

Flexural Modulus and Molecular Motion of PPE and PC by Blending Low Molecular Weight Compounds

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ABSTRACT: Physical and dynamic viscoelastic properties of the blends of polyphenylene-ether (PPE) and aromatic low molecular weight compounds with specific chemical structure were studied. As a result, flexural modulus increase was observed by blending aromatic phosphates, phthalic esters, or aromatic amine, which had similar chemical structure to aromatic phosphates. The observed maximum flexural modulus was 2.94 MPa, whereas PPE alone showed 2.45 MPa. There was a trend that flexural modulus increased according to the molecular weight of aromatic phosphate, though molecular weight dependence was very small for phthalic esters. By calculating the interaction between PPE chains and low molecular weight components using a molecular dynamic simulation program, it was found that there was a peculiar conformation where benzene rings interacted with methyl groups of PPE, then flexural modulus was affected as a result of this interaction. A similar conclusion was obtained by a β -dispersion shift observed by dynamic viscoelastic spectroscopy. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 19–28, 1997

Key words: polyphenylene-ether; organic phosphorous compound; phthalic ester; flexural modulus; methyl/benzene interaction; molecular dynamics

INTRODUCTION

Polyphenylene-ether [poly(2,6-dimethyl-1,4-phenylene oxide) (PPE)] is a polymer synthesized by polymerizing 2,6-dimethylphenol using a copper-amine complex catalyst under the condition of general pressure, room temperature, and oxidizing atmosphere.¹ PPE is a superior material because it has a high glass transition temperature, as high as 211°C, a brittle fracture character, good electronic property, such as low conductivity, and flame retardancy.² In spite of polymerizing under oxidizing conditions, there are few side reactions so that polymer structure is simple, and stable against thermal decomposition.^{3,4} From the or-

ganic molding material point of view, its softening point is rather high due to its high glass transition temperature, and its melt viscosity is hardly said to be easy to handle among other polymer materials. Once PPE is molded by injection under high melt viscosity, there remains molding stress to cause cracks and depreciate physical properties. On the other hand, polycarbonate, poly(1,4-phenylene-2-propane-1,4-phenylene-oxy-carbonyl-oxy), (PC) has a long history of synthesis, though it is relatively recent that its superior brittle fracture character was found to be good. Furthermore, very recent research has led to an understanding of its splendid physical properties as a result of polymer chain movement. PC, as well as PPE, utilizing its low inflammability and high glass transition temperature, is also employed for electronic equipment. Moreover, taking full advantage of its physical properties, it is also used where structural physical toughness is needed.^{5–7}

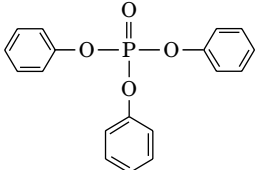
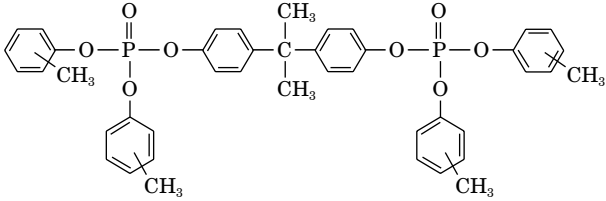
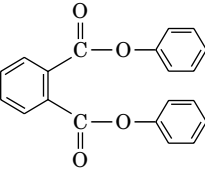
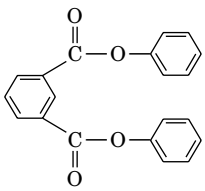
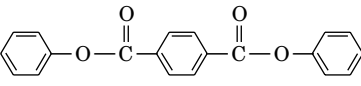
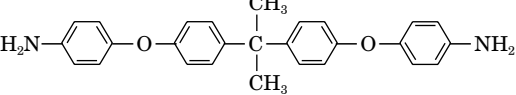
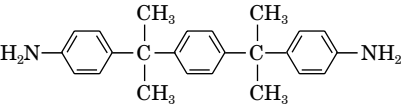
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During a process of research to understand the molding properties and flame retardancy by the interaction between PPE or PC and organic phosphorous compounds (OPC), authors found that there was a remarkable flexural modulus (FM) increase.⁸ In general, blending low molecular weight

compounds with polymer causes plasticity increase and FM decrease. Studies of plasticizer have been active on polyvinylchloride (PVC), and modulus increase by blending some low molecular weight compounds was discovered.⁹⁻¹³ About this phenomenon, Caldwell carried out a systematic work and

Table I Chemical Structure, Molecular Weight, and Melting Point of Compounds Blended with PPE and PC

Abbreviated Symbol of AC	Chemical Structure	Molecular Weight	Melting Point/°C	FM (GPa)	DTUL (°C)
none				2.45	180
TPP		326	49	2.34	112
BBC		748	below room temperature	2.66	123
DPP		318	75	2.48	119
DPIP		318	137	2.64	118
DPTP		318	above R.T.	2.53	121
BAPPP		410	129	2.93	127
BAPIP		344	above R.T.	2.74	128

