Synthesis and Characterization of Poly(ethylene terephthalate-*co*-isophthalate)s with Low Content of Isophthalate Units

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ABSTRACT: The objective of this work was to study the effect of the introduction of low amounts of isophthalate units on the mechanical properties, crystallization rates, and thermal parameters of poly(ethylene terephthalate). For this reason a series of five random poly(ethylene terephthalate-*co*-isophthalate) copolymers, containing 0.5, 1, 1.5, 2, and 4 mol % isophthalic acid, were prepared by the melt polycondensation process. The intrinsic viscosity of copolymers ranged between 0.7 and 0.8 dL/g. The increase of isophthalate content resulted in a significant decrease of the crystallization rates, but in a small decline of tensile strength, Young's modulus, and elongation at break, whereas tensile strength at yield point remained almost unaffected. Also, a decrease in the melting point was recorded, whereas the glass-transition temperature was only very slightly affected. The higher decrease for the aforementioned parameters was noted for the copolymer with 4 mol % isophthalate units content. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1931–1941, 2002

Key words: PET; PEI; copolymer; thermal properties; tensile mechanical properties; crystallization

INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most important thermoplastic materials with a wide field of applications. For many years the largest part of the produced volume was used for textile fiber production. However, in the past few decades much activity has been dedicated to the preparation of suitable materials for films (audio/video tapes, capacitors, and mainly food packaging). The use of PET in this area instead of other polymers provides many benefits. PET has excellent clarity, high resistance to abrasion and stress cracking, and good barrier properties in oxygen and carbon dioxide. Furthermore, when filled with minerals or reinforced with glass fibers, PET can be used for injection moldings in automotive and appliance industries and for electrical and electronic fittings. Recently, foam production from PET gained interest because it offers the advantage of stability at high temperatures.[1] For all the above-noted applications a combination of various properties is demanded and also some problems in industry must be overcome.

The production of PET items such as fibers, film, and bottles for food and household packaging involves many processing steps, which result in changes of morphological and structural characteristics. Almost all films, as well as bottles from PET produced by the blow-molding process, are biaxially orientated above the glass-transition temperature. This orientation, close to the cold crystallization of PET, results in a macromolecular chain alignment parallel to the draw direction, thus increasing the crystallinity of PET and changing the physical properties of the end product. Shrinkage, dimension stability, stiffness, dyeability, mechanical behavior, and gas barrier properties of the final products are related to the degree of crystallinity and the glass transition of PET.

Chemical modification by copolymerization is one of the most attractive techniques to differentiate the properties of PET and, especially, the degree of crystallinity. For this reason glycols with different numbers of methylene groups than that of ethylene glycol, or other dicarboxylic acids instead of terephthalic acid, can be used. The combination of different monomers than that used for PET preparation may result in production of a large variety of copolymers. This technique offers a numerous advantages over other methods, such as the melt blending with other polymers or use of low molecular weight compounds. To prepare mixtures with suitable mechanical properties, the obstacle of compatibility between the various components must be overcome. Production of PET copolymers aims at the solution of complex problems that puzzle the industry.

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Poly(ethylene glycol)s (PEG) with different molecular weights are added to enhance the dye receptivity of PET fibers by increasing their hydrophilic character. Such copolymers are well known as thermoplastic poly(ether–esters).[2,3] PEG increases the chain flexibility by reducing the crystallinity of PET and its glass-transition temperature. The result is an increase in the dye sorption onto fiber and also a decrease in both time and dyeing temperatures. This copolymerization technique has more benefits than the use of carriers, which are low molecular weight compounds, added on PET fibers to increase their dyeability by acting as plasticizers.[4] Low amounts of polyamides or isophthalic acid can be also used to improve the dyeing properties of PET fibers.[5,6] Because of its lower glass-transition temperature and crystallinity, poly(ethylene isophthalate) (PEI) absorbs dye more easily than does PET. Thus, dyeability of PET can be improved by introducing isophthalate units into the PET chains, either by copolymerization or by blending PET and PEI.[7]

For film production cyclohexanedimethanol can be used together with ethylene glycol to produce copolymers with high heat resistance, better impact properties, and hydrolytic stability.[8] These copolymers are used mainly for oriented and cast film production having a brilliant clarity and high tear strength. High shrinkable films can be produced from PET/PEI copolymers, exploiting the high shrinkage ability of PEI. Such copolymers with 40 mol % isophthalate units content exhibit the highest shrinkage ratio.[9] Also, a Japanese patent claims that PET films for videotapes, containing 2 mol % isophthalic acid, can be produced with improved properties.[10]

PET copolymers with 1,4-butanediol or isophthalic acid can be used to coat metallic cans. The prepared polyester films have improved adhesion on the metal plate and excellent shock resistance and barrier properties against corrosive components.[11] Because of its low cost and high chemical stability, PET can be used in the form of films for surface coating of chromium-coated steels that are used in many applications. However, the high crystallinity of PET can reduce the adhesion on the metal surface. PET copolymers with PEI were found to have almost double the bonding energy on chromium-coated steels than that of pure PET, thus increasing the adhesion on the metal surface.[12] Similar copolymers can be used as solution adhesives in a solvent with low boiling point.[13]

