Macromolecules **2003,** *36,* 6791−6796

Temperature-Dependent Transition of Deformation Mode in Poly(1,4-cyclohexylenedimethylene terephthalate)/Poly(ethylene terephthalate) Copolymers

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Received May 20, 2003; Revised Manuscript Received July 7, 2003

ABSTRACT: The temperature-dependent deformation behavior of amorphous thin films of poly(1,4-cyclohexylenedimethylene terephthalate) (PCT), poly(ethylene terephthalate) (PET), and their copolymers was examined with variation of temperature and cyclohexylene linkage content by transmission electron microscopy. When subject to uniaxial tension, thin films of PET homopolymers and copolymers containing low content of cyclohexylene linkage showed a tendency of failure by crazing, whereas a transition from crazing to localized shear deformation occurred as the content of cyclohexylene linkage increased. When temperature was lowered to where secondary relaxation is suppressed, PCT and the copolymers showed transition of deformation mode from shear or mixed deformation to crazing, while no significant change was observed for PET. Whereas it has been considered that the change of deformation mechanism in thin films is governed by entanglement density, it was found that the transition in the deformation behavior obtained in PCT and the copolymers were highly correlated to the conformational transition of the cyclohexylene ring.

Introduction

Mechanical properties of polymeric materials are decisive in applications. Improvement of toughness is of particular interest, since the toughness of polymeric materials is an important selection criterion for many applications. Therefore, understanding of mechanisms of impact resistance or toughness of materials in general and its improvement has been highly noticed to date. Addition of secondary phases with different physical properties into a polymer matrix has been extensively investigated because of its easy accessibility and wide spectrum of properties expectable.[1−3] Toughness is, however, one of the most complex properties and difficult to control because it is greatly affected by morphological and micromechanical parameters.[2,3] Furthermore, incorporating secondary phases is able to induce additional effect that deteriorates impact resistance. For example, while rubber has been known useful in toughening of amorphous polymers, rubber particles placed in semicrystalline polymer matrix can play a role to facilitate crystal nucleation, resulting in drop of toughness.[4]

As an alternative in toughening of polymer, it has been considered to modify chemical structure of polymers to allow polymer chains to dissipate external stresses. A glassy polymer would exhibit various relaxations at temperatures below the glass transition temperature, T_g. These are referred to as secondary relaxations, of which motions are much more localized than those involved in the glass transition. It is generally recognized that secondary relaxations are closely related to mechanical properties, such as ductility and toughness.[5−9] The onset of ductile behavior in tensile tests is correlated with secondary relaxation temperature for bisphenol A polycarbonate (BPA-PC).[10] The secondary relaxation process is believed to involve cooperative chain rearrangements that alter the local volume or shape of the glass and so can relieve stress concentration quickly.[11] On dynamic mechanical spectroscopy, ductile BPA-PC shows secondary relaxation slightly above −100 °C at 1 Hz, while its relative, 3,3′,5,5′-tetramethylbisphenol A polycarbonate (TMBPA-PC), which is more brittle than BPA-PC, presents the secondary relaxation peak around 70 °C at 1 Hz. By investigating copolymers made from these two homopolymers with very different secondary relaxation temperatures, Jho and Yee[12] and Xiao and Yee[13] were able to estimate the extent of the cooperativity producing secondary relaxation. The extensive cooperative motion seems more reasonable for providing the large-scale relaxations conductive to ductile behavior and can be used to explain why TMBPA-PC is not as ductile as BPA-PC. The transition from brittle fracture to ductile yielding in poly(vinyl chloride),[14] amorphous poly(ethylene terephthalate) (PET),[15] and poly(2,6-dimethylphenylene oxide)[15] has been also linked to a major secondary relaxation.

Nearly all the ductile polymer exhibit pronounced secondary relaxations in their dynamic mechanical spectra. However, not all polymers with large secondary relaxation peaks are ductile, and a clear explanation of how the secondary relaxation affects toughness has not been given. A series of previous studies have been done to determine only which molecular groups are involved in the relaxation as well as its nature.[12,13,16−19]

Poly(ethylene terephthalate) (PET) is highly valuable in commercial applications as fibers and films. Despite its extensive use, PET has been long considered to be unsuitable as a thermoplastic molding resin due to the relative brittleness of thick sections when crystallized from the melt. Recent investigations concerning im-

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10.1021/ma034660a CCC: $25.00

