

Review

A NOVEL SECOND-ORDER TRANSITION IN ORGANIC HYBRIDS CONSISTING OF POLYMERS AND SMALL MOLECULES

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Abstract A novel transition appeared above the glass transition temperature of chlorinated polyethylene (CPE) for binary blends of CPE and additives such as organic small molecules or oligomers. This transition was assigned to the dissociation of intermolecular hydrogen bonds between the polymer and additive within the additive rich phase. Of particular interest is that a novel pyramid crystal was observed in the annealed CPE/hindered phenol blends. Another intriguing observation is that these polymer/small molecule blends organized by intermolecular hydrogen bonding have several potential properties, such as shape-memorization, self-restoration, self-adhesiveness and super damping.

Keywords Organic hybrid, Second-order transition, Shape memory effect, Damping, Self-restoration

INTRODUCTION

Recently, many studies have been carried out on the control of morphology in various polymer blends. However, most studies were restricted to either fully compatible or incompatible systems. On the other hand, in some particular polymer/polymer and polymer/small molecule systems^[1-5], a new transition, which was thought to be due to the cooperative motions of constituent components within a new phase formed by incomplete separation of two components, has been observed. However, since the observed loss tangent ($\tan\delta$) peak in these systems was weak, the molecular mechanism underlying this phenomenon is still unclear. Therefore, in order to obtain a relatively large transition, a systematic study on intermolecular interaction and phase-separated structure is needed.

In general, intermolecular hydrogen bonding interaction is important in determining polymer properties and in designing new polymer architectures^[6-8]. We considered here a blend system based on a concept of the sophisticated use of hydrogen bonds. The diffusion of a polymer chain is limited by the repetitive motion on account of its large molecular weight, probably resulting in the incorporation of some polymer segments into another component. Moreover, unlike small molecules, polymers also show a longer relaxation time, giving them some good molding qualities and mechanical properties. Therefore, polymers are suitable for use as a matrix. By contrast, small molecules are superior to polymers in the control of compatibility, the direction and dynamic rearrangement of hydrogen, as well as their selectivity. Therefore, among several possible combinations, a polymer/small molecule system is preferable for experimental study.

The purpose of this work is to obtain a new transition derived from the dissociation of intermolecular hydrogen bonds, and to develop a new material having a variety of functions based on this transition phenomenon. In the present study, the dynamic mechanical properties of some polar polymers hybridized by bi- and multi-functional organic small molecules were investigated to demonstrate that the novel transition is a

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Received February 1, 2001; Accepted February 22, 2001

common phenomenon in polymer/small molecule systems having strong intermolecular hydrogen bonds. Thereupon, the origin of this novel transition was elucidated, and the influence of the aggregation state of the organic small molecules and thermal molding conditions was discussed. Finally, an attempt has been made to clarify the potential abilities for possible application of this novel transition in materials.

A Novel Second-Order Transition^[9-12]

A series of polymer/organic small molecule blends were prepared for studying the relationship between structure and various properties (or functions). The polymers used were chlorinated polyethylene (CPE, unless otherwise specified) with a chlorination degree of 40 wt%, chlorinated polyethylene (CPE30, with a chlorination degree of 30 wt%), epichlorohydrin rubber (CO, with a chlorination degree of 37 wt%), acrylate rubber (ACM) and chlorinated polypropylene (CPP, with a chlorination degree of 26 wt%). The organic small molecular substances used were some multi-functional amines and phenols, the chemical structures of which are shown in Fig. 1. The CPE powders were kneaded for 5 min by two mixing rollers and then the powders of the organic small molecule were added to the kneaded CPE. The mixture was kneaded for 10 min at room temperature into sheets that were directly cut into rectangular pieces as the measuring samples. The organic small molecular substances in the kneaded samples were dispersed into the CPE matrix in the form of crystalline particles which is called the unpressed sample. The kneaded samples were molten for 3 min and were then pressed with a laboratory press at 160°C for 7 min under a pressure of 180 kg/cm², then the pressed samples were quenched in the ice-water bath.

Figure 2 shows the temperature dependence of $\tan\delta$ for CPE, unpressed and pressed CPE/AO-80 (50 wt%), respectively. The unpressed sample shows only one peak, whereas for the pressed sample, a novel peak appears above the glass transition (T_g) of CPE. In addition, the dynamic mechanical behaviors of other polymer/organic small molecule systems also were investigated. As can be seen in Fig. 3, for a CO matrix, the addition of AO-80 also caused a novel transition above T_g of CO. Moreover, the additive effects of three types of small molecules, the chemical structures of which are shown in Fig. 1, on the temperature dependence of $\tan\delta$ of CPE are shown in Fig. 4. All samples clearly exhibit two significant peaks. These results demonstrate that this novel transition appearing above T_g of the matrix polymers is a common phenomenon in polymer/small molecule systems having a strong intermolecular hydrogen bond.

The appearance of two $\tan\delta$ peaks implies that these additives are incompatible with the polymer matrix. However, it should be pointed out that these sheet samples were transparent, suggesting that these polymer/small molecule systems are probably different from the usual completely incompatible polymer blend, that is, a specific molecular-aggregation state may be formed during the hot press process performed above the melting point of small molecule. In the following discussion, attention is mainly focused on the case of a blend of CPE and hindered phenols.

