Microhardness of condensation polymers and copolymers.
2. Poly(ester ether carbonate) thermoplastic terpolymers

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Abstract

The number of phases, transition temperatures and microhardness of a series of poly(ester ether carbonate) multiblock terpolymers with poly(buthylene terephthalate) (PBT) hard segments have been investigated as a function of ether/carbonate (EC) soft segments composition at constant PBT-content. The polymerization degree of PBT and the intrinsic viscosity of the terpolymers was determined by viscosimetry. The degree of crystallinity, long spacing, glass transitions (T_g) and melting temperature were derived by means of X-ray diffraction, DMTA and DSC measurements. Surface mechanical properties were studied by microindentation tests. It is found that the terpolymer consists of two amorphous (EC and PBT) and one crystalline (PBT) phase. The T_g value of PBT does not depend on the chemical composition of the soft segments in contrast to the T_g of the soft segment amorphous phase. Introduction of polycarbonate moities in the soft segments induces an increase of T_g by 50°C without formation of an additional (third) amorphous phase. By this decrease of flexibility of the soft segments it is explained the reduced crystallizability of PBT hard segments (by a factor 3) which causes also a two-fold reduction in the microhardness-values. It is shown the dominating contribution of crystallinity to the microhardness. However, the much lower measured overall microhardness in contrast to the calculated one by means of the additive law is explained by the plasticizing effect of the soft amorphous phase. This assumption is in agreement with the structure model derived from the SAXS and WAXS data.

Introduction

Thermoplastic elastomers are a special type of block copolymers exhibiting an unusual combination of properties: they are elastic, and at the same time tough and they show, low-temperature flexibility, and strength at relatively high temperatures (frequently ca. 150°C) [1,2]. In addition they are easily processable. For this reason, they are nowadays of great commercial importance as engineering materials. In natural rubber and synthetic elastomers, the polymer chains are chemically linked into a three-dimensional network and they are not processable. In thermoplastic elastomers, however, the chemical crosslinks are replaced by thermally labile tie points held together by physical forces: glassy, crystalline, or even hydrogen-bonded segments or ionic associations. In any case, they confer to the material a processability not found in the usual types of elastomers [1,2].

For a copolymer to behave as a thermoplastic elastomer the chains must contain two types of chain sequences: (i) amorphous, rubbery blocks (with T_g below room temperature) referred to as a “soft” segments, and (ii) hard blocks, typically with a T_g value above room temperature and/or extensive crystallinity. The soft segments impart elastomeric character to the copolymer and are bracketed by the “hard blocks” [1,2]. The hard segments can form intermolecular association resulting in a solid phase within a desired temperature range, thus imparting dimension stability to the material. At elevated temperatures, dissociation of the physical bonds occurs, giving rise to processability. In order to meet the continuously increasing demands of thermoplastic elastomers with new or modified properties, copolymers with increasingly complex chemical composition are synthesized. For instance typically representative thermoplastic elastomers, are the poly(ester ether)s based on poly(butylene terephthalate) (PBT) and poly(tetramethylene glycol) (PO4), the PBT sequences forming the hard segments, and the PO4 sequences the soft ones. The latter are chemically modified by introducing polycarbonate moieties in the soft segments.

The thermoplastic elastomers involved in the present investigation are a series of new poly(ester ether carbonate) (PEEC) multiblock terpolymers with varying amount of ether and carbonate soft segment content. Dielectric relaxation experiments of the same poly(ether ester carbonate) revealed the existence of two relaxation processes [3].

The γ -process, appearing at low temperatures, which is due to local mode motions of the polar groups (ether and carbonate from soft segments and ester from PBT segments) in the amorphous phase. For low polycarbonate concentrations the γ -process is mainly governed by the ether groups of PO4 segments. As the amount of PC soft segments increases, a shift of the transition temperature at fixed frequencies is observed and higher activations energies are measured. The dependence of T_g on polycarbonate concentration suggests the existence of good mixing between polycarbonate and PO4 soft segments in the amorphous phase [3].

