Electrical Conductivity and Major Mechanical and Thermal Properties of Carbon Nanotube-Filled Polyurethane Foams

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ABSTRACT: The carbon nanotubes (CNTs)/rigid polyurethane (PU) foam composites with a low percolation threshold of $\sim$ 1.2 wt % were prepared by constructing effective conductive paths with homogeneous dispersion of the CNTs in both the cell walls and struts of the PU foam. The conductive foam presented excellent electrical stability under various temperature fields, highlighting the potential applications for a long-term use over a wide temperature range from 20 to 180°C. Compression measurements and dynamical mechanical analysis indicated 31% improvement in compression properties and 50% increase in storage modulus at room temperature in the presence of CNTs (2.0 wt %). Additionally, the incorporation of only 0.5 wt % CNTs induced remarkable thermal stabilization of the matrix, with the degradation temperature increasing from 450 to 499°C at the 50% weight loss. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3014–3019, 2011

Key words: carbon nanotube; polyurethane foam; electrical properties

INTRODUCTION

Up to now, general methods for preparing electrically conducting polymer materials are based on blending different polymers with various conductive fillers such as carbon black, exfoliated graphite, or carbon nanotubes, which contact with adjacent fillers and construct conductive paths at a certain concentration in the composite, and generate the conductive properties.[1–5] Nevertheless, the porous structure of polymer foams limits the distribution of conductive fillers in the cell walls and cell struts to form effective conductive networks. This is also the very reason why few successful examples have been reported about conductive polymer foam composites based on conventional conductive fillers (carbon black, graphite, etc.).[6–10]

Carbon nanotubes (CNTs), which are widely used to mix with various polymers to manufacture conductive composites,[11–14] can be well dispersed in the polymeric foam composites, as described in our previous work.[15,16] The nanometer-scale diameter CNTs can avoid the limitation of large-size conventional conductivity fillers, and the extremely large aspect ratio allows a low loading of fillers to provide the desired electrical conductivity without sacrificing other inherent properties of the polymer. Therefore, CNTs are regarded as ideal conductive fillers for preparing the conductive polymer foam composites.[17–22]

Yang et al. developed the CNT-filled polystyrene (PS) conductive foams for a lightweight electromagnetic interference (EMI)-shielding materials, reaching the EMI shielding effectiveness around 20 dB with 7 wt % loading of CNT.[20] Rizvi et al. fabricated the porous composites of low density polyethylene and CNTs and achieved substantial improvements in the mechanical and electrical properties with the addition of 5 wt % CNTs.[21] Verdejo et al. prepared CNTs/polyurethane foams, and found that the incorporation of CNTs increased the wettability of the nanocomposite surfaces.[22]

In our previous work, the lightest conductive polymer composite (a density of 0.05 g cm^{-3}) with a weight-reduction rate of 96.2% based on carbon nanotubes and rigid PU foam was prepared and this novel conductive material exhibits an interesting density-dependent conductor-insulator transition.[15] Moreover, the unique negative temperature coefficient (NTC) effect of the solid-state lightweight conductive CNTs/soft PU composite was observed, which usually appeared in the melted conductive polymer composites due to formation of a more perfect conductive network through re-organization of conductive fillers in low viscosity fluid.[16]

Following our previous work, the aim of the current work is to prepare a low conductive percolation

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PU foam composite with excellent temperature–electrical stability, mechanical properties, and thermal stabilization to meet the special requirement in electronic components and precision instruments.

EXPERIMENTAL

Materials

CNTs with a purity of >95 wt % were purchased from Nano Harbor (China), with a diameter of 20–40 nm and a length about 10–30 μm, were grown via the chemical vapor deposition (CVD) method. The polyether polyol, Model GR-4110, originated from polypropylene oxide and sucrose/glycerin base, was obtained from HongQiao Petro (Shanghai, China) and the isocyanate, N200, were purchased from ChangFeng Petro (Chongqing, China). Silicone glycol copolymer, Niax L-580, was used as a surfactant and the catalyst used contain triethylene diamine and stannous octoate. The blowing agent used here was distilled water.

