

Dynamic Thermomechanical and Tensile Properties of Chain-Extended Poly(ethylene terephthalate)

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ABSTRACT: A series of chemically modified poly(ethylene terephthalate) (PET) samples was received after chain extension of a virgin sample at different reaction times with a new diepoxide as chain extender. These samples showed different intrinsic viscosity and degrees of branching or crosslinking. The effect of this differentiation on thermal properties was studied by dynamic mechanical thermal analysis and the determined T_g values were found to be in good agreement with those obtained by differential scanning calorimetry and thermomechanical analysis. Also, the branching or crosslinking exhibited significant improvement in tensile mechanical properties, which were studied, and the results are discussed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 797–803, 1998

Key words: poly(ethylene terephthalate); dynamic mechanical thermal analysis; glass transition temperature; storage modulus; tangent δ ; tensile properties

INTRODUCTION

Poly(ethylene terephthalate) (PET) has become one of the most important engineering thermoplastics. It is used in the manufacturing of synthetic fibers, soft drink bottles, photographic films, recording audio and video tapes, films for food packaging, or even as electrical insulating material for capacitors.

As it is known, a relatively high molecular weight and a low carboxyl content give to the polymer improved mechanical and chemical properties, such as toughness and hydrolytic stability, but this is rarely achieved since further heating during the preparation of the polyester by the melt polycondensation process causes an undesirable degradation reaction with a significant increase in carboxyl end groups. The solid-state polycondensation overcomes this problem, but it is slow and requires special equipment for large-

scale operation, so nowadays, only few companies use this kind of chemical process. For this reason, the use of the so-called chain extenders seems to be very attractive. The chain extenders for polyesters are bifunctional compounds, which react very easily with the end carboxyl or hydroxyl groups of macromolecules. When these compounds are reacted directly with low-molecular-weight polyesters coming, for example, from recycling operations, they form bridges between 2 macromolecules, joining them and increasing the molecular weight significantly. As chain extenders can be used as compounds which are difunctional, easily preparable, thermally stable, non-volatile in the melt temperature of the polymer, and capable for fast reaction with polymer chain ends in a nearly irreversibly manner with no volatile products. It is desirable for such reactions to be of addition or ring-opening type. One of the main chain extenders of this type is bis-epoxides or diepoxides.

On chain extension of the polyesters with diepoxides, secondary hydroxyl groups are produced, which are capable of creating branching, or

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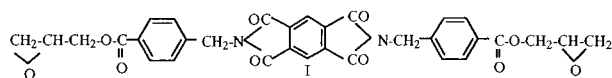
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crosslinking, depending on the reaction conditions.¹⁻³ In our previous work,³ in an effort to prepare new effective chain extenders for polyesters, we received one series of PET samples chain-extended by a diepoxide so we could study by differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA) the effect of molecular weight and branching or crosslinking on some thermal properties such as T_g .⁴ The purpose of this article is to study the dynamic thermomechanical properties, as well as the tensile ones, of the aforementioned chain-extended samples. The results obtained are compared to those received from other techniques.²⁻⁴

EXPERIMENTAL

Materials

The chain-extended PET samples used in this article were the same as those prepared in a previous article.⁴ These were taken from the chain extension of virgin PET ($[\eta] = 0.60$ dL/g, carboxyl content = 42 eq/10⁶ g) with diepoxide I, which was synthesized in our laboratory for the first time, so it is not commercially available (see Scheme 1).



Scheme 1

Viscosity measurements were conducted at $25 \pm 1^\circ\text{C}$ in an Ubbelohde-type viscometer on solutions in 60 : 40 w/w phenol-tetrachloroethane, at a polymer concentration of 1.0%. The intrinsic viscosity $[\eta]$ of each sample was calculated by using the Solomon-Ciuta⁵ equation of a single point measurement, as follows:

$$[\eta] = [2(\eta_{sp} - \ln \eta_{rel})]^{0.5}/c$$

Some samples were partially insoluble in the above solvent mixture at the concentration of 1%. In this case, the insoluble part of the sample was removed by filtration and determined, so the real concentration of the solution was calculated and used in the Solomon-Ciuta equation.

The carboxyl end group content (CC) was determined according to Pohl's method.⁶

The melting points of semicrystalline samples were measured using a differential scanning cal-

orimeter, DSC-2 (Perkin-Elmer) at a heating rate of $20^\circ\text{C}/\text{min}$.