Assignment of Two $\tan\delta$ Peaks

To examine the origin of two $\tan\delta$ peaks, the author first compared the position of the $\tan\delta$ peak for two different polymers admixed with AO-80. Figure 5 shows the temperature dependence of $\tan\delta$ for CPE (with a chlorination degree of 40 wt%)/AO-80 (35 wt%) and CPE30 (with a chlorination degree of 30 wt%)/AO-80 (35 wt%) samples. It was found that the position of the first $\tan\delta$ peaks of the two samples depended on the kind of CPE. Thus, it was confirmed that the first $\tan\delta$ peak was attributable to the glass transition of the matrix polymer.

In addition to the position of the first $\tan\delta$ peak, its magnitude is also remarkable. To determine the dispersion state of AO-80 molecules in a CPE matrix, the dependence of the height of first $\tan\delta$ peak on AO-80 content was investigated. Figure 6 shows the temperature dependence of $\tan\delta$ for the CPE/AO-80 hybrids. The CPE/AO-80 hybrids show a monotonous decrease after an initial increase in the first $\tan\delta$ peak. However, after the addition of a small amount of AO-80 the maximum value of $\tan\delta$ of the first peak becomes higher than that of the pure CPE. In some completely incompatible systems, such as polymer blends^[13], copolymers^[3], and plasticized polymers^[14], the maximum value of the $\tan\delta$ peak of one component decreases by blending with another component. According to the results of previous work^[15] on the additive effects of AO-80 on various polymers such as acrylic rubber, styrene butadiene rubber, nitrile butadiene rubber, polyvinyl acetate, and

chlorinated polypropylene, the maximum values of the $\tan\delta$ peaks of those systems were found to be drastically increased by the addition of AO-80. Therefore, the observed increases in the first $\tan\delta$ peak of compatible CPE/AO-80 systems in which the AO-80 content was lower than 10% can be ascribable to the positive effects of AO-80. From what has been discussed above, we can also conclude that some of the AO-80 molecules are also dispersed in the CPE matrix when the AO-80 content is larger than 15%.

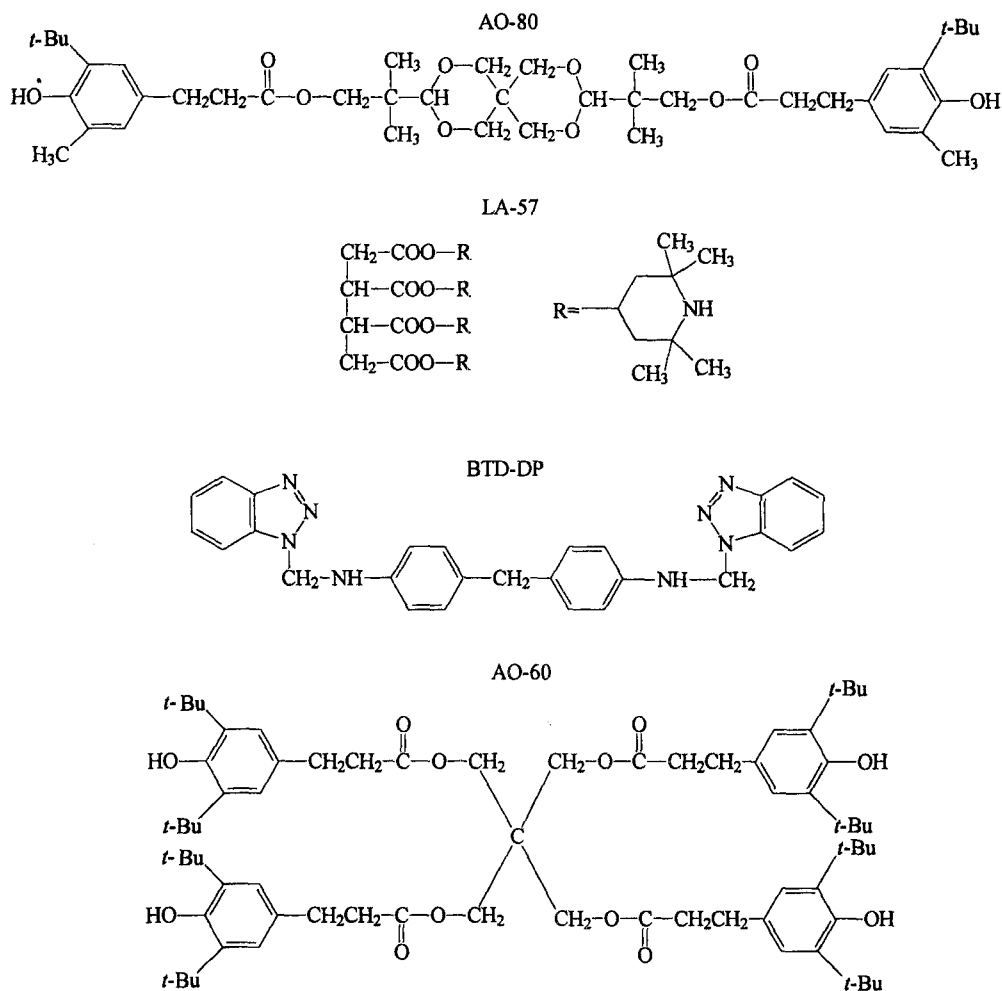


Fig. 1 Chemical structures of some organic small molecular substances used, in the present work

On the other hand, as can be seen in Fig. 6, the position of the second $\tan\delta$ peak is independent of the matrix polymer. This result suggests that the second peak is associated with the AO-80 domains. However, the domain of pure AO-80 does not show a relaxation peak at 50–80°C. Therefore, the appearance of the second peak also seems to be related to the CPE matrix.