Sample preparation

The polyether polyol was dehydrated under vacuum at 100°C for 10 h and the CNTs were dispersed in an ethanol solution by an ultrasonication probe for 30 min. The mixture was subsequently sonicated at 30°C for 4 h to reach uniform dispersion of CNTs in the polyol. Then the ethanol was evaporated until a constant weight was achieved. Subsequently, the surfactant, catalyst and distilled water were added to the mixture, stirred together until a uniform mixture was obtained. Finally, the isocyanate was added and stirred for an additional 15 s before foaming occurred in a mold with a lid. The foams were then transferred. The foam then expanded to fill the entity and postcured in an oven at 100°C for 4 h. In this work, the density of the foams was fixed at 0.2 g cm^{-3} by constant weight of all PU foam composites and the same closed mold with a constant volume. The CNTs content in the foam was controlled from 0 to 2.0 wt %.

Characterization

The morphology of the samples was observed under a JSM-9600 (JEOL, Japan) scanning electron microscopy (SEM) with an accelerating voltage of 20 kV.

In the electrical resistivity measurement, silver paste was coated on the surface of the sample to ensure good contact of the samples with the electrodes. A two-electrode method was used to measure the volume resistivity of the samples with the dimensions of 40 × 10 × 10 mm^3. An *in situ* temperature-resistivity testing system has been introduced

to the resistivity testing upon thermal field, including a silicon oil bath providing thermal field, a high resistivity meter model TH2683, and a computer as a control unit and data acquisition instrument. During temperature (time)/resistivity testing, the sample was immersed in silicone oil of a temperature-controlled apparatus to avoid oxidation and the heating rate were fixed at 2°C min^{-1}. The time and temperature dependence of resistivity was real-time monitored.

The compressive strength and the compressive modulus were measured with a universal electronic tensile machine (Shimadzu, Japan) with compression rate of 2 mm min^{-1} according to ASTM D 1621-94. The specimens for measurement were machined into dimension of 50 × 50 Φ mm^3.

The dynamical mechanical analysis (DMA) were carried out using a Q800 DMA instrument (TA, America) with a heating rate of 3°C min^{-1} from 50 to 250°C. The dimensions of the samples were 35 × 10 × 4 mm^3.

Thermogravimetric analysis (TGA) were used to determine the amount of polymer present in the samples. About 4 mg samples were heated under nitrogen from 25 to 700°C with a heating rate of 10°C min^{-1} on an SEIKO EXSTAR6000 thermogravimetric analyzer.

