Effect of Surface Treatment on Electrical Conductivity of Carbon Black Filled Conductive Polymer Composites

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ABSTRACT: Two different types of surface modifiers, 3-aminopropyltriethoxysilane and formamide, were applied to carbon black (CB) particles to lower electrical resistivity of polymer composites prepared by treated CB. Two different matrices, low-density polyethylene and nylon 6, were chosen to compound with surface modified CB. Surface energy of CB was increased by adding amine or amide functional groups during surface treatment of CB. According to electron spectroscopy for chemical analysis (ESCA), chemical modification in surface chemistry of CB was obtained with the chemicals used for the treatment due to the nitrogen atoms in their structures, which may act as dopant atom. As a result of this, electrical resistivity of composites prepared by treated CB decreased. In addition, there was not any significant change in tensile strength and tensile modulus of the composites with the surface treatment. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3427–3433, 2007

Key words: nylon; composites; conducting polymers; ESCA/XPS; polyethylene

INTRODUCTION

Materials can be divided into three main classes according to the electrical conductivity, which are insulators, semiconductors, and conductors.[1] Conductive polymer composites have great importance among all engineering materials since electrical resistivity of insulating polymer can be lowered to semiconductor level by contribution of conductive filler. Electrical resistivity of polymer composites decreases by several orders of magnitude when the filler composition reaches a certain critical value of percolation threshold concentration, at which conductive fillers start to form a chain structure in polymer matrix.[2]

Different types of conductive fillers are melt mixed with polymer matrices to produce conductive polymer composites. However, electrical resistivity of insulating matrix can be decreased to some extent at relatively high filler compositions.[3–8] To decrease percolation threshold concentration of composites, polymerization filling method can be used as an alternative one to melt mixing method. In this method, polymer is synthesized in the presence of conductive filler particles. Higher conductivity is obtained at lower composition, which can be the result of enhanced interaction between composite constituents and better distribution of filler particles in polymer matrix.[9–15]

Electrical resistivity of conductive polymer composites depends on filler concentration, electrical resistivities of composite constituents, filler dispersion, and process conditions.[2] Thus, any operation, resulting in a decrease in electrical resistivity of conductive filler also decreases the electrical resistivity of prepared composite. As conductive filler, carbon black (CB) is exposed to surface treatments to improve electrical conductivity of polymer composites.[16,17] Bulk structure of CB, which consist of highly conductive graphene layers, and chemical nature of CB surface determine the electrical character of filler. Hence, any type of functional groups except for graphitic structure present on CB surfaces, and added by surface treatment, influence electrical conductivity of CB.[18] Especially surface modifiers containing amine functional groups may improve electrical conductivity of carbon-based filler and its composites.[16,19]

This study was aimed at improving electrical conductivity of polymer composites by altering the surface chemistry of CB. 3-Aminopropyltriethoxysilane, which is a conventional silane coupling agent, and formamide, containing amine and amide functional groups, respectively, were used as surface modifiers for CB. Treated CB was melt mixed with two different matrices, low-density polyethylene (LDPE) and nylon 6. Besides electrical conductivity, the effect of surface modifiers on mechanical properties of LDPE or nylon 6 based conductive polymer composites was also studied.

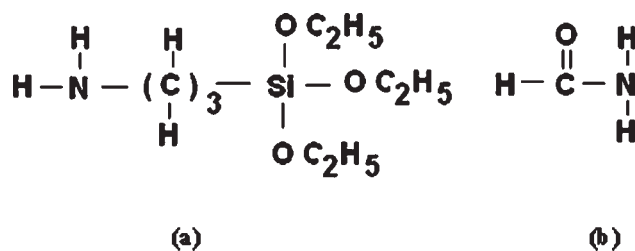*Correspondence to:* G. Bayram (gbayram@metu.edu.tr).

Figure 1 Chemical structure of chemicals used for surface treatment: (a) 3-aminopropyltriethoxysilane, (b) formamide.