Figure 7 shows the temperature dependence of the storage modulus E' for pure CPE, unpressed and pressed CPE/AO-80 (50 wt%), respectively. In the case of pressed CPE/AO-80 (50 wt%), the storage modulus E' curve shows clearly two dispersion regions in which the E' changes rapidly with temperature, as well as three other regions which show a much more gentle decrease in slope, resembling the behavior in a plateau region. While the first dispersion at 10°C is attributed to the glass transition of the CPE-rich matrix, the second dispersion at 60°C corresponds to the transition of AO-80 domains, which is also related to the CPE matrix. The E' in the intermediate plateau is larger than those of pure CPE and the unpressed CPE/AO-80 (50 wt%). It implies that the

AO-80 domains showing higher modulus act as the junction crosslink points. The E' in the last plateau, which is denoted as the rubbery modulus, is smaller than that of pure CPE. Therefore, the agglomeration of AO-80 in the domain structure is released and is unable to behave as a junction point. In fact, AO-80 molecules act as the plasticizer of CPE.

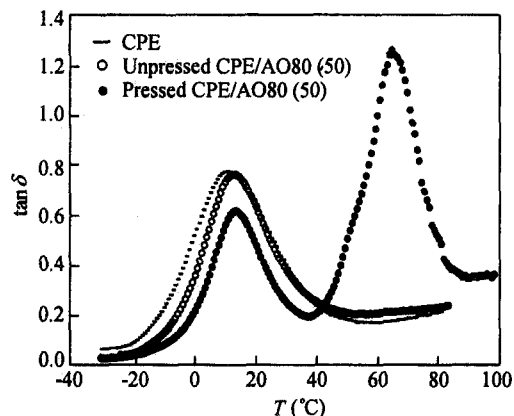


Fig. 2 Temperature dependence of loss tangent ($\tan \delta$) at 11 Hz for CPE, unpressed and pressed CPE/AO-80 (50 wt%)

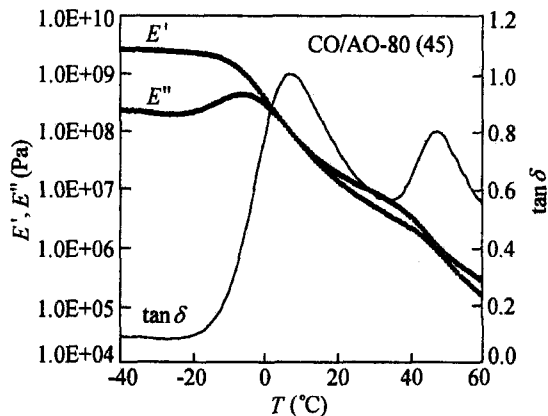


Fig. 3 Temperature dependence of storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) at 11 Hz for CO/AO-80 (45 wt%)

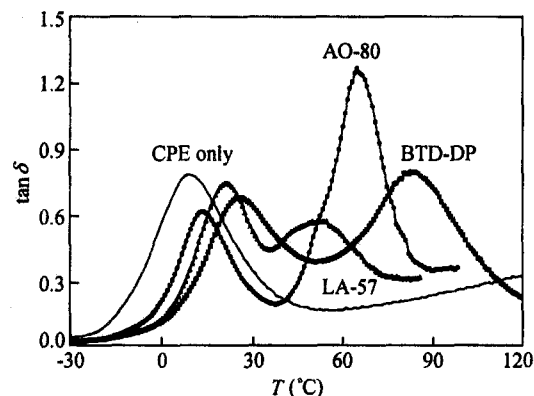


Fig. 4 Temperature dependence of loss tangent ($\tan \delta$) at 11 Hz for CPE/small molecule (50 wt%) systems

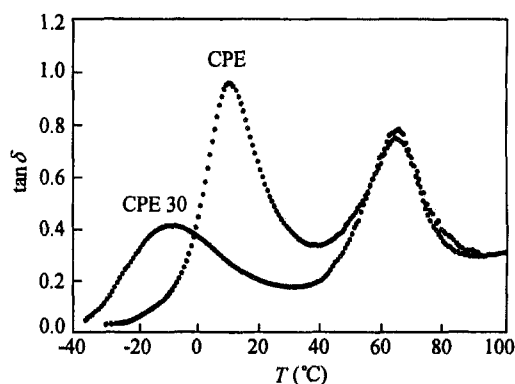


Fig. 5 Temperature dependence of loss tangent ($\tan \delta$) at 11 Hz for CPE/AO-80 (35 wt%) and CPE30/AO-80 (35 wt%)

To elucidate the structure of AO-80 domains, we performed DSC measurements. As shown in Fig. 8, the CPE and AO-80 are crystalline materials, while the unpressed CPE/AO-80 sample exhibits a specific melting peak corresponding to the crystals of pure AO-80. For the pressed sample, both the melting peaks of CPE and of AO-80 disappear. It is well known that organic small molecular substances within a polymeric matrix are easily crystallizable^[16]. Although AO-80 was separated from the CPE, however, the AO-80 molecules within the CPE matrix did not crystallize. This implies that the crystallization of AO-80 molecules was suppressed by some CPE chains, which were incorporated into the AO-80 domains.

Figure 9 shows the DSC curves for CPE, AO-80, unpressed and pressed CPE/AO-80 (50 wt%) with a scanning rate of 10 K/min respectively. Two second-order transitions are clearly observed for pure AO-80, which is regarded as a semi-crystalline organic small molecule. The first transition appearing at 6°C is associated with the glass transition, while the second transition appearing at 69°C is considered to be a phase transformation from a true liquid state to a liquid which is fixed by the hydrogen bonds between hydroxyl groups of AO-80. As a

result, AO-80 at room temperature is supposed to be composed of an amorphous phase, a highly ordered phase and a crystalline phase.