R.T.: Room Temperature

Table II Compositions, DTUL, and Flexural Modulus of PPE/OPC and PC/OPC

Composition (wt %)			DTUL (°C)	Flexural Modulus (GPa)	
PPE	TPP	BBC		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	

^a Measured after immersion of specimen in liquid nitrogen for 20 min.

named these organic compounds which increased modulus by blending “antiplasticizer.”¹⁴⁻¹⁶

Studies on antiplasticizer have been carried out mainly on PVC and PC, and general remarks have been published by Kinjo.¹⁷ Recently, some new findings of antiplasticizer effect on polystyrene (PS) and PC were reported from a viewpoint of viscoelastic properties and microstructures.^{18,19} Because polymer molecules crystallize under a specific condition, it was considered that FM increase was caused by crystallization. For example, PPE (which gives amorphous polymer by molding from a molten state) is known to form very small crystals by treating with particular solvent.²⁰⁻²³ However, subsequent studies on PVC and PC by measuring viscoelastic properties made it clear that an FM increase occurred even when polymers were amorphous.

Authors had reported the antiplasticizer effect occurred in PPE or PC by blending organic phosphorous compounds (OPC), mainly analyzing dynamic viscoelastic spectrum. It is also found that there is a similar FM increase in PPE or PC by blending phthalic esters or aromatic amino compounds. In the case of OPC, there was a tendency

that FM increased according to the molecular weight of OPC. However, in the case of phthalic esters, FM increase differs even among phthalic esters, which have similar chemical structures.

Hence, we studied the restriction of polymer chain movement caused by blending OPC in PPE or PC, using molecular dynamic simulation and dynamic viscoelastic spectroscopy where β -dispersion shift was observed. There are a lot of publications about the movement restriction of polymer chains by means of numerical simulation,²⁴⁻⁴¹ although useful information was obtained by calculating interaction energy between relatively low molecular weight model polymers and blended compounds.

Table III Flexural Modulus of PPE and PC Blends with Organic Phosphates and Other Esters

Composition (wt %)			DTUL (°C)	Flexural Modulus (GPa) at 23°C
PC	TPP	BBC		
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

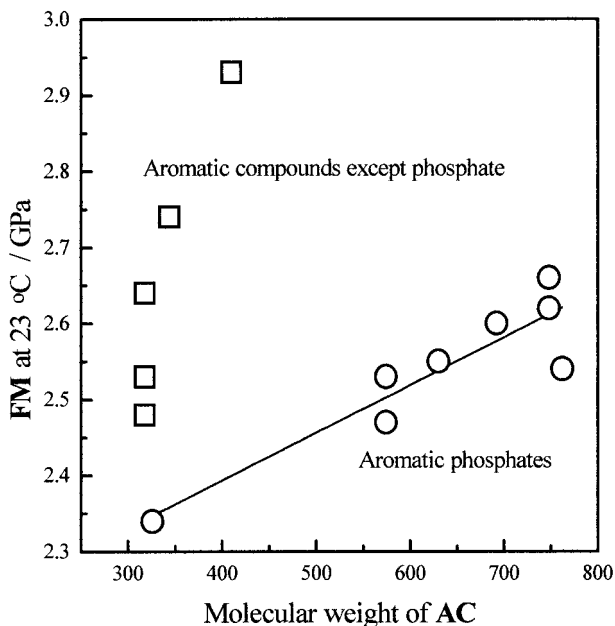


Figure 1 Flexural modulus as a function of molecular weight of blended solvents at 23°C.

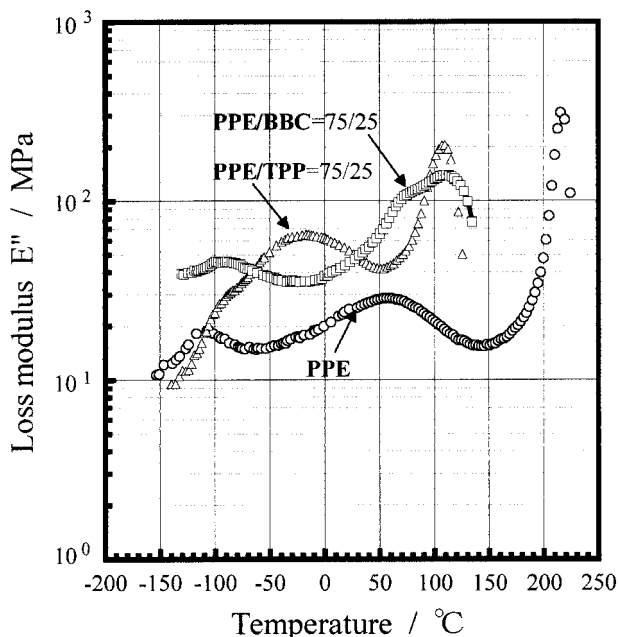


Figure 2 Loss modulus of PPE and PPE/organic phosphates.

