Study of Piezo-Damping Properties of CPE/ZKF/VGCF Composites

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ABSTRACT: The electrical and damping behaviors of chlorinated polyethylene (CPE)/2,2'-methylene-bis-(4-methyl-6-cyclohexylphenol) (ZKF)/vapor-grown carbon fiber (VGCF) have been investigated. CPE/ZKF/VGCF systems exhibit typical percolation characteristics of filled conductive polymer composites. For CPE/ZKF/VGCF composites, dynamic mechanical analysis (DMA) shows that, at the glass transition temperature (T_g) of CPE/ZKF system, the values of loss factor increase with the increasing VGCF content. Within the temperature range of 60–75°C, the values of loss factor for CPE/ZKF/VGCF samples are higher than that of CPE/ZKF and present a peak at 16 vol% VGCF content. This implies that the piezo-damping effect is directly related to the conductive network formation in the composites, and the piezo-damping effect can be regulated by regulating the VGCF content. Therefore, the composite of CPE/ZKF/VGCF is a good damping material with a high and broad loss factor that can be regulated according to practical applications. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3181–3185, 2006

Key words: damping properties; electrical properties; piezo-damping effect; piezoelectric material

INTRODUCTION

During recent years, there has been increased interest in the use of polymers for low-frequency vibration and sound wave damping in the sonic and ultrasonic ranges. This is because noise has become a serious form of pollution. Materials with high damping properties therefore find numerous applications, especially in the aircraft, automobiles, skyscrapers, and appliance industries. However, the damping efficiency for these materials is not very good. In addition, their applications are, to some extent, limited. First, the width and height of the loss peak for a given polymer cannot be independently adjusted, as the broadening of the loss peak usually results in a decrease in its maximum height.[1] In fact, the tanδ values of good damping materials are > 0.3 for a temperature range of $\geq$ 60°C.[2] Second, the dynamic mechanical properties of these materials cannot be changed, once the materials and structures for damping are decided.

Thus, to obtain a damping material with a high and broad loss factor that can be regulated according to practical applications, it is very important to develop a new damping material and mechanism. In recent years, a new damping material has been developed on the basis of a new damping mechanism.[3–5] That is, for some composites, mechanical vibrating energy is first transmitted to the piezoelectric ceramic powder and converted into alternating electrical potential energy by the piezoelectric effect. Then, the electrical potential energy is further converted into joules (J) heat through the networks of electrical conductive particles in polymeric matrix.[6–8] For simplicity, such an energy transferring effect is rather hereafter referred to as the piezo-damping effect hereby.

According to our work, we find that lead zirconate titanate (PZT) damping materials are brittle, fragile, and hard, with the result that not only have some difficulty in processing technology, but also the electromechanical coupling factor is not very good. As a way of improving these inferior properties, we substitute the organic small molecule ZKF with strong dielectric behavior for piezoelectric ceramic powder, and a new damping composite of CPE/ZKF/VGCF has been developed. The piezo-damping behavior of composite of CPE/ZKF/VGCF is investigated by dynamic mechanical analysis (DMA) in the present work.

EXPERIMENTAL

Composite sample preparation

The chlorinating polyethylene (CPE) used in this study, with a chlorination degree of 40 wt%, is commercial grade (from Weifang Yaxing Chemical Plant, Weitang, People's Republic of China). The ZKF (as shown in Figure 1) used as a substitute for piezoelectric ceramic powder, is commercial antioxidant (from Bayer Com-
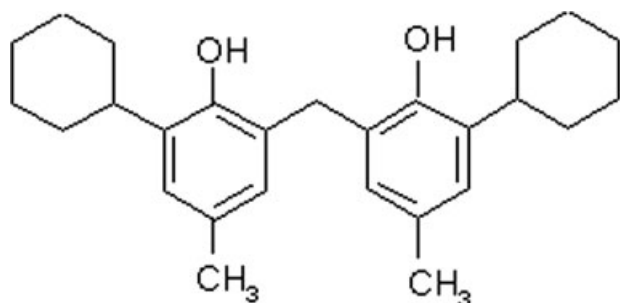
Figure 1 Chemical structure of ZKF.

pany, Germany). Vapor-grown carbon fiber (VGCF) (from Showa Denko Co. Ltd., Japan, with average length of 1.0 μm and a diameter of 0.1 μm, density of 1.8 g/cm³) is used as electrical conductive filler.

