Effect of Structural Characteristic on Physical Properties of Copolyesters from Poly(Ethylene Terephthalate) Oligomer and Polycaprolactone

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1. Introduction

The copolyesters composed of high melting rigid ester unit and low melting flexible aliphatic ester unit have various potential applications as functional materials. Among them, poly(ethylene terephthalate/caprolactone) copolyester, P(ET/CL), has attracted much attention for biodegradable engineering plastics because it possesses biodegradability as well as good mechanical properties.[1-3] Recently, it is expected to be used as thermoplastic elastomers (TPEs), in which ET and CL units act as hard and soft segments, respectively. For example, Tang et al. reported the application and process of P(ET/CL) copolyester fibers to velocity seat belt.[4-5] In this case, P(ET/CL) copolyester gives better transportation safety than PET fiber. This is because the incorporation of CL unit into PET backbone improves the impact-absorbing properties. As well known, the structural characteristics such as chemical composition and sequence length of copolyesters strongly affect their physicochemical properties.[6-8] Although increasing CL content improves the functional properties of P(ET/CL) copolymers such as biodegradability and elasticity, it gives rise to poor thermal and mechanical properties. Thus, determination of a chemical composition which gives a good combination of processability and physicochemical properties is the very technical key for industrial application of P(ET/CL) copolyesters. This study examined the effect of chemical composition on the physical properties of P(ET/CL) copolyester. For this we adopted a novel copolymerization method to prepared the P(ET/CL) copolymer with well characterized chemical composition; PCL is added during polycondensation of PET oligomer to bring about ester interchange reactions, which makes control of chemical composition of the copolyester more precise and easier.

2. Experimental

Materials : PET oligomer and PCL(M_w: 40,000) were supplied by Samyang Corp. and Union Carbide Corp., respectively. They were dried for 24 hours prior to polycondensation. Antimony trioxide(Sb_2O_3) and trimethyl phosphate(TMP, $(CH_3O_3)P$) were used as catalyst and thermal stabilizer, respectively. Reagent grade d-trifluoroacetic acid and $CDCl_3$ were used without further purification.

Preparation of P(ET/CL) copolyesters : P(ET/CL) copolyesters were prepared by addition of PCL to PET oligomer during polycondensation. The feed composition of PCL was varied up to 71.7 mol%(= 60 wt%) of total reactants. The polycondensation was carried out in three neck flask quipped with vacuum pump, mechanical stirrer and thermometer. Sb_2O_3 and TMP dissolved in ethylene glycol were added into previously molten reactant of PET oligomer and PCL at 285 °C under nitrogen atmosphere, and then vacuum pump was applied ($\leq$ 0.03 torr).

Measurement : ^{1}H–NMR spectra were obtained by Varian Gemini 200 spectrometer (200 MHz, U.S.A.) using 1/1(v/v) d-trifluoroacetic acid/$CDCl_3$ mixture as the solvent. Rheological properties were measured by Rheometric Scientific ARES (U.S.A) at melt

temperature + 30 °C under nitrogen purging. In ARES measurement, parallel-plat geometry with a diameter 25 mm was adopted, whose gap 1 mm at the strain level 10 % over the frequency range of 0.05 ~ 400 rad/sec

3. Results and discussion

3.1. Characterization of P(ET/CL) Copolyesters
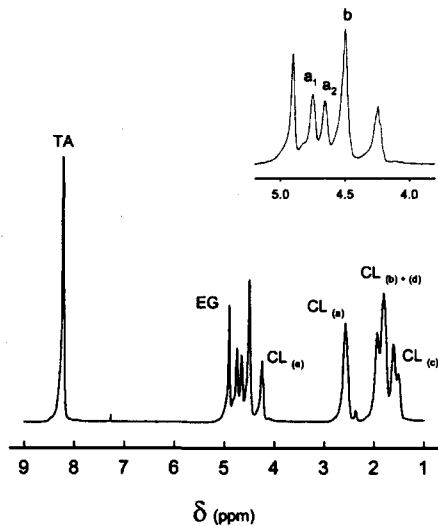

Figure 1. ¹H-NMR spectra of P(ET/CL) ; PET/PCL=40/60 wt.

