Investigation of Free Volume and Damping Property for Polycarbonate/Multiwalled Carbon Nanotube Composites by Positron Annihilation Technology

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ABSTRACT: Microstructure and damping characteristics were investigated for polycarbonate/multiwalled carbon nanotube (PC/MWCNT) composites. Dynamic mechanical analysis results show that the damping factor and the value of the energy loss fraction *w* are significantly increased. Especially, nearly 300% improvement in damping factor is observed in the temperature range from 140 to 150°C. Positron annihilation lifetime measurements indicate that both the o-Ps lifetime and the free volume increase with increasing MWCNT content, leading to decrease in the glass transition temperature and increase in the damping properties. The relationships among the damping, mechanical property, and the free volume have been first observed, that is, the increase of the free volume brings about a reduction in tensile strength and an increase in damping. The interfacial friction slipping of MWCNTs and the free volume play an important role in determining the damping property of PC/MWCNT composites. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: glass transition; microstructure; mechanical properties

INTRODUCTION

Damping materials have been investigated extensively due to their wide applications in various fields, including vehicles, industrial machines, home appliances, precise instruments, military equipments, aero space industries, electronic mechanical equipments, and so on.[1–8] How to reduce the pollution of vibration and noise has been an urgent problem. Although the traditional damping materials (metals and polymers) have been widely applied, they suffer from several limitations (high cost and high weight for metals, poor reliability, low thermal conductivity, and poor performance at elevated temperatures for polymers).[9,10] In order to overcome these drawbacks, many methods have been adopted to improve the damping properties of the damping materials, including graft and block copolymerization, interpenetration, and so on. With the development of nanoscience and technology, the effort of seeking new kinds of high-performance damping materials is rapidly growing.

Since carbon nanotubes (CNTs) were first reported by Iijima[11] in 1991, CNTs and CNT composites have inspired scientists for a range of potential applications. Recent researches indicated that CNT composites have been used not only as a reinforced material, but also as a new kind of promising structural damping material. As reinforced materials, it is integrant to have good adhesion characteristics between CNTs and matrix. On the contrary, it is required that there should be weak CNT-matrix adhesion to improve structural damping properties of matrix. So long as the interface between the CNTs and matrix is not carefully engineered, poor load transfer may result in CNT slipping at interface region and high damping property.[12] Rajoria and Jalili[13] reported the study on the potential of using CNT fillers to inject damping into composite structures, which indicated that the enhancement in damping ratio was more dominant than the enhancement in stiffness. Although significant progress has been made in developing the damping properties of CNT composites, relatively little attention has been given to the damping mechanism. The damping mechanism of CNT filled polymer composites have not been studied in any detail.[14] For example, now that the interfacial slipping is a key factor in determining the damping characteristic, the study on the interfacial defects should be a very important topic. However, we have not found the experimental reports about the interfacial defects up to now. On the other hand, it is well known that the free volume can

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significantly affect the motion of polymer chains and the damping property. The experimental study on the relationship between free volume and the damping property is very lacking except for the work of Zhu et al.[15] How do the interfacial property and the free volume affect damping properties of CNT composites is not very clear.

Positron annihilation technology (PAT) is a very useful tool to probe the atomic-scale free volumes and interfacial defects. The principal advantage of PAT over other techniques is that the formation and annihilation characteristics of positronium (bound state of e^+ and e^-) are localized in nano- or subnanoscale level holes. Therefore, PAT has been widely used to study the microstructure of polymers.

In this study, the polycarbonate/multiwalled carbon nanotube (PC/MWCNT) composites have been prepared. For the composites, the effects of MWCNTs on the free volume and the damping property, and the relationship between damping property and the microstructure have been first studied by PAT, dynamic mechanical analysis (DMA), scanning electron microscope (SEM), and transmission electron microscopy (TEM).