The above-mentioned materials were mixed on a two-roll mill at 65°C. The mixed materials are then molten at 160°C by a sulfuration machine at a pressure of 1–2 MPa for 10 min and then at a pressure of 15 MPa for 10 min. The mixtures are quenched in ice water to obtain the sample films with a thickness of 0.5 mm (volume ratio of the mixture: ZKF 40%; VGCF 0–20%; and CPE 60%–40%).

Experimental method

Measurement of electrical conductivity

The electric conductivity is measured in the thickness direction of the composite films. The silver powder with electrodes is pasted onto the sample surface, with a size of 15 mm × 15 mm. The conductivity is measured at room temperature.

Observation of scanning electron microscopy

The distribution of VGCF in the samples is observed by scanning electron microscopy (SEM).

Dynamic mechanical analysis

Dynamic mechanical measurements are carried out on a dynamic mechanical analyzer (Perkin-Elmer DMA 7e) in tension mode at a frequency of 1 Hz and a varied temperature of −60–100°C with a heating rate of 5°C/min. The dimensions of sample are ∼ 10 mm long × 3 mm wide × ∼ 0.5 mm thick.

RESULTS

Electrical conductivity

The dependence of electrical conductivity on VGCF for CPE/ZKF/VGCF composites is shown in Figure 2. CPE/ZKF/VGCF systems exhibit typical percolation characteristics of filled conductive polymer

composites. At a low content of VGCF, the electrical conductivity of the composites is essentially similar to that of pure CPE, indicating that there are no conductive paths throughout the composites. As the VGCF content is increased, namely percolation threshold, an abrupt increase in the conductivity is observed, suggesting that a continuous conductive network begin to be formed.[9,10] This sharp break in the relationship between the filler content and the conductivity of the composite is well known as "percolation" and the critical filler content is called "percolation threshold."[11] However, the percolation threshold for these systems is relatively higher, which should be attributed to the viscosity of CPE used as the matrix is greater, so that it is more difficult for the VGCF to form the conductive network in the matrix. To ascertain its conductive mechanism, the distribution of VGCF in the composites is observed by SEM, as shown in Figure 3. There are fewer contacts between adjacent fibers and the less VGCF content would make less contribution to the formation of the conducting network in Figure 3(a). However, the conductive networks in this systems have been formed when VGCF content reaches 12 vol%, as can be seen in Figure 3(b).

Dynamic mechanical behavior

Figure 4 shows the dynamic mechanical spectra of CPE/ZKF and CPE/ZKF/VGCF composites at a frequency of 1 Hz. For all the samples, the loss peak (tan δ, the ratio of loss modulus E'' to storage modulus E') that presents a peak shifts to higher temperature, with the increase of VGCF content in the CPE/ZKF/VGCF systems. These phenomena attribute to the present of the VGCF, which reduces the free volume and hinders the motion of the molecules of CPE matrix. The storage modulus also shifts to higher
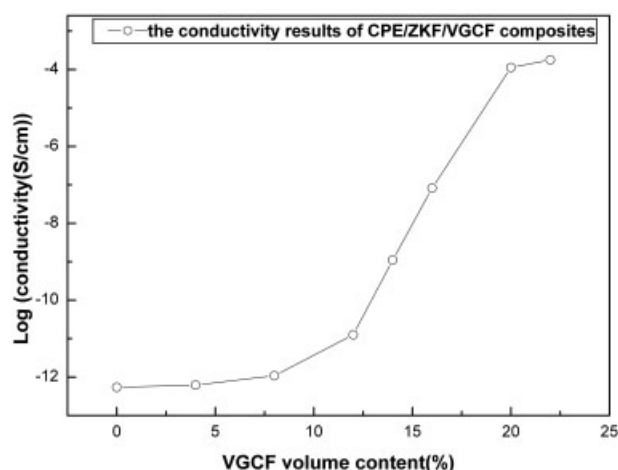

Figure 2 Dependence of electrical conductivity on VGCF content for CPE/ZKF/VGCF composites.

**Figure 3** Scanning electron micrographs of CPE/ZKF/VGCF composites with (a) 4% VGCF and (b) 12% VGCF.

temperature and increases with the increase of VGCF content.

