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Effect of Local Conformational Transition on Craze Initiation in Polyestercarbonates Containing Cyclohexylene Linkages

Jianwei Liu and Albert F. Yee*

Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136

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ABSTRACT: Measurements of craze stresses and impact strengths have been performed on specially designed polyestercarbonates with 1,4-cyclohexylene linkages synthesized in our laboratory. The copolymers became more craze resistant as the cyclohexylene content was increased. On the other hand, the activation volumes of these copolymers, as calculated from the Eyring model for plastic yielding, greatly increased with increasing cyclohexylene ring content. We hypothesize that the conformational transition of cyclohexylene rings can enhance polymer chain mobility and therefore distribute strain over a larger volume. A mechanism is proposed for craze initiation: high chain mobility due to conformational transitions helps to collapse nanovoids that are precursors to stable craze nuclei and increases the stress necessary for the formation of stable nuclei in craze initiation.

Introduction

Extensive research has been conducted on crazing behavior of glassy polymers in the past two decades because, in all high molecular weight thermoplastic polymers, fracture is always preceded by crazing.[1] The occurrence of crazes in polymers can be divided into three stages: initiation, propagation, and breakdown.[2] Most of the previous research focused on the second stage because the process of craze propagation can be monitored directly using optical microscopy, scanning electron microscopy, transmission electron microscopy, low angle electron diffraction, or small-angle X-ray scattering methods.[3−6] The most widely accepted model of craze propagation is the meniscus instability model. However, there is still no general consensus as to the precise nature of the very first stage, i.e., craze initiation, since it is very hard to capture a nanoscopic, localized event. On the basis of the common recognition that cavitation must occur in craze initiation, several models were proposed using dilative stress criteria for crazing.[7−12] However, none of these models provide the details of the molecular process of nanovoid formation. Among these models, Argon's received much attention. He proposed[10] that nascent voids with diameters of about 10 nm may first occur in the material because of chain scission due to mechanical stress. Furthermore, he regarded voiding as a stress-dependent kinetic process. The core of his model assumes that nascent voids can plastically expand as the stress in the surrounding material is elastically unloaded. Kausch proposed another model in which unstable nanovoids could be formed by decohesion of molecular coils in regions of low entanglement, and anelastic deformation of adjacent molecular coils, which are more entangled, will stabilize the nanovoid.[13] This model takes the structure of the condensed glassy state into account. We consider Kausch's supposition about the formation of nanovoids to be quite reasonable because the energy to separate molecular chains bonded by the van der Waals interaction is much smaller than those with covalent bonds. Consequently, plasticity need not be involved at the earliest stage of craze initiation since the local strain is small. Furthermore, the nanovoids must be stabilized before they can grow in size and form crazes. The stabilization of nanovoids is a kinetic process that is closely related to dynamic mobility of polymer segments. We shall attempt to support this assertion in the Discussion.

It is widely accepted that hydrostatic tension must be involved in the crazing process. Hydrostatic tension can result, for example, from loading a specimen in tension or a cracked specimen in mode I. In the case of a material capable of some plastic yielding at the crack tip, the maximum hydrostatic stress caused by plastic constraint can be calculated from Hill's slip-line field theory.[1,12] By assuming that the molecular motions involved in the relaxation of the local hydrostatic stress are the same as those involved in shear yielding, most of the molecular characteristics responsible for yielding would then also affect stress relaxation in the craze initiation process. The duality of crazing and yielding effects of molecular relaxations has been hinted at by describing crazing and yielding as competing processes in the literature. Yielding behavior involves chain segments slipping past neighboring chain segments through large-scale cooperative motions. The more molecular segments participate in this motion, the more delocalized the strain is in the yielding process. We have demonstrated this concept in previous papers.[14−16] While there is no quantitative method to measure how many molecular units are involved in this process, we can consider the "activation volume" from Eyring's yield model to be a parameter that can indicate the size of the mobile units. Eyring's model describes yielding as a stress-biased two-potential-well flow process. An applied external stress σ upsets the equilibrium and shifts the activation barrier between the two potential wells by an amount $\sigma_y V_{act}$, thus favoring the probability of populating one well over the other. V_{act} is the so-called activation volume in this flow process. It was originally used to describe the volume that encompasses the spatial scale of the movement of the chain or chain segment while flowing over the potential energy barrier. If the movement is assumed to involve only one chain, then most of the experimental data produce calculated activation volumes that are too large. For example, Brady and Yeh[17] normalized the activation volume by the repeat unit volume (V_{act}/V_m) for amorphous

