Mobility Control and Modulus Change by the Interaction Between Low Molecular Weight Component and Aromatic Polymer Chain

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ABSTRACT: An increase of flexural modulus was observed by blending liquid organic phosphorous compounds, having specific structure, with polyphenylene–ether (PPE) or polycarbonate (PC). Blending 35 wt % of bisphenol-A type compound with two phosphate atoms in a molecule was especially significant. Flexural modulus increases of 12 and 32% were observed for PPE and PC, respectively. In the case of PPE, the increase tended to depend on the molecular weight of organic phosphorous compounds. The analysis of polymer chain motion of PPE by dynamic viscoelastic spectrum showed a change in shape at the β-dispersion temperature zone. From the trend of activation energy of the dispersion peak top and temperature dependence of both stock and loss modulus, it was concluded that the organic phosphorous compounds formed a complex bonding with the polymer chain with subsequent restricted β-type chain motion. As a result, the increase of modulus was observed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 2269–2277, 1997

Key words: polyphenylene–ether; polycarbonate; flexural modulus; antiplasticizer; dynamic viscoelastic spectroscopy

INTRODUCTION

Some research work has been conducted on blending polymer affinity low-molecular-weight compounds with polymers to change chain conformation and chain entanglement or to cause phase separation due to the differences of those affinities to polymers. Excluding compounds having poor affinity to polymers, the addition of polymer affinity low-molecular-weight compounds activates the motion of polymer chains to enhance plasticity.

At the same time, some exceptions are known in which polymer affinity low-molecular-weight compounds interrupt the plasticizer effect, and these compounds are called antiplasticizer.[1-3] The antiplasticizer effect has been carefully studied on polyvinyl chloride, in which the use of plasticizer is common[4-8] though. These phenomena, found on polycarbonate (PC) and polystyrene (PS), have been studied as well.[9-12] The antiplasticizier effect on polyphenylene ether (PPE) [poly(2,6-dimethyl-1,4-phenyleneoxide] with organic phosphorous compounds have been also researched, and the changes of the glass transition temperature and yield stress have been characterized. The phenomena were analyzed using the viscoelasticity method and the two-dimentional solid-state nuclear magnetic resonance (NMR) study by Kambour and coworkers.[13-16]

PPE, whose glass transition temperature is as high as 211°C, (60°C higher than that of PC), is one of the main engineering plastics. It is synthesized by the Cu catalyst complex polymerization of 2,6-dimethyl phenol.[17,18] Utilizing its low in-

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flammability, PPE becomes an important material for electronic equipment. However, having advantages such as high glass transition temperature and low inflammability [19,20] as a basic material, the polymer structure is known to change easily by heat.[21,22]

PC has a long history of synthesis. However, it is relatively recent that its brittle fracture character has been considered desirable characteristics. Furthermore, it is a consequence of very recent research work that the relationship between its splendid structural properties, as a result of polymer chain movement, has been understood. PC, as well as PPE, using its low inflammability and high glass transition temperature, is also employed for electronic equipment. Moreover, taking full advantage of its dynamic property, it is also used as a material in which structural toughness is necessary.[23–25]

In this work, we report a flexural modulus increase of PPE and PC by blending organic phosphorous compound (OPC) with specific chemical structure and discuss it mainly from dynamic viscoelastic spectrum measurement.

EXPERIMENTAL

Materials

PPE is synthesized by oxidation polymerization of 2,6-xylenohl using copper(II) chloride and N,N,N',N'-tetramethyl–1.3-diaminopropane. Its molecular weight (M_w) as measured by gel permeation chromatography (GPC) was 37,000, and M_w/M_n was found to be 2.6.[26] PC, whose M_w is 23,000, is supplied by GE Japan. OPC, used in this study of the interaction with PPE was supplied from Daihachi Chemical Co., Ltd. Chemical structure, symbols, and melting points of OPC and TPP and PBX are listed in Table I.

OPC is a compound of five-bonding phosphorous, whose substituents are phenol (P : P indicates phenyl group), cresol (C), xylenol (X), resorcinol (R), hydroquinone (H), and bisphenol A (B). All of these OPC are mixtures of different degrees of condensation products and are synthesized by the Friedel Crafts reaction of phosphorous oxychlride and phenol compounds. Only the structure of dimmer compounds are figured in Table I.

