Influence of Nanoclays on Electrical and Morphological Properties of Thermoplastic Polyurethane/Multiwalled Carbon Nanotube/Clay Nanocomposites

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ABSTRACT: Nanocomposites of thermoplastic polyurethanes (TPUs), multiwalled carbon nanotubes (MWCNTs) and clays were prepared via melt processing using polyether- and polyester-based TPUs, MWCNTs, and organically modified nanoclays (Cloisite C30B and C25A). Coaddition of clays and MWCNTs to TPU nanocomposites increased their electrical conductivities above those without any clay. Nanoclay alone is shown to produce no effect on electrical conductivity. TEM results show that the coaddition of nanoclay affects the nanocomposite morphology by changing the MWCNT distribution. Clay C25A and MWCNTs were observed to form network structures in the nanocomposites, resulting in improved electrical conduction. Interaction between MWCNTs and clays as well as an increase in nanocomposite viscosity caused by the coaddition of clays may influence the morphology change. Most of the nanocomposites containing both MWCNTs and clay exhibited higher dielectric constants, indicating higher electrical conductivities. Tensile properties investigations confirmed the reinforcing effects of the MWCNTs and clays. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Carbon nanotubes (CNTs) have been the subject of intensive research activity since their discovery in 1991 by Ijiima.[1] CNTs are known to show excellent mechanical, electrical, and thermal properties.[2–10] Their high aspect ratio in nanocomposites that contain CNTs shifts the electrical percolation threshold to a lower value than that of composites containing carbon black or carbon fiber.[11–13]

Thermoplastic polyurethanes (TPUs) are usually formed from polyether or polyester polyols along with aliphatic or aromatic diisocyanates. Studies on TPU nanocomposites that contain CNTs have shown improved electrical conductivity, mechanical properties, and thermal properties compared to pure TPUs.[14–19]

Polymer nanocomposites containing nanoclays have also attracted attention due to several advantages that can be achieved by the addition of clays, such as improved heat stability, improved mechanical properties, and decreased gas permeability and flammability.[20–23] TPU nanocomposites containing modified clays have been reported to show improved

mechanical and thermal properties compared to pure TPUs.[24–28] TPU nanocomposites containing C30B clays were reported to show a nearly exfoliated structure in the TPU matrix.[29–32]

Carbon black is usually added to polymers to make them conductive. Some researchers have shown that the electrical conductivity can be improved by the coaddition of clay in the polymer/carbon black composites.[33,34] Feller et al.[33] reported that the resistivity of poly(ethylene-*co*-ethyl acrylate)/carbon black decreases by about 2.5 decades when 0.6% clay is added simultaneously. Konishi and Cakmak reported that the percolation threshold of nylon6/carbon black shifts to lower volume fractions of carbon black in the presence of an optimum amount of organic clay.[34] Improved electrical conductivity was explained as arising from the so-called nano-unit structure.

Instead of carbon black, Liu and Grunlan[35] used carbon nanotube and reported that the electrical conductivity of epoxy nanocomposites containing single-walled carbon nanotubes (SWCNTs) can be improved by the coaddition of nanoclay.

TPUs with high electrical conductivity become important in practical applications such as electrostatic coating and electromagnetic shielding. In this study, TPU/multiwalled carbon nanotube (MWCNT) nanocomposites containing clay were prepared and the effect of the coaddition of nanoclay to TPU/MWCNT nanocomposites was studied. TPU nanocomposites were prepared by melt mixing. TEM analyses were performed to study the dispersion states of MWCNTs and clay in the nanocomposites. Electrical conductivities were measured and analyzed in conjunction with the morphology. The rheological and tensile properties were also measured.

EXPERIMENTAL

Materials and Preparation of Nanocomposites

Two types of TPUs were obtained from SK chemicals: polyether-based TPU (Skythane R185A, $M_w \approx 250,000$) and polyester-based TPU (Skythane S185A, $M_w \approx 250,000$), both having a Shore hardness of 87A. Hard segments of both ether- and ester-type TPUs were made using 4,4-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD), but soft segments were made using different compounds, such as poly(tetramethylene oxide) glycol (PTMG, $M_w \approx 1000$) for ether-type TPUs and poly(butylene adipate) glycol (PBAG, $M_w \approx 1000$) for ester-type.

The MWCNT (CM-95) used in this study were purchased from Hanwha Nanotech. These nanotubes were 10–15 nm in diameter and 10–20 μm in length, and they had a very high aspect ratio of around 1000.

Two types of organically modified clays were obtained from Southern Clay Products. Cloisite 25A (C25A, CEC: 95 meq/100 g) is natural montmorillonite modified with a quaternary ammonium salt. Cloisite 30B (C30B, CEC: 90 meq/100 g) is a montmorillonite modified with a quaternary ammonium salt having one methyl, one tallow and two —CH_2CH_2OH groups.

