

Effect of Composite Preparation Techniques on Electrical and Mechanical Properties and Morphology of Nylon 6 Based Conductive Polymer Composites

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ABSTRACT: Nylon 6/carbon black conductive composites were prepared using two different methods, masterbatch dilution and melt mixing. Their effect on the size and distribution of carbon black agglomerates in the matrix was studied in terms of electrical and mechanical properties and morphology. The electrical resistivity of composites prepared by both methods decreased with increasing filler composition. The electrical resistivity of the diluted masterbatch composites and the melt mixed composites was reduced from the resistivity of pure nylon 6,

10^{15} "ohm, cm", to 10^7 "ohm, cm" at 1 and 6 wt % of carbon black, respectively. As the filler content increased, elongation at break and impact strength decreased, but tensile modulus increased. Masterbatch dilution method provided smaller carbon black clusters in composites compared to melt mixing method. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2520–2526, 2006

Key words: carbon black; nylon 6; composites; electrical resistivity; mechanical properties

INTRODUCTION

Conductive polymer composites have attracted much attention since their electrical properties can be altered by changing the composite constituents and their compositions. Therefore, they have been used in several application areas such as electromagnetic interference shielding (EMI) and antistatic discharge capability in electronic devices.¹

When electrically conductive filler is incorporated to a polymer matrix, electrical, mechanical, and other properties of the pure material may change depending on the properties of individual components, the shape, size, and amount of the filler, the morphology of the system, and the interface between the components.² Especially, electrical conductivity of composite systems increases by several orders when the content of conductive filler reaches a definite value that is high enough for the formation of current conductive structures. This critical filler concentration is known as percolation threshold. At percolation threshold concentration, the filler particles are so close to each other that the electron transfer occurs from one particle to the neighboring one. Polymer matrix holds the conductive particles in intimate contact form. Current conduction can be performed by tunneling process or direct con-

tact of electrically conductive particles. However, actual conduction mechanism is unknown.³

Different types of composite preparation methods have been used to prepare electrically conductive polymer composites at lower filler composition. One of these methods is the formation of conductive polymer composites by melt mixing. In this method, carbon black particles are melt-blended with polymer matrices to obtain conductive polymer composites.^{4–6} Various conductive fillers have been especially incorporated into nylon 6 which is of significant commercial interest.^{7–9} Transition from insulator to semiconductor region of nylon 6 based composite is accomplished at around 10 wt % of carbon black.^{6,7} Nylon 6 wets the carbon black and filler particles are isolated from one another owing to high polarity of nylon 6, which retards the formation of conductive carbon black networks in matrix.⁵

An alternative technique to melt mixing is polymerization filling method by which polymer is synthesized in the presence of conductive particles. The electrical properties of polymerization-filled composites are enhanced by improving the distribution of conductive filler in the polymer matrix. This method providing intimate contacts improves the interfacial interaction between conductive particles and polymer molecules by decreasing average agglomerate size. Higher conductivity at lower filler composition may be the result of this enhanced interaction between composite constituents. A few studies were performed on the preparation of conductive polymer

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composites by polymerization-filling method.^{10–15} Especially, expanded graphite-filled nylon 6 composite was prepared by this technique and transition from insulator to semiconductor region was accomplished at around 2 wt % graphite.¹⁵

In this study, both polymerization filling and melt mixing methods were used to prepare conductive composites composed of nylon 6 and carbon black. Different from the previous studies specified earlier, in polymerization filling method, masterbatch composites were first synthesized and then diluted with commercial grade nylon 6 in an extruder. In the melt mixing method, nylon 6/carbon black composites with similar compositions were prepared in the extruder for comparison. It was aimed to obtain semi-conductive nylon 6 composites at relatively low filler concentration and to investigate the effect of composite preparation techniques on the electrical and mechanical properties and the morphology of prepared composites.

