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Effect of the Scale of Local Segmental Motion on Nanovoid Growth in Polyester Copolymer Glasses

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ABSTRACT: We present a study on the effect of the scale of local segmental motion on an important mechanical property of glassy polymers: craze initiation via nanovoid growth. Stress-coupled positronium annihilation lifetime spectroscopy (PALS) is used for this study. A series of polyester copolymer glasses based on poly(ethylene terephthalate) (PET) and poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) are used to vary the scale of local segmental motion. The results show that, in this series of copolymers, nanovoids in the copolymer containing more C-rings have more difficulty in growing. Kinetic analysis suggests that the scale of local segmental motion influences the kinetics in nanovoid growth. Larger-scale local segmental motion results in higher kinetic energy barrier and slower kinetics in nanovoid growth, which might retard craze nucleation and increase craze stress.

Introduction

A. Craze Nucleation and Nanovoid Growth. Crazing is extremely important in the study of fracture in glassy polymers.[1] If we want to understand what gives one glassy polymer a high fracture toughness, but another a low one, we must understand the formation of crazes, which always precede the advancing crack front in a thermoplastic. Extensive research has been conducted on the crazing behavior of glassy polymers over the past three decades. It has been generally recognized[2,3] that there are three stages in the crazing process: nucleation, growth, and breakdown. Most previous research focused on the second stage because craze growth can be monitored directly using optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), low-angle electron diffraction, or small-angle X-ray scattering methods.[4−9] However, very few works have been devoted to the study of the first phase. Consequently, craze nucleation has not been very well understood. For the time being, there is still no general consensus as to the precise nature of craze nucleation, since it is very hard to capture what must be a nanoscopic, localized event. Nevertheless, the importance of craze nucleation in the study of mechanical properties in glassy polymers cannot be overstated, because whether polymers fail in a ductile or brittle fashion is dependent on the competition of the yielding and crazing processes.

Earlier research focused on the macroscopic stress state governing craze nucleation, and several models were proposed using the dilational stress criterion for crazing.[10−16] Among these models, Argon's provides a nanoscale hypothesis.[14] He proposed that voids with diameters of about 10 nm might first occur in the material because of chain scission due to mechanical stress. Furthermore, he regarded voiding as a stress-dependent kinetic process. Kausch[17] 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 nanovoids. This model emphasizes interchain interaction 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 nucleation since the local strain is small. Kramer[9] suggested that there are three types of processes involved in craze nucleation: (1) local plastic deformation by shear in the vicinity of a defect, (2) nucleation of voids to release the triaxial constraints, and (3) void growth and strain hardening of the intervening polymer ligaments as molecular orientation proceeds. In this way the incipient craze structure is stabilized, and the craze can thereafter propagate if appropriate stress conditions hold. It is generally believed[14] that void nucleation is the critical step in this three-stage process.

It was observed[14] that there tended to be a delay in time between the application of a stress and the first appearance of crazing, which suggests the existence of some barrier to craze nucleation. There exists some evidence[18] to show that there is a critical size associated with the critical nucleus. Chen et al. and, more recently, Liu et al.[19,20] proposed a thermodynamic model to further describe craze nucleation. According to this model, a nanovoid must be formed and stabilized before it can act as a nucleus for a craze. They believed that the craze nucleation process is similar to the nucleation process of isothermal crystallization in an undercooled melt. When a polymer is subjected to a hydrostatic tension, chain segments in the less dense regions are eventually able to slide apart. Forming such transient voids reduces the strain energy but increases the surface energy of the system. If the polymer under hydrostatic tension is defined as the system, the free energy for the formation of a spherical void in the system can be expressed by

$$\Delta G = 4\pi r^2\gamma - (4/3)\pi r^3\Delta G_{\mathrm{strain}} \qquad (1)$$

where γ is the surface energy, r is the radius of the nanovoid, and $\Delta G_{\mathrm{strain}}$ is the strain energy per unit volume. The competition between the two energy terms is shown in Figure 1: the new surface energy (γ) and the relaxation of the strain energy ($\Delta G_{\mathrm{strain}}$). Clearly, there is a critical radius (r^*) and the corresponding critical thermodynamic energy barrier (ΔG^*). When the size of a nanovoid is larger than r^*, the void can grow

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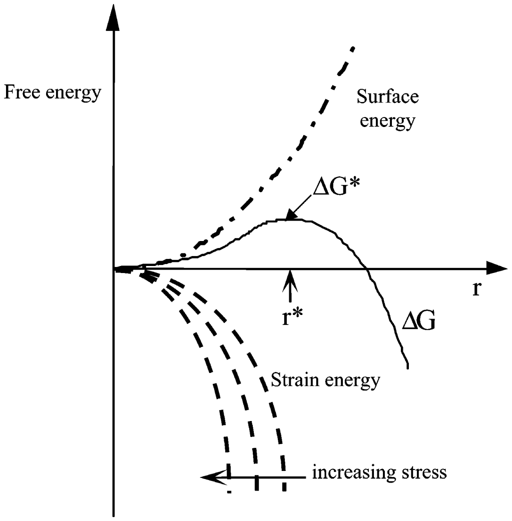

Figure 1. Free energy change in nanovoid growth and craze nucleation.

freely since the free energy will decrease with the void size. However, when the size of a nanovoid is smaller than r^*, the nanovoid growth is a reversible process since the free energy will increase with the void size. Therefore, a nanovoid must grow to a critical size before it can serve as a craze nucleus. This conclusion is strongly supported by experimental results on fatigued polycarbonate (PC) samples.[21,22] In those samples, voids of tens of nanometers in size were observed by TEM; there were no smaller voids. This observation suggests that the lower limit to stable voids, at least in PC, is in the order of tens of nanometers.

