

Thermal Behavior and Tensile Properties of Poly(ethylene terephthalate-co-ethylene isophthalate)

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ABSTRACT: Poly(ethylene terephthalate) (PET) and poly(ethylene isophthalate) (PEI) homopolymers were synthesized by the two-step melt polycondensation process of ethylene glycol (EG) with dimethyl terephthalate (DMT) and/or dimethyl isophthalate (DMI), respectively. Nine copolymers of the above three monomers were also synthesized by varying the mole percent of DMI with respect to DMT in the initial monomer feed. The thermal behavior was investigated over the entire range of copolymer composition by differential scanning calorimetry (DSC). The glass transition (T_g), cold crystallization (T_{cc}), melting (T_m), and crystallization (T_c) temperatures have been determined. Also, the gradually increasing proportion of ethylene-isophthalate units in the virgin PET drastically differentiated the tensile mechanical properties, which were determined, and the results are discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 200–207, 2000

Key words: PET; PEI; copolymers; thermal properties; enthalpy relaxation; DSC; tensile mechanical properties

INTRODUCTION

Although the increase of the melting point of poly(ethylene terephthalate) (PET) is of great importance for some applications (e.g., fibers, insulating films for capacitors), other applications demand all useful characteristics of PET in conjunction with a lower melting point. A good example for this is soft-drink bottles, which nowadays tend to replace the PVC ones in the bottle-packaging of edible oils and drinking water.

In PET bottle manufacturing by stretch-blow molding of injection molded, preforms are subjected to rapid deformation under high strain rates, which results in development of crystallin-

ity by a strain-induced mechanism. Thermal crystallization is generally undesirable because it reduces clarity and can occur during various stages of container manufacturing such as preform cooling following injection molding, or preform heating, prior to stretch blow molding.^{1–4}

The trend toward incorporating modifier comonomers, as, for example, isophthalic acid (IPA), has grown from the need to produce bottles with a high degree of clarity and freedom from residual acetaldehyde. The presence of IPA disrupts PET polymer regularity, resulting in slower thermal crystallization and melting-point reduction. Slower crystallization prevents development of haziness in the molded preform and lowers acetaldehyde content, because lower processing temperatures can be used to reduce degradation.^{1–4}

On the other hand, a Japanese patent⁵ claims that a 2% content of another aromatic dicarboxy-

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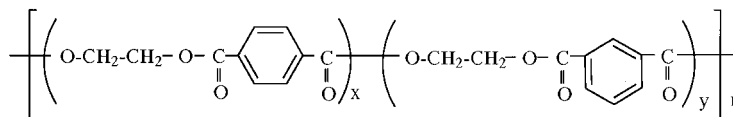


Figure 1 Structure of poly(ethylene terephthalate/isophthalate) copolymers.

lic acid or oxyaromatic carboxylic acid substituted for terephthalic acid in PET provides significant property improvement for video-based films, using apparently ordinary stretching techniques.

Recently,⁶ an article was published on which a series of copolyesters based on different ratios of PET to poly(ethylene isophthalate) (PEI) has been synthesized. As was shown in this work, with the involvement of PEI, the copolyesters become less crystallizable and even amorphous when the PEI percentage is >20%. The WAXD profiles of the crystallizable copolyesters infer that the crystals come from PET homopolymer.

The present work is concerned with the synthesis of poly(ethylene terephthalate/isophthalate) copolymers (Fig. 1) and the effect of IPA content on PET copolymer's thermal behavior and tensile mechanical properties.

The two-step polycondensation process, which was used in their preparation, added Sb_2O_3 as catalyst in the second step and the high vacuum applied resulted in polyester samples with relatively higher molecular weights than those of the aforementioned paper.⁶ Another reason that we tried to prepare these grades is because they are suitable for soft-drink bottles, where higher mechanical properties are needed due to the continuously increasing bottle capacity.

EXPERIMENTAL

Sample Preparation

Both PET and PEI homopolymers, as well as their copolymers, were prepared by the two-stage melt polycondensation method (transesterification and polycondensation) in a glass batch reactor. The starting materials, dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), and ethylene glycol (EG), were of commercial grade and were used without further purification. Zinc acetate [$\text{Zn}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$] was used as catalyst for the first step and antimony trioxide (Sb_2O_3) was used for the polycondensation step.