Figure 1 shows a typical ¹H-NMR spectrum of P(ET/CL) copolyester prepared by the addition of 60 wt% PCL in polycondensation of PET oligomer. The peaks TA and EG at chemical shifts of 8.3 and 4.9 ppm are assigned to the terephthalic acid (TA) and ethylene glycol (EG) units, respectively. The peaks CL $_{(e)}$, CL $_{(a)}$, CL $_{(b)+(d)}$, CL $_{(c)}$ at chemical shifts of 4.2, 2.6, 1.8 and 1.6 ppm are assigned to the CL unit, respectively. New peaks, a_1, a_2 and b appear around 4.9 ~ 4.4 ppm. These new peaks are assigned to the methylene hydrogens adjacent to the ester group whose environment is different from those in EG and CL units. Consequently, the appearance of these new peaks in the ¹H-NMR spectra indicates that P(ET/CL) copolyesters are indeed formed through ester interchange reactions between PET oligomer and PCL. At the increasing feed composition of PCL, the area of new peaks tends to be increase. This suggests that the increase of PCL results in the higher degree of ester interchange reactions. The composition and intrinsic viscosity of P(ET/CL) copolyesters are listed in Table 1. The intrinsic viscosity of the copolyesters are in the range of 0.74 - 0.92 dL/g indicating that they have relatively high molecular weight enough to be used as TPEs.

Table I. Structural Characteristic of P(ET/CL) Copolyestes

Sample Code	Feed Composition (mol%)		Copolymer Composition (mol%)[*]		Intrinsic viscosity[**] (dL/g)
	ET	CL	ET	CL	
CL13	91.9	8.1	86.7	13.3	0.77
CL20	84.2	15.8	79.8	20.2	0.75
CL22	77.1	22.9	78.1	21.9	0.74
CL26	70.4	29.6	73.7	26.3	0.84
CL38	58.1	41.9	62.2	37.8	0.90
CL47	47.1	52.9	52.7	47.3	0.92
CL58	28.4	71.7	41.8	58.2	0.91

[*] Calculated by ¹H-NMR
[**] Measured in phenol/tetrachloroethane = 1 / 1 (v/v) at 25 °C

3.2. Rheological properties

The viscosity curves of PET and the copolyesters at $T_m+30\,°C$ are shown in **Figure 2**. With increasing CL content, viscosity of copolyesters decreases. The copolyesters containing CL unit less than 26 mol%,\ whose ET block is sufficiently long enough to crystallize, show an almost Newtonian flow behavior like PET over the frequency range observed.However, the copolyesters containing CL content higher than 38 mol% show Bingham behavior; disappearance of lower Newtonian flow region at low frequency and Newtonian flow behavior at high frequency. When CL content increases from 38 mol% to 58 mol%, the characteristic of Bingham behavior gets more noticeable, resulting in a heterogeneous system. Bingham flow behavior seems to result from the formation of physically associated pseudostructure by ET blocks. The plots of storage modulus (G') vs. frequency (w) of the copolyesters are shown in **Figure 3**. As well known, homogeneous and isotropic polymer systems show a firm relation of $G' \propto \omega^2$ in the terminal region and block copolymers generally give power law less than 2 on the logarithmic plot of G' against w due to the formation of ordered structure. The copolyesters containing CL unit less than 26 mol% gives slope of ca. 1.70, which is frequently found in PET melts. However, the copolyesters containing CL unit higher than 38 mol% give much reduced slope, suggesting the melt become more and more heterogeneous. The G' is replotted against loss modulus (G'') in **Figure 4**. It is well known that this Cole-Cole type plot gives a master curve independent of measured temperature and the logarithmic plot gives slope of 2 if the polymer system is homogeneous and isotropic. In fact, the copolyesters containing CL unit less than 26 mol% produce a master curve close to PET whose slope is ca. 1.70. However, the copolyesters containing CL unit higher than 38 mol% exhibit an inflection point. As CL content is increased from 38 to 58 mol% the slope decreases from 0.95 to 0.25 in the terminal region and the G'' exhibiting the inflection point decreases. Reduced slope prior to the inflection reflects the breakdown of the physically associated pseudostructure. Thus, critical stress to collapse the physical structure reduces with increasing CL content although heterogeneity becomes more noticeable with increasing CL content. In these copolyester systems the reduced slope at low frequency may be an indication of the existence of phase separation. The heterogeneous systems appear to change to more homogeneous systems by shear mixing effect during rheological measurement, and consequently the slope reincreases. Loss tangent (tan δ) of the copolyesters is plotted against ω in **Figure 5**. In principle, tan δ offers a quantitative measure of solidlike elastic or liquidlike viscous properties. As CL content is increased, the copolyesters exhibit more solidlike elastic characteristic.

