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Microhardness of PET-based liquid crystalline copolyesters: influence of the microstructure

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Abstract

The Vickers microhardness of PET-based liquid crystalline copolyesters has been investigated. The copolyesters have been synthesized by transesterification of PET with equimolar amounts of sebacic acid (S) and hydroquinone (Q) (or 4,4′-dihyroxybiphenyl (B)) and with varying amounts of 4-hydroxybenzoic acid (H). The variation of the Vickers microhardness of PET-S-Q-H and PET-S-B-H liquid crystalline polyesters with the composition have been interpreted by the microstructure of the materials. The increase in the concentration of 4-hydroxybenzoic acid (H) in both types of copolyesters leads to an increase in intermolecular distance and to enlargement of the domain size. This, on its, turn, leads to a decrease in the materials' microhardness. The effect that the mixing time of the reactive blends of equimolar amounts of PET and poly(phenylene sebacate) (PQS) PET/PQS has upon the microhardness values has been also studied. The variation of the microhardness of PET/PQS blends prepared for different mixing times follows the same tendency as that of the melting enthalpy (i.e. the degree of crystallinity). Both parameters have lower values with the longer mixing time. The decreased crystallinity during the transreaction results into materials having higher creep rate under load.

Keywords: PET-based liquid crystalline copolyesters; PET/poly(phenylene sebacate) reactive blends; Microhardness

1. Introduction

Thermotropic liquid crystalline polymers (LCP) are one of the most interesting classes of polymeric materials. The LCP based on poly(ethylene terephthalate) (PET) are considered to be the cheapest and the easiest to process as they require relatively low temperatures. Preparation of different LCPs through the transesterification of PET with selected monomers, such as 4-hydroxybenzoic acid (H), terephthalic acid (T), hydroquinone (Q), 4,4′-dihyroxybiphenyl (B), etc. was performed [1–8]. Our previous articles [7,8] report on PET-based liquid crystalline copolyesters synthesized by transesterification of PET with equimolar amounts of sebacic acid (S) and Q (or B) and with varying amounts of H. The structure, morphology and thermal properties of the PET-S-Q-H copolyesters have been compared with those of PET-S-B-H copolyesters whose components are at the same molar ratio. It has been demonstrated that segregation of the aromatic-rich liquid crystalline phase and the subsequent compositional differentiation of the two phases of the system are more pronounced in PET-S-B-H copolyesters. The latter possess aromaticity higher than that of PET-S-Q-H polymers of similar molar composition. It should be noted too, that liquid crystalline copolyesters prepared by reactive blending of equimolar amounts of PET and poly(phenylene sebacate) (PQS) [9] at temperatures higher than the melting points of the two polymers, contain a segregated phase rich in aromatic units.

It is well known that microhardness is directly related to the microstructural changes in semicrystalline and amorphous polymers [10–12]. On the other hand, hardness is connected to the macroscopic mechanical properties of the materials [10–13]. In the case of polymer blends microhardness is a helpful tool for the assessment of the degree of interpenetration of the blend components [12,14]. Morphological changes during the transreaction in condensation polymers have been detected by microhardness technique [15]. Concerning the microhardness of LCPs it should be noted that the literature data are scarce. In the case of random liquid crystalline copolyesters containing flexible

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spacers [16,17] the dependence between microhardness and crystallinity, crystal thickness and polymorphic crystal forms has been highlighted. The increase in microhardness of amorphous materials with the increasing number of flexible chain sequences has been discussed in terms of a additive behaviour of single components. While that of the crystallized materials has been shown to be an increasing function of the crystallite dimensions (flexible chain domains). The influence of composition and temperature on the microstructure of rigid liquid crystalline copolyesters has been studied by microhardness too [8].

In the present work the microhardness of PET-S-Q-H and PET-S-B-H liquid crystalline copolyesters having similar molar composition was investigated. The aim was to estimate the influence of the polymer composition and the microstructure upon the microhardness values. The effect that the mixing time of the reactive blends PET/PQS has upon microhardness values was also studied.