The microhardness technique has been applied to copolymers for characterization of their micromechanical behaviour [4-6]. The microhardness-structure correlation of glassy random copolymers of PET and poly(ethylene naphthalene-2,6-dicarboxylate (PEN) has been shown to be strongly affected by the composition and by the crystallization conditions of the single components [4]. The microhardness (H) of coreactive blends of PET and bisphenol-A polycarbonate was also investigated over the whole range of compositions and found that the parallel decrease of H and of T_g with increasing PET content in the blends is due to the formation of new copolymer molecules enriched in the component characterized by lower H- and T_g -values [6].

Finally, the microhardness of films of thermoplastic elastomers based on PBT-cycloaliphatic carbonate (PBT-PCc) block copolymers was also studied [7]. The microhardness of the amorphous films was discussed in terms of a model given by the additivity values of the single components H_a^{PBT} and H_a^{PCc} . It was further shown that the deviation of hardness from the additivity law, for the semicrystalline copolymers, is mainly due to the depression of the crystal hardness values of the PBT crystals and partly due to a decrease in crystallinity of the PBT phase [7].

The aim of the present study is to follow the effect of chemical composition, i.e. the introduction of PC moities within the soft segments at cost of polyether while keeping the PBT hard segments content constant, over the number of phases, and to examine their transitions and mechanical properties by means of a joint study of differential scanning calorimetry (DSC) dynamical mechanical thermal analysis (DMTA), X-ray scattering (WAXS and SAXS) and microhardness measurements.

Experimental

Synthesis of the terpolymers

The scheme below shows the general formula representing the poly(ester ether carbonate) terpolymers. For the synthesis of the terpolymers a three-stage polycondensation method, similar to that used in the preparation of poly(ester carbonate) copolymers [8], was used:

- a) Dimethylterephthalate and 1,4-butanediol were first heated in the temperature range of 150–200°C, in the presence of tetrabutoxy-titanate as first catalyst, until more than 90% of the stoichiometric amount of methanol was evaporated.
- b) The temperature was then increased up to 200°C under reduced pressure. Under these conditions oligomers of butylene terephthalate (PBT) were obtained.
- c) Different amounts of α, ω -dihydroxypoly(oxytetramethylene) (PO4), Terathane 1000 from Dupont (USA), $\bar{M}_n = 1000$, $\rho = 0.974 \text{ g/cm}^3$) and/or α, ω -dihydroxypoly(alkylenecarbonate) (PC, Duracarb 124 from PPG Inc. (USA), $\bar{M}_n = 1500$, $\rho = 1.076 \text{ g/cm}^3$) were finally added. At this point, magnesium hydrohexabutoxytitanate was employed as a second catalyst and a phenol derivative (Irganox 1010, Ciba Geigy) as antioxidant agent. The reaction was carried out at 260°C and 0.5–0.7 hPa of reduced pressure until the product of highest melt viscosity, under these conditions, was obtained.

Duracarb 124 is a poly(alkylene ether carbonate) with an ether content of $\approx 8\%$. The poly(ester ether carbonate) terpolymer is schematically represented by the Scheme, where $n \approx 14$, m values given in Table 1, $l \approx 10$ and $x \approx 1.12$, $R = C_6H_{12}$ isomers. The data given in the scheme are average values derived from stoichiometric ratio and NMR analysis.

Terpolymers with a varying content of PO4 and PC segment between 0 to 40% in weight and a constant PBT segment content of 60% (here and further only wt %) were prepared. The degree of polymerization of PBT and the intrinsic viscosity number $[\eta]$ of the terpolymers as determined at 30°C from solution in phenol-trichloroethylene (1:1 vol) of the synthesized terpolymers [3] are given in Table 1.

Sample preparation

The obtained terpolymers were extruded from the reactor, paletisized, dried for 8 h at 70°C under reduced pressure (≈ 7 hPa) and finally injection molded at ≈ 50 MPa. From these 1 mm thick plates, films were prepared by pressing the plates in a hot press at a temperature 5°C above the melting point. The films were removed and immediately placed in a cooled press to obtain of 0.4 mm thick films suitable for physical measurements.

