1.133	g/cm^3
Boiling point	210	ºC
Flash point	154	ºC

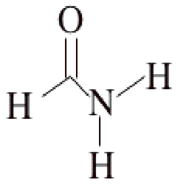


Figure 3.5 Chemical structure of formamide

3.1.5 Release Agent

Poliwax SV-6 supplied by Poliya A.Ş. was used in order to release the cured samples out of the molds easily.

3.2 Experimental Set-up and Procedure

3.2.1 Experimental Procedure

In preparation of the electrically conductive coating materials, two different mixing methods were followed. In the first method, called Grinding, a MOTOREUS SEGAL CO. type engine with a power of 1 kW and its stirrer were used to mix epoxy and carbon black properly. As a coolant fluid, water was circulated in the system. In this method, 300 g glass bead with a 5 mm diameter was added to the system mainly to provide well dispersion of carbon black in the polymer matrix. Besides well dispersion, glass beads also reduce the agglomerate size and as a result help the formation of conductive network. In Grinding Method, mixing time was not a process parameter; it was determined by using a grindometer on which there is a triangular depth with a gradient beginning from 50 μm ascending up to zero level. Mixture was poured into this cavity and excess amount of mixture was removed by a tool. The size of agglomeration was observed by this grindometer. Mixing was continued till no agglomerates bigger than 35 μm was observed. It took longer time for high concentration. The composites contained 0, 1, 2, 3 and 5 vol.% carbon black. For these concentrations, mixing lasted 2-3 hours depending on the carbon black content. After filtration of the glass beads, vacuum was applied to the system for 2 hours to eliminate the bubbles. In this method, again ultrasonic mixing was applied to the system only in composites having 2 vol.% CB. 15, 30 and 45 minutes were selected as ultrasonic mixing time. Then, vacuum was applied to the system for 2 hours to eliminate the bubbles. At this stage, the amine based hardener was added with a ratio of 100:54 parts (epoxy/ hardener) by weight and again vacuum was applied for 15 minutes.

Figure 3.6 and Figure 3.7 represent the experimental set-up and flowchart for Grinding Method, respectively.

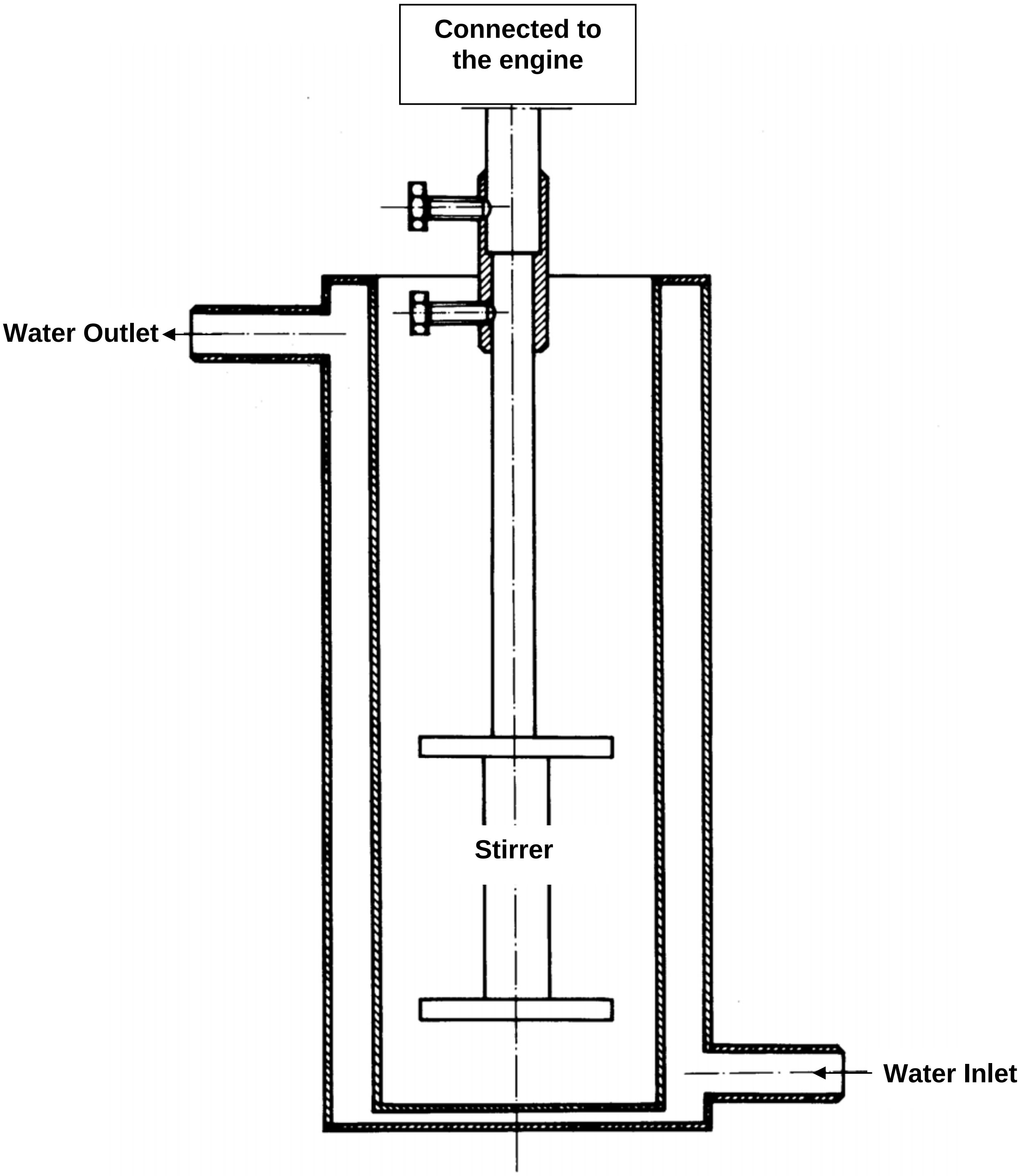


Figure 3.6 Experimental Set-up for Grinding Method

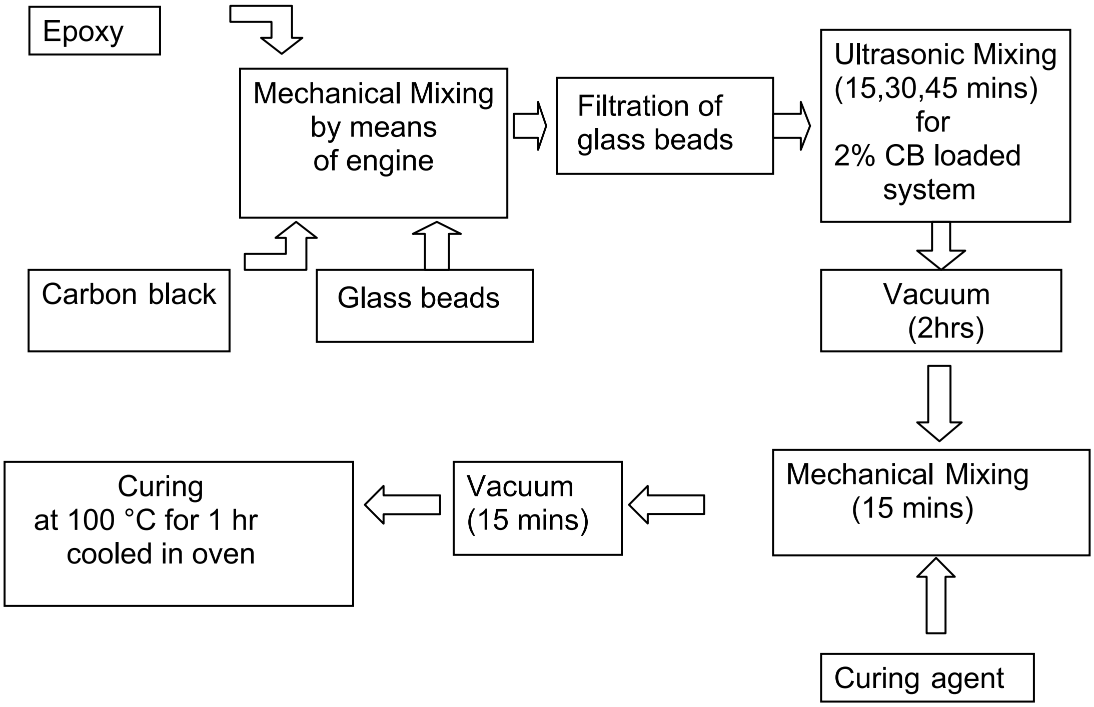


Figure 3.7 Flowchart of Grinding Method

In the second method, called Mechanical Mixing Method, epoxy and carbon black were mixed and stirred by using lab-scale mechanical mixer at 100 rpm for 60 minutes at room temperature. After mixing stage, hardener was added to system as mentioned in Grinding Method. The composites contained 0, 1, 3 or 5 vol.% carbon black. Figure 3.6 illustrates the experimental set-up for Mechanical Mixing Method. Flowchart in Figure 3.7 shows the procedure for this method.

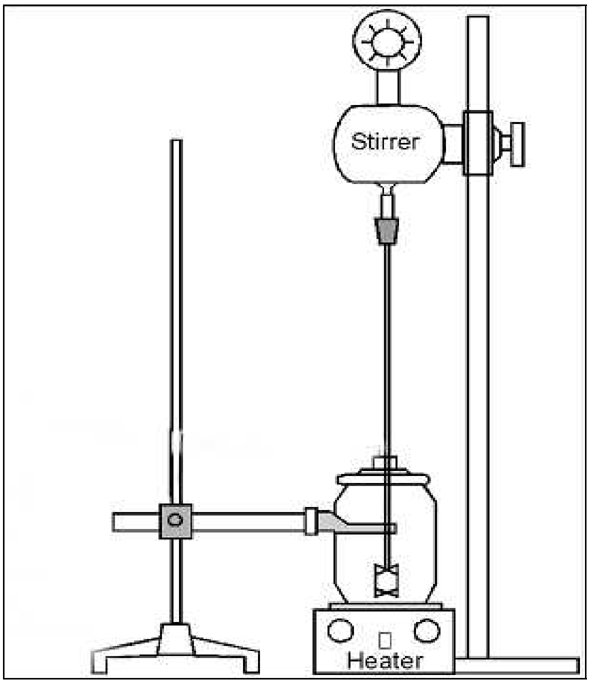


Figure 3.8 Experimental Set-up for Mechanical Mixing Method

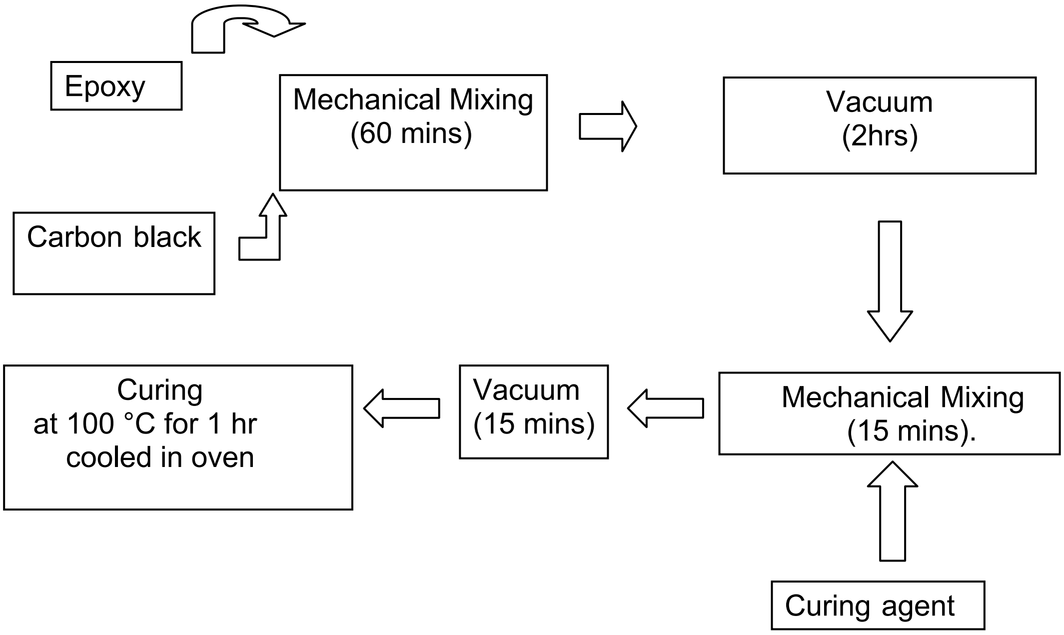


Figure 3.9 Flowchart of Mechanical Mixing Method

3.2.2 Sample Preparation

In order to prepare the specimens for measuring electrical conductivity and tensile properties of the composites, the slurry mixtures were poured into aluminum molds after applying the release agent to the molds. Molds were designed according to ASTM D638 standards [42]

For the hardness, impact and adhesion tests, wet film with 30 μm thickness was applied on glass and aluminum metal panels by a film casting knife (Braive Instrument). All samples were cured in an oven at 100 °C for 1 hour.

3.2.3 Carbon Black Treatment

All four coupling agents and formamide were diluted in water separately to make 1 wt.% solution. 250 ml of each solution was mixed with 100 g of carbon black particles. They were stirred for 10 minutes at room temperature. Then, they were dried at 100 °C for 24 hours to allow complete evaporation of water. Flowchart of the carbon black treatment is given in Figure 3.10.

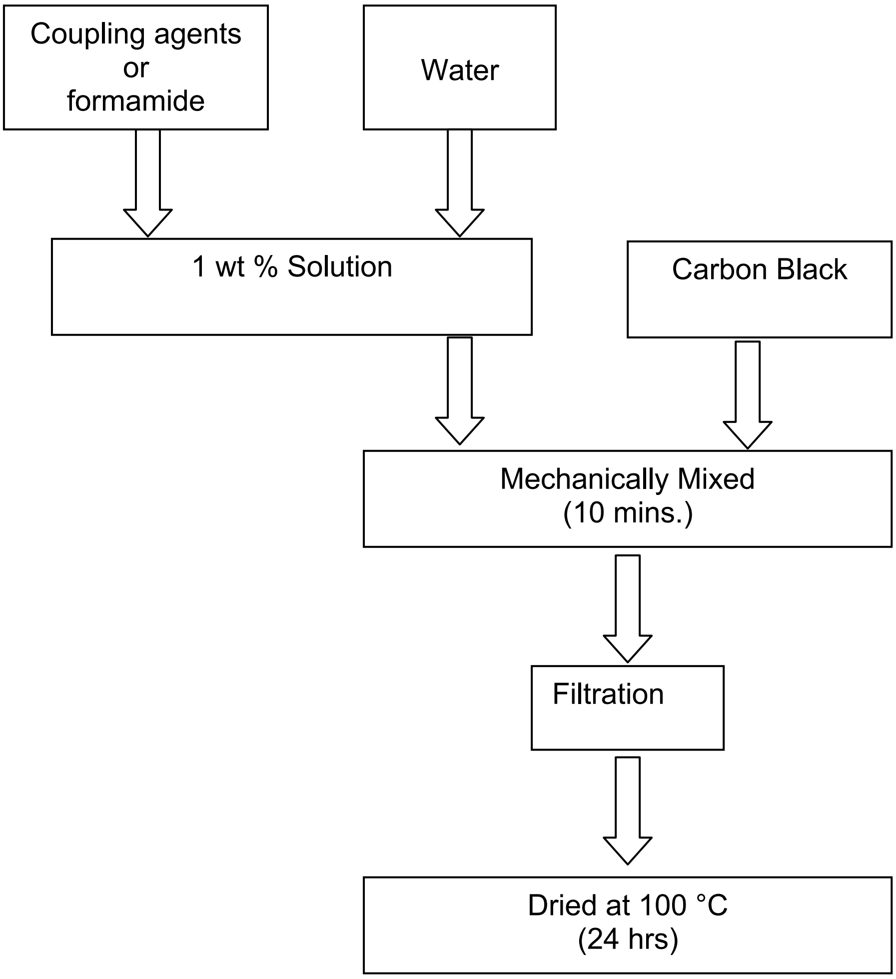


Figure 3.10 Flowchart of the procedure for carbon black treatment

3.3 Chemical Characterization

3.3.1 X-ray Photoelectron Spectroscopy (XPS) Analysis

Surface chemistry of untreated and treated carbon black was analyzed by X-ray Photoelectron Spectroscopy (XPS), also called Electron Spectroscopy for Chemical Analysis (ESCA). Specs model spectrometer (from Central Laboratory, METU) was equipped with aluminum radiation at 1 W to obtain XPS spectra of carbon black.

3.4 Morphological Characterization

3.4.1 Scanning Electron Microscopy (SEM)

A low voltage scanning electron microscopy (JOEL JSM-6400) was used to analyze the impact fracture surfaces of the samples. A thin layer of gold was applied to the fracture surfaces before the analysis in order to obtain conductive surfaces. The SEM photographs were taken at 1000 and 3500 magnification.

3.5 Electrical Properties

Two point probe method by which the test samples are connected to a Keithley 2400 model constant current source, was used in order to measure the volume resistivity of the samples according to ASTM F 43. A constant current of $0.5x10^{-9}$ Amper was supplied to the sample and the resistance values were calculated from voltage drop across the samples. Moreover, four point probe method was used for lower resistivity values.