RESULTS AND DISCUSSION

Dispersion of CNTs in the conductive PU foam composite

The dispersion of CNTs in polymer matrices is a well-known challenge due to the entangled agglomerates resulted from the intrinsically strong van der Waals interactions of nanotubes adjoining with each other.[23,24] In this work, we utilized ethanol as a diluting agent to reduce the viscosity of polyether polyol to optimize the ultrasonic-assisted CNTs dispersion and the uniform dispersion of CNTs in polyether polyol was preserved *in situ* polymerization. Figure 1(a,b) shows the typical cellular structure of both pristine PU foam and CNTs/PU foam composite with 2.0 wt % content of CNTs, respectively. Unlike the instance of Harikrishnan et al.'s work,[25] in the presence of 2.0 wt % CNTs, the cell size shows slight increase, which indicates that CNTs can not serve well as a heterogeneous nucleating agent during the foaming process. However, the composite composed of numerous spherical closed-cells is shown in Figure 1(b), which indicates that the addition of CNTs has little effect on formation of cell in PU foam. The dispersion of CNTs in the PU foam composite is shown in Figure 1(c), in which we can see that many individual CNTs appear in the cell struts, and nearly no aggregates are
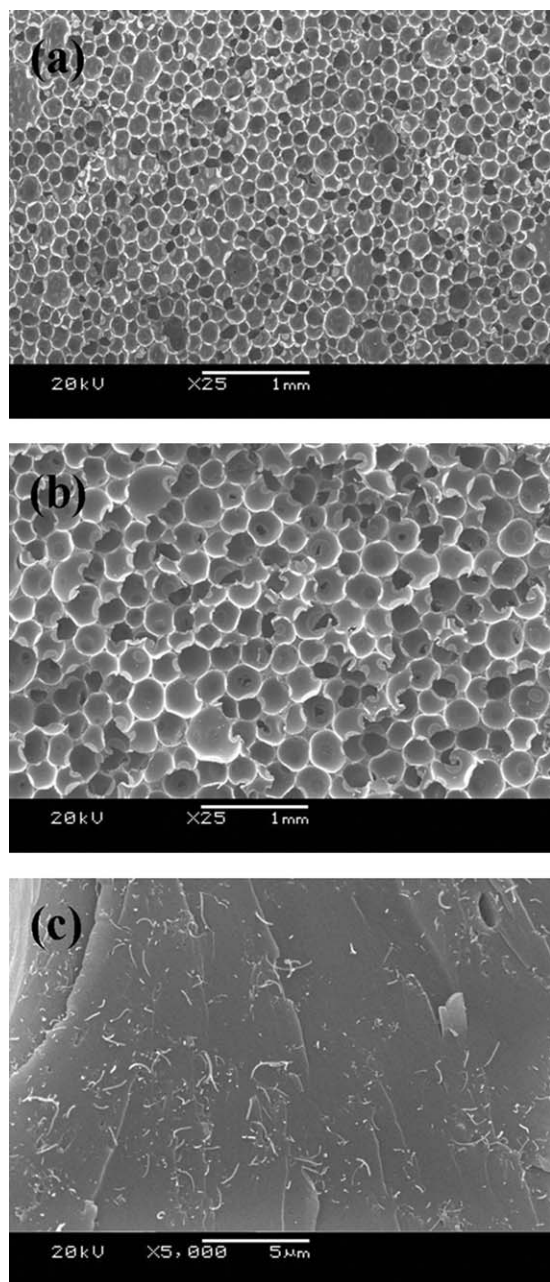
Figure 1 SEM micrographs of (a) Pristine PU foam, (b) CNTs/PU foam composite with 2.0 wt % content of CNTs, (c) high magnification image of CNTs/PU foam composite with 2.0 wt % content of CNTs.

observed, revealing uniform CNTs dispersion in the matrix obtained. The well closed-cells structure and uniform dispersion of CNTs are particularly crucial for the enhancement of the PU foams in electrical and mechanical properties,[17] which will be discussed in the following sections.

Percolation of the conductive PU foam composite

A density percolation of CNTs-PU foam was proposed in our previous research,[15] which showed that

the electrical conductivity increased with the foam density between 0.03 and 0.51 g cm^{-3}, and reached a relatively stable state with the foam density of 0.2 g cm^{-3}. This result indicated that, with such a foam density, the volume of cell walls and struts was large enough for the homogeneous distribution of CNTs, resulting in a relatively superior conductive network. Then, in this work, the foam density was fixed at 0.2 g cm^{-3}; the CNT-PU foam composites with different CNT contents were prepared. As shown in Figure 2, as the CNT loading changes within 1.0 and 2.0 wt %, the foam composites exhibited a typical percolation behavior. The conductivity increases by six orders of magnitude from 1.72×10^{-12} S m^{-1} to 2.03×10^{-6} S m^{-1} when the CNT content rises from 1.0 to 1.2 wt %, while only increases two orders of magnitude when another 0.8 wt % CNTs are added, i.e., a conductive network has been primarily fabricated with incorporation of 1.2 wt % of CNTs, or the CNT concentration percolation value is about 1.2 wt %. It is a very low value for conductive foam composites compared with that reported in the available literatures.[20,21]

