

INFLUENCE OF COMPOSITIONAL HETEROGENEITY ON MORPHOLOGY AND PROPERTIES OF SEGMENTED COPOLYMERS

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ABSTRACT

Polyethylene terephthalate(PET)/polycaprolactone(PCL) segmented copolymers with different hard segment contents and a blend of two of them were studied by using DSC, WAXS, TEM and IR techniques and dynamic mechanical, stress-strain and isothermal crystallization measurements. Emphasis was laid on the studies of influence of compositional heterogeneity on the morphology and properties of these segmented copolymers. It was found that the solution cast specimens of the more heterogeneous sample exhibit better segregation of segments, high crystallinity and melting temperature. They have higher thermal stability of mechanical properties at small deformations. However, they are less stable against large deformations and may become softer than the more homogeneous ones.

INTRODUCTION

Segmented copolymers can be considered as block macromolecules of the general type $-(H-S)_n-$. Usually block S(soft segment) is rubbery, while block H(hard segment)-glassy or crystalline at normal operating temperature. The physical properties of the materials can be varied over a wide range by changing the hard/soft segment ratio. Microphase separation of hard and soft segments, first pointed out by Cooper and Tobolsky in their studies on the properties of segmented polyurethanes,^[1] was accepted as basis for explaining the morphological features and properties of these copolymer^[2-14]. However the real copolymers are more complex than what is expected from the model of microphase separated hard and soft segment domains. Two types of spherulites having different melting temperatures were observed for solution cast poly(ethylene terephthalate)-poly(tetramethylene oxide) specimens^[15]. Domains of micron size have been observed for some noncrystalline segmented polyurethanes^[16-18]. In the case of polybutadiene/toluene diisocyanate/butanediol segmented polyurethanes two hard segment T_g 's have been detected by different techniques^[19-22]. All these phenomena were not consistent with the two phase model based on segment segregation.

It has been found^[15,17,22] that for many segmented copolymers due to the heterogeneity of the reaction system the product is far from a statistically random copolymer, but a mixture of segmented macromolecules with quite different chemical composition and average hard segment length. Therefore, in addition to the microphase separation of segments, the macrophase separation of molecules with different composition should be considered in discussing the morphology and properties of real segmented copolymers.

As this phenomenon is supposed to be common for segmented copolymers, it is important to study the control and characterization of the heterogeneity of segmented macromolecules and also the relationship between properties and the molecular heterogeneity. In this work the influence of compositional heterogeneity on the morphology and properties was investigated for polyester-polyester(PET-PCL) segmented copolymers.

EXPERIMENTAL

Materials

Segmented copolymers PET-PCL were synthesized by a two step method involving ester exchange and polycondensation reactions^[23]. The molecular weight of polycaprolactone segments was about 500. The basic characteristics of the PET-PCL segmented copolymers used in this work are listed in Table 1. The intrinsic viscosity of the samples was measured in *m*-cresol at 30°C, and the hard segment content was determined by NMR measurements. Sample 2 and sample 4 had the same hard segment content, but with different composition distribution. Sample 4 is more heterogeneous, being a blend of samples 1 and 3 cast from their solution in chloroform. A comparison of the behaviour of sample 2 and sample 4 may give some information about the influence of compositional heterogeneity.

Table 1 PET/PCL segmented copolymers

Sample	Hard segment content (wt%)	$[\eta]$ (dl/g)
1	49	0.95
2	64	1.02
3	78	1.13
4*	64	—

* Sample 4 is a blend of samples 1(48.3%) and sample 3(51.7%)

Instrumental

Differential scanning calorimetry was carried out in a temperature range from 210 K to 510 K using a Perkin-Elmer DSC-2. Runs were conducted at a heating rate of 20°C/min.

Dynamic mechanical measurements were performed using a Rheovibron DDV-II at a fixed frequency of 3.5 Hz and a heating rate of 2°C/min.

Wide angle X-ray scattering of the samples was studied using a Rigaku automatic diffractometer type D/max-IIIb with Ni filtered CuK α radiations.

A Hitachi 800 transmission electron microscope was operated at 100 kv for morphological studies. Solution cast films were stained by 0.2% phospho-tungstic acid solutions, and then washed with distilled water for several times.