On the basis of this thermodynamic analysis, craze nucleation is closely related to nanovoid growth in the subcritical region. Both r^* and ΔG^* are determined by surface energy and strain energy, as shown by the following equations:

$$r^* = 2\gamma/\Delta G_{\text{strain}} \qquad (2)$$

$$\Delta G^* = (64\pi/3)\gamma^3/\Delta G_{\text{strain}}^{\ 2} \qquad (3)$$

This thermodynamic model also predicts the effect of applied strain energy on nanovoid growth. With the increase of applied strain energy, both r^* and ΔG^* decrease. The energy barrier for nanovoid growth becomes smaller, and thus nanovoid growth becomes easier. However, the effect of molecular motion cannot be explicitly explained by this model. Molecular motions affect kinetics in nanovoid growth, while only the thermodynamic factors are considered in this model. The major difference between craze nucleation and crystallization is that, in crystallization, mobility is so high in the melt or solution that thermodynamic factors control the process, while in glassy polymers mobility is very limited, causing kinetic factors to play the decisive role.

B. Measurement of Nanovoid Growth by PALS. In the current research, we take advantage of a relatively new and seldom-used technique to investigate nanovoid growth, positronium annihilation lifetime spectroscopy (PALS). PALS has emerged as a unique and powerful tool for studying the “hole” in polymeric materials.[23,24] PALS can directly measure the lifetime (τ_3) and the relative intensity (I_3) of orthopositroniums (o-Ps).[25,26] I_3 is proportional to the number density of the holes, and τ_3 is related to the spherical radius of the hole (R) by the following equation:

$$\tau_3 = 0.5[1 - R/R_0 + (1/2)\pi \sin(2\pi R/R_0)]^{-1} \qquad (4)$$

where $R_0 = R + \Delta R$. ΔR is the depth of penetration of the o-Ps into the surrounding electron layer and has been determined to be 1.61 Å.[27] The total hole volume V_h is proportional to the product of the relative intensity I_3 and the average hole volume v_h, which is calculated from the spherical radius R:

$$v_h = (4/3)\pi R^3 \qquad (5)$$

$$V_h = C v_h I_3 \qquad (6)$$

where C is a normalization constant. Therefore, the size, intensity, and total volume of nanovoids can be obtained using PALS.

To obtain information on nanovoid growth inside glassy polymers when they are under stress, it is desirable to perform a stress-coupled PALS test. Since experimentally it is very difficult to conduct this test, there have been very few reports.[27-29] Hasan et al.[28] investigated PMMA by PALS before and after uniaxial compression. They found that I_3 is unchanged by applied strain, while τ_3, and hence total hole volume, increases. Ruan et al.[29] studied strain-induced nanovoid changes in BPA-PC at room temperature. They found that applications of tensile strain up to a level of around 4% produces an increase in τ_3 and total hole volume, but little change in I_3. Above 4% strain, no apparent variation in τ_3, I_3, and total hole volume was observed. They further compared strain-induced nanovoid volume change to macroscopic volume change and concluded that they have similar trends with respect to the applied strain. Xie et al.[27] conducted a stress-coupled PALS test on BPA-PC. Loadings under both tension and compression conditions were investigated in this research. They found that τ_3 and total hole volume increase when tensile strain is applied and decrease when compressive strain is applied. When the absolute value of strain exceeds 2%, τ_3 levels off. They also found that I_3 remains virtually unaffected by tensile strain before yield occurs. They concluded that o-Ps trapping sites are thermally activated and small tensile strains could not activate more o-Ps trapping sites. Both Ruan and Xie's results showed that, with increasing applied tensile strain, the volume of nanovoids increases. These results support the thermodynamic model proposed by Chen et al. and Liu et al.[19,20] However, since they only studied BPA-PC, the effect of molecular motion on nanovoid growth remains unclear. To better understand the relationship between chemical structure and mechanical properties of glassy polymers, it is crucial to investigate nanovoid growth in polymers with different chemical structures and segmental mobilities. The stress-coupled PALS test is an ideal technique for investigating this issue.

Approach

A. Materials. In the present paper, we studied a series of amorphous polyester copolymers based on poly(ethylene terephthalate) (PET) and poly(1,4-cyclohexylenedimethylene terephthalate) (PCT). The chemical structures of PET and PCT are shown in Figure 2. Chen et al.[19] showed that craze stress increases with C-ring

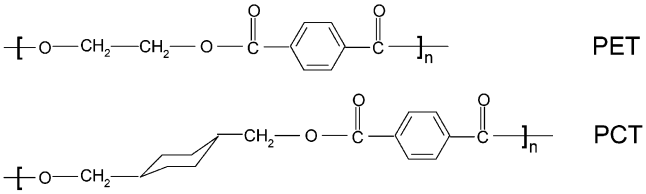

Figure 2. Chemical structure of PET and PCT.

Table 1. Molecular Weights and Molding Temperatures

polymer (PCT/PET)	M_n (g/mol)	M_w (g/mol)	molding temp (°C)
3.5/96.5	25 300	49 900	280
31/69	22 700	44 900	250
62/38	23 700	46 200	265
81/19	22 500	41 800	280

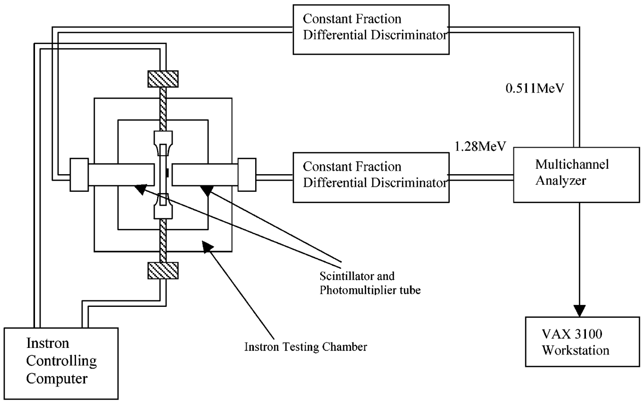

Figure 3. Diagram of the stress-coupled PALS system.

content in this series of copolymers. On the basis of DMA and solid-state NMR results, they[19,30] also concluded that the scale of cooperative segmental motion increases with C-ring content. Since it is believed that[20] the scale of cooperative motion is related to craze nucleation, this series of copolymers is ideal for studying the effect of the scale of local segmental motion on nanovoid growth. The materials were supplied by the Eastman Chemical Co. in the form of amorphous injection molded tensile bars. The dimension of the dog-bone-shaped sample bars is 2.5 in. × 0.5 in. × 0.125 in. (length × width × thickness). The molecular weights and molding temperatures of these copolymers are listed in Table 1. The sample bars were polished with very fine sandpaper (grit size is 1200) before the test to minimize large defects on the surface. Previous work[19] on these specimens showed that they do not contain crystallinity measurable by DSC or X-ray. Since annealing above T_g causes crystallization, all the copolymer specimens were used without further thermal treatment.