In each preparation, the reaction mixture comprised 32.03 g (0.50 mol) of EG, various amounts

(mol %) of DMT and/or DMI (molar ratio of EG/dimethyl ester = 2.2), 50 ppm Zn (OCOCH_3)₂ \cdot $2\text{H}_2\text{O}$, and 950 ppm Sb_2O_3 on dimethyl ester.

The reaction mixture was heated to the final temperature (270°C) under argon atmosphere and stirring at a constant speed (500 rpm). This first step (transesterification) is considered to be completed after \approx 3 h, when the theoretical amount of methanol (18.4 mL) was collected.

In the second step (polycondensation), a vacuum (4.0 Pa) was applied slowly over a period of time (about 30 min), to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. The temperature was increased simultaneously such that when full vacuum was (30 min). The polycondensation was continued for about 1.5 h until the agitator speed decreased to 350 rpm, due to increasing viscosity of the melt. After the polycondensation reaction was completed, the reaction tube had to be broken to get the product out of the tube. In most of the polymerization preparations, the tube was broken due to the adhesion of the polyester to the glass and its shrinkage during cooling. All polyester samples, which had a white color after the glass particles were removed with a grinder, were ground in a mill, sieved washed with methanol, and dried at 110°C for 12 h.

Measurements

Intrinsic viscosity $[\eta]$ measurements were performed by using an Ubbelohde viscometer at 25°C in a mixture of phenol and tetrachloroethane (60 : 40, w : w). The samples were maintained in the above mixture of solvents at 120°C for 20 min to achieve a complete solution. The solution was then cooled to room temperature and filtered through a disposable membrane filter (Teflon).

Thermal analyses (differential scanning calorimetry, DSC) were performed on a Perkin-Elmer DSC-2 by using the following parameters: heating rate, 20°C min⁻¹; cooling rate, 10°C min⁻¹; sample weight, 12.00 \pm 0.01 mg; nitrogen flow rate, 1.5 L h⁻¹; sensitivity, 5 mcal s⁻¹.

Five runs were recorded for each sample. For the first run, the initial sample at a heating rate (0–300°C) of 20°C min⁻¹. For the second run, reheating (0–300°C) of the previous sample which was quenched from the melt just after the completion of the first run by contacting it with an iron bar cooled at -70°C. For the third run, the previous melted sample was cooled (300–0°C) at a cooling rate of 10°C min⁻¹. For the fourth run, the previous solidified sample was reheated (0–300°C). For the fifth run, the sample was reheated (0–300°C) after annealing at a temperature 10°C lower than its melting point for 3 h.

The tensile mechanical properties were studied on relatively thin films of the polymeric samples, which were prepared by an Otto Weber, Type PW 30 hydraulic press at a temperature of 265 ± 5°C under a load of 6 kN on a ram of 110 mm followed by rapid cooling in the molds. Dumbbell-shaped tensile-test specimens (central portions, ~ 5 × 0.5 mm thick; gauge length, 22 mm) were cut from the sheets in a Wallace cutting press and conditioned at 25°C and 55–60% relative humidity for 48 h. The stress-strain data were received by using an Instron tensile testing machine model 1122, which was maintained in the same conditions and operated at an extension rate of 10 mm min⁻¹ recording rate (chart speed), 20 mm min⁻¹, and a loading tension cell 0–200N (CTM 2511–312). The values of Young's modulus, the yield stress, and elongation at yield, as well as the tensile strength and elongation at break, were determined according to ASTM D 1708–66. At least five specimens were tested for each sample and the average values are reported. Typical standard deviation values were found to vary between 10 and 15%.