Molding of Organic Compounds

Purified PPE powder after polymerization or PC pellets were mixed with OPC by a twin screw ex-

truder. 85 wt % PPE powder or PC pellets were mixed with 15, 25, and 35 wt % of OPC. In the case of TPP mixture, it was difficult to mold. The extruder employed was Wellner ZSK-25, and the extrusion temperature was 280°C for PPE. An injection-molded specimen was used for flexural modulus measurement and a heat sag test, and compression-molded specimen was used for dynamic viscoelastic spectrum measurement.

Property Measurement

Flexural modulus (FM; MPa) was measured by Shimazu Aurograph at 23 and 195°C (ASTM-D790). Heat sag temperature (DTUL; C) was measured under a load of 1.82 MPa (ASTM-D648). A dynamic viscoelastic spectrum was obtained by Olientech Rheovibron® where a 1 mm thickness and 5 mm width sample was set between 30 mm of chucks. Measurement was carried out under the conditions where 10 g of load, 20 Hz of vibration and 2°C min of rising temperature from −150 to 200°C.

RESULT AND DISCUSSION

Table II shows the composition of PPE and OPC compounds, flexural modulus (FM), flexural strength (FS), and heat sag temperature (DTUL). The flexural modulus of PPE (which is 2.45 MPa at 23°C under this experimental condition) was increased to 2.62 MPa by adding 15 wt % of BBC (shown in Table I). In this experiment, it was found that (excluding TPP, which is the smallest molecule) the blending of any types of organic phosphorous compounds increased FM.

FS of PPE, which was 108 MPa without blending, was observed to increase by the blending of organic phosphorous compounds, with the exception of TPP. However, the blending of BBC, which showed a significant increase of FM, did not demonstrate a FS increase by blending more than 25 wt %. At the 127 MPa level, there ceased to be further significant change, despite an increase blending of BBC. On the contrary, DTUL dropped by the blending of any types of OPC, and the sample with 35 wt % of TPP resulted DTUL at 56°C.

Kambour and coworkers have reported the effects of low-molecular-weight diluents on the glass transition temperature and the elastic modulus (EM). The increases of EM were not observed in the case of phosphate blends series; instead, the EMs increased for m-phenylene di-

Table I Chemical Structure, Molecular Weight, and Melting Point of Organic Phosphorous Compounds

OPC	Chemical Structure	Molecular Weight	Melting Point (°C)
TPP		326	49
RBP		574	—
HBP		574	—
HBC		630	—
BBP		692	—
BBC		748	—
PBX		762	183

Table II   Flexural Modulus (FM), Flexural Strength (FS), and DTUL of PPE Blending with Various Organic Phosphorus Compounds (OPC)

No.	PPE (wt %)	Abbreviated Symbol of OPC	OPC (wt %)	FM at 23°C	FM at −195°C	FS (MPa)	DTUL (°C)
1	100	none	0	2.45	3.22	108	180
2	85	TPP	15	2.34	3.43	100	112
3	75	TPP	25	2.00	—	80	79
4	65	TPP	35	1.75	—	49	56
5	85	RBP	15	2.47	—	112	119
6	85	HBP	15	2.53	—	121	128
7	85	HBC	15	2.55	—	124	121
8	85	BBP	15	2.60	—	121	127
9	85	BBC	15	2.62	—	122	124
10	85	BBC	15	2.66	4.18	127	115
11	75	BBC	25	2.64	—	127	86
12	65	BBC	35	2.75	—	127	67
13	85	PBX	15	2.54	3.79	113	141

benzoate and Kenflex A naphthalene formalite oligomer, whose structures were not specified.[13]

As blending some types of aromatic phosphorous compounds showed flexural modulus change, flexural modulus of PPE and PC containing TPP and BBC were measured at 23 and −195°C. The results were exhibited in Tables III and IV. PPE, which is known to have hard, stiff, and high glass transition polymer chains and flexural modulus, belongs to polymer groups with the highest FM. However, blending 35 wt % of BBC, which is a viscous liquid at room temperature, surprisingly increased flexural modulus. In general, aromatic phosphorous compounds, whose affinity of PPE is known to be good, are used to improve plasticity. Sometimes aromatic phosphorous compounds causes stress cracking by behaving as a good solvent. Hence, their functioning is considered to enlarge the mobility of the PPE polymer chains.

From the standpoint of the PPE polymer chain mobility, it is interesting that the OPC, with specific chemical structure, increases flexural modulus.