Background

The affinity between filler and polymer is increased to obtain a well-integrated structure by improving surface properties of filler. Surface chemistry of filler is altered by adding functional groups to improve electrical conductivity, wetting property, and dispersion of filler in polymer.[16,17,20] Contact angle measurements are used to investigate surface chemistry of materials. Any change in surface structure of filler can be noticed from a change in surface energy components of this particle. In addition, the interfacial strength can be calculated by using surface energy components of composite constituents.[21,22]

The total surface energy, γ^{TOT}, of a nonmetallic material is composed of London dispersive component, γ^{LW}, and acid/base component, γ^{AB}. Moreover, acid/base component, γ^{AB}, consists of electron acceptor, γ^{A}, and electron donor components, γ^{B}, as given in the following equation:[21,23]

$$\gamma_i^{TOT} = \gamma_i^{LW} + \gamma_i^{AB} \tag{1}$$

$$\gamma_i^{AB} = 2\left(\gamma_i^{A} + \gamma_i^{B}\right)^{1/2} \tag{2}$$

A characteristic property of acid and base components of surface energy is their nonadditivity. If one of the phases has only acid or base component, then this component does not contribute to the total surface energy of the same phase. However, it can interact with the complementary component of the other phase. For a bipolar liquid (L) contacting with the

solid (S), total surface energy and its components such as γ^{LW}, γ^{AB}, γ^{A}, and γ^{B}, can be calculated with "Young Equation" given below by using contact angles of probe liquids measured on the sample surfaces.[21,22,24]

$$(1+\cos\theta_L)\gamma_L^{TOT} = 2\left[\left(\gamma_L^{LW}\gamma_S^{LW}\right)^{1/2} + \left(\gamma_L^{A}\gamma_S^{B}\right)^{1/2} + \left(\gamma_L^{B}\gamma_S^{A}\right)^{1/2}\right] \tag{3}$$

EXPERIMENTAL

Materials

In this study, low-density polyethylene (LDPE) and nylon 6 were selected as two different matrix materials. In addition, carbon black (CB) was used as conductive filler. 3-Aminopropyltriethoxysilane (APS) and formamide were used as surface treatment agents for CB. Chemical structures of these coupling agents are shown in Figure 1. Physical properties of the materials used in this study are given in Table I.

Composite preparation

To modify the surface chemistry of CB by surface treatment, APS and formamide solutions were prepared by diluting these chemicals with distilled water to obtain 1 wt % surface modifier composition. Diluted solutions were mixed with untreated CB particles. The mixture was stirred for 10 min at room temperature in a beaker. Then, it was filtered

TABLE I
Physical Properties of Materials

Material	Trade name and supplier	Specifications
Low-density polyethylene (LDPE)	Petilen G03-5; PETKİM (Turkish petroleum product producer)	Melt flow index: (2.16 kg; 190°C) 0.2–0.4 g/10 min; density, 0.922 g/cm^3
Nylon 6	Domamid 27; Tekno Polimer Ltd. (Tüpraş)	Melt flow index: (2.16 kg; 235°C) 30–35 g/10 min; density, 1.14 g/cm^3
Carbon black (CB)	ISAF N-220; TUPRAS (Turkish petroleum refinery)	Iodine no., 119 mg/g; dibutylphthalate Abs., 114.2 mL/100 g
3-Aminopropyltriethoxysilane (APS)	DYNASYLAN AMEO; Cam Elyaf Sanayi A.Ş.	Density (20°C), 0.95 g/cm^3; flash point, 93°C
Formamide	Formamide; Merck	Density (20°C), 1.13 g/cm^3; flash point, 175°C

to isolate treated CB particles. Afterwards, wet particles were dried at 100°C for 24 h.

Prior to extrusion process, nylon 6 pellets were dried in a vacuum oven for 24 h at 90°C. LDPE and nylon 6 were compounded separately with APS- and formamide-treated CB in a corotating twin screw extruder (Thermo PRISM TSE-16-TC) to obtain 1, 2, 4, 6, and 8 wt % of CB containing composites. For comparison purposes, LDPE and nylon 6 were also compounded with untreated CB. Extrusion of LDPE/CB was performed using the temperature profile of 170-210-210-210-220°C and a screw speed of 300 rpm. Nylon 6/CB composites were melt mixed at the temperature profile of 220-230-235-240-245°C and a screw speed of 80 rpm.

