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Dielectric properties of polyarylate blends

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Dielectric properties and molecular motion were studied by use of dielectric spectroscopy and differential scanning calorimetry for two blends, fully transesterificated polyarylate of bisphenol A with terephthalate/isophthalate (50/50) (PA)/polycarbonate of bisphenol A (PC) blends and PA/poly(ethylene terephthalate) (PET) blends. All the quenched PA/PC and PA/PET blends were amorphous and the glass transition temperature (Tg) was varied with the blends ratio according to Gordon-Taylor equation. The PA/PET blends with more than 60% of PET crystallized above the crystallization temperature. The PA/PC and PA/PET blends showed two dielectric relaxations, α above Tg and γ below Tg, which are related to a glass transition and a local motion of short segment, respectively. The α relaxation moved to lower temperatures as PC or PET content increases, reflecting the lowering Tg faithfully. In the PA/PET blends, the static (ε_0) and the limiting dielectric constant (ε_∞), and the increment ($\Delta\varepsilon$) for the α relaxation decreases with increasing temperature and the decrease falled on one curve, independent of the blend ratio. Any ferro- and piezoelectricity were not observed for two blends. *© 2000 Kluwer Academic Publishers*

1. Introduction

During a few decades, polyarylates have attracted technical and industrial interests as one of useful engineering plastics, because of outstanding physical properties such as high modulus, good thermal and weather resistances, flame retardation, optical transparency and so on. Polyarylates of 2,2-bis (4-hydroxyphenyl) propane (bisphenol A) with terephthalate/isoterephthalate and its blends with other polyesters such as polycarbonate of bisphenol A or poly(ethylene terephthalate) (PET) are commercially available, having been used for electric and automobile parts. In these blends, it is well known that a transesterification reaction frequently occurs between two blended polyesters and the miscibility increases as the transesterification promotes [1–5]. Moreover, it has been pointed out that their physical properties can be controlled by blend ratio and degree of transesterification. However, it is fully transesterified polyarylate blends that have been industrially used. Moreover, dielectric and electric properties are important factors for the use as engineering plastics, but have been scarcely investigated unexpectedly.

From these views, this work is undertaken to disclose dielectric properties of polyarylate of bisphenol A with terephthalate/isophthalate (50/50) and its blends with polycarbonate of bisphenol A or poly (ethylene terephthalate) (PET) which are fully transesterificated, where the chemical structures of polyesters are illustrated in Fig. 1. Dielectric relaxational molecular motion, and ferro and piezoelectricity are discussed for the blends.

2. Experimental

Polyarylate of bisphenol A with terephthalate/isophthalate (50/50) (bisphenol A/phthalate: 50/50) (PA) was U-100 of Unitika Ltd. (Tokyo), which was prepared by interfacial condensation polymerizations of sodium bisphenolate A with phthalic dichlorides. The average-number molecular weight (Mn) was estimated to be about 20000 by a gel chromatography. Polycarbonate of bisphenol A (PC) and PET were Calibre of Sumitomo-Dow Co. (Tokyo) and Unitika Ester Resin of Unitika Ltd. (Tokyo), respectively, whose Mn's are 22000 and 21000, respectively.

The PA blends were prepared by blending PA with PC or PET at 573–603 K, using a Brabender extruder, where the blends were mixed until the torque in the molten state reached a constant value, and so a transesterification reaction was judged to accomplish completely. The blends obtained was compression-molded into sheets of 2–3 mm thick at 573–603 K and quenched into 283 K.