EXPERIMENTAL

Materials

Chemicals used for ring-opening polymerization of nylon 6 were caprolactam (Fluka Chemika), *N*-acetylcaprolactam (Fluka Chemika), sodium hydride (Riedel-de Haen), and polyethylene glycol (Fluka Chemika). Polymerization filling method was used to synthesize nylon 6 in the presence of carbon black particles. Commercial grade nylon 6 pellets supplied by Tekno Polimer was used as matrix material in melt mixing method. Carbon black delivered by Turkish Petroleum Refinery was used as conductive filler. Table I summarizes properties of carbon black.

Composite preparation

Sixteen wt % of carbon black containing masterbatch composites were prepared by polymerization filling method as follows. To synthesize nylon 6, 250 g of caprolactam monomer was melted in a glass reactor, which was placed in a jacketed heater, under nitrogen atmosphere at 70°C. 48 g carbon black, which was dried at 100°C for 24 h, was stirred with molten caprolactam for 4 h at the same temperature and at a speed of 260 rpm. After 4 h mixing, the reaction medium was heated at 235°C. Besides, 2.5 mL of *N*-acetylcap-

rolactam as an activator, and 0.4 g of polyethylene glycol, which was used to shield sodium ion of initiator, were loaded into the reaction medium. Afterwards, 0.4 g of sodium hydride as an initiator was added. The viscosity of the reaction medium increased within 1–2 min. Hence, the polymerization reaction ended up by taking away the reaction mixture from the jacketed heater as soon as possible to prevent further heating. Masterbatch composites, which were synthesized by polymerization filling method, were diluted with commercial grade nylon 6 in a corotating twin screw extruder (Thermo PRISM TSE-16-TC) to obtain 1, 3, 6, 10, and 12 wt % of carbon black containing composites. The extrusion processes were experimented in the temperature profile of 220–230–235–240–245°C and at a screw speed of 80 rpm. This procedure was called as method A.

To compare composite preparation methods, melt mixing method of carbon black and commercial grade nylon 6 was applied with the same extruder. The extrusion process condition was provided to be the same as in the dilution process of masterbatch composites. In this method, commercial grade nylon 6 pellets were fed from the main feeder and carbon black particles were fed into molten polymer from the side feeder. This procedure was called as method B. Carbon black compositions of melt mixed composites were adjusted similar to the compositions of method A.

Neat nylon 6 and also produced composite pellets were dried in a vacuum oven for 24 h at 90°C. Test samples of both methods were prepared by compression molding and injection molding devices. These prepared samples were used in the characterization experiments. Compression molded samples were used to determine electrical property, while injection molded samples were used in mechanical tests and morphological analyses. Compression molding process was performed at 235°C. First, pellets were heated for 1.5 min at 50 bars and then they were compressed for 1 min at 150 bars. After that, the molded samples were quenched to room temperature by water. A laboratory scale injection molding machine (Microinjector, Daca Instruments) was used to prepare test specimens at barrel temperature of 235°C and mold temperature of 40°C.

Composite characterization techniques

The intrinsic viscosities of synthesized and commercial grade polymer were determined by the solution viscosity method in an Ubbelohde viscometer kept in a water bath maintained at a constant temperature of 25°C. Nylon 6/carbon black composite, polymer part of which was dissolved in 85% formic acid, was centrifuged for 1 h at 2300 rpm using CS Model International Centrifuge to separate nylon 6 from carbon black. In the viscometer, the polymer solution flowed

TABLE I
Properties of Carbon Black

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

TABLE II
Intrinsic Viscosity [η] and Viscosity Average Molecular Weight M_v of the Materials

	$[\eta]$ (dL/g)	M_v (g/mol)
Synthesized nylon 6	2.01	65,410
Synthesized and then centrifuged nylon 6 in the presence of 16 wt % carbon black	2.01	65,509
Commercial grade nylon 6	1.98	64,145

through a capillary and the flow times were used to calculate the intrinsic viscosity. Then, viscosity average molecular weight (M_v) was determined with the following Mark-Houwink-Sakurada (MHS) equation:

$$[\eta] = K(M_v)^a \quad (1)$$

MHS constants, K and a , were 22.6×10^{-5} and 0.82, respectively.¹⁶ The constants were relevant to nylon 6 in 85% formic acid at 25°C.