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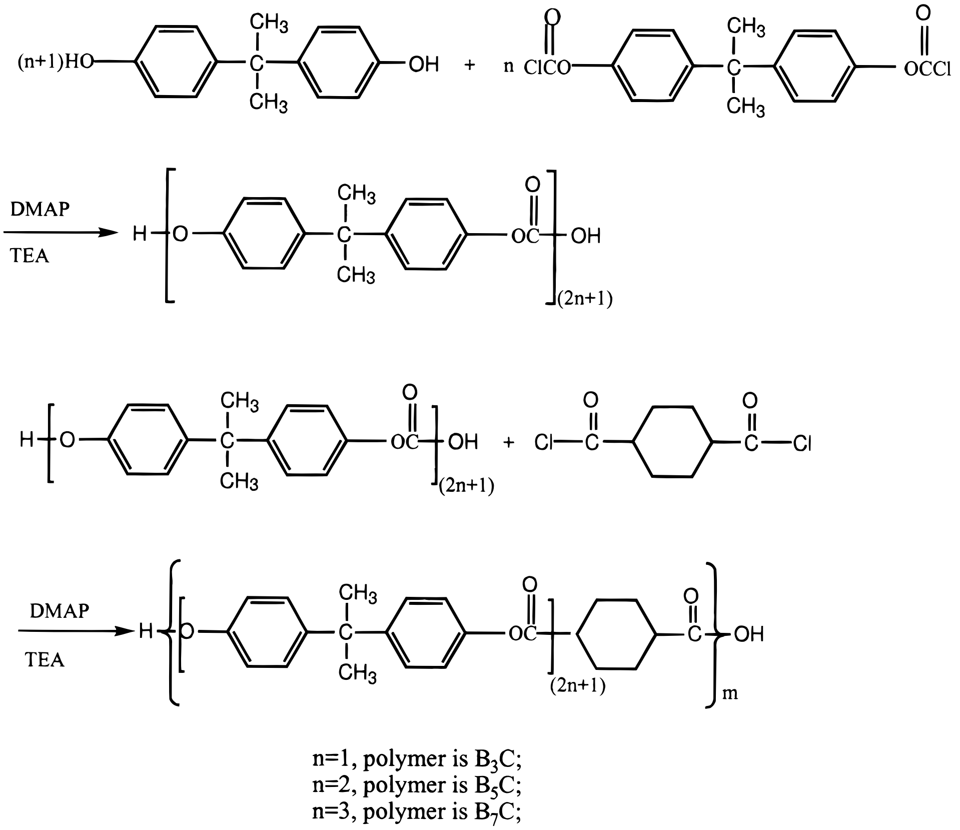
Scheme 1. Synthesis Procedure for B_xC Copolymers



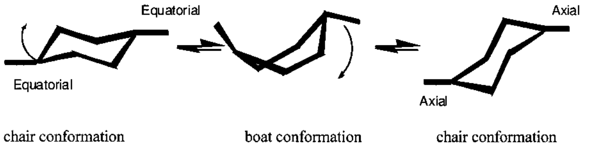


Figure 1. Confromational transition of cyclohexylene ring.

Table 1. Number-Average Molecular Weights (M_n), Polydispersity Indices (PDI) (M_w/M_n) Measured by GPC with THF as Solvent, and T_g's of Copolymers Measured by DSC at a Rate of 10 °C/min

polymers	M_n ($\times 10^4$)	PDI	T_g (°C)
BPA-PC	3.6	2.5	150
B_7C-PEC	3.6	2.3	159
B_5C-PEC	2.8	2.6	161
B_3C-PEC	3.5	2.6	172

BPA-PC, PMMA, and PS and found that these ratios seem unrealistically high (33 for BPA-PC, 10 for PMMA, and 26 for PS). It is hard to imagine how a single molecular unit could move that much during the yielding process. It may be more reasonable to describe the activation volume as the volume of all neighboring chain segments involved in relaxing the stress applied locally at a reference molecular unit. This interpretation of activation volume presents the idea that yielding involves the large-scale cooperative movement of neighboring molecular segments.

As we report in our last paper,[18] the conformational transition of 1,4-cyclohexylene linkages (C-unit) (Figure 1) can enhance polymer chain mobility. In this study, we attempt to discover the effect of large-scale cooperative motions in 1,4-cyclohexylene Bisphenol A polyestercarbonates on their craze initiation process. On the basis of these results, we propose a model of the nucleation process for craze initiation.

Experimental Section

We have shown[18,19] that the incorporation of 1,4-cyclohexylene groups in the polymer backbone can enhance chain mobility due to the coupled chair−boat−chair conformation transitions. In this paper, we further study the effect of this enhanced chain mobility on the craze initiation process. We report on the coefficients of thermal expansion of these Bisphenol A polyestercarbonates since they are a measure of the volume fluctuation.[20] The activation volumes of these copolymers, which indicate how extensively polymer segments are involved in plastic yield, are calculated by measuring yield stresses at various temperatures and strain rates. From the craze stresses obtained, a model on craze initiation is deduced, which gives the reason that chain mobility could retard craze initiation. Furthermore, we report on how the retarded craze initiation affects the notched Izod impact strength.