Techniques

Calorimetric measurements were carried out using a Perkin–Elmer DSC–4 scanning calorimeter. Calibration was made by means of indium standards. The sample was heated at a rate of 10°C/min up to 250°C, kept at this temperature for 1 min and cooled down, at the same rate, to 0°C followed by reheating again up to 250°C. During the first heating a strong entropy relaxation effect in the region of glass transition temperature of PBT was observed. During cooling crystallization takes place showing a crystallization enthalpy ΔH_c which is almost equal to the melting enthalpy ΔH_m observed during the second heating run (Table 1). Another series of DSC measurements was carried out in the temperature interval -100°C up to 25°C in order to evaluate the glass transition temperature of the soft segments. For the evaluation of the T_g the temperature at which $1/2 \Delta C_p$ is observed has been taken. The degree of crystallinity w_c (DSC) of PBT in the copolymer was determined according to the equation:

$$w_c(DSC) = \Delta H_m / \varphi \Delta H^\circ \quad (1)$$

where ΔH_m is the heat of fusion of PBT, F is its weight fraction in the copolymer, and $\Delta H^\circ = 144.5$ kJ/kg [9] is the ideal heat of fusion of PBT.

Wide-angle X-ray diffraction experiments were performed using a Rigaku goniometer and Ni filtered CuK_α radiation from a Rigaku rotating anode generator. X-ray diffraction patterns (WAXS) were taken at room temperature. For determination of the degree of crystallinity w_c the amorphous peak (WAXS taken in the molten state) is fitted to the diffraction curve so that it matches at some points, the area under the amorphous curve is subtracted from the total diffraction curve to yield I_c , the portion of the diffraction from

crystalline regions. w_c is then the ratio of the integrated area under the crystalline peaks I_c to the total integrated area I_t under the WAXS scan, taking into account the wt fraction of PBT φ , i.e. excluding the contribution of the soft segment $(1 - \varphi)$ scattering to the amorphous halo $(\Sigma I_c / \Sigma \varphi I_a)$. The size of the coherently diffracting domains (crystallite size) was calculated from the integral breadth $\delta\beta$ of each reflection according to $\delta\beta \sim 1/D_{hkl}$ [10]. This obviously is providing a minimum value for D_{hkl} .

Small angle X-ray scattering (SAXS) experiments were performed using a double-focusing mirror monochromator on the polymer beam line at HASYLAB (Hamburg). The wavelength (λ) used was 0.15 nm. Scattering patterns were recorded at selected accumulation times using a linear position-sensitive detector and corrected for fluctuations in the intensity of the primary beam and background. The scattering patterns were corrected by Lorentz factor and the long spacing was (L) calculated by the following equation:

$$L = \frac{2\pi}{q_{max}} \quad (2)$$

where $q = \frac{4\pi}{\lambda} \sin(\theta)$ and θ is the scattering angle.

DMTA measurements were performed by means of a Toyo Baldwin Co. instrument at 35 Hz in a tensile mode.

Microhardness (H) was measured at room temperature using a Leitz Tester equipped with a square based diamond indenter. The H -value was derived from the residual projected area of indentation according to the expression:

$$H = kP/d^2(\text{MPa}) \quad (3)$$

where d is the length of the impression diagonal in meters, P , the contact load applied in N and k is a geometrical factor equal to 1.854. A loading cycle of 0.1 min and loads of 0.05 and 0.1 N were used. Ten measurements for each point were averaged.

Results

Calorimetry

Fig 1 shows the DSC traces taken in the low temperature range for the polyblock copolymers with various compositions. The first and the last curves (curves *a* and *e*) correspond to the copolymers of the type $(AB)_n$ and are the poly(ester ether) (PEE) and the poly(ester carbonate) (PEC), respectively. The rest of the curves (Fig 1, curves *b*, *c* and *d*) refer to the copolymers of the type $(ABC)_n$ and are the poly(ester ether carbonate) (PEEC). It is to be noted that with increasing PC content the glass transition interval becomes narrower and the glass transition temperature is shifted systematically to higher temperatures. The numerical values of the respective T_g -value (evaluated as the temperature at which the $1/2 \Delta C_p$ is observed) together with the changes in C_p during softening as well as other data are summarized in Table 1.