RESULTS AND DISCUSSION

Generally, from the literature, we know that poly-(ethylene terephthalate-co-isophthalates) exemplify copolyesters possessing a crystallizing component (PET) and a poorly or noncrystallizing component (PEI).⁷ As the ethylene-isophthalate content increases up to 35%, the crystalline melting points fall and the copolymers acquire broader softening ranges and slower crystallization rates. Composition containing more than 25% ethylene-isophthalate units are freely dissolved by ketones, methyl benzoate, tetrahydrofuran, and dichloroethane to give solutions that can readily be cast to films.⁷

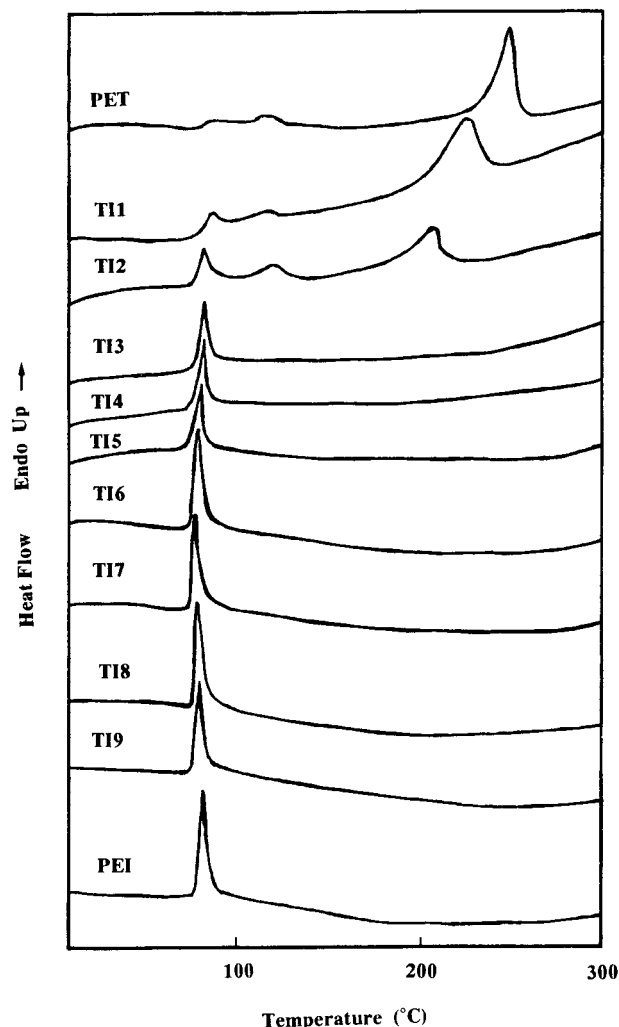


Figure 2 DSC curves of the initial samples of PET/PEI copolymers and their homopolymers.

Thermal Properties

It is worthwhile noting that all samples of this work were prepared about eight years ago and remained in their vials under normal conditions for reasons independent of the target of this research. This long stay in the shelf, especially for the amorphous samples, was the reason for an extremely pronounced enthalpy relaxation phenomenon in the glass transition temperature range (Fig. 2). This relaxation seems to be independent of the copolymer composition, because it applies for all the samples between 79 and 82°C and superimposes the glass transition temperature.

The glass transition temperatures (T_g), the cold crystallization temperatures (T_{cc}), the melting temperatures (T_m), and the crystallization

Table I Feed Composition and Intrinsic Viscosities, as well as Glass Transition, Melting, Crystallization, and Cold Crystallization Temperatures of PET/PEI Copolymers

Polymer	Feed Composition (mol %)		Viscosity ^a (dL/g)	Thermal Parameters			
	TA	IA		T_g (°C)	T_m (°C)	T_c (°C)	T_{cc} (°C)
PET	100	0	0.77	82	257	204	146
TI1	90	10	0.77	79	226	174	162
TI2	80	20	0.74	78	204	136	—
TI3	70	30	0.72	75	—	—	—
TI4	60	40	0.74	73	—	—	—
TI5	50	50	0.74	73	—	—	—
TI6	40	60	0.72	70	—	—	—
TI7	30	70	0.74	69	—	—	—
TI8	20	80	0.76	66	—	—	—
TI9	10	90	0.78	65	235	—	—
PEI	0	100	0.77	65	240	—	—

^a Measured at 25°C in a phenol/tetrachloroethane mixture 60/40 w/w.

temperatures (T_c), where they exist, were determined in this work and are shown in Table I.