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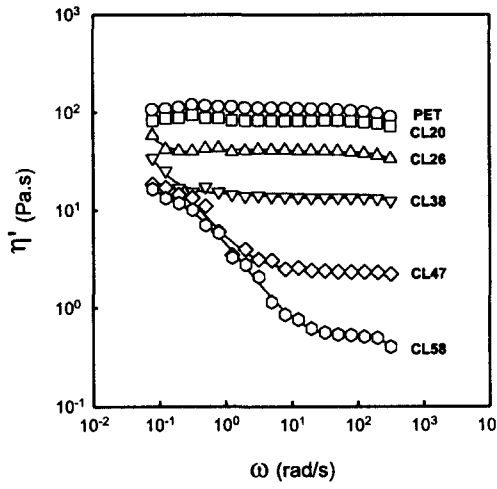9. M. B. Kossuth, D. C. Morse, F. S. Bates, *J. Rheol.*, **43**, 167 (1999).

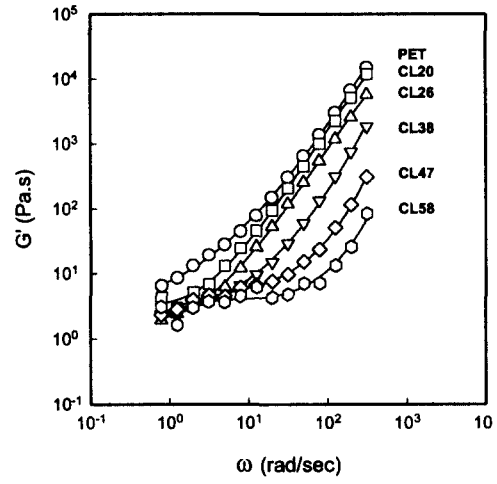**Figure 2.** Viscosity curves of P(ET/CL) copolyesters with frequency.

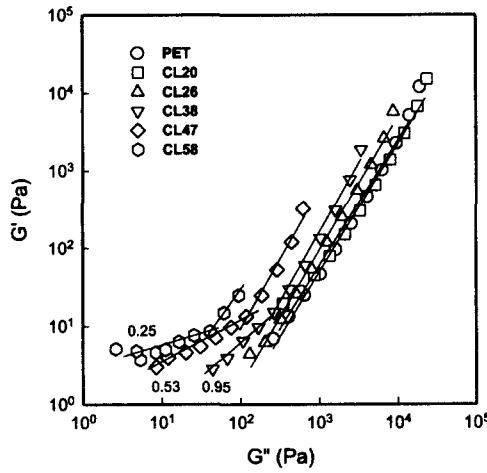**Figure 3.** Storage modulus of P(ET/CL) copolyesters with frequency.
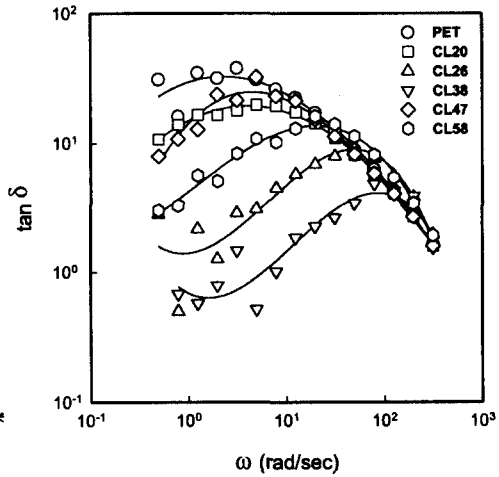

Figure 4. Cole-Cole plots of P(ET/CL) copolyesters.

Figure 5. Tan δ of P(ET/CL) copolyesters.