Table 1
Composition of the samples and degree of aromaticity

Sample	Composition (mol%)			Degree of aromaticity (%)
	PET	PQS	H	
PET-/SQ/-H 1	50	50	–	30.8
PET-/SQ/-H 2	43	43	14	33.3
PET-/SQ/-H 3	33	33	33	37.5
PET-/SQ/-H 4	25	25	50	42.1
PET-/SB/-H 1	50	50	–	40.0
PET-/SB/-H 2	43	43	14	41.6
PET-/SB/-H 3	33	33	33	44.4
PET-/SB/-H 4	25	25	50	47.6
PET	100	–	–	–
PQS	–	100	–	–
PET/PQS 15 min	50	50	–	30.8
PET/PQS 30 min	50	50	–	30.8
PET/PQS 60 min	50	50	–	30.8
PET/PQS 120 min	50	50	–	30.8
PET/PQS 180 min	50	50	–	30.8

2. Experimental part

2.1. Materials

A commercial grade of poly(ethylene terephthalate) (PET) kindly provided by Shell, was used for the preparation of the reactive blends and for the copolyester synthesis. The sample had an intrinsic viscosity of 0.63 dl/g, in a 60/40 (w/w) phenol/tetrachlorethane mixture, at 25 °C. Sebacic acid (S), hydroquinone (Q) and 4,4′-dihydroxybiphenyl (B) were supplied by Merck; 4-hydroxybenzoic acid (H) was supplied by Aldrich.

The copolyesters PET-S-Q and PET-S-Q-H were prepared by reacting PET with the monomers in a Pyrex round-bottomed reactor equipped with a stainless steel stirrer and attached to a vacuum line. The reaction was carried out at 290 °C for 3–4 h, following the procedure described elsewhere [7].

The copolyesters PET-S-B and PET-S-B-H were prepared by a reaction of PET with the monomers, following the above procedure. The synthesis is described in detail elsewhere [8]. The composition of the copolyesters has been chosen to be equal to that of the products prepared from PET, S,Q and H [8].

The polyester poly(phenylene sebacate) (PQS) was prepared by melt polycondensation of sebacic acid (S) and hydroquinone (Q), in the 1:1 mole ratio, as described elsewhere [9]. The reactive blends of PET and PQS, in the 1:1 mole ratio were prepared in a Brabender Plastograph mixing bowl under nitrogen atmosphere, at 270 °C and 100 rpm, in the presence of a catalyst. The procedure has been described in details in Ref. [9]. Several blends were prepared with mixing times of 15, 30, 60, 120 and 180 min.

The composition of the copolyesters PET-S-Q, PET-S-Q-H, PET-S-B and PET-S-B-H and of the reactive blends PET/PQS has been summurized in Table 1. The values of the degree of aromaticity are included too [7–9]. The degree of aromaticity is commonly used to qualitatively measure the stiffness of the LCP macromolecules. It is calculated as the percent ratio of the number of aromatic carbons to the total number of atoms in the backbone [7–9]. All materials were characterized by differential scanning calorimetry, WAXS, optical and electron microscopy [7–9].

2.2. Microhardness measurements

The specimens used for the measurement of microhardness were cylindrical tablets with diagonal 8 mm and height 1 mm, prepared by hot pressing of the materials at ca. 260 °C. For each sample one tablet was rapidly quenched on a metal block, and one tablet was cooled down to room temperature.

Microhardness of the blends was measured on a standard Vickers microhardness tester mhp-160 for light microscope NU-2 (Germany). The indentor was a square shaped diamond pyramid, with top angle of 136°. Loads of 0.4, 0.8, 1.0, and 1.2 N to correct for instant elastic recovery were employed. A loading cycle of 0.1 min was used. The standard Vickers microhardness (H) was determined by the equation [12,19]:

$$H = kP/d^2$$

where P, the applied load, k, a geometric factor equal to 1.854 and d, the mean diagonal length of the imprint after removing the indenter.

At least 10 imprints were made under each load. The H value was determined within $\Delta H/H = 0.05$. Under the loads applied the mean diagonal length of the imprints varies in the range 100–200 μm.

For the determination of the creep constant experiments using different loading times under the indenter were performed.

2.3. Wide angle X-ray diffraction measurements

Wide angle X-ray diffraction patterns of the PET-S-Q-H and PET-S-B-H copolyesters were recorded with a Philips APD diffractometer using a Ni filtered Cu Kα radiation. The values of the size of coherently diffracting domain, D, were obtained from X-ray line broadening data using Sherrer's formula $D = \lambda/\beta_0 \cos\theta$, where λ, the wavelength of the radiation used, β_0, the integral breadth of the scattering reflection in radians, and θ, the Bragg angle [16,18]. The derivation of the spacing d denoting the intermolecular distance was obtained from the X-ray scattering maximum of the reflection.