In recent years PET has been widely used for construction of containers for carbonated drinks not only because of the excellent combination of mechanical properties, chemical resistance, low toxicity of extractants, and gas barrier against carbon dioxide but also mainly because of its reduced cost, compared with that of aluminum and glass, especially because of the high-energy consumption demanded for the production of the latter. However, PET has higher oxygen and carbon dioxide permeability compared with that of either glass or metallic containers. Nowadays, there is an increasing interest to extend the use of PET in new applications like bottles for beers or cosmetics.[14] However, the use of PET in food applications is still limited because of the low barrier properties against oxygen and UV irradiation, in which food exposure could reduce its quality. Most of the research attempts have focused on the preparation of multilayer bottles in which the main layer is composed of PET, whereas others are composed of either polyamide or PEI.[15–17] In addition, copolymers of PET/PEN or PET/PEI with different amounts of either naphthalene or isophthalic dicarboxylic acid can be used to increase the gas barrier properties.[18,19]

From all the preceding information, it seems that PET copolymers with PEI offer an excellent combination of properties of the two homopolymers and can be used in various applications. In the present study, which completes our previous work,[20] PET/PEI copolymers with low isophthalate units content were prepared, to study the effect of introducing isophthalate co-units on mechanical and thermal properties, as well as on crystallization rates of PET.

EXPERIMENTAL

Preparation of the copolyesters

PETI copolymers as well as neat PET 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 [$Zn(OCOCH_3)_2 \cdot 2H_2O$] was used as the transesterification catalyst and antimony trioxide (Sb_2O_3) was used for the polycondensation step.

In each preparation, the reaction mixture was composed of 32.03 g (0.50 mol) of EG, various amounts (mol %) of DMT and DMI esters (molar ratio of EG/dimethyl ester = 2.2), 50 ppm $Zn(OCOCH_3)_2 \cdot 2H_2O$, and 950 ppm Sb_2O_3 on dimethyl ester.

The reaction mixture in the transesterification step was heated to the final temperature (270°C) under argon atmosphere and stirring at a constant speed (500 rpm). It was completed after about 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 (∼ 30 min), to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem

during the melt polycondensation. The temperature was stable at 270°C. The polycondensation was continued for about 1.5 h until the agitator speed decreased to 350 rpm, as a result of the increasing viscosity of the melt. After the polycondensation reaction was completed, the reaction tube was broken to obtain the product from the tube. In most of the polymerization preparations, the tube was broken because of the adhesion of the polyester to the glass and its shrinkage during cooling. After the glass particles were removed with a grinder, all polyester samples, which had a white color, were ground in a mill, sieve-washed with methanol, and dried at 110°C for 12 h.

Measurements

Intrinsic viscosity [η] measurements were performed by using a 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 90°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).

Mechanical properties

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 (Remshalden, Germany) at a temperature 265 $\pm$ 5°C under a load of 6 kN on a ram of 110 mm, followed by rapid cooling in the molds. Dumbbell-shape tensile-test specimens (central portions, $\sim$ 5 $\times$ 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 obtained by using an Instron tensile testing machine model 1122, which was maintained under the same conditions and operated at an extension rate 10 mm/min, recording rate (chart speed) 20 mm/min, and a loading tension cell 0–200 N (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%.

Thermal analysis

Thermal analysis of the copolyesters was carried out using a Perkin–Elmer Pyris 1 differential scanning calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT). The calorimeter was calibrated with indium and zinc standards. For each measurement a sample of about 10 mg was used, placed in an aluminum seal and heated to 300°C at a heating rate 20°C/min. At that temperature samples were held for 5 min to erase any thermal history. After that the samples were quenched to −60°C and scanned again up to 300°C with the same heating rate as before. From this second scan the glass-transition temperature (T_g), the melting temperature (T_m), and the heat of fusion (ΔH_m) were measured. Finally, the samples were held again at 300°C for 5 min and cooled at a cooling rate of 10°C/min to record the crystallization temperature and the enthalpy of crystallization. A final scan up to 300°C at the same heating rate was performed.

Crystallization study

Isothermal crystallizations of the copolyesters were performed using a Perkin–Elmer Pyris 1 differential scanning calorimeter. Samples of about 5 mg were used to reduce thermal lag. The samples were melted at 300°C for a holding time of 5 min to destroy all crystal nuclei. These conditions were similar to those reported in the literature.[22,23] The samples were then rapidly cooled at a rate of 200°C/min to the crystallization temperature and remained at that temperature until no change in the heat flow was recorded in the heat flow versus time plot. From the crystallization enthalpy the kinetics of crystallization was evaluated.

