**Electrical and Thermal Properties of Bisphenol A Propoxylate Diglycidyl Ether-Piperazine Copolyme**r**/Functionalized MWCNT Composites**

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*Abstract:* In this work, bisphenol A propoxylate diglycidyl ether-piperazine copolymer /the functionalized MWCNTs (oxidized MWCNT + aminated MWCNT) composites were prepared and structural characterization was performed using FT-IR and NMR spectra. Composites were investigated in terms of electrical properties and thermal properties. Surface morphology was determined by SEM photographs. It was observed that thermal stability decrease and ac conductivity and dielectric constant increase with increasing in functionalized MWCNT content of the composites. The electrical conductivity increased with increasing temperature and the activation energy of ac conductivity was determined and discussed.

*Keywords:* Bisphenol A; Piperazine; MWCNT; Composite; Copolymer

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**INTRODUCTION**

Carbon nanotubes (CNTs), discovered by lijima 1, have remarkable properties, such as mechanical properties, chemical stability, electrical and thermal conductivity. They have received much attention for their many potential application, such as nanoelectronic and photovoltaic devices 2,3, superconductors 4, electromechanical actuators 5, electrochemical capacitors 6, nanowires 7 and nanocomposites materials 8,9.

Polymer/CNT composites have attracted considerable attention owing to their unique mechanical, surface and multi-functional properties, and strong interactions with the matrix resulting from the nano-scale microstructure and extremely large interfacial area. After the publication of Iijima´s report on CNT in 1991, many research articles and reviews on CNTs and their composites have been published 10-15. In current years, many polymers such as poly(methyl methacrylate) (PMMA), epoxy type polymers, poly(vinyl chloride) (PVC), poly(vinyl alcohol) (PVA), poly (ethylene) (PE), poly(styrene) (PS) 10, poly(glycidyl methacrylate) (PGMA) 16, poly(vinylidene floride) (PVF) 17 have been used widely as matrices for the preparation of polymer/CNT composites. There are reports in the literature on composites of epoxy-based polymers with CNTs. The mechanical properties of bisphenol A diglycidyl ether type epoxy resin were investigated by the addition of polyether polyol and amine functionalized MWCNT 18. Seamus A. Curran and et al. have extensively studied the electrical properties of poly (bisphenol A carbonate) doped with MWCNTs. Particularly, the conductivity of both acid-treatment and pristine MWCNTs have been examined at different nanotube weight percent 19.

In this study, copolymer of bisphenol A propoxylate diglycidyl ether (BPPDE) with piperazine (Pp) was prepared. This condensation copolymer contains functional groups, in its main chain, such as ether, hydroxyl, amine groups, aromatic rings, and epoxide groups at the chain ends. It has been synthesized with the thought that a copolymer with these functional groups and its MWCNT composites will may exhibit interesting electrical and thermal properties. Composites prepared of this copolymer, poly(BPPDE-*co*-Pp) with the mixture of oxidized MWCNT and aminated MWCNT were first time studied in terms of electrical, thermal and surface properties. The effects of the mixture of oxidized MWCNT and aminated MWCNT on the properties of the composite were investigated.

**EXPERIMENTAL**

***Materials***

Toluene, ethanol, 3-aminopropyltrimethoxysilane (3-APTMS) (99%), 1,4-dioxane and bisphenol A propoxylate diglycidyl ether (M.W. 456.6 g/mol, PO/phenol,1, PO: Propylene oxide) were obtained from Sigma-Aldrich and used without any purification. Piperazine was obtained from Sigma-Aldrich and recrystallized from diethyl ether before use. Multi-wall carbon nanotube (MWCNT) (average diameter 9.5 nm, length > 1.5 μm and purity > 95%) was purchased from Grafen chemical Co.

***Synthesis of oxidized MWNT***

Carboxyl-functionalized MWNTs (oxidized MWNT) were prepared by oxidation of MWNTs in a mixture of conc. HNO3 and H2SO4 in 1:3 ratio (by volume).