To determine electrical resistivity of the composites, test samples of LDPE/CB and nylon 6/CB systems were prepared by compression molding device. Compression molding process of LDPE/CB system was performed at 210°C. In addition, nylon 6/CB system was molded at 240°C. First, pellets were heated for 1.5 min under 50 bar gauge pressure and then they were heated for 2 min for LDPE/CB system and 1 min for PA6/CB system under 150 bar gauge pressure. Finally, compression molded samples were quenched to room temperature by tap water. A laboratory scale injection molding instrument (DSM Micro 10 cc Injection Molding Machine) was used to prepare test specimens of surface energy and tensile property measurements. During the injection molding process of LDPE-based composites, barrel and mold temperatures were 210°C and 30°C, respectively, and during the injection molding process of nylon-6-based composites, barrel and mold temperatures were 240°C and 35°C, respectively.

Composite characterization techniques

Electron spectroscopy for chemical analysis (ESCA) was used to analyze surface chemistry of untreated CB and APS type of coupling agent and formamide-treated CB. Specs model spectrometer equipped with aluminum radiation at 1 W was used to obtain ESCA spectra of CB. The high resolution spectra of oxygen (O 1s peak) and of nitrogen (N 1s peak) were recorded with pass energy of 48 eV at a vacuum level lower than 10^{-5} Pa. A nonlinear background was removed from the spectra and XPSPeak 41, which is a curve fitting program, was used to fit the high-resolution spectra of oxygen and nitrogen.

Diiodomethane, ethylene glycol (EG), and formamide, which are probe liquids, were used to determine surface energy of LDPE, nylon 6, and CB by contact angle measurements. Diiodomethane was selected to calculate London dispersive component of surface energy, γ^{LW}. Meanwhile, EG and formamide were used to calculate acid/base component of

TABLE II
Surface Energy Components of Probe Liquids[21] (mN/m)

Liquid	γ_L^{TOT}	γ_L^{LW}	γ_L^{AB}	γ_L^{A}	γ_L^{B}
DIM	50.80	50.80	–	–	–
EG	48.00	29.00	19.00	3.00	30.10
Formamide	58.00	39.00	19.00	2.30	39.60

surface energy, γ^{AB}. Surface free energy components of probe liquids are given in Table II.

According to Sessile drop method, contact angles of probe liquids on injection molded samples of LDPE and nylon 6 were used to calculate surface energy.[24] In addition, CB particles were pressed as discs under 150 bar gauge pressure and contact angles of probe liquids were determined from these pressed surfaces.[22,25] Three different contact angle measurements were performed for each probe liquid and their average was used to calculate surface energy components.

X-ray diffraction (XRD) patterns of composites containing 2 wt % of CB were obtained with a 100 kV Philips twin tube X-ray diffractometer (PW/1050) providing Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA. XRD patterns were obtained at a scan speed of 1°/min, from 5° to 45°. Interlayer spacing between graphene layers of CB (d_{002}) was calculated by using the Bragg equation:

$$n \lambda = 2 d_{002} \sin \theta \tag{4}$$

where n is equal to one for monochromatic radiation, λ is wavelength of radiation, d_{002} is interlayer spacing between graphene layers, and θ is diffraction angle of beam of radiation corresponding to Bragg's maximum.[26,27] Crystalline size along the c-axis (L_c) of CB can be calculated by using the Scherrer equation:

$$L_c = K\lambda/(B \cos \theta) \tag{5}$$

in which K is Scherrer constant, equal to 0.89, L_c is crystalline size along the c-axis of CB, λ is wavelength of radiation, θ is diffraction angle of beam of radiation corresponding to Bragg's maximum, and B is widening of diffraction line measured in the middle of its maximum intensity.[25–27]