Resistivity-temperature behaviors of the conductive PU foam composite

The stability of electrical properties is critical for the applications of conductive foam composites and needs in industrial application as EMI-shielding or electrostatic discharge (ESD) protection materials, especially when they are used in a widely varied temperature range.[26–28] Figure 3 shows the resistivity-temperature behaviors for the CNTs/PU foam
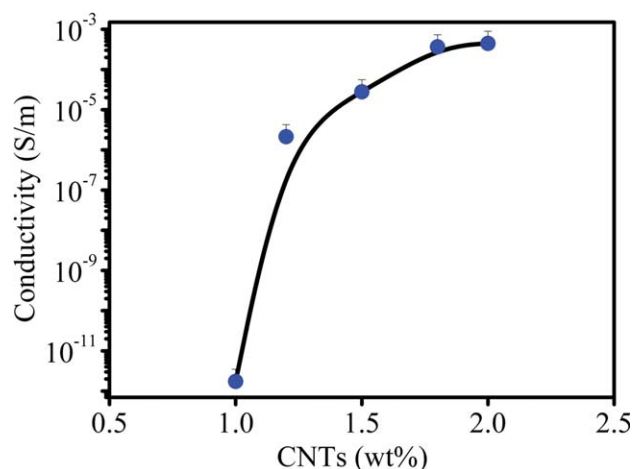

Figure 2 The volume conductivity of the CNTs/PU foam composite as a function of CNTs content with fixed density of 0.2 g cm^{-3}, thereby showing the CNTs content-dependent conductivity and CNTs content-dependent conductor–insulator transition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
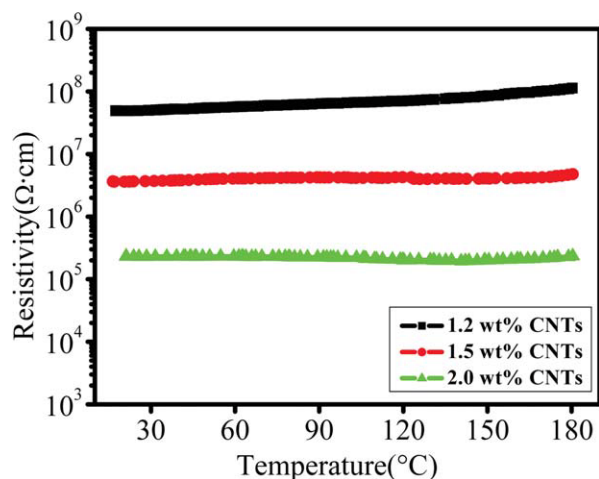
Figure 3 Resistivity–temperature relationship of various CNTs content-filled PU foam electrically conductive composite in the heating process with the heating rate of 2°C min⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composites with different CNT concentration. During heating, the positive temperature coefficient (PTC) and negative temperature coefficient (NTC) are generally not obvious. For conventional conductive polymer composites (CPC), a lot of factors were considered to be related to the PTC and NTC, such as types and concentration of conductive fillers, morphology of the CPC, heating rate, thermal treatment time, and crosslinking of polymer matrix, etc.[2,16,29–31]

Here, in our system, CNTs/PU foam composites, possessing high degree crosslinking, were thermoplastics and amorphous. So we thought that the volume expansion of the composites during heating is drastically restricted and the weak PTC effect of lower CNT loading composite is only due to the slight thermal volume expansion of the conductive foam composite, which was similar to the work by Jana and coworkers,[32] which showed that the shape memory polyurethane composites of CNF and ox-CNF did not show PTC effects due to low levels of soft segment crystallinity. While the higher CNTs loading foam presents almost no change in volume resistivity due to the perfect conductive pathway. The appearance of NTC behavior usually after PTC effect should be mainly caused by the reaggregation of conductive particles above the polymer melting point. Here, the mobility of CNTs has been really suppressed by the high degree crosslinking density of the PU foam matrix, so that few new conductive paths formed to decrease the volume resistivity of CNTs/PU foam composites, i.e., NTC behavior disappeared.