Table 1. Characteristics of Polymers Used in This Study

designation	CHDM content (mol %)[a]	M_w (g/mol)[b]	T_g (°C)[c]
PET	0	42.5K	80.0
PECT31	31	44.9K	82.2
PECT62	62	46.2K	87.3
PECT81	81	41.8K	89.4
PCT	100	30.5K	91.6

[a] The composition of PECT copolymers was identified through FT-NMR using deuterated tetrafluoroacetic acid as solvent. [b] The supplier provided the data for molecular weight. [c] The glass transition temperature was obtained on DSC with a heating rate of 10 °C/min after quenching from the melt state.

provement of toughness in PET have been mainly focused on incorporation of secondary component such as thermoplastics or inorganic fillers.[19−21] Poly(1,4-cyclohexylene dimethylene terephthalate) (PCT) is a new class semicrystalline polyester consisted of terephthalic acid and 1,4-cyclohexanedimethanol (CHDM). When the Izod impact test was conducted for copolymers of PCT and PET, the decrease of ductile−brittle transition temperature was observed with increasing content of CHDM.[4,22] Recently, it has been reported that the shift in the ductile−brittle transition temperature is strongly correlated with an increase in the molecular motion associated with the secondary relaxation.[22] The secondary relaxations of glassy copolymers of PET and PCT involve cooperative motions of the cyclohexylene rings, which gives rise to long-range motions creating significant volume fluctuations that can facilitate macroscopic shear yielding. That is, the motions imparted by the CHDM linkage are expected to facilitate the yield process and bring about the shift in the ductile−brittle transition. At the study about micromechanical behaviors of modified BPA-PC and TMBPA-PC, in which cyclohexylene linkages are incorporated, Liu and Yee[23] extended the usefulness of cyclohexylene linkages as molecular motion activator and intrinsic toughener. Heijboer's early study about the secondary relaxation of poly(cyclohexyl methacrylate) showed that the cyclohexylene ring is capable of chair−chair conformational transition,[16] whose temperature is located around −100 °C.

In this report, the thin films deformation behaviors of PET and PCT homopolymers and their copolymers are extensively examined in terms of the content of cyclohexylene linkage and the temperature dependency on transmission electron microscopy, to obtain visual evidences about the role of cyclohexylene linkage as intrinsic toughener and construct a deformation map which would be highly useful in estimating mechanical properties of copolymers or polymer blends of any composition.

Experimental Section

Materials. The polymers for this study were kindly supplied by Eastman Chemical. The details for the polymers used are described in Table 1. To remove any impurities and additives, all the polymers were purified by way of dissolution/precipitation. As solvent and nonsolvent for washing, a mixture of phenol/1,1,2,2-tetrachloroethane with 70/30 by weight and 2-propanol were used, respectively. Finally, the crude product was washed with hot 2-propanol in Soxhlet apparatus for 6 h and dried in vacuo for 24 h at 120 °C.