Melt flow index (MFI) measurements were performed by Omega model melt flow indexer according to ASTM D 1238 standard. Pure nylon 6 and composites prepared by method A and B were tested at 235°C under 2.16 kg load.

The electrical resistivities of compression molded composites were measured with two point probe method. Test samples were connected to a Keithley 2400 model constant current source. For a 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. The volume resistivity, ρ , was calculated from the relationship:

$$\rho = [V/I]^* [S/L] \quad (2)$$

where V is the voltage drop, I is the current, L is the length, and S is the cross-sectional area of the sample. Average result of six measurements was reported for each material. The electrical resistivity of neat nylon 6 was taken from literature as 10^{15} ohm cm.¹⁵

The tensile properties of the injection molded composites were measured using a Lloyd 30 K universal tensile testing instrument. Five specimens of each composition were tested and average of these test results were illustrated in graphics with their standard deviations. Injection molded specimen had a thickness of 2.1 mm and width of 7.5 mm. According to the gauge length of 80 mm and a strain rate of 0.1 min^{-1} , the crosshead speed of testing instrument was used as 8 mm/min. Charpy impact strength was measured by a pendulum impact tester (Coesfeld Material Test). Fractured surfaces of impact specimens were analyzed using a scanning electron micro-

scope (JEOL JSM-6400). Impact specimens were also analyzed using a transmission electron microscope (Philips CM200 TEM). Samples were trimmed parallel to the molding direction and sections with a thickness of 70 nm were obtained at -100°C . TEM images were taken at an acceleration voltage of 120 kV.

RESULTS AND DISCUSSION

To compare method A with method B, synthesized nylon 6 has to be comparable with commercial grade nylon 6. The comparison can be based on MFI and solution viscosity values of nylon 6. The intrinsic viscosity and viscosity average molecular weight values of synthesized nylon 6, synthesized and then centrifuged nylon 6 in the presence of 16 wt % carbon black and commercial grade nylon 6, are given in Table II. According to the results, viscosity average molecular weights of synthesized and commercial grade nylon 6 are nearly equal. High molecular weight in masterbatch composite (65,509 g/mol) reveals that nylon 6 with a molecular weight similar to commercial grade nylon 6 (64,145 g/mol) is synthesized in the presence of 16 wt % carbon black.

MFI values of method A and B are given in Table III. There is an unusual trend in MFI values of the composites. Both MFI values of masterbatch diluted composites and melt mixed composites fluctuate through the carbon black composition range. Their trends are similar. However, certain MFI values of masterbatch diluted composites are slightly lower compared to melt mixed composites. Possible reason may be the morphological difference. As the carbon black agglomerate size decreases, filler-matrix interaction area increases, this may provide higher melt viscosity for masterbatch diluted composites up to 6 wt % of carbon black composition.

Carbon black tends to form agglomerate structure due to weak van der Waals forces among its particles.² Agglomerates in polymer matrices contain different number of carbon black particles. As the average agglomerate size decreases, the total effective surface area of carbon black increases. Electrical conductivity in conductive polymer composite occurs by means of the transportation of the electrons along the composite. Agglomerates are separated from each other by polymer layers, which are the main reason for electri-

TABLE III
Melt Flow Index Results of Composites Prepared by Method A and B

	Filler content (wt %)					
	0	1	3	6	10	12
Method A(g/10 min)	3.01	3.42	3.33	3.61	3.24	2.56
Method B (g/10 min)	3.34	3.62	3.47	4.77	3.04	2.34