Dynamic Mechanical Thermal Analysis

Dynamic mechanical measurements were performed on a Polymer Laboratories (Model PL-Mk II) dynamic mechanical thermal analyzer at a frequency of 1, 5, or 10 Hz in the temperature range from -120 or 100 to $+100^\circ\text{C}$ at a heating rate of $2.5^\circ\text{C}/\text{min}$. A double cantilever bending geometry was used for beam samples ($0.25 \times 10 \times 30$ mm).⁷ The samples were produced by melt-pressing in a hydraulic heated press (Paul-Otto Weber, Type PW 30) at a temperature $265 \pm 5^\circ\text{C}$ under a load of 6 kN on a ram of 110 mm, followed by rapid cooling in the molds, so they were amorphous.

Tensile Mechanical Properties

Relatively thin films (0.5 mm) of the chain-extended PET samples were prepared by the same above-mentioned hydraulic press. Dumbbell-shaped tensile-test specimens (central portions, approximately 5 mm wide \times 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 using an Instron tensile testing machine Model 1122, which maintained in the same conditions and operated at an extension rate of 10 mm/min, a recording rate (chart speed) of 20 mm/min, and a loading tension cell 0–200 N (CTM 2511-312). Values of tensile strength and elongation at break, yield stress and elongation at yield, and Young's modulus were determined according to the ASTM D 1708-66. At least 4 specimens were tested for each sample, and the average values are reported.

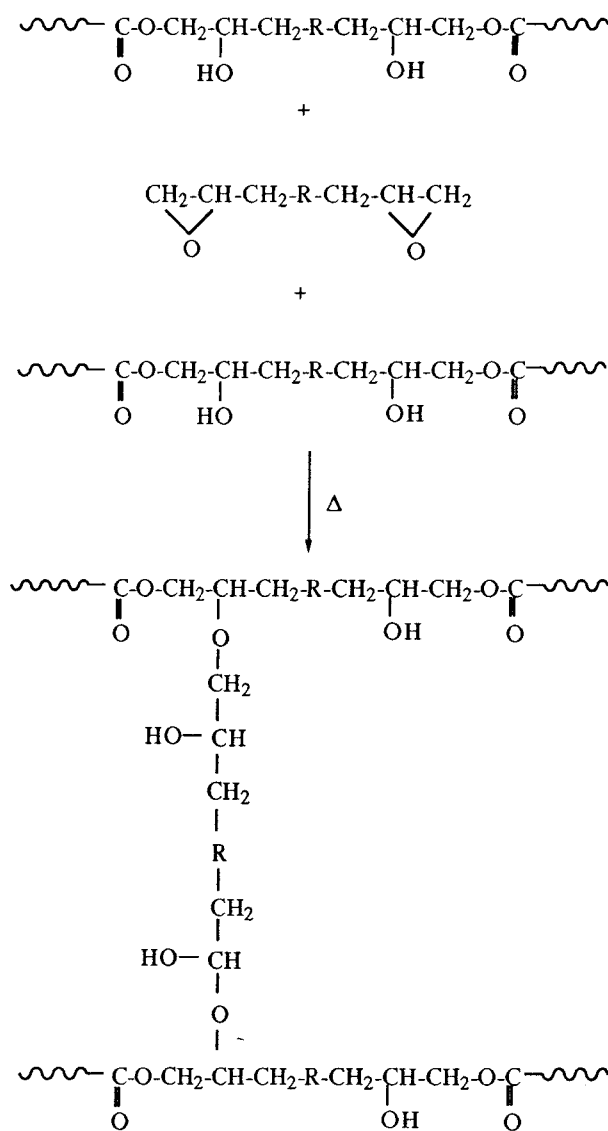
RESULTS AND DISCUSSION

The chain extending reactions of chemical modification of the virgin PET sample with diepoxide I, can be classified as follows.