Stress-strain measurements were carried out using an Instron tester type 1122. The initial length of the stripe specimens was 2 cm and the strain rate was 100%/min.

Isothermal crystallization of samples both from the melt and quenched glass states was studied by means of depolarizing transmittance measurements^[23].

An infrared spectrometer IFS 113V(Bruke) was also used in this work.

RESULTS AND DISCUSSION

Morphology and transitions

The crystallization of these segmented polyesters after solution cast has been studied by DSC measurements. Figure 1 shows the thermograms of the four samples and the corresponding data for the transitions are listed in Table 2. The glass transition temperature of the original samples shifts to high temperatures with increase in hard segment content, which may imply some kind of compatibility between the soft and hard segments of the PET/PCT copolymers in the non-crystalline regions. Sample 1 shows a single endothermal peak at about 66°C. This peak was also observed for the other two original samples at almost the same temperature range. Another endopeak was detected for sample 2 and sample 3 at higher temperatures and the peak temperature increases with increase in hard segment content. As short soft segments of copolymers are usually not crystallizable, the observed endopeaks are all considered as melting effects of crystals of different hard segment lengths. This assignment has found its evidence from direct WAXS measurements. Although the patterns were rather diffuse, especially for sample 1, probably due to their low crystallinity and the small size of crystallites, some intensity maxima can still be detected and their 2θ positions are given in Table 3. The data of a well crystallized PET sample, which are consistent quite well with those reported in the literature^[25], are also listed. It is clear from the

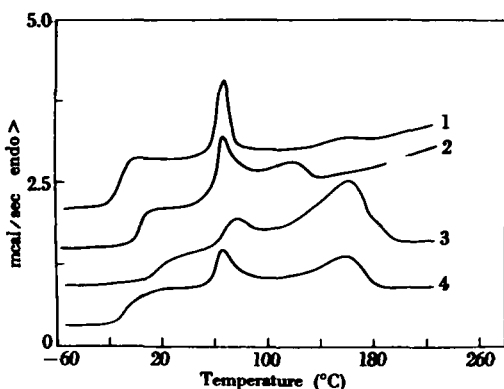


Fig. 1 DSC curves for solution cast samples 1—4.

Table 2 DSC data for segmented polyesters.

Sample	$T_g(^{\circ}\text{C})$	$\Delta T(^{\circ}\text{C})^*$	$T_{m1}(^{\circ}\text{C})$	$\Delta H_{m1}(\text{cal/g})$	$T_{m2}(^{\circ}\text{C})$	$\Delta H_{m2}(\text{cal/g})$
1	-11	23	66	1.60	—	—
2	4	24	66	1.60	117	0.57
3	18	28	75	0.84	159	4.50
4	-7	38	66	1.10	158	2.20
4**	2	38	—	—	155	2.20

* ΔT —temperature range of heat capacity jump during the glass transition.

** Melt cast specimens of sample 4.

comparison that only hard segment crystals are formed in these samples. The separate diffraction peaks from (111) and 110 planes were not observed for the copolymers, it is supposed to be resulted from the interference of the large amorphous halo.

Table 3 WAXS data for the samples

Sample	Peak position 2θ (deg)					
1		17.7	21.2	25.5		
2	16.3	17.8	21.4	25.6	32.7	
3	16.2	17.4	22.0	25.8	32.5	
4	16.3	17.7	21.6	25.8	32.5	
PET	16.3	17.4	21.3	22.7	25.8	32.4
(hkl)	011	010	111	110	100	101

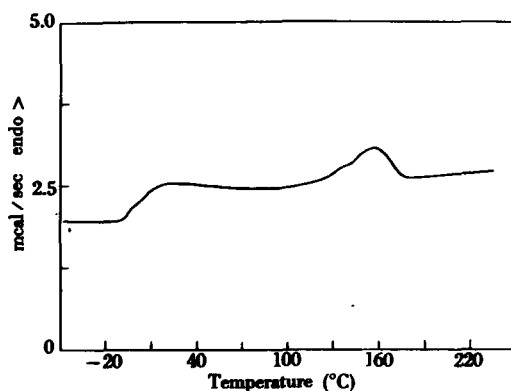


Fig. 2 DSC curve of melt cast specimen of sample 4

The thermal behavior of the melt cast specimens also supported our explanations of the lower endopeak. The DSC curve of the melt cast sample 4 is given in Figure 2. After the melt treatment the lower endopeak disappeared and the glass transition temperature moved to higher temperatures. This can only be interpreted by mixing more hard segments in the soft segment rich domains. The melting behavior of these PET/PCL copolymers indicates the existence of bimodal distribution of hard segment length and the segregation on crystallization according to hard segment length during precipitation from the solution. The heterogeneity of molecules in composition and average hard segment length for these samples is also very possible, if the generality of this phenomenon for segmented copolymers is taken into account.