Taking into account the chemical composition of the copolymers under investigation as well as the fact that the T_g -value of the hard segments of PBT is around 50°C one has to assign the observed glass transition temperatures (T_{g1}) to the amorphous phase arising from the soft segments (Table 1).

It is noteworthy that regardless of the chemical composition, i.e. if one deals with a copolymer of the $(AB)_n$ type or of the $(ABC)_n$ type one observes in this low temperature region only one T_g indicating the presence of only one amorphous phase comprising the soft segments. This is the case for the samples containing chemically uniform soft segments, PO4 or PC, (Fig 1, curves *a* and *e*, respectively). For the rest of cases, when the soft segments are not anymore chemically uniform but copolymeric ones, one has to assume that the presumably two amorphous phases (from PO4 and PC) are miscible or that they do not succeed to dephase during the treatment.

To the same conclusion – existence of a more or less uniform single amorphous phase comprising the two types of soft segments – lead the results of the DMTA measurements. In Figs 2 and 3 the dependence of the loss modulus E'' and storage modulus E' , respectively, are plotted as a function of the temperature for copolymers differing in their soft segments composition. In Fig 2 very well shaped peaks of the β -relaxation (T_β) can be

seen in the same temperature range in which the glass transition temperature of the soft amorphous phase T_{g1} have been observed on the DSC curves (Fig 1). From the position of the T_{β} -maximum in Fig 2 the transition temperatures T_{β} are evaluated for the various copolymers (see Table 1). Once again, the introduction of the PC component in the copolymers results in an increase of the transition temperature of the soft segments T_{β} . As usually occurs, the numerical values obtained by DMTA differ from those derived from calorimetric measurements (Table 1). Common to both techniques is the transition interval. Similarly to the DSC results (Fig 1) in case of the DMTA one can see again the tendency to narrower peaks with rising of the T_{β} -values (Fig 2). What is more important, there is no indication for presence of more than one amorphous phase even for copolymers of $(ABC)_n$ type regardless of the fact that their soft phase consist of two components, the PO4 and PC (Fig 2, curves *b*, *c* and *d*).

The conclusion concerning the number of amorphous phases and their transition temperatures derived from the low temperature DSC measurements (Fig 1) and the temperature dependence of the loss modulus E'' (Fig 2) is supported also by the temperature dependence of the storage modulus E' (Fig 3). One can see that for the same temperature interval (below 0°C) only one transition temperature can be observed for the copolymers of $(AB)_n$ type (Fig 3, curves *a* and *b*) as well as for those of $(ABC)_n$ type (Fig 3, curve *e*).

In addition, on the curves of Fig 3 there is a slight indication for existence of a second glass transition around 50°C. Having in mind the chemical composition of these copolymers, this transition can be assigned only to the glass transition temperature of the amorphous PBT hard segments (T_{g2}).

DSC curves (2nd run) taken in the higher temperature region (between 25 and 225°C) are displayed in Fig 4 for all the samples studied. It is noteworthy that the glass transition T_{g2} for amorphous PBT is particularly well defined for the first heating DSC run (Fig 4, sample *e*, dashed line). Due to the enthalpy relaxation of the glass the T_g transition is presented as a maximum as reported earlier [6]. It should be noted that the first heating scan for the rest of samples also shows a T_{g2} maximum (Table 1). It is to be noted that similar data for T_{g2} were observed for all the chemical compositions of the terpolymers

(of the two types, $(AB)_n$ and $(ABC)_n$. This can be interpreted as an indication that the two types of amorphous phases, the soft and the hard ones, are not miscible.

The DSC curves displayed in Fig 4 also show that, in addition to the two amorphous phases, a third crystalline phase exists. This conclusion is drawn from the presence of the well shaped endothermic peaks of the curves from the second heating (Fig 4, curves *a-e*, solid lines). A further, conclusion can be drawn based on the shape and temperature position of the peaks: the introduction of the PC moities in the copolymers and the increase of its relative amount leads to a less perfect crystalline structure as can be drawn from the strong decrease in melting temperature T_m and broadening of the peaks. The T_m values are evaluated from the peaks (T'_m and T''_m) observed and summarized in Table 1.