EXPERIMENTAL SECTION

Material and sample preparation

In this research, MWCNTs were purchased from Shenzhen Nanotech Port (Shenzhen, China) with a purity of above 95%, a diameter range from 10 to 30 nm, and a length range of 1 ~ 2 μm. Commercially available pure PC powders were purchased from Guangzhou Yangda Plastic (Guangzhou, China) with a specific gravity of 1.2.

To obtain PC/MWCNT composites, we used a solution mixing process. Firstly, the MWCNTs without any disposal were sonicated in a tetrahydrofuran (THF) solution, while the PC powders were dissolved in THF as well separately. Secondly, the two kinds of solutions were mixed and the mixture was sonicated. Thirdly, the mixture was poured dropwise into methyl alcohol. The composite precipitated immediately and the precipitation was filtrated fully and dried out under vacuum.

The composite powders were molded into dumbbell samples and cuboid-shaped samples by mini injection molding machine. The temperatures of charging barrel and mould are set 285 and 95°C. Composite samples with three weight contents of MWCNTs (0.5, 1.5, and 2.0 wt %) were obtained.

Experimental method

Morphology and dispersion of MWCNTs in PC matrix were investigated by SEM (S-4800, Hitachi, Japan) and TEM (H-800, Hitachi, Japan).

DMA measurements were carried out using a Perkin Elmer DMA7e in a three-point bend mode. Specimens were heated from 30 to 160°C with the heating rate of 5°C/min at a constant frequency of 10 Hz.

Positron annihilation lifetime spectroscopy (PALS) has been become a popular way to characterize microstructure of polymers without damnification.[15,16] PALS measurements were made at room temperature using a fast-fast coincident system with a time resolution of about 280 ps. A 20 μCi ^{22}Na positron source was sandwiched in between two pieces of identical samples. Each spectrum contained $\sim 10^6$ and 4×10^6 counts for finite-term lifetime analysis PATFIT program[17] and the maximum entropy lifetime method (MELT),[18–21] respectively. To reduce artificial effects, spectra were analyzed using the same parameters. The lifetime spectra of one million counts were resolved into three components using PATFIT. The first lifetime component (τ_1) and second lifetime component (τ_2) result from the self-annihilation of para-positronium (p-Ps) and free positron annihilation. The third lifetime component (τ_3) is attributed to the pick-off annihilation of orthopositronium (o-Ps) in free volume holes. The average radius of free volume holes can be evaluated according to eqs. (1)[22] and (2):

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi \sin\left(\frac{2\pi R}{R + \Delta R}\right)}\right]^{-1} \tag{1}$$

$$V = 4\pi R^3/3 \tag{2}$$

where R is the radius of free volume holes; $\Delta R = 1.656$ Å derived from fitting the observed o-Ps lifetimes in molecular solids with known hole sizes.[23]

Stress–strain curves were measured using Dumbbell MZ-5000D electronic universal testing machine at a constant stretching speed of 10 mm/min for PC/MWCNT samples.

RESULTS AND DISCUSSION

Dispersion of MWCNTs in composites

SEM images of PC/MWCNT composites containing 0.5 and 1.5 wt % MWCNTs are shown in Figure 1(a,b). It is clear that no agglomeration of MWCNTs was observed. It can be also observed that MWCNTs have been drawn, which indicates that the interfacial interaction is weak. TEM image of PC/MWCNT composites containing 2.0 wt % MWCNTs in Figure 1(c) shows the existence of the middle-empty nanotubes in the composites.

