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Poly(ethylene terephthalate) copolymers with a smaller amount of poly(ethylene glycol)s and poly(butylene glycol)s

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Poly(ethylene terephthalate) copolymers were prepared by melt polycondensation of dimethyl terephthalate and excess amount of ethylene glycol with 2–20 mol% of poly(ethylene glycol) (E) or poly(butylene glycol) (B), where the molecular weights (*MW*) of E and B are 200–7500 and 1000–3000, respectively. Reduced specific viscosity of copolymer increased with increasing *MW* and the content of polyglycol comonomer. Temperatures of glass transition (T_g), cold crystallization and melting (T_m) decreased with increasing *MW* of polyglycol and comonomer content, and their decrease is more remarkable for E-type copolymers than for B-type ones. T_m depression of copolymers suggested that these copolymers are block-type at higher comonomer content. T_g was decreased below room temperature by the copolymerization, which affected the crystallinity and density of the copolymer films. Water content and dye uptake increased with increasing comonomer content, and their increase is higher for E1000 copolymer film than for B1000 one. Alkali resistance increased for B1000 copolymer film, whereas it decreased remarkably for E1000 one. Tensile properties of drawn (3×) film were remarkably affected by the decrease of the T_g of the copolymer, and E1000 5 mol% copolymer film showed high tensile recovery. Shrinkage in boiling water increased for E1000 drawn film, whereas it decreased for B1000 one. Thermal stability increased and then decreased with increasing comonomer content and it was lower for B-type copolymer than for E-type one.

(Keywords: poly(ethylene terephthalate); polyglycol comonomers; physicochemical properties)

INTRODUCTION

Chemical modification of poly(ethylene terephthalate) (PET) by incorporating various glycol or acid comonomers has been intensively investigated in the past[1]. PET copolymers with poly(ethylene glycol)s (PEG) were first studied by Coleman[2] in an attempt to enhance the hydrophilic property and dye receptivity of PET fibre. Subsequently, PET copolymers with large amount of PEG were reported by Charch and Shivers[3] in relation to the elastomeric properties of them. As is well known, this type of copolymers has been developed commercially as thermoplastic copoly(ether–ester) elastomers.

Here, we report the preparation and characterization of PET copolymers with relatively small amount of PEG and poly(butylene glycol) (PBG). The effect of molecular weight, comonomer content and chemical structure of polyglycols on the thermal, physicochemical and mechanical properties of copolymers are studied.

EXPERIMENTAL

Monomers

Commercially available polyglycols used in this study are poly(ethylene glycol)s (PEG) from Wako Pure Chemical Industries, and poly(teramethylene glycol) (PTMG) from Sanyo Chemical Industries. Their codes and molecular weights are PEG 200 (E200), PEG 400 (E400), PEG 600 (E600), PEG 1000 (E1000), PEG 2000 (E2000), PEG 4000 (E3000), PEG 6000 (E7500), PTMG 1000 (B1000) and PTMG 3000 (B3000). These polyglycols and dimethyl terephthalate were used as received. Ethylene glycol was distilled under reduced pressure.

Preparation of copolymers

Copolymers were prepared by a melt polycondensation method. A mixture of dimethyl terephthalate, polyglycol and excess amount of ethylene glycol with a small amount of zinc acetate and antimony trioxide as a catalyst was heated at 200–205°C for 2 h in a stream of nitrogen gas, and then increased to 270–275°C and heated for 1 h followed by heating at 280–285°C for 3 h in a vacuum of 0.3–1.0 Torr.

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Film preparation

Film was melt-pressed between aluminium plates with an aluminium spacing plate of 100 μm thickness and then quenched into iced water. After dissolving off aluminium plates in 10% hydrochloric acid, the film was washed with water and dried overnight at room temperature *in vacuo*.

Characterization

Reduced specific viscosity (η_{sp}/C) was determined at 30°C for a polymer solution of $1.0\,\mathrm{g\,dl^{-1}}$ in phenol/tetrachloroethane (60/40 by weight). Differential thermal analysis (d.t.a.) was performed at a heating rate of $10°\mathrm{C\,min^{-1}}$ in nitrogen atmosphere. Wide-angle X-ray scattering (WAXS) was performed with nickel-filtered Cu Kα radiation. Density was measured in a heptane–tetrachloromethane density gradient column at 30°C. Water absorption was carried out in water at 30°C for 24 h. Alkali hydrolysis was carried out in a 10% NaOH aqueous solution at 70°C for 4 h. Dyeing was carried out in a dye bath of 1 g 1,4-diaminoanthraquinone (disperse dye) in 300 ml water at 80°C for 24 h. Tensile testing was performed with strain rate of $100\%\,\mathrm{min^{-1}}$ under the condition of 20°C and 65% r.h. Thermal shrinkage was carried out in boiling water for 15 min. Thermogravimetry (t.g.) was performed at a heating rate of $10°\mathrm{C\,min^{-1}}$ in nitrogen atmosphere.

