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Synthesis, crystallization and tensile properties of poly(ethylene terephthalate-*co*-2,6-naphthalate)s with low naphthalate units content

George P. Karayannidis*, Nickolaos Papachristos, Dimitris N. Bikiaris, George Z. Papageorgiou

Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Macedonia, Greece

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Abstract

A series of poly(ethylene terephthalate-*co*-naphthalate)s (PETN copolymers) with low naphthalate units content was synthesized. A melting point depression was observed, while the glass transition temperatures were slightly higher than that of Polyethylene terephthalate (PET). Crystallization rates of the copolymers decreased with increasing comonomer content. WAXD patterns showed that only PET crystals were formed. Co-crystallization behaviour was evaluated on the basis of the Wendling–Suter model. The tensile properties of the copolymers PETN 97/3 and PETN 94/6, Young's modulus yield stress and elongation at break was significantly improved compared to PET. WAXD showed that some crystalline precursor was generated during drawing of the specimens. DSC traces of the drawn specimens showed enhanced crystallization rates compared to that of the original amorphous specimens.

Keywords: Poly(ethylene naphthalate); Copolymer; Mechanical properties

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1. Introduction

Polyethylene terephthalate (PET) is one of the most important thermoplastic materials with wide field of applications. For many years the largest part of the produced volume was used for textile fiber production. However, the last decade much activity has been dedicated for the preparation of suitable materials for film and packing industries. 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, good barrier properties in oxygen and carbon dioxide. Also, filled with minerals or reinforced with glass fibers, PET can be used for injection mouldings in automotive and appliance industries, for electrical and electronic fittings [1]. For all the above applications a combination of various properties is demanded and also some problems in industry should be overcome.

The production of PET items such as fibers, films and bottles for food and household packaging involves many processing steps. These steps result in changes of morphological and structural characteristics. Usually, PET films and bottles are biaxially oriented. This orientation, close to the cold crystallization temperature results in a macromolecular chain alignment parallel to the draw direction. This in turn, increases the crystallinity and changes the physical properties of the end product. Shrinkage, dimension stability, stiffness, dye-ability, mechanical behaviour and gas barrier properties of the final products are related to the degree of crystallinity and the glass transition temperature of PET.

Chemical modification via copolymerization is one of the most attractive techniques in order to differentiate the properties of PET and especially the degree of crystallinity. Various glycols for partial replacement of ethylene glycol, or dicarboxylic acids instead of terephthalic acid can be used [2–19]. The combination of different monomers than that used for PET preparation may result in production of a large variety of copolymers. The technique possesses a lot of advantages compared to other methods, such as the melt blending with other polymers. In the last case in order to achieve satisfactory mechanical properties, the blend components must be compatible.

Poly(ethylene-glycol)s (PEG) with different molecular weights are added to enhance the dye receptivity of PET fibers. Thus thermoplastic poly(ether-esters) are produced [2,3]. PEG increases the chain flexibility by reducing the

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* Corresponding author. Tel: +30-2310-997814; fax: +30-2310-997769.
E-mail address: karayan@chem.auth.gr (G.P. Karayannidis).

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crystallinity of PET and its glass transition temperature. The result is an increase in the dye sorption onto fiber and also lowering in time and dyeing temperatures [4]. Low amounts of polyamides or isophthalic acid can be also used [5–7].

Copolymers with high heat resistance, better impact properties and hydrolytic stability can be produced by using cyclohexanedimethanol, for oriented and cast film production [8]. High shrinkable films can be produced from poly(ethylene terephthalate-*co*-isophthalate) (PETI) copolymers [9,10].

PET copolymers with poly(butylene terephthalate) (PBT) or poly(ethylene isophthalate) (PEI) can be used for metallic cans coating since their films offer improved adhesion on the metal plate and excellent shock resistance and barrier properties against corrosive components [11]. PET copolymers with PEI were found to have almost the double bonding energy on chromium-coated steels than pure PET, increasing the adhesion on the metal surface [12]. Similar copolymers can be used as solution adhesives in a solvent with low boiling point [13].