Sample 4 is a blend of sample 1 and sample 3, having the same hard segment content as sample 2. However the thermal behavior of sample 2 and sample 4 is different. Sample 4 exhibits clearly the characteristics of its two components. It has a low glass transition temperature near to that of sample 1 and a significant upper endopeak for hard segment crystals at the same temperature range observed for sample 3. The comparison between samples 2 and 4 indicates that the heterogeneity of segmented copolymers in composition will probably result in mobility of molecular segments in the

rubbery regions at lower temperatures and also the stability of the physical crosslinking at higher temperatures, that are usually hopeful in the applications of segmented copolymers.

Data in Table 2 indicate that the value ΔH_{m2} of sample 4 is almost half of that of sample 3, while the ΔH_{m1} is approximately equal to the average value of those for sample 1 and sample 3. As sample 4 is a blend of sample 1 and sample 3 with a blend ratio of about equal content, it seems that the hard segments of sample 1 and sample 3 in the blend (sample 4) crystallize in the same way as they were not blended with each other. This kind of behavior of sample 4 may imply a well segregation of molecules with different compositions in the blend during crystallization. The glass transition behavior is usually used for discussing the compatibility of components in the noncrystalline regions of multicomponent systems like copolymers or blend. For sample 4, the blend of sample 1 and sample 3, one can not judge the compatibility between the components simply according to the singularity of glass transition, because the T_g values of the components are very close to each other. The temperature width of the glass transition defined as the temperature interval of heat capacity jump was determined for all the samples and are listed in Table 2. It was found to be about 25°C for the three original samples, while that of sample 4, the blend, broadened obviously (38°C). It may imply, at least, that the components are not well compatible in the noncrystalline regions. A broad glass transition was also observed for sample 4 by dynamic mechanical measurements which will be shown below.

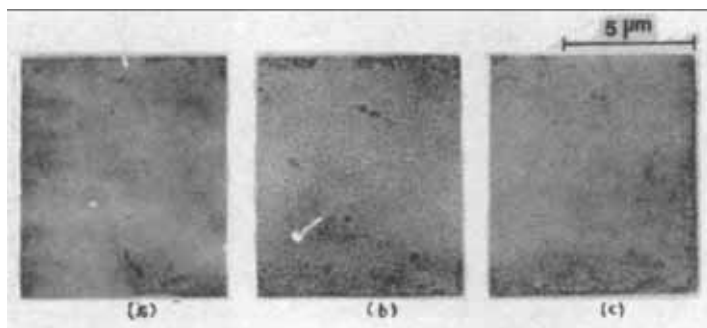


Fig. 3 Transmission electron micrographs of stained
(a) sample 2, (b) sample 3 and (c) sample 4

Information about the domain structure of the samples has been obtained from direct morphological observations by means of transmission electron microscopy. Circular domains of about 0.1 μm diameter uniformly distributed in the matrix can be seen for sample 3, and domains of similar size, but less in quantity, were observed for sample 4 (Figure 3). These domains are considered to be crystalline hard segment rich regions, because they were the unstainable regions and were not observed for sample 1. Circular domains of smaller size, usually less than 50 nm, still could be told in sample 2, but they were rather obscure due to the low contrast. The comparison between the patterns of the two samples of the same hard segment content reveals the influence of compositional heterogeneity of segmented copolymers on their domain morphology.