The electrical resistivities of compression molded composites were measured according to two point probe method using a current source meter (Keithley model 2400). For good electrical contact in two point probe method, copper wires were placed into the compression molded composites during sample preparation. Conductivity measurement was performed by contacting probes with these copper wires. All measurements were done at room temperature and the average of six measurements was
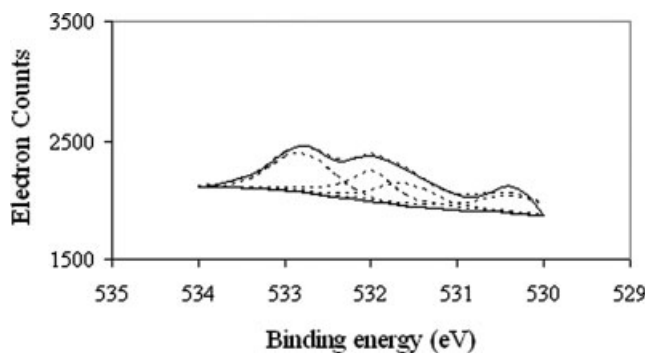
Figure 2 High-resolution spectra of oxygen (O 1s) of untreated carbon black.

Figure 4 High-resolution spectra of oxygen (O 1s) of APS-treated carbon black.

taken into account for each composition of LDPE/CB and nylon 6/CB systems.

The tensile properties of injection molded composites were measured using a Lloyd 30K universal tensile testing instrument. Five specimens of composites containing 2 wt % of CB were tested and average of these five test results are given with their standard deviations. Injection molded specimen had a thickness of 2 mm and width of 4 mm with a gauge length of 20 mm. According to the gauge length and a strain rate of 0.1 min^{-1}, the crosshead speed of testing instrument was selected as 2 mm/min.

RESULTS AND DISCUSSION

The surface chemistry of untreated CB was characterized by ESCA. It is seen that there are different kinds of functional groups present on the surface of CB before any surface treatment, because of the irregular structure of the CB surface. O 1s spectrum of untreated CB, which is given in Figure 2, is fitted to four peaks: a peak for C=O type oxygen at 531.6 eV, a peak for C—O type oxygen (C—OH, C—O—C) at 532.8 eV, a peak for —OH type of oxygen at 532 eV, and a peak for adsorbed oxygen (—O$_2$) at the binding energy of 530.3 eV. In addition, N 1s spectrum of untreated CB, given in Figure 3, is
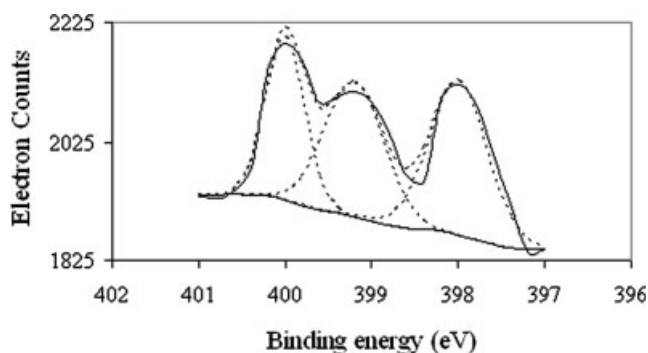
fitted to three peaks: a peak for adsorbed nitrogen at 400 eV, a peak for NH$_2$ type of nitrogen bonded to phenyl, at 399.2 eV, and a peak for nitrogen, which is in conjugated structure of graphene, at 398.1 eV.

O 1s spectra of APS- and formamide-treated CB are fitted to two peaks (Figs. 4 and 5): a peak for C=O type oxygen at 531.6 eV and a peak for C—O type oxygen (C—OH, C—O—C) at 532.8 eV. Bulk structure of CB consists of highly conductive graphene layers.[18] In addition, CB surfaces have active carbon sites, which are known as dangling bonds since regular graphene structure of CB disappears at the surface. CB may have a large amount of these active carbon sites owing to its high surface area, and these active sites are potential centers for a chemical reaction, e.g., oxidation.[28] High resolution spectra of oxygen (O 1s) of APS- and formamide-treated CB reveal the same result that there is an increase in the intensity of peak for C=O type of oxygen (Figs. 4 and 5) due to the oxidation of the active carbon sites during surface treatment of CB.