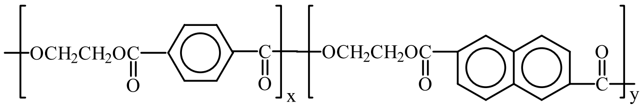
Last years, PET was widely used for construction of containers for carbonated drinks due to the excellent combination of mechanical properties, chemical resistance, low toxicity of extractants and gas barrier against carbon dioxide and mainly due to the reduced cost, comparing to the aluminum and glass containers production, 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 glass or metallic containers. Now a days, there is an increasing interest to extent the use of PET in new applications like bottles for beer or cosmetics [14]. But, the use of PET in food applications is still limited, due to the low barrier properties against oxygen and low resistance to UV irradiation, in which food exposure could reduce its quality. The most of the research attempts are focused in the preparation of multi-layer bottles comprising the main layer from PET, while the others from polyamide or PEI [5–17]. Also, poly(ethylene terephthalate-*co*-naphthalate) (PETN) copolymers or poly(ethylene terephthalate-*co*-isophthalate)s (PETI) with different amounts of naphthalene dicarboxylic or isophthalic acids can be used to increase the gas barrier properties [18,19].

PEN has a glass transition temperature of 122 °C, which is about 40 °C higher than that of PET, and a melting temperature of 267 °C against 254 °C for PET. Poly(ethylene naphthalate) (PEN) also exhibits an increased tensile strength, as well as elasticity modulus and elongation at break. Its gas barrier properties in oxygen and CO_2 are about 70–80% increased compared to PET. Finally, PEN exhibits better UV resistance. However, there are some drawbacks for the use of PEN, which limit its use in bottling. High melt viscosity of PEN results in difficulties in extrusion. Furthermore, increased solid-state polymerization times are needed for high molecular weight PEN. So, at moment, the main problem is its higher price. PEN is about three times more expensive than PET, due to the high cost of 2,6-naphthalene dicarboxylic acid [20].

Reactive blending, as well as thermal and mechanical properties of PET/PEN blends, was studied last years. Only recently some works on PETN copolymers were published [21,22].

Co-crystallization is divided into isomorphism and isodimorphism. In the first case two components of similar chemical structure, occupy approximately the same volume. Since excess free energy of co-crystallization would be very small, the chain conformation of both homopolymers is compatible with either crystal lattice. Then only one crystalline phase is detected at all compositions. In the case of isodimorphism two crystalline phases each one containing comonomer units as a minor component are observed. In this case a melting point depression is observed with increasing comonomer content. Only a few systems have been reported to exhibit co-crystallization accompanied by a clear melting temperature over the entire range of composition [23,24].

In our previous work crystallization and tensile properties of PETI copolymers with low isophthalate units content were studied [25]. In this work synthesis of a series of poly(ethylene terephthalate-*co*-naphthalate) copolymers (**I**) with low naphthalate content was performed. Tensile properties and crystallization of these copolymers were studied.



x+y=1

2. Experimental

2.1. Preparation of the copolyesters

PETN copolymers as well as pure 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 naphthalate (DMN) and ethylene glycol (EG), were of commercial grade and were used without further purification. Synthesis of PET was performed by adding 0.3 mol of dimethyl terephthalate, 0.63 mol of ethyleneglycol and 5×10^{-4} mol $Ti(Obu)_4$ in the polycondensation reactor. Dimethylester of 2,6-naphthalene dicarboxylic acid or dimethyl naphthalate (DMN) was used in amounts of 3, 6, 9, 12 and 15-wt.% on the total amount of the mixture of dimethylesters. 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).

Table 1
Transition temperatures measured from the DSC scans, enthalpies and intrinsic viscosities for PETN copolymers

EN (wt %)	T_g (°C)	T_m (°C)	T_{cc} (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)	IV (dL/g)
0	81	255	146	171	36.9	22.8	0.66
3	82	244	158	165	24.2	19.5	0.61
6	83.5	237	166	159	20.3	7.1	0.73
9	84.5	230	170	153	17.3	5.2	0.61
12	85	225	172	155	9.1	4.7	0.62
15	86.2	220	173	158	9.9	4.6	0.60

T_{cc} : cold-crystallization temperature observed during heating at 20 °C/min, T_c : crystallization temperature observed on cooling at 10 °C/min, ΔH_m : enthalpy of fusion, ΔH_c : enthalpy of crystallization measured from the cooling scan at 10 °C/min, IV: intrinsic viscosity.