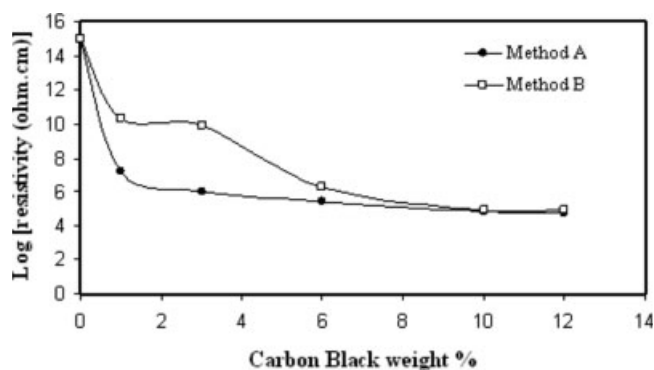


Figure 1 The electrical resistivity values of carbon black filled nylon 6 composites prepared by method A and method B.

cal resistance, and electrons may transfer through the insulating polymer layers by tunneling mechanism during conduction.³ The distance between the agglomerates should be as small as possible. Hence, a decrease in average agglomerate size also reduces the insulating layer between agglomerates. It is aimed to decrease agglomerate size by polymerization filling method in this study. During the polymerization of nylon 6 in the presence of carbon black, filler particles act as catalyst due to their high surface area. Owing to the smaller size of caprolactam in comparison to that of nylon 6 polymer, the monomer can enter the pores of carbon black and polymerize there. As the chain length increases, agglomerates are broken into small pieces and they are separated from each other. Decreased particle size results in increased particle-particle interaction, which increases electron transfer probability between conductive agglomerates.¹⁰ Consequently, lower electrical resistivity is provided by method A compared to method B at the same compositions of carbon black (Fig. 1).

Owing to low melt viscosity of nylon 6 (Table III), carbon black agglomerates can not be broken efficiently in melt mixing method. As a result of this inefficient mixing, low compositions of method B could

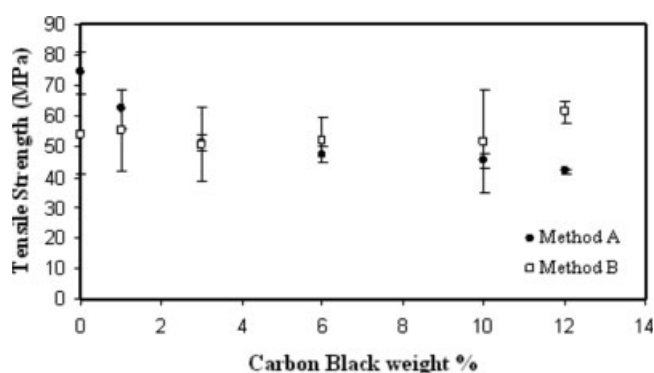


Figure 2 The tensile strength values of carbon black filled nylon 6 composites prepared by method A and method B.

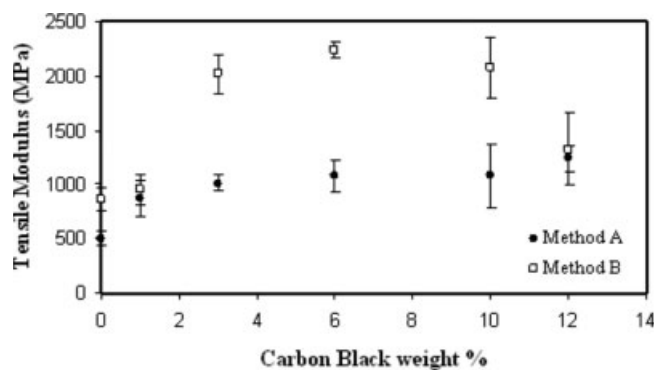


Figure 3 The tensile modulus values of carbon black filled nylon 6 composites prepared by method A and method B.

not provide high conductivity when compared with method A (Fig. 1). However, high loadings of both methods, 10 and 12 wt % carbon black, have similar resistivity values. This improvement in electrical conductivity is the result of increased melt viscosity of composites (Table III) prepared by method B, and also an increase in carbon black content decreases electrical resistivity by reducing the insulating polymer layer between agglomerates. The onset in electrical conductivity of composites, prepared by method A and B, from insulator to semiconductor region is accomplished at around 1 and 6 wt % of carbon black loading, respectively. Since it is aimed to obtain semi-conductive polymer composite at relatively low composition, method A is favorable compared to method B in terms of electrical property.