It was reported for PET/PEG copolymers that the average compositions obtained experimentally were very similar to the theoretical values[4], and the molecular weight of PEG was unchanged during the melt polycondensation[2]. Thus, characterization of the chemical structure of the copolymers prepared was not carried out.

RESULTS AND DISCUSSION

Table 1 shows reduced specific viscosities of copolymers prepared. The value of η_{sp}/C increases with increasing comonomer content in the copolymer and molecular weight (*MW*) of polyglycol, which suggests that the incorporation of the higher-*MW* polyglycol moiety into the PET chain enhances the η_{sp}/C value.

Figure 1 shows d.t.a. curves of melt-quenched samples for copolymers with varying *MW* of PEG comonomers. Glass transition temperature (T_g), cold crystallization temperature (T_{cc}) and melting temperature (T_m) decrease with increasing *MW* of PEG. These results suggest that the mobility of polymer chains is increased while the crystal growth of PET chains is decreased by the incorporation of the longer flexible PEG chains. Endothermic peaks at a temperature around 40–50°C for E-3000 and E-7500 copolymers are due to the melting of crystallized PEG chains.

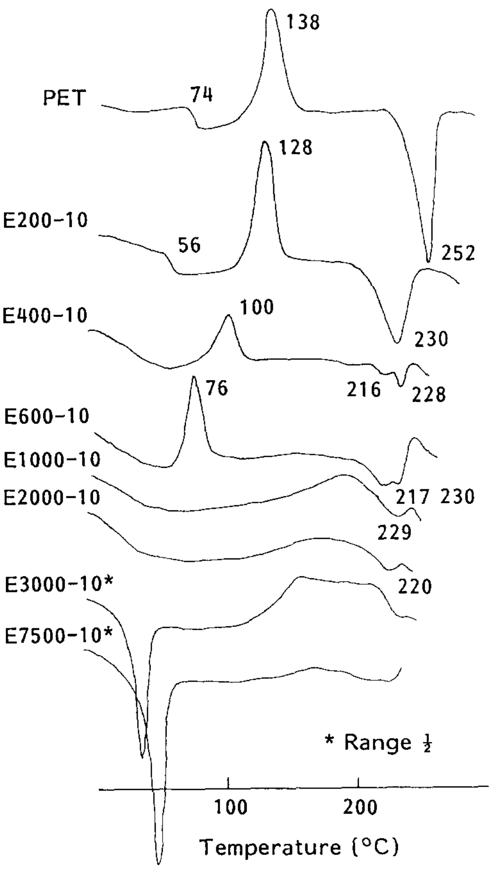

Figure 1 D.t.a. curves of melt-quenched samples for PEG 10 mol% copolymers

Table 1 Reduced specific viscosity of copolymers. Numerals after the hyphen in the polymer code are the comonomer contents in feed (mol%)

Code	η_{sp}/C ($\mathrm{dl\,g^{-1}}$)	Code	η_{sp}/C ($\mathrm{dl\,g^{-1}}$)	Code	η_{sp}/C ($\mathrm{dl\,g^{-1}}$)
PET	0.78	E1000-2	0.88	B1000-2	0.79
E200-10	0.62	-5	0.96	-5	0.63
400-10	0.85	-10	0.85	-10	0.80
600-10	0.94	-20	1.65	-20	1.20
1000-10	0.85	E3000-2	0.93	B3000-2	0.88
2000-10	1.27	-5	1.11	-5	1.44
3000-10	2.21	-10	2.21	-10	1.55
7500-10	2.79	-20	2.67	-20	2.05

Figure 2 shows the d.t.a. curves of melt-quenched samples for E1000 and B1000 copolymers with varying comonomer content. The values of T_g, T_{cc} and T_m decrease with increasing comonomer content. The degree of their decrease is smaller for B1000 copolymers than for E1000 copolymers, which could be ascribed to the lower compatibility of PBG chains with PET chains[5].

Figure 3 shows the d.t.a. curves of E1000 and B1000 copolymers heat-treated at 170°C for 2 h. It is well known that heat-treated PET gives multiple melting endotherms during thermal analysis. The higher melting peak temperatures in the d.t.a. curves are plotted against the comonomer contents in *Figure 4*. The depressions followed by Flory's equation[6] using the reported value of $\Delta H_u = 3980\,\mathrm{cal\,mol^{-1}}$ (ref. 7) and $2200\,\mathrm{cal\,mol^{-1}}$ (ref. 8) are also plotted in the figure. The T_m depressions of both E1000 and B1000 copolymers do not follow the Flory equation, suggesting that these coplymers are not of random type but of block type at higher comonomer content. A similar T_m *versus* molar composition curve was reported by Coleman[2] for PET copolymers copolymerized with PEG with varying *MW* (106–6000) at constant content (10 wt%).