Transesterification was completed after ≈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 maintained at 270 °C. The polycondensation continued for about 1.5 h. All polyester samples were ground in a mill, sieved, washed with methanol, and dried at 110 °C for 12 h. Solid-state post polycondensation under vacuum at 200 °C was applied to increase molar weight of polyesters.

2.2. Measurements

Intrinsic viscosity [η] 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 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). IV values for the copolyesters are shown in Table 1.

2.3. 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 at a temperature 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, ~0.5 mm thick; gauge length 22 mm, width 5 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 10 mm/min, recording rate (chart speed) 20 mm/min, 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%.

2.4. Thermal analysis

Thermal analysis of the copolyesters was carried out using a Perkin–Elmer, Pyris 1 differential scanning calorimeter. The calorimeter was calibrated with Indium and Zinc standards. For each measurement a sample of about 10 mg was used, sealed in an aluminum pan and heated to 300 °C at a heating rate 20 °C/min. At that temperature it was held for 5 min in order 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.

2.5. Crystallization study

Isothermal crystallizations of the copolyesters were performed at several temperatures 30–50 °C below T_m (Table 1) 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 5 min to destroy all crystal nuclei. The samples were then rapidly cooled at a rate 200 °C/min to the crystallization temperature and held 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.

2.6. WAXD study

The crystalline structure of the polyesters was investigated by wide-angle X-ray diffraction, using a SEIFERT 3003T powder diffractometer with Cu K_α radiation in the range 5–90°.

3. Results and discussion

3.1. Thermal analysis

The presence of comonomer units in copolymers is well known that it leads to melting point depression. It is assumed that the probability for introduction of comonomer units in copolymer crystals increases with comonomer

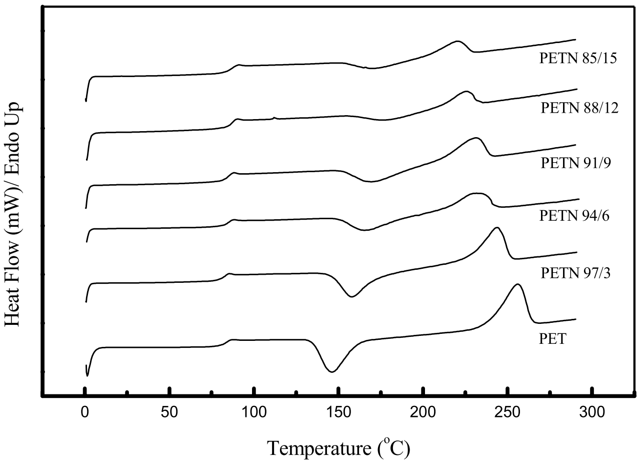


Fig. 1. DSC traces on heating for PETN copolyesters after quenching from the melt. Heating rate 20 °C/min.

content. Thus defects are formed and the excess in free energy results in lowering of the melting point. In the case of the PETN copolymers, with low ethylene–naphthalate units (EN units) content, this trend was confirmed. So, melting temperatures of the copolymers were found to decrease with increasing comonomer content as it is shown in Fig. 1. On the other hand the glass transition temperatures were found to increase with increasing EN content (Table 1).

3.2. Crystallization of the copolyesters

The copolymers are supposed to be random because of the compositions and the method by which they were synthesized.

Crystallization half-time ($t_{1/2}$) is the time needed for half of isothermal crystallization to occur. In this study it was measured directly from the plot of heat of crystallization evolved against time. As one can see in Fig. 2, the