A. Materials. The synthesis procedure of all of polymers, shown in Scheme 1, was reported in our last paper.[18] The series of alternating block copolymers obtained by this approach were $-(-B_xC-)_n-$, but are denoted as B_xC for simplicity, where B represents Bisphenol A, C represents 1,4-cyclohexylene dicarboxylate, and x represents the average number of repeat units within each block.

The molecular weights (M_n), polydispersity indices (PDI), and glass transition temperatures (T_g) of the synthesized copolymers are listed in Table 1. The polymers were precipitated from dichloromethane solutions, purified, dried, and compression molded into test specimens. Molded specimens were heated to T_g + 15 °C and then quenched to room temperature to erase thermal history. Detailed procedures for specimen preparation are reported in ref 18.

B. Coefficient of Thermal Expansion Measurement. Rectangular specimens of B_xC polyestercarbonates were cut from compression molded samples using a low-speed diamond saw. Their dimensions were about 5.0 mm × 5.0 mm × 1.5 mm (length × width × thickness). The coefficients of thermal expansion were measured at 25 °C using a Perkin-Elmer TMA 7 thermomechanical analyzer with a temperature sweeping rate of 1 °C/min.

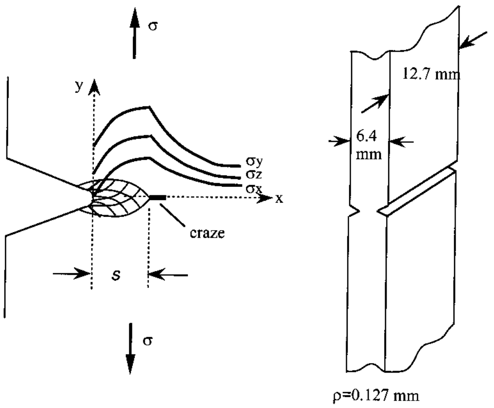


Figure 2. Schematic drawing about the triaxial stress state at notch tip and the geometry of the test sample.

C. Yield Stress at Various Temperatures and Strain Rates. The temperature and strain rate dependencies of the yield stress were determined by performing a series of tensile tests on the B_xC polyestercarbonates using a servohydraulic testing machine (Instron model 1331) equipped with a temperature chamber of ±1 °C stability. The dog-bone-shaped tensile bars for the polymers were compression molded at temperatures 70 °C above their respective T_g's and quenched down to room temperature. The specimens were then polished using fine grit sand paper. Prior to the measurements, the specimens were placed back into the mold and heated to 15 °C above their respective T_g's for 15 min to erase any thermal and mechanical history, before being quenched back down to room temperature. The dimensions of the specimens were 50 mm × 3 mm × 3 mm (length × width × thickness). The gauge length was 12.7 mm.

The tensile specimens were tested at three temperatures −10, 0, and 60 °C and at strain rates between 0.000 33 and 0.026 s^{-1}. The yield stresses were based on the original cross-sectional areas of the specimens and are therefore nominal stresses. The data are presented as plots of nominal yield stress/T vs ln(strain rate) for the temperatures tested. The activation volumes were obtained by the modified Eyring equation:[21,22]

$$\frac{\sigma_y}{T} = \frac{\Delta H}{V_{\mathrm{act}} T} + \frac{R}{V_{\mathrm{act}}} \ln\left(\frac{2\dot{\epsilon}}{\dot{\epsilon}_0}\right) \tag{1}$$

where σ_y is the engineering yield stress, V_{act} is the activation volume, ΔH is the activation energy, $\dot{\epsilon}$ is the testing strain rate, and $\dot{\epsilon}_0$ is a strain rate constant.

D. Craze Stress Measurement. Polymers that can yield in uniaxial tension can be made to craze by imposing a larger hydrostatic tension than possible with uniaxial tension alone. The larger hydrostatic tension can be created by taking advantage of the plastic constraints that arise near the tip of a blunt notch in a thick specimen.

Rectangular specimens of the B_xC polyestercarbonates with dimensions of 76.2 mm × 12.7 mm × 6.4 mm (length × width × thickness) (Figure 2) were cut from compression moldings as described in section B. The rectangular bars were then notched using a TMI notch cutter. Double V-notches of 0.127 mm (0.005 in.) radius were introduced to each long side of the cross section at a depth of 1.3 mm (0.050 in.) as shown in Figure 2. To minimize plastic deformation while cutting the notches, cold N_2 gas was blown into the notch area during cutting.