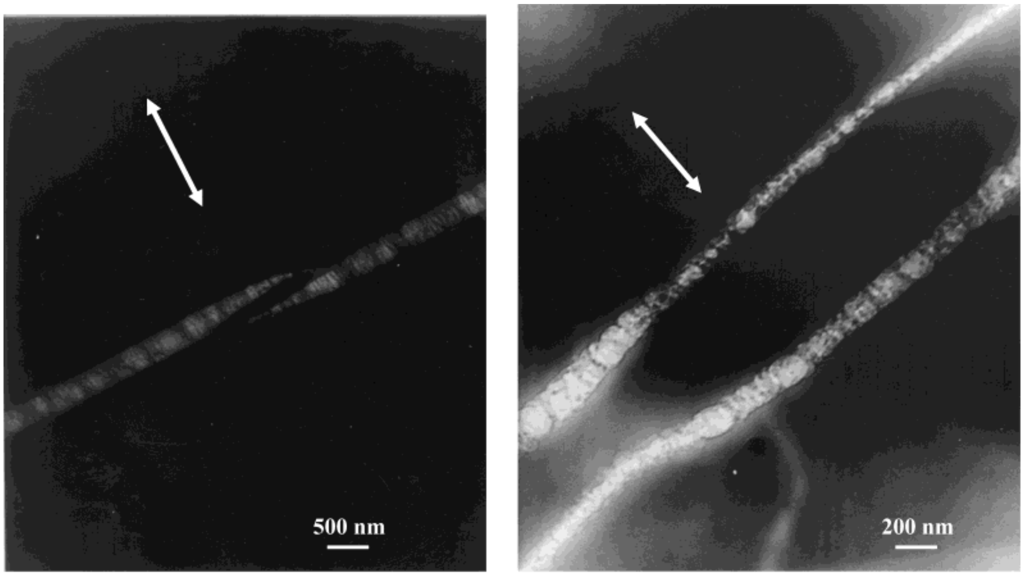
Thin Film Deformation and Testing. To investigate the role of conformational transition of cyclohexylene ring in the deformation behavior, the thin film technique established by Lauterwasser and Kramer was applied.[24] A polymer was dissolved at room temperature in 1,1,1,3,3,3-hexafluoro-2-propanol, and thin films of about 200 nm in thickness were prepared by drawing glass slides at a constant rate out of the polymer solution. After drying, the films were floated off the glass slides on a water bath and picked up on copper grids, whose grid bars were previously annealed under vacuum to sinter the grids and to increase their ductility and coated with a thin layer of polymer that acts a bonding medium between the copper grid and the film. Then, to remove any wrinkle and residual solvent and ensure bonding between grid and film, they were heated for 1 min under vacuum at T_g. After bonding, the films were vacuum-dried for 24 h at the temperature far below each T_g to avoid the possibility of crystallization. In fact, while PET films can be made as fully amorphous state with precise care, it was impossible to obtain PCT films without any crystalline phases, since PCT has a strong tendency to crystallize—a much higher rate of crystallization than that of PET. On the other hand, because of the coexistence of two kinds of diol repeating units, crystallization of copolymers is severely hindered, resulting in amorphous polymers.

Using an Instron CW-2149, a horizontal mechanical tester equipped with double hydraulic actuators, connected to MTS 410 function generator, and environmental chamber, the films were strained at a rate of 4.0×10^{-4} s^{-1}, which corresponds to about 0.1 Hz of oscillation frequency in the DMTA test.[17] Temperature was varied from −130 to 60 °C in each specimen by introducing liquid nitrogen into environmental chamber. In the case of cryogenic experiment, it is common to have a very rapid temperature gradient in an extremely small area. To control temperature as precisely as possible, therefore, two identical specimens were prepared, one for straining and the other as a dummy bearing a thermocouple to monitor temperature change, and they were placed side by side in the environmental chamber. The straining experiment was monitored through optical microscopy, and the final strain was obtained from the deformation of each square of copper grid. The individual film squares of the grid were then inspected with an optical microscope, and a typical square was selected for examination by transmission electron microscopy. The accelerating voltage was 100 kV, and to obtain artifact-free micrographs, the spot size was chosen so that only the field of view was irradiated at the desired magnification and intensity. After focusing, the specimen was slightly displaced and an adjacent fresh portion of the specimen was photographed.