TPUs in pellet form were dried for 4 h prior to melt blending, and MWCNTs and clays were dried in a vacuum oven at 80°C for 12 h. TPUs with different amounts of clays and MWCNTs were melt-blended in a twin screw extruder (Bautek, BA-19ST) at around 195°C, and the extrudate was pelletized. Table I shows the compositions of ester-TPU/MWCNT/clay and ether-TPU/MWCNT/clay nanocomposites prepared in the present study. The pelletized nanocomposites were injection molded into specimens for testing in a mini-injection molding machine (Bautek). Film specimens for testing electrical conductivity and complex viscosity were prepared by compression molding.

Nanocomposites Characterization

The silicate interlayer distance in the polymer matrix was obtained using an X-ray diffraction pattern from X-ray diffractometer (D-8 Advance, Cu radiation $\lambda = 0.154$ nm) at 40 kV, 35 mA. TEM images of nanocomposite specimens were obtained using energy filtered transmission electron microscopy (EM-912 OMEGA, Carl Zeiss) at an operating voltage of 120 kV. Ultrathin sectioning was performed on an ultramicrotome at −100°C. The electrical conductivities were obtained with a digital multimeter (Protek multi tester 608, Protek) and megohmmeter (SM8210, TOA Electronic).

Table I. Composition of Ester-TPU/CNT/Clay and Ether-TPU/CNT/Clay Nanocomposites

TPU (wt %)		CNT (wt %)	Clay (wt %)	
			30B	25A
Ester-TPU	100	–	–	–
	99	1	–	–
	98.5	1.5	–	–
	98	2	–	–
	97	3	–	–
	95.5	3	1.5	–
	94	3	3	–
	92.5	3	4.5	–
	91	3	6	–
	95.5	3	–	1.5
	94	3	–	3
	92.5	3	–	4.5
	91	3	–	6
Ether-TPU	100	–	–	–
	99	1	–	–
	98.5	1.5	–	–
	98	2	–	–
	97	3	–	–
	95.5	3	1.5	–
	94	3	3	–
	92.5	3	4.5	–
	91	3	6	–
	95.5	3	–	1.5
	94	3	–	3
	92.5	3	–	4.5
	91	3	–	6

Tensile tests were carried out on a universal testing machine (LR10K, Lloyd Instruments), according to the ASTM D 638 type V method. The crosshead speed was 50 mmmin^{-1}, and at least five measurements were taken on each sample.

The complex viscosity measurements were performed on a rheometer (MCR 300, Physica) with parallel plate geometry using 25-mm diameter plates. Dynamic frequency sweep tests were conducted at 195°C with angular frequencies ranging from 0.01 to 100 rads^{-1}.

RESULTS AND DISCUSSION

Electrical Conductivity

The electrical conductivities of the ester-TPU nanocomposites containing MWCNTs (ester-TPU/MWCNT) are shown in Figure 1. This data shows that the electrical percolation threshold value is around 2 wt % MWCNT in the ester-TPU/MWCNT. Fairly good conductivity was observed at 3 wt % MWCNT loading.

Nanoclays were coadded to the nanocomposites in addition to MWCNTs to determine if they change the electrical conductivity
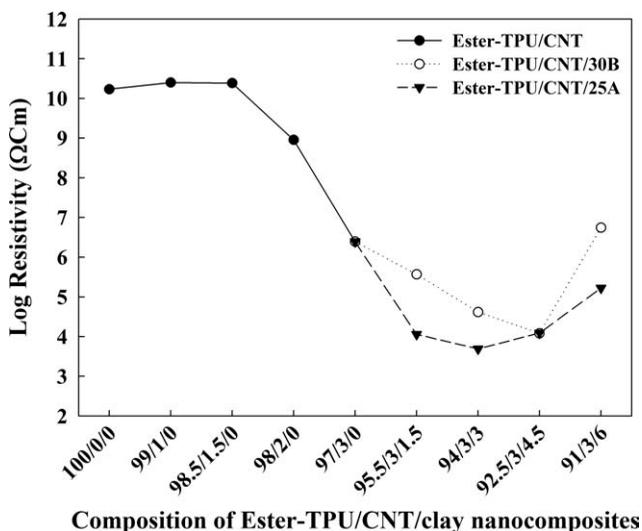
Figure 1. Electrical conductivity of ester-TPU nanocomposites.

of the nanocomposites. Because clays C25A and C30B were reported to show intercalation and near exfoliation, respectively in the ester-TPU/clay nanocomposites,[29–32] up to 6 wt % of clay C25A or C30B was coadded along with 3 wt % MWCNTs. The electrical conductivity results for these ester-TPU nanocomposites containing both MWCNTs and nanoclay (ester-TPU/MWCNT/clay) are also included in the right half of Figure 1. Both clays C25A and C30B were observed to further improve the electrical conductivity as shown in Figure 1; the degree of improvement varies depending on the clay composition.