Similar results were obtained for PC–OPC blends. As is shown in Table IV, DTUL of PC dropped according to the amount of blended TPP and BBC, but flexural modulus increased. What is different for PC from PPE is that the blending of TPP increases flexural modulus at 23°C. As is shown in Table III, the modulus of PPE at −195°C (where the temperature is somewhat too low to guarantee accurate data), a significant increase from 3.22 to 4.18 MPa by BBC and a slight increase to 3.43 by TPP were observed.

In Figure 1, the dependency of DTUL and FM on PS content in PPE–PS blends is shown. PS is well known to have good compatibility with PPE and gives a straight line of DTUL, which is pro-

Table III   Compositions, DTUL, and Flexural Modulus of PPE–OPC

PPE	TPP	BBDCP	DTUL (°C)	at 23°C	at −195°C[a]
100	—	—	180	2.45	3.22
85	15	—	112	2.34	3.43
75	25	—	79	2.00	—
85	—	15	115	2.66	4.18
75	—	25	86	2.64	—
65	—	35	67	2.75	—

Composition (wt %) — PPE, TPP, BBDCP. Flexural Modulus (GPa) — at 23°C, at −195°C[a].

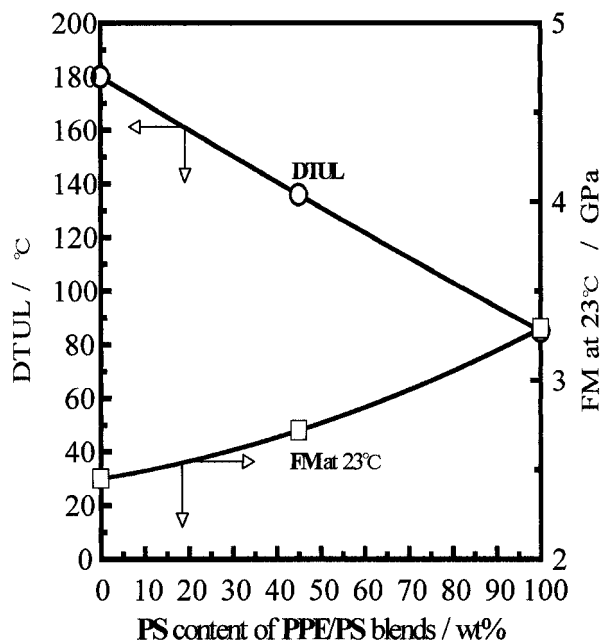[a] Measured after immersion of specimen of liquid nitrogen for 20 min.

Table IV   Compositions, DTUL, and Flexural Modulus of PC–OPC

Composition (wt %)			DTUL (°C)	Flexural Modulus (GPa) at 23°C
PC	TPP	BBDCP		
100	—	—	129	2.16
85	15	—	73	2.45
75	25	—	49	2.6
85	—	15	85	2.82
75	—	25	68	2.75
65	—	35	53	2.83

portional to the blend ratio, as is seen in Figure 1. On the other hand, the line of flexural modulus, which bends slightly downward from the straight line, indicates that PS's stiffer chains are affected by relatively softer PPE chains, even when the content of PS is high.

In Figures 2 and 3, the dependencies of DTUL and FM of PPE on TPP content are plotted. From Figure 3, one see that a significant drop of DTUL and slight drop of FM at 23°C occurs depending on TPP content. However, the rise of FM at −195°C was observed as well. This phenomenon can be explained by noting that TPP, which is a crystal at room temperature and sublimates at 60°C, dissolved well in PPE to allow free polymer chain movement.

Because TPP is a solid at −195°C, it is not clear

how much TPP dissolves in PPE. However, the FM increase is slight, and it may be assumed that TPP dissolves uniformly in PPE to allow free polymer chain movement. However, slight increases of FM by the blending of TPP also indicates the existence of some interaction.

BBC, used in Figure 3, is a viscous liquid, which does not show a clear melting point because of contamination. Blending of BBC significantly changed DTUL and is consistent with the general tendency of DTUL to drop. Nevertheless, FM increase was observed both at 23°C and at low temperature. The increase is especially significant at −195°C. This phenomenon indicates an existence of a strong interaction between BBC and PPE main chain.