Figure 5 shows WAXS curves of the melt-pressed films for E1000 and B1000 copolymers. The melt-pressed films crystallized at comonomer content above 5 mol%

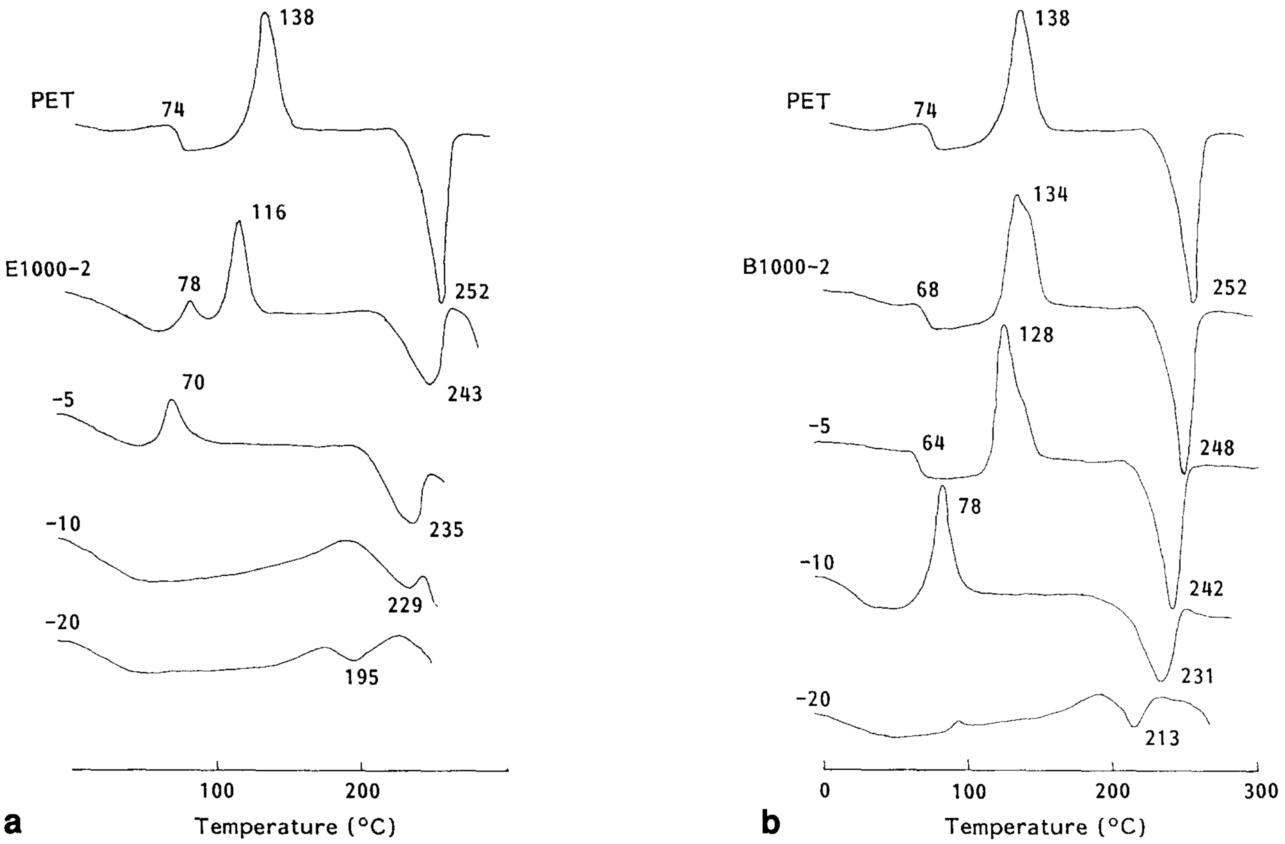

Figure 2 D.t.a. curves of melt-quenched samples for (a) E1000 and (b) B1000 copolymers

