Effects of a Hindered Phenol Compound on the Dynamic Mechanical Properties of Chlorinated Polyethylene, Acrylic Rubber, and Their Blend

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ABSTRACT: The dynamic mechanical properties of binary hybrids of chlorinated polyethylene (CPE) and acrylic rubber (ACM) with 3,9-bis{1,1-dimethyl-2[β-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyloxy]ethyl}-2,4,8,10-tetraoxaspiro[5,5]-undecane (AO-80) and their ternary hybrids were investigated. The addition of AO-80 was successful in tailoring the damping profile. The ACM/AO-80 hybrids show only one relaxation, which is larger than that of pure ACM, whereas for the CPE/AO-80 hybrids, one novel relaxation appears above the glass-transition temperature of CPE. In the case of CPE/AO-80/ACM, a supramolecular network was formed by a crosslink due to hydrogen bonding. The replacement of a part of CPE by ACM increased the value in the middle of two peaks. The AO-80 molecule, which is a bifunctional hydrogen-bonding acceptor, was found to act as a compatibilizer. In addition, in such ternary hybrids, the tan δ value in the middle of the two peaks was found to be proportional to the slope of the E' curve at an identical temperature. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2468–2473, 2001

Key words: dynamic mechanical property; hydrogen bond; supramolecular network; chlorinated polyethylene; acrylic rubber

INTRODUCTION

Numerous applications are being found for polymers with low frequency vibration and sound wave damping in sonic and ultrasonic ranges, particularly in aircraft, automobile, tall building, and appliance industries. Based on the damping theory,[1–5] the magnitude of damping can be determined from dynamic mechanical behavior. The loss modulus E'' or the loss tangent tan δ is a measure of the damping, which requires transformation of mechanical energy into heat. In real damping applications, wide variations of temperature and frequency are usually experienced;

thus, damping systems with a high and broad tan δ range are required. In general, for outdoor or machinery applications, good damping materials should exhibit a high loss factor (tan $\delta > 0.3$) over a temperature range of at least 60–80°C.[6]

The damping properties of a polymer are dominated by its glass transition. When the chain segments in a polymer backbone make de Gennes[7] reptation motions, molecular vibrational energy is converted into heat energy and a loss peak appears in a certain temperature range. The height and width of the loss peak are mutually linked. Therefore, obtaining a loss peak that is both high and wide at the same time is impossible.[8] Usually, for homopolymers, the useful damping range is approximately 20 to 30°C.[9–11] On the basis of the time-temperature superposition principle, this temperature range corre-
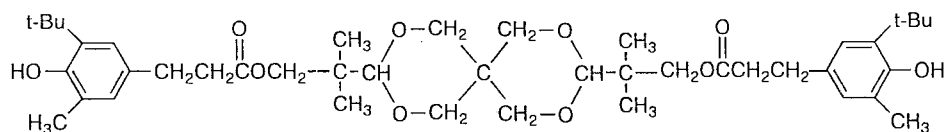
Figure 1 Chemical structure of AO-80.

sponds to two to four orders of frequency range. However, this range can hardly be met.

One solution to the problem lies in the selection of a multicomponent polymer system with controlled degrees of miscibility. Copolymer[12] and mechanical blends[13] have been used for a multicomponent system, but dynamic mechanical spectroscopy has often shown limited damping capability, as indicated by two narrow peaks. Another way to broaden the damping peaks is through the use of interpenetrating polymer networks (IPNs).[14–22]

Organic hybrids consisting of a chlorinated polymer (CPE) and a hindered phenol such as 3,9-bis{1,1-dimethyl-2[β-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyloxy]ethyl}-2,4,8,10-tetraoxaspiro[5,5]-undecane (AO-80)[23–26] and tetrakis [methylene-3-(3,5-di-tert-butyl-4-hydroxy phenyl)propionyloxy]methane (AO-60)[27–28] will have two high tan δ peaks separated by an intermediate region with a low tan δ value. To obtain a very broad, almost rectangular, transition range with high values for the area under the linear tan δ curve, it is important to control the molecular mixing in organic hybrids. When a chemically identical and short compound, such as chlorinated paraffin (CP), is deliberately added into CPE/AO-80, which exhibits two tan δ peaks, a relatively broad tan δ curve is obtained.[26]

