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NOTES

Dynamic Mechanical and Adhesive Properties of Acrylate Rubber/ Chlorinated Polypropylene Blends Compatibilized with a Hindered Phenol Compound

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During recent years there has an increased interest in the use of polymers for low-frequency vibration and sound waves damping in the sonic and ultrasonic ranges. This is because noise and vibration has become a serious form of pollution. Based on the damping theory,[1] 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 damping properties. From an engineering point of view, there are basically two kinds of damping modes of interest when using polymers. Large E'' value is desired for extensional damping, and large tan δ value is desired for constrained-layer damping. Whenever any type of constraining layer is applied on top of a damping layer, the constrained-layer damping is likely to exceed the extensional damping. Therefore, in the present study, the focus was limited to how to enhance tan δ value of some polymers or their blend.

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,[2] On the other hand, homopolymer have narrow glass-transition regions (20–30°C).[3] The glass transition of a given homopolymer at a given frequency can be controlled by many conventional means, such as the additions of plasticizers and fillers.[4] However, the height and width of the loss peak for a given polymer are mutually linked. Therefore, obtaining a loss peak that is both high and wide is impossible at the same time.[5] One solution to the problem lies in the selection of a multi-component polymer system with controlled degrees of miscibility. Copolymer[6] and mechanical blends[7] have been used for a multi-component system. Another method broadening the damping peaks is through the use of interpenetrating polymer networks (IPNs).[8] However, their dynamic mechanical spectroscopes have often shown limited damping capability. Thus, to obtain a more good damping property, a new concept for designing damping material is needed.

Organic hybrids consisting of a chlorinated polymer (CPE) and 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) showed a novel transition above the glass-transition temperature of CPE.[9] This fact will provide a new concept for developing damping material. However, the minimum value between two tan δ peaks is lower. 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 chlorinated paraffin (CP)[10] or acrylate rubber (ACM)[11] is deliberately added into CPE/AO-80, a relatively broad tan δ curve has been obtained.

In another recent study,[12] we also investigated the effects of the addition of AO-80 on a blend of ACM and chlorinated polypropylene (CPP). It was found that a ternary blend of ACM/CPP (7:3) with AO-80 (35 wt%) showed a novel tan δ peak between two peaks corresponding to ACM and CPP. This peak is attributed to an interfacial layer where a super-molecular network is formed.

On the other hand, the polymeric damping material is never used individually because it must be usually affixed to the vibration body by an adhesive or glue. Therefore, in addition to enhancing the tan δ value, the

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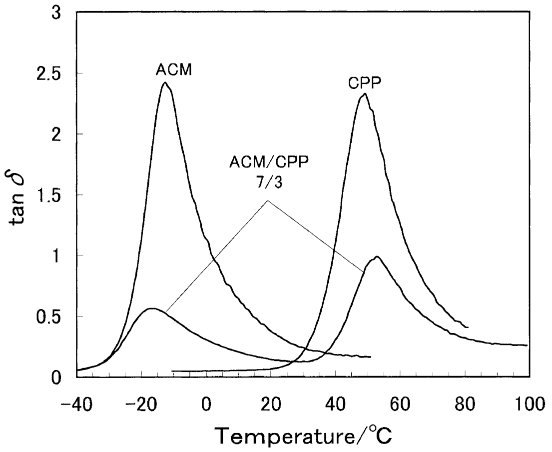

Figure 1. Temperature dependence of tan δ at 11 Hz for ACM, CPP and their blend.

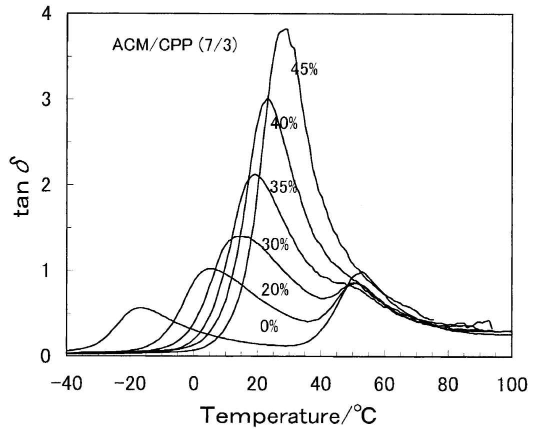

Figure 2. Temperature dependence of tan δ at 11 Hz for ACM/CPP (7:3) with AO-80.

providing of adhesiveness is also very important in real damping applications. In this study, we selected a CPP having more chlorine for enhancing compatibilization of CPP and AO-80 and obtaining more good damping property, and a ACM showing lower glass-transition temperature for shifting the position of the tan δ peak to room temperature. The additive effects of AO-80 on the adhesive properties in addition to the dynamic properties were also investigated. The final goal is to obtain a super-damping material with self-adhesive properties.