3.6 Physical and Mechanical Characterization

3.6.1 Pendulum Hardness Test

Pendulum hardness tests were performed by using a Braive Instruments hardness tester (Model 3034) equipped with a Persoz pendulum (see Figure 3.11) according to ASTM D 4366. The Persoz pendulum is a square frame with a pointer. The hardness of any given coating is measured by the number of oscillations made by the pendulum within the specified limits of amplitude (decrease from 12° to 4° for Persoz pendulum) determined by accurately positioned photo sensors.

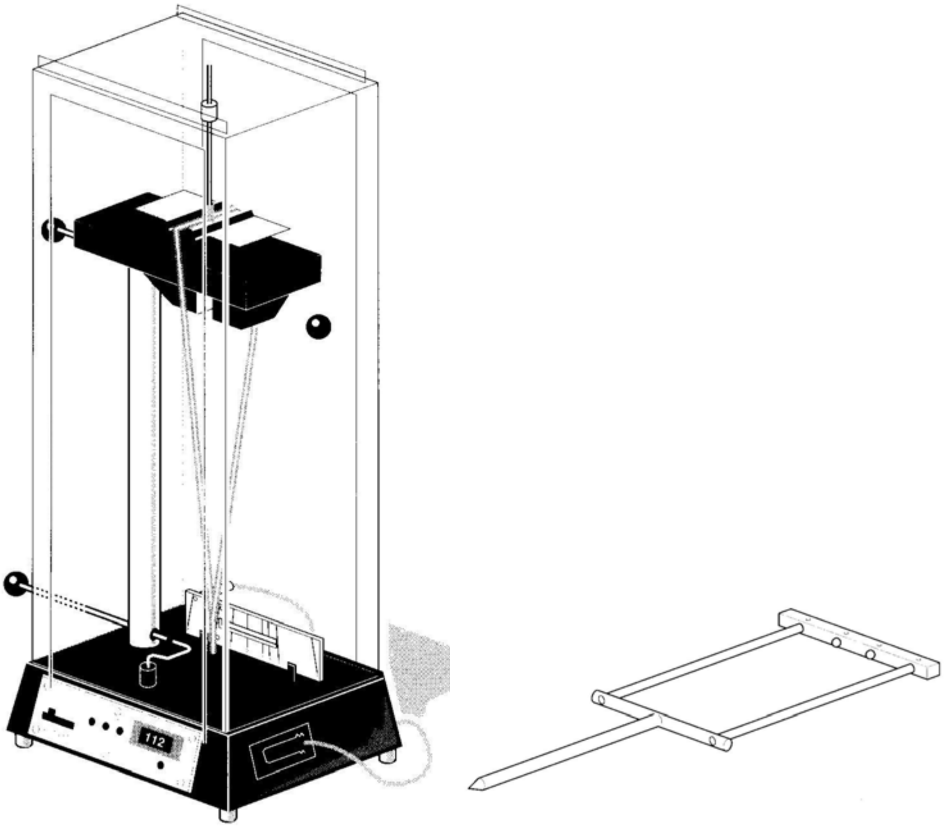


Figure 3.11 Pendulum Hardness tester and Persoz pendulum

3.6.2 Impact Resistance Test

A Gardner Impact Tester (Model 5524) was used to determine the impact resistance of the samples. The weight (1 kg) is raised to the desired height and dropped (See Figure 3.12). The coated sample panel is inspected, and depending on results, the test is repeated by releasing the weight at a higher or lower distance. Impact resistance is determined when cracks first appear in the coating by height as a potential energy according the following equation.

$$\text{Impact Energy (J)} = m \times g \times h \qquad (3.1)$$

m = weight of the dropweight (kg)
g = gravitational acceleration of the earth (m/sec^2)
h = height of dropweight (m)

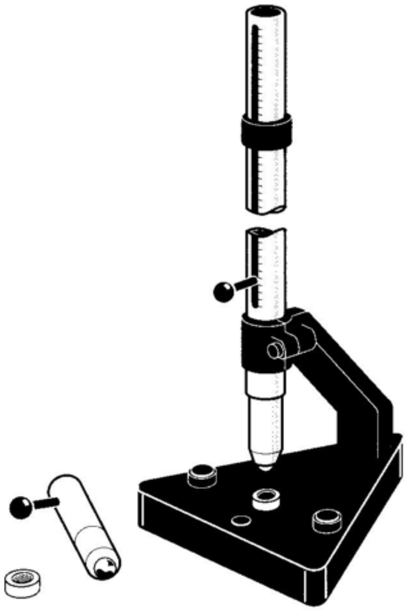


Figure 3.12 Impact resistance tester and dropweight

3.6.3 Tensile Test

Tensile tests were performed according to ASTM D638 (Standard Test Method for Tensile Properties of Plastics) by using a Lloyd LR 30 K Universal Testing Machine. The shape and the dimensions of the specimens were specified according to Type-II in this standard, which are given in Figure 3.13 and Table 3.10. The crosshead speed of the machine was set at 5 mm/min, which was calculated considering the specimen gauge length of 50 mm and strain rate of 0.1 min^{-1}. After strain-stress diagrams were obtained, tensile strength, tensile modulus and percent strain at break values were calculated.

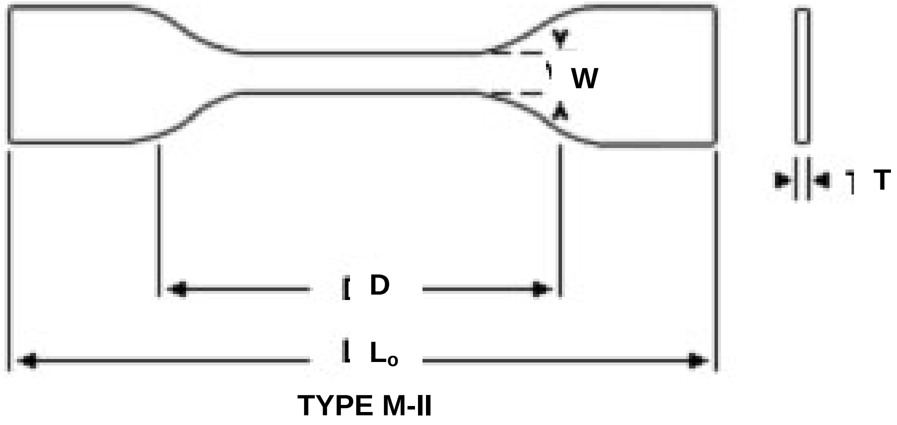


Figure 3.13 Tensile test specimen

Table 3.10 Dimensions of tensile test specimen

D – distance between grips	50 mm
L_0 – length overall	115 mm
T – thickness	4 mm
W – width of narrow section	6 mm

3.6.4 Adhesion Test

Adhesion tests were performed by using an Elcometer Adhesion Tester (See Figure 3.14) which is in convenience with ASTM D 4541. The sample was applied to the aluminum metal surface and cured in an oven at mentioned conditions in Section 3.2.2. Then, a test dolly was glued to the coated surface by using epoxy based adhesive. After curing the epoxy adhesives at 80 °C in an oven for 30 min, the dolly was pulled off in order to measure the stress that is needed to remove the coating from the substrate. It houses spring arrangement, which applies the lift force to a metal dolly attached to the test surface.

Figure 3.14 A photograph of the adhesion tester

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effects of Carbon Black Loading on Morphologies, Electrical and Mechanical Properties of Epoxy/Carbon Black Composites

The aim of this study was to obtain electrically conductive coating materials which have an electrical conductivity between the semi conductive ranges for antistatic applications. In order to observe the effect of carbon black (CB) loading on composite properties, 0, 1, 2, 3 or 5 vol. % CB was added to the epoxy matrix. The Grinding Method is used for sample preparation in this section.

4.1.1 Scanning Electron Microscopy Analysis

In this section, the morphologies of the samples produced by Grinding Method were investigated. Scanning electron microscope analysis was performed to the impact fracture surfaces of all produced samples.

Figure 4.1 shows the fracture surface of unfilled epoxy at magnifications of x1000 and x3500. It can easily be seen that epoxy has a smooth surface and crack propagation lines are clearly observed. Straight propagation lines, rather than tortuous lines, indicate the characteristic morphology of the brittle polymers such as epoxy.

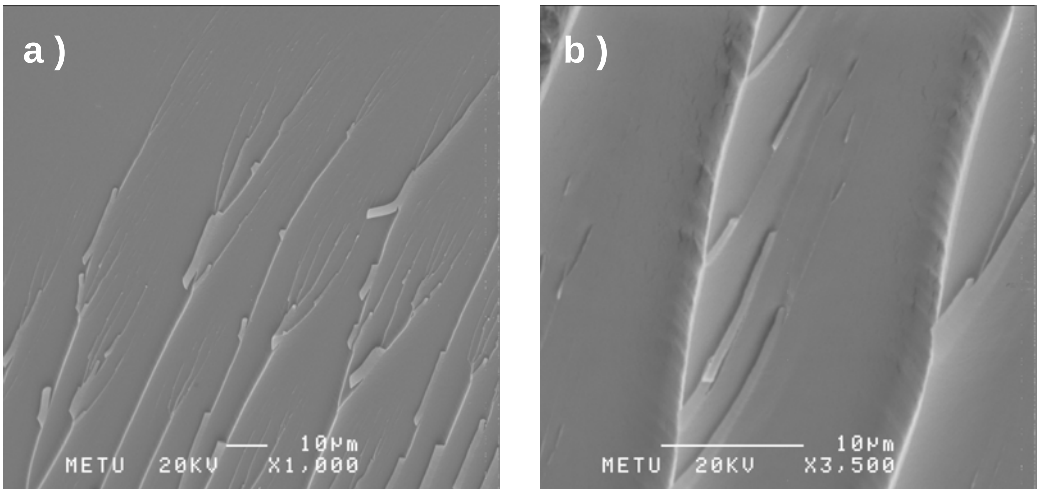


Figure 4.1 SEM micrographs of pure epoxy a) x1000 b) x3500

The effect of carbon black loading (1, 2, 3 or 5 vol %) on the morphologies of the composites can be seen in Figure 4.2. It is inferred that when the carbon black content is increased, agglomerate size decreases by means of glass beads and particles become closer to each other. Then, the continuous network starts to form and as can be seen in later sections, a sharp decrease in electrical resistivity of the samples is obtained at 2 vol % of carbon black.

It can also be observed from the figure that as the filler content was increased, the fracture surface changed into more tortuous structure and crack propagation lines became smaller and non-linear which was the evidence of homogeneous distribution of carbon black particles in the epoxy matrix.

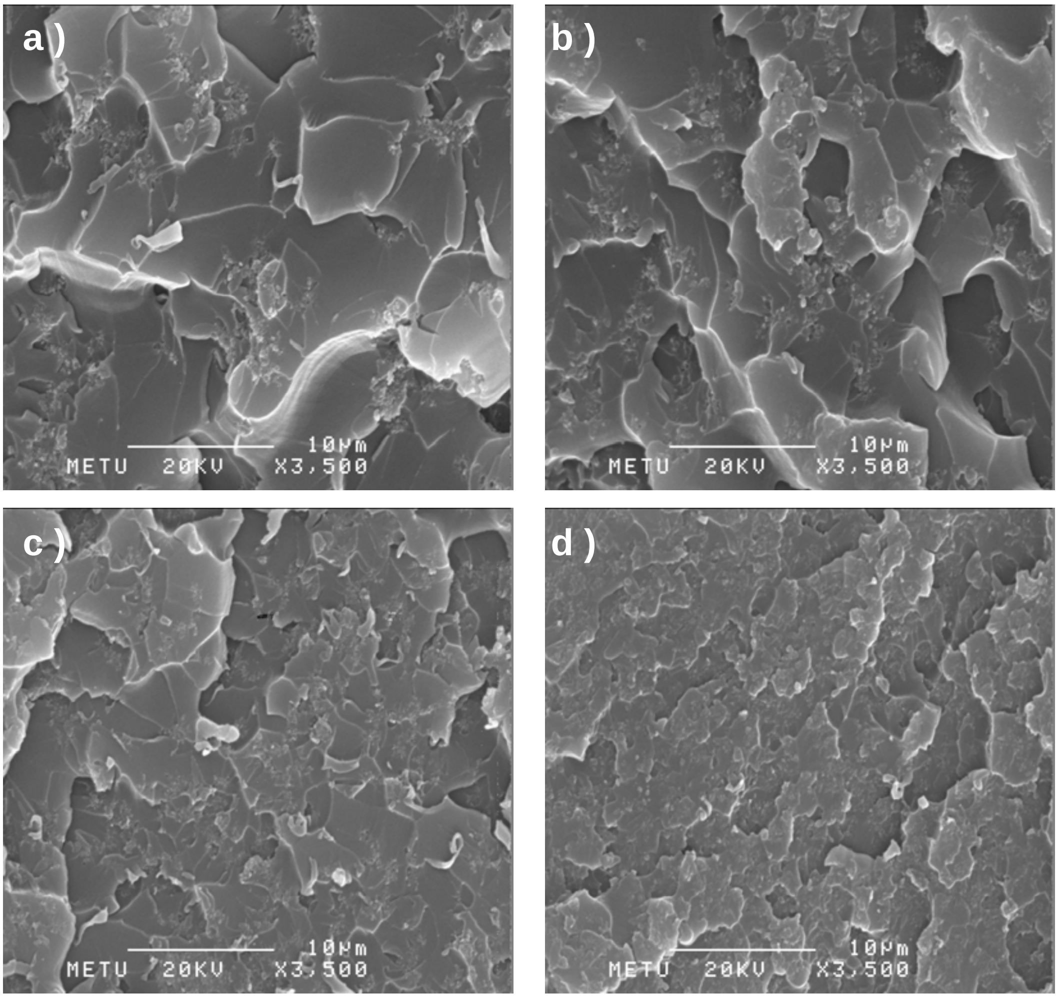


Figure 4.2 SEM micrographs of composites produced by Grinding Method at x3500 magnification containing a) 1 vol %.CB, b) 2 vol % CB, c) 3 vol % CB, d) 5 vol %.CB.

4.1.2 Electrical Properties

The electrical resistivity of the samples produced by Grinding Method is shown as a function of the carbon black content in Figure 4.3. The electrical resistivity decreases with increasing amount of filler. At 2 vol % CB concentration, the electrical resistivity of the sample is reduced to approximately 10^7 ohm.cm. Hence, 2 vol % carbon black content can be set as the percolation concentration which was described previously in Section 2.3.

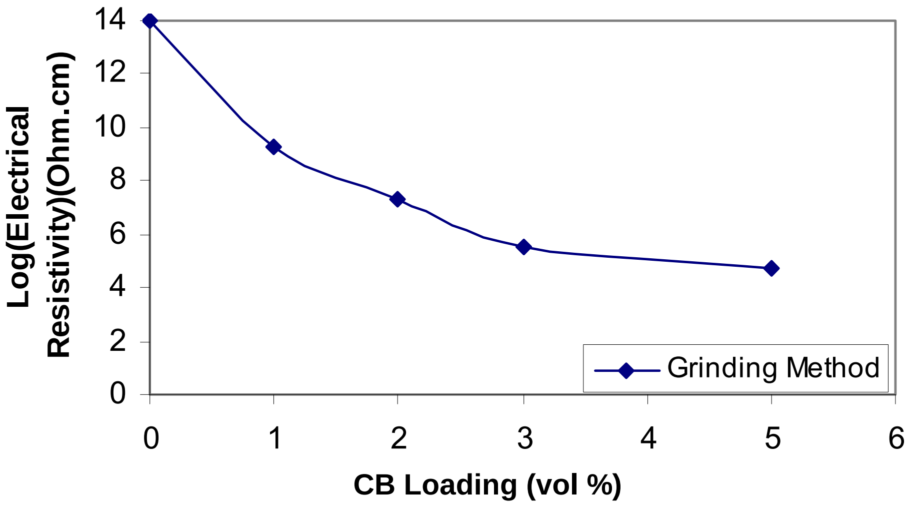


Figure 4.3 Effect of CB loading on electrical resistivity of samples produced by Grinding Method

Furthermore, additional carbon black loading after percolation concentration also results in a decrease in electrical resistivity. However, owing to the difficulty in processing at higher concentrations, it is generally aimed to achieve low resistivity at lowest possible concentrations.

The decrease of the electrical resistivity with increasing filler content can be mainly attributed to decreased distance between particles and it can be obtained by preventing agglomeration and obtaining well-dispersed structure. Good dispersion can be obtained by effective mixing but the size of the agglomerates should also be reduced at the same time.

In Grinding Method, besides more powerful engine, small glass beads were also added to the system in order to mix carbon black and epoxy homogeneously. Introduction of these glass beads to the system helps to decrease the size of the agglomerates and assist in obtaining a more homogeneous structure. Decreasing agglomerate size leads to smaller in distances between the carbon black particles and thus helps them form a continuous network. Moreover, as the distance decreases, the particle-particle interaction increases which allows the carbon black particles to form a conductive network by direct contact or by tunneling mechanism at low concentrations. Therefore, electrical resistivity decreases with conductive filler content. Another reason for having low resistivity values by this method can be attributed to the applied high shear forces via mixing through glass beads, which reduces the potential energy barrier for conductive particles [51].

4.1.3 Mechanical Properties

Mechanical properties of the samples produced by Grinding Method are given in this section as a function of carbon black loading.

4.1.3.1 Tensile Properties

The representative tensile strength, tensile modulus and % elongation at break values of the composites produced by Grinding Method are illustrated in Figures 4.4-4.6 with respect to carbon black loading. The corresponding data are also given in Table A.1 in Appendix A.