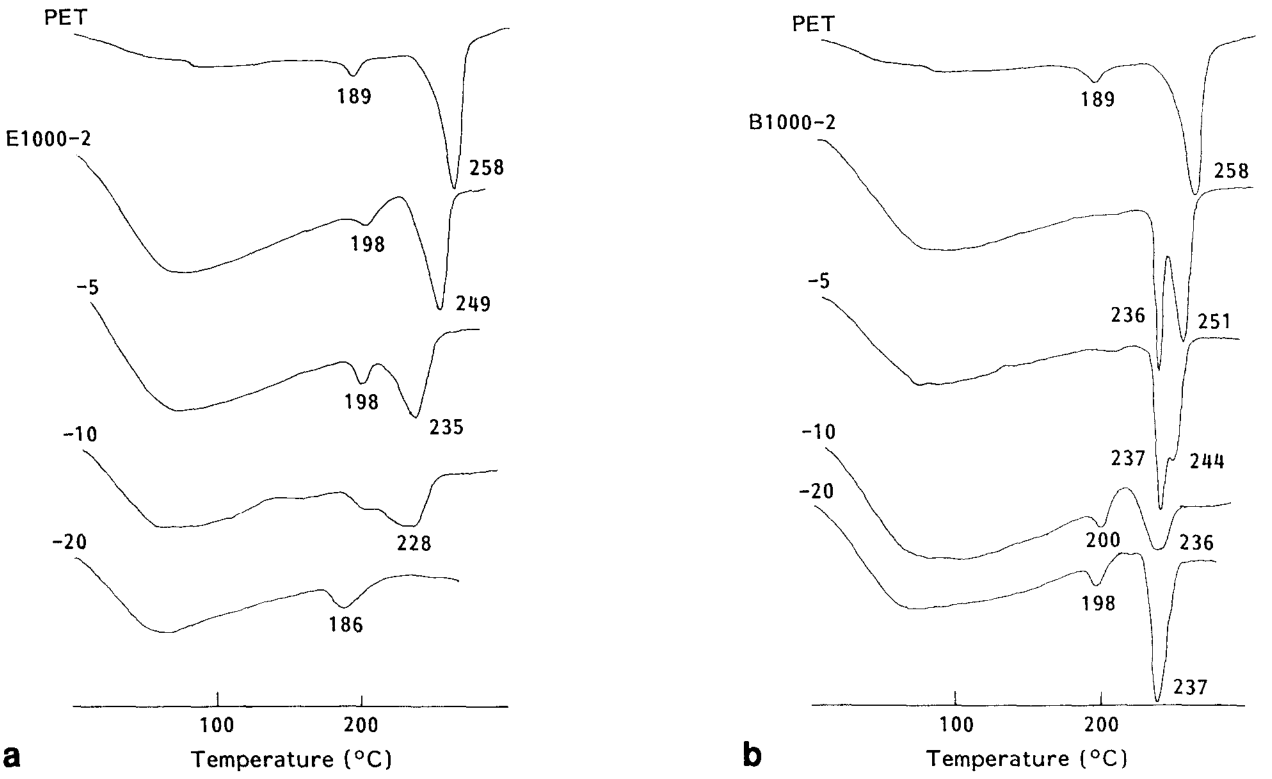

Figure 3 D.t.a. curves of (a) E1000 and (b) B1000 copolymers heat-treated at 170°C for 2 h

for E1000 and 20 mol% for B1000. This is probably due to the fact that the T_g values of these crystallized copolymers are well below room temperature as seen in *Figure 2*.

Figure 6 shows the WAXS curves of E1000 and B1000 films heat-treated at 170°C for 2 h. The intensities of WAXS peaks of E1000 copolymers are lower than those of B1000 copolymers. This result is consistent with the