RESULTS AND DISCUSSION

After their progressive cooling from the melt to room temperature, the prepared PET/PEI copolymers got a milky color, which proves that they were crystallized to some extent. From the determination of intrinsic viscosity it was realized that they have similar molecular weight, given that their intrinsic viscosity values were between 0.72 and 0.81 dL/g. Consequently, the incorporation of isophthalic acid in the macromolecular chains of PET did not have any effect in the growth of chains during melt polycondensation. However, it was observed that isophthalic acid can affect the solubility of the copolymers because the copolymers containing 2 and 4 mol % isophthalic acid dissolved faster in the phenol/tetrachloroethane mixture (60/40 w/w), the solvent that was used for intrinsic viscosity measurements. This property is used for the preparation of copolyester resins, which are used as solution adhesives.[13] PET/PEI copolymers with more than 30 mol % isophthalic acid are soluble in organic solvents like acetone.

Recently, PETI copolymers with low content of isophthalic acid found uses in manufacturing of bottles for carbonated beverages. The use of these copolyesters in soft-drink bottling exhibits a series of advantages. Poly(ethylene isophthalate) as well as isophthalate/terephthalate copolymers have better barrier
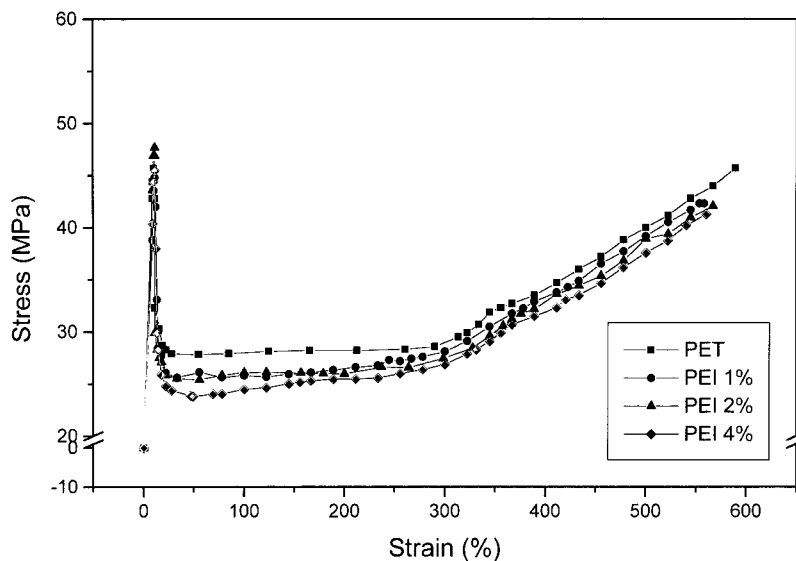
Figure 1 Stress–strain curves of PET and PETI copolymers.

properties with respect to oxygen and carbon dioxide.[21] Besides, these bottles exhibit a greater transparency than that of PET bottles, and thus manufacturers prefer to produce bottles made from copolymers, although the isophthalate content cannot be more than 5 mol %. The main reason for the limited isophthalate content is a significant reduction of the mechanical properties. Most of the studies on PET/PEI copolymers have primarily focused on crystallization kinetics and less on the study of the mechanical properties. In this work a combined study of both crystallization and mechanical properties of PET/PEI copolymers was performed.

The stress–strain curves for the PET homopolymer and for PETI copolymers are shown in Figure 1. From these curves it is concluded that the copolymers exhibit behavior analogous to that of PET. All polymeric samples can be classified as hard and tough materials. A yield point is obvious for all, whereas the increase of the isophthalate content seems to result in a small reduction of the stress at break. After the yield point, orientation of the macromolecular chains parallel to the direction of the applied stress occurs, as the elongation ratio increases. Stress hardening is recorded at an elongation ratio of 3–3.5, which results not only in significant toughening of the materials but also in an increase of the elongation of the strips at break.

The introduction of the isophthalate comonomer does not alter the shape of the stress–strain curves, although it does affect the ultimate strength of the copolymers. As the isophthalate content increases, the tensile strength decreases. However, this decrease is very small for PETI copolymers with up to 2 mol % isophthalate content, as can be seen in Figure 2. A reduction of only 7–8 MPa was observed for the copolymer with 2 mol % isophthalate content compared

to that of PET. Moreover, this reduction is even lower for copolymers containing lower isophthalic content. Furthermore, a comparison of the values of these copolymers shows that they are placed within the limits of experimental error, which means that the first four copolymers have almost the same tensile strength.

