

Damping Properties of Chlorinated Polyethylene-Based Hybrids: Effect of Organic Additives

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ABSTRACT: In this article, the damping properties of organic hybrids consisting of chlorinated polyethylene (CPE), *N,N*-dicyclohexyl-2-benzothiazolylsulfenamide (DZ), and 4,4'-thio-bis(3-methyl-6-*tert*-butylphenol) (BPSR) have been investigated by dynamic mechanical analysis (DMA). It is found that DZ and BPSR seem to have a synergistic effect on the damping improvement of CPE/DZ/BPSR hybrids. For CPE/DZ/BPSR three-component hybrids, when BPSR content is below 20 wt %, the values of damping peak maximum are just the same, while the damping peak position shifts to a higher temperature at a higher BPSR concentration. When BPSR content is fixed at 10 wt %, the damping peak maximum increases with increasing DZ/CPE ratio, while there is little shift in the peak position within the ratio range of 0.75–1.25. The decrease in damping peak maximum against

annealing can be attributed to the phase separation resulting from the crystallization of hybrids components. Such a crystalline phase, which has been formed during annealing, contains not only pure DZ crystallites but also some CPE–DZ or CPE–DZ–BPSR eutectic crystals. Furthermore, the damping stability of the hybrids can be improved excellently by adding a small amount of BPSR or changing hot-pressing temperature. These may imply that a series of high-performance damping materials possessing both high damping peak maximum and controllable damping peak position can be achieved. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3307–3311, 2006

Key words: viscoelastic properties; glass transition; blends; damping material; dynamic mechanical analysis

INTRODUCTION

Typical candidate damping materials for the application of passive damping are viscoelastic polymers. Since the mechanical energy dissipation of a polymer is most efficient in the vicinity of its glass transition temperature, a polymer with a higher damping peak around application temperature is preferred.¹ However, the glass transitions of most polymers are far distant from the room temperature. Therefore, both how to control the damping peak position to locate within a required temperature region and how to enhance the damping peak intensity of a polymeric-based damping material are of great interest.

Although the use of interpenetrating polymer networks obtained from emulsion polymerization has been thought a very effective way to broaden the damping peak, it is often applied as paint instead of a structure material because of the difficulty of water elimination. Blending binary or ternary polymers with

moderate miscibility has been considered as an interval approach to glass transition region broadening, whereas the location of loss peak position is restricted within the glass transitions of polymer components. Furthermore, this approach fails to improve the damping intensity.

The addition of small molecular weight plasticizer indeed causes an increase in the loss peak maximum, but the loss peak position is shifted to a lower temperature and the storage modulus is reduced. On another hand, polymeric composites filled with inorganic particles or fibers can provide high stiffness and strength, whereas the damping peak maximum decreases sharply and there is little shift in the loss peak position. Recently, an organic hybrid damping material consisting of chlorinated polyethylene (CPE) and one kind of hindered phenol compounds has drawn lot of attention.^{2–5} Addition of organic additives in CPE matrix can both improve the damping peak maximum and control the loss peak position in some sort.

From the viewpoint of application, the best damping material should possess both good damping and high stiffness, while its glass transition can be controlled to meet different practical requirements.⁶ In the present work, a CPE-based hybrid damping material is developed to achieve these purposes. It is found that

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either the enhancement of damping peak maximum or the control of its position can be achieved by adding two kinds of organic functional additives *N,N*-dicyclohexyl-benzothia-zolylsulfenamide (DZ) and 4,4'-thio-bis(3-methyl-6-*tert*-butylphenol) (BPSR).

EXPERIMENTAL

Materials

Chlorinated polyethylene (CPE) (from Showa Denko Co., Japan) was used as a base polymer, *N,N*-dicyclohexyl-benzothia-zolylsulfenamide (DZ) (from Oouchi Shinko Kagaku Kougyou Co., Japan) and 4,4'-thio-bis(3-methyl-6-*tert*-butylphenol) (BPSR) (from Seiko Kagaku Co., Japan) were used as organic additives.

Organic hybrid samples preparation

CPE, DZ, and BPSR were first mixed on a two-roll mill at 60°C. Then the mixtures were hot-pressed at 160°C (or 120°C) under 18 MPa for 10 min, followed by quenching into water to obtain a film with the thickness of 0.5 mm. The as-pressed sheets were annealed at 50°C in an oven for further damping stability measurements.