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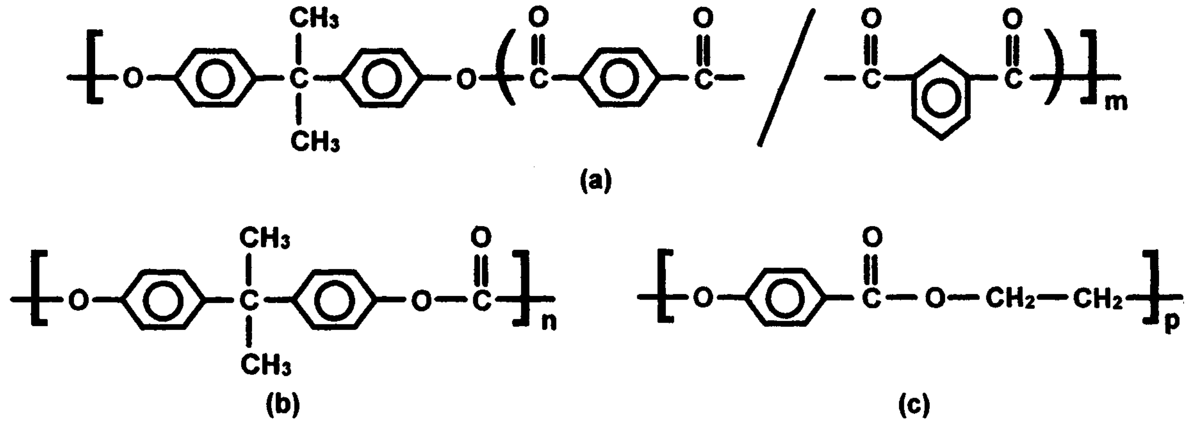

Figure 1 Chemical structures of polyesters. (a) polyacrylate of bisphenol A with terephthalate/isophthalate (50/50) (PA), (b) polycarbonate of bisphenol A (PC), (c) poly(ethylene terephthalate) (PET).

Thermal properties were measured at the heating/cooling rate of 10 K·min^{-1} by use of a Seiko SSC-5000 differential scanning calorimeter (DSC), where indium and tin were used as enthalpy standards. Dielectric measurements were carried out with a Multi-Frequency LCR meter (YHP, Type 4274A) between 100 Hz and 100 kHz at heating rate of about 0.5 K·min^{-1}. The electrode system was used as described previously [6]: The electrode was constructed by the main guarded and unguarded desk electrodes. The main electrode was electrically guarded with a concentric guard ring of 50 mm, respectively. The main electrode was electrically guarded with a concentric guard ring of 50 mm in outer diameter and 39 mm in inner diameter. The polymer disk of 50 mm Φ with ~4 μm thick was mounted between the main and unguarded electrodes, where the electrical contact between the sheet surface and the electrode was ensured by depositing aluminum on sheet surfaces.

Electric displacement (D) vs. electric field (E) curves were measured by the Sawyer-Tower method using a high voltage triangular-wave field of 30 mHz as described elsewhere [7]. The D-E hysteresis measurements were in a temperature range from room temperature up to 450 K at electric field magnitude of 180 MV m^{-1}. Piezoelectric constants were measured for the speciments poled in the D-E hysteresis measurements using a Orientec Corp. Model DDV-II-C Rheovibron equipped with a Model rheo 20 charge amplifier.