The reduction in the ultimate strength becomes maximum for the fifth copolymer with 4 mol % isophthalate content. For this copolymer the ultimate strength decreases from 47 MPa for PET to 32 MPa, which means a reduction of about 33%. This behavior could not be attributed to a different molecular weight because polyesters of comparable molecular weights were used in this study. The PET used in the present study has an intrinsic viscosity of 0.77 dL/g, whereas the intrinsic viscosity of the copolymer containing 4 mol % isophthalic acid is 0.76 dL/g. Besides, the strips were cut from films that were cast following the same procedure, involving quenching from the melt into water, so that they all were amorphous. Thus, differences in the ultimate strength could not be attributed to differences in the morphology of the films. However, another reason could be the different degrees of crystallization that films could gain during tensile testing measurements as a result of the stress-hardening effect. From a previous study, however, it was found that isophthalic acid up to 4 mol % has no significant effect on the crystallinity during the strain hardening.[22] Thus, the only reason for the reduced strength of the copolymers is the *m*-substitution of isophthalate units. It must be mentioned here that in our previous study of PET–PEI copolymers,[20] a dramatic reduction up to 50% was found for copolymers with an isophthalate content of 10 to 20 mol %. Consequently, a reduction in the ultimate strength is also anticipated for copolymers with low isophthalate content, such as those studied in the
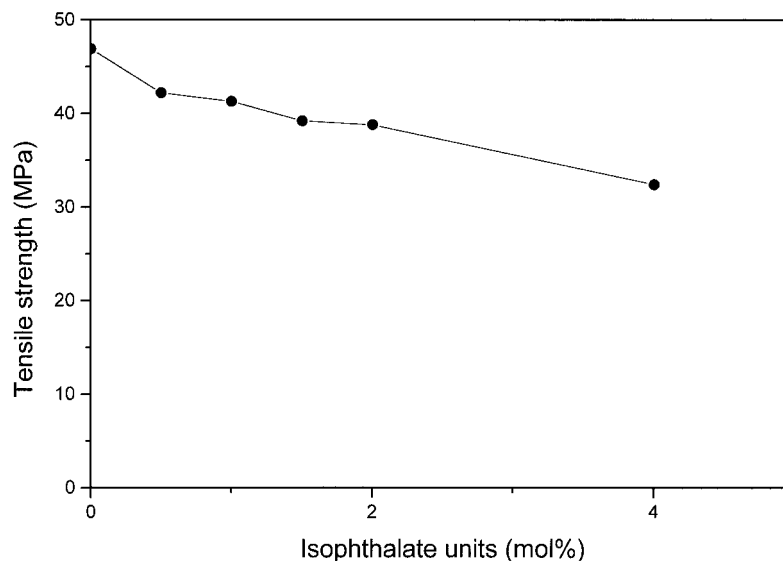
Figure 2 Tensile strength of PET and PETI copolymers.

present work. PEI homopolymer also has slightly lower tensile strength than that of PET.

An analogous reduction was observed for the Young's modulus of copolymers compared with that of PET (Fig. 3). For copolymers with up to 2 mol % isophthalate content the Young's modulus was found to decrease almost linearly with comonomer content, but no extra reduction was observed for the copolymer with 4 mol % isophthalate. Even for this copolymer, Young's modulus still remains at a relatively high level (450 MPa). Further, the tensile strength at the yield point was found to be close to a value 46 MPa for all the copolymers, ranging from 44 to 48 MPa, as can be seen in Figure 4. This means that the isophthalate content has a negligible effect on the tensile strength at yield point.

A satisfactory behavior of the copolymers was found with respect to the elongation at break. For PET homopolymer an elongation up to 600% was found, whereas for the copolymers a slight reduction was observed (Fig. 5). Thus for the copolymers with 2 and 4 mol % isophthalate, an elongation at break of up to 500% was found, which is very close to that of pure PET. These values are also in agreement with those found in our previous work, where for the copolymer with 10 mol % isophthalate the elongation at break was found to be up to 600%.[20]

Thermal analysis

Thermal parameters of the polyesters were measured using the DSC thermograms. From these results (Table
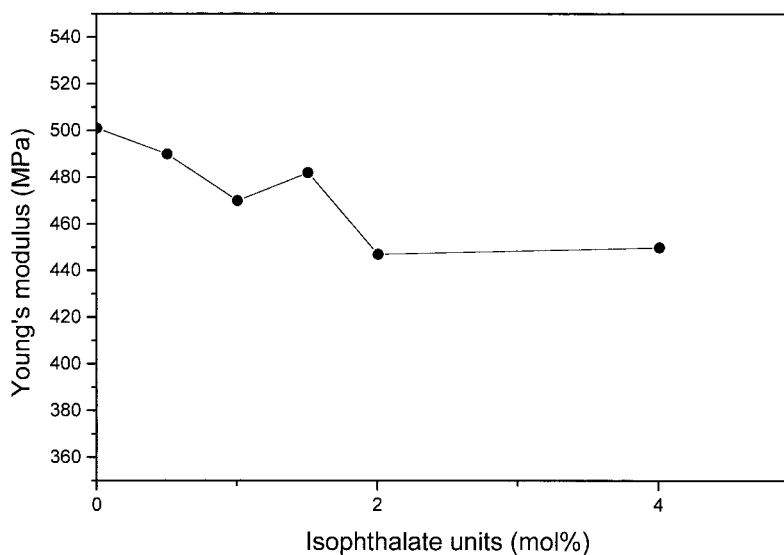