In the same table, one can see the values of intrinsic viscosity of the 11 samples, which range from 0.72 to 0.78 dL/g. This is a good proof that all samples prepared have a relatively high-molecular weight. Taking into account the K and α constants for the Mark–Houwink–Sakurada equation from a work especially for PET and PEI prepared by Aharoni,⁸ we can calculate the \bar{M}_n for PET as 30,300 and the \bar{M}_n for PEI as 40,600. So, our polyester samples have an increased molecular weight compared with other grades. Of course, the fact that PEI with molecular weight higher by 10,000 shows exactly the same intrinsic viscosity (0.77 dL/g) as the PET sample leads us to the concept that PEI is a polyester more flexible than PET and this is true because of the m -substituted isomer dicarboxylic acid (isophthalic acid).

As can be seen from Figure 2, only the three first samples, PET, TI1, and TI2, show clear melting endotherms; that is, only these three polymers can crystallize relatively easily. The melting points of the above samples are 257, 226, and 204, respectively. These values increased by 10°C, when the samples were annealed for 3 h at a temperature 20°C lower than their initial melting point. A premelting endotherm for the above polymers shows characteristically the temperature at which samples were dried eight years before. As is known,^{9,10} this premelting peak appears about 20°C above its previous thermal treatment. In our

case, all samples were dried at 110°C for 12 h and the premelting peak appeared around $\approx 130^\circ\text{C}$.

The melting endotherms for PEI and TI9 can be observed with difficulty on the DSC trace, even when the same thermogram was obtained, by using the new differential scanning calorimeter Pyris-1 (Perkin–Elmer). Special care was given in this determination, but the endotherms could not be obtained as sharp peaks even after annealing.

The T_g 's were determined from the second heating run because the thermogram had to get rid of the relaxation endotherm, as is shown in Figure 3. So, the samples were heated to melting and cooled down quickly to -70°C . As is shown from Table I, the T_g of the homopolymers are not very different, 82°C for PET and 65°C for PEI, therefore, and those of the copolymers do not vary much with copolymer composition.

Figure 4 shows the dependence of T_g on the composition of PET/PEI copolymer. A very fine linear dependence appears, as was shown by other investigators.⁸

From Figure 3, one can also see that only PET homopolymer and TI1 copolymer show cold crystallization (T_{cc}) at 146 and 162°C, respectively (see also Table I). All others samples did not show T_{cc} because they cannot crystallize at all, or they cannot crystallize easily. This is quite true because when they were allowed to crystallize from the melt (third run) only, the above polymers plus copolymer TI2 showed a crystallization exotherm. All other samples remained amorphous.

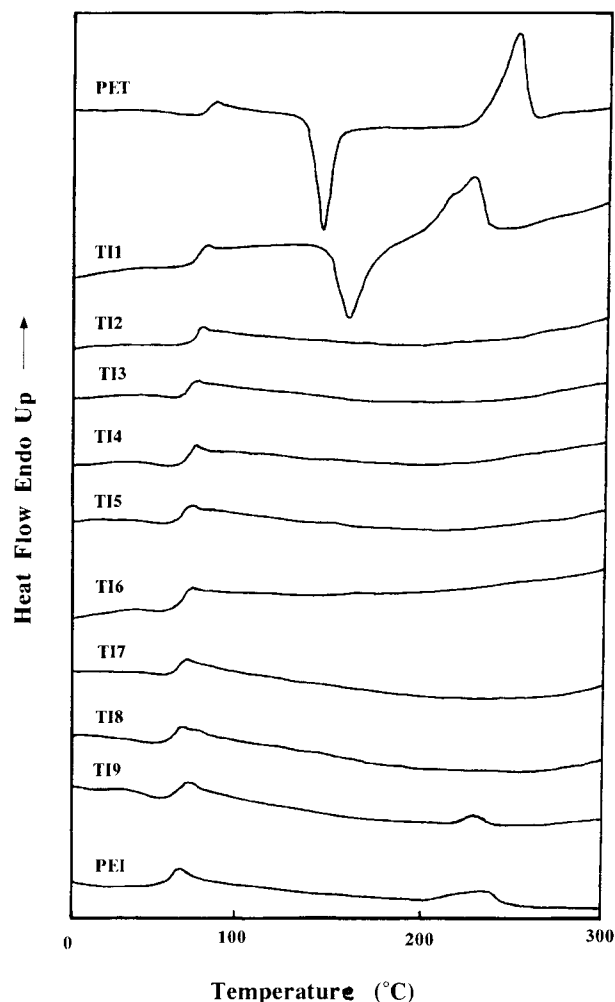


Figure 3 DSC curves of the quenched samples of PET/PEI copolymers and their homopolymers.