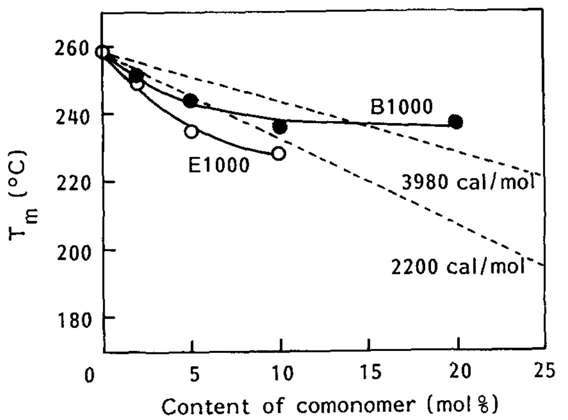

Figure 4 Melting-temperature depression curves for copolymers

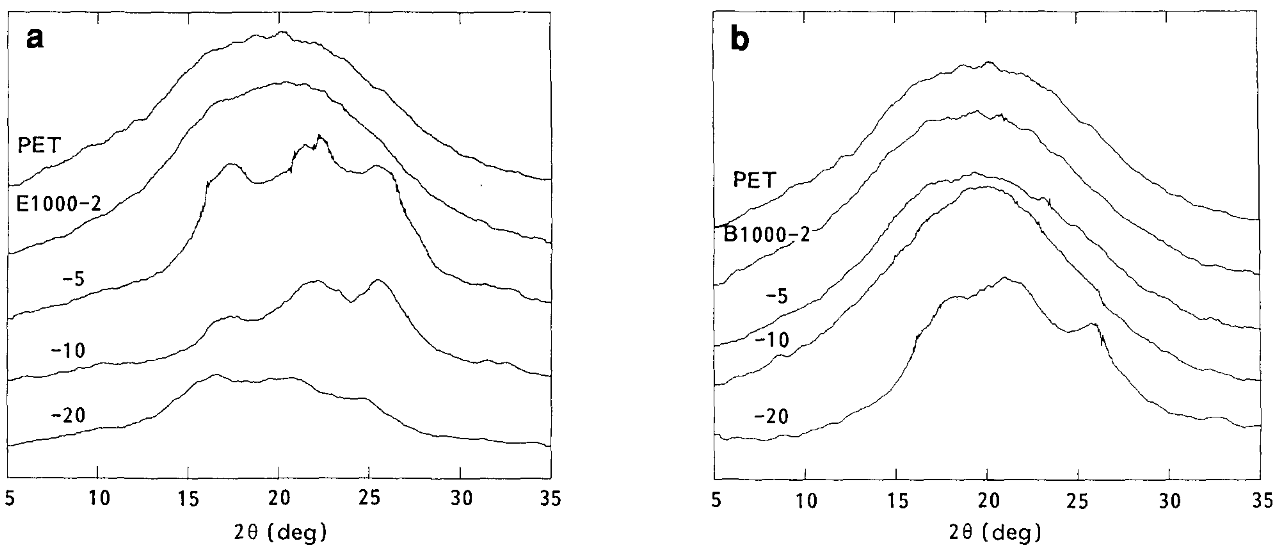

Figure 5 WAXS curves of melt-pressed films for (a) E1000 and (b) B1000 copolymers

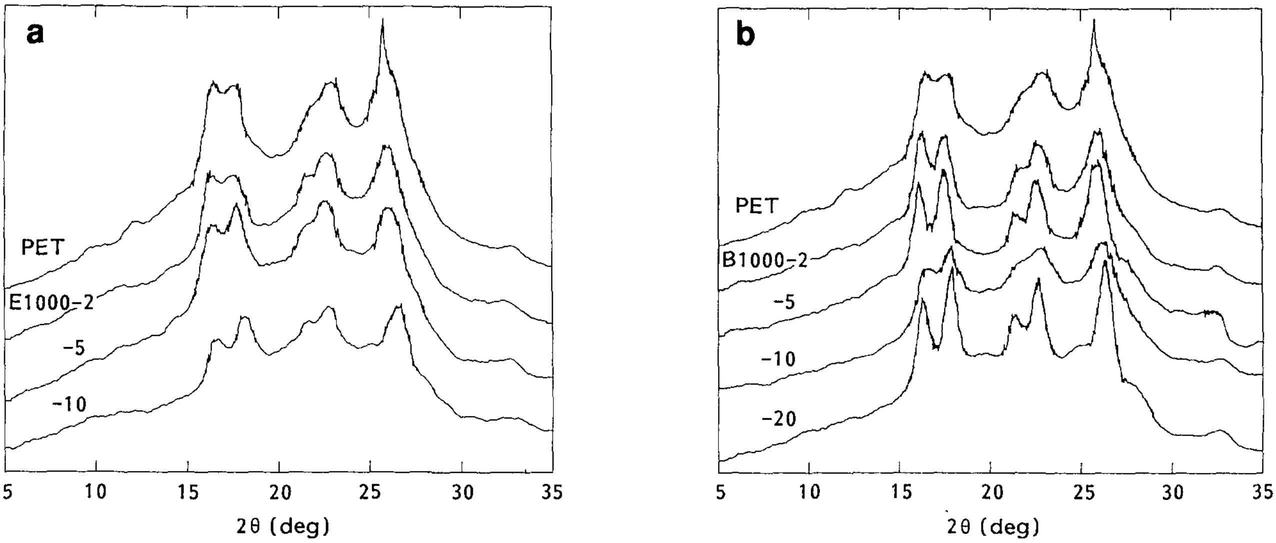

Figure 6 WAXS curves of (a) E1000 and (b) B1000 copolymers heat-treated at 170°C for 2 h

fact that E1000 copolymers have smaller melting peak areas than B1000 copolymers as shown in *Figure 3*.

