Effects of small molecular additives on the damping performance of CPE/ZKF/EBP three-component hybrids

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Abstract The damping performance of CPE/ZKF/EBP three-component hybrid consisting of two kinds of functional organic additives 2, 2′-methylene-bis-(4-methyl-6-cyclohexylphenol) (ZKF) and 2, 2′-methylene-bis-(6-tert-butyl-4-ethyl-phenol) (EBP) have been investigated by dynamic mechanical analysis (DMA). The DMA results show that a part of EBP molecules act as a bulk side group of the CPE chain in the hybrids by intermolecular hydrogen bond interaction between EBP and CPE chain, and there is a synergistic effect between ZKF and EBP on the damping properties of the three-component hybrids. When adding a small quantity of EBP into CPE/ZKF two-component system, not only the loss peak intensity of the CPE/ZKF/EBP hybrids can be further improved, but also its loss peak position can be lowered to a required temperature region. For further studying, it is found that the damping properties of the CPE/ZKF/EBP three-component hybrids mainly depend on the weight ratio of ZKF/CPE and the EBP molecules play a great role in adjusting its loss peak position. These may imply that the CPE/ZKF/EBP three-component system is more efficient in damping performance in comparison with the CPE/ZKF two-component system.

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Introduction

Many efforts have been made for attempting to control the unwanted vibration and noise, and the typical candidate damping materials for the application of passive damping are viscoelastic polymers. On the basis of damping theory [1, 2], the loss factor is a useful measure of material damping, which can be determined from dynamic mechanical behavior. Generally, the vibrating energy is dissipated mechanically through the viscoelastic molecular motion of polymer chains and the damping factor, showing a maximum value of loss peak near the glass transition temperature (T_g). Therefore, in polymeric damping materials, polymers with large damping peak around application temperature are required and preferred [3, 4]. However, most materials used in structural applications have small loss factors. Consequently, various types of polymer systems mixed with plasticizers and fillers have been investigated to obtain larger mechanical loss and adjust T_g to locate within a required temperature region (mostly room temperature) [5–8].

Recently, extensive studies have been carried out on organic hybrid materials and some researchers have been reported advanced damping performance of organic hybrids composed of matrix polymers and low molecular weight organic fillers, aiming at damping applications [9–14]. The addition of bi-functional small molecular weight compounds not only caused an increase in the loss peak maximum, but also the loss peak position was shifted to a higher temperature, such as CPE/DZ hybrids. There were further investigations of the chemical structure, the crystal structure, and the effect of crystallization of the organic low molecular weight compounds on viscoelastic properties of the hybrids. The coexisting of organic low molecular weight compounds and a polymer matrix seems to come about specific vibration phenomena.

However, little attention has been paid to the effect of two kinds of low molecular weight additives on the viscoelastic properties of three-component hybrids so far. In our previous work, we found that 2, 2′-methylene-bis-(4-methyl-6-cyclohexylphenol) (ZKF) and 2, 2′-methylene-bis-(6-tert-butyl-4-ethyl-phenol) (EBP) are effective for improving the damping properties [13, 15]. In this article, the effects of two kinds of organic low molecular weight compounds on characteristic vibrational damping properties and viscoelastic behaviors of three-component hybrids will be studied.

Experimental

Composite sample preparation

The chlorinating polyethylene (CPE) used in this study, with a chlorination degree of 35 wt%, was used as matrix (from Weifang, Yaxing Chemical Plant, Weifang, PRC). The ZKF (from Bayer Company, Germany) and EBP (from Gaoyou Auxiliary Factory, PRC), used as organic functional additives, were both commercially available antioxidant.

The above-mentioned materials were mixed on a two-roll mill at 65 °C. The mixed materials were then molten at 155 °C by a sulfuration machine at a pressure of 1–2 MPa for 5 min and then at a 15 MPa for 10 min. Finally, the mixtures were quenched into water to obtain a film with the thickness of 0.5 mm.

Measurements

Dynamic mechanical analysis (DMA) measurements

Dynamical mechanical measurements were carried out on a dynamical analyzer (Perkin-Elmer DMA 7e) in tension mode at frequency of 1 Hz and a varied temperature from −50 to 100 °C with a heating rate of 5 °C/min. The dimensions of sample were about 16 mm long, 4 mm wide, and around 0.5 mm thick.