The procedure: MWNT (2 g), 40 mL of the acid mixture was added into a 250 mL flask equipped with a condenser, and the mixture was stirred vigorously. The flask was then immersed in an ultrasonic bath at room temperature for 20 min. The stirring of the mixture was continued under reflux for 10 h in an ultrasonic bath. The mixture was allowed to cool at room temperature and was then diluted with 250 mL of water, followed by neutralization with conc. NaOH to pH 7 and then filtered. The residue was washed with water several times, washed with THF to remove the water, and then dried under vacuum for 24 h at 50 oC.

***Synthesis of MWNTCOOSi(OCH3)2-n-propyl-NH2***

For silanization a method modified from literature 20,21 0.5 g oxidized MWCNT was dispersed in an ultrasonic bath in 40 mL toluene for 15 min and then 2 g 3-aminopropyltrimethoxysilane (3-APTMS) was added to the mixture. The mixture was refluxed for 6 h, and after cooled to room temperature, the product, MWNTCOOSi(OCH3)2-n-propyl-NH2 (aminated MWCNT), was separated by filtration, washed with ethanol for a few times, and dried under vacuum at 50 oC for 24 h.

***Copolymerization of Bisphenol A Propoxylate Diglycidyl Ether and Piperazine***

The method which adapted from literature was used for the copolymerization 22. Experimental detail briefly;

To a 25 mL flask were added 3.085 (6.76 mmol) of bisphenol A propoxylate diglycidyl ether and 5 mL of 1,4-dioxane, and dissolved. 0.5820 (6.76 mmol) piperazine recrystallized from diethyl ether was dissolved 5 mL of 1,4-dioxane in a separate flask and was added over the previous solution. After it was passed through nitrogen gas, the resulting mixture was sonicated for 1 h and then refluxed on magnetic stirrer and heater for 3 days. End of this time after 0.55 g bisphenol A propoxylate diglycidyl ether was dissolved in 2 mL 1,4-dioxane, it was added to the reaction flask and was continued to reflux for 1 day more. The reaction content was then cooled to room temperature and diluted with about 20 mL of 1,4-dioxane. The polymer product, poly(BPPDGE-*co*-P), was precipitated by pouring dropwise the reaction mixture into excess methanol/water (1:1 by volume), filtered off and air dried. The product was redissolved in 1,4-dioxane and reprecipitated in the same precipitator, filtered off and dried in vacuum oven at 50 oC for 24 h.

***Preparation of the Composites***

For preparation of the composites, 0.45 g of the copolymer was dissolved in 5 mL of 1,4-dioxane. For a 10 % wt composite, 0.025 g of oxidized MWCNT and 0.025 g of aminated MWCNT were dissolved in 2 mL of 1,4-dioxane, and this mixture was added to the polymer solution. The last mixture was stirred in an ultrasonic bath for 3 h, and then it was stirred using a magnetic stirrer at 80 oC for 1 h. After the mixture was cooled to room temperature, the composite was precipitated by adding dropwise to the methanol-water mixture (1:1 v:v). It was filtered and dried under vacuum at 50 °C for 24 hours. In addition, the composite was ground with an agate morter and pestle, and powdered very fine.

In addition to 10 %, a series of BPDE-Pp copolymer/functional MWCNT composites were prepared with functional MWCNT concentration at 2, 5 and 15 wt% by similar procedure.

***Measurements***

Infrared spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer, using KBr disc in range of 450-4000 cm-1. Calorimetric measurements were carried out on a Shimadzu DSC-50 thermal analyzer under N2 flow a using a heating rate of 20 oC/min. Thermal stability studies were carried out on a Shimadzu TGA-50 thermobalance under N2 flow with a heating rate of 10 oC/min.

For capacitance measurements according to the previous work 23, the composite was ground with an agate mortar and pestle, and the final fine powder was pressed at four tons of pressure into disk-shaped samples with a thickness of 0.68 mm for the composite contained a composite of 2 % and 0.66 mm, 0.64 mm and 0.65 mm for the composites of 5, 10 and 15 %, respectively, and a surface of 1.12 cm2 for all disks. The entire surface of the disk was coated with aluminum foil, which acts as a good contact for capacitance measurements.