Noncarbon atoms and carbon atoms aside from graphitic structure on CB surface affect electrical property of CB. Nongraphitic structures on the CB surface prevent current conduction by direct contact process.[18] Surface carboxyl groups create insulating oxide layer among CB particles. As a result of this, electrical
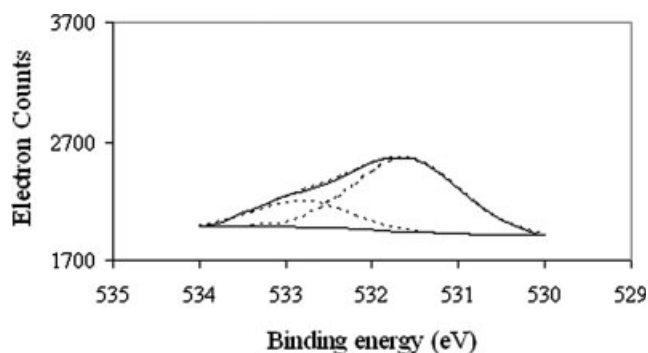

Figure 3 High-resolution spectra of nitrogen (N 1s) of untreated carbon black.

Figure 5 High-resolution spectra of oxygen (O 1s) of formamide-treated carbon black.
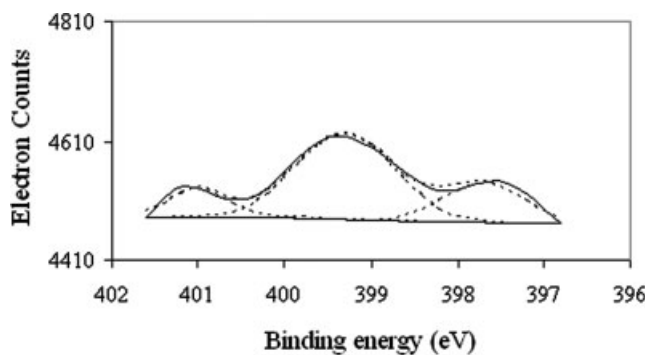
Figure 6 High-resolution spectra of nitrogen (N 1s) of APS-treated carbon black.

resistivity of CB increases with an increase in surface carboxyl groups.[17,19] On the other side, N 1s spectra of APS-treated CB is fitted to three peaks (Fig. 6): a peak for —N type nitrogen at 397.7 eV, a peak for —NH$_2$ type nitrogen at 399.3 eV, and a peak for H$_3$N$^+$CHRCOO$^-$ type nitrogen at 400.9 eV. In addition, N 1s spectra of formamide-treated CB is fitted to three peaks (Fig. 7): 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. Although APS- and formamide-treated CB possess larger amount of surface carboxyl groups when compared with untreated CB (Figs. 2, 4, and 5), treated CB improves electrical conductivity of composites much more than untreated CB does (Figs. 8 and 9). The reason for this improvement is amide functional groups observed on treated carbon filler surfaces.[16,19] Amine group of APS and amide group of formamide react with carboxyl group of CB to obtain amide salt of R-NH$_3^+$—COO$^-$, where nitrogen atom is in quaternary structure (Fig. 10).[29] N 1s spectra of APS- and formamide-treated CB confirm this reaction since there is a peak for H$_3$N$^+$CHRCOO$^-$ type of nitrogen at 400.9 eV (Fig. 6) and a peak for —NH$_3^+$ type of nitrogen at 398.6 eV (Fig. 7) respectively. Quaternary nitrogen, formed during surface treatment, is crucial
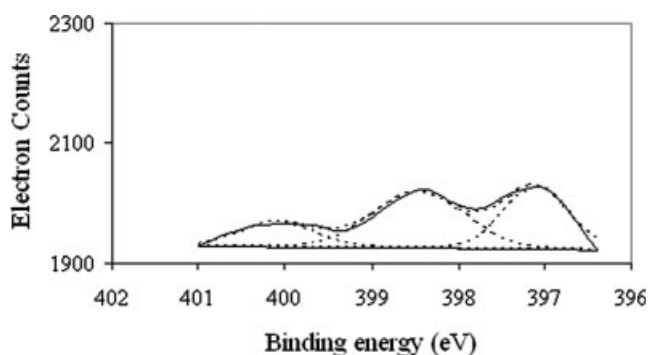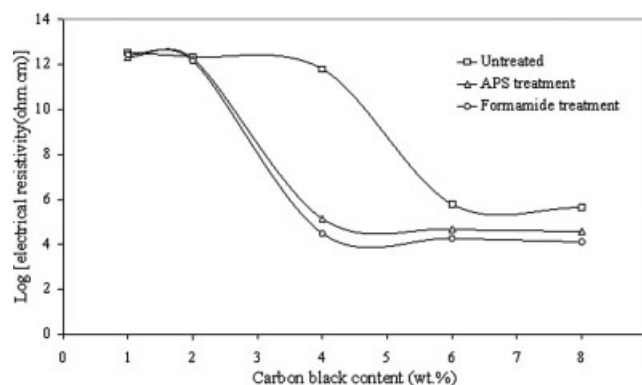