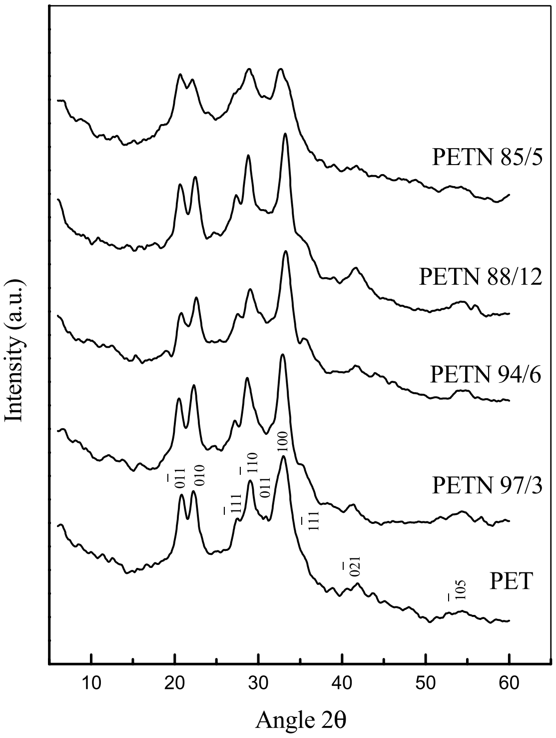


Fig. 3. WAXD patterns of the PETN copolyesters.

crystallization half-time for copolymers increase with increasing comonomer content. This means that crystallization rates of the copolymers become slower as the comonomer content increases. This of course was anticipated [26]. The temperature window for crystallization becomes narrower since melting temperature is decreased, while the glass transition temperature is slightly increased, with increasing comonomer content. The crystallization kinetics is thus strongly affected. It is well known that the driving force for crystallization is the supercooling. Consequently, for a given crystallization temperature

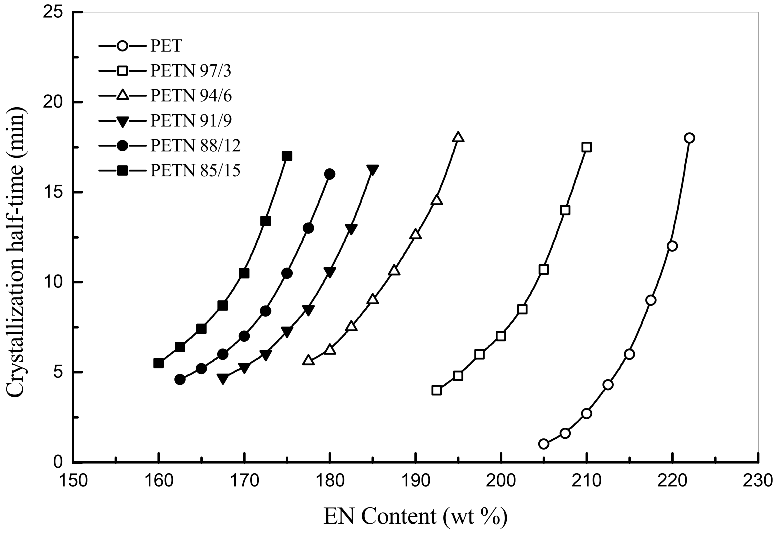


Fig. 2. Crystallization half-times of the PETN copolyesters against isothermal crystallization temperature.

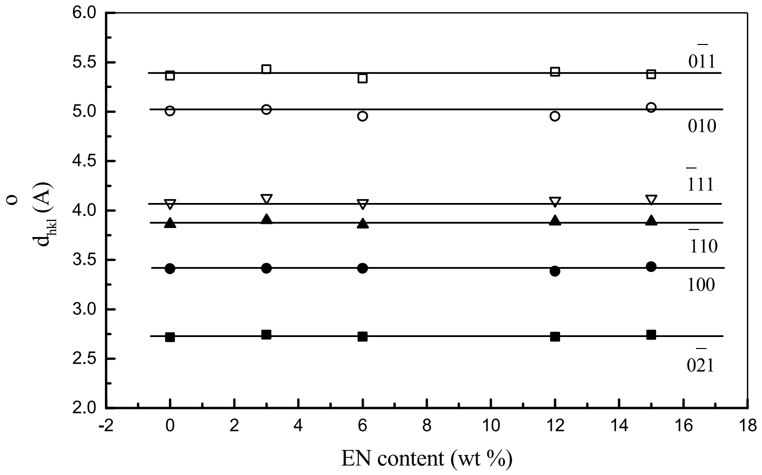


Fig. 4. Plot of interplanar spacings against copolymer composition.

supercooling decreases with comonomer content (due to melting point depression), and thus the crystallization rates of copolymers decrease. Supercooling is defined as the difference between the equilibrium melting temperature and the crystallization temperature, ($\Delta T = T_m^\circ - T_c$). It was also observed that the crystallization rates of copolymers for a given supercooling become slower as the comonomer content increases.