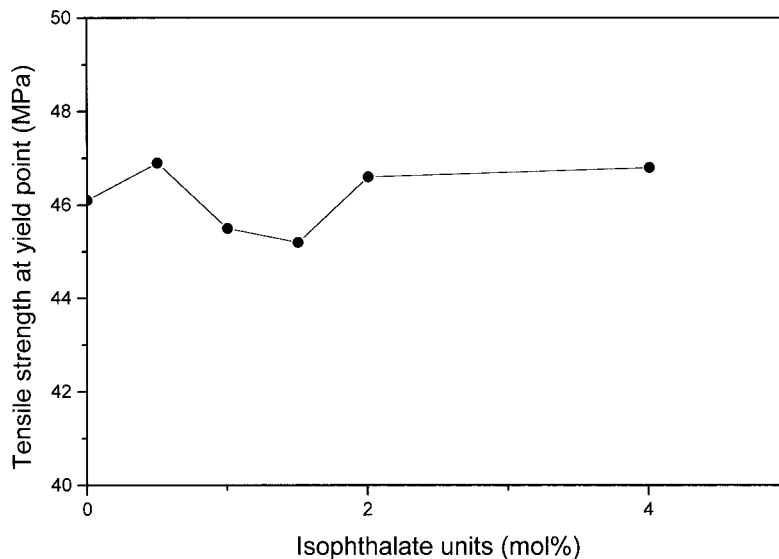**Figure 3** Young's modulus of PET and PETI copolymers.

Figure 4 Tensile strength at yield point of PET and PETI copolymers.

I) it is obvious that the glass-transition temperature (T_g) of the amorphous samples is only slightly affected by the introduction of the isophthalate units. The reduced symmetry of the *meta*-phenyl units of isophthalic acid causes internal plasticization of the material and thus the glass-transition temperature decreases. It is very important to note that the decrease of T_g is not higher than 2°C and only for copolymers containing 2 and 4 mol % isophthalic acid. For copolymers with lower content, T_g values are unaffected. This means that the produced materials can be used instead of PET in similar applications.

On the other hand, the melting points (T_m) of the copolyesters decrease at a higher rate than that of T_g, by increasing the isophthalate content of copolymers. For an isophthalate content of 4 mol %, a drop of 10°C

was observed in T_m. This decrease is attributed to the increase of the population of defects in the crystals. It is known that the introduction of the noncrystallizing comonomer units into the crystal body results in the formation of defects that increase the crystal surface energy, thus decreasing the melting point of the crystals.[23]

The decrease in the melting points for the various PETI copolymers affects their crystallization rates. For copolymers with lower melting point, the supercooling for a given crystallization temperature (T_c) is lower (supercooling is defined as $\Delta T = T_m^\infty - T_c$, where T_m^∞ is the equilibrium melting point). Thus, the driving force for crystallization is reduced, resulting in slower crystallization rates. Lower crystallization temperatures are demanded for the copolymers to obtain the same
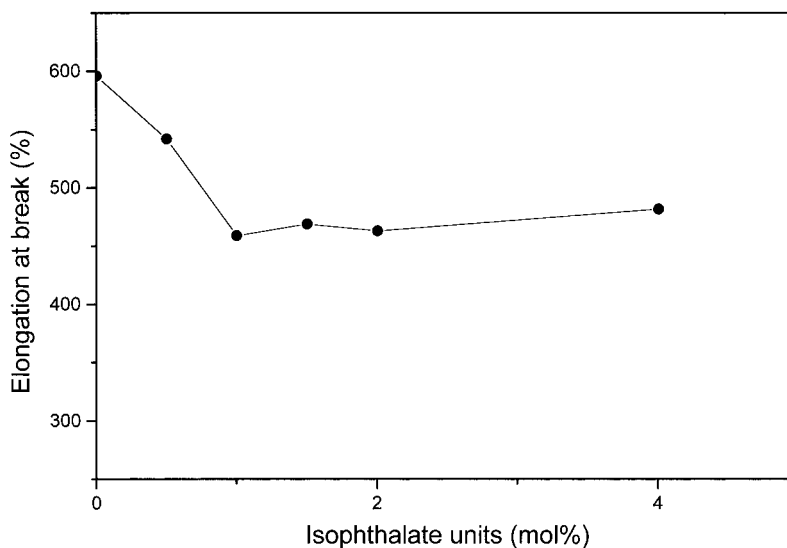

Figure 5 Elongation at break of PET and PETI copolymers.