The test specimens were stretched in the longitudinal direction at a cross-head speed of 254 mm/s. All tests were performed at ca. 23 °C. The gage length of the crazing specimen was 25.4 mm long, so the average strain rate outside the notches is approximate 10 s^{-1}. This relative high strain rate was necessary to cause all the specimens to craze at this temperature. The fracture surfaces were examined using an SEM (Hitachi S800) to determine the craze nucleation site.

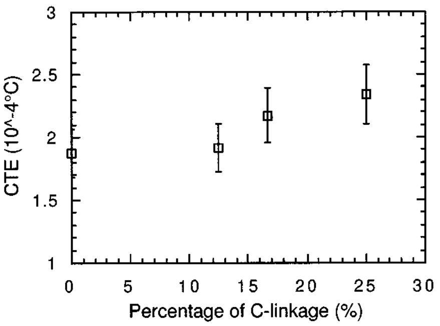


Figure 3. Coefficients of thermal expansion of B_xC at 25 °C.

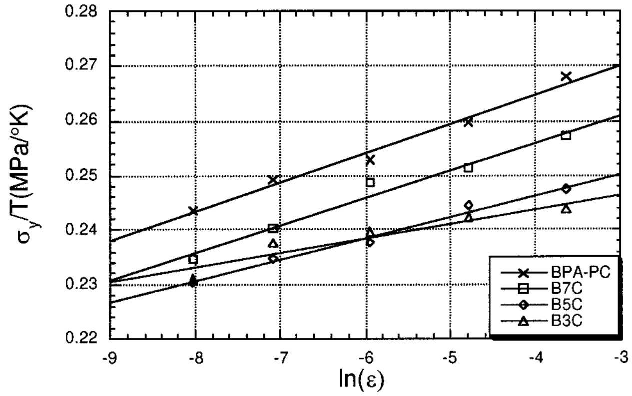


Figure 4. σ_y/T vs ln(ϵ) at −10 °C.

Calculations of the craze stress required determining the yield stress σ_y at comparable strain rates. Values of yield stress at a comparable strain rate of 10 s^{-1} were found from the σ_y vs ln(strain rate) master curves obtained from the yield stress test.

E. Izod Impact Test. Rectangular specimens of the B_xC polyester carbonates with dimensions of 63.5 mm × 12.7 mm × 6.4 mm (length × width × thickness) were cut from compression moldings as described above. The specimens were then notched using a TMI 22-05 notching cutter and tested at 23 °C using a Wiedemann Baldwin impact tester following the ASTM D256, test A procedure.

Results

A. Coefficient of Thermal Expansion. The coefficients of thermal expansion (CTE) of BPA polyester-carbonates at 25 °C are shown in Figure 3. The segmental motions of B_x-blocks and C-units are quite rapid at this temperature.[18] The increase of CTE with increasing 1,4-cyclohexylene content is consistent with the notion that larger volume fluctuation is introduced by the incorporation of C-units. This is consistent with the conclusion we drew[18,19] about the increase of chain mobility with C-unit content in these copolymers.

B. Activation Volume. As we discussed in the Introduction, the calculated value of activation volume describes the volume of the polymer segments involved in relaxing the stress applied locally at a certain molecular unit, causing yield to occur, and the process probably involves more than one chain. The more molecule segments participate in this process, the more the strain can be dispersed.

Figures 4, 5, and 6 show the strain-rate effect on yield stresses of B_xC at −10, 25, and 60 °C. These results indicate that the larger the 1,4-cyclohexylene content, the less strain-rate-sensitive the yield stress of the copolymer becomes. One may think of this as a result of the larger activation volume caused by the incorpora-

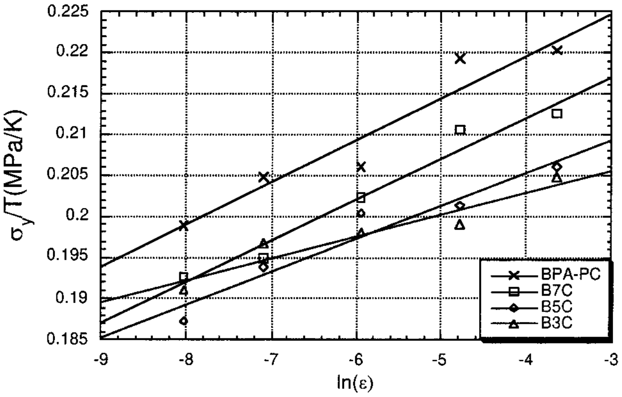


Figure 5. σ_y/T vs ln(ϵ) at 25 °C.