On the other hand, the use of hydrogen bonds for the design of multiphase materials has recently attracted attention because a wide variety of dynamic functional systems can be obtained by such an approach.[29–30] Supramolecular mesomorphic complexes consisting of different and independent molecules have been designed and prepared by intermolecular hydrogen bonds.[31] In a recent preliminary study,[32] the author reported that the addition of AO-80 can increase the height of the tan δ peak of acrylic rubber (ACM), in particular, the peak position of ACM/AO-80 just appears in the intermediate region of the two peaks for CPE/AO-80. In addition, it is also noteworthy that hydrogen bonds exist in organic hybrids consisting of AO-80 and CPE[23–26] or ACM.[32] Thus, when ACM is added into organic hybrids consisting of CPE and AO-80, if a linking between the chains of CPE and the chains of ACM through bifunctional AO-80 molecules is achieved, the compatibility of CPE and AO-80 will be improved, which can lead to a broad damping behavior.

The purpose of this study was to develop a new material that has broader damping behavior. Additive effects of AO-80 on the dynamic mechanical properties of CPE and ACM were investigated. Their ternary systems were then investigated, and the molecular origin of such broad damping behavior was clarified.

EXPERIMENTAL

Materials

The CPE used as a matrix in this study, with a chlorination degree of 40 wt %, is a rubbery grade (Daisolac RA140, Daiso Co.). ACM, used as another matrix, is a kind of acrylic rubber (Nippl AR51, Nippon Zeon Co.). The low molecular weight compound used as dispersing material (AO-80), as shown in Figure 1, is a commercially available antioxidant (ADK STAB AO-80, Asahi Denka Industries Co.).

The CPE and/or ACM were first kneaded with a mixing roller for 5 min. AO-80 powder was then added to the kneaded CPE and/or ACM, and the mixture was kneaded again at room temperature for 10 min. The samples were made molten for 3 min and then pressed for 7 min at 160°C under a pressure of 180 kg/cm². Finally, the samples were cooled by ice water quenching to obtain films with a thickness of about 1 mm.

Dynamic Mechanical Analysis (DMA)

Dynamic viscoelastic measurements were carried out using a dynamic mechanical analyzer (DVE-V4, Rheology Co.) on sample specimens 20 mm in length, 5 mm in width, and about 1 mm in thickness. The temperature dependence of the dynamic tensile modulus was measured at a constant frequency of 110 Hz and at a heating rate of 3°C/min.
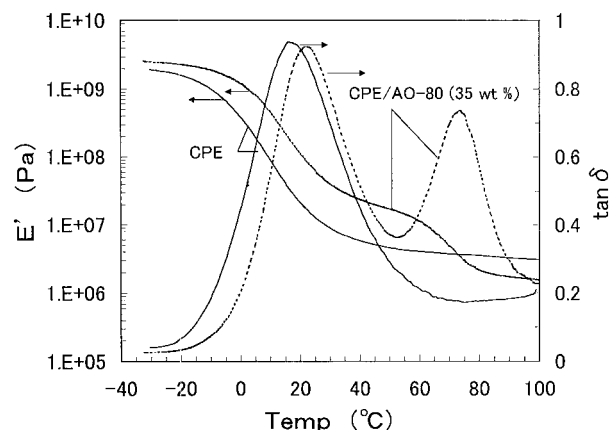
Figure 2 Temperature dependence of E′ and tan δ at 110 Hz for CPE and CPE/AO-80 (35 wt %).

Differential Scanning Calorimetry (DSC)

DSC measurements were carried out using a DSC-7 PerkinElmer calorimeter. The samples were heated from −100 to 160°C at a heating rate of 10°C/min to investigate the glass transition behavior of CPE/AO-80, ACM/AO-80, and CPE/AO-80/ACM hybrids.