Generally, it leads to the decrease in loss peak intensity, when the filler as carbon black (CB) is added into polymer matrix. However, one of the interesting phenomena is observed, as shown in Figures 4 and 5. The loss peak intensity increases with increased VGCF content, reaches the maximum at 16 vol% VGCF content, and finally decreases again. At the glass transition temperature (T_g) of a given homopolymer at given frequency, the peak intensity of loss factor is directly related to the coordinated chain molecular friction, which dissipates mechanical energy as heat. However, at the vitrification point, the piezo-damping effect is not obvious, as the mechanical vibration energy converts into thermal

energy is higher, because of the friction between molecules of CPE matrix. The organic small molecular ZKF is a type of polycyclic compound, as shown in Figure 1. The increase of peak intensity can be explained as follows, which can dissipate mechanical energy as heat: (1) a few VGCF are beneficial to the scatter of the organic small molecule ZKF between molecules of the CPE matrix, increasing the motion of main chain and side chain of the CPE matrix; (2) the vibration of the polycyclic compound can also convert the mechanical energy into thermal energy; and (3) there is friction between the polycyclic compound and the molecules of the CPE matrix. But when a large quantity of VGCF is added into the matrix, the VGCF hinders the molecule motion of CPE matrix and the organic small molecule ZKF, so the
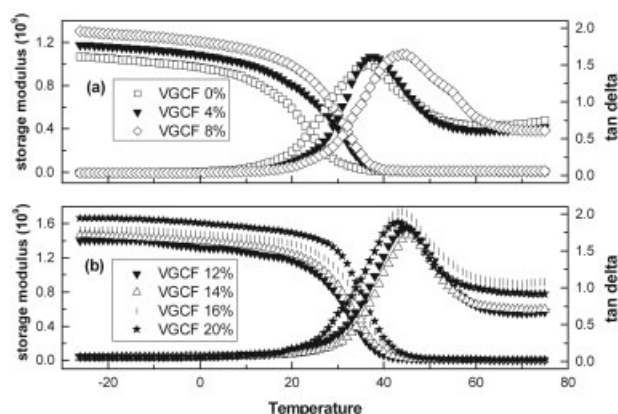
Figure 4 Temperature dependence of storage modulus and loss factor for CPE/[(60–x)vol%]/ZKF(40 vol%)/VGCF (x vol%) composites at 1 Hz.
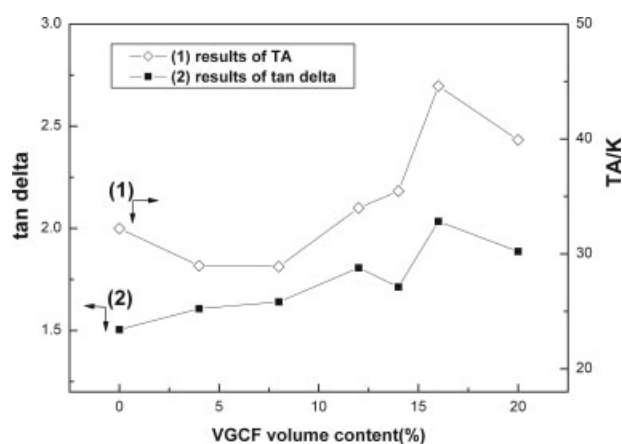
Figure 5 Effect of VGCF content on tanδ peak values and TA in CPE/ZKF/VGCF systems.

intensity of the loss peak decreases at higher VGCF loading.

Another interesting phenomenon is observed within the range of 60–75°C in Figure 4. As the VGCF content exceeds the percolation threshold (i.e., the three-dimensional conductive network is formed), the loss factor is increased dramatically [Fig. 4(b)]. This indicates that the piezo-damping effect really functions in the systems and that the efficient damping temperature region where the tanδ value is even higher than 0.5 is clearly broader as well.

To investigate the CPE/ZKF/VGCF systems further, another index to characterize the damping behavior of materials, TA, denoting the area under the tanδ vs temperature curves around the glass transition, is the energy dissipation of the glass transition, as shown in Figure 5. The VGCF content dependence of loss factor at the T_g for both systems is also plotted in Figure 5.