The infrared spectrum of a molecule is mainly determined by its chemical structure, but it may also reflect some information about its environment and interaction with the surrounding molecules. So valuable data can be obtained by using this technique for studying the structure and morphology of polymer blends. The infrared spectra of PET/PCL copolymers in the wavenumber range 760–940 cm^{-1} and 1300–1500 cm^{-1} are given in Figure 4 and Figure 5 respectively. The

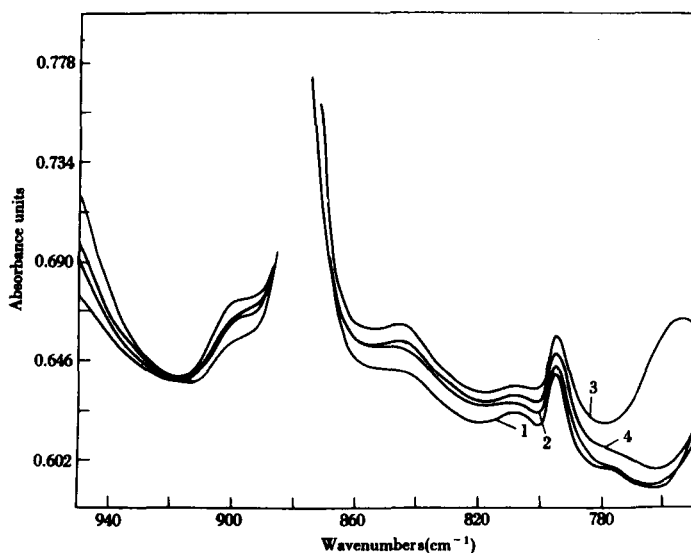


Fig. 4 IR spectra of solution cast PET/PCL copolymers in the wavenumber range from 760 cm^{-1} to 940 cm^{-1} .

(1) sample 1, (2) sample 2, (3) sample 3 and (4) sample 4

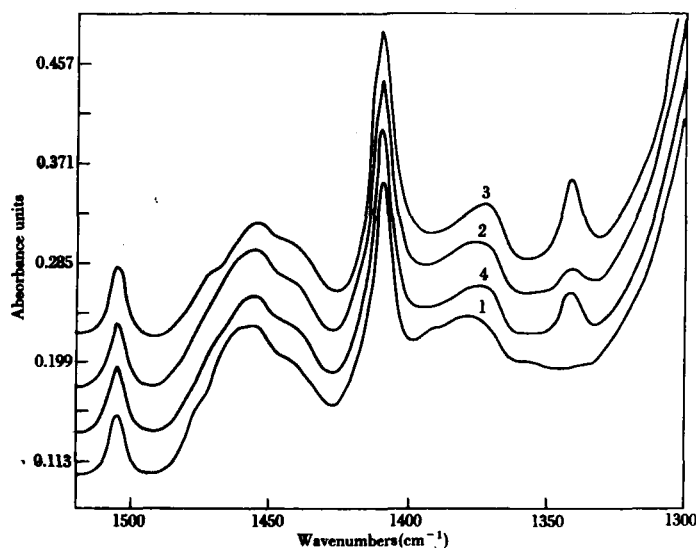


Fig. 5 IR spectra of solution cast PET/PCL copolymers in the wavenumber range from 1300 cm^{-1} to 1500 cm^{-1} .

(1) sample 1, (2) sample 2, (3) sample 3 and (4) sample 4

band of 1340 cm^{-1} is usually supposed to be related to the crystallization of PET molecules and was found to be quite different for the four samples. As PCL does not have IR bands around 1340 cm^{-1} and 795 cm^{-1} , one can use the absorbance ratio of A_{1340} over A_{795} , the latter is generally accepted as the internal standard in PET spectroscopic analysis, to characterize the crystallization of the PET segments in copolymers. The results are given in Figure 6 as a plot of A_{1340}/A_{795} versus hard segment content of the copolymers. It is clear that the crystallinity of PET segments in the copolymers increases with increasing their content, and the compositional heterogeneous sample 4 exhibits much high crystallinity than its counterpart of same hard segment content. These results are consistent with the DSC data discussed above.