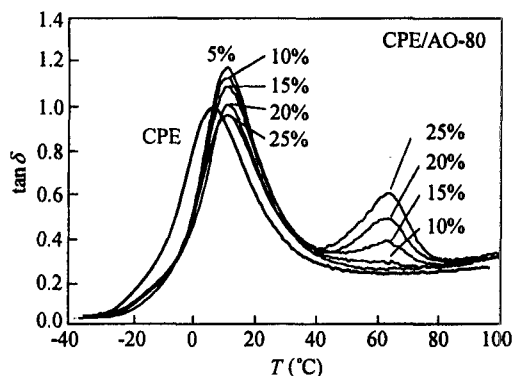


Fig. 6 Temperature dependence of loss tangent ($\tan \delta$) at 11 Hz for CPE/AO-80

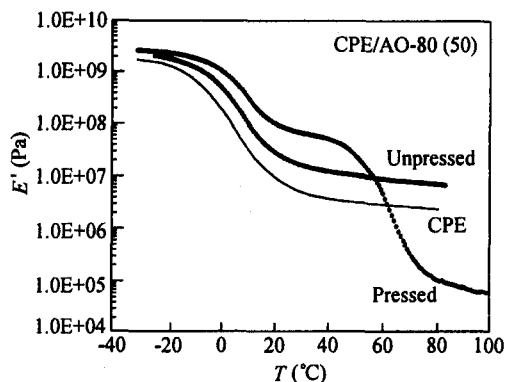


Fig. 7 Temperature dependence of storage modulus (E') at 11 Hz for CPE, unpressed and pressed CPE/AO-80 (50 wt%)

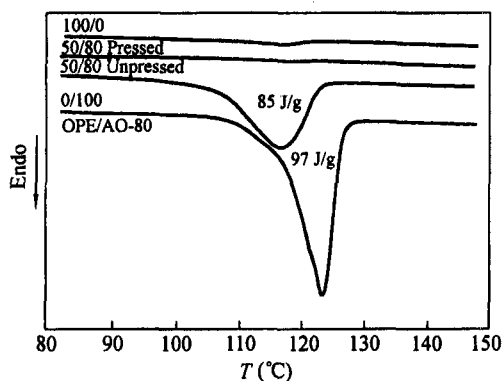


Fig. 8 DSC thermograms of CPE, AO-80, unpressed and pressed CPE/AO-80 (50) measured with a scan rate of 10 K/min

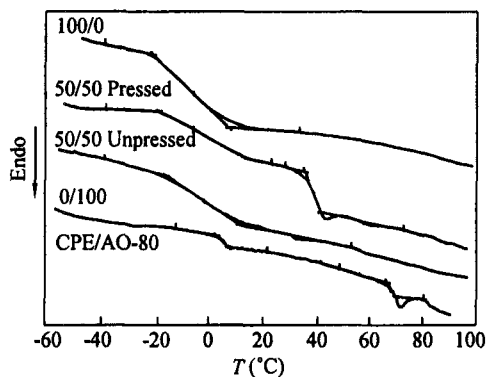


Fig. 9 DSC thermograms of CPE, AO-80, unpressed and pressed CPE/AO-80 (50) measured with a scan rate of 10 K/min

For the unpressed CPE/AO-80 (50 wt%), there is only a single transition in the DSC curve, but the T_g obtained from the DSC curve is slightly higher than that of pure CPE. On the other hand, the second transition seen in pure AO-80 disappeared in both DSC and $\tan \delta$ curves (Fig. 2). By contrast, the pressed CPE/AO-80 (50 wt%) exhibits two transitions in DSC curves, as is also shown in the temperature dependence of $\tan \delta$ (Fig. 2). The second transition is probably associated with the second-order transition of AO-80 domains. In order to confirm the origin of the second transition in the dynamic mechanical properties of pressed CPE/AO-80 (50 wt%), we have attempted to compare the temperature of the second transition of pressed CPE/AO-80 (50 wt%) with that of pure AO-80 from DSC curves. Table 1 shows two transition temperatures obtained from $\tan \delta$ peak at 11 Hz, and from DSC measurement at a scanning rate of 10 K/min, respectively. As can be seen in Table 1, the temperature of the second transition of pressed CPE/AO-80 (50 wt%) is much lower than that of pure AO-80, suggesting that the molecular morphology of AO-80 within the CPE matrix is entirely different from that of pure AO-80. In addition, AO-80 is a semi-crystalline substance but the DSC curve of pressed CPE/AO-80 does not show the melting peak of AO-80 (see Fig. 8). Considering that the second transition of AO-80 is related to the hydrogen bonding between the hydroxyl groups of AO-80, a shift of its transition temperature to a lower temperature in the pressed CPE/AO-80 sample is reasonable because a large amount of the CPE chains has been

incorporated into the AO-80 domains and the intermolecular hydrogen bond between α -hydrogen of CPE and hydroxyl groups of AO-80 is weaker than that between hydroxyl groups of AO-80^[9].