As shown in Figure 5, with the increase of VGCF content, the values of TA for CPE/ZKF/VGCF systems reaches the maximum when the composite contains 16 vol% VGCF for CPE/ZKF/VGCF systems. Such a peak of loss factor at a critical content of electrical conductive filler can also be ascertained as the experimental verification of the piezo-damping effect.[12]

DISCUSSION

Within the range of 60–75°C, the value of tanδ is significantly changed with VGCF content; that is, the electric resistivity of the blends is controlled by VGCF fillers. When VGCF content is $\leq$ 8 vol%, the blends behave electrically as an insulator and here the electric energy generated from ZKF is not fully dissipated. When the VGCF content ranges within 8–16 vol%, the generated electric current flows in the systems through VGCF fillers, thus, becoming well dissipated. However, When the VGCF content is > 16 vol%, the VGCF filler may act rather as electric conductors, and as a result, the electric energy is not fully dissipated.

In comparison with CPE/PZT/VGCF systems, as shown in Figure 6, we can see that the height of loss factor of the CPE/ZKF/VGCF system is higher than that of the CPE/PZT/VGCF system. At 0% VGCF for both systems, the loss peak intensity of CPE/PZT composite is ~ 0.8. However, CPE/ZKF composite exhibits a relatively high tanδ (> 1.5, as shown in Fig. 4). For the CPE/ZKF/VGCF systems, it should be pointed out that the efficient damping temperature region where the tanδ value is even higher than 0.5 is also broader obviously. Therefore, CPE/ZKF/VGCF composites would have the possibility of being used for damping materials.

Consequently, the presence of ZKF and VGCF can result in three effects on the values of the loss factor.
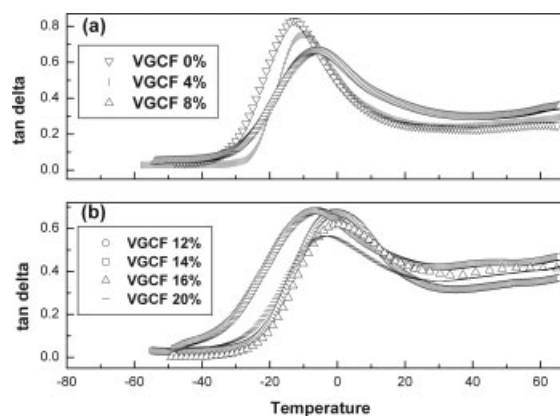
Figure 6 Temperature dependence of loss factor for CPE/[(60–x)vol%]/PZT(40 vol%)/VGCF(x vol%) composites at 1 Hz.

First, the addition of ZKF increases in the loss factor intensity at 0% VGCF, as observed in Figure 4(a); it attributes to the formation of intermolecular hydrogen bonds between the polar polymer (CPE) and functional organic small molecule (ZKF) and that the energy dissipation due to dissociation of the intermolecular hydrogen bonds is larger than that of due to general friction between polymer chains.[13–15] Second, the friction among organic small molecule, VGCF, and CPE chains can be improved by the addition of fillers, supported by a slightly increased loss peak intensity around T_g for CPE/ZKF/VGCF composites, as shown in Figure 4. Third, the piezo-damping effect can improve damping efficiency in CPE/ZKF/VGCF composites.

CONCLUSION

On the basis of the piezoelectric effect and conductivity mechanism, the conductivity and dynamic mechanical properties for the composites of CPE/ZKF/VGCF are discussed, and the conclusions are as follows:

1. The conductivity for CPE/ZKF/VGCF systems has an abrupt increase as the VGCF content is increased to some value, namely percolation threshold. Because of the viscosity of CPE used as the matrix is greater, the percolation threshold for CPE/ZKF/VGCF systems is relatively higher.

2. DMA shows when the composite contains 16 vol% VGCF for CPE/ZKF/VGCF systems, the value of loss factor reaches the maximum in the range of 60–75°C. This implies that the piezo-damping effect is directly related to the formation of conductive networks in the composites.

3. In comparison with CPE/PZT/VGCF systems, CPE/ZKF/VGCF systems not only have better damping properties, but the efficient damping

temperature region where the tanδ value is even higher than 0.5 is also broader.

The formation of intermolecular hydrogen bonds and Fourier transform infrared (FTIR) spectroscopy studies on the CPE/ZKF/VGCF composites will be further reported in our following articles.

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