The effect of carbon black loading on tensile strength is shown in Figure 4.4. Particle size has significant contribution on the tensile strength of the composites related with the interfacial area per unit volume [43]. At 1 vol.% CB loading, a sharp decrease in tensile strength is observed and then the increasing trend is obtained. At 2 vol.% CB content tensile strength reaches a maximum value. This result can be ascribed to obtaining optimum concentration at which epoxy and carbon black have good interaction with each other. Hence, polymer can equally distribute the external forces to the filler. Moreover, at high carbon black loadings the decrease in tensile strength can be attributed to the agglomeration of carbon black particles and dewetting effect. The tensile strength of the sample containing 5 vol.% CB is higher than the tensile strength of the sample with 3 vol.% CB. This can be due to reduced agglomerate size which is obtained by high shear rate of mixing which is more effective at higher CB loadings.

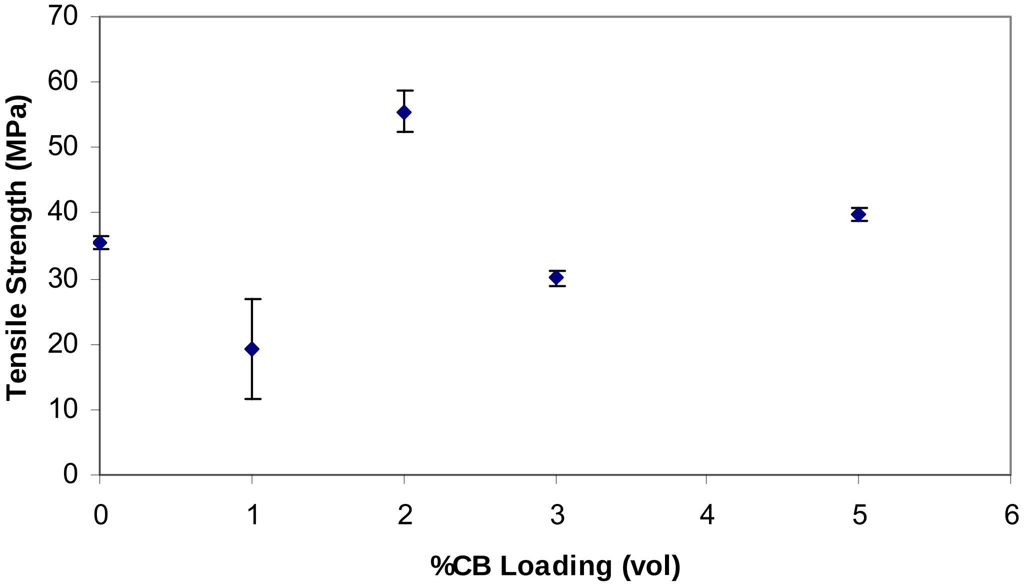


Figure 4.4 Effects of carbon black loading on tensile strength of samples produced by Grinding Method.

The modulus of the composites strongly depends on the ratio of filler modulus to matrix modulus [43]. Since carbon black is among the rigid fillers, it is expected that tensile modulus should increase with increasing carbon black content. However, as can be seen in Figure 4.5 which represents the tensile modulus of the composites with respect to carbon black content, a little decrease in tensile modulus was observed at 1 vol. % compositions of both methods. But, further addition of carbon black resulted in a maximum point in tensile modulus at 2 vol %. This can be explained by enabling small agglomerate size and better dispersion due to the effective mixing.

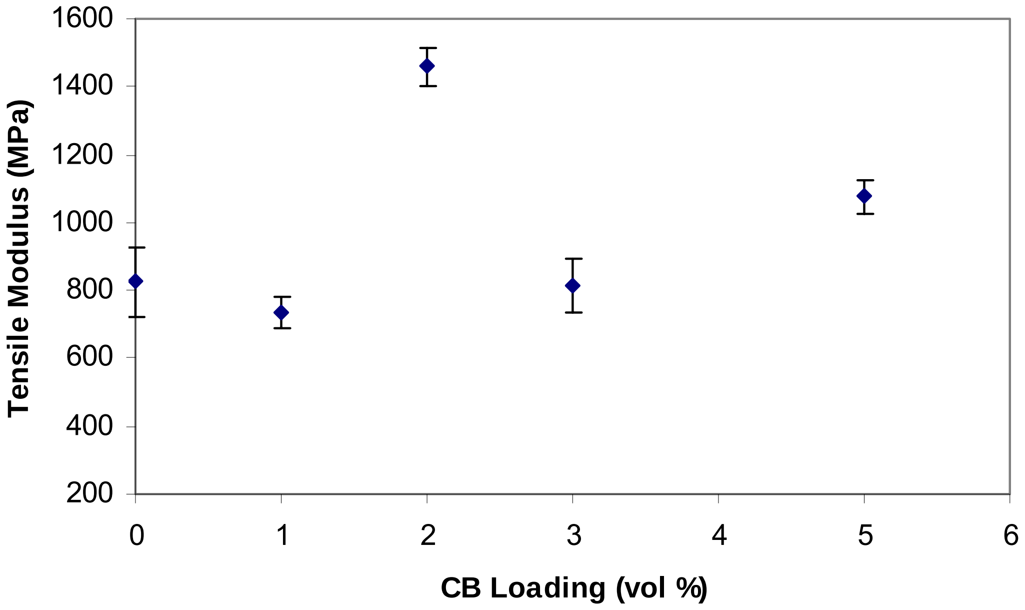


Figure 4.5 Effects of carbon black loading on tensile modulus of samples produced by Grinding Method.

Generally, an increasing trend is obtained in tensile modulus as carbon black content increases since carbon black is rigid filler. It is evident that at 2 vol % CB loading, a maximum point is observed for the modulus which can be due to small agglomerate size of carbon black, homogeneous structure within the matrix and/or possibilities of having high interaction between CB and epoxy.

Figure 4.6 shows the % elongation at break values of composites produced by Grinding Method with respect to carbon black loading. In general, addition of rigid particulate fillers to a polymer matrix decreases the % elongation ar break since a more brittle structure is obtained. At 1 vol % composition, there exists an expected sharp decrease in elongation at break value because of the rigidity of the carbon black. Only in rare instances, if there is a good adhesion between the polymer and the filler, the fracture goes from particle to particle rather than following a direct path, such filled polymers have higher elongation at break when compared to neat resin [43]. As can be seen in Figure 4.6, additional loading of carbon black causes an increase in elongation at break values of the composites.

These results can be attributed to the aforementioned case, but all of the % elongation at break results of the filled samples are still lower than the neat polymer as expected.

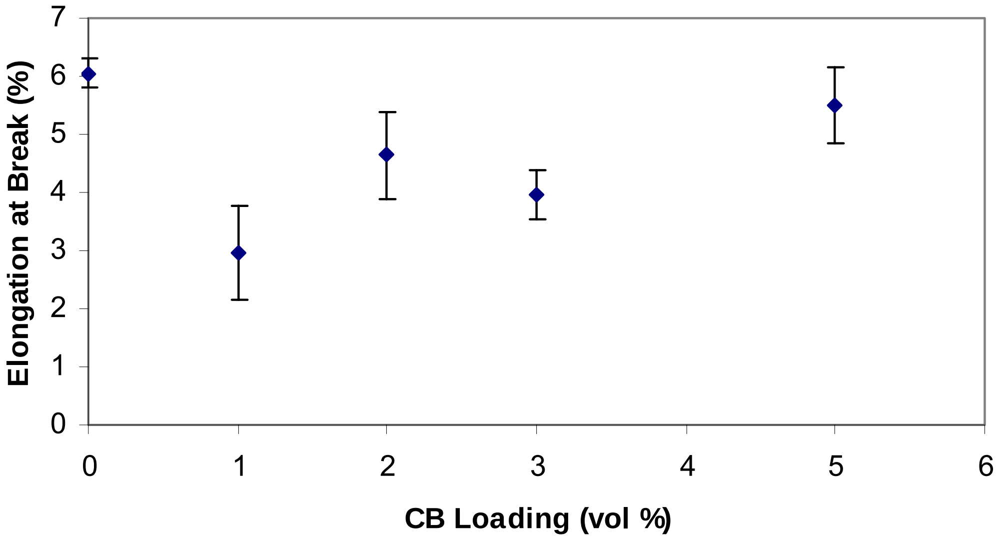


Figure 4.6 Effects of carbon black loading on tensile strain at break of samples produced by Grinding Method.

4.1.3.2 Hardness Properties

In Figure 4.7, the dependency of hardness on carbon black addition is displayed. It is clearly seen that small amount of carbon black addition results in significant increase of hardness, because of rigidity of carbon black. At 2 vol % CB loading, conductive network is started to form which can be confirmed by electrical resistivity values and make the composite harder. This increasing trend in hardness with increasing filler content can also ascribed to additional physical crosslinks which are formed due to the possible filler-matrix interactions.

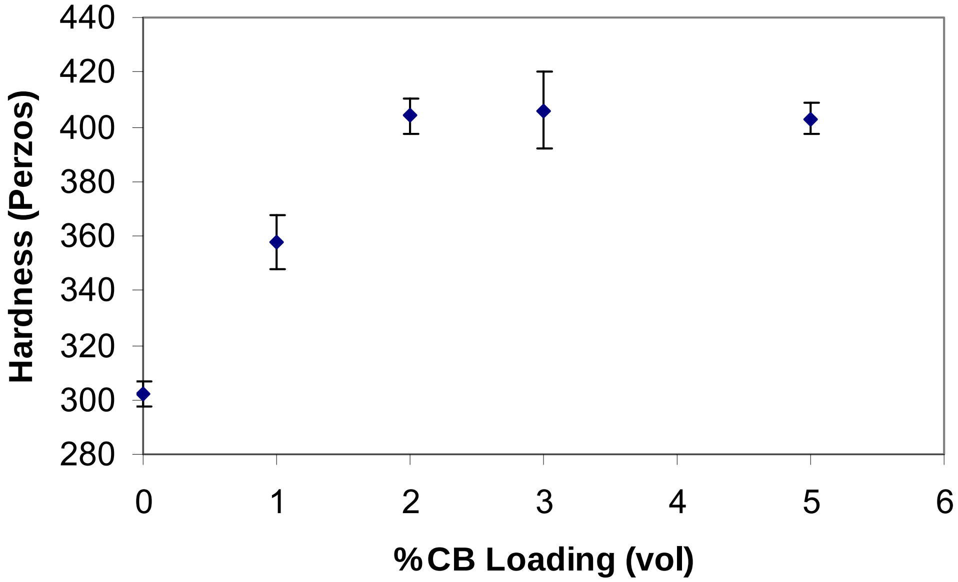


Figure 4.7 Effects of carbon black loading on hardness of samples produced by Grinding Method.

4.1.3.3 Impact Properties

In Figure 4.8, the change of impact energy as a function of carbon black addition is depicted. Impact energy of the composites decreases with carbon black loading. At the concentration at which continuous internal network is formed, as observed from electrical resistivity results, the minimum point is obtained. This fact can be associated with the obtained continuous network which reduces the flexibility of the composites.

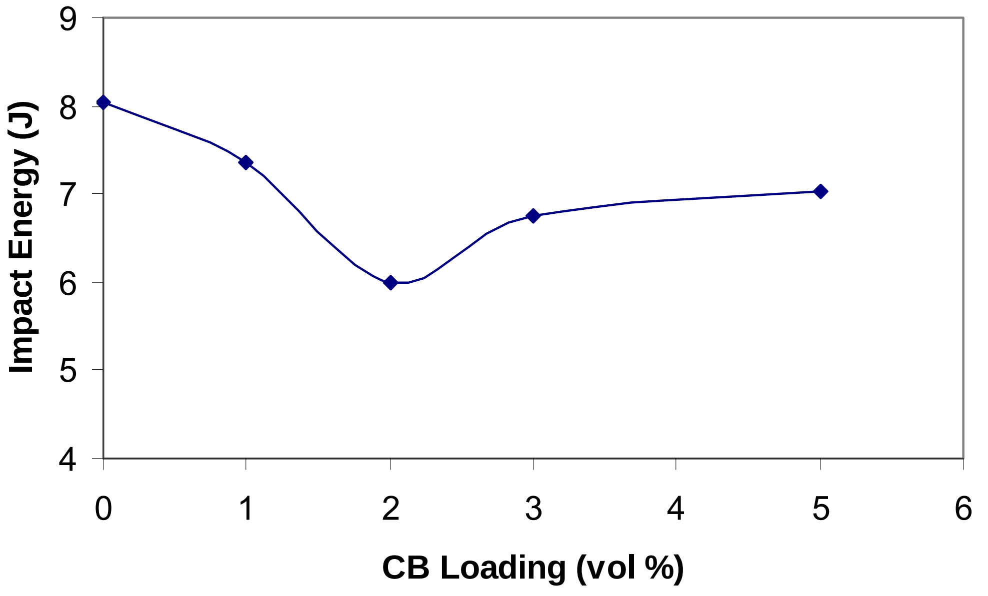


Figure 4.8 Effects of carbon black loading on impact energy of samples produced by Grinding Method.

4.1.3.4 Adhesion Properties

In Figure 4.9 the relation between the adhesion strength and carbon black content is illustrated. The adhesion strength decreases with an increase in carbon black content. This result may be due to the reduced wettability of the epoxy matrix because of carbon black loading.

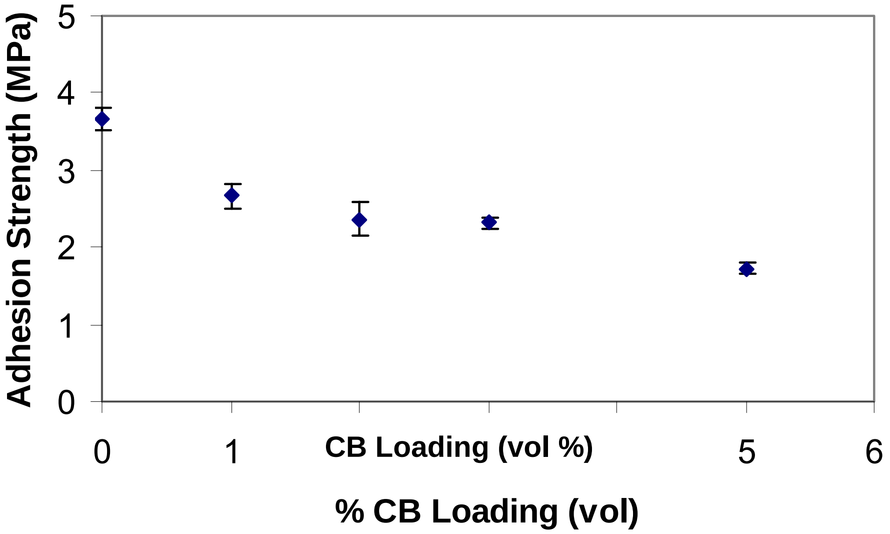


Figure 4.9 Effects of carbon black loading on adhesion strength of samples produced by Grinding Method.

4.2 Ultrasonic Mixing Effects on Electrical and Mechanical Properties of Samples Produced by Grinding Method

In order to produce composites having desired electrical resistivity at lower carbon black loading, application of different process parameters were investigated through literature survey. Then, it was decided to apply ultrasonic mixing on the system just after the mixing process of Grinding Method. Three different ultrasonic mixing times (15, 30 and 45 mins) were selected and applied while CB content was kept constant at 2 vol %. The effect of ultrasonic mixing was studied on electrical and mechanical properties of the samples as can be seen in Figures 4.10-4.13.

4.2.1 Ultrasonic Mixing Effect on Electrical Properties of the Composites

The electrical resistivity of the samples produced by Grinding Method as a function of ultrasonic mixing time is shown in Figure 4.10. It is clear from the Figure 4.10 that the samples obtained by applying ultrasonic mixing during processing have higher resistivity values than the samples obtained without ultrasonic mixing. These results can be due to the reagglomeration of the carbon black particles during ultrasonic mixing. The formed conductive carbon black chains can be broken by additional ultrasonic mixing and these broken conductive carbon black chains results in higher electrical resistivity.

Considering only the results with ultrasonic mixing i.e.; excluding point zero (0 min) the optimum value for electrical resistivity is obtained at a 30 minute ultrasonification. At this point, the broken carbon black chains are reformed and a decrease in electrical resistivity is obtained. However, considering all data, Figure 4.10 clearly depicts that the zero point which corresponds to mixing without ultrasonification has lower resistivity compared to the data with ultrasonic mixing. With respect to the figure, it would be true to state that ultrasonic mixing has no positive effect on electrical conductivity of the composites.

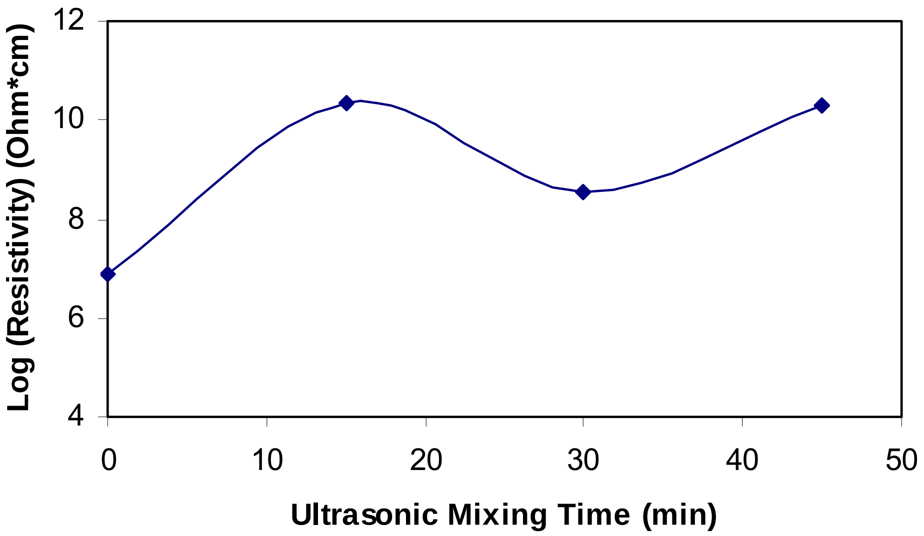


Figure 4.10 Effect of ultrasonic mixing time on electrical resistivity of the samples containing 2 vol % CB produced by Grinding Method.