Damping property

The measurements of damping properties for PC and composites filled with MWCNTs have been

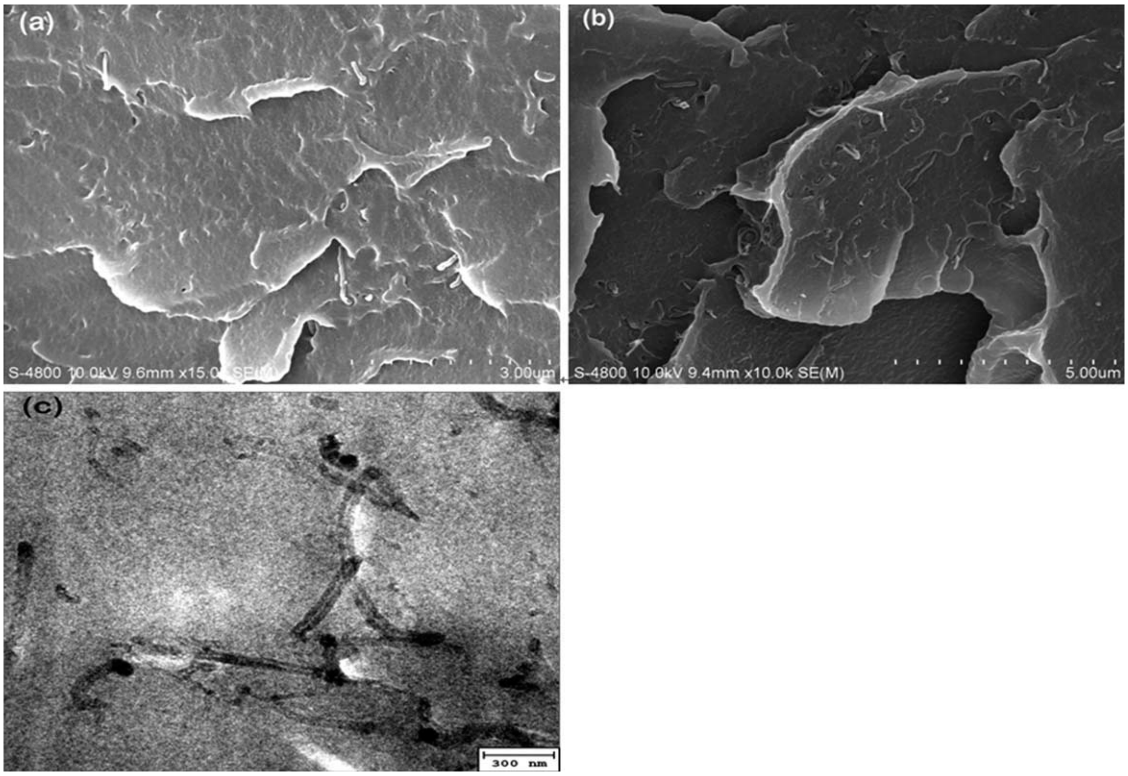

Figure 1 SEM image of composites with (a) 0.5 and (b) 1.5 wt % MWCNTs; TEM image of composites with (c) 2.0 wt % MWCNTs.

carried out by DMA. Storage modulus (E') representing the elasticity of samples, describes the response of the sample under periodic stress. Loss modulus (E'') represents the ability of the energy converted from mechanical energy to heat energy. tan δ (E''/E') is well known as the loss factor related to the damping property of the material.[24,25] Generally speaking, the storage modulus of a polymer will decrease rapidly if the loss modulus and tan δ go through a maximum. The glass transition temperature (T_g) is usually identified by half height of E' curves or the peak of either loss modulus or tan δ curves. Here we choose the peak of tan δ curves as T_g.

The variations of the storage modulus and tan δ versus temperature are shown in Figure 2(a,b), respectively. In Figure 2(a), the storage moduli of the PC/MWCNT composites decrease compared with pure PC in the low temperature region (glassy state). In the higher temperature region (rubbery or even fluid state), however, the storage modulus of the composites filled by MWCNTs is much higher than that of pure PC, which indicates that MWCNTs improve the elasticity of PC at relative higher temperatures.