TABLE I
Thermal Parameters of PET and PETI Copolymers

Sample	Isophthalate (mol %)	$[\eta]$ (dL/g)	T_g (°C)	T_m (°C)	T_{cc} (°C)	T_c (°C)	$T_m^{\infty a}$ (°C)
PET	0.0	0.77	83.0	250.0	150.0	194.0	291.0
PETI 1	0.5	0.77	83.0	249.0	149.5	193.0	289.0
PETI 2	1.0	0.81	83.0	246.5	150.0	192.0	286.5
PETI 3	1.5	0.77	82.5	246.5	150.5	193.6	284.0
PETI 4	2.0	0.72	81.4	246.0	150.7	194.0	282.0
PETI 5	4.0	0.76	81.5	240.5	153.9	185.0	279.0

[a] Values calculated after the empirical scheme proposed by Bicerano.[37]

supercoolings as for the homopolymer. This is proved by the increased values for cold-crystallization temperatures (T_{cc}'s) and the decreased T_c's on cooling. For cold crystallization there is a need for sufficient supercooling to achieve significant rates, although there is also a need for a significant distance from T_g, given that increased mobility of the polymer chains is demanded for adequate diffusion rates. For crystallization during cooling from the melt, significant supercoolings are demanded. Thus, the decreased T_c's found for copolymers were anticipated.

Crystallization kinetics

Crystallizations of PETI copolymers were performed at a series of crystallization temperatures, corresponding to large supercoolings. For a given supercooling, the crystallization rate is quite closely associated with two energy quantities: (1) the nucleation free energy and (2) that belonging to the transport at the liquid/crystal interface.

The weight fraction of crystalline material $x(t)$ (relative crystallinity) at time t can be calculated according to the equation

$$x(t) = \int_0^t (dH/dt)\, dt \Big/ \int_0^\infty (dH/dt)\, dt \qquad (1)$$

where the first integral is the heat generated at time t and the second is the total heat generated up to the end of the crystallization process.[24] As expected, the sample at a higher crystallization temperature requires a longer time to complete crystallization.

The study of crystallization kinetics included the following steps. First, after the Avrami treatment the relative crystallinity as a function of crystallization time is plotted. The slopes of the curves at each point are a measure of the rate of crystallization. Beyond the induction period, the rate of crystallization increases and then remains constant for a certain time, decreasing afterward to zero.

The isothermal crystallization kinetics of PETI copolymers were analyzed on the basis of the Avrami equation[25]

$$\log\{-\ln[1 - x(t)]\} = \log K + n \log t \qquad (2)$$

where $x(t)$ is the weight fraction of crystallinity, n is the Avrami exponent, K is the overall kinetic constant, and t is the time of crystallization. Both K and n depend on the mechanism of the nucleation as well as the growth geometry.

By plotting $\log\{-\ln[1 - x(t)]\}$ against $\log t$ for different T_c values, the Avrami exponent n and the overall rate constant K were obtained from the slope and the intercept, respectively. The Avrami plots for PET and PETI4 are shown in Figures 6 and 7, respectively. The n values found in this work for PET as well as for PETI4 copolymer, ranging from 2.3 to 2.7, are listed in Table II. For PET, n values from 2 to 4 have been reported. For slow crystallization at 90–160°C, $n = 2$, whereas for fast crystallization, $n = 3$; for slow crystallization at T_c values higher than 230°C, n values close to 4 were reported.[26–33]

The K values decrease rather exponentially with increasing temperature, as can be seen in Figure 8, indicating the reduction in crystallization rates with temperature. The K values decrease with isophthalate content as was also reported by other investigators.[34]

The half-times of crystallization were calculated from the equation

$$t_{1/2} = (\ln 2/K)^{1/n} \qquad (3)$$

The half-times of crystallization decrease exponentially with decreasing crystallization temperature, indicating that the rate of crystallization increases with supercooling for all polyesters. The half-times of crystallization are plotted against temperature in Figure 9. The results are similar to those reported by other investigators.[35,36]

For the copolyesters, it must be noted that the introduction of the comonomer units into the polymer chains causes a decrease in the melting point, which
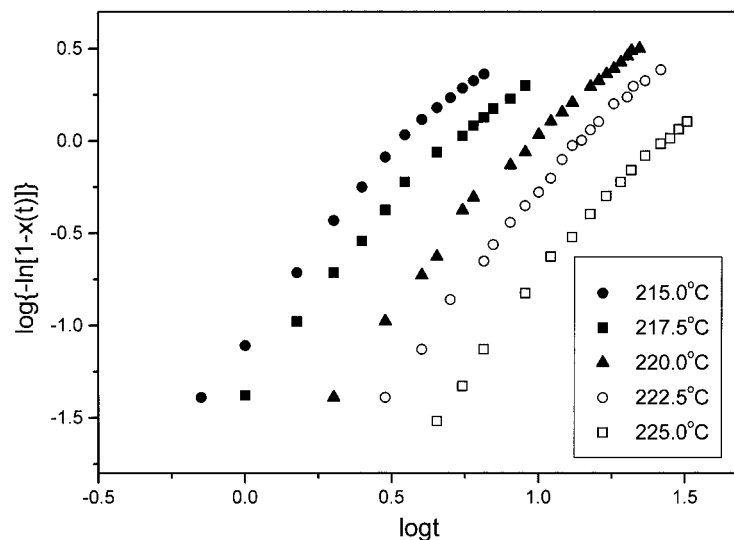
Figure 6 Avrami plots for PET.