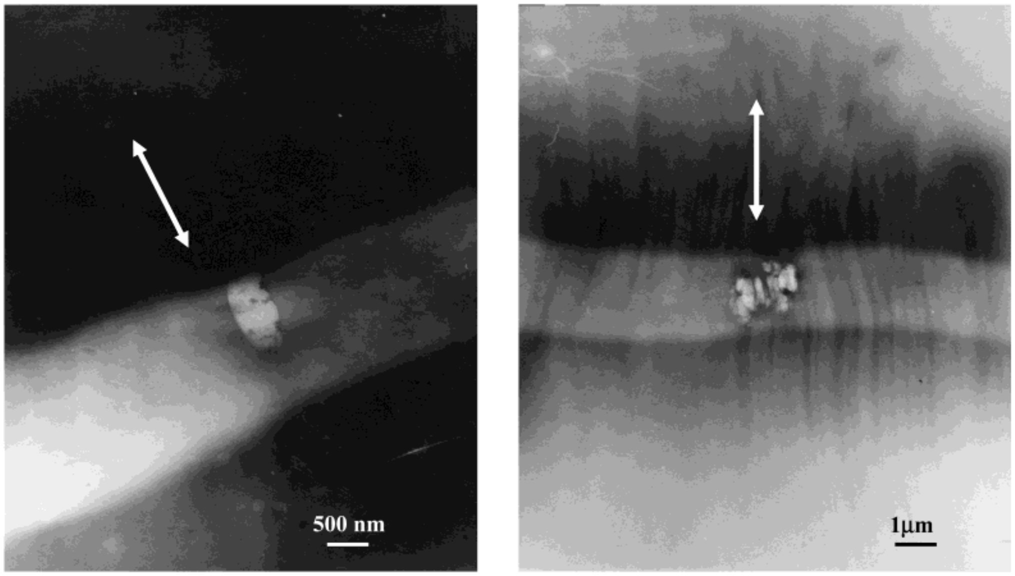
Results

Transmission electron micrographs in Figure 1 show the deformation mode of thin films at room temperature. As appeared in each electron micrograph, the deformation mode was varied with the content of CHDM. Figure 1a is a micrograph for amorphous PET subject to uniaxial tension and showed well-developed fibrillations and midribs, which are regarded to be characteristic of crazing failure.

When the content of CHDM incorporated in the PECT copolymers reached 31 mol %, as shown in Figure 1b, the deformation mode appeared to change as a mixed mode of crazing and deformation zone (DZ), which are thin film analogue of necking in bulk samples. Although crazing was dominant as ever, the development of fibrillation became coarser, and DZ generally restricted to the craze−bulk interfaces were observed. As the content of CHDM increased further beyond 50 mol %, the transition of the dominant deformation mechanism from crazing to localized DZ was found. The aspect ratio of regions that were locally deformed was highly reduced, and disappearance of fibrillated structure and midrib was observed, as shown in the micrographs of PECT62 and PECT81 in Figure 1. Consequently, it can be said that at room temperature the PECT copolymers with high content of CHDM is likely to be deformed by



(a) PET (b) PECT31



(c) PECT62 (d) PECT81

Figure 1. Thin film deformation microstructure in (a) PET, (b) PECT31, (c) PECT62, and (d) PECT81 obtained at 25 °C. Note the well-developed fibrils typical for crazing of (a) and the increasing tendency of the DZ as the CHDM content increases. The arrow represents the direction of extension.

shear deformation, whereas PET exhibits failure by crazing.

When test temperature was dropped to −100 °C, in amorphous PET thin film, failure by crazing was retained (Figure 2). On the other hand, all the copolymers underwent a change in the deformation behavior with decreasing temperature. In the range between −20 and −50 °C thin film of PECT62 showed that, as shown in Figure 3a, DZ became smaller and rather localized. Moreover, in Figure 3b of PECT62 strained at −100 °C it was demonstrated that a transition of deformation mode from localized DZ to crazing occurred between −70 and −90 °C. As found in Figure 4, PECT81 also showed the same transition of deformation mode in the similar temperature ranges; while shear bands seemed dominant up to −50 °C, long and high-aspect-ratio crazes were observed below −90 °C, and DZ was no longer visible. As shown in Figure 5, however, for PCT crazes did not occur until −110 °C, which is below the onset temperature of secondary relaxation of PCT, and even below that temperature, continued to be in competition with localized DZ.

In Figure 6, a summary of these results is presented in the form of a deformation map in which the observed deformation mechanisms are given as a function of temperature and cyclohexylene group content. As shown, DZ is a favorable deformation mechanism as the content of CHDM or temperature increases.

Discussion

On a microscopic level, brittle failure is often associated with crazing while ductile failure is associated with shear yielding. The ultimate mode of failure is then the result of a competition between yielding and crazing. Many studies have been conducted on the crazing,[25,26] and it has shown that the craze is deeply correlated to

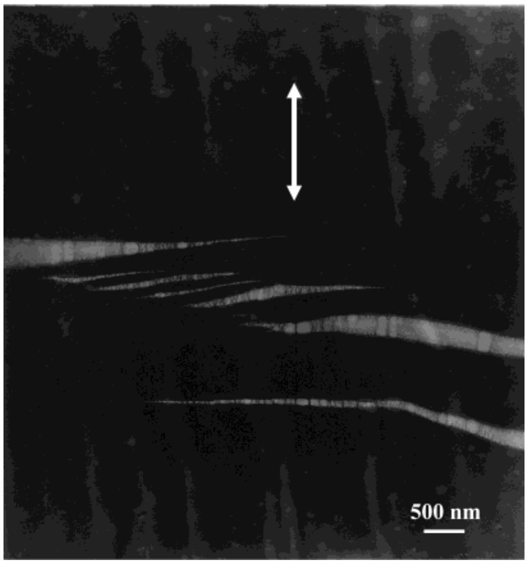
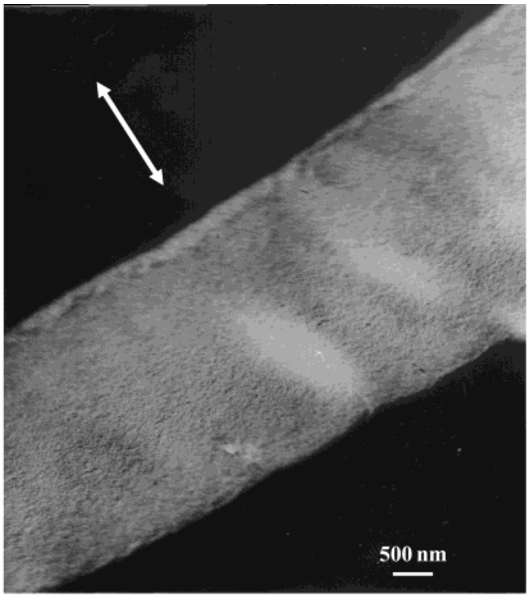