From the data derived from DSC and DMTA techniques (Figs 1–4) one can conclude that the copolymers under investigation contain three phases – two amorphous and one crystalline. The PBT hard segments give rise to the crystalline and one of the amorphous phases; the soft segments – to the second amorphous phase. It should be emphasized again that one observes a single soft-segment amorphous phase regardless of the number (one or two) of the soft-segment components.

X-ray scattering

To obtain a more complete information about the effect of the PC component on the structure formation of the block copolymers, X-ray diffraction patterns from the samples were taken (Fig 5). All the WAXS patterns show well defined crystalline reflections typical for the α -polymorphic form of the PBT phase [11]. With increasing PC content at expenses of the PO4 component, a relative decrease in intensity of the Bragg peaks and the disappearance of the higher scattering angle reflections is observed. Such changes suggest the formation of less perfect crystals and a decrease in the degree of crystallinity. A quantitative support of this observation is found in Table 2 where the values of the crystallinity w_c are collected. Crystallite dimensions in the range of 100 Å are obtained for D_{100} and D_{010} , in a good agreement with the reported values for similar systems [12,13].

Fig 6 illustrates the SAXS curves taken from these copolymers containing different amounts of PC in the soft segments. It is seen that the position of the scattering maxima slightly shifts towards higher scattering angles with increasing PC content. The decreasing long spacings L are summarized in Table 1 together with the calculated values of the crystal thickness l_c assuming ($l_c = L.w_c$).

Microhardness

Table 1 shows the clear influence of PC content on the microhardness values. It is well known the dominating contribution of the crystallinity in the mechanical properties of polymers [4-6]. Therefore, to understand better the correlation between the chemical composition and the microhardness of the copolymers one has first to examine the behaviour of the crystalline phase. Fig 7 shows the parallel dependence of the microhardness and of the crystallinity on the PC content within the copolymers. H drops continuously with increasing PC content almost in the same manner as the crystallinity does. Such a parallel behaviour of H and w_c shows that the effect of chemical composition on the microhardness is transferred via the crystallinity.

The plot of H versus w_c for copolymers with various compositions (see Fig 8) offers the opportunity to derive, by means of extrapolation, the values of the H for a completely amorphous copolymer (H_a^{PEEC}) and for a copolymer with 60% fully crystallized PBT component. The extrapolation of the straight line in Fig 9 to $w_c = 0$ and 100% leads to the following values: $H_a^{PEEC} \simeq 6,0$ MPa and $H_c^{PEEC} \simeq 106$ MPa. It is noteworthy that these values are notably lower than those for the homopolymer PBT because the samples studied contain only 60 wt% of this polymer. The remaining molecular strains belong to a much softer material which causes the drop in the H -values.

Discussion

Effect of chemical composition on the number of phases and transition temperatures

As shown in the previous sections the data obtained from calorimetric, dynamic mechanical and X-ray analysis indicate the existence in the copolymers of three phases – two amorphous and one crystalline. The hard PBT segments give rise to the crystalline phase and to one of the amorphous phases; the soft segments – contribute to the second amorphous phase. These three phases are characterized by their transition temperatures T_m , T_{g2} and T_{g1} , respectively. Their dependence on the PC content in the samples is plotted in Fig 9.

In contrast to the amorphous PBT phase (Figs 2 and 3) the crystalline PBT phase shows a strong dependence on the PC content in the copolymers.

From Fig 4 one sees that almost all the samples show two or even three melting peaks, the first one T'_m and the third one T'''_m being very weak in contrast to the strong central one T''_m . It is well known that this phenomenon can have two origins: the recrystallization processes during scanning in DSC or the presence in the sample of more than one population of crystallites each one distinguished by different crystal size and perfection [14]. The curves in Fig 4 (second heating) are in favour of the second alternative, at least concerning the T'_m and T'''_m values. Otherwise the second, main peak T''_m should be of the same size, shape and position regardless of the sample history [14]. The last peak T'''_m (Fig 4, curves *a* and *b*) seems to be more a result of recrystallization processes.