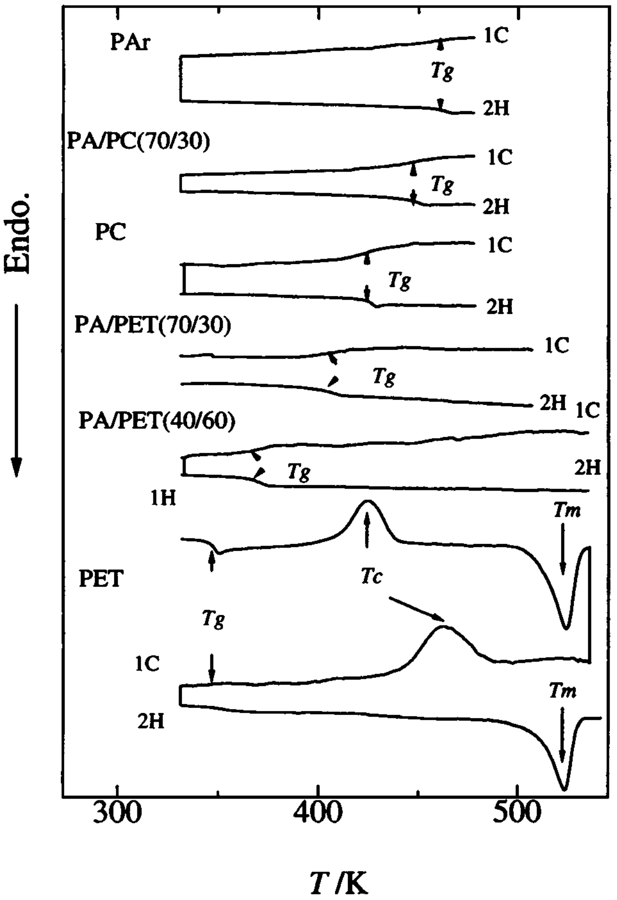

Figure 2 DSC curves of PA/PC and PA/PET blends at a heating/cooling rate of about 10 K·min^{-1}. 1H and 2H: 1st and 2nd heating, 1C: 1st cooling.

3. Results and discussion

Fig. 2 shows typical DSC curves for PA/PC and PA/PET blends. In PA and PC, one bend is observed near 461 and 425 K, respectively, corresponding to the glass transition temperatures (Tg). The PA/PC (70/30) blend shows one bend near 446 K corresponding to Tg, and a similar bend was seen for all other PA/PC blends. This result suggests that the PA/PC blends are amorphous over all the blend ratio. In PET, at the 1st heating, a bend corresponding to Tg is seen near 343 K, and then an exothermic peak and an endohthermic peak are seen near 424 and 523 K, respectively, which correspond to crystallizing (Tc) and melting temperatures (Tm), respectively. There are the quenched original PET is amorphous at room temperature, because the enthropy change of the crystallizing is canceled by that of the melting. However, once DSC measurements are run above Tc, PET become crystalline, showing an endothermic peak near 523 K. On DSC thermograms, the PA/PET blends with less than 60% PET were amorphous, almost regardless of thermal treatment. In the PA/PET (40/60), a bend is seen near 367 K at the heating but any thermic peak was not seen on DSC thermogram but a small amount of crystalline region was detected above Tc on the first heating on dielectric data described later. These results means that PA obstracts the formation of crystallites in PA/PET blend. Both Tg and Tm values are listed in

TABLE I Phase transition parameters obtained from DSC

Polyesters	T_g/K	T_m/K	T_c/K
PA/PC blends			
100/0	461		
90/10	458		
70/30	446		
50/50	438		
0/100	425		
PA/PET blends			
100/0	461		
70/30	399		
60/40	387		
50/50	376		
40/60	367		455[a]
0/100	343	523	424 (1st. H) 462 (1st. C)

[a] Obtained from dielectric measurements at a heating rate of about 2 K·min^{-1}.