Differential scanning calorimetry (DSC) Testing

Differential scanning calorimetry measurements were carried out with a DSC-7 Perkin-Elmer calorimeter. Samples about 8 mg in weight and sealed in aluminum were heated from 35 to 160 °C at a scanning rate of 10 °C/min under the nitrogen atmosphere to investigate the melting temperature and degree of crystallinity of organic hybrids. The melting temperature was obtained at the top of the DSC endothermic peak in the heating scan.

Scanning electron microscope (SEM)

The films of samples were cryofractured in liquid nitrogen. The fracture surfaces were then sputter-coated with gold and observed with a JSM-5600LV (JEOL) SEM using an accelerating voltage of 10–20 kV.

Results and discussion

Figure 1 shows the concentration dependence of loss peak maximum and its position for CPE/ZKF and CPE/EBP organic hybrid materials. It is clear shown that for CPE/EBP organic hybrids, with increasing the EBP content, the maximum value of the damping peak corresponding to pure CPE relaxation decreases dramatically, while the loss peak position of that shifts to high temperature. As analysis of the thermal properties of CPE/EBP hybrid materials listed in Table 1, more and more organic filler EBP crystallizes with increasing the EBP content and the crystallization of EBP may act as physical crosslinking points, which hinder the motion of the molecules of CPE matrix and result in the shift of the loss peak position. However, for CPE/ZKF organic
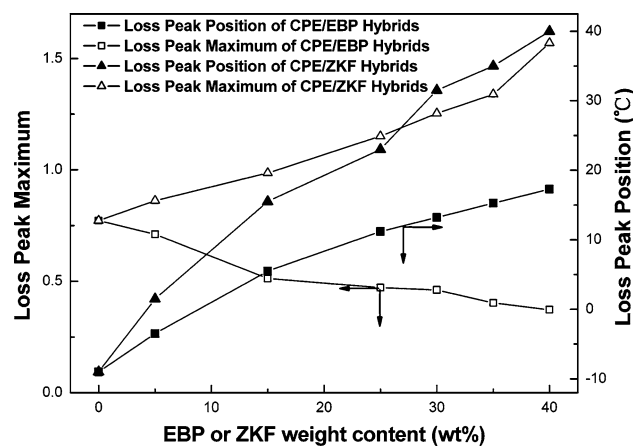

Fig. 1 Concentration dependence of loss peak maximum and its position for CPE/ZKF and CPE/EBP organic hybrid materials

Table 1 The thermal properties of CPE hybrid materials with low molecular compounds

Sample CPE/EBP	T_m (°C)	Melting enthalpy (J/g)	Sample CPE/ZKF/EBP	T_m (°C)	Melting enthalpy (J/g)
95/5	0	0	60/40/0	121.848	1.702
85/15	103.469	8.062	57/38/5	118.243	1.924
75/25	112.874	14.755	54/36/10	110.554	1.624
65/35	116.3	24.683	51/34/15	110.893	1.813
60/40	119.9	36.538	48/32/20	96.831	5.164

hybrids, the loss peak position even shifts to higher temperature and the loss peak maximum increases markedly with increasing the ZKF content. In our previous work [15], we found that a small molecule ZKF formed two hydrogen bonds with two CPE chains at the same time, and the ZKF is compatible with the CPE matrix. The energy dissipation due to dissociation of the intermolecular hydrogen bond network is larger than that of due to general friction between polymer chains. Therefore, the increase of the height of the loss peak can be attributed to the dissociation of the intermolecular hydrogen bonds between CPE and ZKF within hybrids. However, most of EBP formed EBP-rich domains due to the intermolecular hydrogen bond between hydroxyl groups of EBP and Cl atom of CPE, and the EBP is incompatible with the CPE matrix.