The measurements were carried out at room temperature with a QuadTech 7600 precision LRC meter impedance analyzer over the frequency range 0.1 - 2 kHz. The dielectric features against the frequency and temperature were examined, and ac conductivity of the composites against the temperature were also examined at 1 kHz constant frequency.

Scanning electron microscopes (SEM) (Jeol JSM-700IF) were used to examine the distribution in the composite materials of nanoparticles, and they were taken with a Jeol JSM-7001F instrument from gold coated powder samples.

**RESULTS AND DISCUSSION**

***Characterization of the Matrix Copolymer and the Composites***

FT-IR spectra of the mixture of oxidized MWCNT and aminated MWCNT, the matrix copolymer, poly(BPPDGE-*co*-P) and the composite containing 10 % of (oxidized MWCNT + aminated MWCNT) are shown in Figure 1. In the spectrum 1(a), the O-H and C=O stretching vibrations in acid group of oxidized MWCNT are seen at 3440 cm-1 and 1735 cm-1 (small peak), respectively. The broad peak at 1380 cm-1 and the broad band at 1600-1650 cm-1 may be assigned to O-H bending vibration (in addition to acidic O-H, probably O-H of atmospheric moisture on the surface) 21 and aromatic C=C stretching vibration (and also N-H in plane bending vibration)24, respectively. The FT-IR spectrum (a) also shows the characteristic bands at 3290 cm-1 (symmetric stretching vibration of N-H, the asymmetric vibration of N-H is under the band at 3440 cm-1), 2925 and 2850 cm-1 (C-H stretching in CH2 groups), the bands at 1200-1000 cm-1 (Si-O-Si, Si-O-C and C-O stretching vibration), 780 cm-1 (N-H out-of-plane bending vibration).

The FT-IR spectrum of poly(BPPDGE-*co*-P) shows the characteristic peaks of the matrix copolymer. In this context, the six intense bands at 3430 cm-1, 2970-2818 cm-1, 1604 cm-1, 1241 cm-1, 1155-1000 cm-1 and 827 cm-1 are the characteristic poly(BPPDGE-*co*-P) peaks that correspond to O-H stretching vibration, aliphatic C-H stretching vibration, aromatic C=C stretching vibration, C(aromatic)-O-C(aliphatic) asymmetric stretching vibration, aliphatic ether C-O-C, C-N stretching vibrations and p-disubstituted aromatic C-H out-of-plane bending vibration, respectively. The bands at 3054 cm-1, 1885 and 1764 cm-1, 1365 and 1384 cm-1, 913 cm-1 and 740 cm-1 can be attributed to epoxide C-H and aromatic C-H stretching vibration, overtone and combination bands of p-disubstituted aromatic, in plane bending vibration of C(CH3)2 group, epoxide symmetric ring stretching vibration and epoxide C-H bending vibration, respectively. The peaks corresponding to epoxide group (3054, 913 and 740 cm-1) are seen as weakened in the spectrum of the composite (10 wt%), when compared those of the matrix copolymer. This is probably due to opening by the acid and amine groups of some part of the epoxide ring.

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| Fig. 1. FT-IR spectra of (a) poly(BPPDGE-co-P), (b) the composite (10 wt%) and (c) mixture of oxidized MWCNT and aminated MWCNT |

The 1H NMR spectrum (Fig. 2a) shows characteristic signals that confirm the structure of the copolymer. The signals at 7.12 ppm and 6.76 ppm assigned to aromatic meta proton and aromatic ortho proton according to oxygen, respectively. The signal between 3.25-4.7 ppm are due to CH and CH2 protons bonded to oxygen, and the signal between 2.25-3.0 are due to epoxide ring protons and CH2 protons bonded to nitrogen. Peaks between 1.0 and 2.0 ppm include methyl protons at side chain of aromatic ring and CH2 protons not bonded to oxygen. All the assignments are shown in the copolymer formula in Fig. 2. 13C-NMR spectrum (Fig. 2b) shows characteristic signals for bisphenol A propoxylate diglycidyl ether at 156 ppm, 143 ppm, 128 ppm and 114 ppm due to quaternary carbon (p) bonded to oxygen, quaternary carbon (q) bonded to aliphatic carbon, CH carbons in meta and ortho position on aromatic ring, respectively. The other assignments are shown in the copolymer formula in Fig. 2.