Next, the results of the blending of TPP and BBC with PC are exhibited in Figure 4. Both PC,
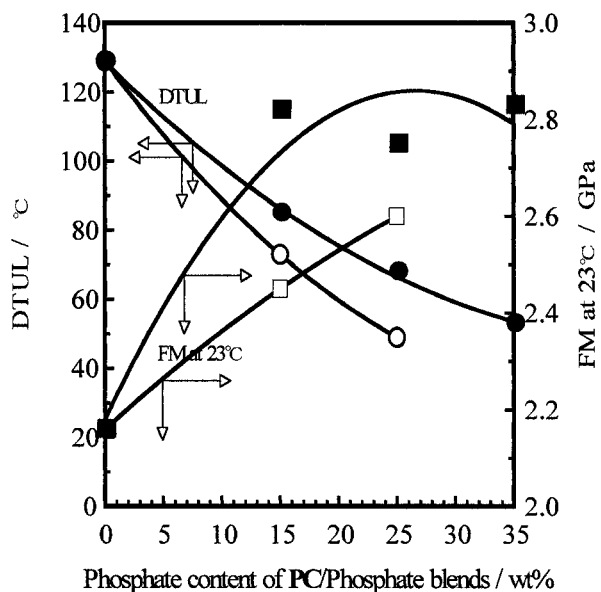
Figure 1   Dependency of DTUL and FM on PS content of PPE–PS blends.
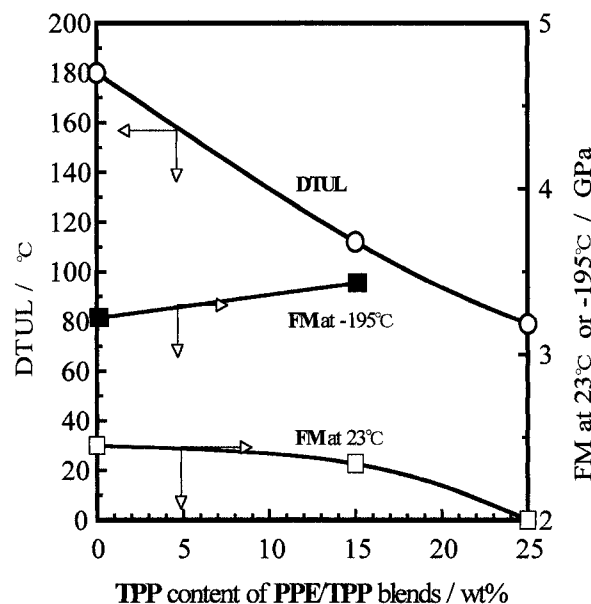
**Figure 2**   Dependency of DTUL and FM on TPP content of PPE–TPP blends.
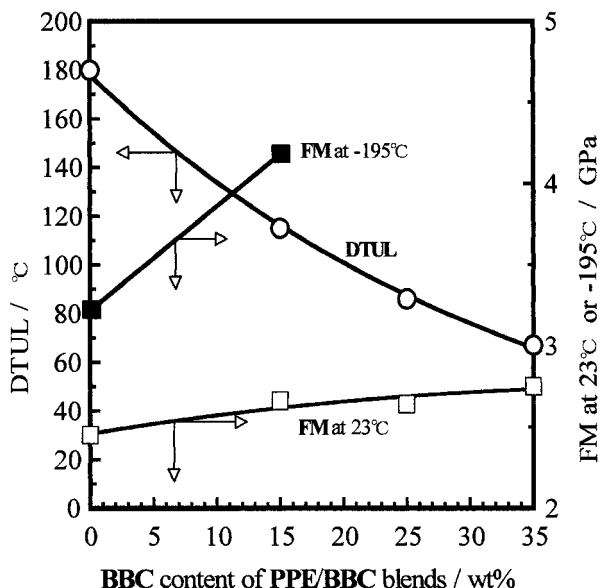
Figure 3 Dependency of DTUL and FM on BBC content of PPE–BBC blends.

as well as PPE, when blended with TPP or BBC showed a decrease of DTUL and an increase of FM. What is characteristic for PC is that the blending of even TPP results in significant FM increase.