B. Equipment. To study nanovoid growth inside the glassy polymers when they are under stress, we set up a stress-coupled PALS device (shown in Figure 3). This device is capable of collecting PALS data when specimens of polymers are under stress in various temperature environments.

The PAL spectra are obtained by a conventional fast-timing coincidence method. Signals from the start and stop detectors, consisting of plastic scintillators coupled to photomultipliers (Amperex XP2020 with bases S563), are processed by two constant fraction differential discriminators (CFDD, Ortec583) with the start energy window set for the ^{22}Na 1.28 MeV nuclear γ-ray indicating the birth of a positron and the stop set for 0.511 MeV annihilation γ-rays. The CFDD outputs went to a time-to-amplitude converter (TAC, Ortec567) that produces output pulses with heights proportional to the time interval between the start and stop signals from the CFDDs. The TAC output pulses are then digitized by an analog-to-digital converter (ADC, ND581) and are recorded by an integrated multichannel analyzer (ND9900) through an ethernet compatible module (AIM, ND556) into a micro-VAX station that performs both data acquisition and analysis. The three lifetimes and relative intensities are determined by a FORTRAN program POSFIT. Since we are only interested in the lifetime and intensity of o-Ps, only τ_3 and I_3 are analyzed.

Mechanical loading is provided by a servo-hydraulic testing machine (INSTRON 1332), which is under displacement control and interfaced with a computer to carry out a preprogrammed loading sequence suitable for PALS measurement. For each copolymer a strain−displacement master curve was constructed by a uniaxial tensile test before the stress-coupled PALS test. Since the dimensions of different sample bars for the same copolymer are identical, the applied strain is controlled by displacement based on the master curve.

A 100 μCi ^{22}Na positron source, deposited on the surface of an aluminum disk, is placed on the surface of the specimen. At the beginning of a stress-coupled PALS test, a preprogrammed loading sequence is applied to the specimen. In the meantime, PALS data collection is started and continues until the loading sequence is finished. This instrumentation setup enables us to study nanovoid growth inside the polymers when they are under stress.

Experimental Section

A. Uniaxial Tension at Constant Strain Energies. Chen et al.[19] and Liu et al.[20] proposed that the driving force in nanovoid growth is determined by applied strain energy and surface energy on the basis of their thermodynamic model. In the series of PET/PCT copolymers we study, surface energies are almost the same.[31] Therefore, the driving force for nanovoid growth is only determined by the applied strain energy. In previous research using stress-coupled PALS,[27−29] a constant strain was applied to the polymers. In this series of PET/PCT copolymers, the modulus decreases with C-ring content significantly.[30] If a constant strain is applied to different copolymers, the applied stress and strain energy will both be different. In this case, we cannot tell whether the difference in nanovoid growth in different copolymers is due to different scales of local segmental motion or different driving forces. Therefore, we decided to apply uniaxial tension at constant strain energy levels to all copolymers to keep the driving force constant. To this end, we used a computer program to keep the applied strain energy constant, taking advantage of the servo-hydraulic control in our testing machine. The applied strain energy is determined by both stress and strain, as shown by the following equation:

$$\Delta G_{\text{input}} = \sigma\epsilon/2 \qquad (7)$$

where ΔG_{input} is the applied strain energy (per unit volume), σ is stress, and ϵ is strain. When the test started, uniaxial tension corresponding to a preset strain energy was applied to the specimen. Since the stress will decrease gradually due to relaxation, the strain energy will also decrease. To keep the strain energy constant, the strain must be increased gradually. This was done by the servo-control. A typical loading sequence

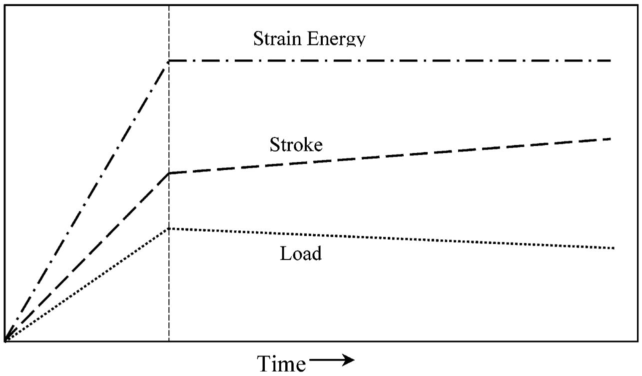

Figure 4. Schematic of the loading program used. Strain energy was maintained at constant value. The changes in load and stroke are exaggerated. The initial loading took less than 1 s.

is shown schematically in Figure 4. The fluctuation of applied strain energy is smaller than ±1.5% for up to 20 h.

As it turned out, by keeping the strain energy constant, neither the stress nor the strain varied significantly with time, thus obviating the need for a debate on whether stress or strain is the correct criterion to use. This fortunate result is perhaps due to the fact that we mostly kept away from stress/strain levels that would cause measurable plastic (permanent) deformation.