EXPERIMENTAL

Materials

PPE was obtained by oxidation polymerization of 2,6-dimethylphenol using copper(II) chloride and *N,N,N',N'*-tetramethyl-1,3-diaminopropane. Its molecular weight (M_w) as measured by GPC was 37,000, and M_w/M_n was found to be 2.6.²⁴ PC, whose M_w is 23,000, was supplied by GE Japan. Chemical structure, symbols, and melting points (as long as the puerility was high enough to measure), or state at room temperature of OPC are listed in Table I. Low molecular weight compounds used in this study were aromatic phosphorous ester, carboxylic di-ester, and two kinds of aromatic amines. Molecular weight of these compounds were chosen from 300 to 400, because relatively high molecular weight phosphorous esters of this molecular weight range showed characteristic behavior with PPE. Phosphorous esters are phosphates of five-bondings and whose substituents are phenol (P : P indicates phenyl group), cresol (C), xylenol (X), resorcinol (R), hydroquinone (H), and bis-phenol A (B). All of these compounds were synthesized by the Friedel Crafts reaction of phosphorous oxychloride and phenol compounds.

Molding of Organic Compounds

Purified PPE powder after polymerization or PC pellets were mixed with OPC by a twin-screw extruder. Standard weight content of PPE in blend was 85%. The extruder employed was Wellner ZSK-25 and the extrusion temperature was 280°C. An injection-molded specimen was used for FM measurement and heat sag test, and the compression-molded specimen was used for dynamic viscoelastic spectrum measurement. Cylinder and mold temperature of injection molding were of 320 and 100°C for PPE, and 270 and 90°C for the blend of PPE and low molecular weight compounds, respectively. In the case of compression, the molding temperature was 320°C for PPE and 250°C for the blends.

Property Measurement and Molecular Dynamics Simulation

Flexural modulus (MPa) was measured by a Shimadzu Autograph at 23 and -195°C (ASTM-D790). Distortion temperature under load (DTUL : °C) was measured under a load of 1.82 MPa (ASTM-D648). 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 with 10 g of

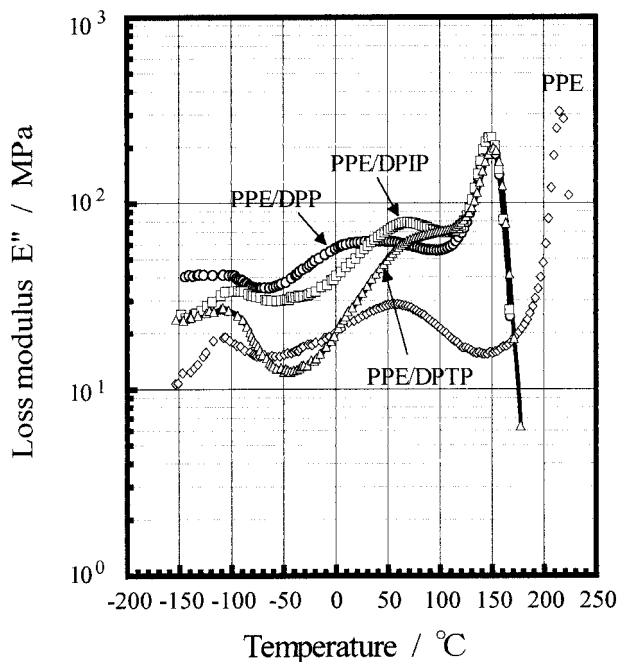


Figure 3 Loss modulus for PPE/AC = 85 : 15 blends.

load, 20 Hz of vibration, and 2°C/min of rising temperature from -150°C to 200°C. The molecular dynamics simulation system employed was HyperChem Release 4 (Structure optimization MM+) provided by Simulation Technology.

RESULTS AND DISCUSSION

Table II shows the DTUL and FM of PPE and TPP or BBC blends measured at 23 and -195°C. PPE is known to have hard and stiff polymer chains with high glass transition temperature, and its FM belongs to polymer groups with the highest FM. However, an FM increase was observed even by blending BBC, which is a viscous liquid at room temperature. In general, aromatic phosphorous compounds were used to increase plasticity of PPE because they have a high affinity for each other. When there is mold stress, aromatic phosphorous compounds behave as if they are solvent and cause stress cracks. Hence it is considered that OPC releases polymer chain movement.

In the case of the PC/OPC blend, DTUL decreased according to the amount of TPP or BBC; however, FM increased. For PC, different from PPE, even TPP increased FM at 23°C. Furthermore, by blending 35% of BBC, the increase of FM was 35% for PC, where only a 12% increase occurred for PPE. FM is one of the polymer properties which does not alter significantly by polymer structure, so that it is quite interesting that FM increased by blending viscous liquid.