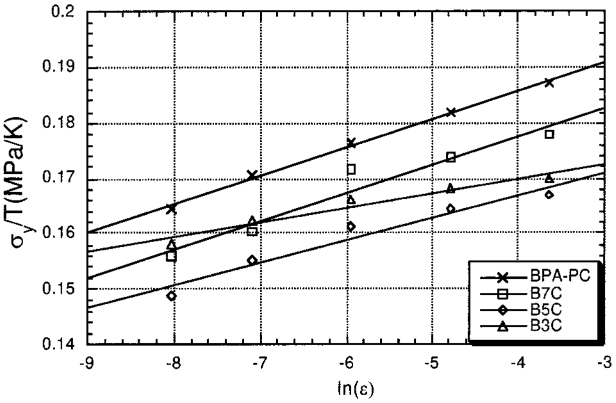


Figure 6. σ_y/T vs ln(ϵ) at 60 °C.

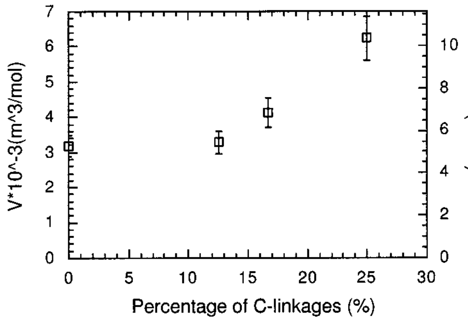


Figure 7. Activation volume of B_xC.

tion of 1,4-cyclohexylene linkages (Figure 7). The conformational transition of a given C-unit requires a large scale of cooperative motions, which was also observed by Chen et al.[19,23] in a series of PET/PCT copolymers. Evidently, this facilitates the shear yielding process.

It may also be noted that the yield stress data of B_3C cross over those of B_5C at low strain rates. From eq 1, the stress bias effect is reduced as strain rate is lowered. In other words, activation energy (ΔH) is dominant in the yielding process at low strain rates. This is the cause for the high yield stresses of B_3C at low strain rates, since in B_xC copolymers, ΔH increases with the content of C-unit, as shown in Figure 8. In addition, the activation energy may be further increased if a cooperative conformational transition begins to be involved. As we described in ref 18, the conformational transition of a 1,4-cyclohexylene ring forces its neighbors to move excursively. When the block between two neighboring C-units in the same chain is short and rigid, it is obvious that the independent conformational transition of cyclohexylene rings becomes less likely. On the basis of positron annihilation lifetime spectroscopy (PALS) results and mechanical behaviors of the PET/PCT copolymers, Chen et al. postulated that two neighboring C-units could undergo conformational transition cooperatively when the block between them was short and rigid.[19] As the content of C-units increases in B_xC, blocks between C-units become shorter and less mobile,[15] and consequently conformational transitions of C-units must be more cooperative (Figure 9). Further PALS results to support this explanation will be presented in a following paper.

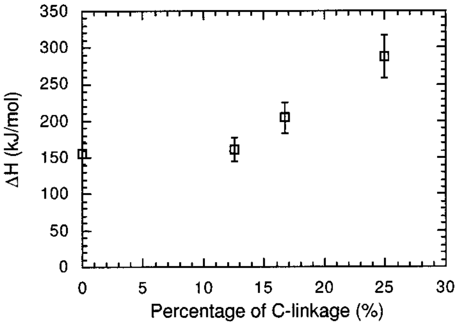


Figure 8. Activation energy of B_xC for yielding according to eq 1.

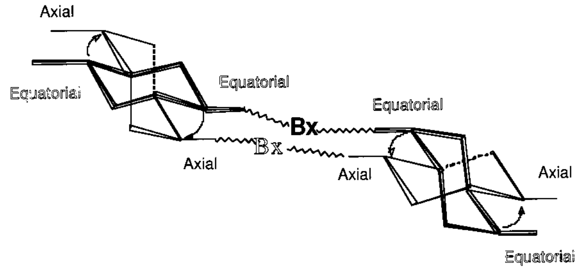


Figure 9. Schematic drawing of the prossible concerted conformational transition of cyclohexylene linkages when B_x-blocks are short. The backbone connectivity is illustrated by labels.