To examine the effect of the two bi-functional small molecular compounds ZKF and EBP on the damping properties of CPE/ZKF/EBP three-component organic hybrids, the temperature dependence of storage modulus and loss factor for CPE, CPE/ZKF (60/40), and CPE/ZKF/EBP (54/36/10) are shown in Fig. 2. Compared with CPE/ZKF two-component hybrid, when ZKF/CPE = 2:3 and EBP content is 10 wt%, one interesting phenomenon is that the loss peak maximum of CPE/ZKF/EBP three-component hybrid increases significantly and exhibits a high loss peak. The other interesting point should be noted that the loss peak position of the three-component hybrid shifts to lower temperature range. It is also worth pointing out that there are five domains on the E' curve of the CPE/ZKF/EBP hybrid showed in Fig. 2, two dispersion regions in which E' decreases rapidly with temperature, as well as three regions that show a much more gentle decrease in slope. However, there is only one sharp and narrow relaxation peak on the corresponding tan δ curve. Compared to the idealized multi-event DMA scanning curve as shown in Fig. 3 [16], the first dispersion region at −20 °C on the E' curve may be caused
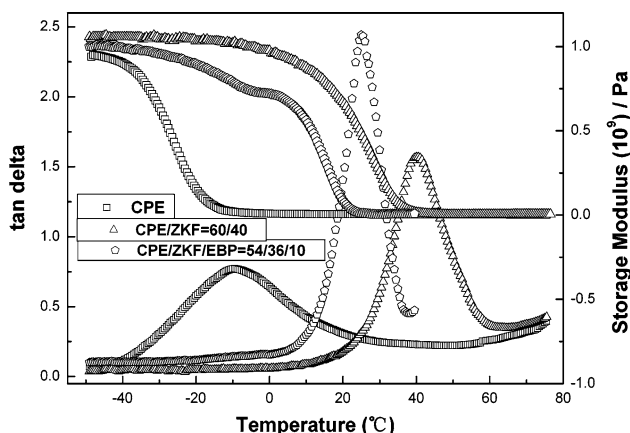
Fig. 2 Temperature dependence of storage modulus and loss factor for CPE, CPE/ZKF (60/40) and CPE/ZKF/EBP (54/36/10)
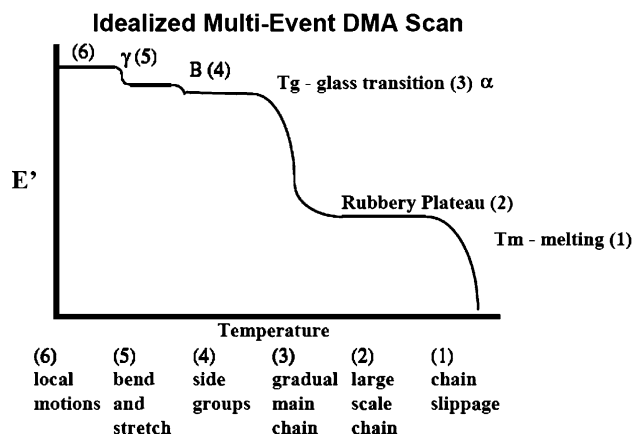
Fig. 3 The idealized multi-event DMA scanning curve

by the side group, and the second dispersion at 10 °C corresponds to the transition of ZKF and EBP domains, which is also related to the CPE matrix. Therefore, a part of EBP molecules may act as a bulk side group of the CPE chain in the hybrids by intermolecular hydrogen bond interaction between EBP and CPE chain [17]. The presence of the bulk side group may increase the flexibility and the free volume, resulting in a shift of the loss peak to lower temperature comparing to the CPE/ZKF hybrid with the same ZKF weight ratio. These imply that there is a synergistic effect between ZKF and EBP on the damping properties of the hybrids. When a small amount of EBP was incorporated into CPE/ZKF hybrid, there might be three different kinds of intermolecular hydrogen bonds related to the small molecule EBP: (1) some EBP molecules might act as a bulk side group of the CPE chain by intermolecular hydrogen bond, (2) the EBP might also form two hydrogen bonds with two CPE chains at the same time due to the present of the hydrogen bond network between ZKF and CPE, and (3) the hydrogen bond network might be formed between EBP and ZKF. Both the physical bulk side group and hydrogen bond network should cause the synergistic interaction between EBP and ZKF.