results in a decrease of the corresponding supercooling for a given crystallization temperature. Finally, the decreased supercooling results in a decrease of the crystallization rate compared to that of the homopolymer PET. However, the introduction of the comonomer units causes a decrease in the crystallization rate because of the reduced symmetry and similarity of the chains and the appearance of noncrystallizing segments along the chains. These noncrystallizing segments are responsible for reduced crystallization growth rates, given that their deposition onto the growing surface of a crystal results in formation of pinned surfaces. Besides, the nucleation rates are also probably affected by the presence of the noncrystallizing segments along the polyester chains. Thus, it must be assumed that the reduction of the overall crystalli-

zation rates of the copolyesters is a consequence of these three factors. At high crystallization temperatures, the reduction in the nucleation rates is probably predominant. At lower T_c values the growth rates are more important, given that the melt viscosity increases and also the enhanced supercooling results in introduction of defects (comonomer units) into the crystals, almost with the same probability at which they occur in the polymer chains. Thus, the deposited noncrystallizing segments cannot support nucleation of new segments and, finally, they can cause reduction at least of the growth rates. Besides, the reduced mobility may cause an increase of the concentration of the noncrystallizing segments in the crystal/liquid surface and thus also a reduction of the growth rates because of the limited transportation of the crystallizing seg-
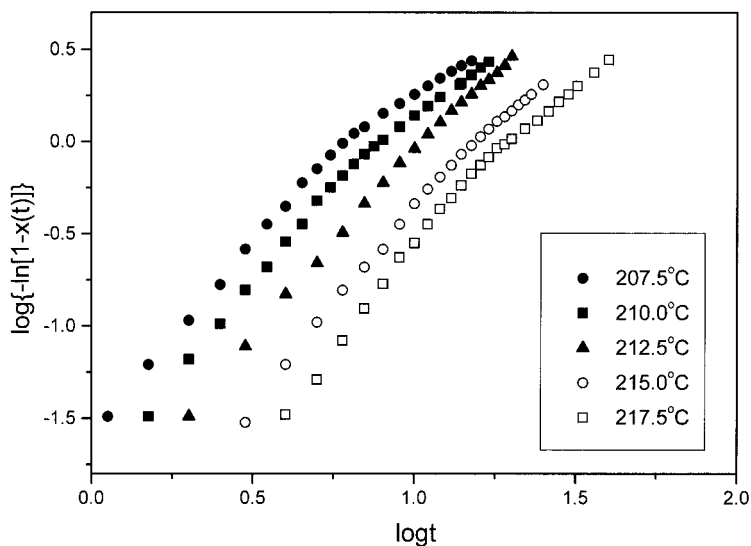

Figure 7 Avrami plots for PETI containing 4 mol % isophthalic acid.

TABLE II
Avrami Exponent (n), Growth Function (K), and Crystallization Half-Times ($t_{1/2}$) for PET and PETI Copolymers

T_c (°C)	Crystallization parameter	PET	PETI copolymer				
			0.5	1	1.5	2	4
207.5	n						2.28
	K						0.018587
	$t_{1/2}$						4.89
210.0	n						2.19
	K						0.013849
	$t_{1/2}$						5.97
212.5	n			2.33	2.18	2.20	2.39
	K			0.061907	0.056821	0.044043	0.004061
	$t_{1/2}$			2.82	3.15	3.50	8.59
215.0	n	2.31	2.48	2.44	2.56	2.26	2.42
	K	0.069983	0.021861	0.015089	0.011855	0.014954	0.001699
	$t_{1/2}$	2.75	4.03	4.80	4.90	5.46	11.99
217.5	n	2.39	2.30	2.30	2.69	2.29	2.61
	K	0.029065	0.012915	0.004588	0.003068	0.007283	0.000135
	$t_{1/2}$	3.77	5.65	7.10	7.50	8.58	26.42
220.0	n	2.46	2.37	2.72	2.31	2.49	
	K	0.005739	0.005665	0.000367	0.002009	0.001043	
	$t_{1/2}$	7.02	7.60	10.95	12.55	13.60	
222.5	n	2.53	2.62	2.72	2.66	2.63	
	K	0.001724	0.000555	0.000307	0.000279	0.000221	
	$t_{1/2}$	10.70	15.20	17.10	19.10	21.34	
225.0	n	2.71	2.58				
	K	0.000262	0.000152				
	$t_{1/2}$	18.32	26.07				

ments. In contrast at high T_c values, the increased mobility of the chain segments may be assumed to result in some kind of fractionation of segments and exclusion of the comonomer units from the crystal body.[37]

The overall crystallization rates are found to decrease with the increase of the isophthalate content, as can be seen in Figure 9, where the increase of the crystallization half-times with isophthalate content is obvious. For the estimation of supercooling $\Delta T = T_m^\infty - T_c$, the equilibrium melting points of the copolyesters should first be calculated. For simplicity and also validity, the empirical scheme proposed by Bicerano[37] was used in this work. According to Bicerano a reasonable value for the equilibrium melting point of PET is 291°C.