B. Stress-Coupled PALS Test. The test procedure was as follows: before loading, a PALS test was conducted on a polymer specimen for 20 h. Data were collected every 2 h. Thereafter, the test was temporarily halted. Then a uniaxial tensile strain corresponding to a preset strain energy was applied to the specimen and kept constant for 18 h. PALS data collection was restarted right after loading at 2 h intervals until the loading sequence was finished. After unloading, PALS data were collected for another 14 h at 2 h intervals. By comparing the PALS data before and under loading, we obtained information on nanovoid growth inside the polymers. Similarly, by comparing the PALS data before and after loading, we obtained information on structure change. In the first sequence of tests, the same copolymers were tested at different strain energies. In the second sequence of tests different copolymers were tested at the same strain energy levels. This part is the core of the current research. On the basis of these results, we expect to discover how the scale of local segmental motion affects nanovoid growth.

Although the test is actually a “strain energy-coupled PALS test”, for simplicity, we still call it stress-coupled PALS test in this paper. The true driving force for nanovoid growth is the hydrostatic component of the uniaxial tensile stress. In the rest of the paper, we will simply use “stress” to represent the driving force.

C. Data Analysis. τ_3 and I_3 were obtained in stress-coupled PALS tests. To characterize nanovoid growth induced by stress, we normalized data using PALS data before loading as reference. ν_{τ_3}, ν_{I_3}, and ν_{hole} were used to characterize the stress-induced change of nanovoids. ν_{τ_3} and ν_{I_3} are defined in eqs 8 and 9 as following:

$$\nu_{\tau_3} = \tau_3(\text{under loading})/\tau_3(\text{before loading}) \qquad (8)$$

$$\nu_{I_3} = I_3(\text{under loading})/I_3(\text{before loading}) \qquad (9)$$

ν_{hole} is the normalized total hole volume. According to eq 6, the total hole volume is proportional to R^3I_3, where R is the average radius of the nanovoid. R was calculated from τ_3 according to eq 4. Therefore, ν_{hole} could be determined from eq 10:

$$\nu_{\text{hole}} = {R_3}^3I_3(\text{under loading})/{R_3}^3I_3(\text{before loading}) \qquad (10)$$

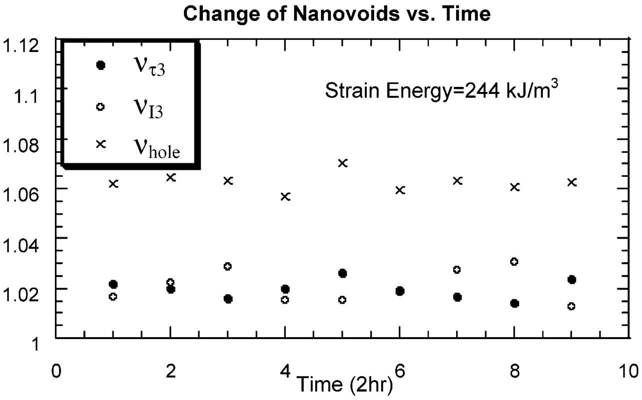

Figure 5. Change of nanovoids during loading in PET/PCT-31% C.

On the basis of the above definitions, ν_{τ_3}, ν_{I_3}, and ν_{hole} are the parameters for characterizing the change in size, number density, and total volume of nanovoids induced by stress, respectively. The PALS data after unloading were normalized in the same way except that the data under load were replaced by the data after unloading in eqs 8−10.

Results

A. Crystallinity of Copolymers before and after Loading. Previous research showed that crystallinity has a significant effect on I_3 and thus on total hole volume.[32,33] It was found that I_3 decreases with increasing crystallinity in some semicrystalline polymers. In the current research, all the copolymers used are amorphous, which has been confirmed by wide-angle X-ray scattering. To demonstrate that crystallization did not occur during mechanical loading, wide-angle X-ray scattering was also conducted after unloading at different strain energy levels. There was no observable change in crystallinity after unloading for the copolymers. For this reason, the X-ray data are not shown here. On the basis of these results, we conclude that the volume change of the nanovoids cannot be attributed to the change in crystallinity.

B. Effect of Applied Strain Energy on Nanovoid Growth. The change in nanovoid characteristics under the applied strain energy of 488 kJ/m^3 in the PET/PCT copolymer containing 31% C-rings is shown in Figure 5. ν_{τ_3}, ν_{I_3}, and ν_{hole} do not show any observable change with time up to 20 h. For other copolymers, similar results were obtained at various strain energy levels. Although data collection was started immediately after loading, it took 2 h to get the first set of data. Some relaxation in the size and number of nanovoids will have occurred during this period. Therefore, not all of the growth process could be followed by PALS. However, the net effect was measured. This information is still valuable for investigating the effect of applied strain energy on nanovoid growth. After the early stage, nanovoids inside the polymer may still grow as long as the polymer is under load. Yet, the number of “growing” nanovoids is apparently so small that it did not contribute to the total hole.

As shown in Figure 6, ν_{τ_3} rises with strain energy until yield occurs. This is true for all of the copolymers regardless of C-ring content. The strain energy at yield is around 800 kJ/m^3 for all of the copolymers. This result is consistent with previous reports[27,28] on BPA-PC. It suggests that the applied strain energy drives nanovoid growth. The extent of growth increases with the driving force. The effect of strain energy on ν_{I_3} is shown in

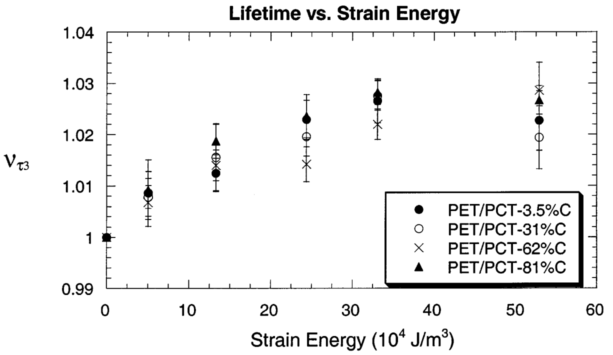

Figure 6. Effect of strain energy on ν_{τ_3} in PET/PCT copolymers.