Table 1. The position of $\tan\delta$ peak and T_g (DSC) for various samples

Sample	First transition		Second transition	
	T_g (DSC) (°C)	T_g ($\tan\delta$) (°C)	T_g (DSC) (°C)	T_g ($\tan\delta$) (°C)
CPE	-6.5	10.6	—	—
CPE/AO-80 (50 wt%), unpressed	-4.0	13.5	—	—
CPE/AO-80 (50 wt%), pressed	-3.4	13.5	41.6	65.1
AO-80	5.9	—	68.8	—

The morphology of pressed CPE/AO-80 (50 wt%) is shown in Fig. 10. It has a CPE-rich phase and a AO-80-rich phase, in the former phase a part of AO-80 molecules are dissolved in the CPE matrix and simply act as an anti-plasticizer, in the latter phase the CPE chains penetrate through the AO-80 domains. These results demonstrate that AO-80 and CPE were hybridized during the quenching process. Thus we refer to the pressed CPE/AO-80 (50) as a hybrid. It should be noted here that a novel transition originating neither from CPE component nor from AO-80 component which was observable above the glass transition temperature of CPE in DMA and DSC measurements arises from their hybridization.

Figure 11 shows the SEM photograph of another hybrid CPE/AO-60 (30 wt%), which also exhibits two transitions. The domains of AO-60 are clearly observed. The results of elemental analysis of the AO-60 domain and CPE continuous phase are shown in Fig. 12. Both the chlorine atoms within the AO-60 domain and the oxygen atoms within the CPE matrix are clearly observed. This indicates that a part of the CPE component is included in the AO-60 domain, and that a part of AO-60 component is dispersed in the CPE matrix. These facts support the concept of partial compatibility of AO-60 in CPE matrix. Consequently, there is considerable validity in the structural image of the CPE/AO-80 hybrid shown in Fig. 10.

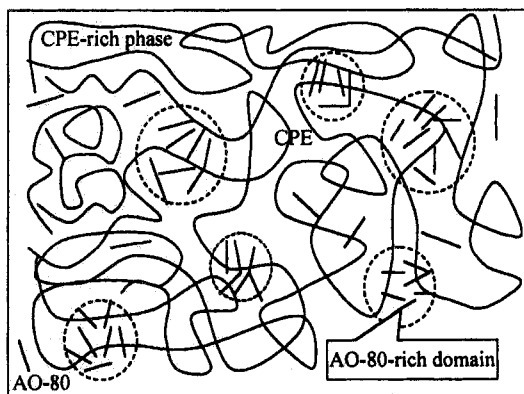


Fig. 10 Schematic illustration of the morphology of CPE/AO-80

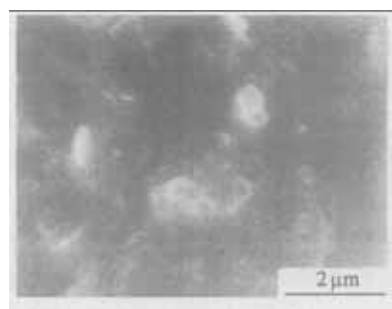


Fig. 11 SEM photographs of CPE/AO-60 (30 wt%) after being pressed for 30 days

Figure 13 shows the infrared spectra of pure AO-80, the unpressed and the pressed CPE/AO-80 (50 wt%). The spectrum of pure AO-80 shows the presence of two infrared bands which are associated with the OH stretching vibration. The band at 3555 cm^{-1} is assigned to "free" —OH group (non-hydrogen-bonded), while the band at 3470 cm^{-1} is assigned to "OH—OH" interaction, respectively. The same spectral characteristic was also observed in the unpressed CPE/AO-80 (50). For the CPE/AO-80 (50 wt%) hybrid, these bands disappeared, but another band clearly appeared at 3503 cm^{-1} , which can be attributed to an intermolecular hydrogen bonded OH ($\alpha\text{-H—OH}$). This illustrates that the domains of AO-80 within CPE matrix contain a large amount of CPE segment. Moreover, we have also observed that the wave number of the ($\alpha\text{-H—OH}$) hydrogen bond is higher than that of the (OH—OH) hydrogen bond, indicating that the bond energy of the former is smaller than that of

the latter. This fact can successfully explain that the second transition of CPE/AO-80 hybrids which is observed from DMA and DSC measurements, occurs at a temperature below the second transition temperature of the pure AO-80.

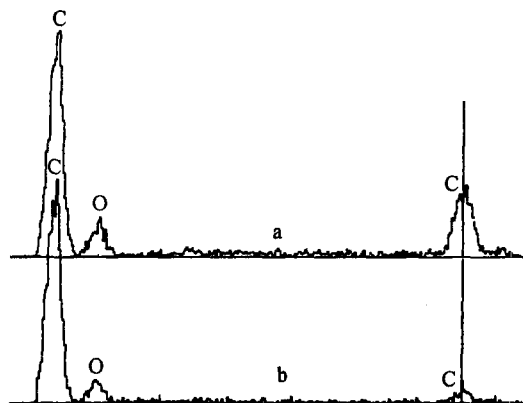


Fig. 12 Elemental analysis of CPE-rich phase (a) and AO-60-rich phase (b) for CPE/AO-60 (30 wt%) after being pressed for 30 days