Since these observations were very interesting, the effect of OPC on PPE or PC polymer chain motion using dynamic visoelastic spectroscopy were studied. First, observing loss modulus of

Figure 4 Dependency of DTUL and FM as a function of phosphate content of PC–TPP and PC–BBC blends.
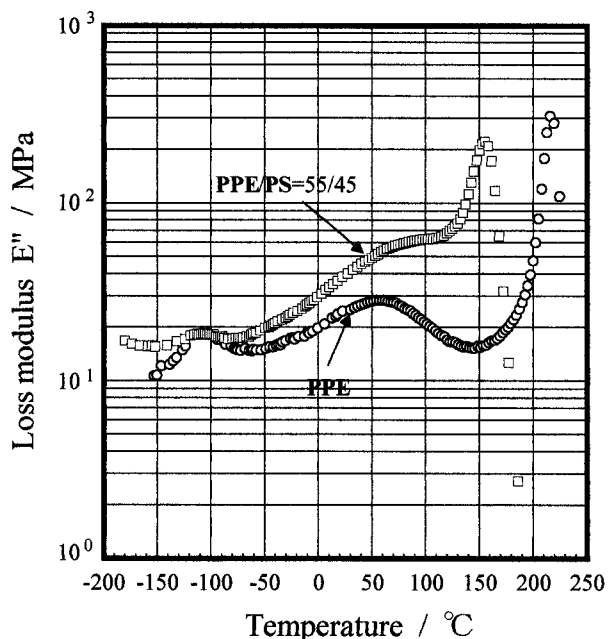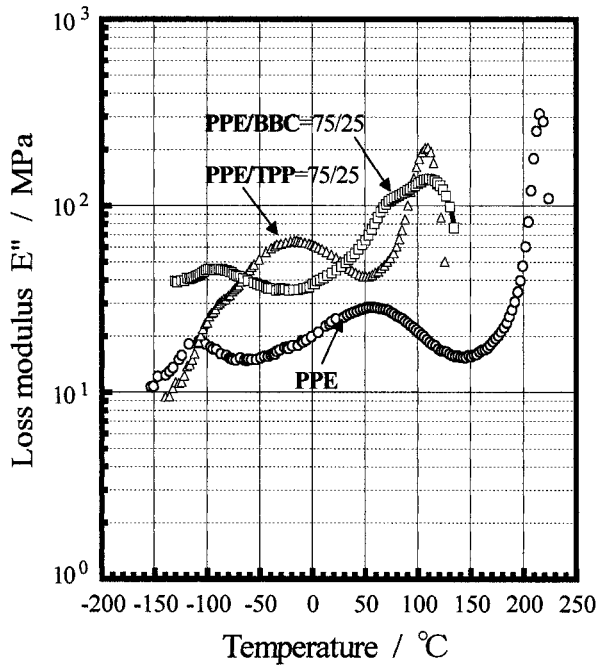

Figure 5 Loss modulus of PPE and the PPE–PS blend.

PPE and PS missible polymer pair, as is shown in Figure 5, it was found that the α dispersion temperature of PPE depreciates, and β and γ dispersion became smaller by blending PS. At the same time, a small β dispersion temperature increase was observed, indicating the restriction of movement of PPE chain by PS.

If movement of the entire chains or movement of units on the chain (local motion) occur in the similar mode, the changes of α and β dispersion must be similar. Hence, it is clear that, even in a missible polymer pair, movement of the entire chains and local motion have different modes.

Subsequently, loss modulus of PPE–OPC blends are exhibited in Figure 6. Both the TPP and BBC blends showed a similar tendency to the PS blend. In the case of the TPP blend, where little flexural modulus increase occurred, a drop of β dispersion temperature that relates to local chain motion by 20°C is shown. The movement of the entire chains indicated by α dispersion temperature dropped as well; but the γ dispersion temperature, which is not clear enough, does not seem to change. On the other hand, for the BBC blend, where a significant flexural modulus increase occurred, the absolute value of loss modulus at β dispersion zone rose and temperature itself increased by 10°C. It is reasonable that PS, which is a high polymer and chain movement at room temperature, is negligible and gives a high modulus by blending. Assuming that the mis-
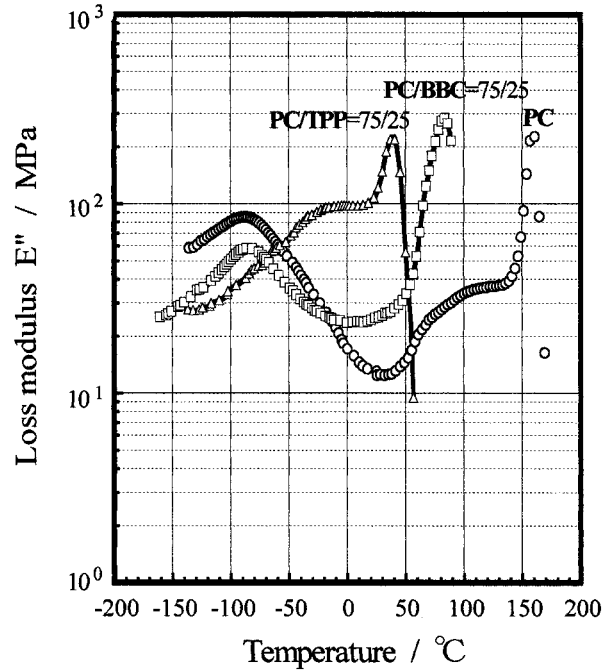
Figure 6 Loss modulus of PPE and the PPE–phosphate blends.