1. Esterification of carboxyl end groups.
2. Etherification of hydroxyl end groups; these reactions are shown in detail in our previous article.²
3. Branching or crosslinking created from the

Table I Intrinsic Viscosity, Carboxyl Content, and Insoluble Residue of the Chain-Extended PET Samples

Sample Number	Time ^a (min)	[η] ⁴ (dL/g)		CC (eq/10 ⁶ g)		T_m ⁴ (°C)	Insoluble Residue ⁴ w/w (%)
		Blank	CE ^b	Blank	CE ^b		
1	0	0.60	0.60	42	42	254	—
2	10	0.54	0.85	44	13	249	2.9
3	20	0.54	0.98	48	9	243	5.1
4	30	0.55	1.19	50	6	242	6.8
5	60	0.58	0.94	52	5	237	25.3

^a Time of chain extension.^b Chain-extended sample with diepoxide.**Scheme 2**

reaction of secondary hydroxyl groups that were produced from the above chain-extending reactions. A crosslinking reaction by etherification on chain-extended macromolecules is shown in Scheme 2.

This crosslinking, along chain extension reactions, are responsible for the improved tensile properties (higher strength or elastic modulus) of samples 2, 3, 4 and 5, as will be discussed later.

The intrinsic viscosity, the carboxyl content, and the melting points, as well as the insoluble residue due to crosslinking of the PET samples, are given in Table I.

As one can see from Table I, in the blank experiment, that is, in the case in which the melted sample is heated under stirring for 10, 20, 30, or 60 min in the absence of chain extender, the intrinsic viscosity decreases during the first 20 min of reaction because of the presence of moisture traces, and the thermal decomposition that takes place.² After this period, a small increase seems to appear. On the contrary, in the presence of the chain extender, the intrinsic viscosity gradually increases with reaction time up to 30 min; longer chain extension leads to a decrease of viscosity due to branching.

The chain-extended PET samples were characterized also by the determination of carboxyl content. From Table I, one can also see the clear increase of the control (blank) run, that is, from 42 to 52 eq/10⁶ g. This increase is due to thermal decomposition of the samples because of the high temperature. On the contrary, in the presence of chain extender, the decrease of CC was very intense (from 42 to 5 eq/10⁶ g) so that it overbalanced the aforementioned increase.

The T_m values of more chain-extended samples are lower. This is quite reasonable because these

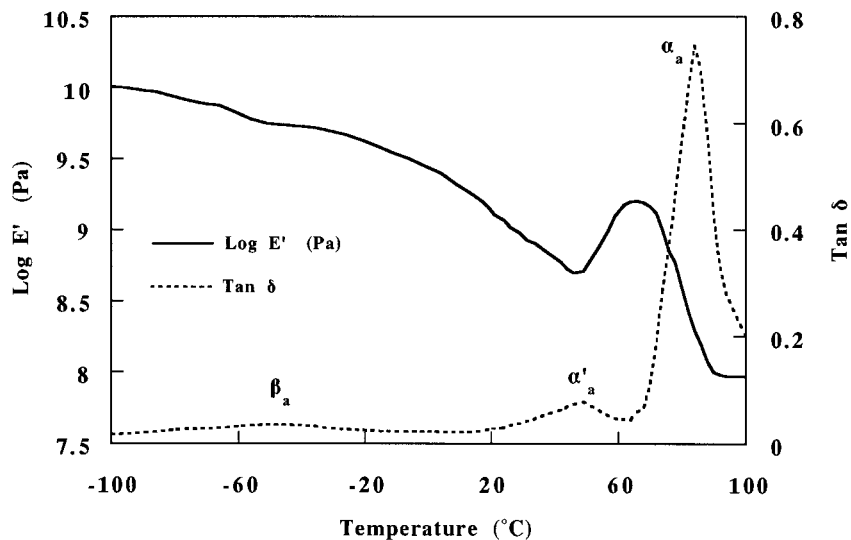


Figure 1 Tangent δ ($\tan \delta$) and log storage modulus ($\text{Log } E'$) versus temperature for the chain-extended PET sample 4 at a frequency of 1 Hz and a heating rate of 2°C/min.

samples, having a significant extent of crosslinking, cannot crystallized easily.

An insoluble matter, due to crosslinking, was detected in the viscometric trials and was determined gravimetrically. In the case of the sample, which remained for 60 min in the reactor, this insoluble residue rose to 25.3%.

Dynamic Mechanical Thermal Analysis

DMTA, according to International Confederation for Thermal Analysis (ICTA),⁸ is the thermomechanical technique in which the storage modulus (elastic response) and loss modulus (viscous response) of the sample, under oscillating load, are monitored against time, temperature, or frequency of oscillation, while the temperature of the sample in a specified atmo-

sphere is programmed. This technique was used in this work and the dynamic mechanical behavior under various conditions, for example, the temperature or frequency of oscillation was studied.