Lu and Windle who studied PETN copolymers with larger comonomer content, reported a eutectic behaviour [22]. They also concluded isodimorphism for PETN copolymers, since they found a transition in crystal structure parameters from those of PET crystal to those of the PEN crystal. For the PET copolymers of low EN content, as one can see in Fig. 3, only crystal reflections associated with PET crystals were observed in WAXD patterns, and there was no evidence for PEN crystal diffractions [27,28]. Thus, only PET crystals may form. However, melting point depression is an evidence for crystal defects or reduced size of crystals. The introduction of EN units into the PET chains leads to shorter sequences of ethylene–terephthalate units. Thus, thinner lamellae are anticipated to form. Besides, the introduction of EN units in PET crystals, it is expected to result in formation of crystal defects. In Fig. 4 variation in the interplanar spacings (d_{hkl}) calculated using the Bragg's equation are plotted against the copolymer composition. The d values remained almost unchanged for any of the Miller planes. This probably means that only a very limited amount of EN units is introduced in PET crystals.

The melting point depression of the PETN copolymers was analyzed, by using the equations of Flory [29–30] Baur [31], Sanchez–Eby [32] and the new model of Wendling–Suter [33,34] for co-crystallization of copolymers of A and B comonomers. The Flory and the Sanchez–Eby approaches were tested here, but the results did not fit to the experimental values.

Baur [31] treated copolymer crystals as a 'pseudo-eutectic' system, where the homopolymer sequences of length ξ may be included into crystals of lamellar thickness corresponding to that length. The melting point is calculated as follows:

$$\frac{1}{T_m^\circ} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^\circ}[\ln(1 - X_B) - \langle\xi\rangle^{-1}] \qquad (1)$$

where X_B is the concentration of the minor comonomer B units in the polymer and $\ln(1 - X_B)$ equals the collective activities of A sequences, T_m° and ΔH_m° are the homopolymer equilibrium melting temperature and heat of fusion and R is the gas constant. Also, $\langle\xi\rangle = [2X_B(1 - X_B)]^{-1}$ is the average length of homopolymer sequences in the melt.

The new model of Wendling and Suter [33,34] combines the Sanchez–Eby [32] model (comonomer inclusion model) with the Baur [31] model (a comonomer exclusion model). This model is given by:

$$\frac{1}{T_m^\circ} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^\circ} \times \left[\frac{\in X_{CB}}{RT} + (1 - X_{CB})\ln\frac{1 - X_{CB}}{1 - X_B} + X_{CB}\ln\frac{X_{CB}}{X_B} + \langle\tilde{\xi}\rangle^{-1}\right] \qquad (2)$$

where $\in$ is the excess free energy of a defect created by the incorporation of one B unit into the crystal and X_{CB} is the concentration of the B units in the crystal.

In the equilibrium comonomer inclusion, the concentration of B units in the crystal is given by:

$$X_{CB}^{eq} = \frac{X_B e^{-\in/RT}}{1 - X_B + X_B e^{-\in/RT}} \qquad (3)$$

Here, $X_B e^{-\in/RT}$ is the equilibrium fraction of repeat units B that are able to crystallize. When X_{CB} in Eq. (2) is substituted by Eq. (3), Eq. (2) is simplified to the following equilibrium inclusion model:

$$\frac{1}{T_m^\circ} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^\circ}\{\ln(1 - X_B + X_B e^{-\in/RT}) - \langle\tilde{\xi}\rangle^{-1}\} \qquad (4)$$