The slower crystallization rates for copolymers result in reduced crystallinity that may be derived from a standard cooling process. Besides, the temperature
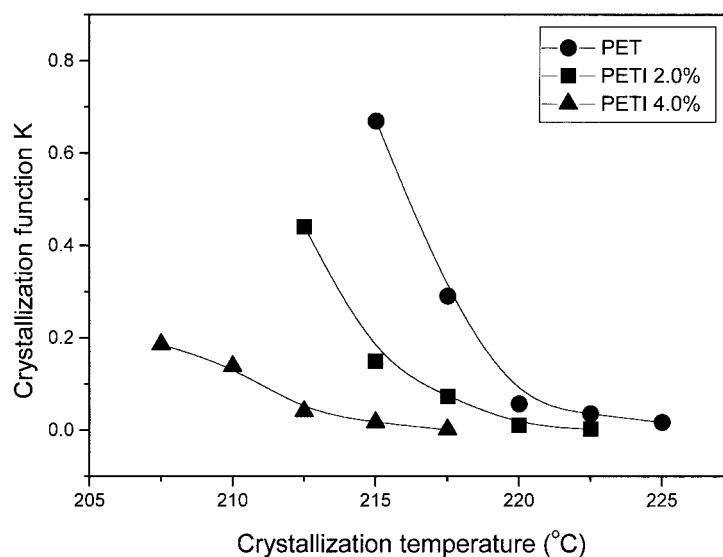

Figure 8 Plot of K values of PET and PETI copolymers (2.0 and 4.0 mol %) against crystallization temperature.
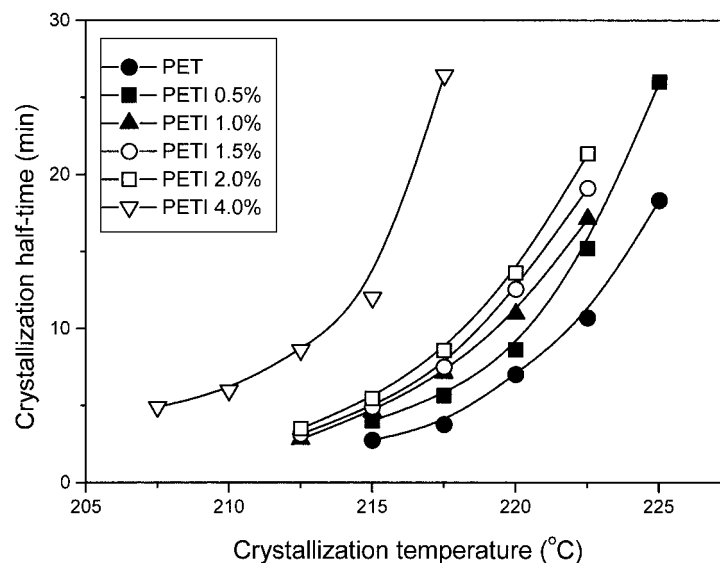
Figure 9 Plot of crystallization half-time of PET and PETI copolymers against crystallization temperature.

window for crystallization is narrower for copolymers because it is defined as the region from T_m to T_g and for the copolymers there is practically only a drop of T_m.

During blow molding for the production of soft-drink bottles, it is obvious that slow crystallization kinetics is demanded for increased clarity. It is very important that, in contrast to crystallization rates, the T_g and the mechanical properties of the copolymers are not significantly reduced with the introduction of small amounts of isophthalate units.

CONCLUSIONS

In this study it was found that the introduction of a small amount of isophthalate units in PET results in a significant decrease of the crystallization rates. The crystallization rates decrease with isophthalate content. On the other hand, it was found that mechanical properties are practically unaffected by the introduction of the isophthalate units, when the isophthalate content is up to 2 mol %. Tensile strength constitutes a critical parameter for PET applications and product formations, especially for carbonated soft-drink bottles. For an isophthalate content of 4 mol %, the decline in mechanical properties was rather significant. Thus, isophthalate content should be less than 4 mol % to achieve the best combination of properties.

The interruption of macromolecular chain regularity of PET affects the thermal properties of the copolymers, given that it causes a melting point reduction, which should be attributed to the presence of defects in copolymer crystals. The reduction in the melting point in the case of the copolymer with 4 mol % isophthalate content was about 10°C. However, only a very small reduction (of about 2°C) was found in the

glass-transition temperature of copolymers containing 2 and 4 mol % isophthalate units content, compared to the T_g of neat PET. The fact that the T_g remains practically constant is very important for high-dimension stability of the final products.

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