The tensile strength values of carbon black filled nylon 6 composites prepared by both methods have different trends (Fig. 2). As the filler concentration increases, tensile strength of the composites prepared by method A decreases slightly. However, composites of method B show fluctuations in tensile strength values. Carbon black particles have a strong tendency to agglomerate. Agglomerates are weak point of composites and should be broken into small pieces as much

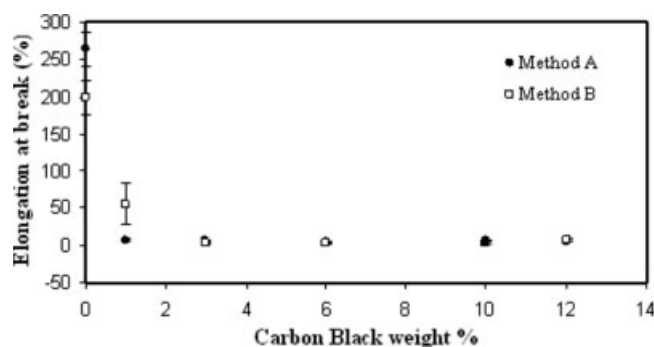


Figure 4 The elongation at break values of carbon black filled nylon 6 composites prepared by method A and method B.

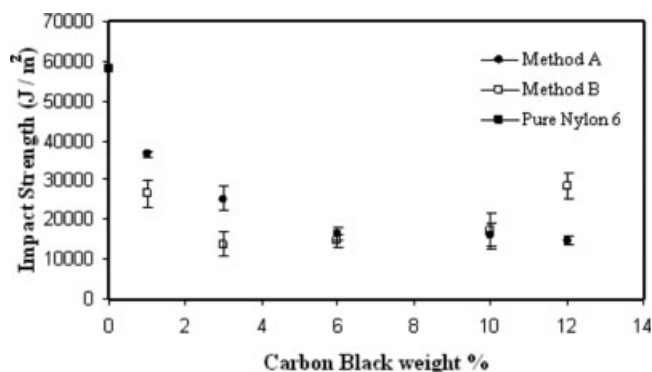


Figure 5 Charpy impact strength values of carbon black filled nylon 6 composites prepared by method A and method B.

as possible. The tensile strength of the composite increases due to the decrease in filler size.² Masterbatch preparation and then dilution process of method A may prevent agglomeration into some extent, which results in an increase in the tensile strength at low compositions up to 6 wt % compared to method B. Method A provides also lower electrical resistivity at low compositions. Improvement in tensile strength and electrical property can be attributed to the increasing interfacial area of particles at the same carbon black concentration.

Relatively high melt viscosity (Table III) increases the shearing effect of rotating screws, which may lead to decrease in agglomerate size of carbon black particles in 12 wt % composite of method B when compared with other compositions of the same method. Hence, melt mixed composites filled with 12 wt % carbon black have higher tensile strength value (Fig. 2). All composites of method B show high standard deviations from average tensile strength values at the same composition. Large standard deviations may be

resulted from less homogeneous filler distribution. In contrast to method B, tensile strength values of method A show small deviations from the average values, which may be the evidence of more homogeneous distribution provided by method A.

The addition of carbon black increases the modulus of prepared composites since carbon black is a rigid filler.² Tensile modulus values of filled composites obtained by methods A and B are different from each other, which may be the consequence of the difference in agglomerate size of carbon black (Fig. 3). The trend of tensile modulus increases slightly as the filler content increases in method A. However, modulus values of method B increase sharply with filler contribution and decrease after 6 wt % of carbon black composition. Below a critical size, the filler loses its effect on tensile modulus.² As it is observed from electrical resistivity results and also given further in TEM micrographs, method A provides a decrease in agglomerate size. As a result, tensile modulus does not change significantly due to small sizes of carbon black agglomerates in composites prepared by method A.