In order to correlate the two $\tan\delta$ peaks with certain kind of molecular motion, the evaluation of activation energies for the first and second transitions of various CPE/AO-80 hybrids were carried out. From the width of the peak of the $E''-1/T$ plot:

$$E_a' = 2.63/\delta_{1/2} \quad (1)$$

$$\delta_{1/2} = 1/T_2 - 1/T_{\max} \quad (2)$$

where T_2 is the temperature at which $E'' = E''_{\max}/2$, $T_{\max}$ is the temperature at which $E'' = E''_{\max}$. The E'' data are obtained from a related study^[12] for CPE/AO-80 hybrids. As seen in Fig. 14, the activation energies of the first transition remain constant whereas that of the second transition increase with the increasing AO-80 content. The first transition can be attributed to the onset of the micro Brownian motion of the CPE chains containing AO-80 molecules. If the second transition were attributed to the dissociation of the intermolecular hydrogen bonds, the magnitude of the second transition would depend on the number of the intermolecular hydrogen bonds. The origin of the second transition is most probably due to the dissociation of the intermolecular hydrogen bond within the AO-80-rich domain; in addition, it is also due to the repetitive motion of the CPE chains within the CPE-rich phase accompanied by this dissociation. This implies that the second transition is not an indication of the glass-transition. This hypothesis is confirmed from the fact that the second transition occurs over a relatively narrow temperature range; that the AO-80 content dependence of the second-transition temperature obtained from the peak maximum of E'' , $\tan\delta$ and onset temperature obtained from DSC are different from each other^[12]. The observed increase in the activation energy of the second transition with increasing AO-80 content may be due to a significant increase in the number of intermolecular hydrogen bond per CPE chain.

INFLUENCE OF MOLECULAR AGGREGATION STATE^[17-19, 10]

The novel transition caused by the addition of organic small molecular substance into the polymer is attributed to the dissociation of intermolecular hydrogen bonds. Therefore, it is conceivable that the intensity of this novel transition varies with the number of intermolecular hydrogen bonds in the additive-rich domains. On the other hand, it was found that the AO-60 molecules within the CPE matrix crystallize easily during an aging or heating process, and the crystallization of AO-60 molecules results in an increase of the number of intermolecular hydrogen bonds between CPE and AO-60. Consequently, this novel transition can be controlled by heat-

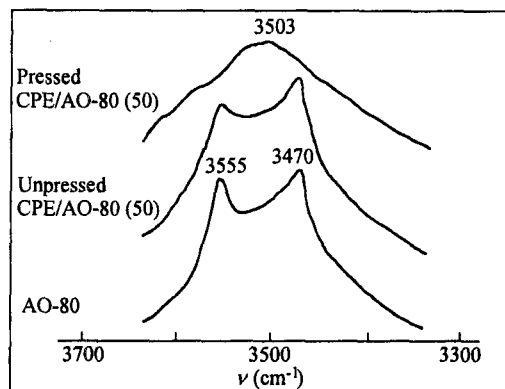


Fig. 13 Infrared spectrum of AO-80, unpressed and pressed CPE/AO-80 (50) in the hydroxyl groups stretching region

treatment below the melting point of AO-60. This is important for further understanding the molecular mechanism of such novel transition.

Figure 15 shows the DSC curves of various annealed CPE/AO-60 (40 wt%) hybrids. For untreated sample, the melting peak due to the AO-60 crystals is very small, implying that most AO-60 molecules did not crystallize. With increasing annealing time (up to 8 min), the melting peak of AO-60 crystals increased. This is thought to be due to crystal growth from the AO-60-rich domain or the micro-crystal that became highly disordered. With further increase in the annealing time from 16 to 45 min, there was almost no change in the magnitude of this peak, but another shoulder peak appeared near 100°C. This shoulder peak was probably caused by the melting of an imperfect micro-crystal, which is thought to be a result of slight adjustment of the AO-60 molecules packed randomly in terms of position and direction as well as conformation in the AO-60-rich domain. The relatively low melting point is thought to be due to the disorder of the formed AO-60 crystals and/or of the incorporation of the CPE segments into the AO-60-rich domain. Furthermore, when the annealing time was extended to 300 min, the above mentioned shoulder peak conversely became smaller, but the melting peak of AO-60 crystals, which appeared at 115°C, increased again. This suggests that there is a transition from an imperfect micro-crystal to a lamellar crystal during the annealing process of more than 45 min. The result showed that the amount and regularity of the AO-60 crystals that formed during the annealing process varied greatly according to the annealing time. In summary, the process of annealing in a span of 300 min can be classified into three regimes: (1) growth of micro-crystal, (2) formation of imperfect micro-crystal, and (3) transition from an imperfect micro-crystal to a lamellar crystal.

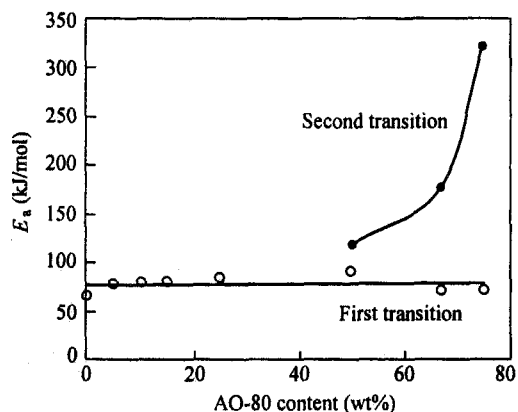


Fig. 14 Apparent activation energies of CPE/AO-80 hybrids as a function of AO-80 content

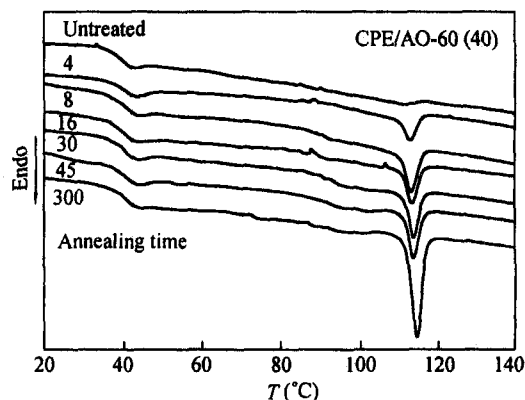


Fig. 15 DSC thermograms of various annealed CPE/AO-60 samples, measured at an annealing temperature of 90°C, and a scan rate of 10 K/min. The numbers shown in the figure denote the annealing times (min)