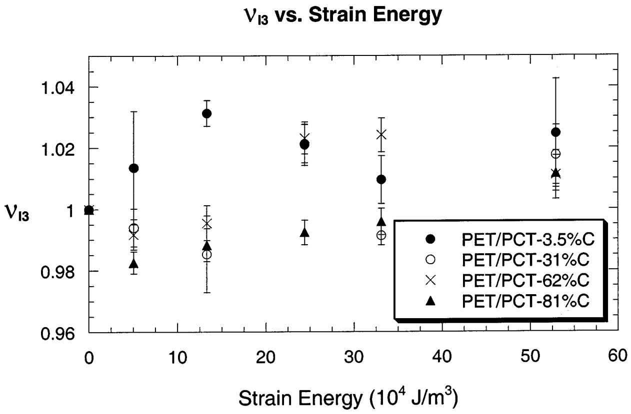

Figure 7. Effect of strain energy on ν_{I_3}.

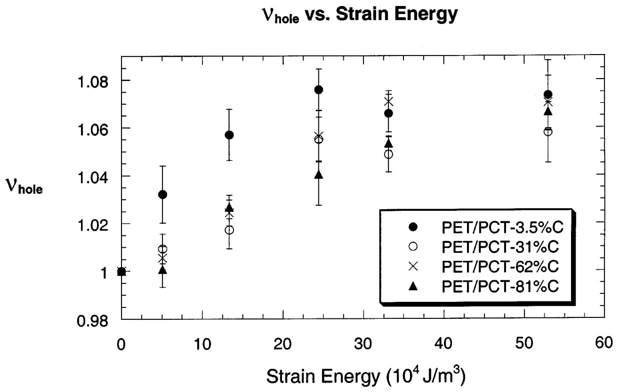

Figure 8. Effect of strain energy on ν_{hole}.

Figure 7. There is no clear trend among the different copolymers. It seems that ν_{I_3} fluctuates from 0.98 to 1.02 randomly. Previous reports on BPA-PC[27,28] also show that applied strain does not change I_3. These results suggest that the number density of nanovoids does not change significantly with strain energy. Therefore, the change in total hole volume arises solely from the change in the size of the nanovoids. As shown from Figure 8, for different copolymers, ν_{hole} increases with strain energy before yield occurs and levels off after that, which is similar to the behavior of $\nu_{\tau 3}$, as expected. Because τ_3 and I_3 are both obtained from fitting and are correlated, changes in these two parameters always go to opposite directions. The total hole volume is proportional to R^3I_3. According to eq 4, R is proportional to τ_3 when the change in τ_3 is small. Therefore, the error in total hole volume is smaller than the error in τ_3. For this reason, we decided to use ν_{hole} to characterize nanovoid growth in the current research.

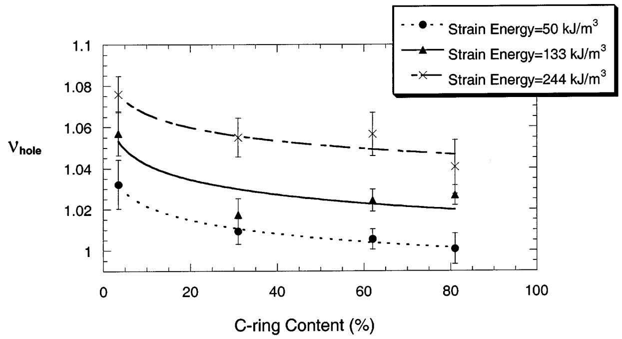

Figure 9. Effect of C-ring content on ν_{hole} before yield.

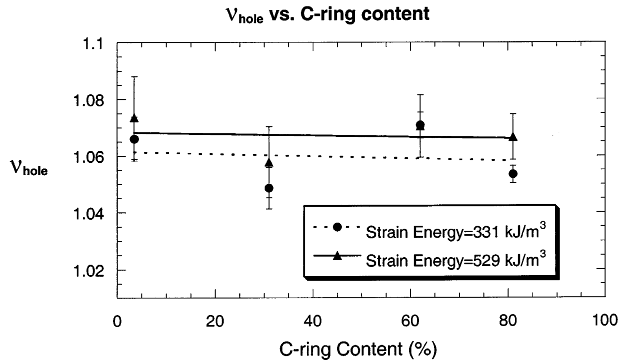

Figure 10. Effect of C-ring content on ν_{hole} after yield.

Clearly, these results support the previously proposed thermodynamic model.[19,20] Our results also suggest that the volume of nanovoids stop increasing around the yield point. For the time being it is still not known what happens at the molecular level when plastic deformation occurs. But our results are consistent with previous research on strain-induced macroscopic volume change in BPA-PC. It is well established that plastic deformation in glassy polymers occurs at nearly constant volume.[3] Powers and Caddell[34] followed volume changes by measuring local axial and transverse logarithmic strains during tensile elongation. They found that bulk volume increases with tensile strain up to 3.5% and begins to levels off after that. Since the change in bulk volume arises mainly from the change in hole volume,[35,36] our results agree very well with Powers and Caddell's results.

C. Effect of Local Segmental Motion on Nanovoid Growth. As shown in Figure 9 and Figure 10, when the applied strain energy is low, ν_{hole} decreases with C-ring content. Actually, ν_{hole} decreases significantly when C-ring content increases from 3.5% to 31% and only changes slightly after that. With further increase in applied strain energy, the difference in ν_{hole} between different copolymers becomes smaller. Eventually, after yield occurs, ν_{hole} of different copolymers are almost the same.

This result suggests that the scale of local segmental motion does correlate with nanovoid growth when the polymers are under stress. It shows that nanovoids inside the copolymers containing more C-rings have a lower tendency to grow. In this series of copolymers, Chen et al.[19] showed that the craze stress increases with C-ring content. They also found that the scale of the cooperative segmental motion increases with C-ring content due to chair–boat–chair (CBC) conformational transitions of C-rings. They proposed that large-scale cooperative segmental motion might retard nanovoid growth and craze nucleation, thus increasing the craze stress. Our results do show that nanovoid growth in the copolymers containing more C-rings is retarded.