RESULTS AND DISCUSSION

Binary Systems

Figure 2 shows the additive effects of AO-80 on the storage modulus E′ and loss tangent (tan δ) for CPE. The pure CPE exhibited only one relaxation, while the CPE/AO-80 samples clearly exhibited two relaxations. According to preliminary studies,[23–26] there is a CPE-rich phase and an AO-80-rich phase for CPE/AO-80, and these two transitions are attributed to the onset of micro-Brownian motion of the CPE chains within the CPE-rich phase, and to dissociation of the intermolecular hydrogen bonds within the AO-80-rich domains, respectively. Following the appearance of a novel relaxation on the high temperature side, CPE/AO-80 thinks about various applications. In the present study, the focus was limited to the damping material. In this case, the magnitude of the second peak is of particular interest. According to preliminary results,[25] it was found that the height of the second peak increases with increases in the AO-80 content, particularly when the AO-80 content is larger than 40 wt %. The magnitude of the second peak is larger than that of the glass transition of pure CPE. Consequently, a CPE/AO-80 mixture is a good candidate for a damping material. As seen in Figure 2, however,

the value in the middle of the two peaks for CPE/AO-80 is relatively low. Therefore, it is necessary to improve the temperature dependence of tan δ.

Figure 3 shows the additive effects of AO-80 on E′ and tan δ of ACM. With the addition of AO-80, it was observed that the height of the tan δ peak increases and the position of the peak shifts to a higher temperature. The single tan δ peak and the transparency of the sample demonstrate that ACM is compatible with AO-80. The increase and shift of the tan δ peak result from the formation of intermolecular hydrogen bonds between the hydroxyl groups of AO-80 and the side chains of ACM.[32–33]

A comparison of ACM/AO-80 with CPE/AO-80 showed that the effects of AO-80 vary depending on the kind of the matrix polymers. In addition, a relatively high peak for ACM/AO-80 just appeared in the relatively low intermediate region of two peaks for CPE/AO-80. Thus, the addition of ACM to CPE/AO-80 will improve the temperature dependence of tan δ. This is considered to be a useful approach for designing a broader damping material.

Ternary Systems

The replacement effects of a part of the matrix polymer CPE by ACM on the temperature dependence of tan δ are shown in Figure 3. With an increase in the ACM content, the first peak decreases, whereas the second peak increases. It is possible that these two peaks are made the same at a certain content of ACM (about 88/12). Moreover, it is remarkable that the value in the middle region of the two tan δ peaks also increases with an increase in the ACM content. Thus, it was
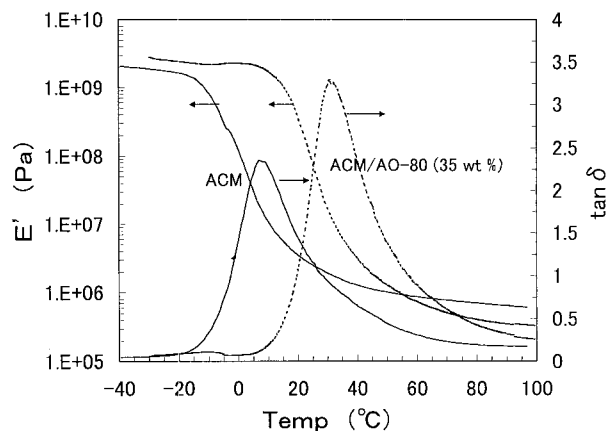