Figure 16 shows the effects of annealing treatment at 90°C on the temperature dependence of $\tan\delta$. There was no great change in the first peak with change in the annealing time; this strongly demonstrated that the first peak could be attributed to a glass transition of the matrix polymer. By contrast, the second peak decreases monotonously with increases in the annealing time. Because the second transition is associated with the intermolecular hydrogen bonds between CPE and AO-60 within the AO-60-rich domain, the observed reduction in the second peak seems to be due to the dissociation of intermolecular hydrogen bonds during the crystallization process of AO-60 molecules occurred in annealing. The results demonstrated that the second transition caused by the dissociation of intermolecular hydrogen bonds is controlled through annealing treatment so that the number of intermolecular hydrogen bonds changes.

It is also noteworthy that there was almost no change in the position of the second peak for all samples, indicating that neither the annealing time nor the temperature influences the second transition temperature. This

implies that the second transition temperature depends on the intensity of the intermolecular hydrogen bonding but not on the number of intermolecular hydrogen bonds, which might determine the height of the second peak.

In many biphasic systems^[20, 21], it has been identified that the magnitudes and the location of a glass transition caused by a single phase are dominated by its content. On the other hand, the compatibility of AO-80 and CPE is considerably enhanced with increasing thermal forming temperature and time. It is therefore possible to dissolve still more AO-80 molecules in a CPE matrix by quenching the sample from the melt; this, of course, decreases the amount of AO-80-rich phase when the AO-80 content remains constant.

The temperature dependence of E' and $\tan\delta$ are shown in Fig. 17 for CPE/AO-80. The $\tan\delta$ curves of two samples, which were pressed at different temperature and time, show two transition peaks at the same temperature. The first peak of a sample that was pressed at 180°C for 30 min is higher than that of another sample that was pressed at 130°C for 10 min and conversely its second peak is lower. The E' in the intermediate plateau of the former sample is lower than that of the latter one.

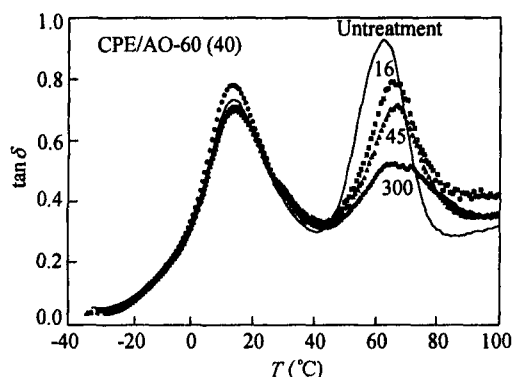


Fig. 16 Temperature dependence of loss tangent ($\tan\delta$) at 11 Hz for CPE/AO-60 (samples B and C). The numbers shown in the figure denote the annealing times (min)

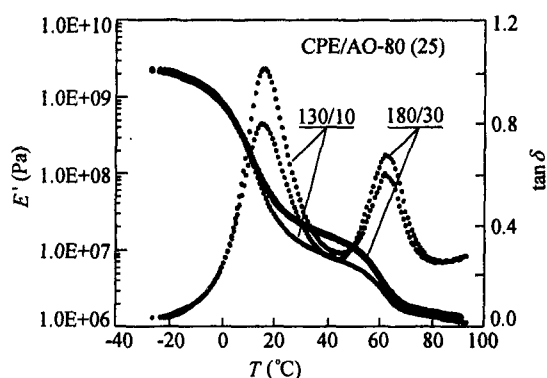


Fig. 17 Temperature dependence of loss tangent ($\tan\delta$) at 11 Hz for CPE/AO-80 (25). The numbers shown in the figure denote the pressing temperature (°C) and pressing times (min)

By comparing the $\tan\delta$ curves, and or the E' of the two samples, it was found that both the first and the second transitions appear at the same temperature. In the case of the CPE/AO-80 hybrid, the intensity of two transitions is dependent on the amount of each phase, whereas the temperature of two transitions is independent of that. It was reported that the transition temperature is strongly dependent on the amount of each phase in many phase-separated systems^[20, 21]. Therefore, the second transition observed in the CPE/AO-80 hybrid is a new type of transition different from the general glass transition in terms of its mechanism.

DISCOVERY OF MULTI-FUNCTIONS^[9, 22-24]

The additive-rich domain organized by intermolecular hydrogen bonding is very interesting from both the scientific and the industrial points of view. The crystals with various shapes, such as polyhedron, platelet, needle and imperfect crystals, have been cultured through annealing treatment from amorphous domains^[13]. It should be noted here that the pyramidal crystals (Fig. 18) were observed when annealing was carried out at 100°C for 20 min. Pyramidal crystals of some polymers or paraffin have usually been cultured from a dilute solution of the polymers^[25]. However, a pyramidal crystal of small molecules formed within a thick polymer matrix is very rare. In fact, our observation of such a crystal formed within a thick polymer matrix may be the first such finding. The observed pyramidal crystal may be formed only by the hybridization of two constituent components. Further discussion will be presented in a later paper.

In addition, the additive-rich domain can also be regarded as a dynamic multifunctional cross-linking point. The additional plateau observed in the E' -temperature curves (Fig. 7) is attributed to the cross-linking effects and

filling effects of the additive-rich domains. Some physical functionality is induced by a thermally reversible change in this additive-rich domain.