Another issue we will discuss here is the volume relaxation during loading. In our experiments, there are two stages in the loading sequence: loading and holding. In the first, loading stage, the strain energy and the volume increase. In the second, holding stage, the strain energy is constant but the volume relaxes (decreases). The first set of PALS data was obtained after 2 h. But the time for loading is much shorter than that. Therefore, the PALS data were mainly collected in the second, volume relaxing stage. Since we are more interested in nanovoid growth in the first stage, we need to determine how much the volume relaxes in the second stage and whether this relaxation will affect the trend of ν_{hole} in different copolymers in the low strain energy region (i.e., equivalent strain is smaller than 1%). When a small stress (or strain) is applied to a glassy polymer which has a nonequilibrium structure, the volume change is very complex. In this case the viscoelastic response and the structure relaxation occur simultaneously. In the rubbery state, structure relaxation in a polymer proceeds extremely rapidly. The relaxation time is on the order of seconds around T_g and 10^{-10} min at 30 K above T_g.[37] By constrast, rubbery polymers are always in the equilibrium state and structure relaxation does not affect stress relaxation. However, structure relaxation is very slow in the glassy state. The relaxation time is about 10^{10} min at 30 K below T_g. The rate of stress relaxation is faster than structure relaxation below T_g.[37] As mentioned above, there are two stages in the loading sequence in this stress-coupled PALS test: loading and holding. The PALS data were mainly collected in the second stage. Now, the question is, how different would the hole volumes be between the end of the first stage and the second stage? To our knowledge, there is no experimental data to answer this question. However, previous research on macroscopic volume change in BPA-PC during stress relaxation and creep may help to clarify this question. Colucci et al.[38] reported that, during the stress relaxation process, the bulk volume of BPA-PC decreases by 0.1% at 1% strain. If we compare this result to Xie et al.'s PALS results,[27] it becomes evident that the difference between hole volume change and bulk volume change is about 1 order of magnitude. So the total hole volume change is estimated as 1% during stress relaxation. During creep testing of BPA-PC, the bulk volume change is much smaller (0.002% up to 500 s) although volume still relaxes (decreases) during the creep test.[39,40] Therefore, the hole volume change is estimated to be around 0.02%. In our experiment, we kept the strain energy constant. Therefore, the hole volume change should be around 0.5% in stage two. The error of measurement is between 0.5% and 1%. Obviously, PALS cannot probe such a small change. That is probably the reason why there was no observable change in ν_{hole} up to 20 h for all the copolymers. The difference in ν_{hole} values between the copolymers containing 3.5% C-ring and 81% C-ring is around 3% in our test range. We can therefore conclude that the volume change in the second stage should not change the trend of ν_{hole} in different copolymers.

D. Effect of Applied Strain Energy on Structure Change in the Copolymers. The change in nanovoids after unloading in the PET/PCT copolymer containing 31% C-rings is shown in Figure 11. ν_{τ_3}, ν_{I_3}, and ν_{hole} do not show any observable change up to 14 h. For other copolymers, similar results were obtained at various strain energy levels. Clearly, after unloading, the rate of volume relaxation is very slow. ν_{hole} (hole volume after unloading over hole volume before loading) is plotted with respect to applied strain energy for different copolymers in Figure 12. The results show that ν_{hole} is close to 1 for most of the data, which suggest that those nanovoids are "elastic" in nature and their growth is a reversible process. The nanovoids inside the copolymers expand when tensile stress is applied and shrink to the original size after unloading.

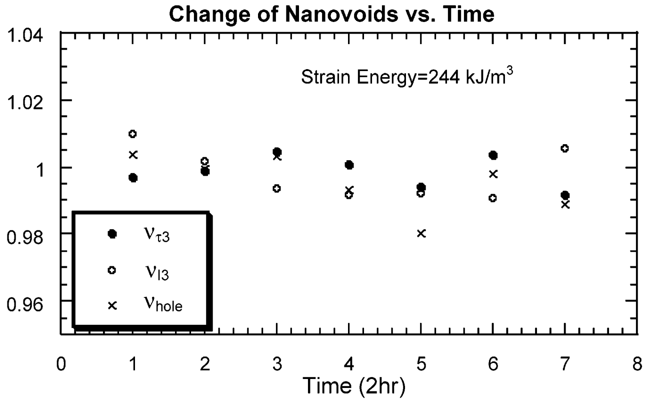

Figure 11. Change of nanovoids before loading and after unloading in PET/PCT-31% C.

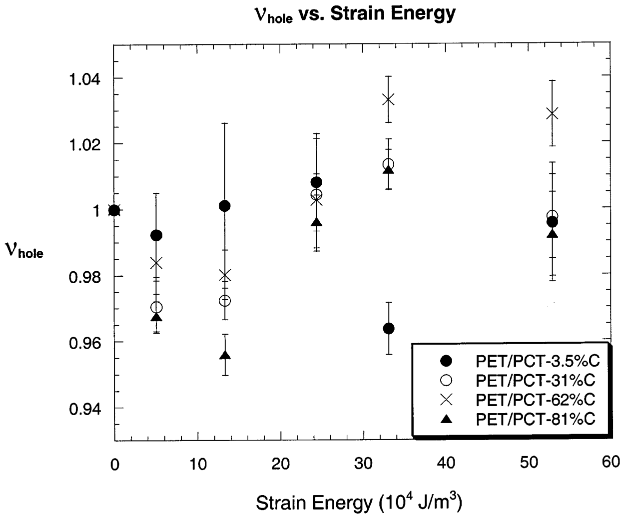

Figure 12. Effect of strain energy on ν_{hole} after unloading.