2.4. DSC measurements

DSC measurements of PET, PQS and of the reactive blends PET/PQS were performed using DSC-7 Perkin Elmer apparatus, in nitrogen atmosphere with heating/cooling rate 10 °C/min.

3. Results and discussion

3.1. Microhardness–microstructure relation of PET-S-Q-H and PET-S-B-H liquid crystalline polymers

The data for the Vickers microhardness of the quenched and cooled copolyesters are listed in Table 2. The values of the size of the coherently diffracting domains (D) and the values for the cross-sectional area of the molecules (d^2), both types of values determined from X-ray patterns of the samples are included in Table 2 as well. It should be noted that the microhardness values of the quenched and slow cooled tablets do not differ substantially. Evidently, this is due to the liquid crystalline order in the copolyesters, which almost does not change during the different preparation procedures of the tablets. This suggestion has been confirmed by the X-ray patterns of the samples, which are very similar for the quenched and slow cooled tablets [18]. Wide angle X-ray diffraction patterns of the copolyesters, taken at room temperature show the existence of one main reflection at $2\theta \approx 20°$, which is due to the lateral packing of copolyester chains having longitudinal disorder and it is typical for polymers with liquid-crystalline properties. It should be mentioned that the microhardness values obtained are much lower than the microhardness values reported for other LCPs [16,18]. In the latter [16,18] microcrystals coexist with the liquid crystalline domains, leading to higher microhardness values. On the other hand, the microhardness values for the PET-S-Q-H and PET-S-B-H copolyesters are in perfect agreement with the value obtained for the semiflexible LCP S-B-H [20].

Table 2
Microhardness of quenched ($H_{quenched}$) and slow cooled (H_{cooled}) tablets and the cross-sectional area (d^2) and domain size (D) of the slow cooled polyesters

Sample	$H_{quenched}$ (MPa)	H_{cooled} (MPa)	d^2 (Å^2)	D (Å)
PET-/SQ/-H 1	28	32	17.57	46
PET-/SQ/-H 2	23	26	17.90	77
PET-/SQ/-H 3	15	20	18.85	108
PET-/SQ/-H 4	16	18	19.71	108
PET-/SB/-H 1	27	30	18.59	70
PET-/SB/-H 2	22	23	18.59	104
PET-/SB/-H 3	15	17	19.33	135
PET-/SB/-H 4	16	16	19.52	141

The dependence of microhardness on the sample composition is shown in Fig. 1. The microhardness descreases with increasing the content of 4-hydroxybenzoic acid for both types of the copolyesters in an almost similar way. The substitution of Q with B does not affect significantly the hardness values. These results show that the degree of aromaticity of the samples does not influence the microhardness values. For that reason two other main parameters must be taken into account: molecular packing and domain size [16,18]. The packing of polymer chains and, respectively, changes in cohesive energy of the crystals has been shown to play a role in determining the hardness value. Hence, the closer molecular packing of crystalline polymers leads to an increase in microhardness [21,22].

The molecular packing could be described in terms of molecular cross-sectional area. The liquid crystalline phase in the copolyesters studied consist chiefly of rigid rod molecules with cylindrical symmetry along their chain axes.

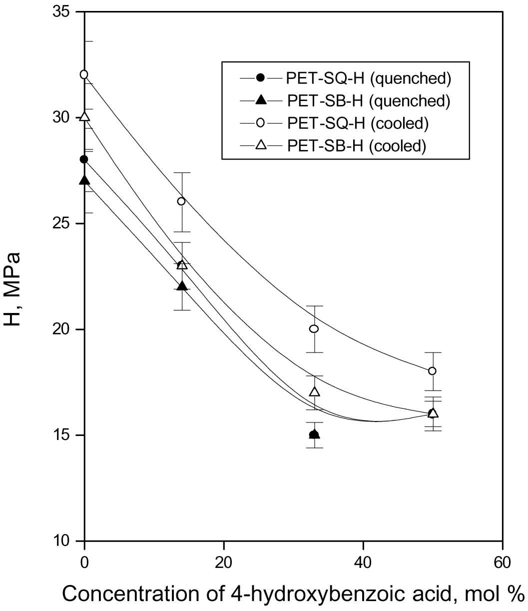

Fig. 1. Dependence of microhardness on the content of 4-hdroxybenzeoic acid (H) for both types of the copolyesters (PET-S-Q-H and PET-S-B-H).