EXPERIMENTAL

The ACM used in this study was commercial grade (Nippon Zeon Co., Ltd. Nipol AR42W); CPP with 29.5% of the weight content of chloride was a thermoplastic resin (Nippon Paper Industries Co., Ltd. Superchlon 803MWS). The AO-80 (as shown in Figure 1 of ref 12) used as a compatibilizer, was a commercial antioxidant (ADK STAB AO-80; Asahi Denka Kogyo K.K.). The ACM and CPP were kneaded by mixing rollers for 5 min at 90°C and then the AO-80 powders were added to the kneaded ACM/CPP mixture. The kneaded samples were made molten for 3 min and then were pressed in a laboratory hot press at 160°C for 7 min under a pressure of 19.6 MPa. Finally, the samples were cooled to obtain films by quenching into ice-water bath.

The dynamic mechanical measurements were carried out using a dynamic mechanical analyzer (Rheology Co., DVE-V4) on sample specimens of the following dimensions: 20 mm long, 5 mm wide, and 1 mm thick. The temperature dependence of dynamic tensile moduli was measured at a constant frequency of 11 Hz and at a heating rate of 3°C min^{-1}. In addition, for peel test, films, approximately 0.5 mm thick, were compression mold at 160°C between 0.1 thick polyester film. The peel adhesion to stainless steel of strips with dimensions $25 \times 150\ \mathrm{mm}^2$ were carried out in 90° using Toyoseiki Strograph V at 10, 25, 40°C, respectively. The grip separation rate was 50mm min^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of tan δ for ACM, CPP and their blends. ACM and CPP exhibited a relatively high tan δ value (> 2.3). The peak area under the tan δ temperature curves, which is abbreviated as TA, can be considered to be a damping index, which is a measure of the energy dissipation of a transition.[13] Both of ACM and CPP showed relatively large TA value (52.9 and 43.4°C), they therefore can be considered to be a good damping homopolymer. If the TA value of ACM/CPP blend obeys the simple additive mixing rule reported by Ogawa *et al.*[14] for a compatible copolymer, their blends will have a possibility to use for damping materials. However, the tan δ curve of their blend has shown limited damping capability as indicated by two narrow peaks (its TA value is only 30.7°C). This is because the blends of ACM and CPP are immiscible.

To obtain a very broad transition range with high value for the area under the tan δ curve, it is of great importance to modify the compatibility of ACM/CPP blends. AO-80 has been found to heighten the tan δ value of ACM and CPP, indicating that AO-80 interacts strongly with both ACM and CPP by intermolecular hydrogen bond.[12] Consequently, adding such AO-80 containing two hydrogen-bonding acceptors into their blends makes it possible to compatibilizer ACM and CPP phase. The additive effects of AO-80 on the tan δ curves of a polymer blend of ACM and CPP (7:3) are shown in Figure 2. As shown in the figure, the addition of 35% AO-80 pronounced these tan δ peaks and leads to a higher temperature shift of ACM peak but did not affect the location of CPP peak. This result suggests that the AO-80 molecules may preferentially mix with ACM polymers. Furthermore, when the AO-80 content is more than 35%, those ternary blends show only one peak apparently, implying that ACM and CPP are compatibilized by AO-80. That is, AO-80 can be considered to be a new type of compatibilizer. This is due to formation of a super-molecular network where ACM and CPP chain couples by an AO-80 molecule that is a bi-functional hydrogen bonding acceptor.

The magnitude of the maximum value of the tan δ peak is worthy of notice. In the case of a given polymer blend, the magnitude and shape of its tan δ peak depends on the size of the dispersion domain. In general, the tan δ peak of the compatible blend becomes relatively low and broad.[15] However, in the case of ACM/CPP blends with AO-80 of more than 40 wt%, its tan δ peak is higher and broader than that of pure ACM or pure CPP. Such peculiarity may have never seen before. So far, obtaining a loss peak that is both high and wide is impossible at the same time because the height and width of the loss peak for a given polymer are mutually linked. In addition, we also note that the value of tan δ of ACM/CPP (7/3) with 45 wt% of AO-80 at room temperature is about 4. This value is markedly higher than that of common damping materials (< 2). This signifies that such ACM/CPP/AO-80 ternary blend has the potential to be a new type of damping material with very high performance.