Elongation at break values (Fig. 4) of both methods decrease sharply with 1 wt % filler content due to brittle character of carbon black and do not change significantly upon further increase in filler composition. In addition, the values in both methods are close to each other, except for 1 wt % of carbon black composition. At 1 wt % composition of method B, test samples elongate more compared to other filled composites. Electrical conductivity in insulator range was obtained at this composition of method B, which is the consequence of incomplete carbon black network in the composite. Hence, incomplete filler network results in higher elongation at break value.

Pure matrices of the study could not be broken with the available impact tester. Thus, the impact

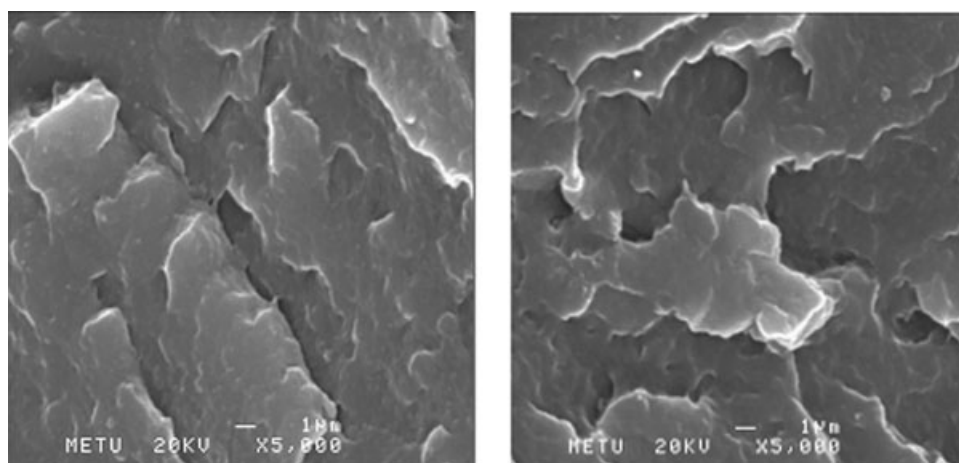


Figure 6 SEM micrographs of impact fractured samples containing 6 wt % carbon black. (a) Method A ($\times 5000$) and (b) Method B ($\times 5000$).

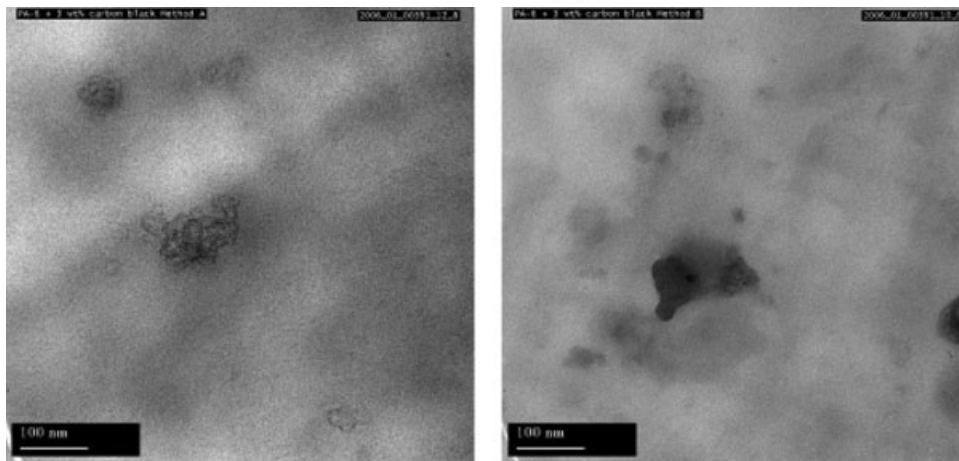


Figure 7 TEM micrographs of impact samples containing 3 wt % of carbon black. (a) Method A and (b) Method B.