C. Craze Stress. The double-notched specimens depicted in Figure 2 developed slip-line fields ahead of the notches. The slip-line field is visible as a series of intersecting shear bands inclined along slip planes. These propagate ahead of the notch. The slip lines can be described as a logarithmic spiral.[1,12] The elastic material outside the yielded zone provides a constraint to the zone and a triaxial stress state at the elastic−plastic boundary of the material (Figure 2). The stress distribution in the plane strain yielded zone has been described by Hill's slip-line field theory[1,12] which assumes that the material is elastic−perfectly plastic with no strain hardening. In addition, the dilational stress produced by the stress triaxiality at the elastic−plastic boundary is assumed to be responsible for craze and fracture initiation. Hill's slip-line field analysis can be used to calculate the critical hydrostatic stress for craze nucleation, σ_{cr}, by the following equation:[12]

$$\sigma_{cr} = \sigma_p = \tau\left[1 + 2\ln\left(1 + \frac{s}{\rho}\right)\right] \qquad (2)$$

where τ is the shear yield stress, s the distance from the notch tip to the craze nucleation site, and ρ the notch tip radius. The shear yield stress τ can be calculated from the uniaxial yield stress by assuming that the yield criterion of the polymer obeys the von Mises yield criterion, viz. $\tau = \sigma_y/\sqrt{3}$. Studies of plane strain fracture

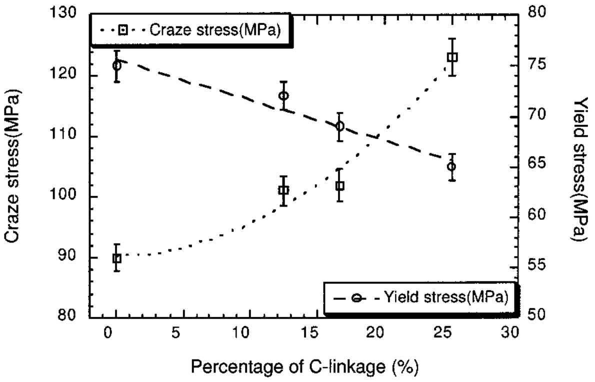


Figure 10. Craze stress and yield stress of B_xC at a strain rate of 10/s.

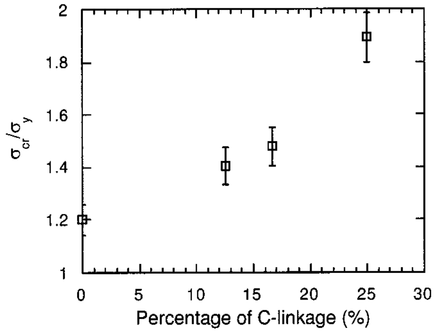


Figure 11. σ_{cr}/σ_y of B_xC at a strain rate of 10/s and room temperature.

of notched, polymer specimens using Hill's slip-line field theory are well documented,[12,24] demonstrating the validity of this convenient method of determining σ_{cr}.

The craze stress and the yield stress at 25 °C and a strain rate of 10/s are plotted in Figure 10. The yield stress values at this strain rate were extrapolated from experimental results at lower strain rates shown in Figure 5. These results show that, with the increase of 1,4-cyclohexylene content in B_xC, the yield stress decreases while the craze stress increases. The correlation that immediately suggests itself is that, as local segmental mobility increases, shear yielding is facilitated while crazing is retarded. Alternatively, this could be explained in terms of increasing the ester content. However, Chen et al.[23] found decreasing yield stress with increasing cyclohexylene content while the ester content remained constant. Their results suggest that the changes in mechanical properties are not determined by the ester content, but rather related to the cyclohexylene content.

The ratio of σ_{cr}/σ_y increases with C-unit content. This ratio is proportional to the size of the yielded zone between the notch tip and the craze initiation point (Figure 11). It should therefore be proportional to the notched Izod impact "strength" when the plane strain condition prevails. As in PET/PCT copolymers (Figure 12) reported in ref 23, the higher the C-unit content in B_xC, the larger the size of yielded zone. The correlation between the ratio of σ_{cr}/σ_y and the C-unit content suggests that a larger yielded zone was formed in B_xC, perhaps due to the cooperative conformational transition of C-units. To develop a larger yielded zone, the craze initiation process must be retarded. The retardation of craze initiation can be explained by the larger thermal fluctuation in the polymer glassy due to the enhanced polymer mobility. This point will be discussed in detail in subsequent sections of this paper.

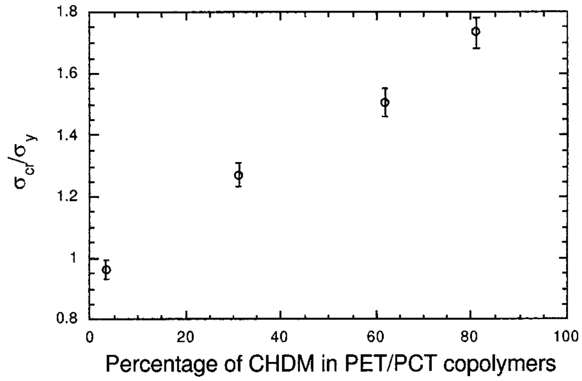


Figure 12. σ_{cr}/σ_y of PET/PCT copolymers at a strain rate of 22/s and room temperature.