As shown in Figure 2(b), it can be clearly seen that the damping properties of PC/MWCNT composites are higher than that of pure PC. Especially in the temperature range of 140–150°C, the tan δ of composites with 0.5 wt % MWCNTs is 300% superlatively higher than PC matrix. The energy loss fraction w of the composites can be calculated in terms of the peak value of tan δ using the following equation[26,27]:

$$w = \frac{\pi \tan \delta}{\pi \tan \delta + 1} \tag{3}$$

The values of tan δ peaks and w are shown in Table I. The energy loss fraction of the composites increases evidently compared with that of pure PC. This result can be explained as follows. First, the ability of chain motion increases near T_g, which results in the increase of internal friction energy dissipation between chains due to higher viscoelastic nature and the increase of loss factor. Second, the friction slipping of MWCNTs occurs, which also brings about an increase of the damping properties and the energy loss fraction w.

From Figure 2(b), it can also be seen that the T_g of nanocomposites obviously decrease compared with that of PC. The similar phenomenon has been observed in other polymer/CNT composites.[28,29] It is assumed that the decrease of glass transition temperature results from the increase of free volume. As we all know, the more easily polymer chains can move, the less heat it takes for the chains to break out of glassy state and then into rubbery state. As a result, the increase of free volume is favorable for chain moving, which induces the decrease of glass

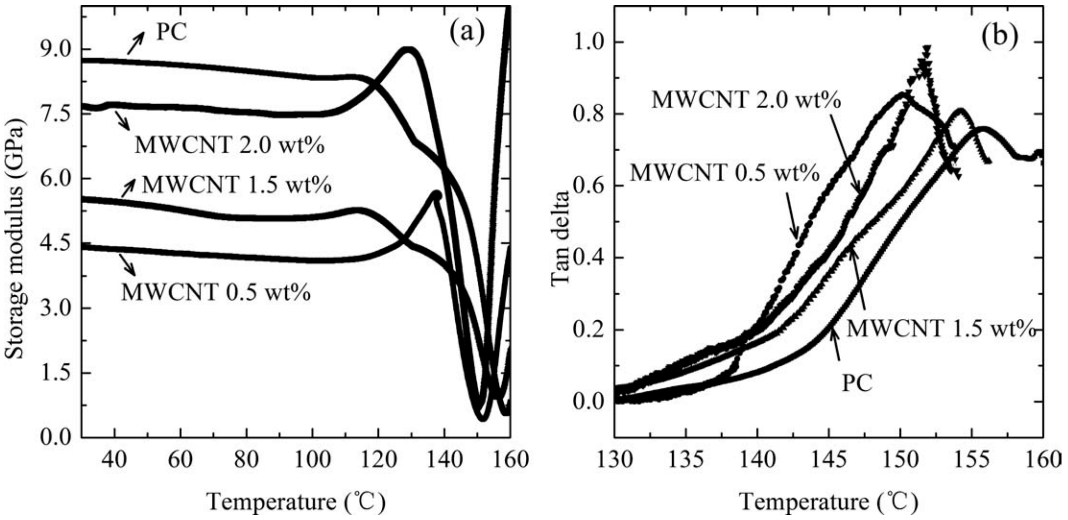

Figure 2 Dynamic mechanical spectra: Storage modulus (a) and tan δ (b) as a function of temperature for PC and PC/MWCNT composites with 0.5, 1.5, and 2 wt % MWCNTs. Test was carried out using three-point bend mode, and at a constant frequency (ω = 10 Hz).

transition temperature ultimately. This can be testified by PALS in the following study.

Effect of free volume on mechanical and damping properties

Positron spectroscopy is a very useful tool to probe the atomic scale free volume. PATFIT analysis gives an average value of positron annihilation lifetime as shown in Figure 3. From Figure 3, it is clear that the o-Ps lifetime and the average free volume size of the composites increase with increasing the MWCNT content. This is attributed to the increase in motility of molecules. As MWCNTs were added into the matrix, the packing modes of PC molecular segments were partly disarranged and a large amount of segment chains were adsorbed on the surface of nanotubes. The increase of average free volume size is beneficial to the chain segment movement of PC as well as the slippage of MWCNTs in the matrix, which leads to increasing the damping properties. This is in good agreement with the increase of loss factor tan δ measured by DMA as shown in Figure 2(b).