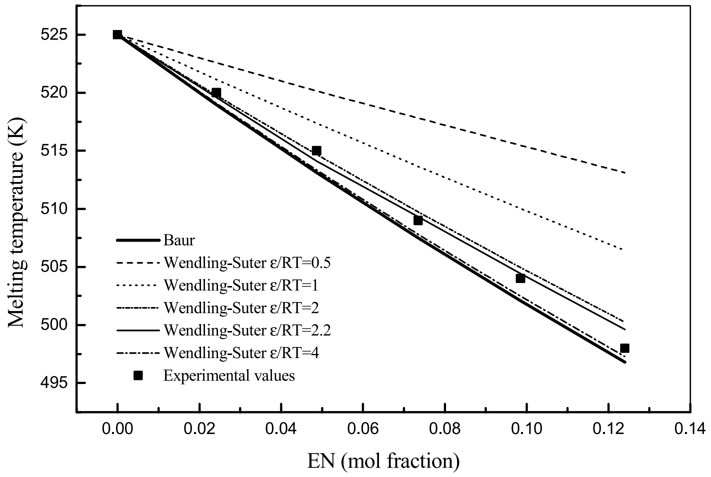


Fig. 5. Comparison of the theoretical melting temperatures of PETN copolymers, calculated using the Baur and Wendling–Suter equations, with the experimental melting points measured from DSC traces.

where

$$\langle\tilde{\xi}\rangle^{-1} = 2(X_{\rm B} - X_{\rm B}{\rm e}^{-\in/RT})(1 - X_{\rm B} + X_{\rm B}{\rm e}^{-\in/RT}) \qquad (5)$$

When $X_{\rm CB} = X_{\rm B}$ and $X_{\rm CB} = 0$ Eq. (2) reduces to the uniform inclusion model and the exclusion model, respectively.

In Fig. 5 the plots of the above theoretical estimations, in comparison with the experimental values for melting temperatures of the copolymers are shown. For the calculations the apparent melting temperatures of PET and the copolymers were used instead of the equilibrium values. The equilibrium melting enthalpy was assumed to be 26.9 kJ/mol [35]. It is obvious that the new model of Wendling and Suter fits well to the experimental data. The value of the function $\in/RT$ is determined as an adjustable parameter. The model gives the constant $\in/RT$ value regardless of the comonomer composition. When the average defect free energies were calculated from value of $\in/RT$ for PET ($X_{\rm EN} = 0$) it was found that $\in = 9.6$ kJ/mol. This rather high defect free energy is associated with a trend for comonomer exclusion, for the copolymers with low EN units content.

By use of Eq. (3) the equilibrium concentrations $X_{\rm CB}$ of comonomer units in the crystals are estimated. The plot of $X_{\rm CB}$ against $X_{\rm B}$ is shown in Fig. 6. It is revealed that the comonomer concentration in crystals increases with increasing the comonomer composition in bulk. But the comonomer concentration in crystal is significantly lower than the copolymer concentration in uniform inclusion model $X_{\rm CB} = X_{\rm B}$.

3.3. Mechanical properties

The mechanical behaviour of PET and poly(ethylene terephthalate-*co*-naphthalate) films was investigated with a tensile testing instrument. In Fig. 7 the stress–strain curves for the neat PET homopolymer, as well as for the copolymers are shown. From these curves it was concluded that the copolymers exhibit an analogous behaviour to that of PET. A yield point was obvious for all. After the yield

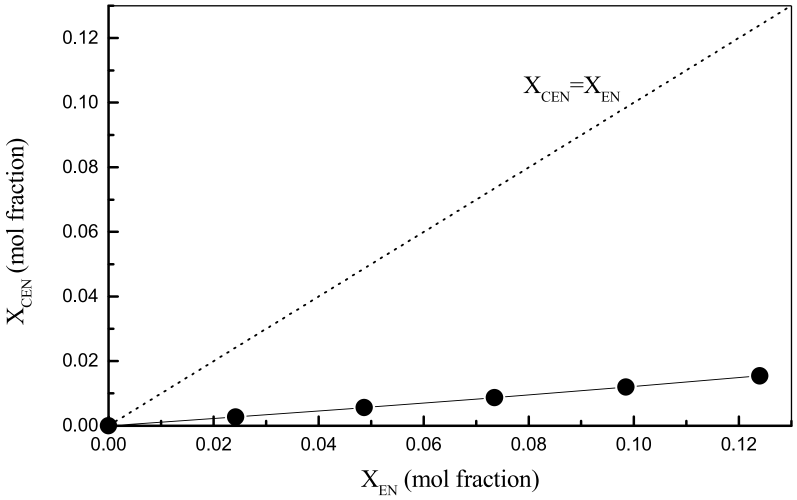


Fig. 6. Equilibrium concentrations of EN units incorporated in the PET crystal as a function of copolymer composition.