Coaddition of clay C25A produced better improvement in electrical conductivity than C30B. As the amount of either coadded clay increased, the electrical resistivity of the nanocomposite decreased to a minimum value, after which it began to increase again. The maximum improvement of the electrical conductivity, more than three orders of magnitude, was observed when 3 wt % of C25A was coadded. In the case of C30B, the minimum electrical resistivity was observed at 4.5 wt %.
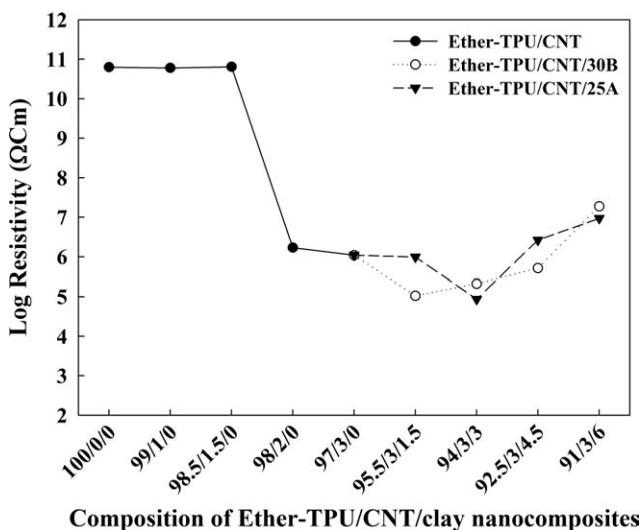
Ether-TPU nanocomposites containing MWCNTs (ether-TPU/MWCNT) were also prepared to see if a similar trend to that for ester-TPU nanocomposites could be observed. The electrical resistivities of ether-TPU/MWCNT are shown in Figure 2. The electrical percolation threshold value of ether-TPU/MWCNT was between 1.5 and 2 wt % MWCNTs, which is similar to that of ester-TPU/MWCNT.

Clays C25A and C30B were also coadded to ether-TPU/MWCNT nanocomposites. The electrical conductivities of the ether-TPU nanocomposites containing both MWCNTs and nanoclay (ether-TPU/MWCNT/clay) are shown in the right half of Figure 2.

In ether-TPU/MWCNT/clay, the improvement in electrical conductivity by coaddition of clay was also observed to vary depending on the amount of clay added, but the degree of improvement was much less than in the ester-TPU nanocomposites. When 3 wt % of C25A or 1.5 wt % of C30B was coadded along with 3 wt % MWCNTs, a decrease in resistivity of around one order of magnitude was observed. At other clay loadings, the resistivity decreased slightly or even rose above that of ether-TPU/MWCNT without any clay.

The decrease in resistivity or increase in electrical conductivity by the coaddition of clay along with MWCNTs can potentially be explained from two points of view. One is a change in the dispersion state of the MWCNTs by the addition of clays. The other may be a role of the clay itself. To check if the clay itself contributes to the improvement in conductivity, ester-TPU/C30B and ether-TPU/C30B nanocomposites were prepared without the addition of MWCNTs. The electrical conductivities of the ester- and ether-TPU nanocomposites as a function of C30B clay loading are shown in Figure 3. This figure demonstrates that the electrical resistivities of ester-TPU/C30B and ether-TPU/C30B nanocomposites remain almost the same, regardless of the addition of clay C30B. This indicates that the clay itself does not provide any increase in electrical conductivity. The electrical resistivity results in Figures 1 and 2 also
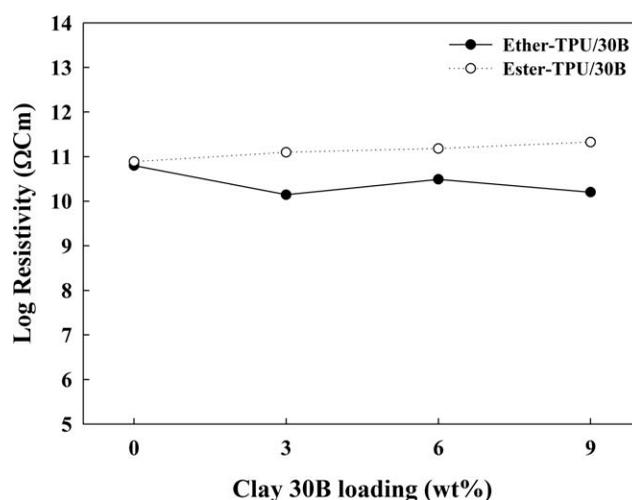

Figure 2. Electrical conductivity of ether-TPU nanocomposites.

Figure 3. Electrical conductivity of ester- and ether-TPU nanocomposites containing C30B.

indicate that the clay itself does not affect the conductivity; if the clay acts as a conductivity contributor, then the conductivity of the nanocomposites should always increase with an increase in the amount of clay. However, a minimum resistivity is reached at specific clay content in the results presented in Figures 1 and 2. The remaining possible explanations for the effect of clay addition are changes in the morphology or the dispersion of the MWCNTs in the nanocomposites.