Characterization

Dynamic mechanical analysis (DMA)

DMA measurements were carried out using a dynamic mechanical analyzer (DVA-200S) in a tension mode at a frequency of 3 Hz and a varied temperature from -50°C to 150°C with a heating rate of 5°C/min. An oscillating dynamic strain of 0.15% was used. The specimens were 20 mm long, 5 mm wide, and around 0.5 mm thick.

Differential scanning calorimetry (DSC)

DSC measurements were carried out using a Shimadzu DSC-50 differential scanning calorimeter within a temperature region from -80°C to 200°C at a heat rate of 10°C/min. The Al₂O₃ powder was used as a reference.

Scanning electron microscopy (SEM)

The sheet samples were fractured in liquid nitrogen, etched with an Eiko IB-3 and coated with Pt-Pd, and observed by a FE S800 scanning electron microscopy.

RESULTS AND DISCUSSION

The damping properties of CPE-based organic hybrids are investigated by means of DMA. The magnitude of damping can be determined from dynamic mechani-

cal behavior, in which loss tangent $\tan\delta$ are usually used as a measure of damping. The studies are concentrated on $\tan\delta$ peak maximum and its position. Figure 1 shows the concentration dependence of damping peak maximum and its position for CPE/BPSR and CPE/DZ hybrids, to examine the effect of small molecular organic additives on the damping properties of CPE. The test specimens were cut from the centers of the as-pressed sheets.

It is clear that for CPE/BPSR two-component hybrid, the damping peak maximum decreases sharply with increase in BPSR content, while there is no obvious shift in the damping peak position. In this case, BPSR crystals, which have been formed during the quenching procedure, seem to behave as a reinforcement filler-like conventional inorganic particles or fibers.⁷ As a result, although the material with a higher BPSR content exhibits a relative high value of storage modulus, the damping efficiency of CPE/BPSR is too poor to meet the practical requirements.

However, for CPE/DZ samples, the damping peak shifts to a higher temperature and its maximum increases markedly with the increase of DZ content. Such an antiplasticization-like phenomenon cannot be explained by the dilution effect, but should be attributed to the strong interaction between DZ and CPE chains.^{8,9} One of the interesting points should be noted that if a small amount of BPSR is incorporated into CPE/DZ hybrid, damping peak maximum is enhanced significantly, while its position shifts to a very high temperature (Fig. 2). This implies that BPSR and DZ may have a synergistic effect on the damping of the hybrids. To confirm this suggestion, DMA experiments are carried out by fixing the ratio of CPE/DZ (1:1) and changing the concentration of BPSR in the CPE/DZ/BPSR three-component hybrids.

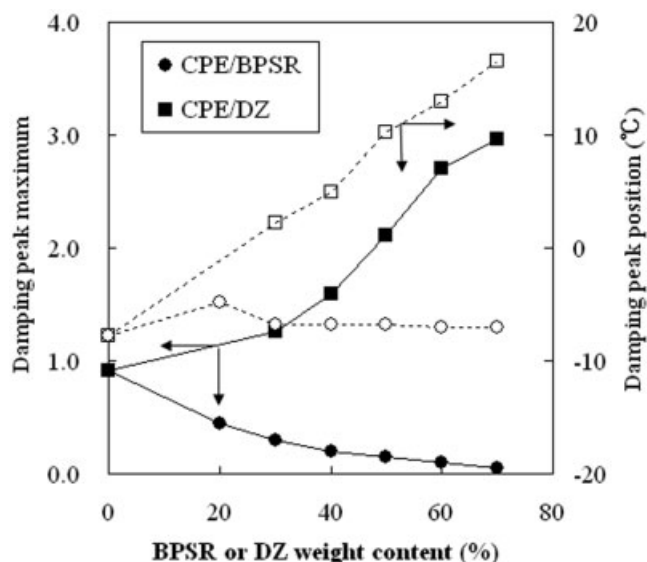


Figure 1 Composition dependence of damping peak maximum and its position.