Therefore, the cross-sectional area of molecules could be considered approximately equal to $\pi(d/2)^2$; i.e. proportional to the squared intermolecular distance d^2. Fig. 2 shows the variation of microhardness with d^2 in the liquid crystalline polyesters. It can be immediately observed that the decrease in the cross-sectional area of the molecules, i.e. the closer molecular packing, leads to an increase in the microhardness. These results are in agreement with those in Ref. [18].

Concerning the dependence of the microhardness on the size of liquid crystalline domains, *D*, Fig. 3 shows clearly that the microhardness decreases with *D* increasing.

The results obtained show that the microhardness of PET-S-Q-H and PET-S-B-H copolyesters decreases with increasing the content of 4-hydroxybenzoic acid in the samples. This is due to an increasing size *D* of the liquid crystalline domains, as well as to the larger intermolecular distance, *d*.

3.2. Microhardness–microstructure interdependence for 1:1 mol:mol blends PET-PQS, prepared for different mixing time

In Table 3 the values of the microhardness of the slow cooled tablets are collected together with the enthalpy of fusion of the components. The phase transition of the blends was studied by DSC and the second heating scan was considered for the determination of the enthalpy of fusion. The increase in the mixing time leads to a continuous decrease in the melting enthalpy of the two crystalline components PET and PQS [9]. That means the crystalline phase of both components decreases during the transreaction between them, which at sufficient time (180 min) leads to a random copolyester exhibiting liquid crystalline properties [9]. Fig. 4 shows the variation of microhardness and of fusion enthalpy for both components on mixing time.

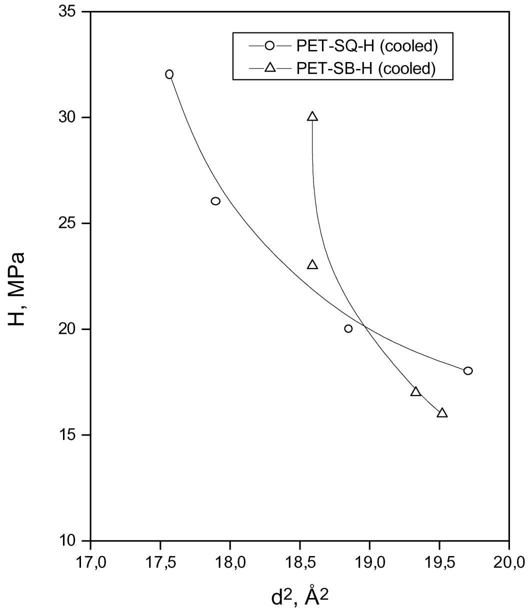

Fig. 2. Microhardness versus the squared intermolecular distance d^2 in the liquid crystalline polyesters.

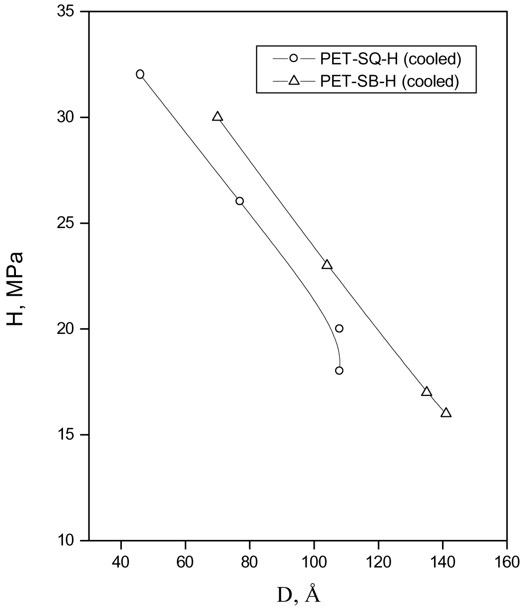

Fig. 3. Dependence of the microhardness on the size of liquid crystalline domains, *D*, for both types of the copolyesters (PET-S-Q-H and PET-S-B-H).