As Liu and Grunlan[35] reported, the electrical conductivity of epoxy nanocomposites containing single-walled carbon nanotubes (SWCNTs) can be affected by the coaddition of nanoclay. The interaction of SWCNTs with clay resulted in the formation of a SWCNT network, which was explained to be one of the main reasons for the improvement in electrical conductivity. In their study, SWCNTs were observed to migrate around the clay in an optical microscope under polarized light. A slight decrease in electrical conductivity at high clay concentrations was also observed, which is similar to our results.

Konishi and Cakmak reported that the electrical conductivity of nylon6/carbon black composites was improved in the presence of clay and there was an optimum level of clay content for maximum enhancement. Clay was explained to act as a dispersion-control agent to induce self-assembly of a carbon black network while simultaneously partially blocking the electron hopping pathway.

In previous study on polyethylene oxide with lithium perchlorate, electrical conductivity was reported to increase by the addition of clay.[36] Dissociation of lithium salts is increased due to the interaction between negative charges on silicate layers and lithium cation of lithium salt resulting in the increase of electrical conductivity.

Interaction of CNT with clays can play some role in the change of CNT distribution in our study. Other factors may be important as well since the intensity of interaction between clays and CNTs may not be strong. Change in nanocomposite viscosity by adding clay may contribute also to change in CNT distribution such as network structure formation.

Above factors may be used to interpret the results from ester-TPU/MWCNT/clay and ether-TPU/MWCNT/clay in this study. Clays C25A and C30B are considered to induce a MWCNT morphology change favoring electrical conduction. Because the clay itself cannot contribute to the electrical conductivity improvement and instead interferes with the electron path, coaddition of a high concentration of clay beyond some optimum level along with MWCNT may again lower the electrical conductivity. This is consistent with our results.

Because a clay-induced morphology change is an important factor in explaining the above results, TEM images were taken and are presented in the following section.

XRD and TEM Results

XRD results of ester-TPU/MWCNT and ether-TPU/MWCNT containing C30B or C25A are shown in Figure 4(a, b), respectively. These XRD results exhibited that gallery distances between silicate layers of C30 and C25A are increased indicating good dispersion of clay similar to intercalation.
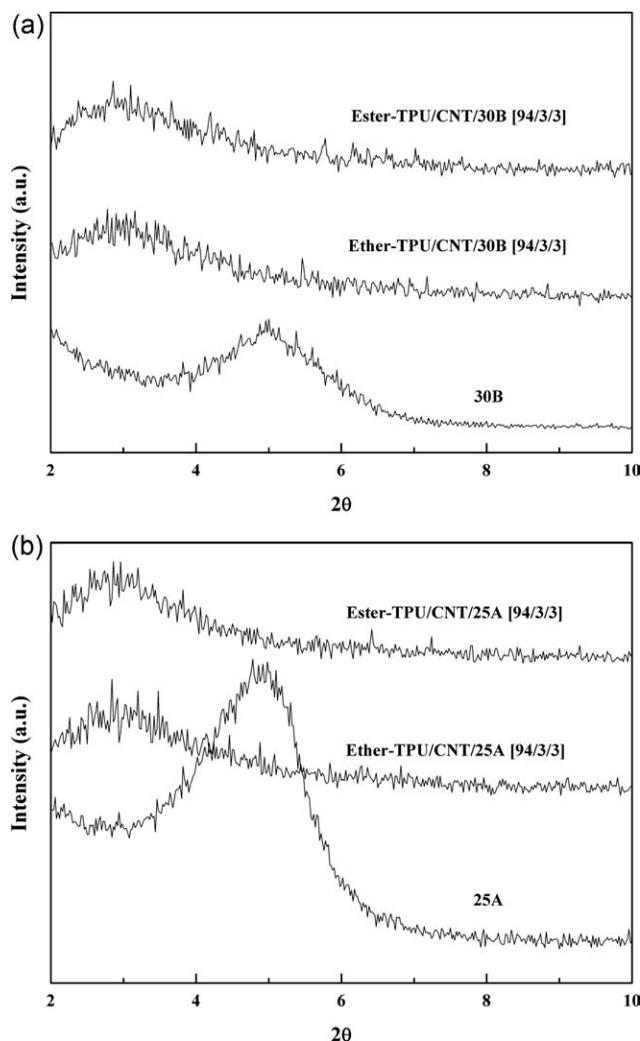

Figure 4. XRD patterns of TPU nanocomposites containing 3 wt % MWCNT and 3 wt %; (a) C30B and (b) C25A.

The TEM images of the ester-TPU/MWCNT containing 3 wt % MWCNTs are shown in Figure 5(a), and images of the ester-TPU/MWCNT/clays containing 3 wt % MWCNTs with 3 wt % of C30B or C25A coadded are shown in Figure 5(b, c), respectively. Both the MWCNTs and clay C30B show fairly good dispersion in Figure 5(b). The MWCNTs in Figure 5(b) appear to show better dispersion than those in the ester-TPU/MWCNT in Figure 5(a). This indicates that coaddition of C30B improves the dispersion of MWCNTs, which agrees with the electrical conductivity results that exhibit conductivity improvement by the coaddition of C30B.