The drastic increase of T_g (by 50°C) and the narrowing of the transition interval (from 40 to 7°C) with increasing PC content are a result of a decrease in the chain flexibility. Such a change in the flexibility of the soft segments will affect in turn the flexibility of the copolymer chains bracketing the PBT hard segments. The proper flexibility of PBT chains remains unaffected by the presence of PC-moities, as can be concluded from the constancy of the T_g of PBT (Table 1, T_{g2}). What is changed is the mobility of PBT hard segments dispersed in the amorphous soft segment matrix. The crystallization of PBT segments presumes such a mobility. In addition one has to take into account the fact

that the hard segments are not only “embedded” in the soft segments matrix but they are also chemically bonded with each other by means of these soft segments with varying flexibility. By introducing the PC moieties in the soft segments one decreases dramatically their flexibility thus restricting the mobility of the hard segments which in its turn hampers the crystallization process. As a result, when the PC content in the copolymers increases one can expect a decreasing degree of crystallinity and more imperfect crystallites as we actually observe (Figs 4 and 5, Table 1).

These considerations allow one to affirm that the effect of PC content on the crystallizability of PBT hard segments is transferred by the drastic changes in the flexibility of soft segments interconnecting the crystallizable hard segments. The strong influence of PC component on the flexibility of the soft segments is enhanced by another peculiarity of this amorphous phase. As we shall see below the introduction into the PO4 soft segments of the chemically different component (PC) does not yield a new amorphous phase, even if the PC component dominates. One deals with an uniform amorphous phase regardless of the chemical composition of this phase. Nevertheless, its glass transition temperature T_g , increases with the PC content. This means that the PC-moieties increase the rigidity of the soft segments by introducing chemical bonds with a higher rotation potential.

The conclusion drawn with respect of the effect of PC content on the crystallinity is important for the interpretation of the mechanical properties.

Microstructure from X-ray scattering

The data from Table 2 reveal that the crystal size values derived from SAXS are smaller than those derived from the broadening of the WAXS reflections.

While the D_{hkl} values are derived from the coherence length along the hkl directions perpendicular to the chain direction within the PBT crystallites, the l_c -values are derived from the long period L defined by the electron density fluctuation within the sample. Since the PBT crystallites are distributed at random L and therefore l_c cannot be assigned to any particular crystallographic direction.

Since the densities ρ_a^{PBT} and ρ_a^{soft} are very close to each other ($\rho \sim 1 \text{ g/cm}^3$) from the scattering viewpoint they behave as one single phase. Consequently the long spacing

will correspond to the average distance between adjacent PBT crystallites which are separated by the amorphous phase composed of PBT disordered segments and the soft segments. For a better evaluation of the average size of the PBT particles, comprising both the crystalline and amorphous PBT phases one has to use their mass fraction φ in the terpolymer. Values of $l_\varphi = L\varphi$ between 77–90 Å are obtained (see Table 2) which lie between the values of l_c and those of D_{hkl} .

The fact that the hard PBT crystallites are acting as scattering centers embedded within the amorphous material (amorphous PBT and soft segments phase) is in accordance with the length of the hard segments of about 70 Å [15]. The reported PBT crystallite size values in chain direction are around 50–60 Å [13,15]. This means that the rest of the segments, being also in the amorphous state, are located at the surface of the crystallites. In addition some fraction of PBT segments may also be fully in the amorphous phase near to the crystallites. This type of PBT amorphous phase giving rise to strong restricted flexibility has been invoked by dielectric relaxation measurements [3].

From the above calorimetry data and specially from the SAXS results one can conclude that PBT particles comprising crystalline and amorphous partners are embedded in a much softer amorphous phase arising from the soft segments. Fig 10 illustrates schematically a model for the microstructure of these block copolymers.