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| Fig. 2. (a) 1HNMR and (b) 13CNMR spectra of poly(BPPDGE-*co*-P) (solvent: CDCl3) |

Fig. 3 shows the SEM images of reference pure the matrix copolymer (3a), original MWCNT (3b), MWCNT silanized with aminopropyltrimethoxysilane (aminated MWCNT) (3c) and the composite containing 15 wt% the mixture of oxidized MWCNT and aminated MWCNT (3d). The SEM micrograph of the pure matrix copolymer suggests a smooth surface. A clear distribution of MWCNT is observed after silanization. In addition to this, the morphology of MWCNTs after functionalization is observed to have remained intact with minimal visible tube damage. No serious MWCNT destruction is observed which indicates that the MWCNTs are strong enough to withstand the functionalization process. SEM photograph of the composite (3d) shows that the functional MWCNT particles in the polymer matrix are homogeneously dispersed. This is because the presence of the carboxylic groups and amino groups on the nanotube surface is likely to give the strong interfacial interaction between the polymer matrix and the nanotubes in polymer composites 25. That is, oxygen (–O–) in epoxide at the end groups and oxygen in etheric groups of polymer main chain and -N- in piperazine unit of the matrix copolymer may form the hydrogen bonds with –COOH and -NH2 groups of the functionalized MWCNTs.

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| Fig. 3. SEM images of the matrix copolymer (a, m: x2000), original MWCNT as received (b, m: x30000), aminated MWCNT (c, m: x70000) and the composite (15 wt%) (d, m: 50000). m: Magnification |
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To be knowledgeable the viscosity of the poly (BPPDGE-co-P), the limiting viscosity number ([η]) was determined using the Huggins equation, ηsp/c = [η] + k´[η]2 c. Flow times of the solutions with concentration (c) at between 0.556-0.280 g copolymer / dL solvent and pure chloroform using Ubbelohde viscometer were determined. The Huggins line was obtained from

plot of ηsp/c versus c. Where ηsp is the specific viscosity. From these measurements, the limiting viscosity number of the polymer in chloroform solution and the Huggins constant, k´, were obtained as 0.34 dL / g and 0.38 (generally 0.3 <k '<0.4) at 22 oC, respectively.

***Electrical Investigation***

The dielectric constant which is one of the electrical properties of materials is a measure of the influence of a particular dielectric on the capacitance of a condenser. When a dielectric is put between two electric charges, it reduces the force acting between them, just as if they had been moved apart from each other. The dielectric constant of a material affects how electromagnetic signals move through the material. It is calculated from capacitance measurements using the following equation:

Where *Cp* is parallel capacitance, *εo* is permittivity in free space, *d* is thickness of sample material and A is surface area of the sample. Fig. 4 shows how the dependence of dielectric constant (4a) and dielectric loss factor (4b) on frequency (0.10-2.5 kHz) for all samples and on the percentage of functional MWCNT (4c) in composites. It is distinctly observed that the dielectric constant and dielectric loss decrease with the increase in frequency. As shown in the Fig. 4, for the composite in concentration of 2 wt%, the dielectric constant remained approximately constant with increasing frequency from 0.1 kHz to 2.5 kHz, while that of the composite in concentration 5 wt% decreased slightly. When MWCNTs loading is 10 wt% and 15 wt%, dielectric constant decreases rapidly up to about 0.6 kHz, then the decline slows down. Similar behavior in the composites, it is also observed for calcium copper titanate/MWCNT/polyarylene ether nitrile composites25, for some ceramics26 and poly(urethane)/poly(aniline) composites27. The large value of dielectric constant at low frequency is due to the presence of electric polarization of polar groups. The decrease in the value of dielectric constant with frequency is due to the fact that the frequency of electric charge carriers cannot follow the alternation of the electric field applied beyond a certain critical frequency. The very low value of dielectric constant at higher frequencies is important for the fabrication of materials for ferroelectronic, photonic and electro-optic devices. Fig. 4b shows that the dielectric constant is more dependent on the frequency in the composites at higher concentrations.