Tensile Mechanical Properties

The stress-strain relationship for all polymeric samples of this study was measured by using an Instron tensile tester. Such a test enables the determination of the mechanical tensile strength and the elongation at break of the polymer sample (film) in lateral direction. The Young's modulus was calculated from the slope of the linear part (elastic range) of the stress-strain curve. The average values of the main tensile properties (Young's modulus, yield stress, elongation at yield, tensile strength at break, and elongation at break)¹¹⁻¹³ of all samples are shown in Table II. Also, some representative diagrams of the above relationship are given in Figures 5-7.

Polymers that are characterized by a high modulus and a high tensile strength at large elongations are considered hard and tough materials. In this study, the PET sample, which is a semicrystalline polymer, seems to be classified between them, because it has the relatively highest Young's modulus (610 MPa) as well as a high tensile strength (45 MPa) and elongation at break (335%) (Fig. 5).

PET, TI1, and TI2 showed the characteristic phenomenon of necking, which usually appears in hard and tough polymeric materials. At a certain cross section of the polyester specimen, a narrowing suddenly appeared, which then grew at the expense of the gradually diminishing initial thick part of the specimen. The formation of such a

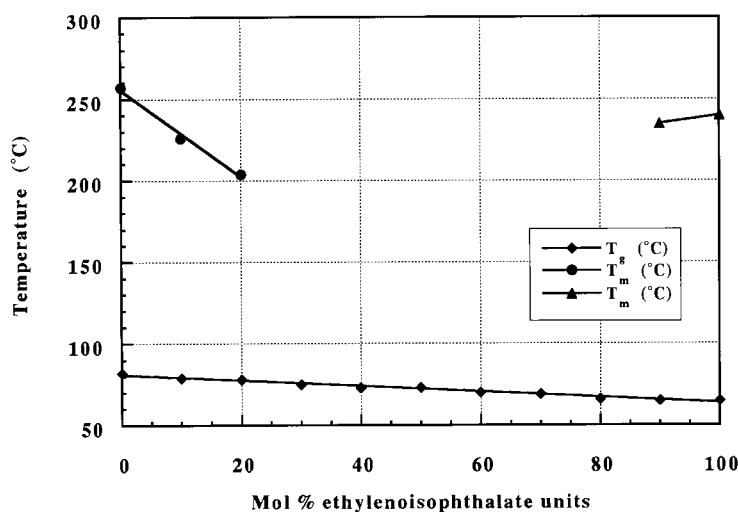


Figure 4 Glass transition temperature (T_g) and melting temperature (T_m) as a function of copolymer composition, expressed as ethylene-isophthalate units molar fraction.

Table II Tensile Mechanical Properties of PET/PEI Copolymers

Polymer	Young's Modulus (MPa)	Yield Stress (MPa)	Elongation at Yield (%)	Tensile Strength at Break (MPa)	Elongation at Break (%)	Type ^a
PET(100 : 0)	610	61	10	45	335	HT
TI1(90 : 10)	242	46	19	34	617	HT
TI2(80 : 20)	200	34	17	21	274	HT
TI3(70 : 30)	240	12	5	49	21	ST
TI4(60 : 40)	280	14	5	50	16	ST
TI5(50 : 50)	300	12	4	51	13	ST
TI6(40 : 60)	283	17 ^b 48 ^c	6 ^b 23 ^c	42	31	ST
TI7(30 : 70)	360	18 ^b 46 ^c	5 ^b 15 ^c	43	21	ST
TI8(20 : 80)	333	20 ^b 45 ^c	6 ^b 16 ^c	42	35	ST
TI9(10 : 90)	316	19 ^b 45 ^c	6 ^b 16 ^c	41	38	ST
PEI(0 : 100)	350	14 ^b 42 ^c	4 ^b 24 ^c	39	27	ST

^a HT: hard and tough. ST: Soft and tough.

^b Values derived from the first yield point.