Table III shows the effect on FM of PPE by blending OPC-analogous compounds shown in Table I. Aromatic amines dramatically increased PPE FM where 2.93 MPa and 2.74 MPa were observed by blending BAPPP and BAPIP, listed in Table I, respectively. In the case of low molecular weight OPC, FM increased according to OPC molecular weight as shown in Figure 1. However, almost no relationship between molecular weight and FM increase was observed for phthalates and aromatic amines. The reason why FM increased with increasing the molecular weight of OPC was considered that the larger OPC made a complex with the polymer. Excepting OPC, compounds used in this study were chosen considering viscoelastic β -dispersion shift and the relationship between FM increase and molecular weight. The effect of conformation on molecular interaction was calculated using molecular dynamic simulation.

A characteristic change was observed on loss

modulus among viscoelastic properties when two kinds of OPC used in this study were blended with PPE. Figure 2 shows observed loss modulus of PPE and the blend of TPP or BBC. PPE showed α -dispersion at $\sim 210^\circ\text{C}$, and at 50 and -100°C for β - and γ -dispersion, respectively. Blending of TPP caused the curve shift toward low temperature where α - and β -dispersion were observed at 110 and at -20°C , respectively. While in the blend of BBC, only α -dispersion temperature decreased and β -dispersion temperature was found at the same temperature zone to that of PPE.

Figure 3 shows the loss modulus of three types of phthalic ester blends where the chemical structures of these phthalic esters are analogous to each other. As well as blending OPC, α -dispersion temperature shifted to 120°C for all samples. The β -dispersion temperature of the PPE/DPP blend dropped, and the peak became moderate. However, in the case of the PPE/DPIP blend, both the temperature and the peak of the β -dispersion stayed the same as PPE alone.

The largest modulus change was observed in

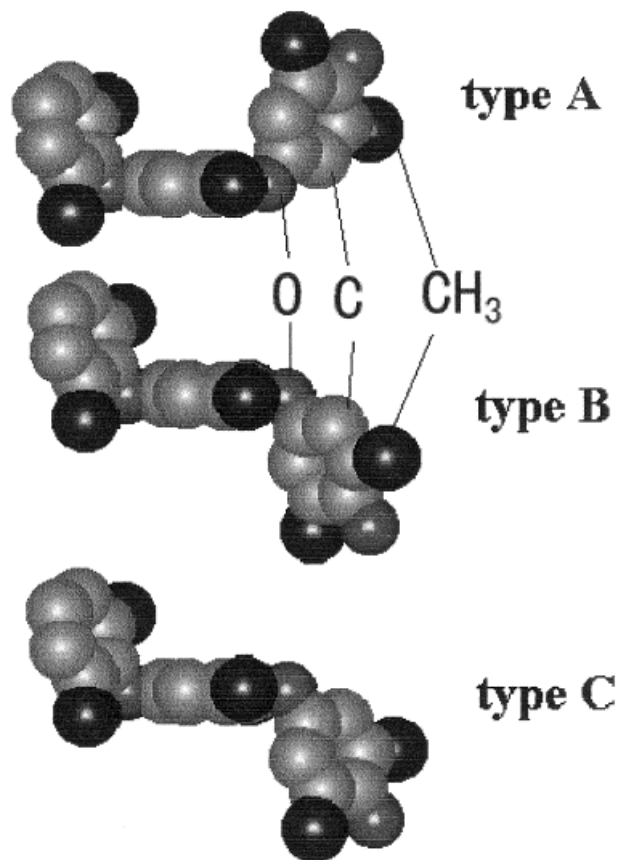


Figure 4 Three-dimensional structure of PPE with three repeating units.

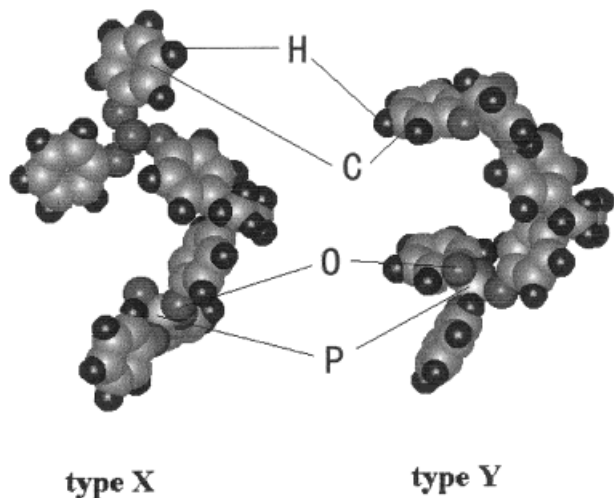


Figure 5 Three-dimensional structure of BBC.

the PPE/BAPP blend, where the FM of PPE was 2.45 MPa. Among compounds with analogous chemical structures (where the substitution positions are ortho, meta, and para for DPP, DPIP, and DPTP, respectively), only DPIP showed a significant FM increase. DPP dropped β -dispersion temperature of loss modulus and the FM was 2.48 MPa, which was almost the same as that of PPE alone. However, the blends which exhibited a β -dispersion temperature of loss modulus increase, for example in the case of DPIP, showed FM increases.