When fixing the EBP content at 10 wt% and changing the weight ratio of ZKF/CPE, it is noted that the loss peak maximum of the three-component increase with increasing the ratio of the ZKF/CPE as shown in Fig. 4. In comparison with the CPE/ZKF two-component hybrids, it is found that the damping properties of the three-component hybrids can be improved by adding a small amount of EBP content. The damping peak maximum of CPE/ZKF/EBP (ZKF content is 50 wt%) is higher than 3, while that of the CPE/ZKF (ZKF content is also 50 wt%) is about 2. On the other hand, its loss peak position is lower than that of the CPE/ZKF two-component hybrids with the same ZKF content, namely, the loss peak position of the three-component hybrid shifts to lower temperature region due to the presence of the EBP. These
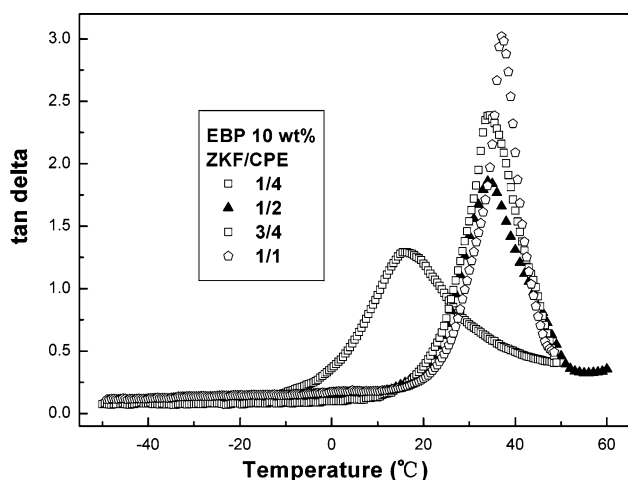
Fig. 4 Temperature dependence of loss peak intensity of the CPE/ZKF/EBP hybrids with fixing the EBP content = 10 wt% and changing the weight ratio of ZKF/CPE

results imply that the damping performance of the CPE/ZKF/EBP three-component hybrids mainly depends on the weight ratio of ZKF/CPE and the presence of the synergistic effect between ZKF and EBP on the damping properties of the hybrids is also confirmed.

For further investigating the three-component hybrids, DMA measurements are carried out by fixing the CPE content (60 wt%), the weight ratio of ZKF/CPE (2:3) and changing the concentration of EBP in the CPE/ZKF/EBP hybrids, respectively. Figure 5 depicts the composition dependence of loss peak maximum and its position of the CPE/ZKF/EBP three-component hybrids. It can be seen from Fig. 5, when fixing the ratio of ZKF/CPE (2:3) and changing the EBP content, the maximum value of the damping peak and its position are significantly changed with EBP content. The loss peak position of the CPE/ZKF/EBP hybrid shifts to lower temperature when the EBP content is
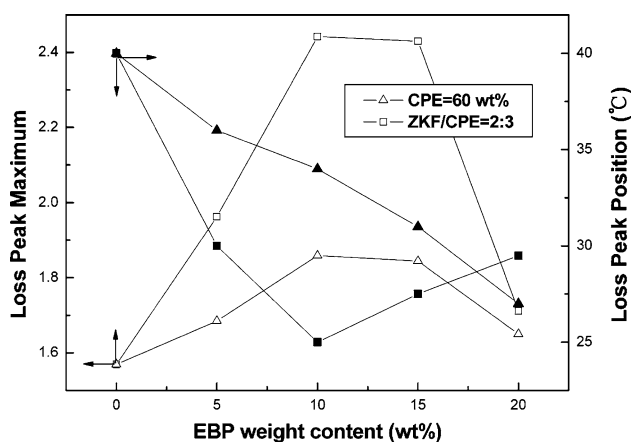
≤10 wt%, and then there is a slightly shift to higher temperature with increasing the EBP content. The shift of the loss peak position to lower temperature may be due to a part of EBP molecules acting as a bulk side group in the hybrids, which increasing the flexibility and the free volume. As can be seen from SEM observation as shown in Fig. 6 and the DSC results of the thermal properties of the three-component hybrids as listed in Table 1, with increasing EBP content, more and more EBP crystallizes, which may behave as a reinforcement filler-like conventional inorganic or fibers, resulting in a shift of the loss peak to higher temperature at higher EBP content. However, the loss peak position shifts to lower temperature ranges nearly linearly when fixing the CPE content (60 wt%) and changing the EBP content. This phenomenon suggests that the EBP molecules play a great role in adjusting the loss peak position of the three-component hybrid.