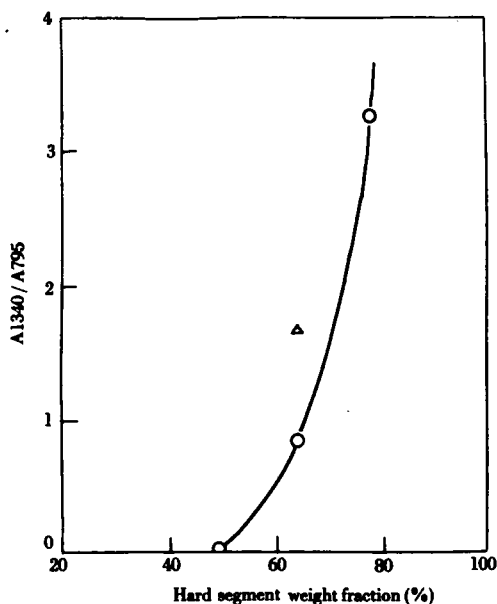


Fig. 6 Dependence of A1340/A795 on the hard segment content of the PET/PCL copolymers. Δ sample 4

Band 874 cm^{-1} is related to the C-H vibration of the PET benzene rings. It was found that for the copolymers this band deviates from its original position for PET homopolymers, shifting to higher wavenumber. We suppose that the shift of this band is related to the change in environment of the PET benzene rings and can be used to estimate the segregation of PET segments in multicomponent systems. The shift toward higher wavenumber was found to increase with decreasing PET segment content (Figure 7). The shift for sample 4 was about 1 cm^{-1} less than that for sample 2, which means a better segregation of PET segments in the compositionally more heterogeneous samples of PET/PCL copolymers.

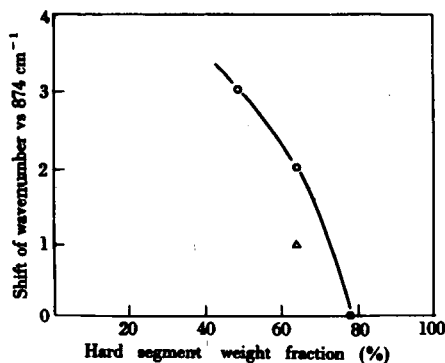


Fig. 7 Relationship between the shift of band 874 cm^{-1} and the hard segment content of the samples Δ sample 4

The crystallization kinetics of the hard segments of the copolymers has been studied isothermally by depolarizing transmittance measurements. It was unable to detect the crystallization process by this technique for sample 1 and sample 2. This is believed to be due to the small size, as shown by TEM observations, of their crystallites or the aggregates of the crystallites, which is much

less than the wavelength of the visible light used for the depolarizing transmittance experiments. Isothermal crystallization curves were obtained for sample 3 and sample 4, and the results of the latter are given in Figure 8. The exponent value n in the Avrami analysis of the kinetic process was found to be 3.5–4.5 both sample 3 and sample 4 in the used temperature range. The half-crystallization time $t_{\frac{1}{2}}$ was determined, and its reciprocal was used for characterizing the crystallization rate of the samples at the given temperature. The temperature dependence of crystallization rate of the two samples is illustrated in Figure 9. The crystallization rate increases at first with supercooling and then decreases after a maximum. Samples 3 and 4 have the same melting temperature of hard segment crystals, but their maximum crystallization rate temperatures T_k 's

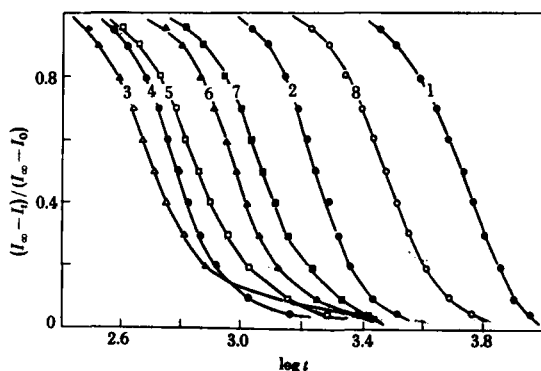


Fig. 8 Isothermal crystallization curves of sample 4 at (1) 60°C, (2) 70°C, (3) 80°C, (4) 90°C, (5) 95°C, (6) 100°C, (7) 105°C and (8) 130°C respectively

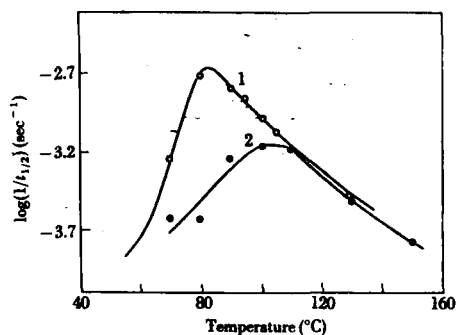


Fig. 9 Temperature dependence of $\log t_{\frac{1}{2}}^{-1}$ for (1) sample 3 and (2) sample 4

are different in about 20°C. It is probably resulted from their difference in T_g 's, as it was accepted that T_k can be roughly estimated from the average of T_g and T_m [26].