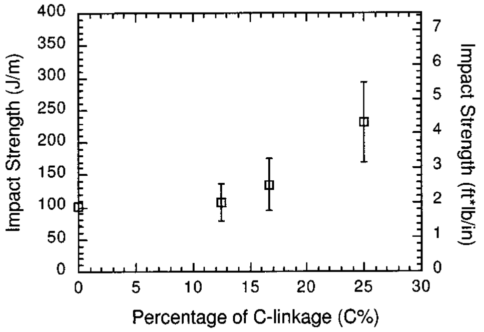


Figure 13. Izod impact strength of B_xC at room temperature, for 0.25 in. thick samples.

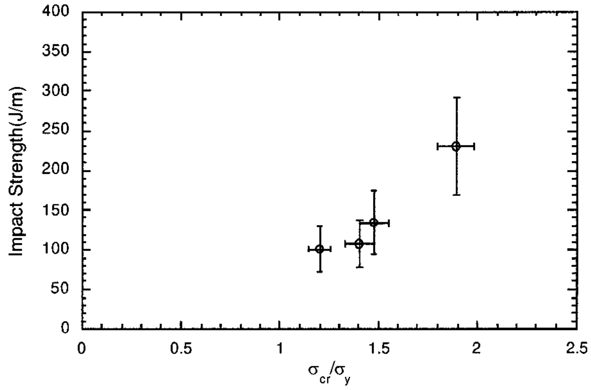


Figure 14. σ_{cr}/σ_y vs Izod impact strength in B_xC.

D. Izod Impact Test. To produce the plane strain condition during fracture, the Izod impact test was performed on $^1/_4$ in. thick specimens. In the $^1/_4$ in. specimens, the impact strength was found to increase dramatically with the C-unit content (Figure 13) because crazing truncates the plastic yield process. σ_{cr}/σ_y was also found to correlate strongly with Izod impact strength (Figure 14). These results are all expected on the basis that increased craze resistance increases the amount of plastic yielding prior to fracture. To our knowledge, these polymers are the only ones ever reported in the literature that show higher notched Izod impact strength values than BPA-PC under predominantly plane strain conditions.

Discussion

From the experimental results presented above, we can clearly see that the cooperative conformational

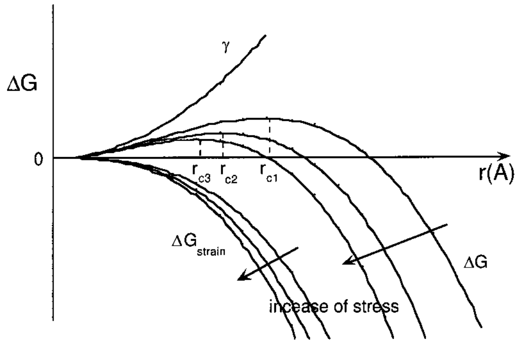


Figure 15. ΔG for the microvoid formation under external stress, where γ is the surface free energy, and ΔG_{strain} is the strain energy relaxed by growing the void. R_{ci} are the critical radii at different stress levels *i*.

transition of C-units correlates with the difficulty of craze initiation. According to a recently proposed mechanism of craze initiation,[23] a nanovoid must be formed and stabilized before it can act as a nucleus for a craze. The following discussion is presented to explore the void nucleation process in polymer glasses subjected to a dilative stress.

The craze nucleation process we envision is similar to the nucleation process of isothermal crystallization in an *undercooled* melt. In the latter, two energy components compete in the nucleation of crystals, assuming that the diffusion of molecules in or out of the nascent nucleus is rapid and not the rate-limiting step. One component is the surface energy, which increases the system energy due to the increase in surface area. The other is the latent heat of crystallization, which reduces the system energy by forming the crystalline phase. The competition between these two components determines the size of the critical nucleus beyond which a crystal will grow. Moreover, this nucleation is also a kinetic process. In this process, density fluctuation from thermal movements of molecules determines how fast a nucleus can be formed or dissolved again. In the craze initiation case, density fluctuation exists in the polymer glass, and when the polymer matrix is subjected to a hydrostatic tension, stresses in the less dense regions are high enough to force the molecule chains to slide apart. Forming such transient voids reduces the strain energy but increases the surface energy of the system. According to Hristov et al., the stabilization of these voids is the necessary condition for the craze initiation process.[23] These stabilized voids, observable by transmission electron microscopy,[2,3] which are several to tens of nanometers in diameter, eventually coalesce to form crazes. The competition between the two energy terms is shown in Figure 15: the new surface free energy, γ, and the relaxation of the strain energy (ΔG_{strain}) by growing the void. Thus, we can introduce the following free energy equation for the formation of a spherical void in a system under hydrostatic tension:

$$\Delta G = \gamma - \Delta G_{\text{strain}} = \Gamma^* 4\pi r^2 - \Delta G_{\text{strain}} \qquad (3)$$

where γ is the surface energy, Γ is the surface tension, and ΔG_{strain} is the released strain energy, which is proportional to the volume of the void and the hydrostatic stress level in the region. In a manner analogous to the nucleation of crystals, a critical void radius r_c must be reached before the void can be stable. r_c is stress-dependent. If the stress level is small, the critical radius for stable void growth will be increased correspondingly (Figure 15). This is consistent with experimental observations which show that craze initiation is easier at higher stresses.[1]