Ruan et al.[28] reported that hole volume continues to decrease in a BPA-PC sample subjected to 200 h aging at 3% tensile strain. They also found that the hole volume after unloading is smaller than the hole volume before loading. The difference between our results and their results can be attributed to the differences in strain levels and aging times. In their test, the applied tensile strain is large and the aging time is very long. In this situation, it is possible for some observable change in chain packing to occur. As a result of physical aging, polymer chains pack more efficiently, which would cause the hole volume to continue to decrease. Eventually, the hole volume after unloading is smaller than the hole volume before loading due to densification. However, in our test the applied strain energy is small (equivalent strain is smaller than 2%) and the loading time is short (20 h). In this case, there is no observable change although physical aging must still occur.

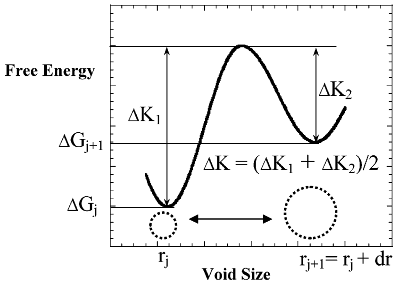

Figure 13. Effect of kinetic energy barrier on nanovoid growth.

Discussion

We consider how the scale of local segmental motion will influence nanovoid growth inside the glassy polymers when they are under uniaxial tension. Becker[41] proposed the following type of expression for the rate of nucleation in condensed systems where kinetics cannot be ignored (liquid−solid or solid−solid transformation):

$$r_n = A \exp[-(\Delta G^* + \Delta K)/RT] \tag{11}$$

where r_n is the rate of nucleation, ΔG^* is the thermodynamic energy barrier, ΔK is the activation energy for diffusion across the phase boundary, and A is an undetermined constant. Later, Turnbull[42] arrived at a very similar expression for r_n on the basis of the theory of absolute reaction rate. Following Turnbull's approach, we consider nanovoid growth in the subcritical region as a set of reversible chemical reactions and study the role of kinetics in this process. In glassy polymers, nanovoid growth is realized by segmental motions of the polymers.[20] Rearrangement of the segments around the surface of a nanovoid results in the growth of a nanovoid. The energy profile in an elementary growth step is shown in Figure 13. For a nanovoid with the radius of r_j to grow by dr, the net free energy change is ($\Delta G_{j+1} - \Delta G_j$). Since segmental mobility in glassy polymers is limited, there is a kinetic energy barrier for nanovoid growth. Assuming the kinetic energy barrier for "forward reaction" is ΔK_1 and for "backward reaction" is ΔK_2, then the rates of forward and backward reactions are

$$r^+ = n_j a r_j^2 (kT/h) \exp(-\Delta K_1/RT) \tag{12}$$

$$r^- = n_{j+1} a r_j^2 (kT/h) \exp(-\Delta K_2/RT) \tag{13}$$

Here n_j represents the concentration of the voids with the radius of r_j, n_{j+1} represents the concentration of the voids with the radius of r_{j+1}, and ar_j^2 is the concentration of mobile segments available for the growth of the void. Here we assume that the number of mobile segments available for each r_{j+1} void is also ar_j^2. Therefore, the net forward rate is

$$r_n = r^+ - r^- = r_j^2 (kT/h) a [n_j \exp(-\Delta K_1/RT) - n_{j+1} \exp(-\Delta K_2/RT)] \tag{14}$$

We define the ΔK (number-average of ΔK_1 and ΔK_2) as the kinetic energy barrier. Noting that

$$\Delta K_1 = \Delta K + 0.5(\Delta G_{j+1} - \Delta G_j) = \Delta K + 0.5\ \mathrm{d}(\Delta G_r)/\mathrm{d}r$$

$$\Delta K_2 = \Delta K - 0.5\ \mathrm{d}(\Delta G_r)/\mathrm{d}r$$

$$r_n = (-akT/h) \exp(-\Delta K/RT)[n_j((2/3)Aj^{-1/3} - B) + \mathrm{d}n_j/\mathrm{d}j]j^{2/3} \tag{15}$$

Equation 15 can be rewritten as

$$r_n = \mathrm{A} \exp(-\Delta K/RT) \tag{16}$$

According to eq 16, the rate of nanovoid growth will decrease with the increase of ΔK. In polymers, ΔK is the activation energy for segmental motions that contribute to nanovoid growth. To clarify the nature of ΔK, we must first examine different modes of motion in glassy polymers. A polymer molecule is so large that an attempt to characterize its motions in terms of the three spatial coordinates of each atom becomes an almost impossible task. However, it is possible to divide the possible motion modes into a number of groups:[43] (1) very localized vibrational and torsional movements of individual atoms, (2) local motions undergone by short segments, and (3) large-scale cooperative motions involving large sections of the chain.

For the first type of motion, its amplitude is too small to contribute to the nanovoid growth. The effect of these high-frequency motions can be safely neglected. In the temperature and strain energy range of our interest, the third type of motion is not available. This large-scale cooperative motion can only be activated at temperature near T_g or very high strain energy levels. Therefore, the only motion mode that could contribute to nanovoid growth would be the local segmental motions. In this type of motion, the moving unit may consist of a few monomer units. Chen[30] found that the molecular origin of the secondary relaxations of this series of PET/PCT copolymers is the local segmental motion triggered by chair−boat−chair (CBC) conformational transitions. Moreover, the energy barrier for this segmental motion can be characterized by the activation energy in secondary relaxations. Therefore, it is reasonable to assume that the kinetic energy barrier for nanovoid growth in this series of copolymers is the activation energy in the secondary relaxations. Since the activation energy is crucial in the current research, we decided to conduct DMA tests on this series of PET/PCT copolymers.