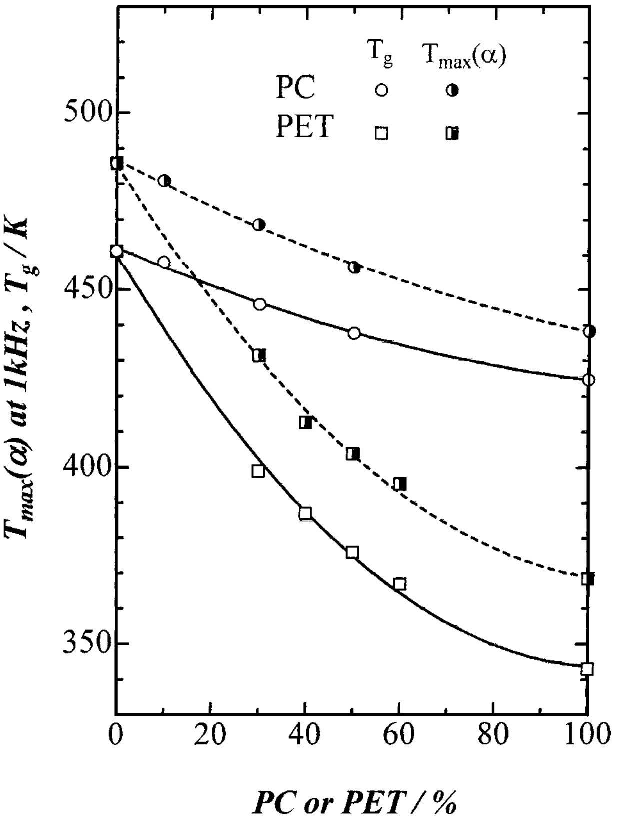

Figure 3 Plots of glass transition temperature obtained with DSC (Tg) and relaxation temperature of α relaxation at 1 kHz [$T_{max}(\alpha)$] versus PC or PET content (%) in PA/PC or PA/PET blends.

Table I. The values of Tg are plotted versus blend ratio in both PA/PC and PA/PET blends in Fig. 3. The plots for both blends well obey the Gordon-Tayler equation,

$$Tg = (w_1 Tg_1 + k w_2 Tg_2)/(w_1 + w_2),$$

where w_1, w_2, Tg_1, Tg_2 and k are weight fraction of PA, weight fraction of PC or PET, Tg of PA, Tg of PC or PET and parameter, where k was estimated as ~1.8 in PA/PC and ~2.14 in PA/PET. It is concluded that in both PA/PC and PA/PET blends, the transesterification change are accomplished, because only one glass transition is observed over all blend ratios from 0 to 100% in both PA/PC and PA/PET blends and obeys the Gordon-Tayler equation.

Fig. 4 shows temperature dependence of dielectric constant (ε') and the loss (ε'') for PA at several frequencies. There are observed two relaxation, α near 486 K and γ near 243 K at 1 kHz, which are attributable to a re-orientational molecular motion of long segments above Tg and a local molecular motion of short segments below Tg, respectively, as have been conventionally seen in amorphous polymers [8, 9]. Fig. 5 shows temperture dependences of dielectric loss (ε'') at 1 kHz for PA/PC blends. As PC content increases, the α relaxation moves to lower temperatures, which corresponds to the lowering of Tg with blending PC [9], and the γ relaxation also shifts to lower tempertures slightly (Table III). Fig. 6 shows temperture dependence of dielectric constant (ε') (a) and the loss (ε'') (b) at 1 kHz for PA/PET blends. In PA/PET blends as well as PA/PC blends, the α relaxation moves to lower temperatures, as PET content increases, and the γ relaxation is seen below Tg. In PET, the α relaxation is seen near 370 K at 1 kHz, and an abrupt change, an abrupt decrease in ε' and a peak in ε'' (see arrow in the figure), is seen near 400 K, which may be caused by the crystallizing of PET, because the temperture corrsponds to Tc on DSC (Table I), independent

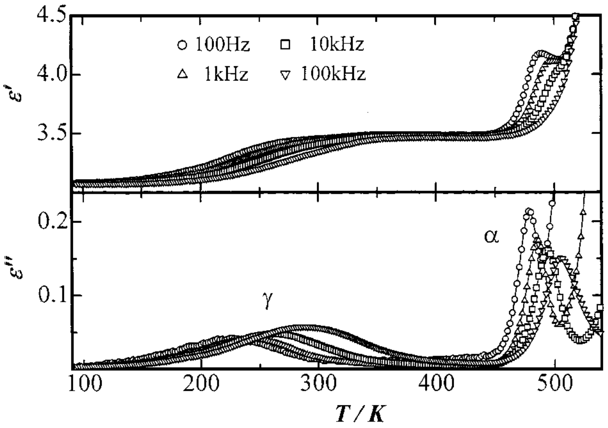

Figure 4 Temperature dependence of dielectric constant (ε') and the loss (ε'') in PA at different frequencies.