strength value of nylon 6 was taken from the literature.¹⁵ The impact strength of the composites prepared by both methods decreases with filler contribution, excluding 10 and 12 wt % compositions of method B. Low compositions of method A have higher impact strength values compared to method B (Fig. 5), which can be attributed to the reduction in agglomerate size. Moreover, higher impact strength values of method A at low carbon black content is the result of improved interfacial interaction between composite constituents since a decrease in agglomerate size enhances interfacial interaction between the polymer and the filler.

Figure 6 shows SEM micrographs of impact fractured surfaces of the composites containing 6 wt % carbon black for both method A and method B. Carbon black agglomerates could not be detected on SEM micrographs at higher resolution around micron size. From these micrographs, it can be concluded that the carbon black agglomerates are under micron size for both composite preparation methods. The size and dispersion of carbon black particles in the composites

are investigated by TEM analyses. Figures 7 and 8 illustrate TEM micrographs of the composites prepared by method A and method B with 3 wt % carbon black. In Figures 7(a) and 8(a), a few small carbon black clusters are observed as less dense areas with the size smaller than 200 nm. In Figures 7(b) and 8(b), more dense areas and larger agglomerate sizes are recognizable for method B. Therefore, method A provides smaller and less dense agglomerates, which result from the entering of nylon 6 monomer into the pores of carbon black particles during polymerization reaction. As a result, lower electrical resistivity and improved tensile strength and impact strength were obtained for the composites prepared by polymerization filling method at lower concentration of carbon black.

CONCLUSIONS

Polymer composites prepared by masterbatch dilution technique showed lower electrical resistivity at

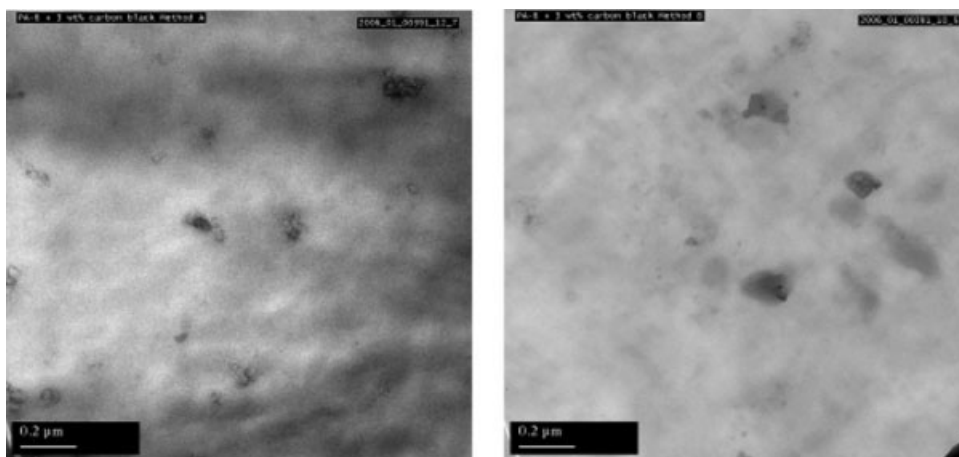


Figure 8 TEM micrographs of impact samples containing 3 wt % of carbon black. (a) Method A and (b) Method B.

each composition of carbon black when compared with melt mixing method. Transition from insulator to semiconductor range was achieved at 1 wt % carbon black content. This improvement was attributed to the decrease in agglomerate size of carbon black. Composites prepared by both methods did not differ so much in elongation at break values. At low compositions of the filler, polymerization filling method gave higher tensile strength and impact strength results. In addition, melt mixing method gave higher tensile modulus values at intermediate compositions. According to these results and especially based on the improved electrical conductivity values, polymerization filling method together with masterbatch dilution can be chosen as an alternative composite preparation technique to melt mixing method.

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