However, the loss peak intensity increases significantly with increasing the EBP content, reaches the maximum at 10 wt% EBP content and the damping peak maximum are just the same when the EBP content ranges within 10–15 wt%, and finally decreases dramatically when the EBP content is >15 wt%, implying that a small quantity of EBP can further improve the loss peak intensity. This phenomenon can be attributed to as follows. The loss peak intensity increases after the addition of EBP, which may be related to the phase structure and density of the hydrogen bond network increasing with the EBP content, and the energy dissipation due to dissociation of the intermolecular hydrogen bond network is larger than that of due to general friction between polymer chains[18–20]. On the other hand, the presence of bulk side group increases the friction between the EBP molecules and the main chains of the hybrid, which also increases the efficiency of the energy dissipation. However, the crystallization of the hybrids not only causes the phase separation, but also hinders the motion of the main chains due to the crystallization of the hybrids acted as physical crosslinking points, resulting in the dramatically decrease of the loss peak intensity at higher EBP content.

Conclusions

A new damping material of CPE/ZKF/EBP three-component hybrid consisting of two kinds of bi-functional organic additives was prepared. For CPE/ZKF/EBP three-component hybrids, the DMA results showed that a part of EBP molecules acted as a bulk side group of the CPE chain in the hybrids by intermolecular hydrogen bond interaction between EBP and CPE chain. It was found that there was a synergistic effect between ZKF and EBP on the damping properties of the three-component hybrids. When adding a

Fig. 5 Composition dependence of loss peak maximum and its position for CPE/ZKF/EBP hybrids with fixing the CPE content and ratio of ZKF/CPE, respectively

Fig. 6 SEM micrographs of CPE/ZKF/EBP three-component hybrids: **a** CPE/ZKF/EBP = 54/36/10 and **b** CPE/ZKF/EBP = 48/32/20
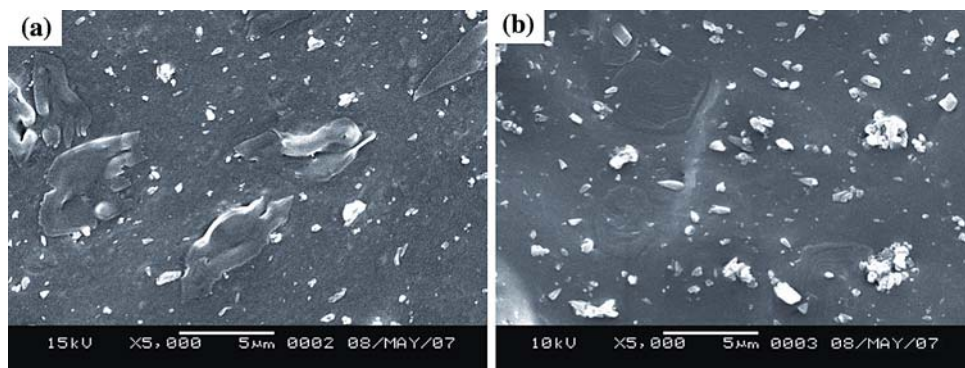
small quantity of EBP, not only the loss factor tanδ of CPE/ZKF/EBP hybrid could be further enhanced, but also its loss peak position could be adjusted to a required temperature region.

For further studying, it was found that the damping performance of the CPE/ZKF/EBP three-component hybrids mainly depended on the weight ratio of ZKF/CPE and the EBP molecules played a great role in adjusting its loss peak position. Therefore, the three-component damping material not only possessed good damping, but also its loss peak position could be adjusted to meet different practical requirements. In comparison with two-component system such as CPE/ZKF, the CPE/ZKF/EBP three-component system was more efficient in damping performance.

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