Figure 8 The electrical resistivity values of LDPE/carbon black with different types of surface treatments.

in terms of doping mechanism, since nitrogen as n-type of dopant atom increases the electrical conductivity of CB by increasing the number of charge carriers.[16,19,30]

Nitrogen atoms of APS and formamide, treated on CB particles, may act as dopant atoms following the reaction between nitrogen atoms of these surface modifiers and carboxyl groups of CB (Fig. 10) and this doping reaction increases electrical conductivity of CB and its composites (Figs. 8 and 9). Thus, when compared with polymer/untreated CB system, lower electrical resistivity is obtained at each composition of LDPE/CB and nylon 6/CB systems, in materials containing surface modified CB. APS and formamide types of surface treatments lower percolation threshold concentrations of LDPE/CB and nylon 6/CB systems from 5 wt % to 3 wt % of CB content because of the improvement in electrical conductivity of treated CB. Formamide seems to be more effective in decreasing the electrical resistivity of CB when compared with APS, which may be due to relatively large chemical structure of APS when compared with that of formamide. During surface treatment of CB, formamide molecules being smaller in size react with CB easily (Fig. 10) and nitrogen atoms of
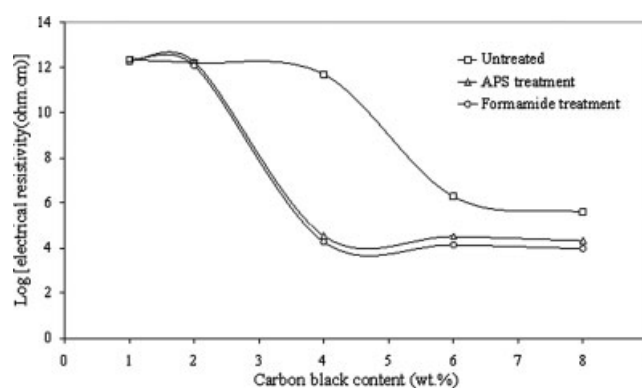

Figure 7 High-resolution spectra of nitrogen (N 1s) of formamide-treated carbon black.

Figure 9 The electrical resistivity values of nylon 6/carbon black with different types of surface treatments.
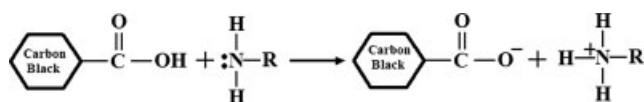
Figure 10 Doping mechanism of nitrogen atom during surface treatment of carbon black.[29]

formamide act more effectively as dopant atoms than nitrogen atoms of APS. Also, at the same weight percent of the surface modifiers, the number of molecules of formamide is higher than the number of molecules of APS owing to the lower molecular weight of formamide. Hence, formamide-treated CB improves electrical conductivity of matrices more than APS-treated CB does (Figs. 8 and 9).