Figure 2. Thin film deformation microstructure in PET strained at −100 °C. The arrow represents the direction of extension.

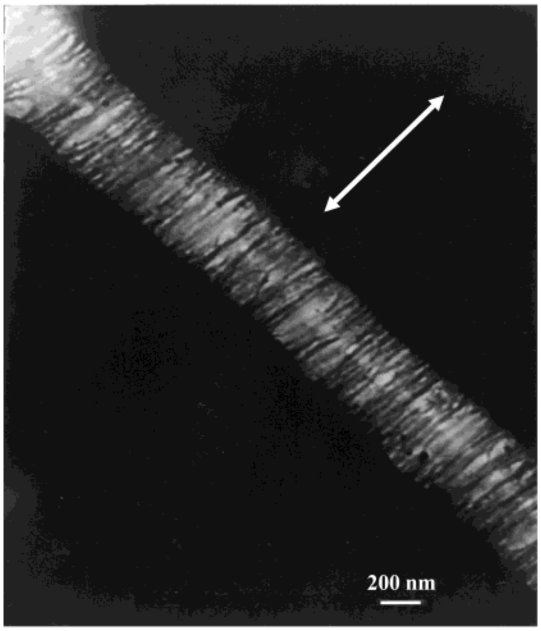
entanglement, which refers to the degree of topological constraint on relative chain motion, and it was demonstrated that the yield−craze transition could be understood in terms of the relative ease of shear yielding vs crazing, as entanglement density is changed.[27] Furthermore, it has been generally known that the deformation mode would be highly affected by test temperature.[28−30]

The entanglement density ν_e can be obtained from the rubbery plateau modulus $G_N°$ by treating the small strain response in the regime of rubberlike behavior just above T_g. Fetters et al. presented that the packing length density p controls the entanglement density, and from the values of p in the literature $\nu_e = 2.4 \times 10^{26}$ m^{-3} for PET was obtained.[31] For PECT62 the dynamic viscosity measurement in our lab produced $G_N° = 1.4$ MPa,[32] corresponding to $\nu_e = 2.8 \times 10^{26}$ m^{-3}. Given the uncertainty, this result tells us that the entanglement density would not be varied significantly with the concentration of cyclohexylene linkage. Therefore, the prevailing discussion of entanglement about the competition between crazing and shear yielding cannot explain the ductility change with the content of cyclohexylene linkage, and it is demanded to suggest an alternative mechanism to elucidate the higher ductility of PCT.

The Role of Cyclohexylene Linkage. It is generally recognized that localized molecular motions of polymer chain along a few repeating units affect macroscopic mechanical properties, although the specifics of this relationship are not well-defined. The typical example for the correlation was established on the basis of the observation that ductile materials such as BPA-PC have pronounced secondary loss peaks in their dynamic mechanical spectra.[6−9] Also, brittle−ductile transition temperatures were often correlated to secondary relaxation peak temperatures. The work of Plummer et al.[33] about the microdeformation mechanism in methyl methacrylate−glutarimide random copolymers demonstrated that in addition to the entanglement density, which has been considered to be a primary parameter in microdeformation mechanism, chemical modification can influence the competition between shear and crazing in thin films and the macroscopic behavior.



(a) PECT62 at –40 °C



(b) PECT62 at –100 °C

Figure 3. Change of thin film deformation microstructure in PECT62 as temperature decreases: strained at −40 °C (a) and at −100 °C (b), which show a transition of the microdeformation mode from DZ to crazing. The arrow represents the direction of extension.