Densities of melt-pressed and heat-treated films are plotted against the comonomer contents in *Figure 7*. The densities of melt-pressed films at a comonomer content of 10 mol% increase at first (E200 < E400 < E600) and then decrease with increasing *MW* of PEG (E600 > E1000 > E3000 > E7500). This increase of density could be ascribed to the higher crystallinity of E400 and E600 copolymers due to the low T_g values below room temperature as seen in *Figure 1*. The decrease of density of copolymers above *MW* of 1000 could be ascribed to the increase of content of low-density PEG component in these copolymers. The densities of all the E1000 copolymers and some E3000 copolymers (*Figure 7a*) are higher than that of PET homopolymers, which is also ascribed to the increase of crystallinity due to low T_g values of these copolymers. The heat treatment increases the density (*Figure 7b*), and thus the degrees of crystallinity calculated from the densities for PET homopolymer films are 9 and 50% for melt-pressed and heat-treated films, respectively. The densities of heat-treated B1000-2, B1000-5 and E1000-2

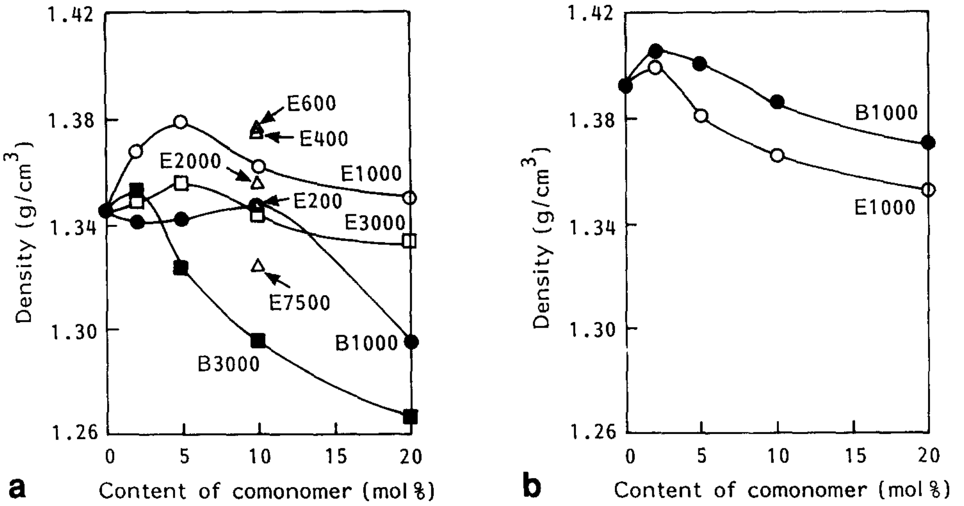

Figure 7 Change of density with copolymer composition for (a) melt-pressed films and (b) heat-treated films at 170°C for 2 h

copolymer films are higher than that of heat-treated PET homopolymer film, which is ascribed to the increase of crystallinity as shown in *Figure 6*. The higher densities of B-type copolymers than those of E-type copolymers could be ascribed to the higher crystallinity of B-type copolymers due to the lower compatibility of PBG chains with PET chains as described above.

Water contents of melt-pressed films are plotted against the copolymer composition (wt%) in *Figure 8*. Coleman^2 reported that the plot of moisture regain *versus* PEG content (wt%) is nearly linear for PET/PEG copolymer fibres. Similar linearity is also obtained for E1000 and B1000 films between the water content and the copolymer composition. The higher water content of E1000 copolymer than that of B1000 copolymer could be ascribed to the higher hydrophilicity of PEG.

Weight losses of melt-pressed B1000 films in an alkali solution are plotted against the copolymer composition in *Figure 9*. The weight loss of B1000 film decreases, which is probably due to the decrease of ester linkage concentration. On the contrary, E1000 films were completely dissolved in alkali solution after a short period of time, except for E1000-2 film whose weight loss was 79.8 g m^{-2}. This difference for alkali resistance between B1000 and E1000 films is quite noticeable, and the low alkali resistance of E1000 film may be ascribed to the higher hydrophilicity of PEG as shown by the water absorption. In relation to this easy degradability of PET/PEG copolymers, PET/PEG elastomers have been studied by Gilding and Reed for their biodegradability^{4,9}.

Figure 10 shows dye uptake of melt-pressed films against the copolymer composition. The dye uptake increases with increasing comonomer content, which was also reported by Coleman^2 for PET/PEG copolymer fibres. The increase of dye uptake for disperse dye may be attributed to the decrease of crystallinity of copolymer, which may be more remarkable for E1000 copolymer than for B1000 copolymer, and so the dye uptake is also higher for E1000 film than for B1000 film.