The surface energy components of CB particles are given in Table III. Untreated CB has a lower surface energy when compared with APS- and formamide-treated CB. With chemical treatment, surface chemistry of CB is altered by adding polar groups on the surface of CB. Total surface energy of treated CB increases with a parallel increase in acid/base component of surface energy, and this increase may be an evidence for chemical modification of CB surfaces, in addition to ESCA results. According to surface energy measurements, base component of total surface energy increases with surface modifications, which may be a result of added amide groups to CB surface (Table III). In addition, acid component of total surface energy of treated CB is higher with respect to untreated one, owing to NH_3^+ structure formed following the reaction between surface modifiers and CB (Fig. 10), which is an evidence for quaternary nitrogen on the surface of treated CB. On the other hand, the higher intensity of the peak for C=O type of oxygen for modified CB, when compared with that the untreated one (Figs. 2, 4, and 5), contributes to acid/base component of total surface energy of modified CB. In addition, the London dispersive component of modified CB particles increases, which may result from an increase in effective surface area, since the particle size and effective surface area determine the London dispersive component.[22,31]

One of the critical points in surface modification is to alter the chemical structure of the surface to obtain desired property without sacrificing the bulk properties of the materials. In the current study, chemical treatment changes the surface chemistry of CB as observed from ESCA analysis and surface

energy measurements. The effect of APS and formamide treatment on structural properties of CB is also analyzed by XRD. Graphene layers of CB are held together with weak van der Waals forces.[32] As can be seen from Table IV, interlayer spacing (d_{002}) between these layers does not change significantly with the treatment because of the low concentration of APS and formamide solutions. Also, there is not a distinctive effect of chemical treatment on crystalline size along the c-axis (L_c) of CB.

Tensile strength and tensile modulus can be used to evaluate structural changes of the bulk material. Table V shows the tensile properties of the composites containing untreated and treated CB. Both tensile strength and modulus remain almost constant with APS or formamide treatment for both LDPE/CB and nylon 6/CB systems. As a result, it can be said that both APS and formamide treatments do not significantly affect the bulk properties of these composites.

CONCLUSIONS

According to surface energy analysis and ESCA results, surface structure of CB was modified during APS or formamide chemical treatments. Surface

TABLE III
Surface Energy Components of Carbon Black (mN/m)

Specimen	γ_S^{TOT}	γ_S^{LW}	γ_S^{AB}	γ_S^{A}	γ_S^{B}
Untreated CB	42.46	35.17	7.29	1.07	12.45
CB+APS	50.05	38.73	11.32	1.31	24.49
CB+formamide	54.79	40.41	14.38	1.96	26.38

TABLE IV
Structural Properties of Untreated, APS-Treated, and Formamide-Treated Carbon Black (CB) in Nylon 6 and LDPE Matrices

System	2θ	B	d_{002} (A)	L_c (A)
2 wt % untreated CB/nylon 6	23.11	5.31	3.848	0.264
2 wt % APS-treated CB/nylon 6	20.83	5.52	4.264	0.253
2 wt % formamide-treated CB/nylon 6	21.17	5.5	4.197	0.254
2 wt % untreated CB/LDPE	21.38	0.65	4.156	2.148
2 wt % APS-treated CB/LDPE	21.25	0.72	4.181	1.939
2 wt % formamide-treated CB/LDPE	21.27	0.61	4.177	2.289

TABLE V
Tensile Properties of Composites Containing Untreated and Treated Carbon Black (CB) with their Standard Deviations

	Tensile strength (MPa)	Tensile modulus (MPa)
Nylon 6		
2 wt % untreated CB	43.11 ± 1.98	1277 ± 65
2 wt % APS-treated CB	43.79 ± 0.99	1483 ± 46
2 wt % formamide-treated CB	46.48 ± 2.12	1485 ± 95
LDPE		
2 wt % untreated CB	24.68 ± 3.66	272 ± 29
2 wt % APS-treated CB	25.05 ± 1.70	290 ± 27
2 wt % formamide-treated CB	27.42 ± 2.47	273 ± 8

energy of treated CB increased mainly because of an increase in acid/base component of surface energy. APS and formamide, which have nitrogen-based functional groups in their structures, increased electrical conductivity of composites by improving electrical conductivity of CB. According to ESCA results, nitrogen atoms of APS and formamide turned into quaternary structure following the doping reaction between CB and surface modifiers. Nitrogen atoms behaved as dopant in this quaternary structure by increasing the number of charge carriers. Hence, APS and formamide treatments decreased percolation threshold concentrations of LDPE/CB and nylon 6/CB systems from 5 wt % to 3 wt % of CB content. In addition, surface treatment of CB did not significantly change the tensile strength and modulus of nylon 6 and LDPE composites, compared with untreated CB.

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