Representative traces of DMTA recording of $\tan \delta$ and $\text{log } E'$ for the chain-extended PET sample (30 min) are shown in Figure 1.

One can distinguish 3 peaks on the $\tan \delta$ curve (broken line): the α_a peak, which is attributed to the glass transition and is related of course to the acquisition of main chain molecular motion (this loss process can be used as a definitive measure of T_g , provided that it is measured at a low frequency and that this frequency is specified); the α'_a peak, which is unknown in the literature; and the β_a peak, which was attributed to a very restricted degree of molecular mobility, probably in

Table II Glass Transition Temperatures Determined from Relaxation Spectra of $\tan \delta$ of Chain-Extended PET Samples at a Frequency of 1 Hz

Sample Number	Chain Extension Time (min)	$T\alpha_a$ or T_g (°C) Determined from			Determined from $\tan \delta$	
		$\tan \delta$	DSC ⁴	TMA ⁴	$T\alpha'_a$	$T\beta_a$
1	0	82	82	81	52	-66
2	10	83	82	82	54	-62
3	20	84	83	82	55	-56
4	30	84	83	83	56	-50
5	60	81	83	84	58	-45

Table III Mechanical Properties (Average Value) for Chain-Extended PET Samples

Sample Number	Chain Extension Time (min)	Tensile Strength at Break (MPa)	Elongation at Break (%)	Yield Stress (MPa)	Elongation at Yield (%)	Young's Modulus (MPa)
1	0	31.4	275	43.4	3.9	1315
2	10	36.2	300	50.8	5.0	1455
3	20	43.3	315	61.3	6.5	1767
4	30	52.9	335	63.7	6.5	1826
5	60	62.3	350	66.3	6.5	1852

the glycol residue,⁹ or to carbonyl groups and ethylene unit motions.¹⁰

The T_g s determined from $\tan \delta$ of DMTA relaxation spectra at a frequency of 1 Hz and those obtained by DSC or TMA are given in Table II. These T_g values determined by $\tan \delta$ are in very good agreement with those determined by DSC and TMA (maximum difference 2 and 3°C, correspondingly).

When higher frequencies were used for the determination of T_g from $\tan \delta$, the received values were higher indeed (Fig. 2). So, this characteristic temperature is frequency-dependent and must be measured at low frequency ≤ 1 Hz. However, sample 5's behavior did not permit us to use lower frequencies.

The same shift to higher temperatures with higher frequencies was observed from $\log E'$ spectra (Fig. 3), but the determination of T_g from these curves was impossible because of the presence of an unusual maximum ($\approx 70^\circ\text{C}$) of the curve, just opposite of the α'_a peak in $\tan \delta$ curve. This unusual maximum is unknown in the liter-

ature and, in our opinion, it could be attributed to the small thickness of the samples (0.25 mm).

The α'_a peak is very clear for the first 3 samples, while for the last samples, its intensity is decreased significantly. This observation, in combination with the fact that the samples are amorphous, gave us the sense that this peak consists of the starting of T_g peak, which is interrupted by a partial crystallization of the sample due to orientation. This probable explanation is enhanced by the increase of $\log E'$ in the vicinity of 70°C and the very low intensity of this peak for the last 2 samples (4 and 5) because of the high degree of crosslinking, especially for the last one. All samples after annealing at 200°C changed their behavior, and this peculiar peak, α'_a , disappeared. Also, this peak seems to be unchanged with frequency (Fig. 2).

It is worthy to note that the value of T_g for sample 5, determined by $\tan \delta$ (81°C), is unexpectedly lower than that obtained by DSC (83°C) or TMA (84°C). It is known that at high crosslinking, the glass transition temperature is shifted to higher temperatures, or even it disappears. In this case,

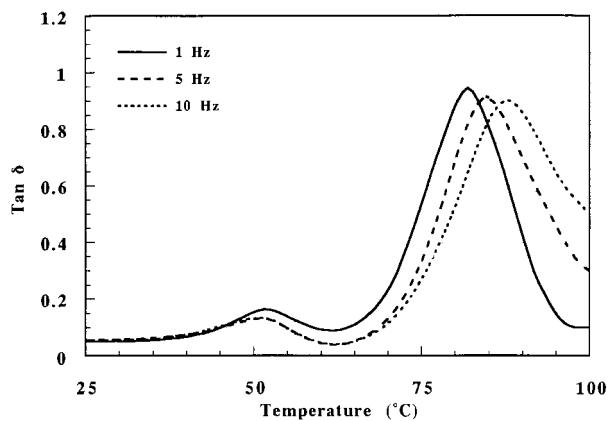


Figure 2 Tangent δ ($\tan \delta$) versus temperature at 3 frequencies (1, 5, and 10 Hz) and a heating rate of $2^\circ\text{C}/\text{min}$ (sample 1).