Fundamental viscoelastic properties and the activation energy of β -transition was first determined to be ~ 80 kJ/mol by Petris et al. using a polymer with 30,000 of molecular weight.^{25–28} Sauer reported that the activation energy of γ - and β -transition of PPE were 20 kJ/mol and 40 kJ/mol, respectively. Activation energy of diffu-

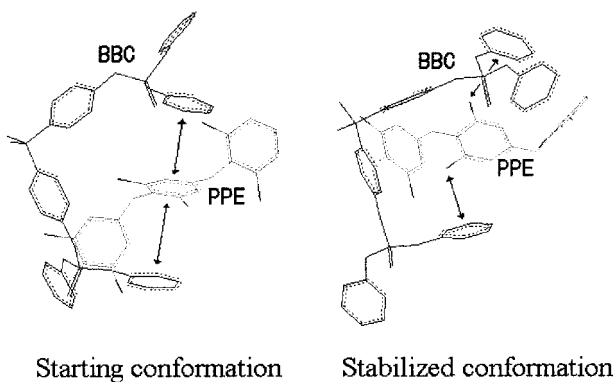


Figure 6 Interaction between PPE (type C) and BBC (type X) started from π - π stacking.

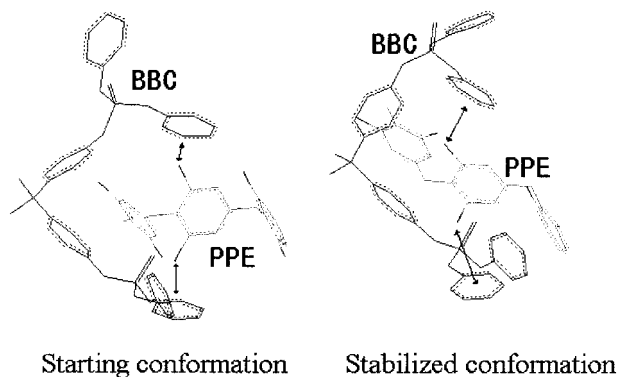


Figure 7 Interaction between PPE (type C) and BBC (type Y) started from π -hydrogen bond.

sion of low molecular weight components, whose molecular weight is ~ 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 suggests that it is a diffusion 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. Sauer clarified the dispersions of PPE by detailed studies.²⁹ The γ -dispersion peak, appearing from -173 to -93°C , was considered to belong to the phenylene group rotation, and the β -dispersion peak of -93 to -83°C to the interaction with water because its 40–50-kJ/mol of activation energy was largely affected by the presence of water molecules. Another β -dispersion-like peak appearing at 7 to 127°C was considered to be caused by the molecular motion due to defects. Because PPE has low melt viscosity and a hard-to-remove polymerization solvent such as toluene, the effect of residual molding stress and solvents should be taken into consideration. For example, comparing spectra of samples of PPE prepared immediately after poly-

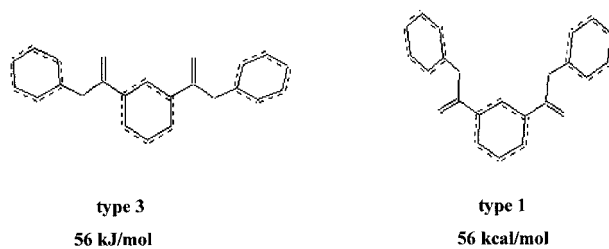


Figure 8 Three-dimensional structure of DPIP.

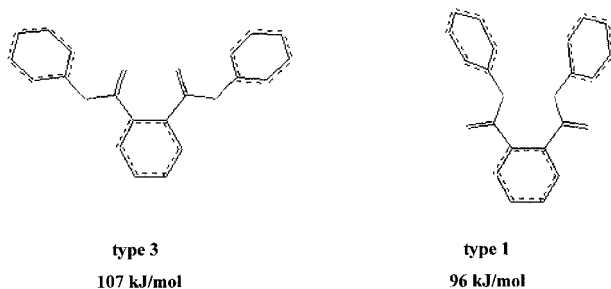


Figure 9 Three-dimensional structure of DPP.

merization with the one purified by reprecipitating benzene solution into methanol, the latter sample showed slight β -transition temperature increases and the peak itself became smaller. Since γ -dispersion disappears by purification, it may be concluded that γ -transition is caused by the interaction with the solvent. Some other researchers reported that γ -dispersion largely altered according to the amount of water included.³⁰

Considering these findings and reports, it is difficult to consistently discuss dispersion temperature or peak pattern change. The conclusion differs from researchers who measured viscoelastic spectra or read publications. However, from many findings about activation energy, the state of γ -dispersion of PPE consisting solvent, NMR observation, and the study on PPE chain conformation, it is reasonable to conclude that γ -dispersion relates to very local movement such as rotation of main chains or benzene rings, and β -dispersion relates to relatively larger scale movement including several monomer units. Hence, in a study dis-

cussing the viscoelastic property change, especially about β -dispersion, by blending OPC or phthalic ester compounds, it is necessary to consider the interactions between low molecular weight compounds and PPE chains which consist of several monomer units. From this reason, a numerical simulation about the interaction between low molecular weight compounds and PPE chains based on molecular dynamics was carried out. BBC, which showed significant FM increase, was chosen as an object. Other objects were DPIP, which has a chemical structure akin to BBC and showed characteristic change in FM or viscoelastic loss modulus, and DPP, which did not show such a change in spite of having isomeric structure.