Figure 7 Loss modulus of PC and the PC–phosphate blends.

sible blend gives an average of properties, blending viscous liquid BBC should decrease β dispersion temperature. The γ dispersion temperature, which indicates the rotation of the chain and is known to be affected by impurities such as water, showed some increase. And β dispersion initiated by large-scale local chain motion has significant reemergence. Hence, it may be possible to conclude that BBC limits the motion of PPE main chain.

When we change the polymer from PPE to PC, it is not easy to detect the β dispersion change because there is an enormous main dispersion shift, as one can see in Figure 7. Then, storage modulus, which directly relates to flexural modulus, is plotted in Figure 8.

For the PC–BBC blend, storage modulus above 60°C is apparently higher than that of PC alone. As seen in Figure 7, α and β dispersion can be explained to overlap each other. Storage modulus of the PC–BBC blend is higher than PC alone, even at low temperatures; but that of the PC–TPP blend, which is higher at room temperature, changed to a more similar level at low temperatures then became reversed at below −150°C. In Figure 7, one can find γ dispersion in samples with BBC and PC alone, but one cannot find it in a sample containing TPP. The fact that there exists no storage modulus drop caused by γ dispersion change signifies that polymer chain relax-

ation at low temperature is caused by a quite local chain motion so that the flexural modulus, which relates to the entire chain movement, is not affected by this.
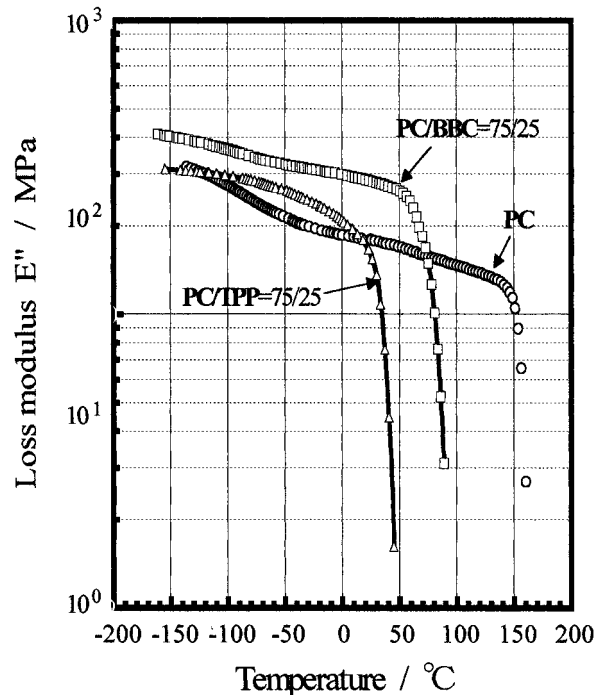
Figure 8 Storage modulus of PC and the PC–phosphate blends.

Table V   Activation Energy of Each Transition

		Activation Energy (kcal/mol)		
Sample	Molding	α-Transition	β-Transition	γ-Transition
PPE	injection	220	240	10
PPE	compression	220	32	7
PPE–TPP = 75 : 25	compression	96	38	9
PPE–BBC = 85 : 15	compression	79	120	9
PPE–BBC = 75 : 25	compression	138	140	37

Calculated from the transition temperature at 10 and 100 Hz.