Compared with other thermal-sensitive conductive composites, the inherent crosslinking in the thermosetting CNTs/PU foam composite could stabilize the distribution of conductive filler and the gel network structure of the conductive network in the matrix. At a high temperature, the superior conductive network could still be maintained because of the poor mobility of the macromolecular chains, which were crosslinked in the synthesis process of PU. Therefore, PTC and NTC intensities were reduced, which corresponded to the decreased sensitivity of the foam composite to thermal field, leading to the potential application over a wide temperature range.

Compression properties of the conductive PU foam composite

A CPC material not only needs good electrical properties, but also a certain mechanical strength, especially when they are used as structural materials. To verify the mechanical properties of the PU foam composites, the compressive strength and the compressive modulus of the composites were measured. As revealed in Table I, the compressive performance of the CNTs/PU foam composites increases gradually with the increase of CNTs content. For example, the compressive strength increases by 31% from 3.7 MPa for polyurethane foam to 4.8 wt % CNTs/PU foam composite, and the compressive modulus increases by 31% from 85.9 to 112.7 MPa.

Compressive strength mainly reflects the damage of the external force required, while the compressive modulus reflects the ability to resist deformation. To nanofiller-reinforced polymer composites, ultimate mechanical improvement can only be realized when the nanofiller is dispersed uniformly, and the external load is efficiently transferred via the strong interface interaction between filler and the matrix.[33–37] For the CNT/PU foam composites, homogeneous dispersion of CNTs in the PU matrix is achieved, as shown in Figure 1. Furthermore, in the compression process, the electrostatic interaction and van der Waals forces, along with the radial stress caused by the thermal expansion differences between CNTs and PU probably induce significant load transfer across the nanotube–matrix interface, so that the formation of the cracks under the action of compression deformation is suppressed by linking of CNTs. The enhancement of the compressive performance in our system can thus be understood. Therefore, when the CNTs loading increased, more energy was required to destruct the composites and the compressive strength and modulus were improved.

Dynamical mechanical analysis (DMA) of the conductive PU foam composite

When PU foams are used as packaging materials, their damping performance, usually known as dynamic properties, is of great importance, which

TABLE I
Compressive Properties of Various CNT Content-Filled PU Foam Composites

Foam type	Compressive strength (MPa)	Compressive modulus (MPa)
PU	3.7	85.9
0.5 pphp CNTs	3.8	102.8
1.0 pphp CNTs	4.1	105
2.0 pphp CNTs	4.8	112.7

can be characterized by dynamic mechanical analysis (DMA). Figure 4 shows the temperature dependence of the storage modulus (E') of CNTs/PU composites with different CNTs loading. Similar dynamic mechanical properties spectra were recorded for the different samples. The storage modulus of all samples decreases slowly and progressively with increasing temperature, showing a very strong decay in the temperature range between 140 and 160°C, which correlates with the glass transition of the polymer.

Below the glass transition temperature (T_g), the incorporation of increasing contents of CNTs induces a progressive rise in the storage modulus of the matrix with $\sim$ 50% increase for CNTs (2.0 wt %)-filled PU at room temperature. The observed enhancement in the mechanical response was attributed to the effective load transfer from the PU matrix to the high-strength, homogeneously dispersed CNTs, and the strong interface friction.[38–40] However, above the T_g, there are no obvious differences in modulus for these three composites, revealing that the load transfer declines for the debilitate interface interaction between PU and CNTs and the dynamical mechanical properties mainly derive from the intrinsic properties of the PU matrix.
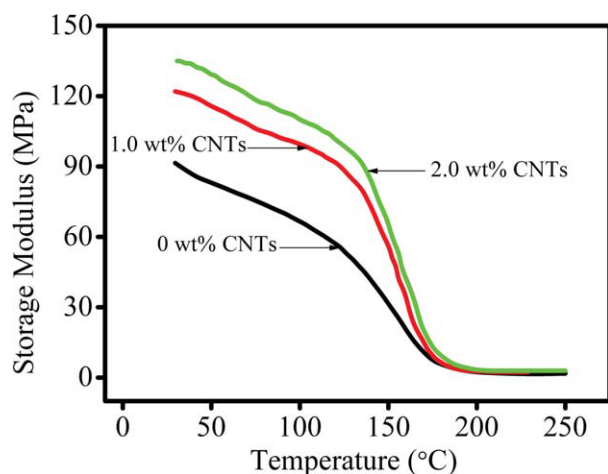