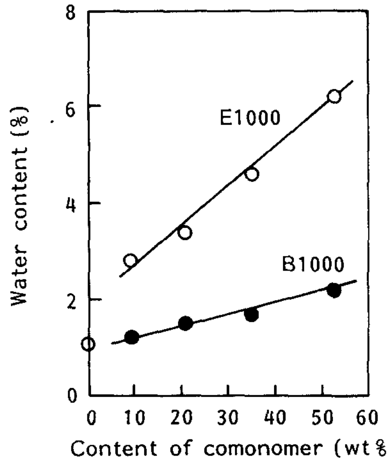

Figure 8 Change of water content of melt-pressed films with copolymer composition

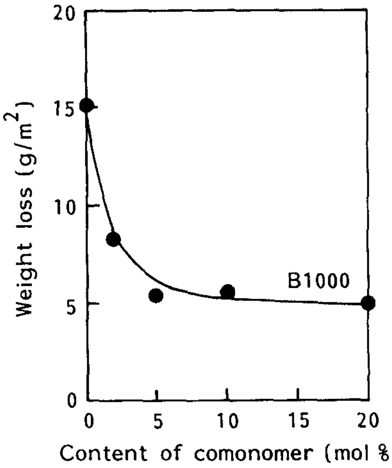

Figure 9 Alkali resistance of melt-pressed films in 10% NaOH aqueous solution at 70°C for 4 h

Table 2 shows the results of tensile tests for drawn (3×) films. Tensile strength and elongation are increased by copolymerization with a small amount of comonomer. The disturbance of the interaction of polymer chain by the comonomer and the increase of chain length by the

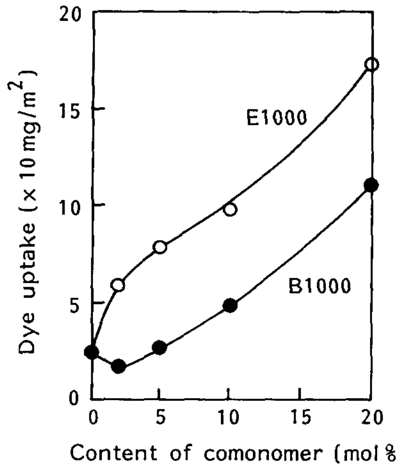

Figure 10 Dyeability of melt-pressed films for disperse dye at 80°C for 24 h

longer comonomer chain may lead to the increase of extensibility of the polymer chain, and thus increases the tensile strength and elongation. The tensile strength and Young's modulus are decreased by copolymerization with a higher amount of comonomer, which could be caused by the decrease of T_g below room temperature as shown above. This decrease of tensile properties is more pronounced for E1000 films than for B1000 films, which corresponds well to the higher decrease of T_g.

Table 3 shows tensile recovery at 10% stretching for the drawn (3×) films. Charch and Shivers[3] reported that PET/PEG 4000 copolymers show elastomeric properties in the range of 40–70 wt% PEG. E1000-5 film whose PEG content is 21 wt% shows high tensile recovery, which suggests that PET modified with a relatively small amount of PEG also has potential use as a stretching material.

Figure 11 shows shrinkage of drawn (4×) films in boiling water. It is noted that the shrinkage increases for E1000 films and decreases for B1000 films. This difference is consistent with that for the alkali resistance shown above. Thus, it is considered that the hydrophilicity of PEG also promotes the shrinkage in boiling water.

Table 4 shows thermal stability of 10 mol% polyglycol copolymers. The thermal stability decreases with increasing *MW* of polyglycol comonomer. *Figure 12* shows the t.g. curves of E1000, B1000, E3000 and B3000 copolymers. In general, the thermal stability increased at first and then decreased with increasing comonomer content. It is found that the thermal stability of PBG copolymer is lower than that of PEG copolymer.

Table 2 Tensile properties of drawn (3×) films

Code	η_{sp}/C (dl g^{-1})	Tensile strength (kg mm^{-2})	Elongation (%)	Young's modulus (kg mm^{-2})
PET	0.61	6.5	39	259
E1000-2	0.63	11.2	114	239
-5	0.64	1.1	42	112
-10	1.21	3.9	51–104	20
B1000-2	0.61	16.7	82	282
-5	0.49	10.6	82	241
-10	0.98	6.9	23	61

Table 3 Tensile recovery (%) at repeated cycles for drawn (3×) films

	Cycle of 10% stretching		
Code	1st	2nd	3rd
PET	48	43	38
E400-5	44	34	24
E1000-2	38	35	28
E1000-5	99	94	94
B1000-5	50	43	38

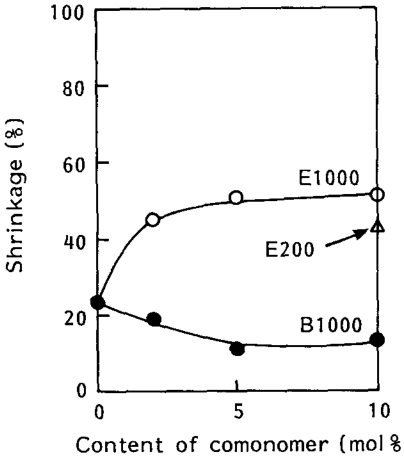

Figure 11 Shrinkage of drawn (4×) films after treating in boiling water for 15 min