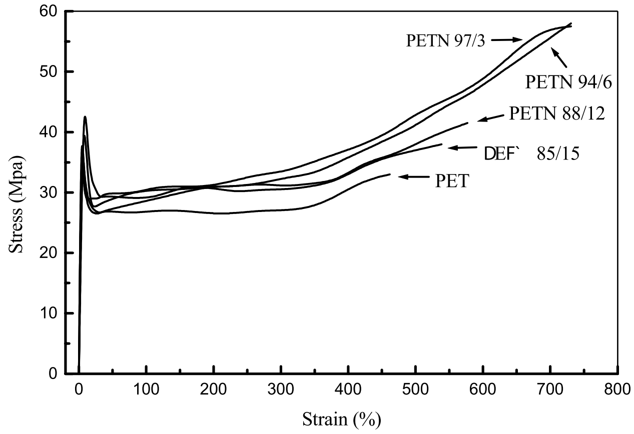


Fig. 7. Stress–strain curves for the PETN copolymers. Strain rate 10 mm/min.

point, orientation of the macromolecular chains parallel to the direction of the applied stress occurred, as the elongation ratio increased. Stress hardening was recorded after a draw ratio 3–3.5. This resulted in significant toughening of the materials, and also in an increase of the elongation of the strips at break. As one can see at Fig. 8 elongation at break increased from 470 to 730% for the PETN 97/3. For PETN 94/6 it was about 700%, but it fell to about 550% for PETN 88/12 and 85/15.

The introduction of the naphthalate comonomer did not alter the shape of the stress–strain curves, but it affected the ultimate strength of the copolymers. Tensile properties of copolymers were found to increase for low content of naphthalate units as could be seen in Fig. 9 where the variation of yield stress and stress at break with comonomer content is observed. Yield stress for PETN 97/3 and PETN 94/6 was slightly increased (about 6%). For copolymers PETN 88/12 and PETN 85/15, the yield stress was maintained at about the same levels, and no further increase was observed. The stress at break however was significantly increased for the copolymers. Especially for PETN 97/3 and PETN 94/6 the stress at break was about 80% higher than for PET. Further increase of comonomer content did not result in further increase of the stress at break. However the latter was still about 35% higher than for PET.

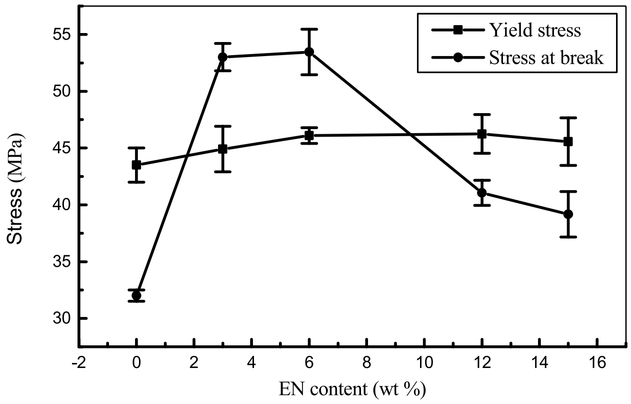


Fig. 9. Yield stress and stress at break as a function of copolymer composition.

Elasticity modulus of the copolyesters is more than 10% higher comparing to that for PET (Fig. 10). However, when naphthalate units content exceeds 12%, Young's modulus does not increase any more.

The improvement in mechanical properties of the copolyesters should be attributed to the rigidity of the naphthalene rings. As it has been referred for PEN, the presence of the naphthalene ring, which replaces the benzene ring of PET [36] results in increased stiffness of the polymer chains. This in turn leads to higher mechanical properties of PEN comparing to PET.

Findings of this work lead to the conclusion that small amounts of naphthalene units in PET chains improve the properties of PET, while at the same time cost remains at low level.