4.2.2 Ultrasonic Mixing Effect on Mechanical Properties of the Composites

Mechanical properties of the samples produced by Grinding Method with ultrasonic mixing are given in Figures 4.11-4.13. The dependence of tensile strength, tensile modulus and % elongation at break values of the samples containing 2 vol % CB on ultrasonic mixing time are presented in this section. The corresponding data are also given in Table A-2.

Ultrasonication yields a high energy density in the mixture and increase the collision between the particles which leads to break carbon black agglomerates. This results in an improvement in mechanical properties of the composites. However, at the same time, high energy may also damage the formed connective network which will decrease the electrical conductivity as mentioned in previous section [53]. As can be observed in Figures 4.11-4.13, it is evident that the effect of ultrasonic mixing on tensile properties is not significant compared to the case for the process without ultrasonic mixing.

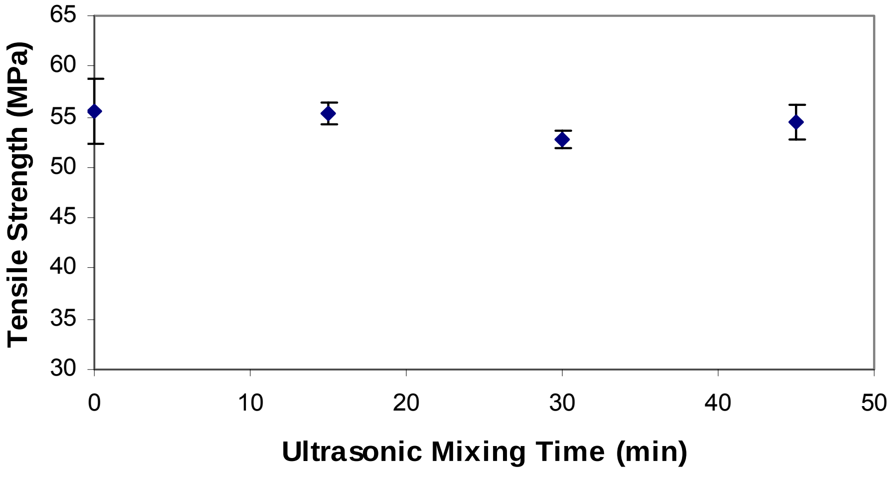


Figure 4.11 Effect of ultrasonic mixing time on tensile strength of the samples containing 2 vol % CB produced by Grinding Method

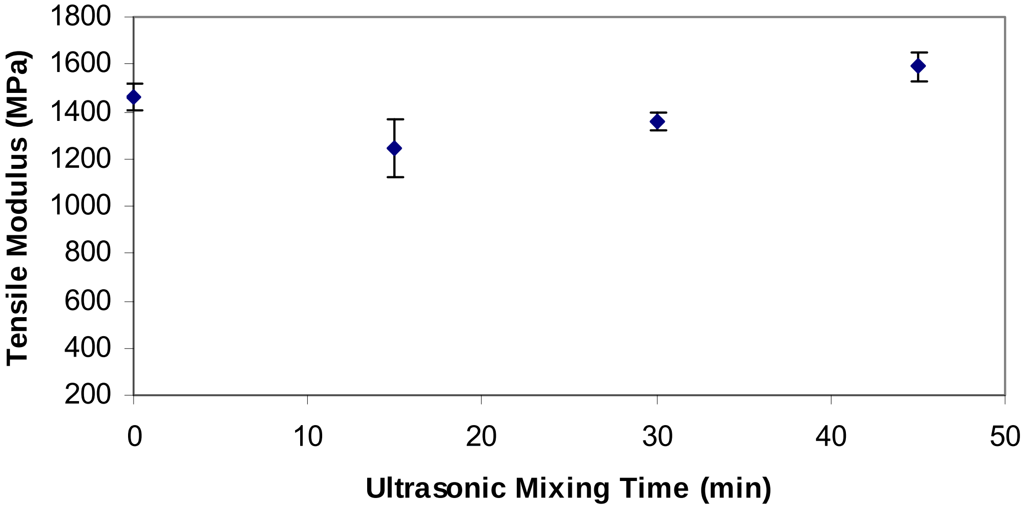


Figure 4.12 Effect of ultrasonic mixing time on tensile modulus of the samples containing 2 vol % CB produced by Grinding Method

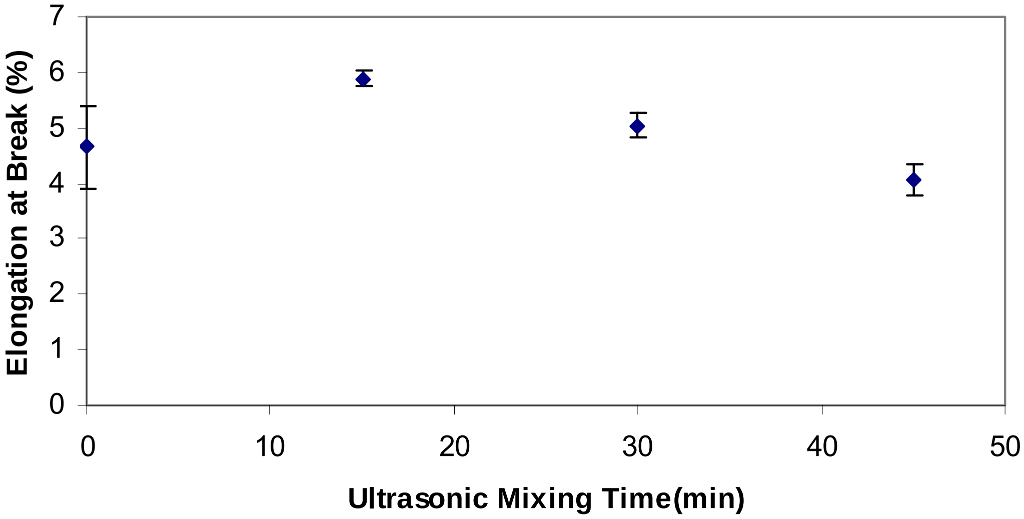


Figure 4.13 Effect of ultrasonic mixing time on elongation at break of the samples containing 2 vol % CB produced by Grinding Method.

4.3 Effects of Mixing Type on Morphologies, Electrical and Mechanical Properties of Epoxy/ Carbon Black Composites

In this study, samples filled with carbon black were also prepared by using the Mechanical Mixing Method in order to compare the results of different mixing processes. In Mechanical Mixing Method three different concentrations (1, 3 and 5 vol %) were studied at 100 rpm for 60 minutes.

4.3.1 Scanning Electron Microscopy Analysis

In order to observe the effect of mixing type on morphologies of the carbon black/epoxy composites, SEM analyses were performed on the fractured surfaces of the composites which were produced by two different methods namely Mechanical Mixing and Grinding Method.

Figure 4.14 - 4.16 show the micrographs of samples containing, 1, 3 and 5 vol % CB respectively. In these figures a) and b) represent the fracture surface of samples produced by Mechanical Mixing Method at magnification of x1000 and x3500, on the other hand, c) and d) represent the fracture surface of samples produced by Grinding Method at magnification of x1000 and x3500, respectively.

In Figures 4.14 through 4.16, the distribution of the carbon black agglomerates in the epoxy matrix can be seen. It is known that when considering the dispersion of conductive filler in the polymer matrix, diffusion process and particle-particle interaction forces play significant role in network formation [51].

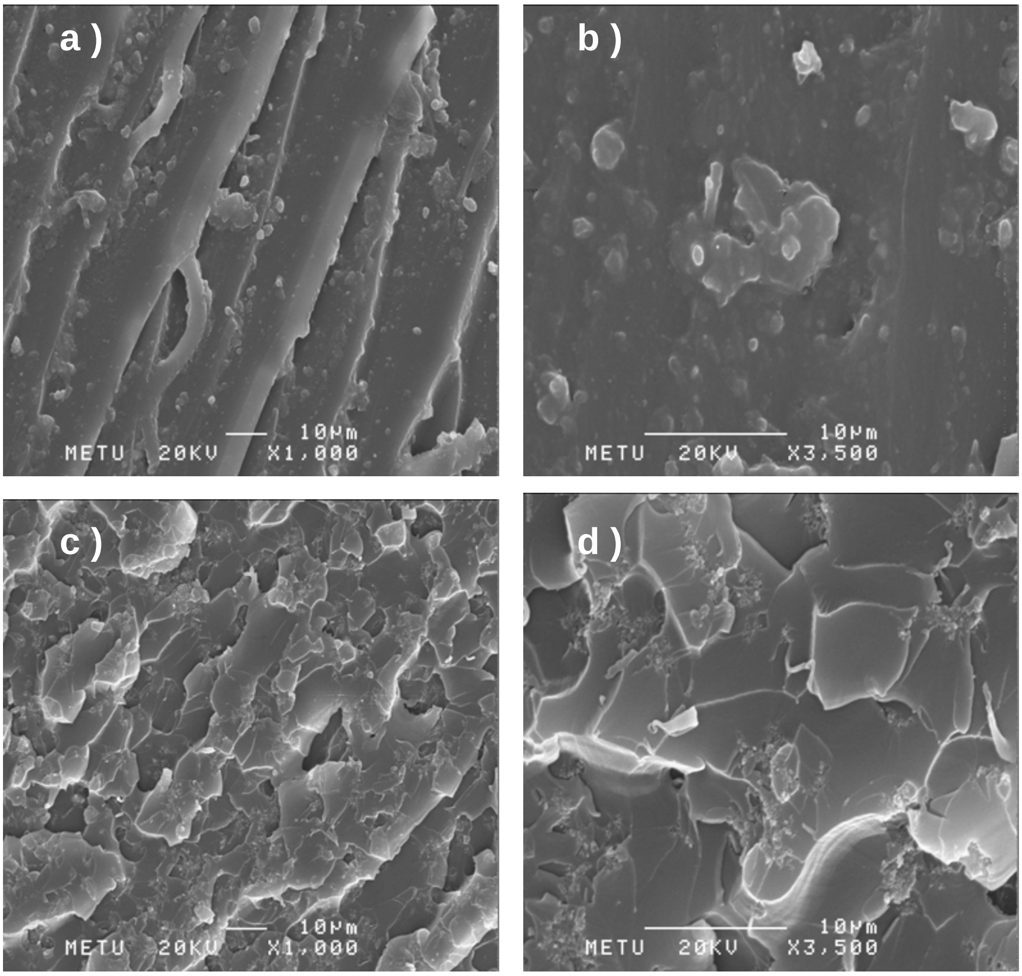


Figure 4.14 SEM micrographs of composites containing 1 vol % CB, a) produced by Mechanical Mixing Method x1000, b) produced by Mechanical Mixing Method x3500, c) produced by Grinding Method x1000, d) produced by Grinding Method x3500.

It is observed from Figure 4.14 that the fracture surfaces of the samples produced by two methods are different. Sample obtained by Grinding Method has tortuous crack propagation path while the sample produced by Mechanical Mixing Method has parallel crack lines similar to neat epoxy. From a structural point of view, many non-linear cracks are formed simultaneously in the case of well-dispersion [43].

From Figures 4.15 and 4.16, it can be noticed that the degree of compacting increased with increasing carbon black content, but this effect is more obvious in samples produced by Grinding Method. This compact structure is called as “spongelike” structure [54], and in accordance with this structure; the dispersed particle morphology forming a continuous network is obtained in the epoxy as seen in the micrographs. This can be also supported by electrical resistivity values of the samples prepared by Grinding Method.

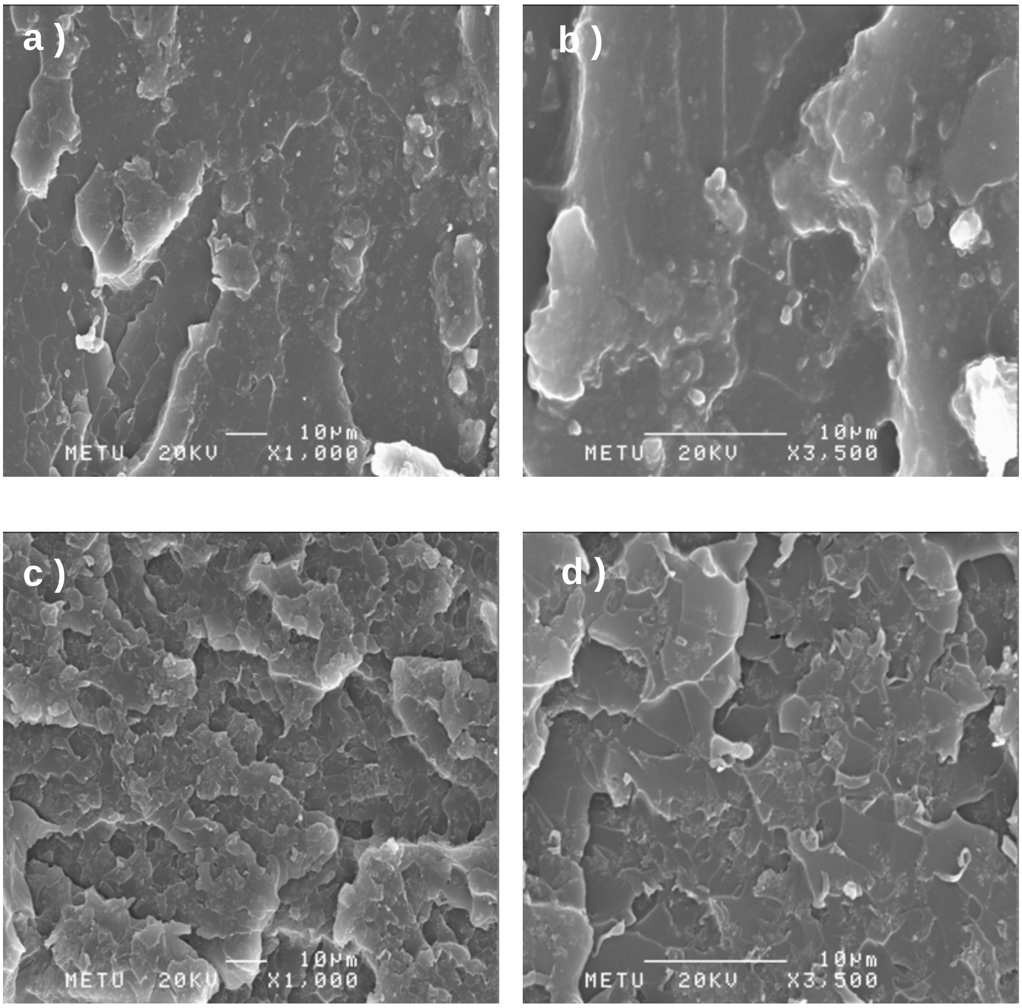


Figure 4.15 SEM micrographs of composites containing 3 vol % CB, a) produced by Mechanical Mixing Method x1000, b) produced by Mechanical Mixing Method x3500, c) produced by Grinding Method x1000, d) produced by Grinding Method x3500.

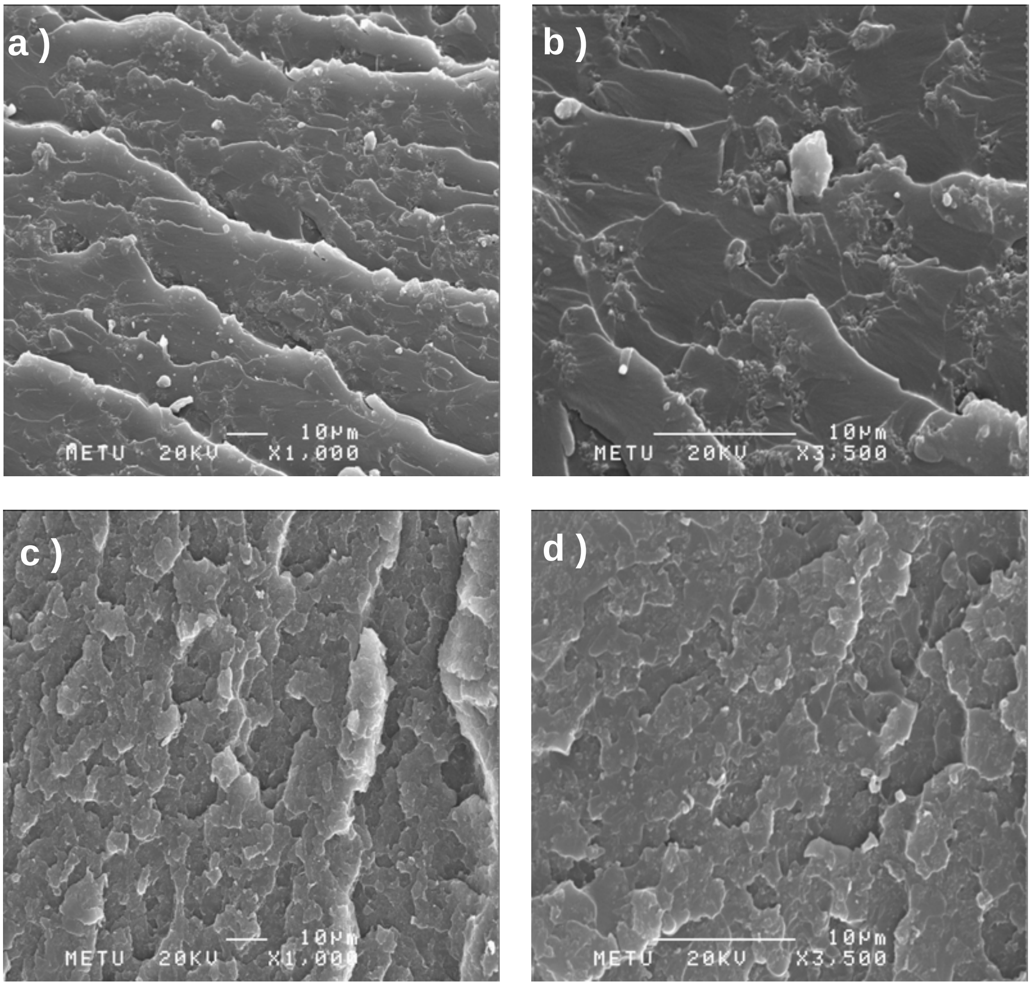


Figure 4.16 SEM micrographs of composites containing 5 vol % CB, a) produced by Mechanical Mixing Method x1000, b) produced by Mechanical Mixing Method x3500, c) produced by Grinding Method x1000, d) produced by Grinding Method x3500.