The *H* value of PET can be interpreted by the formula [23]:

$$H = \alpha H_c + (l - \alpha)H_a$$

where H_c and H_a are the microhardness of the crystalline and amorphous phase, respectively; and α, the degree of crystallinity.

The degree of crystallinity, calculated by the enthalpy of fusion is 0.235, the values for H_c and H_a taken from Ref. [23] are, respectively, $H_c = 360$ MPa, $H_a = 75$ MPa; so the calculated value for *H* is 142 MPa. The experimental obtained value $H = 144$ MPa is in perfect agreement with the theoretical one. That means the microhardness of PET is determined mainly by its degree of crystallinity. PQS is a crystalline polymer too [9], and its *H* values are also

Table 3
Microhardness of slow cooled tablets and the enthalpy of melting of the two components of the reactive blends

Sample	ΔH_m (J/g)		H_{cooled} (MPa)
	H_m (PQS)	H_m (PET)	
PET	–	33.0 (0.23)	144
PQS	75.4	–	107
PET/PQS 15 min	26.0	33.2	116
PET/PQS 30 min	17.5	20.7	88
PET/PQS 60 min	12.6	12.6	47
PET/PQS 120 min	No peak	No peak	36
PET/PQS 180 min	No peak	No peak	35

The value in the brackets is the degree of crystallinity, calculated from the measured enthalpy of melting. The value of 140 J/g has been taken as the enthalpy of melting of 100% crystalline PET.

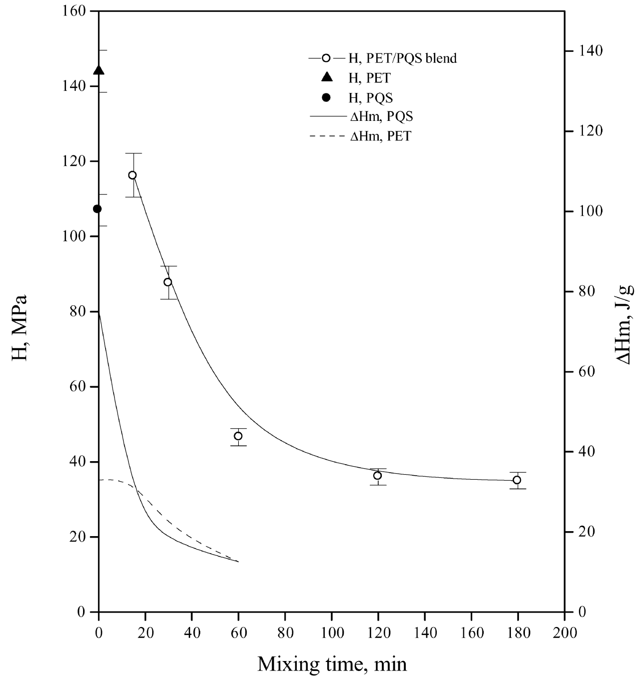

Fig. 4. Dependence of microhardness and of fusion enthalpy for both components of the reactive blends PET/PQS 1:1 (mol:mol) on mixing time.

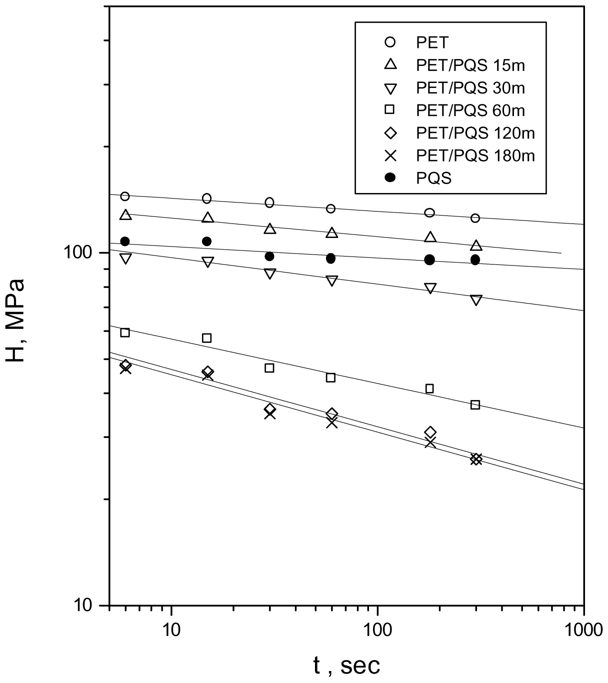

Fig. 5. Microhardness variation as a function of the loading time for the reactive blends PET/PQS, prepared at different mixing times.