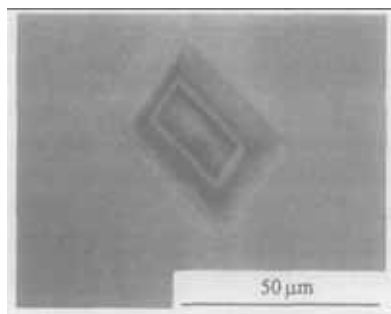


Fig. 18 Polarized light micrograph of a pyramidal crystal of CPE/AO-60 (50 wt%) annealed at 100°C for 30 min

The CPE cross-linked by the additive-rich domains is not only a new type of elastomer, which can be recycled, but it also shows a good shape-memory effect. It is known that polymers showing shape memory characteristics basically consist of two phases, i.e., a frozen phase and a reversible phase in which the reversible action often used is due to the melting transition and glass transition, and the shape memory behavior is mainly dominated by a softening-hardening transition^[26]. Reversible change in E' of an organic hybrid is dramatic and shows high reproducibility as compared with the changes in other shape-memory materials. In addition, the elasticity in the intermediate range near room temperature can be retained. Therefore, the organic hybrid can be regarded as a good and highly desirable shape-memory rubber that has not been developed until now.

The additive-rich domain is thermally reversible as well as mechanically reversible. The magnitude of the second transition was found to decrease with increases in strain (Fig. 19). This is due to the dissociation of intermolecular hydrogen bonds during the strain process. Assuming that once the dissociated hydrogen bonds can be recombined, it is estimated that the height of the E' in the intermediate plateau increases with relaxation time. This was demonstrated from the results shown in Fig. 20. The mechanical reversibility is due to the recombination of intermolecular hydrogen bonding between the two constituent components. This finding is also very interesting because the organic hybrid can be regarded as a self-restorable material.

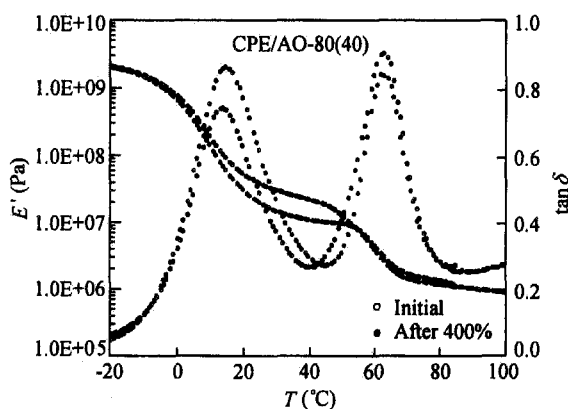


Fig. 19 Temperature dependence of storage modulus (E') and loss tangent ($\tan \delta$) of initial CPE/AO-80 (40%) and after it has been extended to 400%

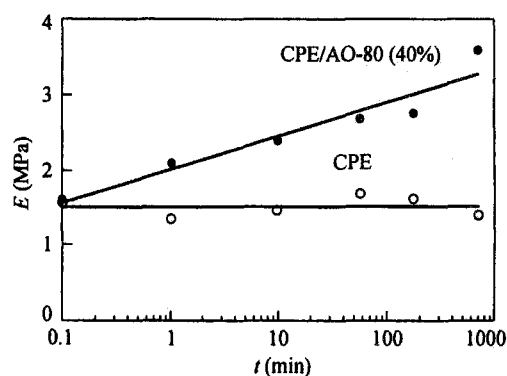


Fig. 20 Time dependence of tensile modulus (E) of CPE and CPE/AO-80 (40%) which has been extended to 400%

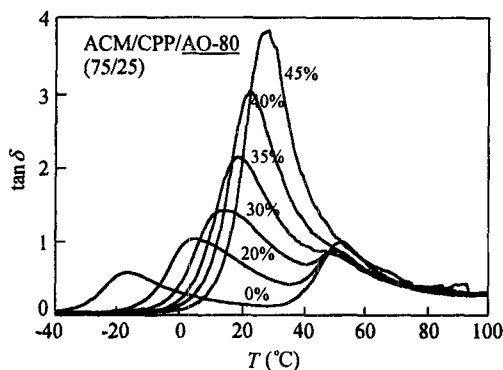


Fig. 21 Temperature dependence of $\tan\delta$ for ACM/CPP (75/25) with AO-80

Another interesting finding is that the second peak is larger than the first peak in the case of a CPE/AO-80 hybrid (see Fig. 2). By definition, $\tan\delta$ is determined by both the viscous and the elastic moduli. While the elastic modulus is a measure of the energy returned to the system, the viscous modulus is 90° out of phase and is related to the component of lost energy. Therefore, $\tan\delta$ is a ratio of the work converted into heat to the work recovered, for a given work input. The fact that the second peak is larger than the first peak indicates that the energy dissipation due to the dissociation of intermolecular hydrogen bonds is larger than that due to general friction between polymer chains. Thus, the addition of small molecules with bi- or multi-functional hydrogen-bonding acceptors should greatly improve the damping behavior of a given polymer or polymer blend. We here considered a ternary system consisting of ACM, CPP, and AO-80. The additive effects of AO-80 on the $\tan\delta$ of ACM/CPP (7:3) are shown in Fig. 21. While the ACM/CPP blends exhibit two relatively small peaks, for ternary blends the addition of AO-80 drastically increases the ACM peak. In addition, we also found that the addition of AO-80 will produce highly desirable self-adhesiveness. Therefore, such a ternary blend can be considered as a new type of super-damping material for damping low vibration and sound waves.

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