DMTA spectra in Figure 7 demonstrated that the secondary relaxation of PCT occurs with a higher energy loss than that of PET, and the secondary relaxation temperature of PCT is close to that of the transition of the thin film deformation mode. In the study by Chen et al.,[22] comparison of the secondary loss peaks and activation energies by dynamic mechanical spectroscopy between the PECT copolymers and poly(cyclohexyl methacrylate) and poly(1,4-cyclohexylenedimethylene 2,5-dimethyl terephthalate) demonstrated that secondary relaxation of the PECT copolymers involves motion of the cyclohexylene ring, which is suppressed below ca. −80 °C. They postulated that two neighboring cyclo-

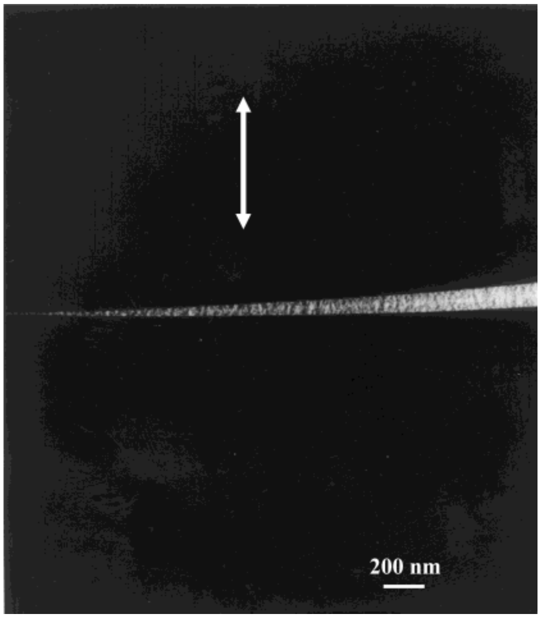


Figure 4. Thin film deformation microstructure in PECT81 strained at −100 °C, which show a transition of the microdeformation mode from DZ to crazing. The arrow represents the direction of extension.

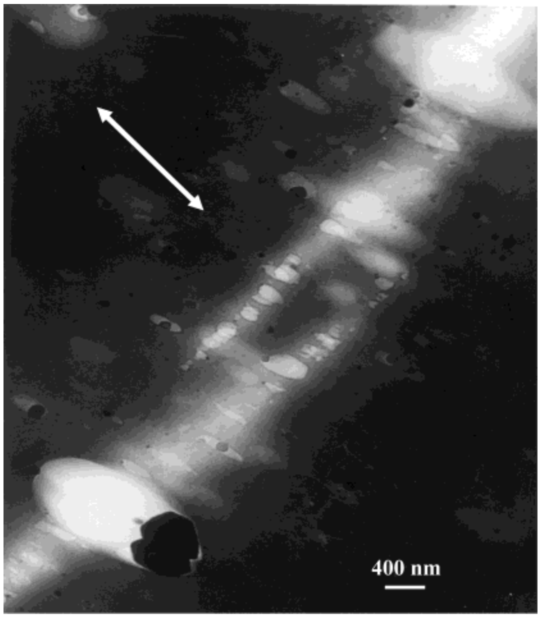


Figure 5. Deformation microstructure of PCT thin film strained at −110 °C. The arrow represents the direction of extension.

hexylene linkages could cooperate in affecting a conformational transition, which would consequently lead to a high level of chain mobility. This postulate was strongly evidenced by ^{13}C NMR experiments.

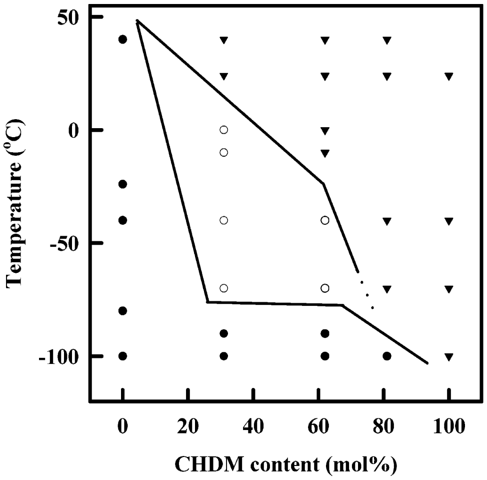


Figure 6. Deformation map for PET, PCT, and their copolymers. Note the dominant mode of deformation determined at each test temperature marked as (●) for crazing, (○) for mixed deformation of DZ and crazing, and (▼) for DZ.