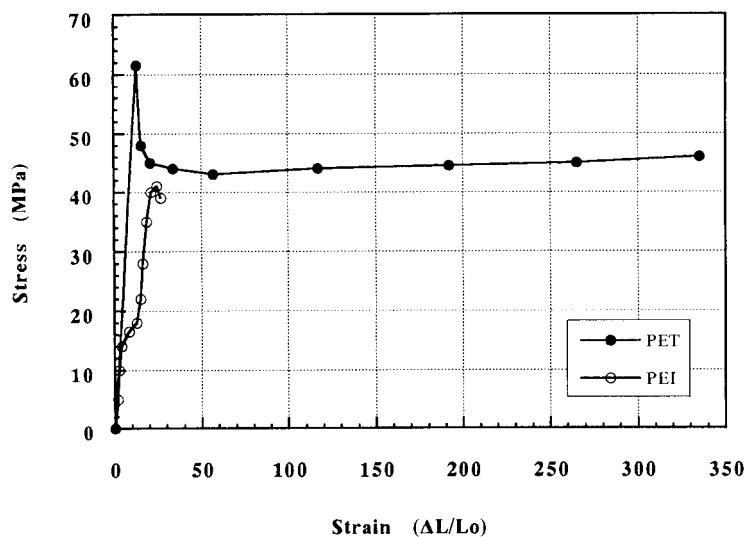
^c Values derived from the second yield point.

neck corresponds to the transition of the horizontal part of the stress–strain diagram (Figs. 5, 6).

From Figure 5, the very different behavior of PEI against PET can be seen. This polymer, as fully amorphous material, initially (up to ≈ 15 MPa) behaves as a hard and tough sample such as PET. Just after this point, a small yield (first yield point) takes place due probably to a partial orientation of the macromolecules. On further extension, when the macromolecules have practically exhausted their capacity for straightening, very large stress is again required. This part of

the curve seems to be parallel to the first one, until a second yield point around 42 MPa appears before breaking. The elongation at break reaches the value of $\approx 30\%$ and according to this criterion, PEI cannot be classified as a hard and brittle nor as a hard and strong material. However, PEI is not an elastomer because its $T_g = 65^\circ\text{C}$ is higher than room temperature; so, it could be classified as a soft and tough material.

Copolymers TI1 and TI2 are also semicrystalline materials like PET, but not to the extent that was shown from the previous thermal study. Con-


Figure 5 Stress–strain curves for PET and PEI homopolymers.

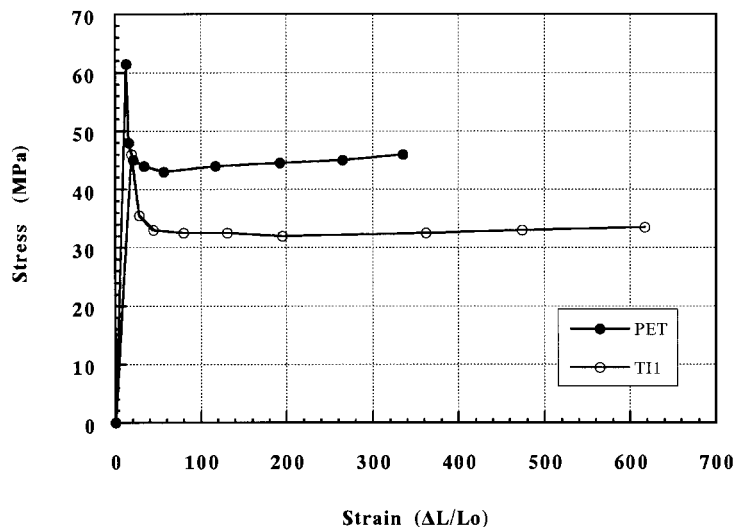


Figure 6 Stress–strain curves for PET homopolymer and TI1 copolymer.

sequently, their Young's modulus is lower, although TI1 showed surprisingly the higher elongation at break (617%) (Fig. 6). These two copolymers could also be characterized as hard and tough materials.

All the other copolymers TI3–TI9, including homopolymer PEI, show a peculiar behavior, which can be explained if we remember that these polymers are fully amorphous. The samples studied were taken from the press after quenching as fully amorphous films, but during tensile testing, just after yield points, they changed from transparent into opaque materials due to orientation.

The T_g of the above samples (75–65°C) are higher than that of mechanical testing (25°C). So, they must behave as rigid solids. Their stress–strain curves seem to have an S shape, especially for those TI3, TI4, and TI5, whereas TI6–PEI seem to show a second yield point before breaking (Fig. 7). The first yield point is considered to be the onset of the middle of the S shape.