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| Fig. 4. Frequency dependence of (a) dielectric constant (*εʹ*), (b) dielectric loss factor (*εʹʹ*) (c) the composite concentration dependence of dielectric constant at different frequencies |

Fig. 5 indicates the change of dielectric constant (*εʹ*) with temperature for the composites at different concentration at 1 kHz. With increasing temperature, the dielectric constant increases moderately from 320 to 340 K for a 15% composite and from 320 to 360 K for a 10% composite, later it increases rapidly up to 375 K for a 15% composite and up to 390 K for a 10 % composite. For a 5% and 2% composites, the dielectric constant increases slightly with increasing temperature from 320 to nearly 390 K, then increases rapidly up to 420 K for a 5 % composite and up to 430 K for a 2% composite.

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| Fig. 5. Temperature dependence of dielectric constant of the composites at 1 kHz |

The variation of ac conductivity with frequency and temperature at different the modified MWCNT content are shown in Fig. 6. The electrical conductivity (log *σ*) of the composites increases approximately linearly with increasing the applied frequency (log *f*, f kHz from 2 to 3.4) (Fig. 6a), moderately for the composite with 2%, slowly for the other composites. The conductivity increases also with increasing MWCNT content in composites.

The composite samples with increasing MWCNT content are thermally activated by heating at higher temperature. Activation energy of ac conductivity was obtained using Arrhenius equation 28.

Where *σ* is the conductivity, *σo* is the pre-exponential factor of conductivity, *kb* is the Boltzmann constant, T is the temperature in Kelvin, and *Ea* is the activation energy. Fig. 6b shows plot of log *σ* vs 1/*T* at 1 kHz. The ac activation energies were calculated from the slopes linear region (range of 320-440 K) of the plots. It is clear from these plots that above ~320 K the ac conductivity increases with increasing temperature and increase in MWCNT content. The incorporation of the modified MWCNT increased the conductivity from 0.18x10-7 to 8.19x10-7 at 320 K and from 1.18x10-5 to 17.06x10-5 S/cm at 400 K when the filler content was increased from 2 to 15 wt%. The resulting from the plot of log *σ* vs 1/*T*, is a firsthand indication that the observed conductivity does not correspond to single thermally activated process and cannot be described by a simple exponential relationship 29. Under this point of view, it can be concluded that ac conductivity depends on temperature and it is reasonable to assume that a range of activation energies is involved. The activation energy values are shown in Table I.

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| TABLE I. Activation energy of ac conductivity at 1 kHz | |
| Composite | *Ea* / eV |
| 2 wt% the modified MWCNT | 0.396 |
| 5 wt% the modified MWCNT | 0.335 |
| 10 wt% the modified MWCNT | 0.327 |
| 15 wt% the modified MWCNT | 0.312 |

As can be seen in this table, there is a decrease in the activation energy of ac conductivity as the modified MWCNT concentration increases. A similar trend for activation energy has also been observed in polyester / MWCNT composites 30 and carbon black/epoxy composites 31. Similar to the comments in the literature 30, 31 degrease in *Ea* values with the MWCNT content may be due to an increase of polarization energy and/or charge carrier density leading to a decrease of the domain boundary potential of MWCNT aggregate into the matrix polymer.

Since it could not be prepared the disc, electrical properties of the matrix copolymer could not be measured.

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| Fig. 6. Variation of ac conductivity with (a) frequency, (b) temperature |

***Thermal Investigation***

TGA measurements (Fig. 7) of the copolymer, the mixture of oxidized MWCNT and aminated MWCNT and the composites showed that initial decomposition temperature (IDT), at which the rapid decomposition begins, shifted lower values (260 oC for the matrix copolymer, 248, 246, 246 and 240 oC for the nanocomposites with 2 wt%, 5 wt%, 10 wt% and 15 wt%, respectively) when the modified MWCNT content was increased. This result shows that the mixture of oxidized MWCNT and aminatid MWCNT decreased thermal stability of nanocomposites according to the temperature at which decomposition begins. Probably, the radicals which have remained within the MWCNT during the oxidation have initiated decompose of the polymer at a lower temperature.