Microhardness of systems comprising very soft (liquid-like) components

The measured H-values for the terpolymer studied (Table 1) are very low in comparison to the values known for common synthetic polymers, some of them, even being in the amorphous state [16]. What is more H-values are more than 3 times smaller than the calculated ones for the same terpolymer by means of the additive law:

$$H = \varphi H^{PBT} + (1 - \varphi) H^{soft} \quad (4)$$

where φ is the weight fraction of the hard PBT segments.

Taking into account that the soft segment amorphous phase has T_g -values between –50 and 0°C, depending on the PC content (Table 1) one can expect that at room temperature such a phase will be a very soft material much closer to a liquid than to a solid. For this

reason one may expect that $H^{soft} \simeq 0$ and, as a result, that H will be depressed with increasing values of φ according to the simple expression:

$$H = \varphi H^{PBT} = \varphi [H_c^{PBT} w_c + H_a^{PBT} (1 - w_c)] \quad (5)$$

By applying the numerical values, $\varphi = 0.6$, $H_c^{PBT} = 287$ MPa and $H_a^{PBT} = 54$ MPa one [7], can derive the calculated values H_{cal} for the terpolymer depending on w_c (Table 2). It is seen that the H_{cal} values are notably larger than the measured ones.

In order to explain such a hardness depression it is convenient to consider the behaviour of the harder component dispersed in the liquid component (with “zero” hardness). It seems reasonable here to assume that the total hardness of such a system will depend also on the viscosity of the soft component where the particles of the harder component are “floating”. The deviation of the H values from the H_{cal} ones actually may reflect the viscosity of the soft segments phase which also contributes to the resistance of the total system against the applied load.

The viscosity of the soft phase introduces two important effects:

The first one is related to the above mentioned “floating” effect of the hard segments within the liquid matrix. Actually, the soft phase plays a plasticizing role reducing strongly the H^{hard} value depending on its viscosity. The lower the viscosity, i.e. the lower the T_g^{soft} (T_{g1}) the stronger the plasticizing effect, i.e. the larger the depression in H^{hard} .

The second effect caused by the viscosity of the soft phase concerns the crystallization ability of the hard segments. As discussed in the foregoing paragraphs the crystallization process presumes the mobility of the crystallizing segments. In the present case the hard segments are linked to each other through the soft segments. It is quite obvious that the higher flexibility of the soft segments, (lower T_g^{soft}) and consequently the lower viscosity will enhance the crystallization capability of the hard segments. At the same time the higher crystallinity results in higher H-values. It turns out that the viscosity of the soft amorphous phase creates two competitive effects: on the one hand the plasticizing effect leading to the decrease of the overall microhardness H, and on the other the enhanced crystallizability results in an increase of the overall microhardness H.

Conclusions

The data of the present study show a large decrease in the overall H with increasing PC content within the soft segments. Such a decrease is due to the decrease in crystallinity but not to the plasticizing effect. The latter should act in the opposite direction since the introduction of PC moities in the soft segments creates a strong increase in T_g -values (from -50 up to 0°C , Table 1) and consequently an increase of viscosity. In other words, the increase of PC content will contribute to a decrease of the plasticizing effect, but does not eliminate it as long as the T_g -values are below room temperature. The plasticizing effect will be always present when one of the components is liquid. Consequently one can conclude that this plasticizing is the main factor controlling the overall microhardness depression. Indeed, the measured H values are strongly depressed representing only about 25% of the calculated values.

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Figure captions

Fig 1 DSC curves taken in the low temperature region for polyblock copolymers with the following composition PBT/PO4/PC (wt%): *a* – 60/40/0 (PEEC); *b* – 60/32/8 (PEEC); *c* – 60/20/20 (PEEC); *d* – 60/12/28 (PEEC) and *e* – 60/0/40 (PEC).

Fig 2 Dependence of the loss modulus E'' on the temperature T for polyblock copolymers with the following composition PBT/PO4/PC (wt%): *a* – 60/40/0 (PEE); *b* – 60/32/8 (PEEC); *c* – 60/20/20 (PEEC); *d* – 60/12/28 (PEEC) and *e* – 60/0/40 (PEC).