Instead of calculating a whole polymer chain of PPE, a model component consisting of three repeating units was chosen to calculate stable PPE conformation. Figure 4 shows that there were three types of stable conformations, named A to C, where the energy of these were almost the same as 64 kJ/mol. From this calculation it is possible to assume that there is no particular stable repeating unit conformation in PPE. In the case of BBC, there were two stable conformations, as shown in Figure 5. The energy of type Y was 209 kJ/mol, where two benzene rings of phosphorous esters confront each other across bis-phenol A-type molecular center, and that of type X, where these rings locate in the opposite side, had relatively smaller energy of 191 kJ/mol, indicating that type X conformation was slightly more stable for BBC. The absolute energy value is not

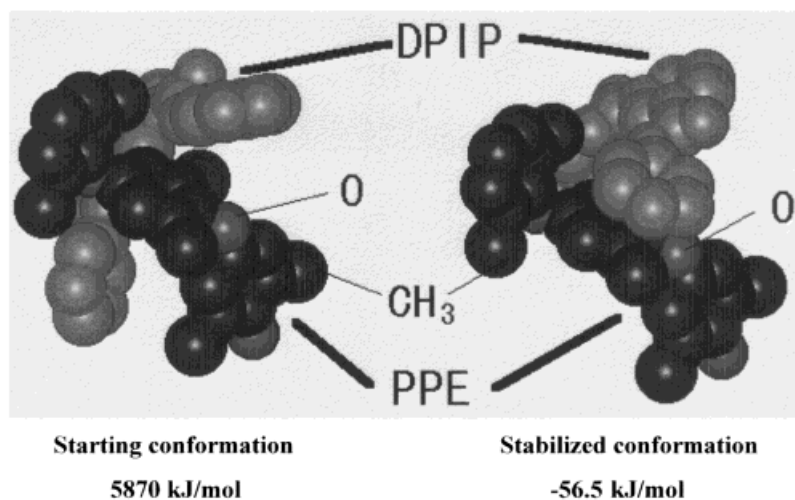


Figure 10 Interaction between PPE (type C) and DPIP (type 1) started from π - π stacking.

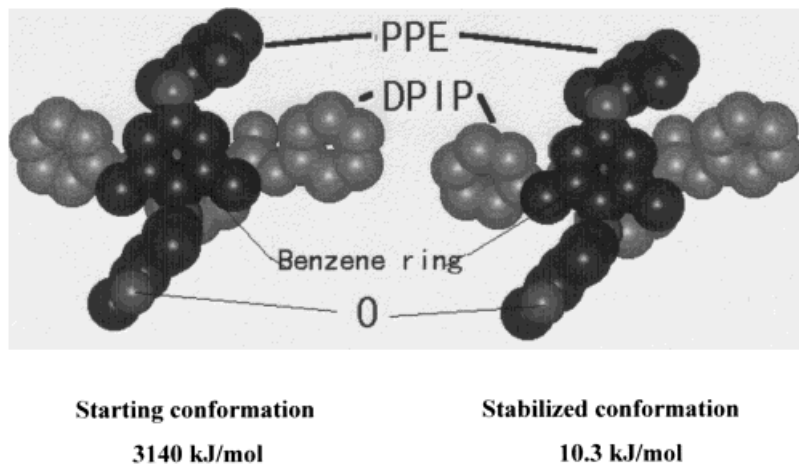


Figure 11 Interaction between PPE (type C) and DPP (type 3) started from π - σ stacking.

important since the simulation was started from the easiest conformation for calculation.

It is expected that benzene rings between PPE and BBC form a π - π complex. From NMR observation, unusual miscibility of PPE/PS alloy suggests that the polymer chains must closely approach each other. The interaction between benzene rings possibly exists when their chains approach so closely. Hence, in the simulation of PPE and BBC interaction, the starting conformation (Fig. 6, left) was built assuming a π - π complex, then calculating the most stable conformation. However, against the expectations, the stability of the starting conformation consisting of a π - π complex (Fig. 6, left) was low, where the

energy was as high as 1900 kJ/mol. It was also found that the conformation shown in Figure 6, right, where both PPE and BBC occupy twisted positions (stabilized conformation) had the energy of 29 kJ/mol. This result indicates that the blend of PPE and BBC has a higher probability to have twisted conformation by forming a m - π complex between methyl groups of PPE and BBC benzene rings.