The test condition was as follow: the aged copolymers were studied with a TA-DMA 2980 instrument in the cantilever mode on bulk specimens. The specimens were run in an iso-step mode and held for 10 min at each temperature interval to allow for thermal equilibration. To maximize accuracy, the tests were run at 2.5 °C intervals at frequencies of 0.3, 1, 3, 10, and 30 Hz. The specimens had typical dimensions of 31.5 mm × 12.5 mm × 3.14 mm (length × width × thickness). Activation energies are calculated on the basis of the following equation:[44]

$$\mathrm{Ln}(f) = B \exp(-\Delta E_a/RT) \tag{17}$$

where f is the frequency, ΔE_a the activation energy, and T the peak position of E''. Therefore, by plotting Ln(f) with respect to $1/T$, the activation energy can be obtained. The activation energy of the series PET/PCT copolymers is shown in Figure 14. The result shows that ΔE_a increases with C-ring content. It is generally

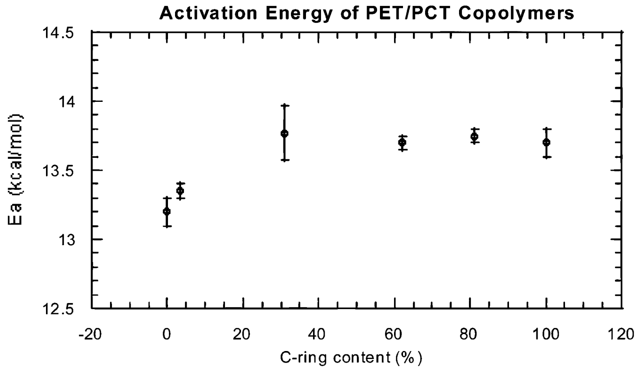

Figure 14. Activation energies of secondary relaxations of PET/PCT copolymers.

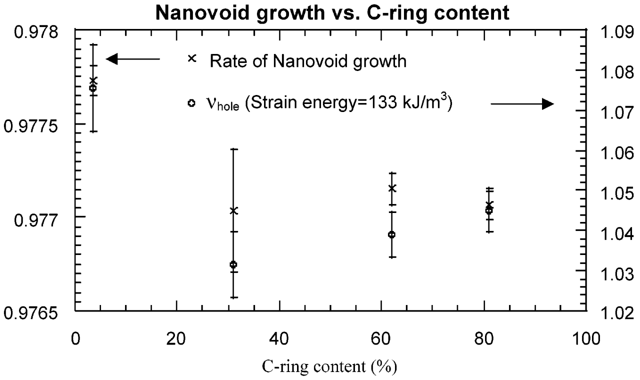

Figure 15. Comparison of the rate of nanovoid growth (in arbitrary units) and ν_{hole}.

believed that larger scale motions require higher activation energy and the higher activation energy results in slower molecular motion.[30,43,44] For example, the activation energy of glass transitions in glassy polymers is always higher than that of secondary relaxations in the temperature regime between T_α (T_g) and T_β (secondary relaxation temperature). Moreover, the molecular motion responsible for the glass transition is slower than that of secondary relaxations. Therefore, we conclude that in this series of PET/PCT copolymers the activation energy increases with C-ring content due to the rise of the scale of cooperative segmental motion.

Since ΔK increases with C-ring content, according to eq 16, the rate of nanovoid growth will decrease with the C-ring content. Therefore, ν_{hole} (ratio between total hole volume during and before loading) decreases with C-ring content as shown in the stress-coupled PALS results. In Figure 15, we compare the rate of nanovoid growth and ν_{hole} for different copolymers. The rate of nanovoid growth is calculated according to eq 16. The preexponential factor A in eq 16 is unknown for the time being. A should be related to the number of available mobile segments per mole of bulk material for nanovoid growth. It increases with the number and the size of the nanovoids but decreases with the number of monomer units in a mobile segment. Previous research[19] showed that the number and the size of nanovoids increase with C-ring content. But the scale of cooperative segmental motions also increases with C-ring content. Therefore, we assume that the effect of A on the rate of nanovoid growth is small, and we ignore this factor in our calculation. Thus, the rate of nanovoid growth (in arbitrary units) shown in Figure 15 is only determined by the kinetic energy barrier. As shown in Figure 15, the rate of nanovoid growth and ν_{hole} have the same trend with respect to the C-ring content. On the basis of this result, we propose that the larger-scale segmental motions give rise to higher kinetic energy barrier in nanovoid growth. As a result, the nanovoids grow more slowly, which might retard craze nucleation and cause the rise of craze stress. This result also suggests that the preexponential factor may have either little effect or similar effect as the kinetic energy barrier.

Previous research[19,20,30] suggests that the C-ring serves as a "motor" in the polymer chain. When C-rings undergo chair−boat−chair conformational transitions, the neighboring segments are forced to move cooperatively. Therefore, the scale of cooperative segmental motion increases with C-ring content in a polymer. In the current research, interestingly, we find that the activation energy changes significantly when the C-ring content increases from 3.5% to 31% in copolymers and very little after that. A similar trend is observed for ν_{hole} in stress-coupled PALS test. Moreover, Chen[19] also found that the craze stress of these copolymers exhibit the same trend. These results strongly support the idea that the C-ring serves as a motor, and its motion couples with the neighboring segments. If C-rings move independently, we are supposed to observe a "concentration effect". However, the results show that there is no "concentration effect". A possible explanation for our results is that when small amount of C-rings are inserted in the polymer chain, the scale of cooperative motion increase significantly because C-rings drag the neighboring segments to move cooperatively. But when there are more and more C-rings in the polymer chain, their effects may overlap, and eventually the system is saturated with these "motors". In this case, further addition of C-rings would have little effect on the scale of cooperative segmental motion. Certainly, this idea requires further demonstration.

Summary

PALS measurements undertaken at constant strain energies have been used to study nanovoid growth in glassy polymers. A series of polyester copolymer glasses based on PET and PCT have been investigated by stress-coupled PALS at different strain energy levels. The results show that the total hole volume of nanovoids increases with the applied strain energy, which support a previously proposed thermodynamic model. It is also found that the scale of local segmental motion does affect nanovoid growth. In this series of copolymers, nanovoids in the copolymer containing more C-rings has a lower tendency to grow. We studied the kinetics in nanovoid growth and proposed that larger-scale cooperative segmental motions result in higher kinetic energy barrier and slower kinetics in nanovoid growth, which might retard craze nucleation and increase craze stress.

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