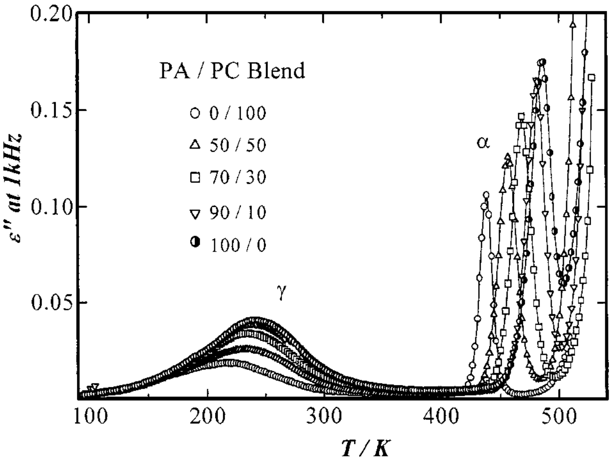

Figure 5 Temperature dependence of dielectric loss (ε'') at 1 kHz in PA/PC blends.

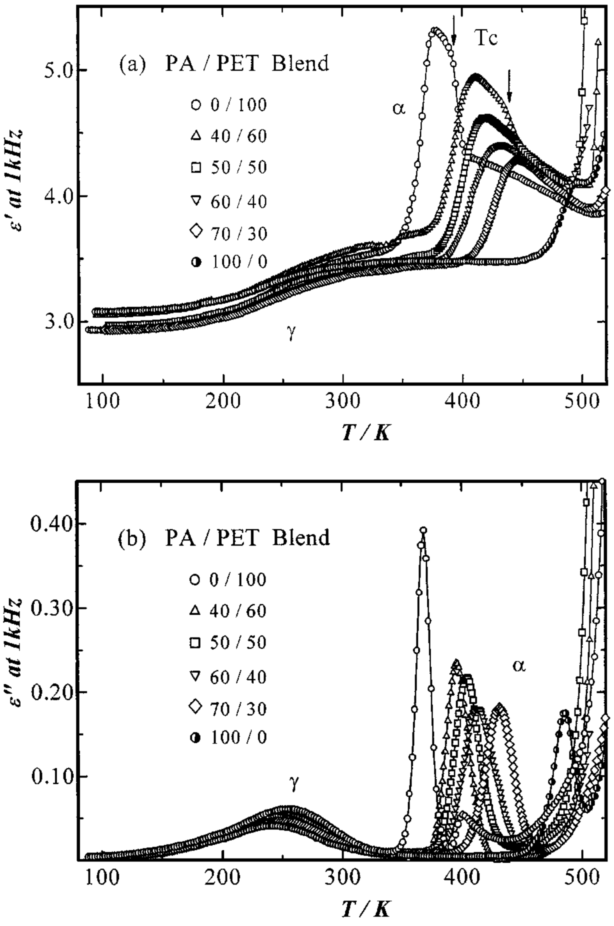

Figure 6 Temperature dependence of dielectric constant (ε') (a) and the loss (ε'') (b) at 1 kHz in PA/PET blends.

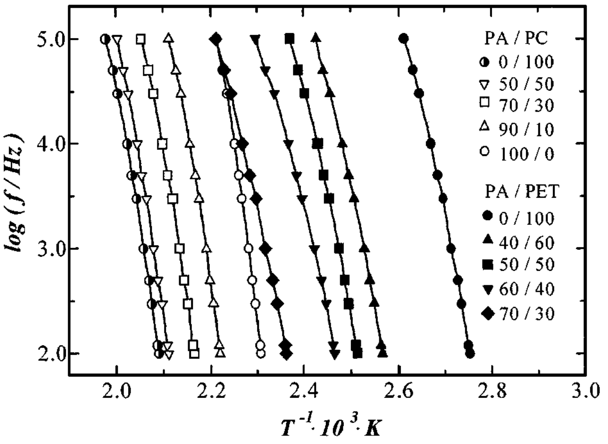

Figure 7 Arrhenius plots of α relaxation in PA/PC and PA/PET blends.