It is clearly seen from the micrographs that homogeneous dispersion of carbon black particles is obtained by Grinding Method. This can be attributed to the more effective mixing capability of this method due to the existence of glass beads providing high shear forces in the system.

4.3.2 Electrical Properties

The effect of type of mixing process on electrical resistivity of the composites is seen in Figure 4.17. It is clear from the figure that the samples obtained by using Grinding Method have lower resistivity values than samples produced by Mechanical Mixing Method. It can also be seen that addition of carbon black to neat polymer matrix results in a decrease in resistivity values for both two methods but further addition has no positive effect on resistivity of samples produced by Mechanical Mixing Method. This might be due to inefficient mixing properties. The force applied by this method might be inadequate to breakdown carbon black agglomerates. On the other hand, for the samples produced by Grinding Method, dramatical decrease in resistivity is obtained with the addition of carbon black concentrations higher than 1 vol %. This significant difference between two methods can be attributed to the efficiency of the mixing processes.

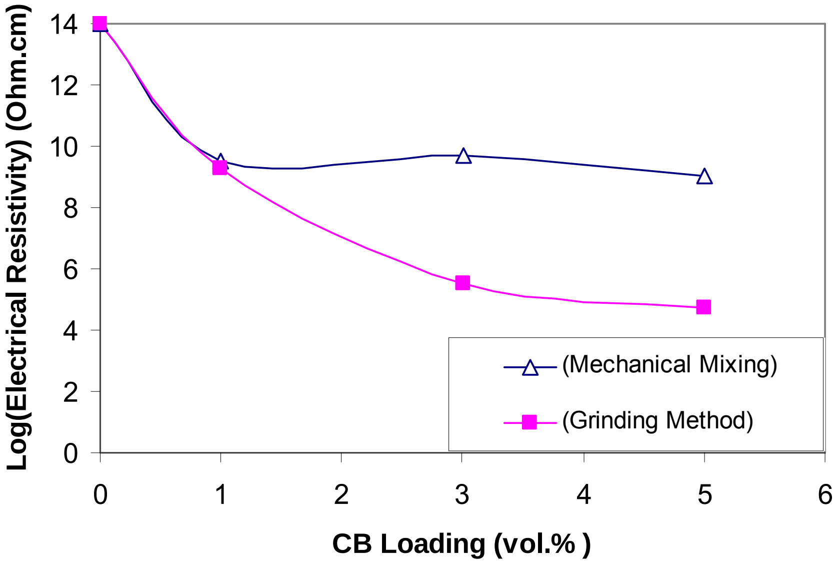


Figure 4.17 Effects of mixing process on electrical conductivity of samples filled with carbon black.

In this study, it was aimed to obtain polymer composite which have electrical conductivity in semi-conductive region at relatively low composition. So, Grinding Method yields favorable results compared to Mechanical Mixing Method in terms of electrical property.

4.3.3 Mechanical Properties

Another aim of the study was to obtain electrically conductive polymer composites in semiconductive region without sacrifying mechanical properties. As mentioned previously, two different mixing processes were used in the study. In order to investigate the effects of mixing type on the mechanical properties of the produced composites, tensile, hardness, impact and adhesion tests were performed on the samples produced using both methods.

4.3.3.1 Tensile Properties

Tensile strength, tensile modulus and elongation at break results for the samples produced with both methods are compared in Figures 4.18-4.20. Table A-3 in Appendix A shows the corresponding data for the samples produced by Mechanical Mixing Method.

As mentioned in section 4.1.3 dimension of filler has a strong effect on tensile strength. Since the carbon black particles have a tendency to form agglomerate, more effective mixing should be applied to prevent agglomeration and to obtain homogeneous structure. By Grinding Method, it was aimed to reduce agglomerate size of carbon black and increase the interaction surface area of polymer and filler which contributed to obtaining higher tensile strength values. As demonstrated in Figure 4.18, at 3 and 5 vol % CB compositions, samples produced by Grinding Method have higher tensile strength values than those of Mechanical Mixing Method. These results might be the due to better dispersion of the particles and decreased agglomerate size produced by Grinding Method. However, at loading of 1 vol % carbon black, lower tensile strength is obtained for samples of Grinding Method.

The reason for this may be the entrapped air which might not be eliminated totally during the vacuum application. Therefore the tensile strength decreases as the amount of entrapped air increases [43].

However, it can also be seen from Figure 4.18 that addition of carbon black to neat epoxy matrix showed no significant positive effect on tensile strength. Only at 5 vol % carbon black loading, higher tensile strength value is obtained for the samples produced by Grinding Method that may be the consequence of well-dispersion and small agglomerate size of the carbon black particles which increase the interaction area between the polymer and the filler.

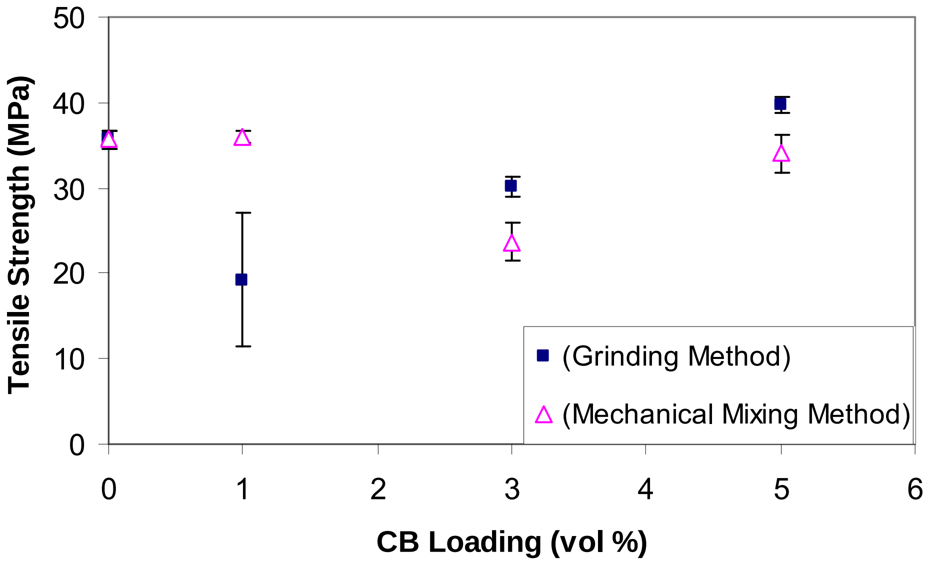


Figure 4.18 Effects of mixing process on tensile strength of samples filled with carbon black.

In Figure 4.19, the tensile modulus values of samples produced by two methods are given.

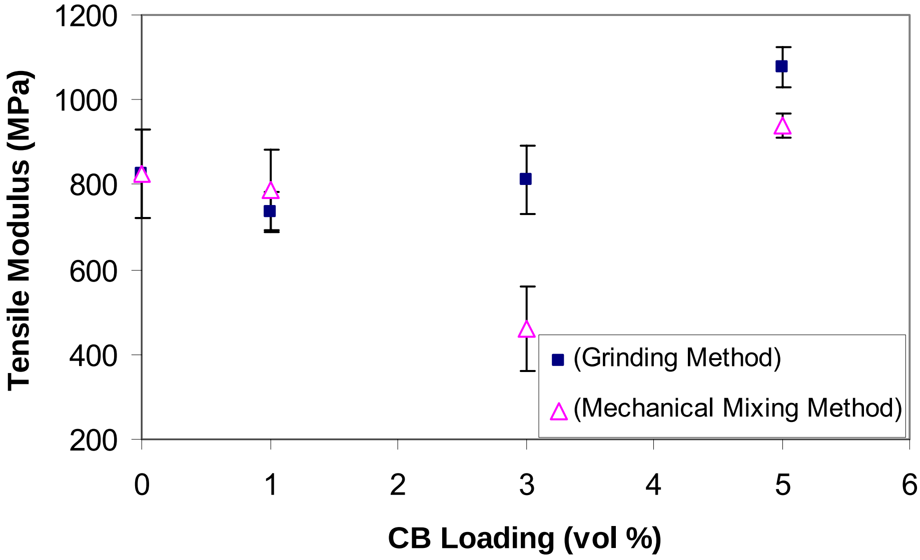


Figure 4.19 Effects of mixing process on tensile modulus of samples filled with carbon black.

In the case of Grinding Method, the materials have higher tensile modulus especially at high concentrations of CB. The differences between the samples produced by two methods are due to the different mixing capabilities of the methods. For the materials produced by Mechanical Mixing Method, carbon black particles may form agglomerates destroying the adhesion between the matrix and the filler resulting in a decrease in modulus.

Elongation at break values of samples prepared by both methods as a function of filler content is shown in Figure 4.20. For Mechanical Mixing Method, a fluctuation was seen which is the result of inefficient mixing and incompleteness of the conductive network. In the Mechanical Mixing Method, the electrical conductivity does not change with CB content in the 3-5 vol % CB range; this also shows that the mixing is inefficient with this method. The reasons given in Section 4.1.3 for Grinding Method are also valid here.

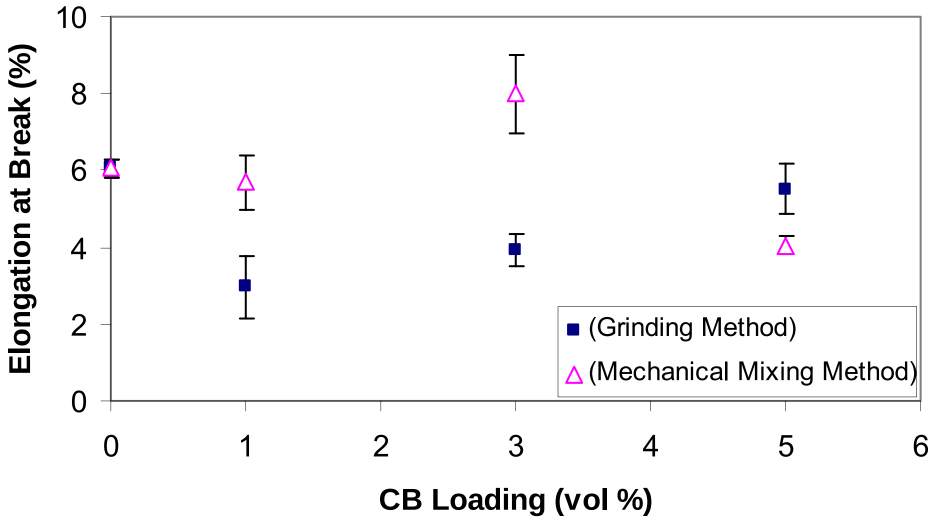


Figure 4.20 Effects of mixing process on percent elongation at break of samples filled with carbon black.

4.3.3.2 Hardness Properties

Pendulum hardness test method was applied to the samples produced by both methods. However, for the samples produced by Mechanical Mixing Method, the surface of the specimens applied to the metal and glass surfaces was not suitable for the coating applications. The surfaces were too rough to apply this test; consequently the test could not be applied for this method. Hardness results for Grinding Method were given in Section 4.1.3.

4.3.3.3 Impact Properties

Impact test was not also applied because of the reason mentioned above for Mechanical Mixing Method. Impact results for Grinding Method were given in Section 4.1.3.

4.3.3.4 Adhesion Properties

Adhesion test could not be applied because of the same reason given for Mechanical Mixing Method. Adhesion test results for Grinding Method were given in Section 4.1.3.

4.4 Effects of Surface Modification on Morphologies, Electrical and Mechanical Properties of Epoxy/Carbon Black Composites

4.4.1 X-Ray Photoelectron Spectroscopy (XPS) Analysis

In order to compare the surface functional group of the neat carbon black and chemically modified carbon black, X-Ray Photoelectron Spectroscopy analysis was used. The information of possible chemical bonds on the surface can be obtained by XPS as well as elemental information. Only hydrogen atom can not be detected by XPS because of its high binding energy. The obtained elemental XPS results can be seen in the following Table 4.1

Table 4.1 Elemental Composition of Untreated Carbon Black Surface by XPS

Element	(%)
Carbon	94.9
Oxygen	3
Nitrogen	1.7
Sulphur	0.4

Carbon black has graphite like structure and the imperfections of this structure strongly affect the electrical conductivity of the black negatively. The non-carbon atoms might damage graphitic structure of the carbon blacks. However, Pantes et al. [55] showed that the concentration of non-carbon elements is not a determining factor for electrical conductivity. It is thought that intrinsic conductivity of carbon black might depend on electrical character of surface functional groups. Hence, detailed information on the graphite structure is extracted from the XPS spectra.

4.4.1.1 Carbon Spectra of Neat Carbon Black

The C 1s spectra (see Figure 4.21) of untreated carbon black used in this study are fitted to five peaks; a sharp graphite peak in polyaromatic structure at 284.4 eV, four small peaks for carbon atoms with one, two or three bonds with oxygen.

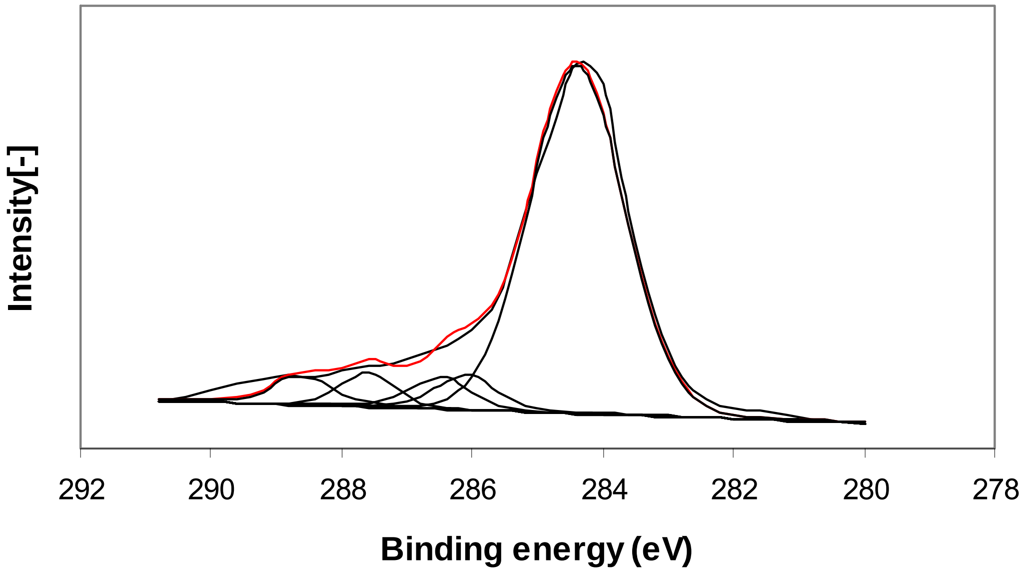


Figure 4.21 XPS spectra of carbon (C 1s) of neat carbon black

The probable functional groups on carbon black surfaces, their relative peak areas and also binding energies (B.E) are given in Table 4.2.

Table 4.2 Carbon XPS spectra of neat carbon black and relative peak areas of functional groups

Sample	C 1s spectra	B.E (eV)	Peak Area (%)
Neat Carbon Black	(C-C (or graphite peak))	284.1	37.4
	(C-OH)	286.1	15.9
	(C-O)	286.5	15.7
	(-C=O- or -O-C-O-)	287.6	15.5
	(COOH)	288.6	15.6

As can be understood from the table, C 1s spectra of carbon black are dominated by an intense graphite peak. In addition, the results of the elemental analysis of neat carbon black mentioned in previous section show that carbon black consists of 94.9 % C element, but in order to obtain high conductivity, C elements should be in graphite structure.

4.4.1.2 Oxygen Spectra of Neat Carbon Black

In addition to carbon, other elements are present on the commercial carbon black surfaces. Thus, oxygen spectra are also extracted from XPS spectra. Figure 4.22 shows high resolution spectra of oxygen (O 1s) of neat carbon black. It is seen that different types of oxygen groups are present on the surfaces of carbon black. The possible oxygen groups on neat carbon black, the relative peak areas and binding energies of these groups are given in Table 4.3.