Fundamental viscoelastic properties and the activation energy of β transition was first determined by Petris et al. in 1967, using a polymer with 30,000 molecular weight.[27] From the viewpoint that dynamic viscoelastic data provides an important understanding of polymer properties, many studies have been carried out[28–30]; and it becomes clear that mechanical properties of polymers strongly relate to β dispersion. Sauer reported that the activation energy of PPE γ and β transition were 20 and 40 kJ/mol, respectively, as measured several kinds of aromatic polymers. Activation energy of diffusion of low-molecular-weight components, whose molecular weight is about 100 to 200 inside entangled polymer chains, which limit diffusion, is known to be 15 kJ/mol. Compared with this, 40 kJ/mol of PPE β transition activation energy indicates that it is a movement of several monomer units. However, 20 kJ/mol of γ transition activation energy indicates that it is a quite local motion, even though it is under conditions in which the motion is highly restricted by polymer chains. Activation energy obtained in our study is greater than those publications show, although the trend agrees well with those findings.

In Table V, transition activation energy of injection and compression-molded samples are listed. Compression-molded samples of PPE–BBC blend in which the interaction with solvent has a more direct effect than injection-molding samples, the increase of activation energy of β transition rises significantly from 32 to 120 and 140 kcal/mol. Slight increases of γ transition activation energy are observed as well. Since there are several factors that raise γ transition activation energy, it is possible to assume that even a small motion of polymer is restricted by blending with phosphorous compounds.

There are many reports about dynamic viscoelastic dispersion peaks of PPE included above. For example, Sauer reported in 1973 that γ dis-

persion peak, appearing from -173 to $-93°C$, belonged to the phenylene group rotation and that β dispersion peak of -93 to $-83°C$ belonged to the interaction with water because its activation energy was 40 to 50 kJ/mol and largely affected by the presence of water molecules.[31] The viscoelastic study on the blends PPE with low-molecular-weight diluents has also been achieved and the changes and shift of γ dispersion peak[13] discussed. The peak of PPE disappeared by blended trioctylphosphate ($TOPO_4$). However, the modulus decreased with increasing the content of the phosphates.

The interaction with the solvent used during polymerization (such as toluene) is consistent because it is hard to remove from stiff PPE polymer chains. Stiff chains might also cause residual molding stress. For example, comparing spectrums of sample of PPE prepared immediately after polymerization with the one purified by reprecipitating benzene solution into methanol, β transition temperature increases, and the peak itself becomes smaller by purification. Since the purified sample shows no γ dispersion, it may be concluded that γ transition is caused by the interaction with the solvent. Furthermore, some other researchers reported that γ dispersion changes according to the amount of water included.[32] Viscoelastic spectrums differ from one another by the existence of impurities or molding conditions; hence, it is not easy to get a consistent conclusion. However, from storage and loss modulus observation of PPE or PC blend with OPC, it is probable that OPC restricts the motion of polymer chains with several monomer units, which is equivalent to β transition, then causes a flexural modulus increase, even if OPC is a viscous liquid. As was found, large-scale polymer chain motion is limited so that there may exist complex-type bonding or some other possible interactions in this scale. In-

termolecular movement of polymer chains may be related as well.

The interaction between PPE and low-molecular-weight compounds have been researched by nuclear magnetic resonance (NMR) and other methods in order to elucidate the molecular motion of PPE chain in solution.[14–16] They revealed the dynamics of the glass transition and the micromotion of PPE and PC chains in the solutions. We are measuring the viscoelastic behavior of PPE and PC blends more preciously and analyzing the steric effects of the interaction by computer simulation in our further works.

CONCLUSIONS

1. Blending liquid OPC with PPE increased flexural modulus, and the rate of increase tended to rise according to OPC molecular weight.
2. TPP, (a low-molecular-weight compound including one phosphate atom), slightly increased flexural modulus when the blending amount was small, then decreased when the blending amount was increased.
3. Any kind of OPC studied here decreased DTUL, and the observed DTUL was consistent with calculation, assuming that OPC did not contribute to DTUL.
4. Blending OPC with PC showed a similar tendency to PPE, where TPP had some difference from PPE.
5. The results of dynamic viscoelastic spectrum analysis indicated that there was a strong interaction between PPE or PC and OPC.
6. Blending BBC restricted an intermediate-scale motion of the PPE chain. Blending a certain amount of TPP instead of BBC resulted in freer polymer chain movement, and the movement among plural chains became possible.
7. The reason for flexural modulus increase might come from a restriction of polymer chain movement, which was caused by an interaction between PPE and OPC molecules.

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