Table 4 Temperatures of 5% and 50% weight loss by t.g. for 10 mol% polyglycol copolymers

Code	5% weight loss temp. (°C)	50% weight loss temp. (°C)
PET	364	400
E200-10	375	429
E400-10	347	420
E600-10	355	415
E1000-10	327	405
E2000-10	305	402
E3000-10	315	400
E7500-10	275	397
B1000-10	330	414
B3000-10	265	386

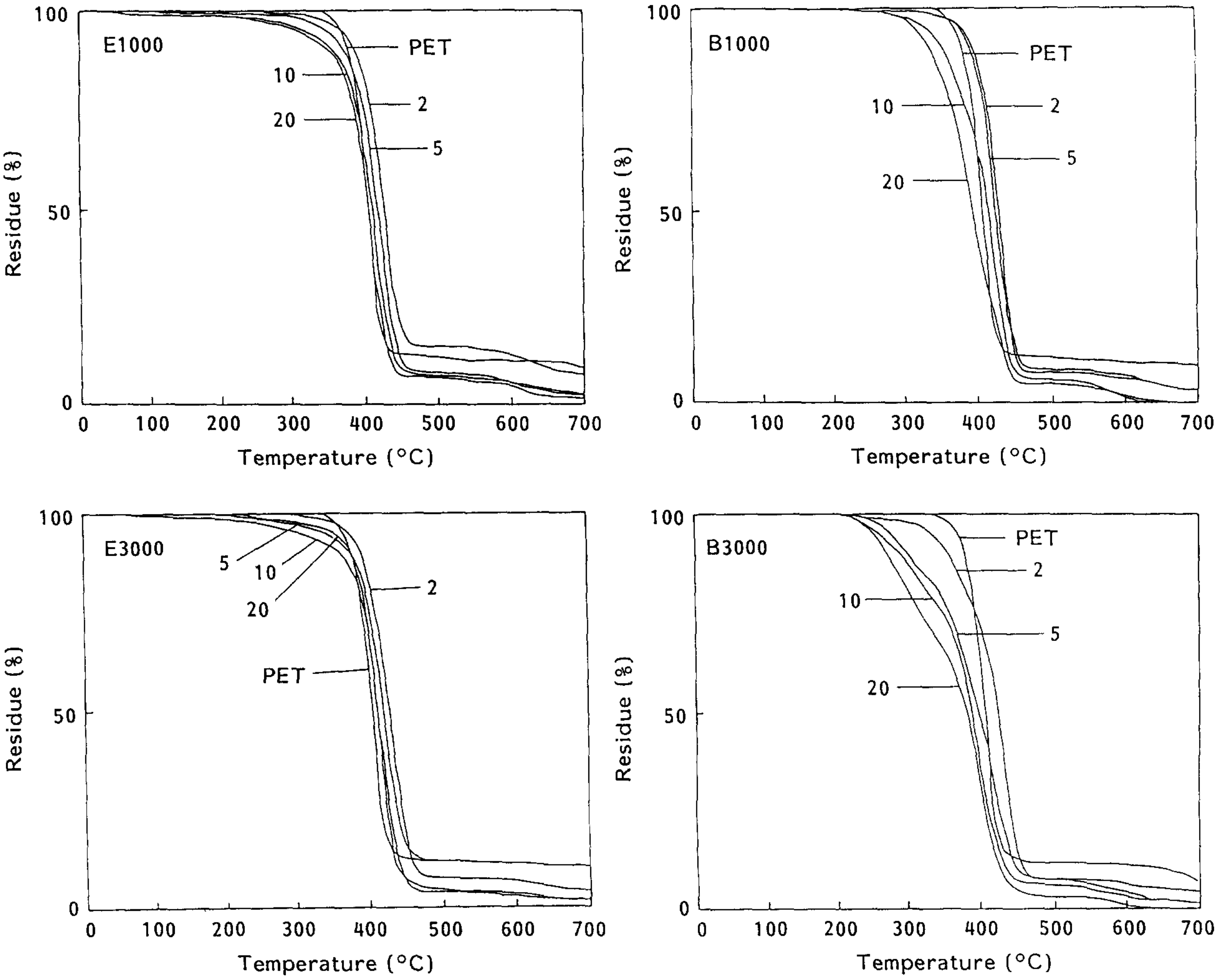

Figure 12 T.g. curves of E1000, B1000, E3000 and B3000 copolymers

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