Fig 3 Dependence of the storage modulus E' on the temperature T for polyblock copolymers with the following composition PBT/PO4/PC (wt%): *a* – 60/40/0 (PEE); *b* – 60/32/8 (PEEC); *c* – 60/20/20 (PEEC); *d* – 60/12/28 (PEEC) and *e* – 60/0/40 (PEC).

Fig 4 DSC curves taken in the higher temperature region for polyblock copolymers with the following composition PBT/PO4/PC (wt%): *a* – 60/40/0 (PEE); *b* – 60/32/8 (PEEC); *c* – 60/20/20 (PEEC); *d* – 60/12/28 (PEEC) and *e* – 60/0/40 (PEC). Dashed line – first heating run (shown only for one sample), solid lines – second heating run.

Fig 5 WAXS diffractograms for polyblock copolymers with the following composition PBT/PO4/PC (wt%): *a* – 60/40/0 (PEE); *b* – 60/32/8 (PEEC); *c* – 60/20/20 (PEEC); *d* – 60/12/28 (PEEC) and *e* – 60/0/40 (PEC). Solid lines – taken at room temperature, dashed line – taken in a molten state.

Fig 6 SAXS curves for polyblock copolymers with the following composition PBT/PO4/PC (wt%): *a* – 60/40/0 (PEE); *b* – 60/32/8 (PEEC); *c* – 60/20/20 (PEEC); *d* – 60/12/28 (PEEC) and *e* – 60/0/40 (PEC).

Fig 7 Dependence of: a) microhardness H and b) total degree of crystallinity φw_c (referred to the sum of PBT plus PO4 and PC components), on the PC-content of polyblock copolymers.

Fig 8 Dependence of microhardness H on degree of crystallinity $w_c(\rho)$ for polyblock copolymers with various PC-content.

Fig 9 Dependence of melting temperature T_m'' and glass transition temperatures T_{g1} on PC content w_{pc} for polyblock copolymers. A: $-T_m'$; Ba -DSC b-DMTA. The data are derived from the respective curves (Figs 1,2 and 4, Table 1).

Fig 10 Schematic model showing the hard PBT particles (composed of crystalline cores and surface amorphous regions) embedded in the amorphous phase from the soft segments.

SCHEME

Table 1 Thermal properties of poly(ester ether carbonate) block terpolymers.

Composition (wt %) (PBT/PO4/PC)	Polym. degree of PBT [3] m	$[\eta]$ [3] (dL/g)	First heating			Second heating				
			T_{g1} DSC	T_{g1} DMTA	T_{g2} DSC	T_c (°C)	ΔH_c (J/g)	T'_m (°C)	T''_m (°C)	$\Delta H''_m$ (J/g)
100/0/0	—	—	55	—	—	—	—	—	—	—
60/40/0	7.7	1.16	-56	-50	57	171	39.7	170	201	39.7
60/32/8	8.4	1.19	-45	-34	55	145	25.1	146	179	31.8
60/20/20	9.4	1.16	-32	-17	54	111	20.2	108	151	19.0
60/12/28	10.1	1.04	-10	-3	53	70	20.2	—	131	18.1
60/0/40	11.1	1.02	1	19	52	56	13.9	—	102	12.8

Table 2 Structural data and mechanical properties of poly(ester ether carbonate) block terpolymers

Composition (wt %) (PBT/PO4/PC)	WAXS			SAXS			Microhardness (MPa)		
	w_c %	D_{100} (Å)	D_{010} (Å)	L (Å)	l_c (Å)	l_φ (Å)	H_{exp}	H_{cal}	ΔH
100/0/0	59.0	–	–	–	–	–	–	–	–
60/40/0	37.7	84.7	116.6	146.0	55.0	83.7	29.6	85.1	55.5
60/32/8	25.8	87.8	93.8	130.8	33.8	77.2	22.8	68.5	45.7
60/20/20	24.3	105.0	113.9	118.5	28.8	89.6	18.6	66.4	47.8
60/12/28	21.2	86.2	119.6	118.5	25.1	85.3	17.5	62.0	44.5
60/0/40	13.0	77.9	104.0	116.3	15.1	77.3	15.5	50.6	35.1

Fig 1

Fig 2

Fig 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 3

Fig. 10