The TEM image of ester-TPU/MWCNT/C25A in Figure 5(c) shows that the MWCNTs and clay form some kind of network structure. Neither the MWCNTs nor clay C25A is commonly seen in the bright open area. The MWCNTs appear to a have good affinity for C25A. This kind of conductive network formation due to C25A may explain the good electrical conductivity results from ester-TPU/MWCNT/C25A.
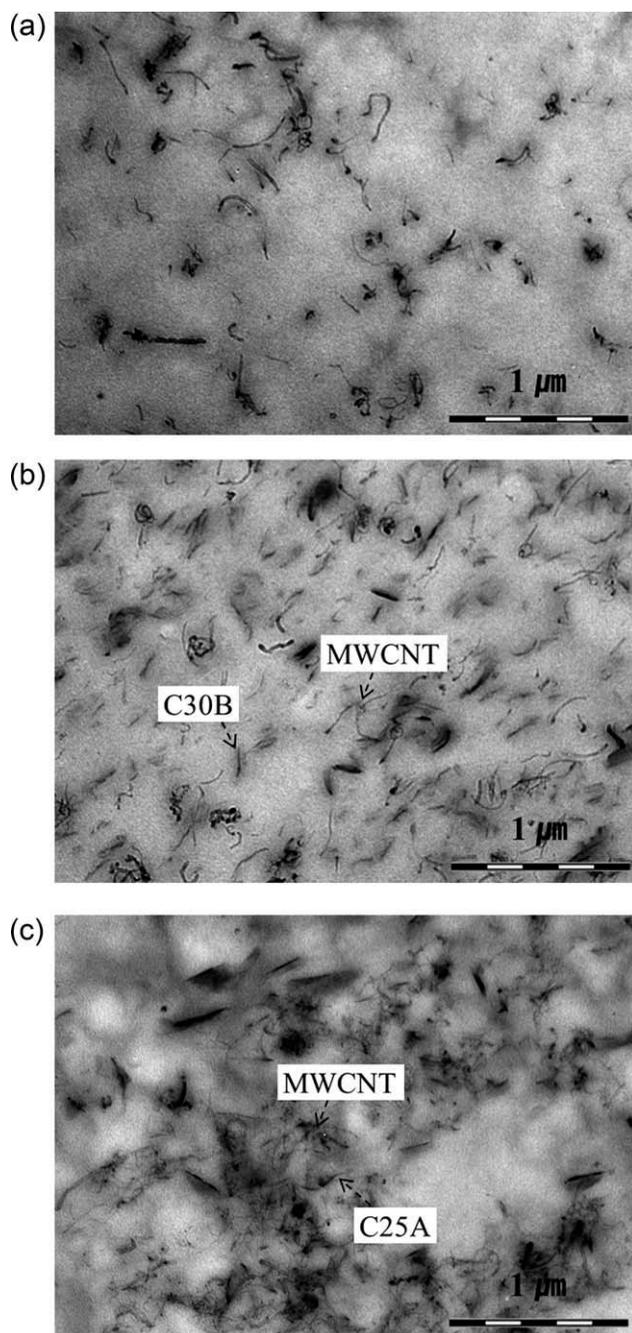
Figure 5. TEM images of ester-TPU nanocomposites containing 3 wt % MWCNT and 3 wt %; (a) none (b) C30B and (c) C25A.

The TEM image of the ether-TPU/MWCNT containing 3 wt % MWCNT is shown in Figure 6(a). TEM images of the ether-TPU/MWCNT/clay cocontaining 3 wt % of C30B or C25A and 3 wt % MWCNTs are shown in Figure 6(b, c), respectively. MWCNT dispersion in Figure 6(b) is better than that in Figure 6(a), which is consistent with the electrical conductivity results in Figure 2 that show that 3 wt % C30B improves the electrical conductivity. Clay C25A in Figure 6(c) appears to form an aggregated structure with MWCNT, which is somewhat similar to that seen for ester-TPU/MWCNT/C25A in Figure 5(c). This

may again explain the good electrical conductivity result for the ether-TPU/MWCNT/clay cocontaining 3 wt % C25A.