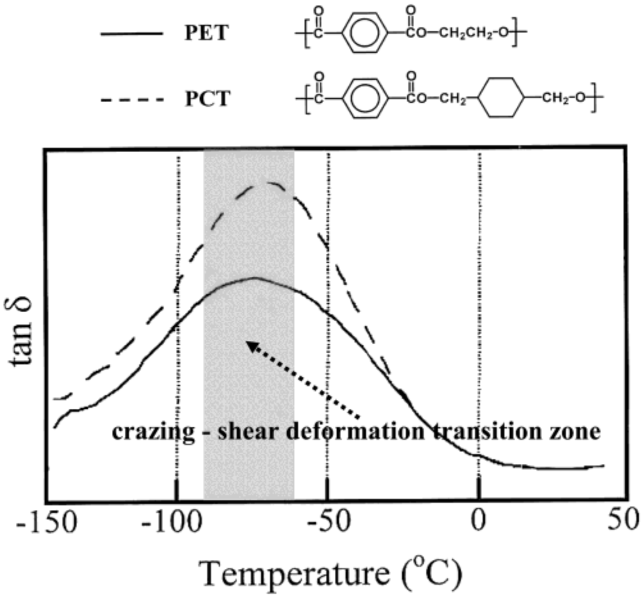


Figure 7. Secondary relaxation behaviors of PET and PCT obtained on DMTA at 1.0 Hz.

As found in the deformation map for PET, PCT, and PECT copolymers in Figure 6, PET thin films were deformed by only crazing in the whole range of test temperature. On the other hand, the PECT copolymers showed a distinct change in microdeformation behavior when temperature varied. Transition of microdeformation mode from shear deformation to crazing occurred in the range of −70 to −90 °C, which coincided well with the temperature range of secondary relaxation involving the conformational change of cyclohexylene ring. On the basis of these findings, it is allowed to speculate that if temperature decreases as low as the conformation transition of cyclohexylene ring is suppressed, the PECT copolymers would be failed in brittle mode rather than ductile deformation. The results in the deformation map also correspond to the previous results[22,23] concerning the effect of the conformational transition of cyclohexylene ring and are strongly supportive to the ductile−brittle transition in terms of CHDM content in the PET/PCT system.

The motions of the rings corresponding to conformational transition give rise to small translational motions of adjoining terephthalate units such as in Figure 8. The cyclohexylene motions are also likely to behave cooperatively, giving rise to a long-range motion along the polymer chain that create greater volume fluctuations. We believe this volume fluctuations can have a large effect on the competition between shear yielding and crazing.

By the way, it was previously reported that crazing appears to be prevented by strain-induced crystallization.[34] Because of the great tendency of PCT to crystal-

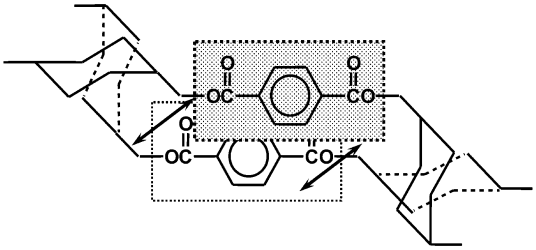


Figure 8. Schematic representation of translational motion of terephthalate moiety induced by cooperative conformational transition of adjoining cyclohexylene linkages (from Figure 13 in ref 22).

lize, it was impossible to obtain a perfectly amorphous thin film. Therefore, that PCT showed the suppression of disentanglement even below secondary relaxation temperature can be partly interpreted as a result of the hindrance of craze formation by the crystalline phase.

Conclusions

The temperature-dependent behavior of PCT/PET copolymers has been investigated with variation of cyclohexylene unit content. The results are summarized as follows:

1. PET and copolymers with low content of cyclohexylene linkage showed crazing failure, whereas a transition from crazing to localized shear deformation occurred as the content of cyclohexylene linkage increased.

2. When temperature was changed, polymers containing a cyclohexylene linkage showed a transition of the deformation mode from shear deformation to crazing, while no change in the deformation mode was observed in PET.

3. These facts in the deformation behavior are attributed to the conformational transition of a cyclohexylene ring.

4. While it can be referred that the entanglement density usually governs the deformation mode determined by the thin film test, it is necessary to consider the molecular motion correlated with secondary relaxation of the polymeric main chain.

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MA034660A