on frequency. This abrupt change in ε' and ε'' (see arrow) is also seen for 60% PET blends near 430 K in Fig. 6, higher than that in PET (400 K); the abrupt change in ε'' at 1 kHz is not visualized on the figure but certainly exists as a very small peak which is larger at the lower frequencies. This means that PA obstracts the crystallizations, and in the other words, lowers the crystallization speed, resulting in shifting the crystallization temperture to higher tempertures. Therefore, the 60% PET blends is certainly crystalline, but the crystallinity is too low to detect the peak in DSC measuremests (Fig. 2). In less than 60% PET blends, any crystallizing or melting was not detected on both DSC and dielectric data. Consequently, PA obstracts the formation of crystallites in PA/PET blends. As a result, when PET is 60%, the blend is crystalline but the crystallinity is very low, and when PET is less than 60%, the PA/PET blends are amorphous.

In Fig. 7, Arrhenius plots in the α relaxation are shown for PA/PC and PA/PET blends. The plots are curved, indicating a WLF type and moves to higher tempertures as PC or PET content increases. The activation parameters for α and γ relaxations are listed in Table II. In the α relaxation, the free volume fraction at Tg (fg) was between 0.024–0.034 and $T_{\max}$ at 1 kHz are higher by about 25 K than Tg, as shown in Fig. 3. The plots for γ relaxation showed a straight line, being in a Arrhenius type, and the activation enthalpy $[\Delta H(\gamma)]$ was estimated to be about 55–59 kJ·mol^{-1} for PA/PC blends and 60–65 kJ·mol^{-1} for PA/PET blends, respectively. The value of static dielectric constant (ε_0'), limiting dielectric constant (ε_∞') and dielectric increment ($\Delta\varepsilon' = \varepsilon_0' - \varepsilon_\infty'$) were obtained from Cole-Cole plots. The plots obey the Cole-Cole equation [10] for

TABLE II List of dielectric relaxation parameters

	γ relaxation		α relaxation				
				WLF parameters			
Polyesters	$T_{\max}$/K at 1 kHz	ΔH (kJ·mol^{-1})	$T_{\max}$/K at 1 kHz	T_0/K	C_{1g}	C_{2g}	f_g
PA/PC blends							
100/0	243	60	486	411	14	50	0.030
90/10	239	55	481	418	13	41	0.034
70/30	235	57	469	413	13	34	0.035
50/50	233	54	456	382	14	56	0.030
0/100	220	59	438	363	16	62	0.027
PA/PET blends							
100/0	243	60	486	411	14	50	0.030
70/30	251	62	431	334	17	65	0.026
60/40	248	67	413	352	13	35	0.034
50/50	252	65	404	341	16	35	0.027
40/60	256	64	395	335	18	32	0.025
0/100	256	65	369	315	18	28	0.024

γ relaxation and showed a skewed arc for α relaxation, which were well fitted to the Williams-Watts equation [11],

$$\varepsilon^* = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)\sum_{n=1}[(-1)^{n-1}/(\omega \mathrm{T}_0)^{\mathrm{nb}} \times \Gamma(n\beta + 1)/\,\Gamma(n+1)\cdot \cos(\pi\beta n/2) - \mathrm{i}\ \sin(\pi\beta n/2)],$$

where the distribution parameters of relaxation time (β) were estimated as 0.36–0.42 for PA/PC blends and 0.29–0.40 for PA/PET blends, as listed in Table III. The values of ε_0', ε_∞' and $\Delta\varepsilon$ for the α relaxation were plotted against temperture in Fig. 8. In PA/PET blends, the values of ε_0' and ε_∞' and $\Delta\varepsilon$ decrease with decreasing temperature, and rather interestingly, appear to fall on one curve, respectively, independent of the blend ratio. In PA/PC blends, on the other hand, the values of ε_0 and $\Delta\varepsilon$ become larger, as PC content decreases, and fall on each $\Delta\varepsilon$–temperature curves for each PC content, while the value of ε_∞, slightly increases as temperature increases and fall on one curve for all PA/PC blends. The value of ε_∞' are nearly equal to n^2 (n: refraction index) which may be associated with electric polarization. In