Figure 3 Temperature dependence of E′ and tan δ at 110 Hz for ACM and ACM/AO-80 (35 wt %).
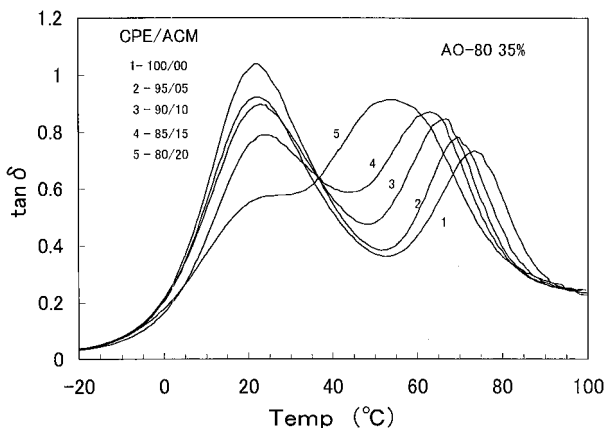
Figure 4 Temperature dependence of tan δ at 110 Hz for CPE/AO-80 and CPE/ACM/AO-80.

concluded that the temperature dependence of tan δ for CPE/AO-80 can improve by replacing a part of the matrix polymer CPE with ACM, which is compatible with AO-80. In particular, it is noteworthy that as a result, the same performance as that of many IPNs can be obtained.[14–22] Therefore, this is considered to be a new approach to improving the temperature dependence of tan δ.

To examine the distribution of ACM molecules within the CPE/AO-80 hybrid, in which two phases exist, the positions of the two relaxations should be considered. As seen in Figure 4, the second peak, which is attributed to the AO-80-rich phase, shifted greatly toward a lower temperature, and the first peak similarly shifted toward a higher temperature; however, the shift of the first peak was not as great as that of the second peak. The same tendency was also observed from the DSC, as shown in Figure 5. It is inferred from those data that the ACM molecules were distributed preferentially in the AO-80-rich phases.

Moreover, the dispersion state of the ACM molecules in the CPE/AO-80 hybrids should be noted. The ACM/CPE samples were nontransparent, indicating that ACM is incompatible with CPE. In contrast, the ACM/CPE/AO-80 samples were transparent. Thus, the AO-80 molecules can be considered to be a kind of compatibilizer. However, as seen in Figure 4, ACM/CPE/AO-80 clearly exhibited two relaxations, and it therefore cannot be said to be completely compatible. These findings suggest that the morphology of ACM/CPE/AO-80 is very complicated.

As seen in Figures 2 and 3, the peak positions of pure ACM and of the CPE-rich phase of CPE/AO-80 (35%) are 7 and 22°C, respectively. Thus, if ACM is compatible with the CPE-rich phase, the

peak positions of their blends should appear between 7 and 22°C. However, the peak positions were actually above 22°C in each case. For this reason, the position of the first peak for ACM/CPE/AO-80 cannot be explained in terms of compatibility. This suggests that other mechanisms may exist.

The following two basic facts should be noted. One is that only a little AO-80 existed in the continuous phase of CPE for the CPE/AO-80 hybrids. Another is that AO-80 can be considered to be a bifunctional hydrogen-bonding acceptor. It has been shown in previous studies[23–26,32–33] that in hybrids consisting of AO-80 and CPE or ACM, hydrogen bonding occurs between a hydroxyl group of AO-80 and an α-hydrogen of CPE or a carbonyl group of ACM. When AO-80 was added to a continuous phase of CPE containing ACM, a super-molecular network was probably formed, as shown in Figure 6. Thus, the relatively high position of the first relaxation can be explained in terms of the crosslinked structure of CPE/AO-80/ACM.

In addition, the same discussion applies to the AO-80-rich domain that leads to the second relaxation. The picture that emerges of such ternary systems described above can be summarized as follows. There is a CPE-rich continuous phase and an ACM/AO-80-rich domain in CPE/ACM/AO-80. In the former, some of the AO-80 and the ACM molecules are dispersed in the CPE matrix, and those AO-80 molecules simply act as a crosslinking of ACM and CPE chains. In the latter, the CPE chains are incorporated into the domains in which ACM is compatible with AO-80.