Figure 4 Dependence of the storage modulus of various CNTs content-filled PU foam electrically conductive composites on temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
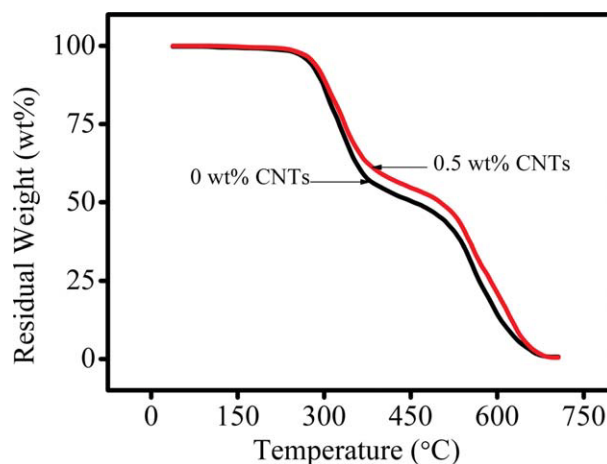
Figure 5 TGA curves of CNTs/PU foam composites filled with 0 wt % CNTs and 0.5 wt % CNTs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DMA study suggested that CNTs-filled PU foam enjoyed fine damping properties coupled with good stiffness and deformation resistance due to the interface interaction between CNTs and PU, displaying the potential application of this material as damping structural materials.

Thermal properties of the conductive PU foam composite

Figure 5 shows the thermogravimetric analysis (TGA) results of the CNTs/PU foam composites with different CNTs loading under a flow of nitrogen and the quantitative data are summarized in Table II.

Both pure PU foam and its nanocomposites decompose in a two-step process, and the TGA curve of the 0.5 wt % CNTs-filled composite shifted toward a higher temperature compared to that of pure PU foam, as shown in Figure 5. In Table II, it can be seen that the degradation temperatures for 1, 5, and 50% weight loss of conductive PU foam with 0.5 wt % CNTs loading all increase, especially for 50% weight loss, from 450 to 499°C, compared to the pure PU foam. This indicated that the incorporation of CNTs at such a low concentration somewhat induced a remarkable thermal stabilization of the matrix. The results also revealed that the uniform and fine dispersion of the CNTs improved the interfacial adhesion between the CNTs and the matrix,

TABLE II
Degradation Properties of CNTs/PU Foam Composites

Foam type	1%	5%	50%
PU	220	275	450
PU: 0.5 wt % CNTs	237	281	499

which restricted the thermal motion of the PU chains as well as the diffusion of the volatile decomposition products, improving the thermal stability of the CNTs/PU composites.[41]

CONCLUSIONS

We have fabricated the low conductive percolation PU foam composite with CNTs simultaneously dispersed in the cell walls and struts of the PU foam by utilizing the ethanol as diluting agent, which reduces the viscosity of polyether polyol to optimize the ultrasonic-assisted CNTs dispersion. The electrical stability of the PU composite at high-temperature reveals the application over a wide temperature range with long-term using. Homogeneous distribution of CNTs and significant load transfer between CNTs and PU matrix result in the 31% enhancement in compression properties as well as and 50% increase in storage modulus at room temperature. TGA measurements display that the introduction of low-content CNTs induces a remarkable thermal stabilization of the matrix.

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