Dielectric Analysis

It was reported in the literature that electrical conductivity could be directly related to the dielectric constant such that both the dielectric constant and electrical conductivity increase concurrently with increasing MWCNT content in polymer/MWCNT nanocomposites.[37] For this reason, dielectric constants
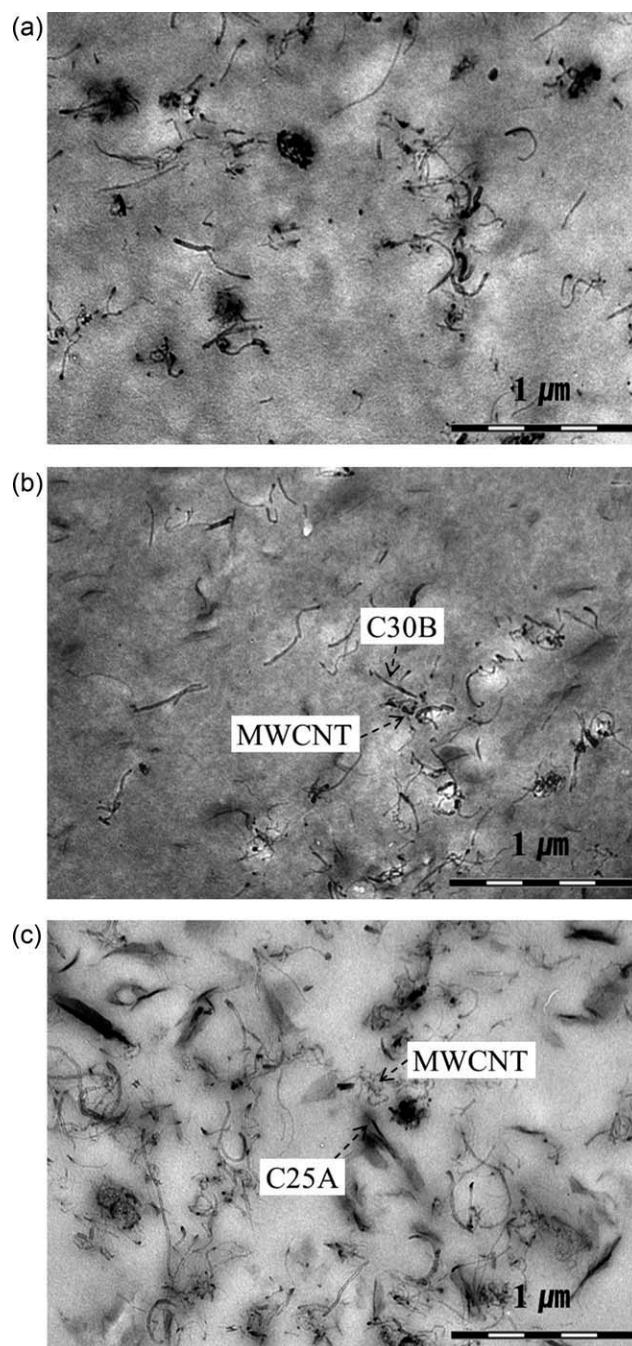

Figure 6. TEM images of ether-TPU nanocomposites containing 3 wt % MWCNT and 3 wt %; (a) none (b) C30B and (c) C25A.
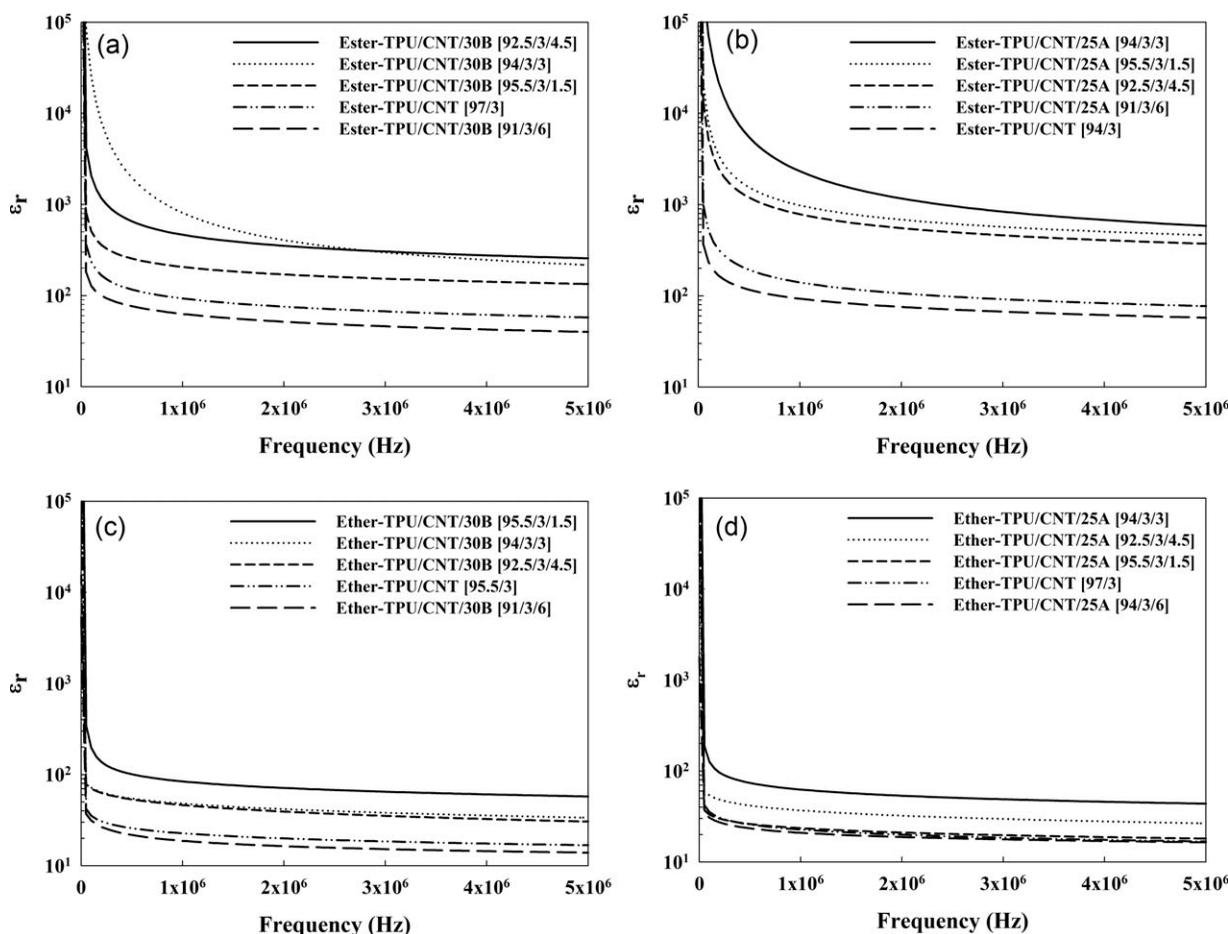
Figure 7. Dielectric constants as a function of frequency for (a) ester-TPU/MWCNT/C30B, (b) ester-TPU/MWCNT/C25A, (c) ether-TPU/MWCNT/C30B and (d) ether-TPU/MWCNT/C25A.