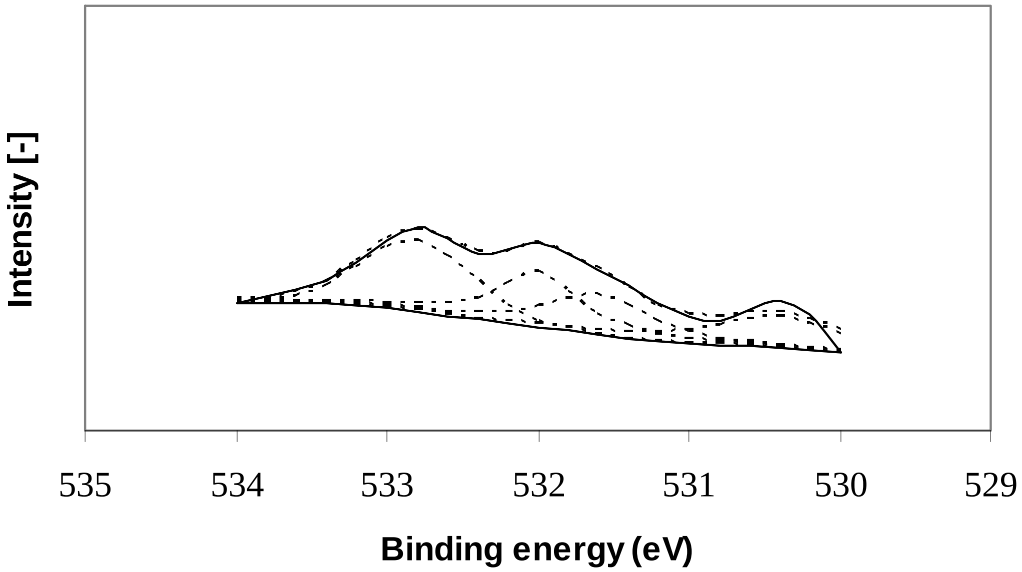


Figure 4.22 XPS spectra of oxygen (O 1s) of neat carbon black

It is clear from the figure that there exists certain amount of surface oxygen in the form of carboxyl or hydroxyl type surface functional group. In addition, adsorbed oxygen may contribute at 530.4 eV.

Table 4.3 Oxygen XPS spectra of neat carbon black and relative peak areas of functional groups

Sample	O 1s spectra	B.E (eV)	Peak Area (%)
Neat Carbon Black	Adsorbed O_2	530.3	25.5
	(C=O or –OH)	531.6	25.0
	(OH-)	532	24.7
	(C-OH and/or C-O-C)	532.8	24.8

4.4.1.3 Nitrogen Spectra of Neat Carbon Black

The detailed investigation of XPS spectra of carbon black shows that some functional groups containing nitrogen are present. High resolution spectra of nitrogen (N 1s) of neat carbon black are illustrated in Figure 4.23.

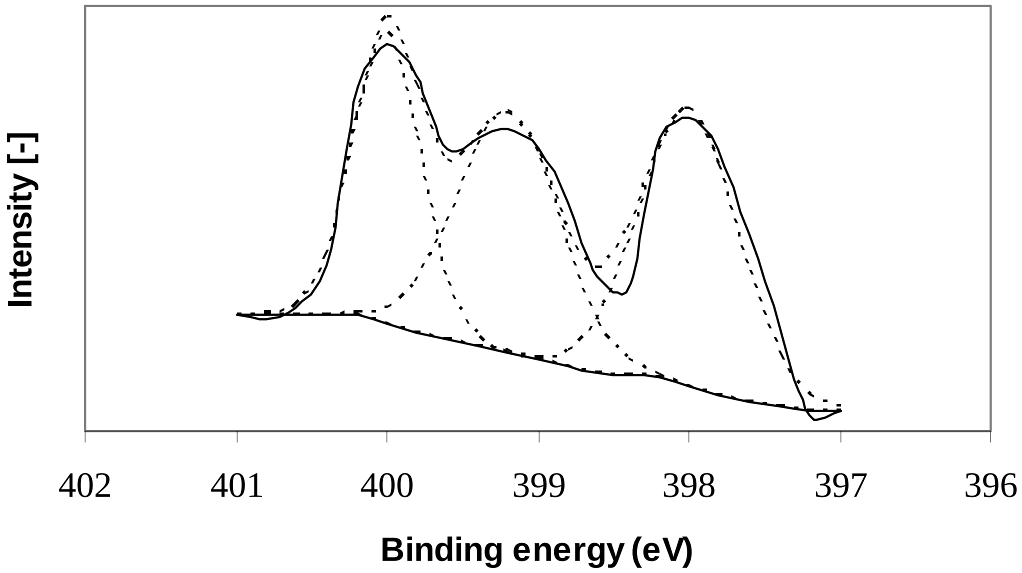


Figure 4.23 XPS spectra of nitrogen (N 1s) of neat carbon black

As it is clear from the figure, the nitrogen spectra are fitted to three peaks; one peak for adsorbed nitrogen, one peak for N-C type and one for nitrogen in conjugated structure of graphene. The relative peak areas of the fitted groups can be seen in Table 4.4.

Table 4.4 Nitrogen XPS spectra of neat carbon black and relative peak areas of functional groups

Sample	N 1s spectra	B.E (eV)	Peak Area (%)
Neat Carbon Black	Nitrogen in the conjugated structure of graphene	398.1	33.5
	NH_2-Ph	399.2	33.4
	Adsorbed N_2	400	33.1

4.4.2. XPS Analysis for Surface-Treated Carbon Black

Four different types of coupling agents, 3-Aminopropyltriethoxysilane (Ameo), 3-Aminopropylmethyldiethoxysilane (1505), N-(n-Butyl)-3-aminopropyltrimethoxysilane (1189), 3-Glycidyloxypropyltrimethoxysilane (Glymo), and formamide were used in this study to modify the surface chemistry of the carbon black particles. In order to observe the effect of surface modification on functionality of the surfaces, the XPS analysis was performed for the carbon blacks modified with Ameo and formamide. The reason for selecting these two chemicals is based on the goal of obtaining high electrical conductivity for the composites treated with these chemicals.

4.4.2.1 Carbon Spectra of Modified Carbon Black

The change of the intensity of the chemical bonding of carbon element by surface modification is given in Table 4.5. It is clear from Table 4.5 that chemistry of the carbon black surface is altered by chemical treatment.

In Table 4.5, the intensity of the functional groups on untreated and treated carbon black is compared according to their relative peak areas so that each column should be considered separately. It is also valid for Table 4.6 and 4.7.

Table 4.5 Change of carbon XPS spectra and relative peak areas of functional groups by surface modification

C 1s spectra	Relative Peak Area (%)		
	Neat Carbon Black	Modified CB with Ameo	Modified CB with formamide
(C-C (or graphite peak)	37.4	26.0	32.2
(C-OH)	15.9	15.0	17.4
(C-O)	15.7	15.0	17.0
(-C=O- or -O-C-O-)	15.5	29.0	16.8
(COOH)	15.6	15.0	16.6

High resolution of C 1s spectra of modified carbon black with Ameo type silane coupling agent and formamide are given in Figures 4.24 and 4.25 respectively.

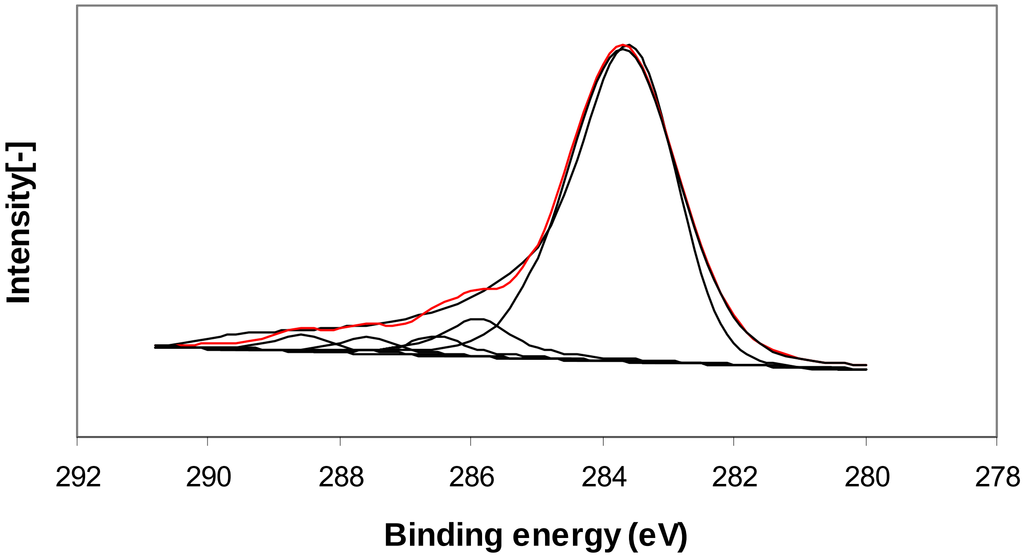


Figure 4.24 XPS spectra of carbon (C 1s) of modified carbon black with ameo

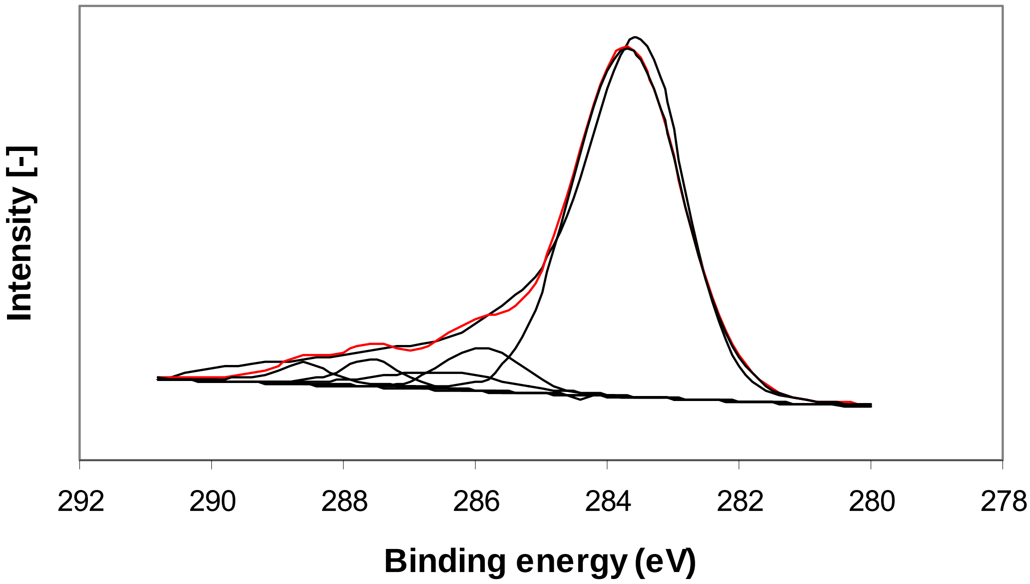


Figure 4.25 XPS spectra of carbon (C 1s) of modified carbon black with formamide

4.4.2.2 Oxygen Spectra of Modified Carbon Black

XPS spectra of oxygen (O 1s) of modified carbon black with ameo and formamide are fitted to only two peaks; a peak for C=O type oxygen and a peak for C-O type oxygen (C-OH, C-O-C). As seen in Table 4.6, there is a significant change in concentration of C=O and C-O type functional groups on the surfaces. This may be due to the oxidation reactions occurring on the carbon black surfaces.

Table 4.6 Change of oxygen XPS spectra and relative peak areas of functional groups by surface modification

O 1s spectra	Relative Peak Area (%)		
	Neat Carbon Black	Modified CB with Ameo	Modified CB with formamide
Adsorbed O_2	25.5	a	a
(C=O or –OH)	25.0	53	52
(OH-)	24.7	a	a
(C-OH and/or C-O-C)	24.8	47	48

a: No peak detected

High resolution spectra of oxygen (O 1s) of treated carbon black with Ameo and formamide are also given in Figures 4.26 and 4.27, respectively.

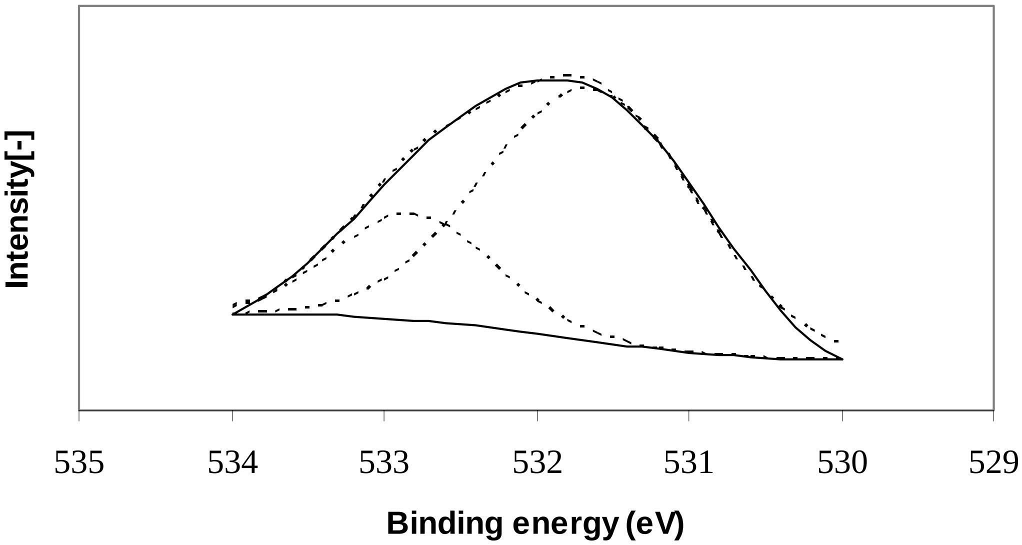


Figure 4.26 XPS spectra of oxygen (O 1s) of modified carbon black with ameo

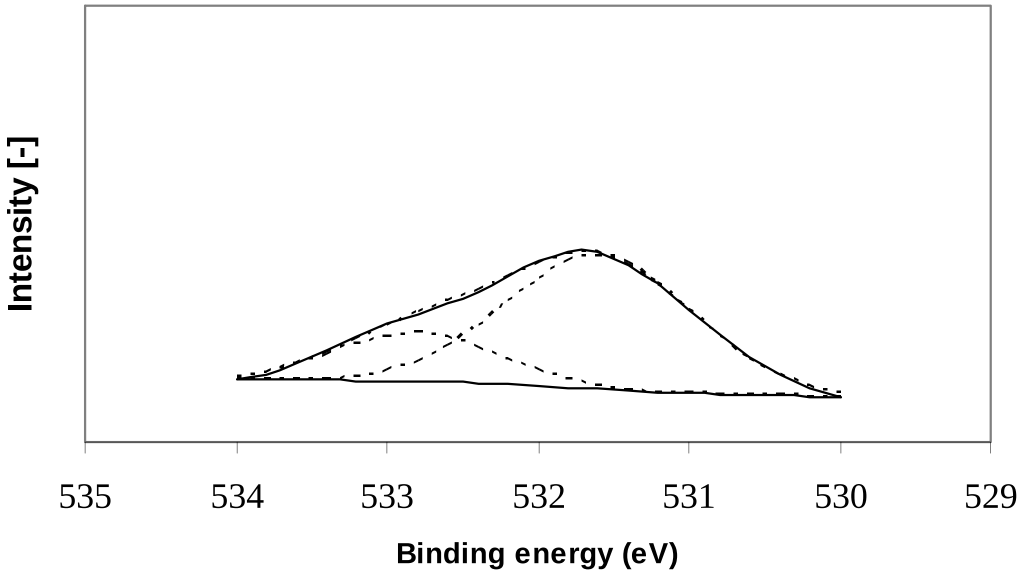


Figure 4.27 XPS spectra of oxygen (O 1s) of modified carbon black with formamide

4.4.2.3 Nitrogen Spectra of Modified Carbon Black

Table 4.7 represents the comparison of neat and modified carbon black surface chemistry. As seen in the table, there is a significant change in surface chemistry of treated carbon black.

Table 4.7 Change of nitrogen XPS spectra and relative peak areas of functional groups by surface modification

N 1s spectra	Relative Peak Area (%)		
	Neat Carbon Black	Modified CB with Ameo	Modified CB with formamide
Nitrogen in the conjugated structure of graphene	33.5	a	a
Nitride	a	33.3	a
NH_2-Ph	33.4	a	a
NH_2		33.4	a
NH_3	a	a	33.8
N-H or N-O	a	a	33.2
Adsorbed N_2	33.1	a	33.1
($H3N^+CHRCOO^-$)	a	33.3	a

a: No peak detected

High resolution spectra of nitrogen (N 1s) are given in Figures 4.28 and 4.29. The N 1s spectra of Ameo treated carbon black are fitted to three peaks; a peak for nitrogen of nitride at 397.7 eV, a peak for NH_2 type nitrogen at 399.3 eV and a peak for $H_3N^+CHRCOO^-$ type nitrogen at 400.9 eV. In addition, N 1s spectra of carbon black treated by formamide exhibited three different peaks; a peak for adsorbed nitrogen at 397 eV, a peak for NH_3 type nitrogen at 398.6 eV and a peak for nitrogen (N-H or N-O) at 400.2 eV. The observed new functional groups show that the surface of the carbon black was modified successfully.