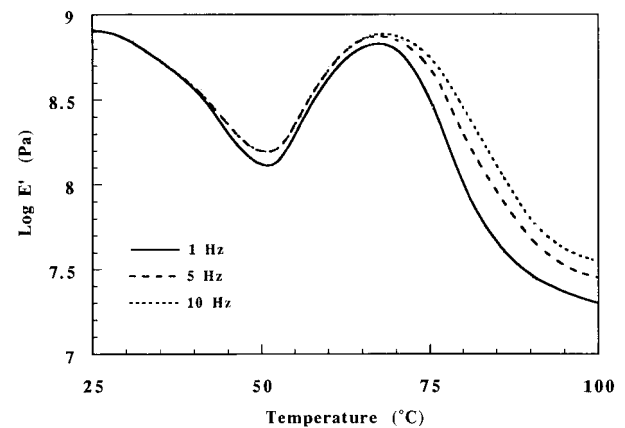


Figure 3 Log storage modulus ($\log E'$) versus temperature at 3 frequencies (1, 5, and 10 Hz) and a heating rate of $2^\circ\text{C}/\text{min}$ (sample 1).

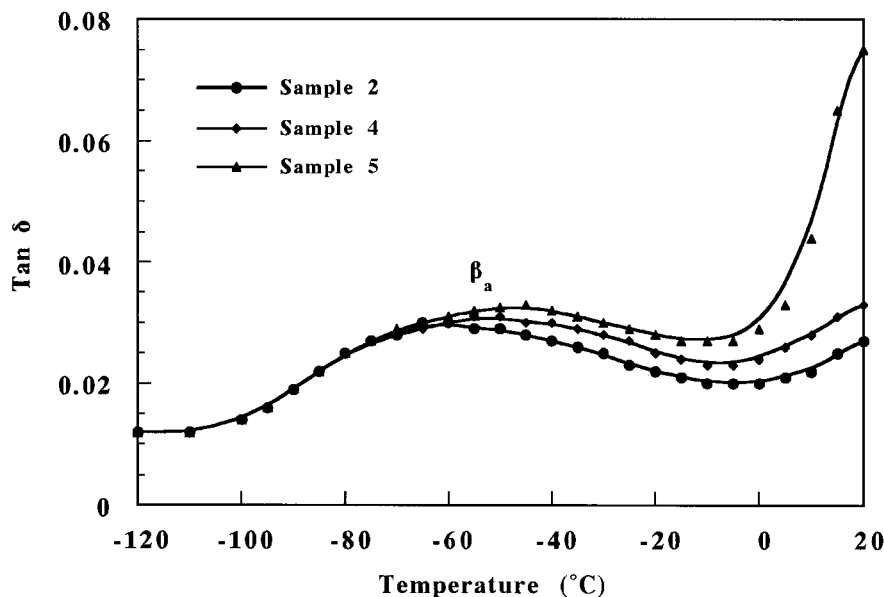


Figure 4 Tangent δ (peak β_a) of the chain-extended PET samples (2, 4, and 5) versus temperature.

the most probable explanation could be based on the lower crystallinity of the sample 5. The heats of fusion of the samples determined by DSC confirm this explanation. Sample 5 has the lowest value (≈ 40 j/g),¹¹ so the lowest degree of crystallinity and, consequently, the lower T_g . Such a lower T_g was not determined by DSC or TMA, of course, because the sensitivity of these techniques is clearly lower by a factor of approximately 1000.

A shift to higher temperatures with branching or crosslinking was observed in the β_a peaks (Fig. 4). Since the response of the samples changes

with both temperature and impressed frequency of oscillation, it was decided to take a three-dimensional thermogram for virgin PET sample 1 (Fig. 5). The α_a and α'_a processes are both visible, and the rate of change of the first one in position is seen clearly.