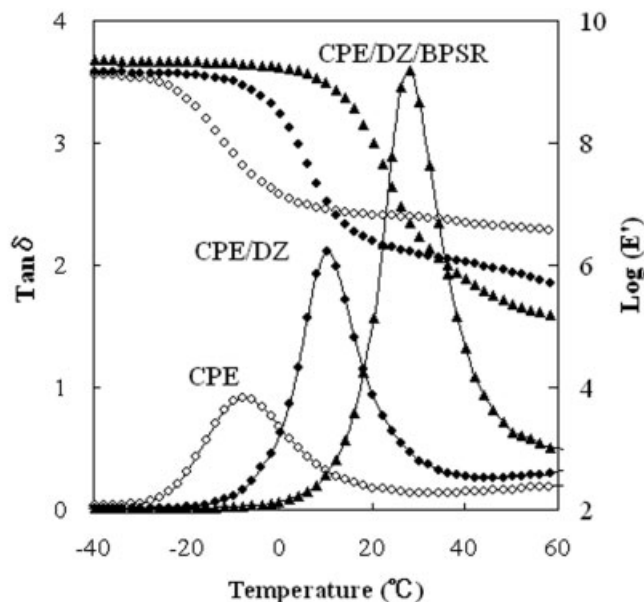


Figure 2 Dynamic mechanical behaviors for CPE, CPE/DZ (50/50), and CPE/DZ/BPSR (30/60/10).

It is found that for CPE/DZ/BPSR three-component hybrids, when $DZ/CPE = 1$ and BPSR content is below 20 wt %, the values of damping peak maximum are just the same, while damping peak position shifts to a higher temperature at a higher BPSR concentration [Fig. 3(a)]. Further studies show that damping peak maximum depends on the weight ratio of DZ/CPE [Fig. 3(b)]. When BPSR content is fixed at 10 wt %, the damping peak maximum increases with increasing DZ/CPE ratio, while there is little shift in the peak position within the ratio range of 0.75–1.25. These results suggest that either damping peak maximum or its position can be controlled by changing the CPE/DZ/BPSR hybrid composition. A series of high-performance damping materials suitable for different practical temperatures may be designed and obtained by adding a small amount of BPSR in the hybrids.

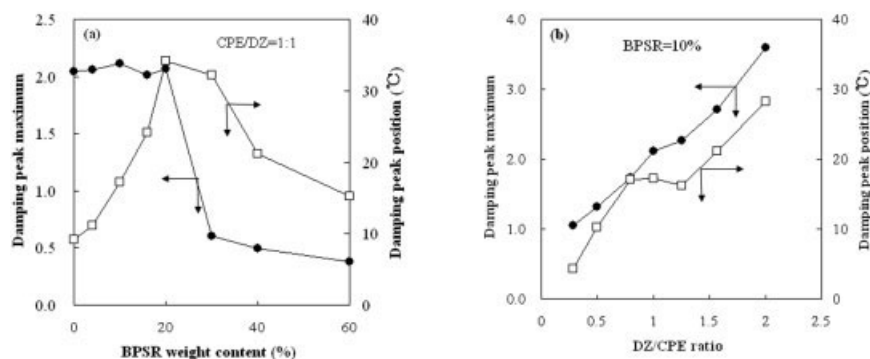


Figure 3 Composition dependence of damping peak maximum and its position for CPE/DZ/BPSR hybrids: (a) $CPE/DZ = 1:1$ and (b) $BPSR = 10$ wt %.

The addition of a small amount of BPSR not only achieves to enhance damping peak maximum and control damping peak position, but also can improve the stability of damping properties against ageing or isothermal treatment successfully. Figure 4 presents the variations of damping peak maximum and its position with annealing time for CPE/DZ (50/50) and CPE/DZ/BPSR (45/45/10) hybrids hot-pressed at different temperatures. The test specimens were cut from the centers of the sheets, which were annealed at 50°C for annealing different times in an oven.

Compared with CPE/DZ two-component systems, the decrease of damping peak maximum values for CPE/DZ/BPSR hot-pressed at 160°C is relatively slow, and damping peak maximum value at equilibrium is much higher than that of CPE/DZ. Furthermore, for CPE/DZ/BPSR hybrid hot-pressed at 120°C, there is no obvious decrease in damping peak maximum and no shift in its position against annealing, indicating a perfect improvement of damping stability. It also worth pointing out that because the damping peaks of such hybrids are around the room temperature, more efficient damping can be expected for the practical use.