Fig. 7 also showed that as the content of modified MWCNT in the composites increased, the residues at 500 oC also increased from 10.8 to 18.3 wt%, while the matrix copolymer left 8.3 wt % of a residue at 500 oC. The thermal data are summarized in Table II. The original polymer and the composites gave a three-stage decomposition curve. The residues at 350 oC are 51.5 % for the matrix copolymer, 59.2 %, 61.0 %, 62.0 and 64 % for the composites (from 2% to 15%, respectively).

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| TABLE II. Some thermal properties of the materials used in this study | | | | | | |
| Material | *Tg*/ oC) | *TIDT*/oC)1 | Tsecd2 | Ttrd3 | Residue(% by weight)  at 350 oC | Residue(% by weight)  at 500 oC |
| The mixture of oxidized and aminated MWCNT | - | 340 | - | - | > 95 | 40.0 |
| Poly(BPPDGE-*co*-P) | 152 | 260 | 374 | 446 | 51.4 | 8.3 |
| Composite : 2 wt% | 57 | 248 | 363 | 449 | 59.2 | 10.8 |
| 5 wt% | 54 | 246 | 349 | 447 | 61.0 | 14.2 |
| 10 wt% | 54 | 246 | 391 | 465 | 62.0 | 15.8 |
| 15 wt% | 58 | 240 | 364 | 454 | 64.2 | 18.3 |
| 1*TIDT*: Initial decomposition temperature (at which the first stage decomposition begins), 2 the temperature at which the second decomposition stage begins, 3 the temperature at which the third decomposition stage begins. | | | | | | |

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| Fig. 7. The TGA curves of the materials used in this study |

DSC curves in Fig. 8 show that the matrix copolymer, poly(BPPDGE-*co*-P), has 152 oC of a glass transition temperature (*Tg*), whereas the composites have 57 oC for 2%, 54 oC for 5% and 10%, 58 oC for 15%. *Tg* Value for bisphenol A propoxylate diglycidyl ether (BPPDGE) has given as 125 oC in the literature. 32 When the *Tg* value obtained for the copolymer is compared with that the BPPDGE, the copolymer is due to containing the rigid piperazine units in the main chain, it is reasonable to be higher than that the BPPDGE. The increase of *Tg* value of the copolymer is because rigid piperazine units in the main chain of the copolymer prevents chain mobility and leads increase of free volume in the copolymer. It is also interesting that the *Tg* values of the composites are very low compared to the copolymers. The copolymer contains etheric groups, amine groups and hydroxyl groups in its main chain, and epoxy end groups. Strong dipole-dipole interactions and hydrogen bond interactions occur between these groups along the chain. Strong dipole-dipole interactions and hydrogen bond interactions occur between these groups along the chain. When MWCNT nanoparticles introduce between the copolymeric chains in the composites, these strong physical interactions are broken and the chains are separated from one another, which means that the free volume increases in the polymer and the *Tg* value decreases. It has been given that the addition of a mono amine with a long hydrocarbon chain or an aliphatic diepoxy compound to the EPON 826 polymer which bearing epoxy end groups and ether and OH groups in the main chain significantly reduces the *Tg* temperature of the polymer 33. While the matrix copolymer also shows a melting point at about 260 oC, only one (2 wt%) of the composites shows at about 270 oC.

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| Fig. 8. The DSC curves of the matrix copolymer and the composites |

**CONCLUSIONS**

FT-IR and NMR characterization of composites prepared from this copolymer and functionalized MWCNT have been made and surface morphologies have shown that a homogenous composite is formed. It has been observed that the ac electrical conductivity, the dielectric constant, and the dielectric loss factor of the composites increase with the MWCNT concentration in the composites. The increase in dielectric constant with MWCNT content is an indication that these composites can be used as capacitors. It was also found that activation energy related to ac conductivity decreased with composite concentration. The thermal stability of composites decreased with MWCNT content. The glass transition temperatures of composites decreased considerably with MWCNT concentration.

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