The E' curve is also of particular interest. Figure 7 shows the temperature dependence of E' for
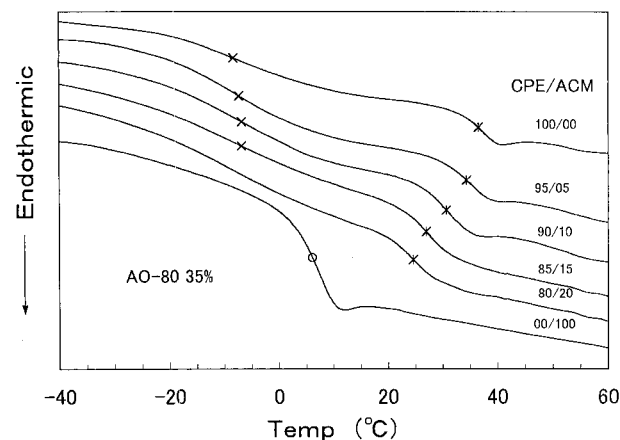

Figure 5 DSC thermograms of CPE/AO-80 and CPE/ACM/AO-80 at a heating rate of 10°C/min.
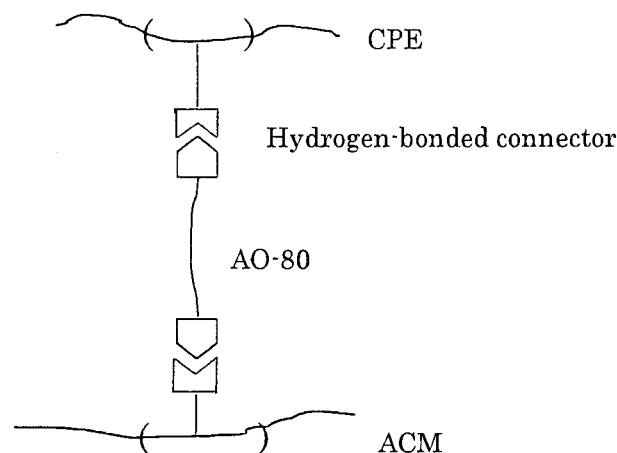
Figure 6 Schematic structure of supramolecular crosslinked polymers obtained from AO-80, CPE, and ACM.

CPE/ACM/AO-80 (35 wt %). The E′ curve clearly shows two relaxation regions in which E′ changes rapidly with temperature, as well as three regions that show a much more gentle decrease in slope, resembling the behavior in the region of a plateau. For CPE/ACM/AO-80 (35 wt %), the E′ values at the first plateau and at the last plateau are smaller than those of CPE/AO-80 (35 wt %). It follows from what has been said thus far that ACM is a kind of plasticizer. In contrast, with an increase in the ACM content, the E′ value in the intermediate plateau initially decreases and then increases. For CPE/AO-80, the rise in the E′ value in the intermediate plateau is caused by the additive effect as filler particles and the crosslinking effect of the AO-80-rich domain. The decreases in the E′ value at the intermediate plateau can be regarded as a plasticization effect of such an AO-80-rich domain. However, the increase in the E′ value can be explained in terms of the appearance of a super-molecular network.

For CPE/ACM (85:15)/AO-80 (35 wt %), though the second peak is higher than the first peak (Fig. 4), the drop in the second relaxation is larger than that of the first relaxation (Fig. 7). From this comparison, it was also confirmed that the second relaxation is different from the glass transition. It is conceivable that the second relaxation does not originate in the micro-Brownian motion of either a polymer component such as CPE or ACM, or a small molecule component such as AO-80, but rather that it arises due to their cooperative motion accompanying dissociation of the intermolecular hydrogen bonds.

As seen in Figure 7, it was also found that the slope of the E′ curve, in an intermediate region in which tan δ showed a minimum value, increases with an increase in the ACM content. This can be explained by considering the variety of interactions between AO-80 molecules and CPE or ACM chains (for example, AO-80CPE or AO-80ACM or CPEACM).