The change in dynamic mechanical properties against annealing may be attributed to phase separation resulting from the crystallization of hybrid components. This is confirmed by SEM observation. As shown in Figure 5, for CPE/DZ (50/50) hybrid hot-pressed at 160°C, a crystallite phase is formed throughout the sample. However, for CPE/DZ/BPSR hybrid hot-pressed at 160°C, there is only a small amount of flower-like crystallites dispersed in the amorphous phase. Moreover, for the CPE/DZ/BPSR hybrid hot-pressed at 120°C, no crystallite can be observed. Therefore, the addition of BPSR seems to hinder the crystallization of the hybrids, in turn delays the phase separation process, and finally improves the damping stability.

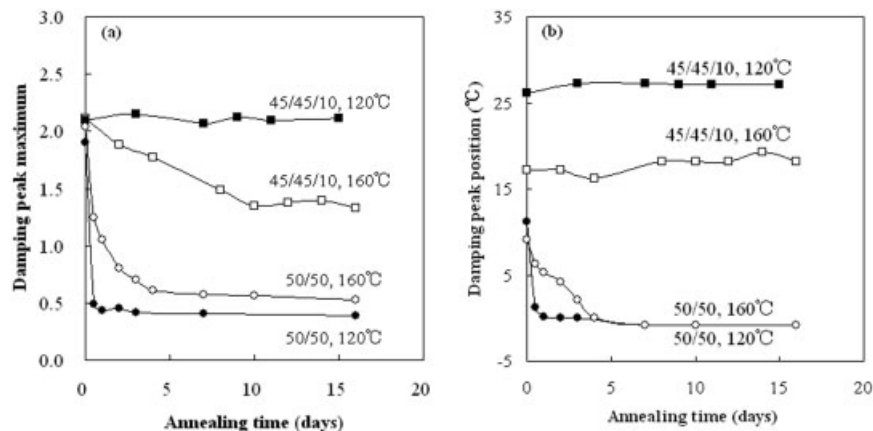


Figure 4 Effect of composition and hot-pressing temperature on damping stability for CPE/DZ and CPE/DZ/BPSR annealed at 50°C for different annealing times: (a) damping peak maximum and (b) damping peak position.

DSC results agree with SEM observation. As can be seen in Figure 6(a), when the measurements are carried out just after hot-pressing, DSC heating curves exhibit a small melting peak for the samples hot-pressed at 120°C, and no melting peak can be observed for the samples hot-pressed at 160°C. The small peak around 120°C should be attributed to the melting of a small amount of polyethylene crystallites, considering the melting points of DZ and BPSR are 96°C and 160°C, respectively. However, as shown in Figure 6(b), for the CPE/DZ (50/50) hybrids annealed at 50°C for 16 days, a large peak can be observed around 90°C, corresponding to the melting of DZ crystallites. Therefore, the sharp decrease in the damping peak maximum against annealing for CPE/DZ (50/50) hybrids should be attributed to the phase separation resulting from the crystallization of the components.

An interesting point should be noted that for annealed CPE/DZ/BPSR (45/45/10) hybrid hot-pressed at 160°C, a novel melting peak appears around 70°C, corresponding to the melting of flower-like crystal-

lites. Moreover, for annealed CPE/DZ (50/50) hybrids, a shoulder peak at the same position can also be observed. Since the melting point of DZ is 96°C, it is certain that these peaks can't be attributed to pure DZ crystallites. Further studies show that the crystalline phase, which has been formed during annealing, contains not only pure DZ crystallites but also some CPE-DZ or CPE-DZ-BPSR eutectics crystals, according to the elemental analysis. By means of energy-dispersion X-ray spectrometry (EDAX), both chlorine and sulfur can be detected in either the crystalline or the amorphous phase. A deeper investigation is being carried out by X-ray diffraction to characterize the crystal structure of such supermolecular complexes, and the results will be reported in a following article. Similar crystal structures have been reported for polyethylene oxide (PEO)-based complexes, such as PEO/*p*-dihalogenobenzenes,¹⁰ PEO/*p*-nitrophenol,¹¹ PRO/2-methyl resorcinol,¹² and PEO/hydroquinone.¹³ It was found that the interaction, such as van der Waals interaction and hydrogen bond between polymer