According to the diagrams obtained, the amorphous polymers, which behave as elastic solids during the first step (the initial portion of the tensile curve exhibits elastic deformation up to the yield point), reorient their macromolecules at this point

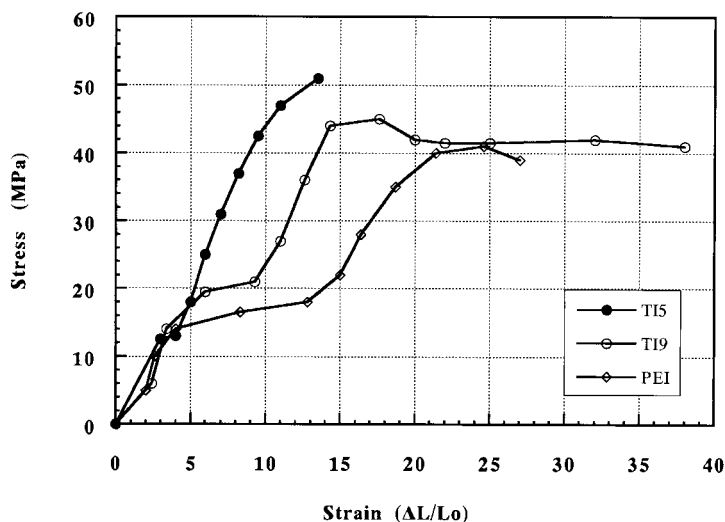


Figure 7 Stress–strain curves for PEI homopolymer, as well as TI5 and TI9 copolymers.

with the aid of the exerted stress and after a while they continue to behave as elastic materials again. This could be an explanation for the S-shaped curves obtained. This behavior could be paralleled with that of forced rubbery deformation before breakdown (hard and tough solids/with cold-drawing or necking), but with the difference being that the plateau in this case is very small to about non-existent and the yield stress low enough.

It is worth noting that copolymers TI3–TI9 showed stress–strain diagrams resembling this one of PEI. The various values obtained from these diagrams seem to be independent from the copolymer composition. One probable explanation could be that all these polymeric samples are fully amorphous and their T_g 's are not very different. Only the first three samples (e.g., PET, TI1, and TI2) can be crystallized easily; PEI and TI9 were crystallized with difficulty after a long annealing time for 12 h at 220°C.

The very different behavior of sample TI1 in respect to PET as it may concern the elongation at break is something that needs further investigation. For this reason, a series of PET–PEI copolymer samples are now being prepared with a composition ranging between 0 and 5% of PEI, and the results of this work are expected in the near future.

REFERENCES

1. Sakellarides, S. L. ANTEC 1996, 938.
2. Sakellarides, S. L. ANTEC 1997, 822.
3. Tsutsumi, N.; Nagata, M. in *Encyclopedia of Polymeric Materials*, Vol. 8; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p 6110.
4. Tirell, D. in *Encyclopedia of Polymer Science and Engineering*, Vol. 4, 2nd ed.; Kreschwitz, J. I., Ed.; Wiley: New York, 1988; p 192.
5. Fukuta, Y. Jpn. Pat. 62–198439, 1987.
6. Li, B.; Yu, J.; Lee, S.; Ree, M. *Eur Polym J* 1999, 35, 1607.
7. Goodman, I. in *Encyclopedia of Polymer Science and Technology*, Vol. 11; Mark, H.; Gaylord, N.; Bikales, N., Eds.; Interscience: New York, 1969; p 78.
8. Aharoni, S. *Makromol Chem* 1978, 179, 1867.
9. Yagpharov, M. *J Therm Anal* 1986, 31, 1073.
10. Karayannidis, G. P.; Kokkalas, D. E.; Bikiaris, D. N. *J Appl Polym Sci* 1995, 56, 405.
11. ASTM D 638–67T. *Annu ASTM Book Stand* 19XX, p 189.
12. ISO Recommendation R 527; *Plastics Determination of Tensile Properties*; November 1966.
13. Nielsen, L. E. *Mechanical Properties of Polymers and Composites*, Vol. 1; Marcel Dekker: New York, 1974.