To deeply investigate the effect of MWCNT on the size and the distribution of free volume, the continuous analysis of o-Ps lifetimes using MELT program was performed as shown in Figure 4. It is evident that two well-separated o-Ps lifetimes τ_3 and τ_4 are observed for all tested samples. It is very interesting that the values of τ_3 and τ_4 of composites are higher than that of PC, which is in good agreement with the results analyzed by PATFIT.

According to the reports,[30,31] the variation of the second lifetime intensity I_2 is related to the interfacial interaction in the composites. Both Liu et al.[32] and Zhou et al.[33] reported an increase in the interaction parameter β, which is an intuitionistic characterization of the interfacial interaction between filler and matrix. In the latter report, Zhou et al. reported that the absolute values (max. 1.5) of β in epoxy/MWCNT-NH_2 with amined-modified MWCNTs composites were very high, indicating that strong interfacial interaction existed in the composites. To investigate the interfacial interaction between MWCNTs and

TABLE I
Peak Value of tan δ and Calculated *w* of PC and PC/MWCNT Composites

Sample	Peak value of tan δ	Energy loss fraction *w*
PC	0.758	0.704
PC/MWCNT 0.5 wt %	0.854	0.728
PC/MWCNT 1.5 wt %	0.807	0.717
PC/MWCNT 2.0 wt %	0.985	0.756

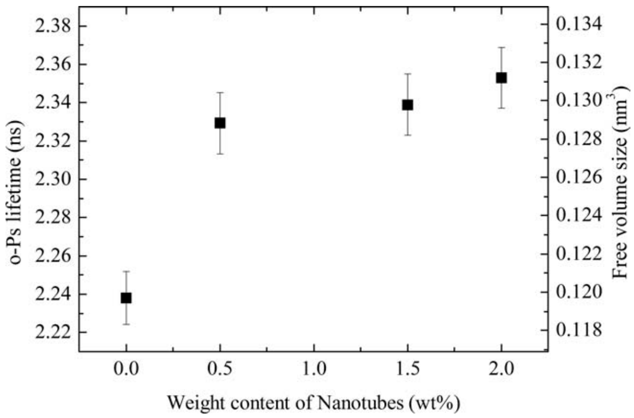

Figure 3 Lifetime of o-Ps and average free volume size versus weight content of MWCNTs.

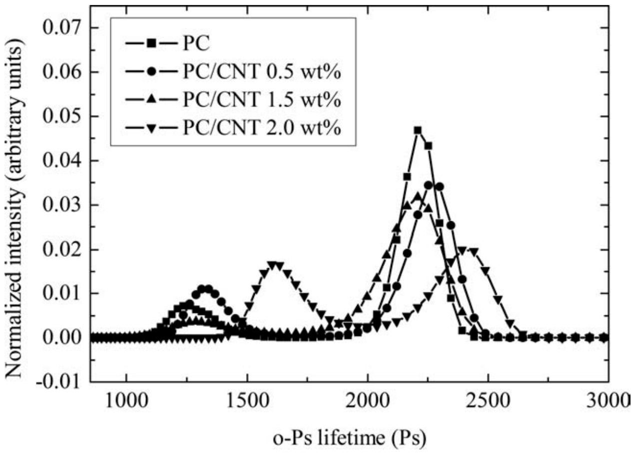

Figure 4 o-Ps lifetime distributions for pure PC, composites with 0.5, 1.5, and 2.0 wt % MWCNTs. The lines are drawn to guide the eyes.