Tensile Mechanical Properties

The main tensile properties of the chain-extended PET samples, including the virgin one, are shown in Figure 6. As a group, all samples behave as hard

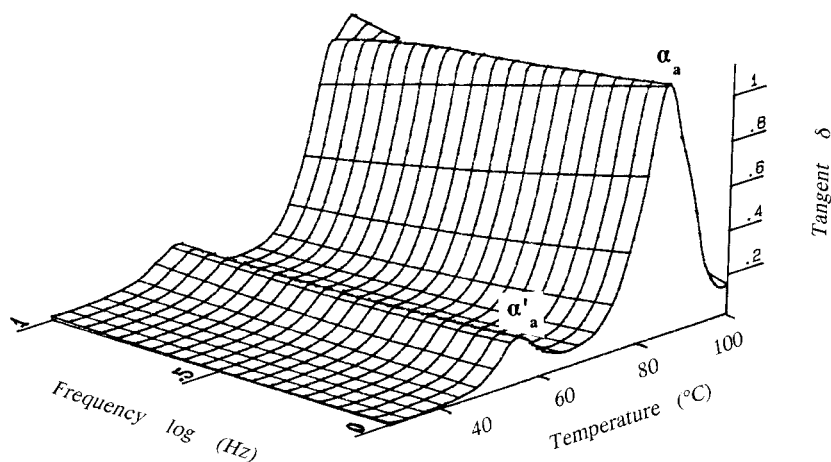


Figure 5 Effect of temperature and frequency on $\tan \delta$ for the virgin, nonchain-extended amorphous PET (sample 1).

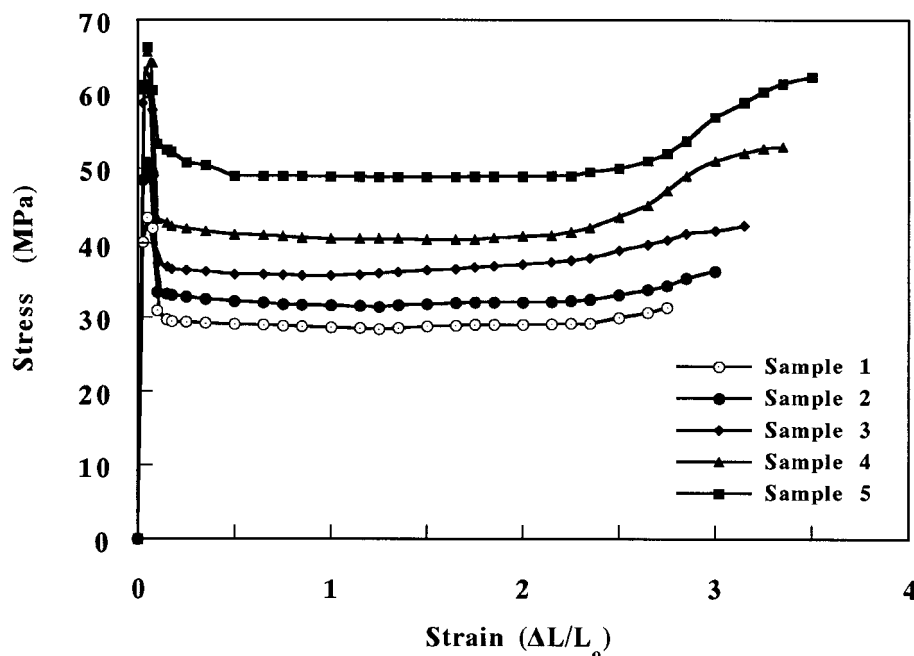


Figure 6 Stress-strain curves for the chain-extended PET samples.

and tough materials, with high tensile strengths and elongations at break. The samples studied were taken from the press after quenching as amorphous films, but during tensile testing, just after yield points, they changed from transparent into opaque materials, due to orientation.

From the curves of Figure 6, the tensile strength and elongation at break, the stress and elongation at yield, and Young's modulus were determined, and are given in Table III.

It is interesting to note the high increase of tensile strength from 31.4 MPa (sample 1) to 62.3 MPa (sample 5), due to chain extension, branching, and crosslinking; the significant increase of Young's modulus from 1315 (sample 1) to 1852 MPa (sample 5); and, of course, the elongation at break, which rose up to 350%.

This significant improvement in tensile mechanical properties of PET, after modification with the aforementioned diepoxide, can open new possibilities for the recycling and reusing of this interesting thermoplastic polyester.

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