For a number of polymers that do not contain diluents, Heijboer[33] analyzed the relationship between the temperature coefficient of the elastic modulus and the tan δ value. He found that the tan δ value is proportional to a temperature coefficient of the modulus at a corresponding temperature where there is no relaxation process. As shown in Figure 4, the value in the middle of the two tan δ peaks decreases with increases in the ACM content when the addition of AO-80 is the same (35 wt %). Compared with this result, as seen in Figure 7, the order in the slopes of the E′ curve agreed with that of the tan δ value at an identical temperature. The tan δ value in the middle of the two peaks is plotted against the slope of the E′ curve at an identical temperature in Figure 8. From this figure, a correlation between the tan δ value in the middle of the two peaks and the slope of the E′ curve at an identical temperature was obtained. This agreed with the relationship observed for a ternary system consisting of CPE, chlorinated paraffin, and AO-80.

CONCLUSION

The dynamic mechanical properties of binary hybrids of CPE and ACM with AO-80 and their ternary hybrids were investigated. The ACM/AO-80 hybrids show only one relaxation, whereas for the CPE/AO-80 hybrids one novel relaxation
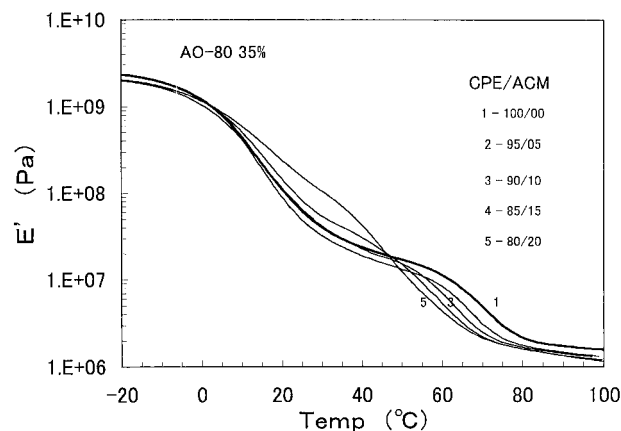

Figure 7 Temperature dependence of E′ at 110 Hz for CPE/AO-80 and CPE/ACM/AO-80.
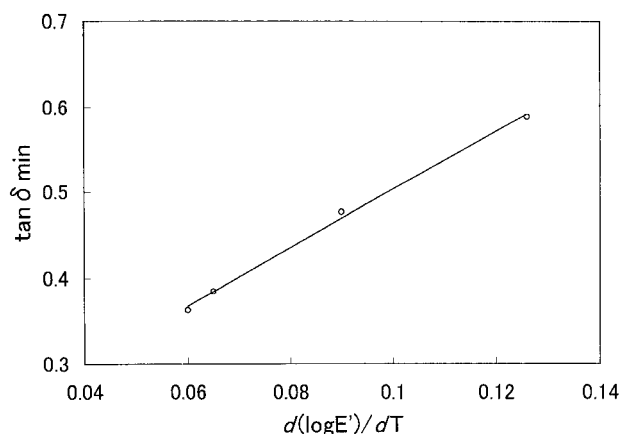
Figure 8   Height of the tan δ peak as a function of the temperature coefficient in the E′ curve for CPE/ACM/AO-80.

appears above the glass-transition temperature of CPE. The replacement of a part of the matrix polymer CPE by ACM, which is compatible with AO-80, cannot only adjust the height of the two peaks, but it can also increase the value in the middle of the two peaks. In addition, in such ternary hybrids, the tan δ value in the middle of the two peaks was found to be proportional to the slope of the E′ curve at an identical temperature.

For CPE/ACM/AO-80, most of the ACM molecules were preferentially distributed in an AO-80-rich domain. The improvement of many behaviors, such as the temperature dependence of tan δ and the degree of transparency by the replacement of ACM, is thought to be due to the formation of a super-molecular network. In addition to the discovery of the damping property and the shape-memory effect, the AO-80 molecules can be considered to be a kind of compatibilizer.

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