However, one must be careful about the calculation output because of its uncertainty. For example, if there were a quasi-stable conformation close to the starting one, the simulation might terminate at this stage. In order to check the possibility whether the final stable structure differs from starting con-

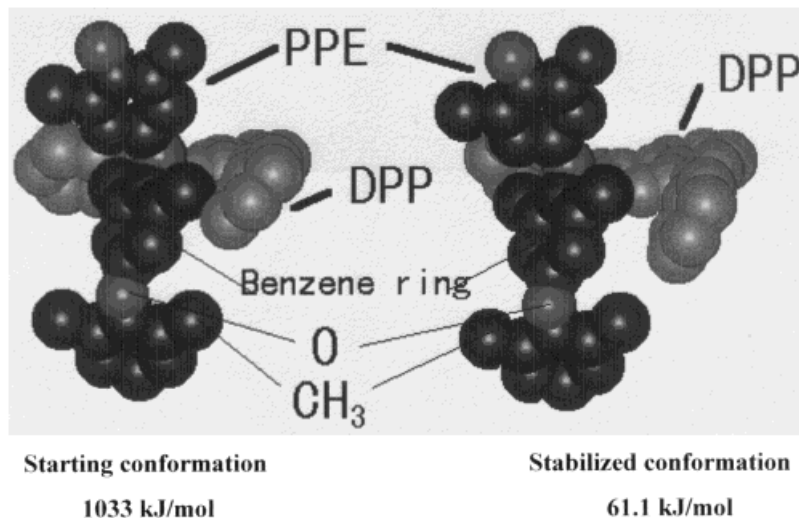


Figure 12 Interaction between PPE (type C) and DP/IP (type 3) started from π - σ stacking.

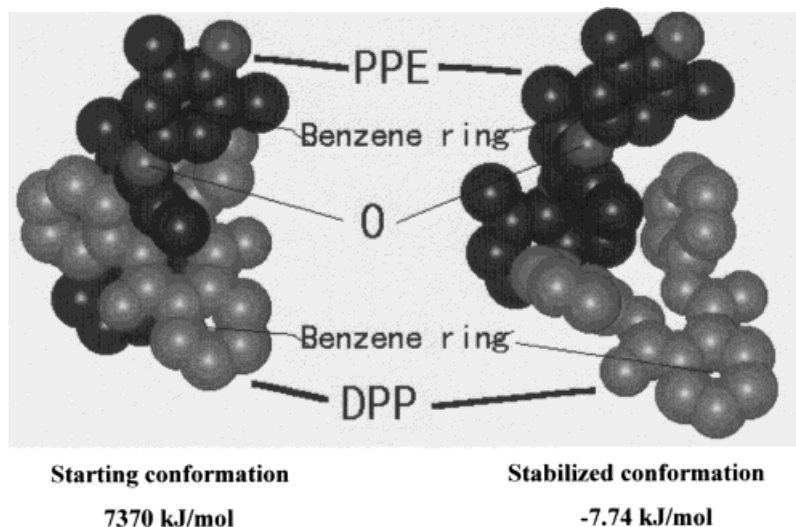


Figure 13 Interaction between PPE (type C) and DPP (type 1) started from $\pi-\pi$ stacking.

formations, a calculation was tried starting from the conformation where BBC did not twist and form a $\sigma-\pi$ complex between methyl group and benzene rings. The starting conformation shown in Figure 7, left, where the energy was 623 kJ/mol, transformed to result in the conformation shown in Figure 7, right, where the energy was 32 kJ/mol. This conformation was the same as previous case. Hence it was concluded that the interaction between PPE and BBC caused the conformation where $\sigma-\pi$ complex between the methyl group of PPE and benzene ring of BBC.

Similar simulations between PPE and DPIP or DPP, which are phthalic ester compounds, were studied. The stability of phthalic ester compounds alone did not exhibit significant difference due to the conformations shown in Figures 8 and 9. The energy of the strait conformation shown on the right-hand side in Figure 8, which appeared to be unstable, did not differ from the bent conformation, which seemed more stable. From the output that there was little difference on energy from starting conformations, it was expected that the chemical structure of phthalic ester compounds would directly reflect the stable conformation of the blend controlled by the interaction with PPE.

The interaction between DPIP (type 1) and PPE was calculated and the result is shown in Figure 10. Starting from a quite unstable conformation where the energy was 1300 kJ/mol, 5900 kJ/mol of stabilization energy was obtained. Similarly, stabilization energy obtained by calculating DPIP (type 3) and PPE was 3100 kJ/mol as shown

in Figure 11. In both cases, DPIP surrounded PPE units and methyl groups of PPE closely approached the DPIP benzene ring.

On the other hand, completely different results were obtained by calculating interaction between DPP and PPE, where FM increase was not observed. Calculation started from type 3 conformation (Fig. 12), as well as from type 1 conformation (Fig. 13), terminated at a stable conformation where the DPP molecule was repelled out from the PPE chain (this conformation was clearly explained in the right side of Fig. 13). Even when the calculation was started from the conformation where DPP was inserted in PPE as shown in the left side of Figure 13, the calculation terminated, indicating that DPP could not come close and the blend stabilized where DPP was distant from PPE.