were measured for the ester- and ether-TPU nanocomposites investigated in the present study.

Figure 7 shows the variation of the relative dielectric coefficients (ε_r) with frequency changes at room temperature for ester-TPU nanocomposites containing 3 wt % MWCNTs as a function of the concentration of clays (a) C30B and (b) C25A. Corresponding data for ether-TPU nanocomposites are shown in Figure 7(c, d), respectively. The dielectric constant value was highest in ester-TPU/MWCNT with 3 wt % C25A, followed by 1.5 and 4.5 wt %. This result is consistent with the electrical resistivity results shown in Figure 1, since a high dielectric constant is known to produce high electrical conductivity.

Figure 7(a–c) also show similar trends: with few exceptions, the nanocomposites with higher electrical conductivities in Figures 1 and 2 exhibit higher dielectric constants.

Like the changes in electrical conductivity, these dielectric constant results are thought to be related to morphology changes induced by the addition of clays.

Rheological Properties Measurements
An increase in nanocomposite viscosity can increase the shear force acting on MWCNTs resulting in a better dispersion of MWCNTs. Therefore, the complex viscosities of the nanocom-

posites were measured, since the improvement in MWCNT dispersion by the coaddition of clay may be caused by an increase in nanocomposite viscosity. The plots of complex viscosity $\eta^\star$ vs. frequency ω for ester-TPU/MWCNT/clay and ether-TPU/MWCNT/clay are shown in Figure 8(a, b), respectively.

As can be seen from these figures, the addition of MWCNTs to ester- and ether-TPUs increased the viscosity of the nanocomposites. An increase in nanocomposite viscosity by the addition of MWCNTs was reported in previous studies.[5,11–13] In the present study, coaddition of clays produced an even further increase in the nanocomposite viscosity, as shown in Figure 8(a, b), which indicates that coaddition of clay may also help improve the dispersion of MWCNTs due to this increased viscosity.

Therefore, the morphologies of the nanocomposites and the resulting electrical conductivity are thought to be the combined result of several factors, including the nanocomposite viscosity and the relative affinity of the MWCNTs or clays for the TPUs.

Tensile Properties
Stress–strain diagrams of ester- and ether-TPU/MWCNT containing several concentrations of MWCNTs as well as ester- and ether-TPU/MWCNT/clay cocontaining 3 or 6 wt % of C30B or C25A are shown in Figure 9(a, b).

The tensile modulus of TPU/MWCNT increased slightly with additional MWCNTs. Coaddition of clays caused a remarkable increase in the tensile modulus, as seen in Figure 9(a, b). The tensile modulus increased most significantly for both ester- and ether-TPUs when C30B was added. This indicates that a very good interaction exists between C30B and ester- or ether-TPUs, which is consistent with the good dispersion of C30B observed in TEM images.

CONCLUSIONS

The effects of nanoclays on the electrical and morphological properties of nanocomposites were investigated by coadding nanoclay C30B or C25A to ester- and ether-TPU/MWCNT nanocomposites.

Coaddition of clay C25A or C30B along with MWCNTs to ester-TPU nanocomposites increased the electrical conductivity by more than three orders of magnitude. An improvement in electrical conductivity by the coaddition of clay was also observed in ether-TPU nanocomposites, although to a lesser extent.