The morphology that is generated due to drawing of the initially amorphous specimens was also examined. WAXD patterns of the drawn specimens showed no crystalline reflections, but the intensity of the amorphous halo increased. Besides, it was observed from DSC traces that the drawn specimens crystallize much faster than the undrawn specimens, when they are heated above T_g.

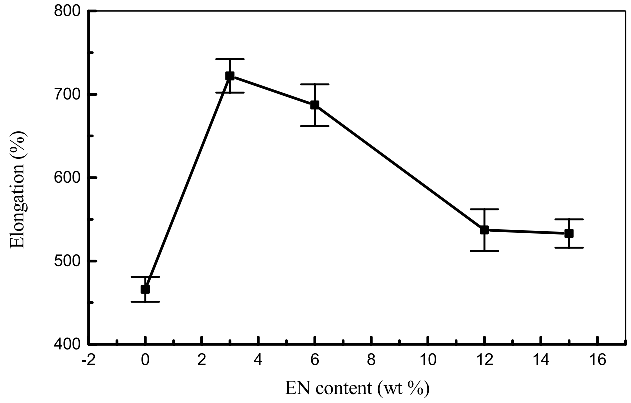


Fig. 8. Elongation at break as a function of copolymer composition for the PETN copolymers.

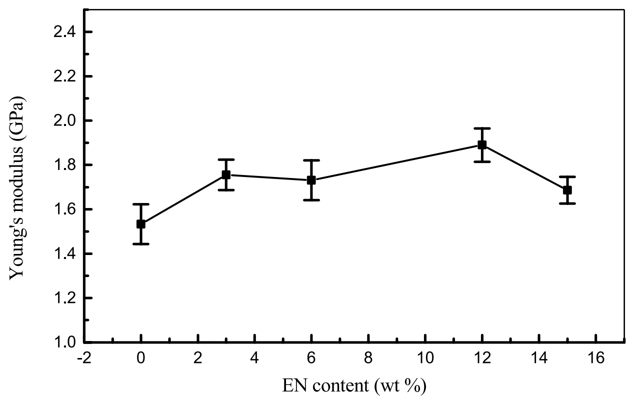


Fig. 10. Young's modulus as a function of copolymer composition for the PETN copolymers.

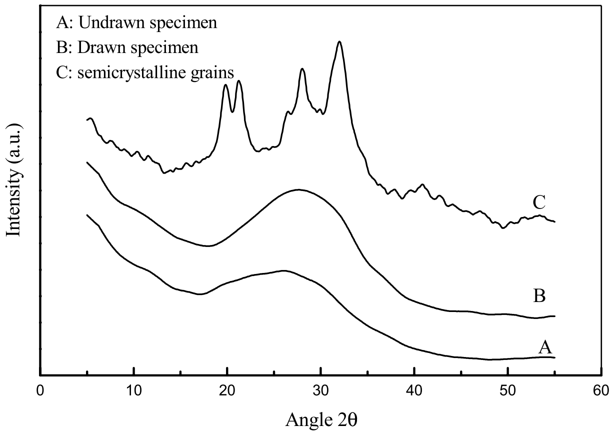


Fig. 11. Comparison of the WAXD patterns for PET. A: original specimen. B: Drawn specimen. C: semicrystalline grains.

These observations lead, to the conclusion that probably, some crystalline precursors were formed and also the rigid amorphous phase fraction may be increased [37–39]. Crystallization is not anticipated at a temperature lower than T_g (Fig. 11).

4. Conclusions

In this work a series or poly(ethylene terephthalate-*co*-naphthalate)s with low naphthalate content were synthesized. It was anticipated such copolymers to offer advantages in applications where PET is traditionally used. Their crystallization rates were found to be slower comparing to PET and thus transparency of films can be achieved. They also exhibit a melting point depresssion with increasing naphthalate content. WAXD studies showed that only PET crystals are formed. The mechanical properties were found to increase in contrast to what was observed for poly(ethylene terephthalate-*co*-isophthalate)s with low isophthalate units content. In general properties of PET can be improved with the use of small amounts of naphthalate, with no significant increase of cost.

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