Thereupon, we shift focus on the TA values of ACM/CPP blends with AO-80. The additive effects of AO-80 on the TA values of ACM/CPP are summarized in Figure 3. The TA value against the AO-80 content exhibits a bend point at the critical content of *ca.* 30 wt%. When the AO-80 content is smaller than the critical content, the increase of the TA was found to be obeying the simple additive mixing rule, signifying that AO-80 is compatible with ACM phase. In contrast, a sharp increase of the TA value above 35 wt% of the AO-80 content was observed. This trend agrees with our previous result.[12] Therefore, it can be considered to be due to the appearance of a new tan δ peak between both glass transitions of ACM and CPP, and it is attributed to the formation of an interfacial layer between ACM and CPP. The magnitude of the TA value of ACM/CPP blends with more AO-80 is also particular interest. As can see in Figure 3, the TA value of ACM/CPP (7/3) with AO-80 of 30 wt% is above 90, it is 3 times of ACM/CPP (7/3).

Briefly, the discussion above suggests that AO-80 plays a critical role in determining the dynamic mechanical properties of ACM/CPP blend. Thereupon, we shift attention to how the addition of AO-80 into ACM/CPP blend results the adhesive properties. The relationship between the peel strength and the content of AO-80 is shown in Figure 4. The addition of AO-80 of more than 30 wt% results in a very large increase in the peel strength. The magnitude of the peel strength is above 10 times than that of general adhesive type. The high adhesive performance is very useful in real damping application. Such damping material not only can reduce the total cost, but also is mild to the environment as well. The discussion about the mechanism that the addition of AO-80 into ACM/CPP blend can cause the grant of the adhesion will be present in a later paper.

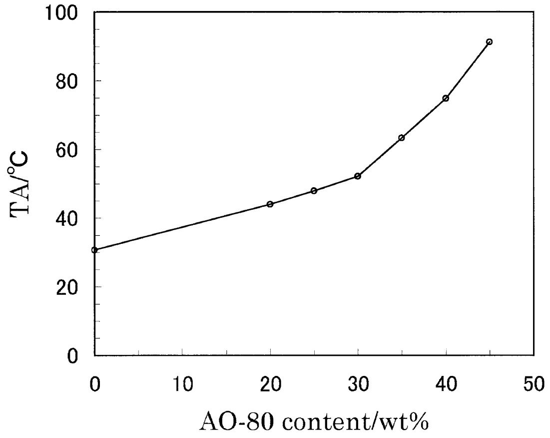

Figure 3. Dependence of TAs (the peak area under the tan δ-temperature curves) of the ACM/CPP/AO-80 ternary systems on the AO-80 content.

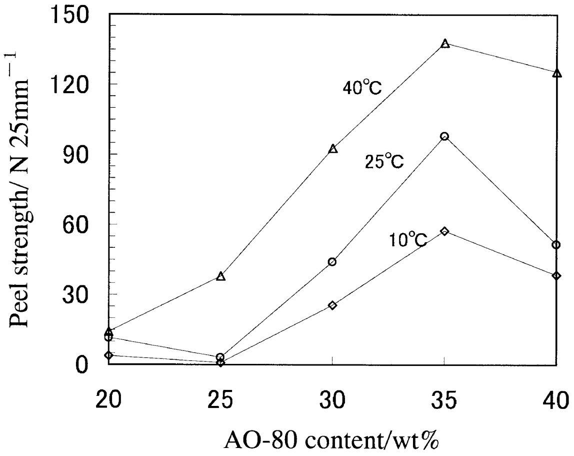

Figure 4. Dependence of peel strength (90°) of the ACM/CPP/AO-80 ternary systems on the AO-80 content.

CONCLUSIONS

The dynamic mechanical and adhesive properties of the ternary blends of ACM/CPP with AO-80 were investigated. From what has been discussed above, we can concluded that the addition of the hindered phenol compound such as AO-80 into a incompatible ACM/CPP blend can cause not only a remarkable enhancement of the damping properties but also the grant of very large peel strength.

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