TEM results showed that clay addition changed the morphology in TPU/MWCNT/clay nanocomposites. Clay was observed to
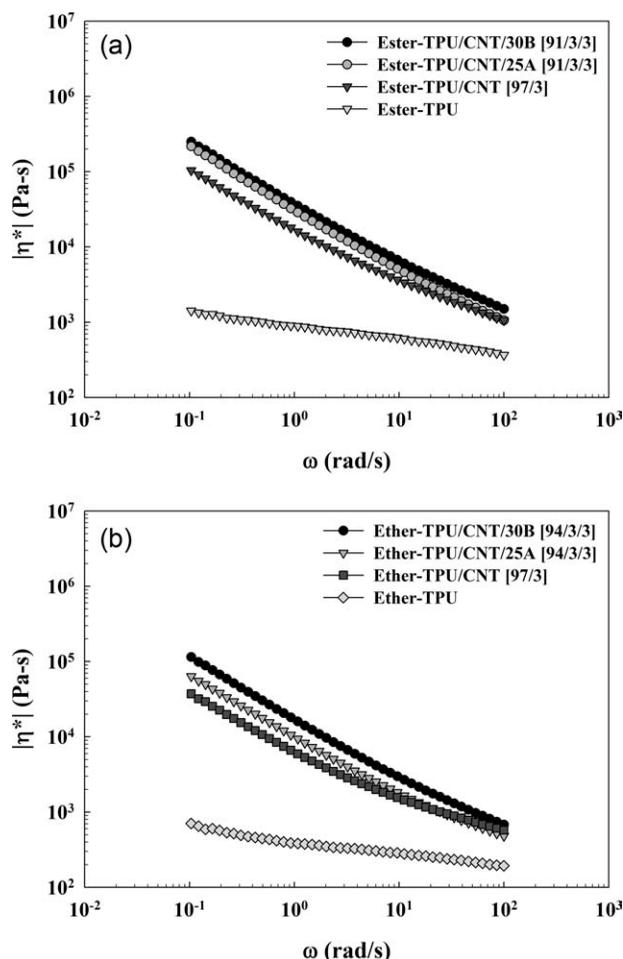

Figure 8. Complex viscosity vs. frequency for (a) ester- and (b) ether-TPU nanocomposites containing MWCNT and clay.
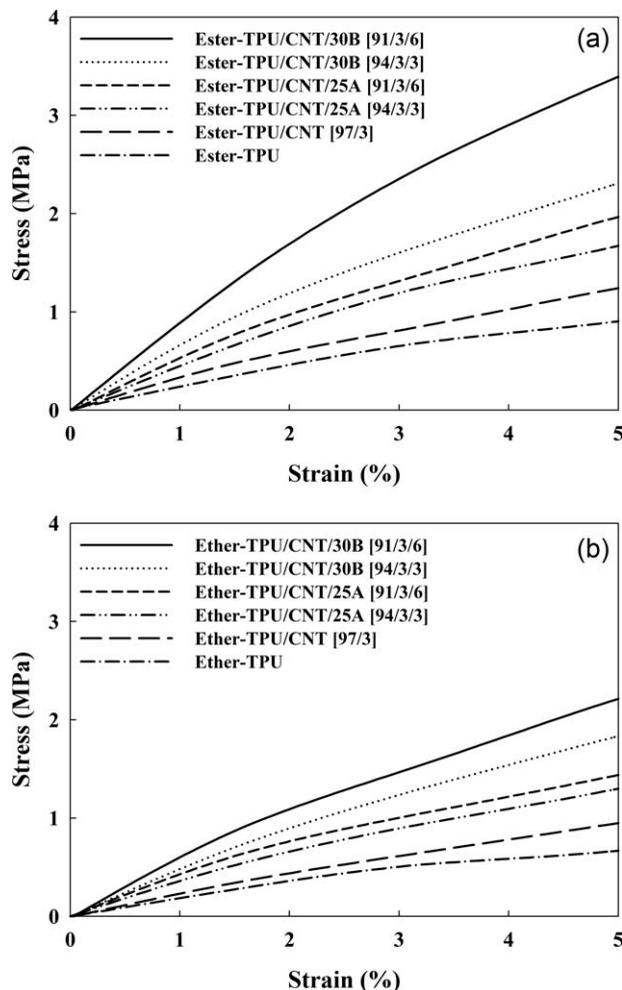

Figure 9. Stress–strain curves of (a) ester- and (b) ether-TPU nanocomposites containing MWCNT and clay.

induce a better MWCNT dispersion and in some case, the MWCNTs and clay formed a network structure. The factors that lead to creation of these morphologies may be the interaction between CNT and clays as well as the viscosity increase in the nanocomposite by coaddition of clay, since the viscosity of the nanocomposites notably increases with increasing MWCNT and clay contents.

The results of dielectric constant measurements were also consistent with the electrical resistivity results, where most of the nanocomposites with higher electrical conductivities also exhibited higher dielectric constants.

Tensile properties measurements exhibited the reinforcing effects of the MWCNTs and clays.

ACKNOWLEDGMENTS

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