Mechanical properties

The dynamic modulus of the samples at different temperatures are given in Figure 10. A rapid decrease of modulus occurs in a transition temperature range, which moves to higher temperatures with increasing the hard segment content of the sample, and the amount of the modulus decrease becomes smaller for samples with higher hard segment content. The more heterogeneous sample 4 was different from sample 2, exhibiting the influence of its two fractions. The curves of sample 2 and sample 4 intersect each other in the transition temperature range. Sample 4 has higher modulus than

sample 2 in the high temperature region, but – lower modulus at temperatures below the intersection point. These results are consistent with the morphological observations discussed above. The data of mechanical loss tangent for the samples are given in Figure 11. The loss peak, being related to the glass transition of the samples, shifts to higher temperatures with increasing hard segment content similar to the results from DSC measurements. The peaks of the original samples were relatively narrow, however that for sample 4, the blend, was rather broad, indicating a not well compatibility between the components of the blend in its noncrystalline regions.

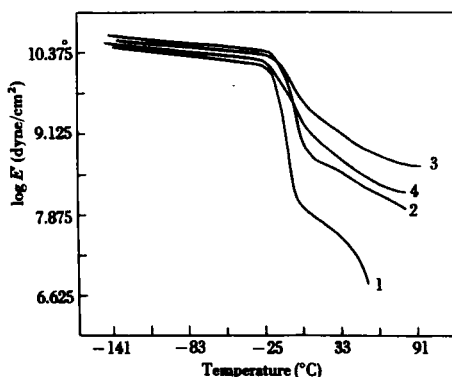


Fig. 10 Temperature dependence of the storage modulus E' at 3.5 Hz for PET/PCL copolymers:

(1) sample 1, (2) sample 2, (3) sample 3 and (4) sample 4

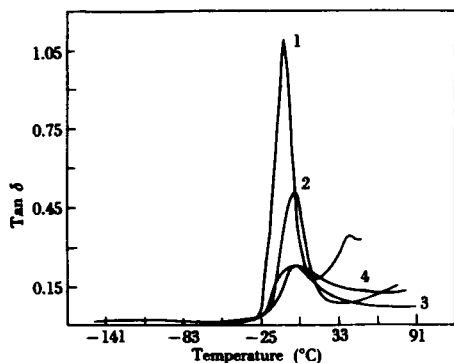


Fig. 11 Temperature dependence of $\tan \delta$ at 3.5 Hz for (1) sample 1, (2) sample 2, (3) sample 3 and (4) sample 4

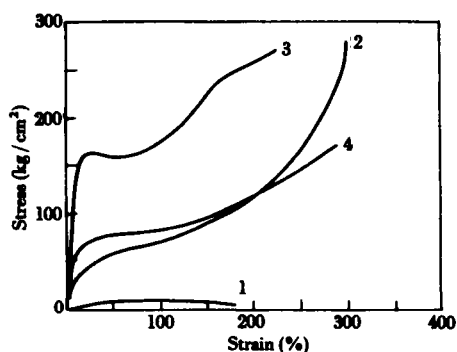


Fig. 12 Stress-strain curves for (1) sample 1, (2) sample 2, (3) sample 3 and (4) sample 4 at 16°C.