Flexural modulus increase was clearly explained by viscoelastic analysis and by the result of conformation simulation. For the blend of PPE and low molecular weight compound where FM increase was observed, viscoelastic β -dispersion remains without change. Because γ -dispersion at lower temperature did not change, it was concluded that there was no difference in local chain movement by blending. When solvents activate polymer main chain movement, β -dispersion temperature decreases. Because of the fact that β dispersion temperature decrease did not occur by blending liquid low molecular weight compound, it was indicated that the interaction restricted the movement of the PPE

polymer chain. The results of experiments and simulation, studied using phthalic ester isomers, suggested that the substance of restriction was due to its conformation, where the interaction between PPE and the benzene ring of those compounds is possible.

CONCLUSIONS

A strong interaction between PPE and OPC with a particular structure was observed; an FM increase was related to OPC molecular weight. There were some esters with structures similar to OPC which caused FM increase by blending with PPE. However, molecular weight dependence of the FM increase was small. A relationship between viscoelastic β -dispersion temperature change and FM increase was found, and there was a possibility of complex formation between PPE methyl groups and benzene rings of OPC. In the combination of PPE and phthalic esters with isomeric structure, an FM increase was observed only when the substitution position of phthalic esters to benzene ring was suitable to surround PPE.

REFERENCES

1. A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6335 (1959).
2. A. S. Hay, *Adv. Polymer Sci.*, **4**, 496 (1967).
3. K. Takeda, N. Ooki, K. Shichijo, and S. Takayama, *Materials Life*, **7**, 126 (1995).
4. K. Takeda and S. Takayama, *J. Polymer Degradation and Stability*, **50**, 277 (1995).
5. D. W. van Krevelen, *Polymer*, **16**, 615 (1975).
6. D. W. van Krevelen, *Chimia*, **28**, 504 (1974).
7. D. W. van Krevelen, J. Bicerano, Ed., *Computational Modeling of Polymers*, Chap. 1, Marcel Dekker, New York, 1991.
8. K. Takeda and S. Takayama, *J. Society of Materials Science, Japan* **45**, 1259 (1996).
9. A. T. Walter, *J. Polym. Sci.*, **13**, 207 (1967).
10. U. Jacobson, *Brit. Plastics*, **32**, 152 (1959).
11. P. Ghera, *Modern Plastics*, **36**, 135 (1958).
12. O. Fuchs and H. Frey, *Kunststoffe*, **49**, 213 (1959).
13. G. Grunwald, *Kunststoffe*, **50**, 381 (1960).
14. W. J. Jackson, Jr. and J. R. Caldwell, *Adv. Chem. Ser.*, **48**, 185 (1965).
15. W. J. Jackson, Jr. and J. R. Caldwell, *J. Appl. Polym. Sci.*, **11**, 211 (1967).
16. W. J. Jackson, Jr. and J. R. Caldwell, *J. Appl. Polym. Sci.*, **11**, 227 (1967).
17. N. Kinjo, *Japan Plastics*, **7**, 6 (1973).
18. S. L. Anderson, E. A. Grulke, P. T. DeLassus, P. B. Smith, C. W. Kocher, and B. G. Landes, *Macromolecules*, **28**, 2944 (1995).
19. R. P. Kambour, J. M. Caraber, C. L. Fasoldt, G. T. Seeger, N. M. Sowa, and D. M. White, *J. Polym. Sci., Part B*, **33**, 425 (1995).
20. C. C. Price, W. A. Butte, and R. E. Hughes, *J. Polym. Sci.*, **61**, 28 (1962).
21. J. M. Barrales-Rienda and J. M. Fatou, *Koolid. S.S., Polymer*, **244**, 317 (1971).
22. S. Horikiri and K. Kodra, *Polymer J.*, **4**, 213 (1973).
23. W. R. Wenig, W. Hammel, J. MacKnight, and F. E. Karasz, *Macromolecules*, **9**, 253 (1976).
24. USP 4, 788, 277.
25. S. de Petris, V. Frosini, E. Butta, and M. Bacca-redda, *Die Makromolekulare Chemie*, Vol. 109, No. 2534, 1967, p. 54.
26. J. Heijboer, *J. Polym. Sci., Part C*, **16**, 3755 (1968).
27. J. Stoelting, F. E. Karasz, and W. J. MacKnight, *Polym. Eng. Sci.*, **10**, (1970).
28. C. I. Chung and J. A. Sauer, *J. Polym. Sci., Part A-2*, **9**, 1097 (1971).
29. J. A. Sauer, *Polym. Eng. Sci.*, **13**, 51 (1973).
30. G. Allen, J. McAinsh, and G. M. Jeffs, *Polymer*, **12**, 85 (1971).