TABLE III List of static dielectric constant (ε_0), limiting dielectric constant (ε_∞), dielectric increment ($\Delta\varepsilon$), and distribution parameter of relaxation time (β) at the relaxation temperature of 1 kHz

	γ relaxation					α relaxation				
Polyesters	$T_{\max}$/K	ε_0	ε_∞	$\Delta\varepsilon$	β^a	$T_{\max}$/K	ε_0	ε_∞	$\Delta\varepsilon$	β^b
PA/PC blends										
100/0	243	3.432	3.110	0.322	0.36	486	4.319	3.462	0.857	0.37
90/10	239	3.376	3.124	0.252	0.41	481	4.156	3.425	0.731	0.41
70/30	235	3.327	3.085	0.242	0.35	469	4.040	3.339	0.701	0.36
50/50	233	3.200	2.969	0.231	0.29	456	3.818	3.200	0.618	0.37
0/100	220	3.153	3.033	0.120	0.38	438	3.621	3.137	0.494	0.42
PA/PET blends										
100/0	243	3.432	3.110	0.322	0.36	486	4.319	3.462	0.857	0.37
70/30	251	3.328	3.027	0.301	0.44	431	4.451	3.437	1.014	0.32
60/40	248	3.356	3.022	0.334	0.43	413	4.566	3.485	1.081	0.29
50/50	252	3.406	3.064	0.342	0.42	404	4.792	3.556	1.236	0.31
40/60	256	3.537	3.151	0.386	0.39	395	5.081	3.727	1.353	0.31
0/100	256	3.474	3.083	0.391	0.40	369	5.450	3.729	1.720	0.40

[a] The Cole-Cole distribution parameter of relaxation time.
[b] The Williams-Watts distribution parameter of relaxation time.

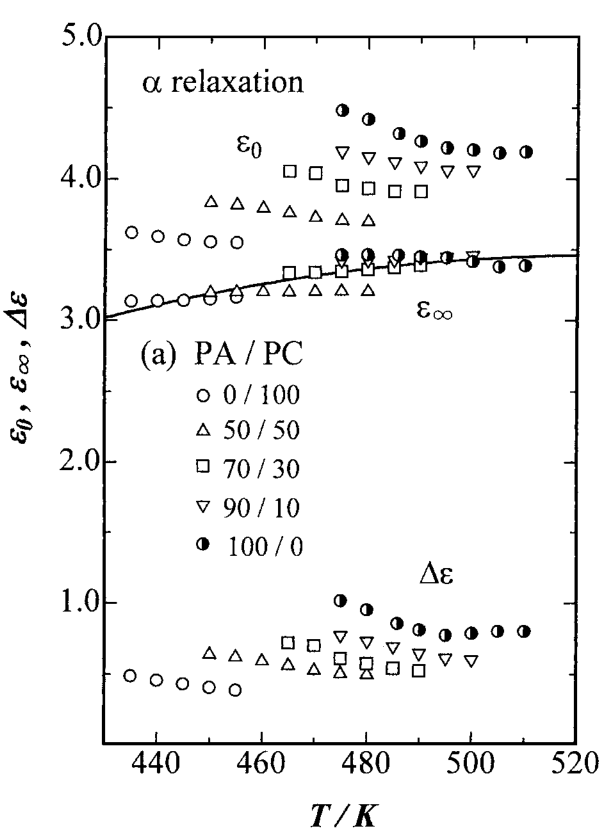

Figure 8 Variations of static dielectric constant (ε_0), limiting dielectric constant (ε_∞) and dielectric increment ($\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$) with temperature for PA/PC (a) and PA/PET (b) blends.

both PA/PET and PA/PC blends, the electric polarization may come mainly from the ester group in addition to benzene ring. The electric polarization per unit volume may be scarcely changed by the blend ratio in both PA/PC and PA/PET blends, and as a result, the value of ε'_∞ may be not changed so much with the blend ratio. The values of ε_0, ε_∞ and $\Delta\varepsilon$ at $T_{\max}$ (1 kHz) for γ relaxation were listed, also in Table III. These values were somewhat changed with temperature between 200 and 300 K but the change was very small.