determined by H_c, H_a, and α. However, we could not find literature data about this material. The H value for the reactive blend PET/PQS 1:1 (15 min) is slightly lower than the theoretical value, calculated from the additivity law and taking into account the PET degree of crystallinity:

$$H^{\mathrm{blend}} = H^{\mathrm{PET}} w^{\mathrm{PET}} + H^{\mathrm{PQS}} w^{\mathrm{PQS}}$$

$$= (\alpha H_c + (1-\alpha)H_a)0.5 + H^{\mathrm{PQS}} \times 0.5$$

where H^{PET} and H^{PQS} are experimental data and w^{PET} and w^{PQS} are the corresponding weight parts.

With mixing time increasing the H values of the blend drastically decrease and became much lower than the additive value. The variation of the microhardness (Fig. 4) follows dependence quite similar to that of the decreasing fusion enthalpy. In the reactive blend prepared at 180 min none of the DSC melting peaks can be detected. For this sample microhardness reaches the lowest values, which, however, is in agreement with the H value obtained for the liquid crystalline polymer PET-S-Q-H1 with the same composition (Tables 2 and 3).

In order to determine the rate of creep under load for the reactive blends, the microhardness was measured using different loading intervals under load. Fig. 5 shows the microhardness variation for the various samples as a function of the loading time. This function follows equation of the type [18]:

$$H = H_0 t^{-k}$$

where H_0, the hardness value at a reference time (0.25 min), and the slope k of the straight line provides a quantitative measure for creep rate under load. Fig. 6 shows the variation of the creep constant k as a function of mixing time.

The creep constant should decrease when the crystallinity of the sample increases [18]. In fact the creep constant increases continuously with the increasing mixing time, i.e. with the decreasing crystallinity of the samples. The lowest k values have been obtained for the homopolymers PET and

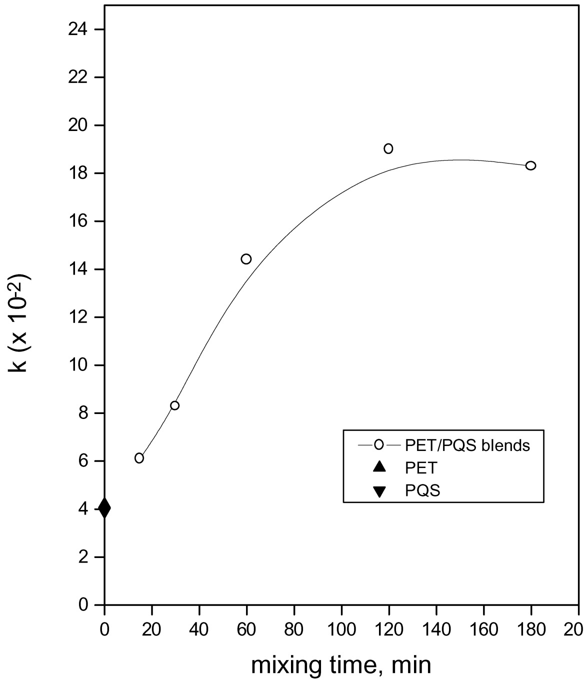

Fig. 6. Variation of the creep constant k as a function of mixing time for the reactive blends PET/PQS.

PQS. The liquid crystalline random copolyester, obtained at mixing times of 120 and 180 min shows the highest *k* value.

4. Conclusion

The variation of the Vickers microhardness of PET-S-Q-H and PET-S-B-H liquid crystalline polyesters with the composition have been interpreted by their microstructure. The increase in the concentration of 4-hydroxybenzoic acid (H) in both types of copolyesters leads to an increase in intermolecular distance, i.e. to wider molecular packing and greater domain size. This, on its turn, leads to a decrease in the materials' microhardness. The results show that the microhardness does not depend on the substitution of Q with B in the copolyesters.

The variation of the microhardness of PET/PQS blends prepared for different mixing times follows the same tendency as that of the melting enthalpy (i.e. the degree of crystallinity), which decreases with the longer mixing time. The decreased crystallinity during the transreaction results into materials having higher creep rate under load.

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