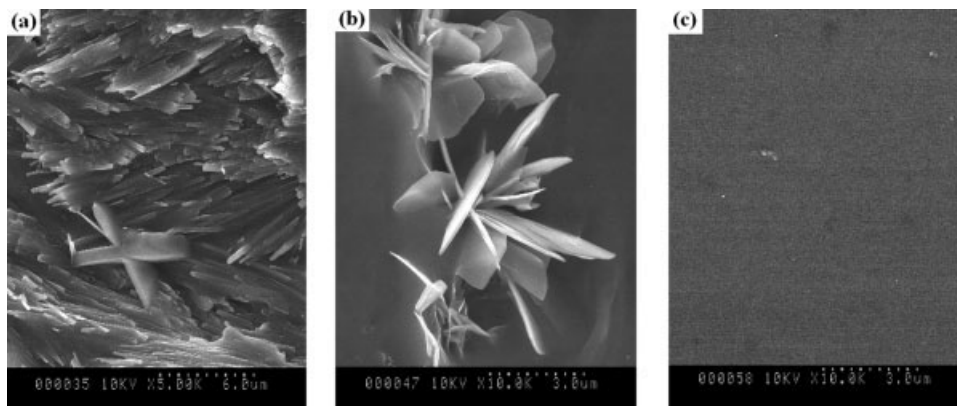


Figure 5 SEM micrographs of CPE/DZ and CPE/DZ/BPSR after annealing at 50°C for 7 days: (a) CPE/DZ = 50:50 hot-pressed at 160°C; (b) CPE/DZ/BPSR = 45:45:10 hot-pressed at 160°C; and (c) CPE/DZ/BPSR = 45:45:10 hot-pressed at 120°C.

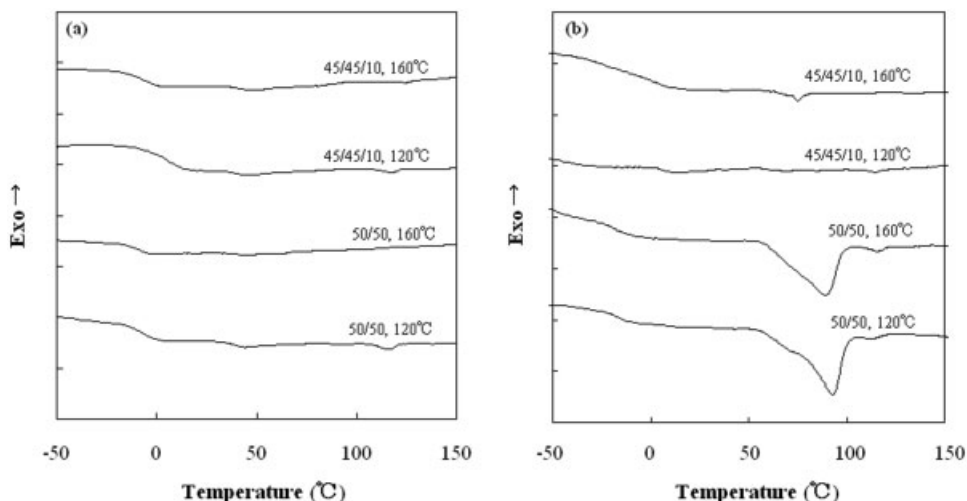


Figure 6 DSC heating curves for CPE/DZ and CPE/DZ/BPSR hybrids hot-pressed at 160°C and 120°C: (a) after hot-pressing and (b) annealed at 50°C for 16 days.

chains and organic small molecules plays a leading role in the stability of the crystalline phase.

CONCLUSIONS

An effort has been made to design a high-performance damping material by incorporating small molecular weight organic additives in CPE-based hybrids. It is found that either the enhancement of damping peak maximum or the control of its position can be achieved by adding DZ and BPSR.

The decrease in damping peak maximum against annealing for CPE/DZ hybrids can be attributed to the phase separation resulting from the crystallization of hybrids components. The damping stability can be improved excellently by adding a small amount of BPSR or changing hot-pressing temperature.

CPE–DZ or CPE–DZ–BPSR eutectics crystals may be formed in the crystalline phase during crystallization process. The characterization of phase morphology and crystal structure of such supermolecular complexes will be carried out in a following article.

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