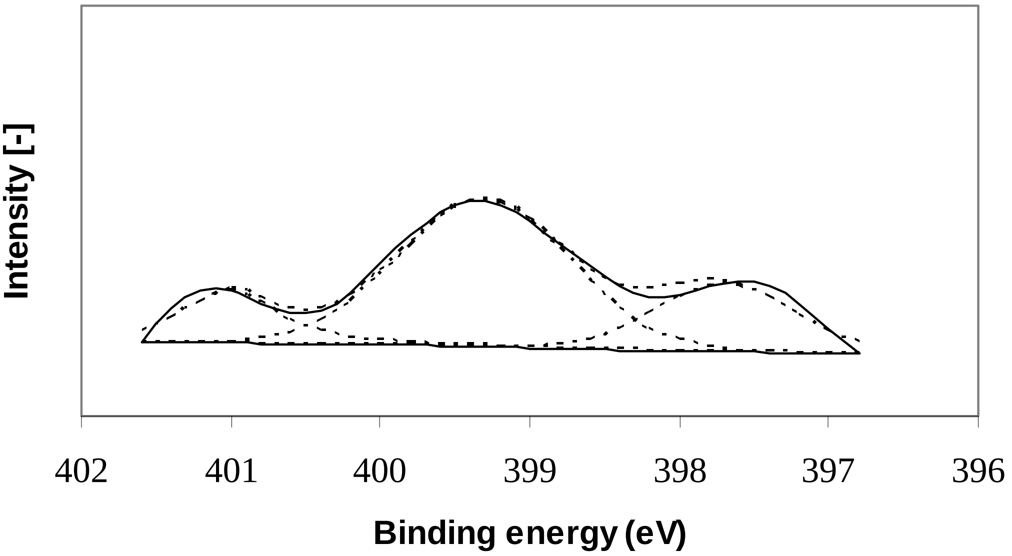


Figure 4.28 XPS spectra of nitrogen (N 1s) of modified carbon black with ameo

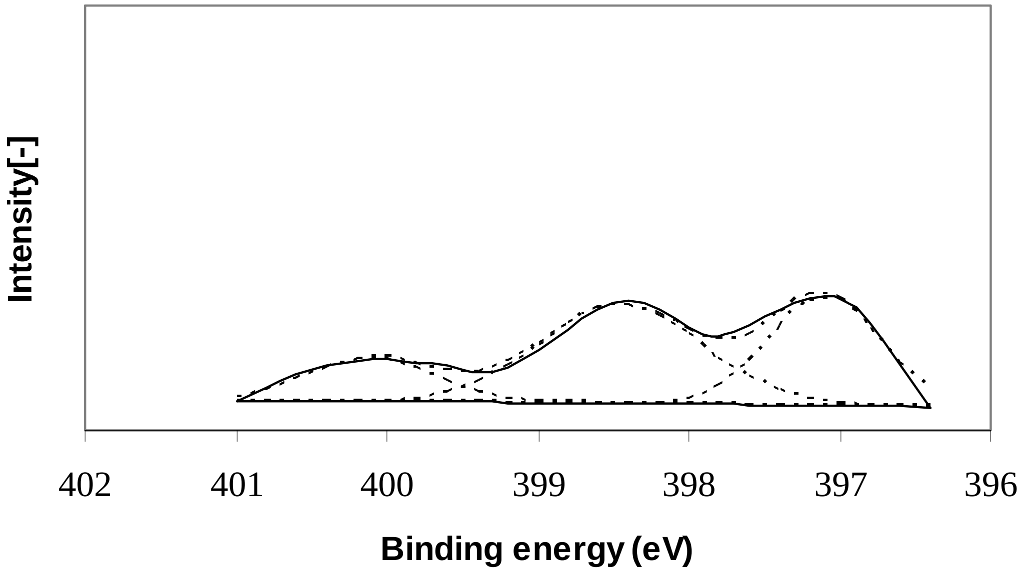
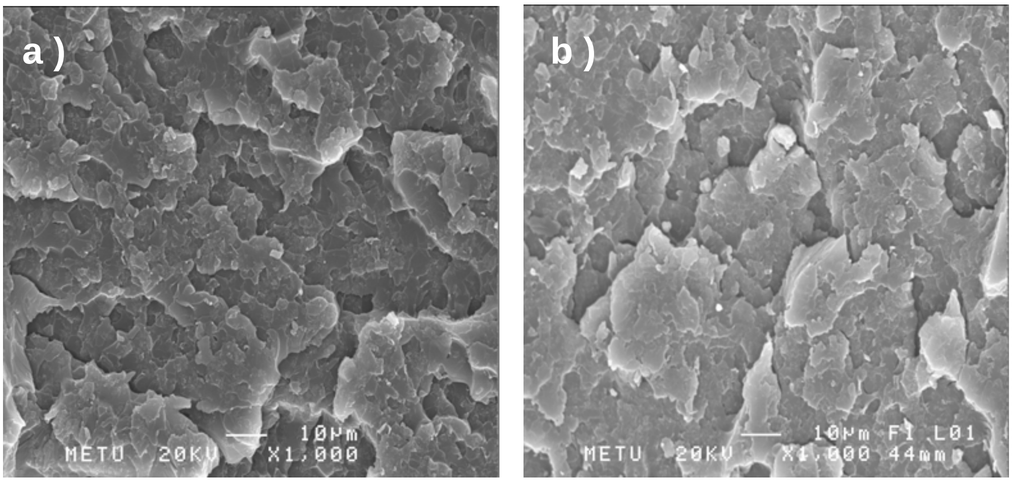


Figure 4.29 XPS spectra of nitrogen (N 1s) of modified carbon black with formamide

4.4.3. SEM Analysis of the Composites Prepared by Surface-Treated Carbon Black

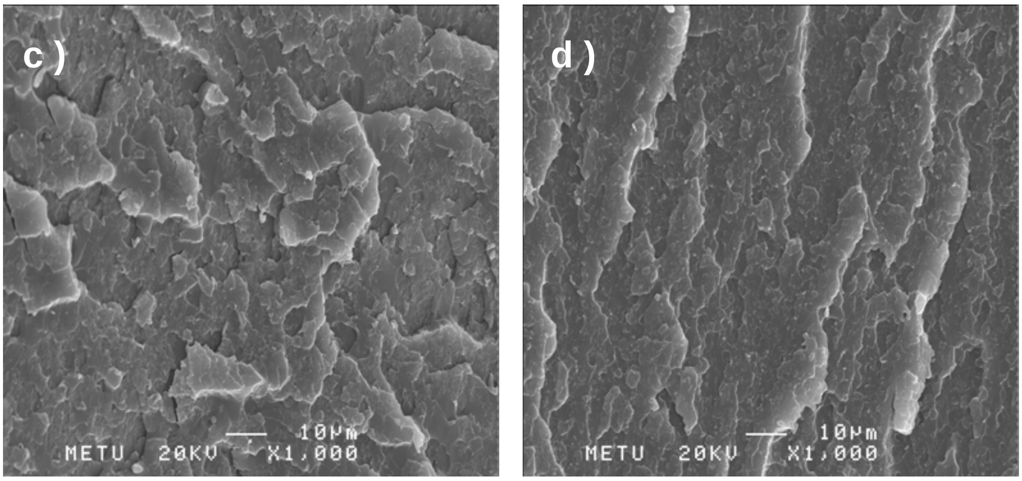
The SEM Micrographs of epoxy/carbon black composites with different types of coupling agents are shown in Figures 4.30. For this part of the study, the carbon black content is kept constant at 3 vol %.

Although different chemicals are used to modify the carbon black surfaces, no remarkable differences are observed in the morphology of epoxy/CB composites. Generally, the surfaces of the materials prepared by treated carbon blacks are similar and all of them have tortuous crack propagation lines. However, in Figure 4.30 e) which shows the fracture surface of the samples treated with 1505, the propagation lines become bigger and parallel, and are responsible for low mechanical properties. In the case of well dispersion of filler, crack propagation lines become shorter and closer. Since the cracks tend to grow until they interfere with each other, these small and nonlinear cracks formed prevent further growth by reducing the stress concentration [42].

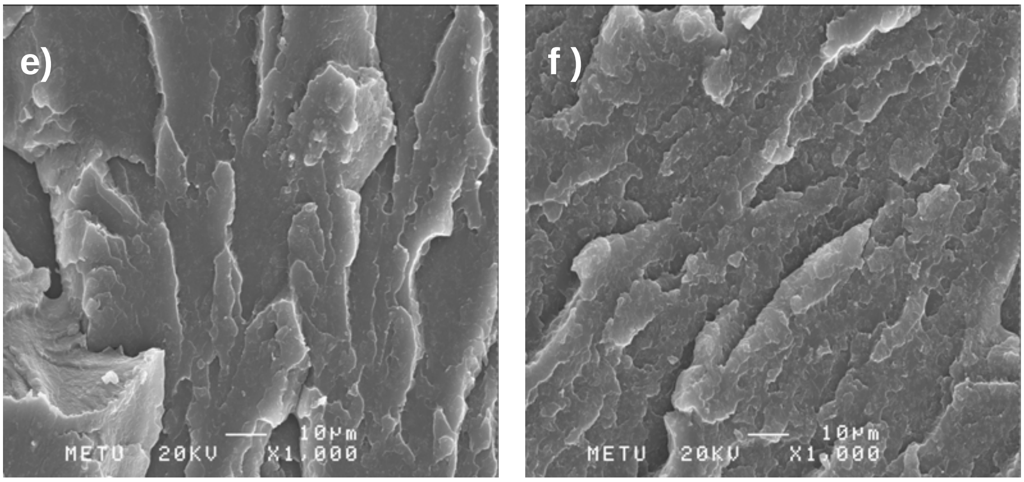


Untreated

Ameo



Glymo 1189



1505 Formamide

Figure 4.30 SEM Micrographs of CB/epoxy composites containin 3 vol%.CB treated with different chemicals a) untreated, b) Ameo, c) Glymo, d) 1189, e) 1505, f) formamide

4.4.4 Electrical Properties

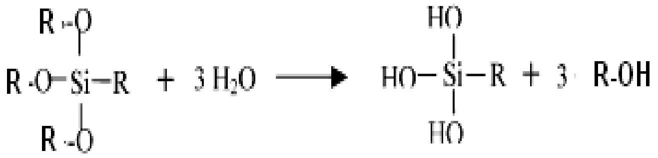
Electrical resistivity of composites strongly depends on the volume fraction of the conductive filler; however, in this section another behavior of the conduction mechanism, the effect of chemical treatment of CB is studied by keeping the filler concentration constant at 3 vol %. The surfaces of the carbon blacks were treated with four different coupling agents and formamide, as a result, the chemistry of the CB surfaces was modified. The effect of the chemical treatment on electrical resistivity of the materials can be seen in Figure 4.31.

Figure 4.31 Effect of coupling agent type on electrical resistivity of the samples containing 3 vol % CB.

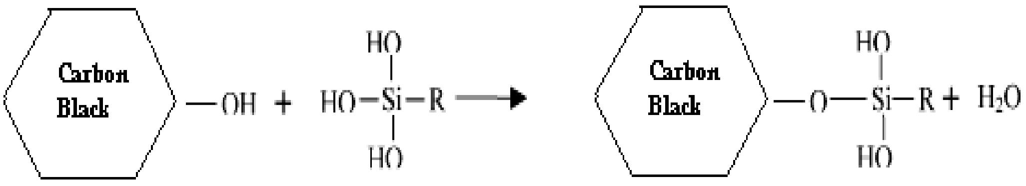
As shown in the figure, the electrical resistivity of the samples containing the same amount of conductive filler (3 vol %) has been altered by chemical treatment of the CB surfaces. The sample prepared with formamide treated CB has yielded the lowest electrical resistivity whereas the sample prepared with glymo treated CB showed no significant improvement in electrical resistivity. In addition, the other three samples obtained by using CB modified with Ameo, 1189 and 1505 have shown a relative decrease in electrical resistivity when compared to untreated CB containing composite.

General structure of typical silane coupling agents is $(X)_3Si(CH_2)_3$-Y where X is the short-chain alkoxy group, OCH_3 [2] and Y is an amino functional group for silane coupling agents used in this study except for Glymo. For the case of glymo, Y is the epoxy functional group. The differences in electrical resistivity of the prepared samples containing treated CB are probably due to two factors which are based on chemical reactions taking place between functional groups on CB surfaces and silane agents.

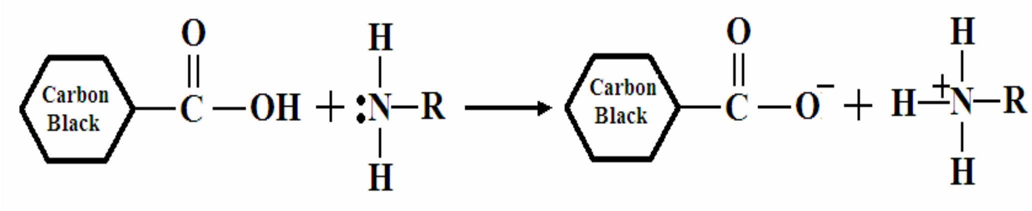
First, the hydroxyl groups onto the CB surface might form hydrogen bonds with silanol groups, Si-OH which are formed by hydrolysis of silane in aqueous media, while the amine groups might react with the carboxyl group on the CB surfaces and form amine salts as $R\text{-}NH_3^+COO^-$ (see Figure 4.32).



a) Hydrolysis Reaction of Silane Coupling Agent



b) Reaction of Silanol with hydroxyl group of carbon black



c) Reaction of carboxyl group on CB with amine functional group of coupling agents

Figure 4.32 Reactions of silane coupling agents with carbon black [56, 57]

Then these salts are dissociated in the electrical field. Consequently, the formed amine salts should decrease the energy barrier that is needed to hop charge carriers from one CB cluster to another and this transfer of charge carriers could take place faster [52]. This theory may be explains the improvement in electrical conductivity because the samples having better electrical conductivity were prepared with chemicals that have amine functional group in their chemical backbone. Gylmo is the only silane which has no amine functional group in its chemical structure and showed no remarkable effect on electrical resistivity.

Other reason which can cause a decrease in electrical resistivity of the samples is also based on the salt formation during the reaction between functional groups on carbon black surface and chemicals used for treatment (silane coupling agents and formamide). As stated in Section 4.4.2, high resolution nitrogen (N 1s) spectra of Ameo treated carbon black are fitted a peak for $H_3N^+CHRCOO^-$ type nitrogen and N 1s spectra of formamide treated carbon black give a peak for $-NH_3$ type nitrogen. In these structures nitrogen atoms have four bonds that is crucial in terms of doping mechanism. Thus, nitrogen atom might behave as n-type of dopant and increase the electrical conductivity by increasing the number of charge carriers instead of speeding up the charge carrier.

Since glymo does not have amine functional group in its chemical structure, these two theories can not be valid for this coupling agent which is also verified with electrical conductivity results. There is no significant improvement in electrical conductivity of samples produced with Glymo treated carbon black.

Moreover, it should be discussed why formamide yields the lowest electrical resistivity. This comes from the simple structure of formamide. Because of its simplicity, the percentage of possible reactions with carbon black is much higher compared to silane coupling agents which have more complex, branched chemical structure. Also, formamide is a smaller molecule than silane coupling agents studied here and it can easily enter between the CB particles and promotes the conductivity.

Owing to the lowest electrical resistivity values of the samples containing 3 vol % CB treated with formamide, it was investigated whether formamide has the same effect at other compositions. The composites consisting of 1, 2, 3 and 5 vol % formamide treated CB were prepared and their resistivity values were measured. The results can be seen in Figure 4.33. At all compositions, samples prepared with formamide treated carbon black ensured the lower electrical resistivity in comparison with untreated sample.

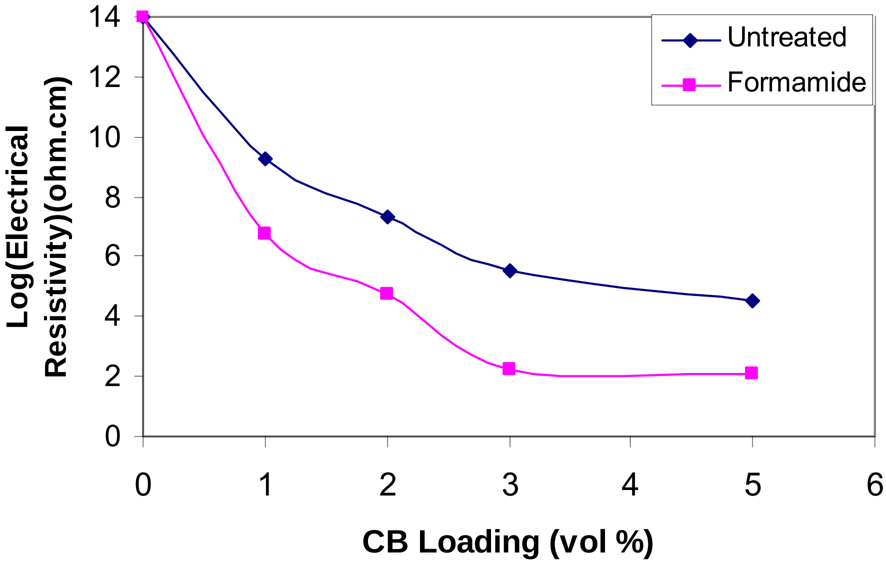


Figure 4.33 The effect formamide treatment of carbon black on electrical resistivity with respect to carbon black content.

4.4.5 Mechanical Properties

The effects of the surface modification of the carbon black on the mechanical properties were also investigated in this study.