We now elaborate on the possible influence of the local fluctuation due to thermal energy on nanovoid formation. The argument we present above is for an equilibrium system in which craze initiation is discussed as a thermodynamic process. However, there is necessarily a kinetic aspect to craze initiation just as in crystal nucleation. Subcritical nanovoids can be formed and collapsed quickly by molecular fluctuations unless the stress increases even more rapidly. As we showed in the Results section, strain can be dispersed more effectively by incorporating C-units in B_xC copolymers. Therefore, the hydrostatic tension around nanovoids could be reduced. As a result, a higher energy barrier must be overcome before nanovoids can grow. Furthermore, the amplitude of the fluctuation determines the size of the nascent void that can collapse. For a given $r < r_c$, the larger the amplitude of the fluctuation, the more likely it will collapse the nascent void. On the other hand, a craze can be started from a subcritical void as long as it collapses slowly enough relative to the rate of increase of the hydrostatic tensile stress. High segmental mobility, causing large local fluctuation, can prevent this kind of premature craze nucleation. In other words, the local fluctuation, though small in amplitude, could help to restore the system to the energy minimum state if the system is away from the critical region.[20] A nanovoid could collapse much faster with fluctuation. Thus, we arrive at the same conclusion as in the shear yielding case; i.e., if the polymer chains are able to move sufficiently rapidly and extensively to relax the stress applied, then the strain energy could not build up locally. Consequently, the larger the fluctuation, that is, the higher the mobility of the polymer chains,[26] the more difficult it is to stabilize the nascent voids. As a result, the craze initiation process is retarded. The ideas discussed here are also consistent with the fact that the crazing stress for a given polymer increases with temperature.[1] Further studies on the nanovoid formation with the positron annihilation lifetime spectroscopy technique (PALS) will be reported in a following paper.

We now compare our hypothesis with the craze initiation models proposed by Argon[10] and Kausch.[13] Both of these previous models propose the occurrence of nanovoids, although Argon's nanovoids are created by chain scission due to mechanical stress while Kausch's are by density fluctuations. Since chain scission requires more energy than the separation of van der Waals bonds, Argon's model can be easily be modified with no change in the calculation of subsequent void growth. Kausch did not specify whether the density fluctuation is static (i.e., due to the frozen-in, amorphous structure) or dynamic. However, in the temperature range of our investigation, it is clear that there is significant dynamic fluctuation on a local scale. This picture finds support in the use of PALS to study temperature effects on nanovoid expansion in polymer glasses by Hristov et al.[25] It also finds support in the CTE results presented here. The new element introduced in our hypothesis is that dynamic fluctuation can collapse nascent voids if the *rate* of void growth due to the hydrostatic tension is slow compared to the fluctuation time scale and that the fluctuation is directly related to the local segmental motion enhanced by the cyclohexylene linkage. It is important to note that the movement of the cyclohexylene linkage must involve at lease the nearest chain neighbors. This cooperative motion of neighboring chains as well as neighboring segments along the same chain means that the anelastic or plastic (i.e., flow) of neighboring chains with a significantly different time scale from the reference chain is highly unlikely. The local anelastic or plastic deformation do stabilize the nascent voids given sufficiently high stress and time. This explains why copolymers with more molecular fluctuation have higher crazing stress.

The qualitative hypothesis we offer must be verified by a more detailed calculation, an understanding which is well beyond the scope of this paper.

Conclusion

In this paper we show that by CTE measurement a larger local fluctuation is introduced in the B_xC copolymers by the conformational transitions of C linkages. In addition, these transitions cause an increase in activation volume for the yielding process in B_xC, which means that the transitions allow the shear strain to be dispersed over a large volume. Furthermore, results of craze stress measurements suggest that craze initiation is retarded by the incorporation of the C-units. This can also explain why the notched Izod impact strength increases dramatically with the C-unit content. Our results support the notion that craze initiation involves a nanovoid nucleation process. A nanovoid must reach a certain size before it can act as a nucleus for a craze. Moreover, thermal fluctuation, which can be enhanced by the local conformational transition of the C-units, helps to collapse unstable nanovoids and prevents premature craze initiation.

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References and Notes

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