Recently, piezoelectricity and ferroelectrocity have been discovered for amorphous polyamides of isophtalic acid with aliphatic diamine and of meta-xylenediamine with aliphatic dicarboxylic acid by Murata, Tsunashima and Koizumi [12, 13]. In the present work, we measured piezoelectricity and ferroelectricity for PA, PA/PC and PA/PET blends containing isophthalic acid moiety but these polyesters had no piezoelectricity and no ferroelectricity which may be explained by no existence of hydrogen bonding, because it has been pointed out that the appearance of piezoelectricity and ferroelectricity in amorphous polyamides may be closely connencted with an existence of hydrogen bonding.

In conclusion, the fully transesterified PA/PC and PA/PET blends are amorphous and the change of Tg with the blend ratio was well explained by the Gordon-Tayler equation. The quenched PET are amorphous at room temperature but a peak due to crystallizations was observed near 424 K at the 1st heating on DSC and dielectric measurements. In the PA/PET (40/60) blends, a very small change was seen near 455 K only on dielectric data, but not at all in the less than 60% PET blends. These results indicate that PA obstracts a formation of crystallites in PET.

Both PA/PC and PA/PET blends show two dielectric relaxations, α above Tg and γ below Tg, which are attributable to a reorientational molecular motion of long segments above Tg and a local molecular motion of short segments below Tg, respectively. The values of ε_0, ε_∞ and $\Delta\varepsilon$, for the α relaxation change with temperature. In PA/PET blends, the ε_0, ε_∞ and $\Delta\varepsilon$, values decrease with increasing temperature and their decreases fall on one curve, roughly independent of PET content, while in PA/PC blends, the value of ε_∞ slightly increases with increasing tempertature, almost independent of PC content but the values of ε_0 and $\Delta\varepsilon$ decrease with temperature due to thermal fluctuation (kT term) and differ by PC content. These dielectric data should serve a molecular design for an industrial application of PA blends.

References

1. T. R. NASSER, D. R. PAUL and J. W. BARLOW, *J. Appl. Polm. Sci.* **23** (1979) 85.
2. R. N. MOHN, D. R. PAUL, J. W. BARLOW and C. A. CRUZ, *ibid.* **23** (1979) 575.
3. I. MONDRAGON, *ibid.* **32** (1986) 6191.
4. I. EUIAZABAL, M. CORTAZAR, E. CALAHORRA, J. J. IRUING and G. M. GUZMAN, *Rev. Rlast. Mod.* **337** (1984) 48.
5. M. KIMURA, G. SALEE and R. S. PORTER, *J. Appl. Polym. Sci.* **29** (1984) 1629.
6. N. KOIZUMI and S. YANO, *Bull. Chem. Res. Kyoto Univ.* **47** (1969) 320.
7. N. KOIZUMI, Y. MURATA and K. TSUNASHIMA, *IEEE. Trans. Electr. Insul.* **21** (1986) 543.
8. N. G. MCCRUM, B. E. READ and G. WILLIAMS, "Anelastic and Dielectric Effects in Polymeric Solids" (Wiley, New York, 1968).
9. J. P. RUNT, in "Dielectric Spectroscopy of Polymeric Materials," edited by J. P. Runt and J. J. Fitzgerald (Amer. Chem. Soc. Washington D.C., 1997) Ch. 10.
10. K. S. COLE and R. H. COLE, *J. Chem. Phys.* **9** (1941) 341.
11. G. WILLIAMS and D. C. WATTS, *Trans. Faraday Soc.* **66** (1970) 80.
12. Y. MURATA, K. TSUNASHIMA, N. KOIZUMI, K. OGAMI, F. HOSOKAWA and K. YOKOYAMA, *Jpn. J. Appl. Phys.* **32** (1993) L8494.
13. Y. MURATA, K. TSUNASHIMA and N. KOIZUMI, *ibid.* **34** (1995) 6458.

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