4.4.5.1 Tensile Properties

The tensile strength, tensile modulus and % elongation at break graphs of the samples containing 3 vol % CB treated with different coupling agents and formamide are shown in Figures 4.34-4.36. All data in the figures are given in Table A.4 in Appendix A.

As reported in Figures 4.34 and 4.36, the tensile strength and tensile modulus increase for the samples produced with carbon black treated by Ameo, 1189 and 1505 type silane coupling agents when compared to the untreated sample. The increase in tensile strength and tensile modulus is possibly attributed to the improvement of the adhesion between carbon black and epoxy. The silane coupling agents react with polymer matrix and hydroxyl group on the carbon black surfaces, and thus they increase interfacial adhesion between the constituents of the composites [42]. Due to this improvement in adhesion, the stress can be transferred from the polymer matrix to the fillers more efficiently and thus, higher tensile strength is expected [58]. Glymo and formamide show no significant changes in tensile strength and modulus.

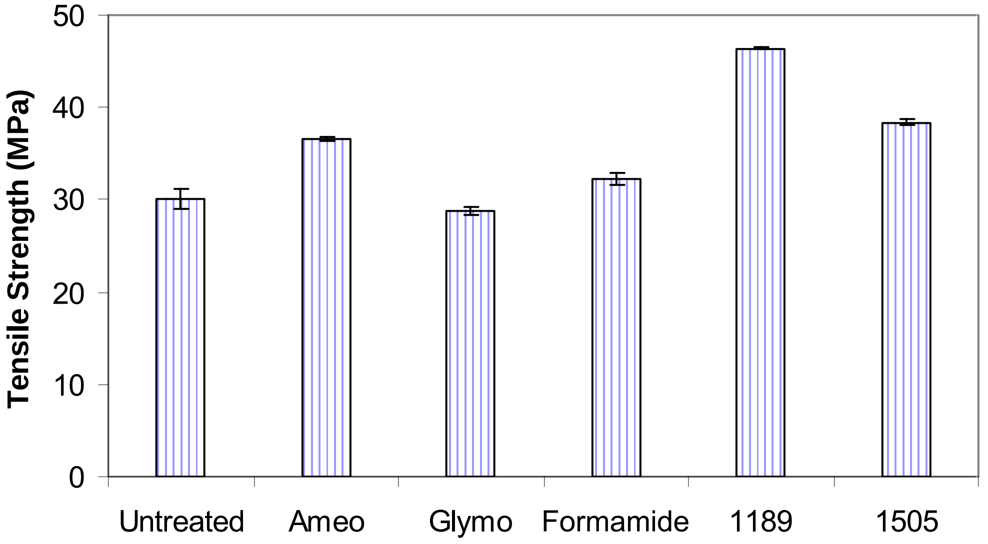


Figure 4.34 Effect of different surface modifiers on tensile strength value of the epoxy/carbon black composites containing 3 vol.% carbon black.

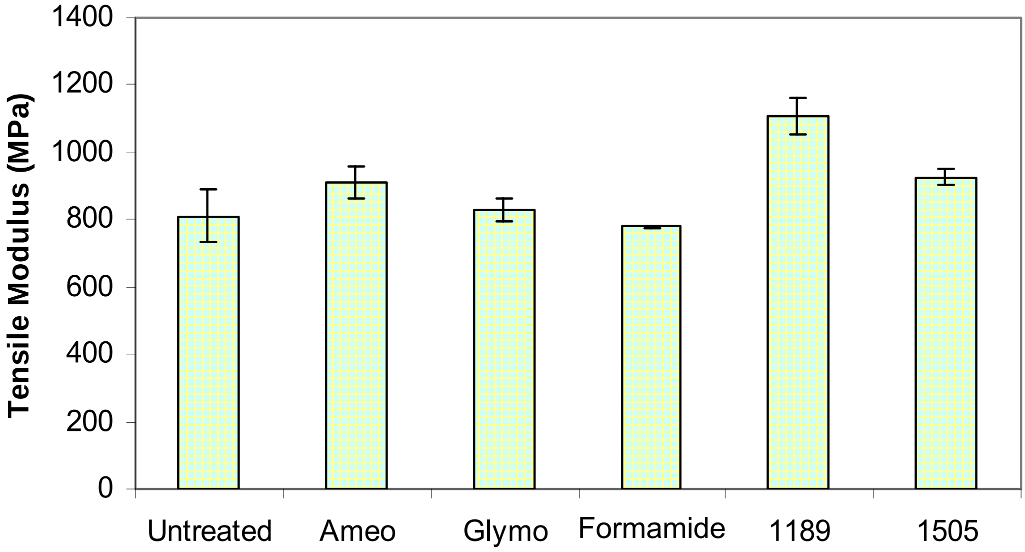


Figure 4.35 Effect of different surface modifiers on tensile modulus value of the epoxy/carbon black composites containing 3 vol.% carbon black

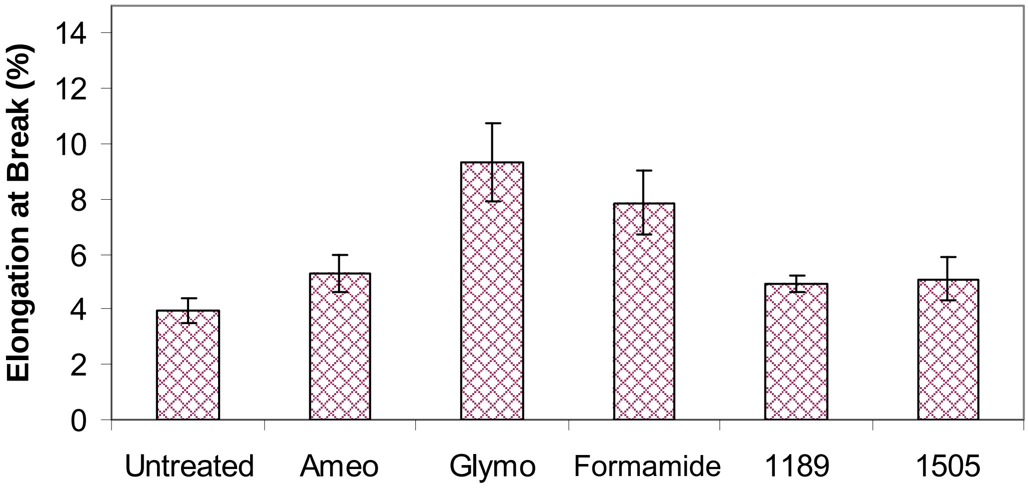


Figure 4.36 Effect of different surface modifiers on elongation at break value of the epoxy/carbon black composites containing 3 vol.% carbon black.

There is a remarkable change in elongation at break values as can be seen in Figure 4.36 with the treatment of the carbon black surfaces. The samples with glymo treated carbon black show the highest elongation at break value that may be due to the low degree of interactions.

4.4.5.2 Hardness Properties

As illustrated in Figure 4.37, treatment of carbon black surfaces with Ameo type silane coupling agent and formamide increase the hardness slightly. However, the hardness of the sample containing 1189 treated carbon black decreases. But in general, the changes in hardness of all the samples are not significant in comparison to the untreated sample.

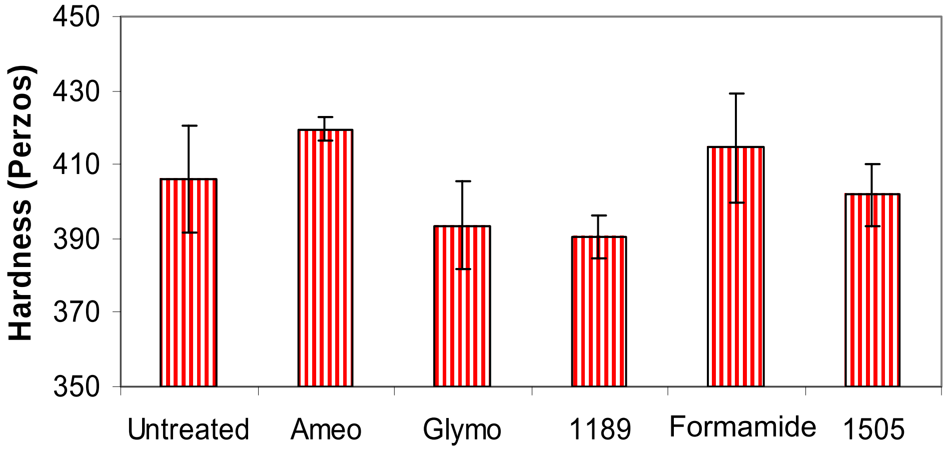


Figure 4.37 Effect of different surface modifiers on hardness value of the epoxy/carbon black composites containing 3 vol.% carbon black.

4.4.5.3 Impact Properties

The impact test results of materials produced with treated carbon black by different modifiers are shown in Figure 4.38. A significant improvement is not observed on the impact energy of the samples; except for the formamide treated carbon black/epoxy system. However, all samples show better results compared to untreated carbon black/epoxy system which may be due to the enhanced polymer-filler interaction between the treated CB and the functional groups of epoxy.

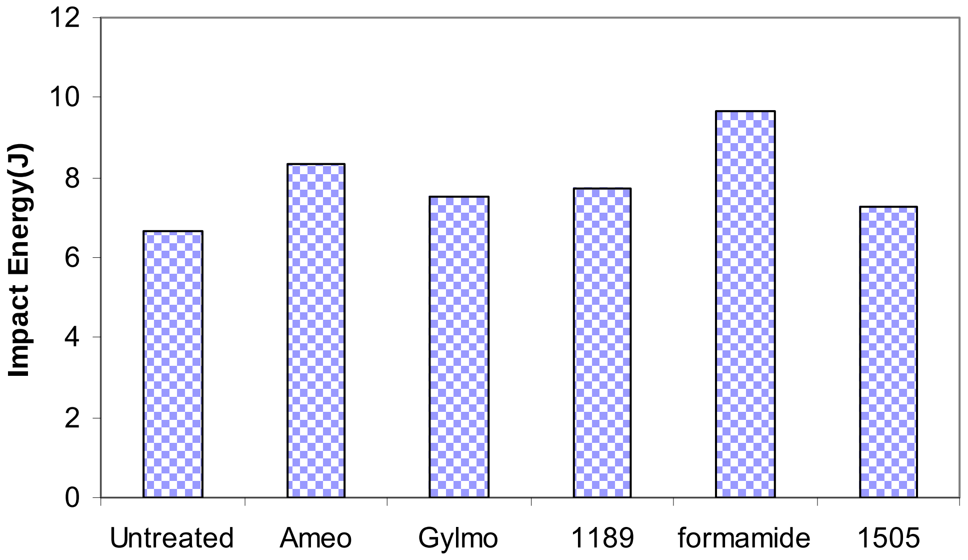


Figure 4.38 Effect of different surface modifiers on impact energy values of the epoxy/carbon black composites containing 3 vol % carbon black

4.4.5.4 Adhesion Properties

Figure 4.39 shows the effect of surface modifiers on adhesion strength of the samples prepared by treated carbon black. It can be said from the figure that, silane coupling agents slightly decrease the adhesion strength while formamide has the opposite effect. Since the molecules of formamide are very small and contain amine functional groups, its reaction possibility with carbon black is much higher than the coupling agents having longer molecules. Also, modification of carbon black with formamide forms new polar groups on carbon black surfaces, which not only result in chemical bonding but also makes the surfaces rougher than the others. Therefore, formamide treatment on carbon black provides improved adhesion strength in the epoxy/carbon black composites.

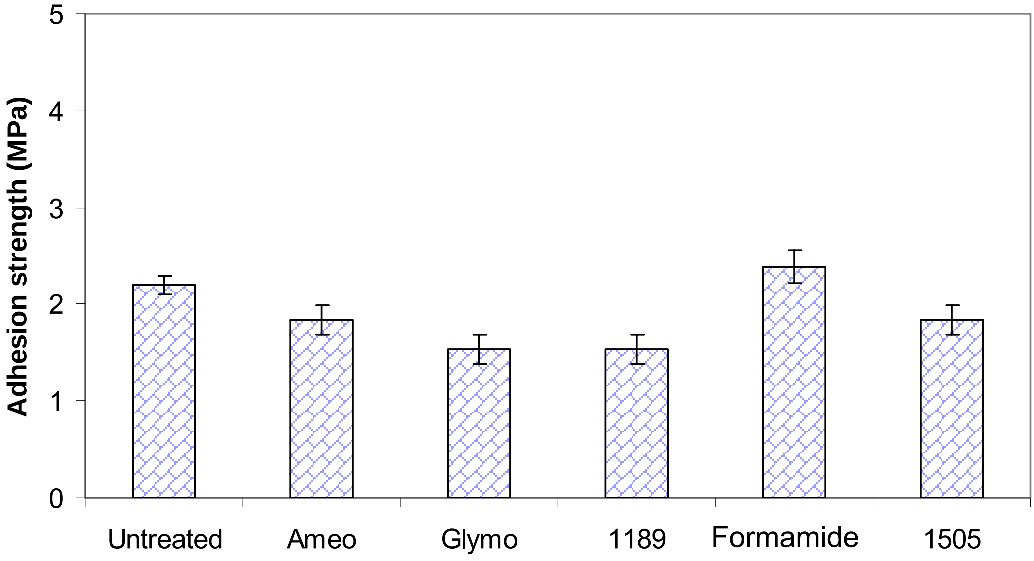


Figure 4.39 Effect of different surface modifiers on adhesion strength values of the epoxy/carbon black composites containing 3 vol % carbon black.

CHAPTER 5

CONCLUSIONS

In this study, electrically conductive epoxy/carbon black composites were produced by applying two different mixing processes called as Grinding and Mechanical Mixing Methods at 1, 2, 3 and 5 vol % carbon black loading. Effects of carbon black content, type of mixing process, ultrasonic mixing time and the surface modification of carbon black with four different silane coupling agents and formamide were investigated on the final properties of the composites.

SEM analysis showed that the crack propagation lines were rather straight and smooth for the neat epoxy resin. As carbon black content increased, it is clearly observed that the crack propagation occurred in a tortuous manner in materials prepared by both methods.

The electrical resistivity of the samples decreased further while increasing the carbon black content in the Grinding Method. The percolation concentration was obtained at 2 vol % CB content in this method. However, no improvement of electrical conductivity was obtained for the samples prepared by using the Mechanical Mixing Method beyond 1 vol % CB loading.

In addition, at 2 vol % carbon black concentration, maximum tensile strength and tensile modulus values were obtained for the samples prepared by the Grinding Method.

Ultrasonic mixing was applied to the system produced by the Grinding Method on samples containing 2 vol % carbon black to reduce the resistivity value further, but no positive effect on electrical and mechanical properties was observed.

The effects of surface modification on electrical and mechanical properties of the samples prepared by carbon black treated with four different silane coupling agents and formamide were also studied.

Formamide which is a small molecule and has the simplest chemical structure exhibited lowest electrical resistivity value which was around 10^2 ohm.cm. This is a significant improvement when compared to the resistivity of the epoxy. Also, samples prepared with formamide treated carbon black had better impact energy, hardness and adhesion strength values than the neat epoxy and the composites prepared with other chemicals.

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APPENDIX A

MECHANICAL TEST DATA

Table A.1 Tensile strength, tensile modulus and (%) elongation data of the samples produced by Grinding Method with respect to CB loading

CB (vol.%)	Tensile Strength (MPa)	Std. Deviation	Tensile Modulus (MPa)	Std. Deviation	%Elongation at break	Std. Deviation
0	35.6	1.0	825	103	6.1	0.25
1	19.3	7.7	736	49	2.3	0.79
2	55.5	3.3	1459	58	4.7	0.75
3	30.1	1.1	812	80	4.0	0.42
5	39.7	1.0	1076	49	5.5	0.66

Table A.2 Tensile strength, tensile modulus and (%) elongation data of the samples containing 2 vol.%CB produced by Grinding Method with respect to Ultrasonic Mixing Time.

U.Mixing Time (min)	Tensile Strength (MPa)	Std. Deviation	Tensile Modulus (MPa)	Std. Deviation	%Elongation at break	Std. Deviation
0	55.5	3.3	1459	58	4.7	0.75
15	55.3	1.1	1242	121	5.9	0.13
30	52.8	0.9	1357	36	5.0	0.23
45	54.6	1.7	1589	62	4.1	0.28

Table A.3 Tensile strength, tensile modulus and (%) elongation data of the samples produced by Mechanical Mixing Methods with respect to CB loading

CB (vol.%)	Tensile Strength (MPa)	Std. Deviation	Tensile Modulus (MPa)	Std. Deviation	%Elongation at Break	Std. Deviation
0	35.7	1.0	825	104	6.1	0.25
1	38.3	0.8	787	96	5.7	0.69
3	23.7	2.3	461	101	8.0	1.02
5	34.1	2.2	939	23	4.1	0.22

Table A.4 Tensile strength, tensile modulus and (%) elongation data of the samples containing 3 vol %CB with respect to surface modifier type

Modifier Type	Tensile Strength (MPa)	Std. Deviation	Tensile Modulus (MPa)	Std. Deviation	%Elongation at Break	Std. Deviation
Untreated	30.1	1.1	812	80	4.0	0.42
Ameo	36.6	0.2	913	47	5.3	0.67
Glymo	28.8	0.4	830	32	9.3	1.39
Formamide	30.2	0.6	779	2.3	7.9	1.16
1189	46.4	0.1	1107	55	5.0	0.30
1505	38.4	0.3	926	23	5.1	0.80