PC, the interaction parameter β has been calculated according to the eq. (4)[32,33]:

$$I_2^c = I_2^{pc}\phi_{pc} + I_2^M\phi_M + \beta I_2^{pc}\phi_{pc} I_2^M\phi_M \tag{4}$$

where ϕ is the weight content of MWCNTs or PC, and the superscripts C and M refer to the composite and MWCNTs, respectively. Calculated results show that the absolute values (max. 0.314) of β in PC/MWCNT composites are very small compared with that (max. 1.5) of epoxy resin composites with the surface decorated CNTs as shown in Figure 5, which indicates that the interfacial interaction between the MWCNTs and PC is very weak. The weak interfacial interaction makes MWCNT slipping occur more easily at the interface, which leads to enhancement in the damping properties. This agrees well with the reports.[14,34] This result can also be confirmed by the mechanical analysis as below.

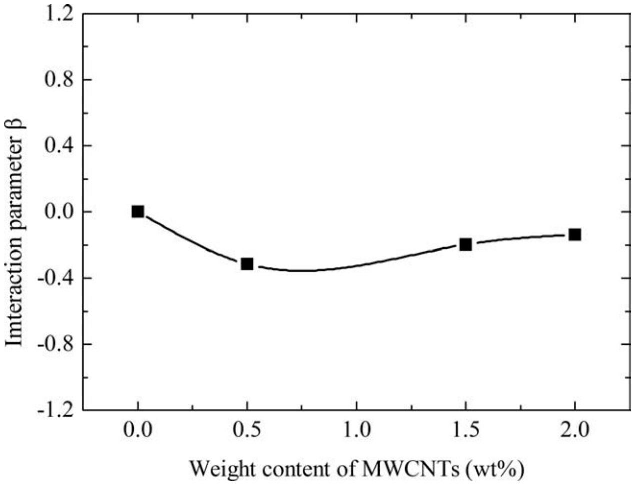

Figure 5 Interaction parameter β versus weight content of MWCNTs. The line is drawn to guide the eye.

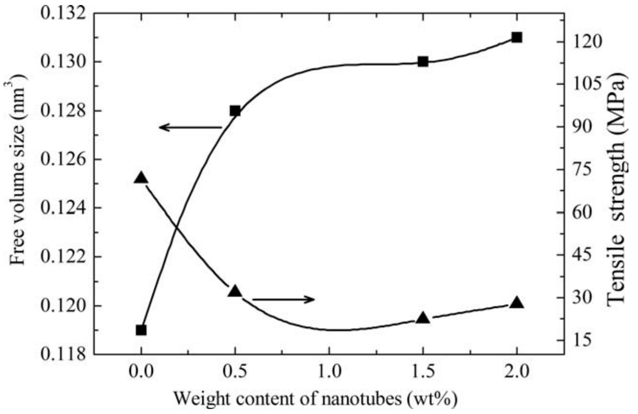

Figure 6 Variations of free volume size (left vertical axis) and tensile strength (right vertical axis) as a function of the weight content of MWCNTs. The lines are drawn to guide the eyes.

The variations of tensile strength and free volume versus content of MWCNTs are shown in Figure 6, from which we can see that the free volume increases with increasing MWCNT content, whereas the tensile strength decreases. After incorporation of MWCNTs, a drastic reduction in tensile strength from 75.51 to 22.32 MPa is observed. On the contrary, the free volume size increases from 0.119 to 0.131 nm^3 with increasing MWCNT content. The larger the free volume, the weaker the tensile yield strength. This can be explained by MWCNT slipping resulting from the weak interfacial interaction. This phenomenon has also been observed by Schmidt et al.[35] and Ravikumar et al.[36]

CONCLUSION

In this article, the microstructure, damping, and mechanical properties of PC/MWCNT composites have been systemically studied. The experimental results indicate that the damping properties and the values of the energy loss fraction w have a marked increase for PC/MWCNT composites, which is contributed to the much weaker interfacial interaction between MWCNTs and PC matrix confirmed by interaction parameter β evaluated in terms of positron annihilation parameter. A correlation between the damping and the free volume has been given for the first time, suggesting that the larger the free volume, the higher the damping. The experimental results reveal that the free volume and slipping of MWCNTs at interface region play an important role in determining the damping for PC/MWCNT composites.

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