The strain rate is 100%/min

Figure 12 shows the typical stress-strain curves of the PET/PCL samples. The features of samples 1, 2 and 3 are quite different. Sample 1 is very weak. Sample 2 is rubber-like and the stress rises to the breaking point with a sigmodal relationship to the strain. The stress-strain curve of sample 3 shows a yield point and subsequent cold-drawing phenomenon. Their various mechanical behavior reveals the versatility of segmented copolymers to different kinds of applications. The stress-strain curve of sample 4 was more complicated. It shows a much larger initial Young's modulus, as expected, than that of sample 2, but the stress increases slowly with elongation, and the sample 4 appears softer than sample 2 at strain values more than about 200%. It may indicate the necessity of considering the instability of morphological structures for samples under large deformations. It is anticipated especially for segmented copolymers to be the case, because the

crosslinks, being physical in nature, are very weak, and some of them may become points of stress concentration and collapse in elongation process. Of course, new physical crosslinks are also possible to form in the elongated samples and have their influence on the further elongation. Therefore it means that the true morphology within the samples should be considered for interpreting the properties during large deformations, and only the behavior under small deformations can be related to the morphology of samples before the experiments, the initial or quiescent morphology.

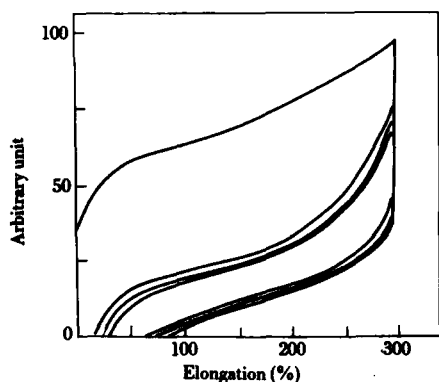


Fig. 13 Stress-strain curves of sample 2 in cyclic deformation experiments at 16°C

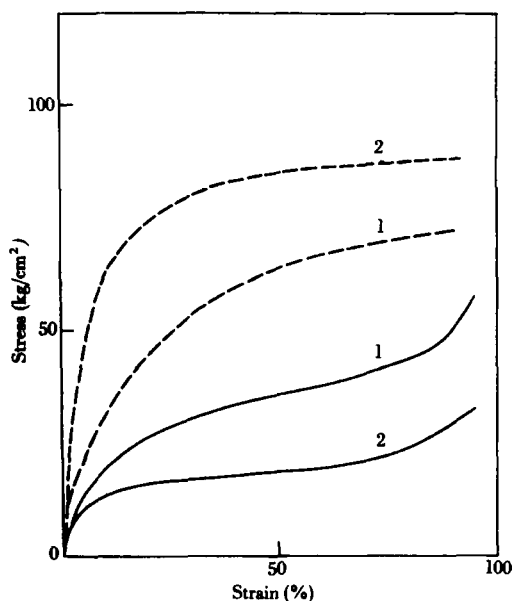


Fig. 14 Stress-strain curves for (1) sample 2 and (2) sample 4 at 16°C after prestraining to 200%. The strain rate is 100%/min. Dash curves are the corresponding curves replotted from Figure 12 for comparison

Lilaonitkul and Cooper have studied the hysteresis of polyether/polyester segmented copolymers in cyclic strain experiments. They found that higher hard segment content will result in a higher percent hysteresis due to the higher crystallinity and plastic deformation of the samples^[5,6]. The stress-strain curves of sample 2 in cyclic deformation process are shown in Figure 13. It is obvious from these curves that the subsequent straining results in lower stress levels at extensions lower than those previously applied; it appears that the specimens do not return to their initial situation at the end of the cycle. After three or four cycles the tensile behavior of the specimen become almost reversible, and the hysteresis in cyclic strain experiments – mainly due to viscoelasticity, but not the unreversible further structure changes. Thus it is very interesting to use prestrained specimens for studying the true morphology and the mechanical behavior of the samples in real applications. A comparison of specimens of samples 2 and 4 after prestraining treatment to a strain level of 200% is given in Figure 14. It can be seen that the curves of both samples are rubber-like and sample 4 becomes softer than sample 2 after the prestraining. The difference of these curves from those shown in Figure 12 may reflect the difference between the initial morphology and the true morphology of the samples after a straining to 200% and explain their tensile behavior under large deformations.

CONCLUSIONS

The heterogeneity of PET/PCL segmented copolymers in composition may give evident influence on their morphology and mechanical properties. The solution cast specimens of the more heterogeneous sample exhibit better segregation of segments, higher crystallinity and melting temperature, but lower glass transition temperature. They have higher thermal stability of mechanical properties related to small deformations. However, they are less stable against large deformations and may become softer than the more homogeneous ones.

Keywords:

Segmented polyester; compositional heterogeneity; morphology; mechanical properties.

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