

DYNAMIC MECHANICAL RESPONSE OF CRAZES IN POLYSTYRENE*

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ABSTRACT

Dynamic mechanical analysis was used to study the mechanical properties and microstructure of crazes in polystyrene produced in air or in methanol at different temperatures. A new loss peak was found at about 82°C, which is assigned to glass transition peak of craze fibrils. The decrease of glass transition temperature of polymer in craze fibrils is due to the high values of surface to volume ratio. The glass transition temperature ratio of craze fibrils to bulk material (T_g'/T_g) has been expressed as a function of the fibrils diameter (d). From T_g' of craze fibrils, the value of fibril diameter can be calculated. Annealing the crazed specimen at room temperature makes the fibrils plastically deform and cause the fibrils to thin slightly, whereas annealing the crazed specimen at the temperature near T_g of the craze fibrils makes the fibrils bundle together.

INTRODUCTION

Crazes form in many glassy polymers under an applied tensile stress and grow in width by the mechanism of surface drawing^[1,2]. Many investigators suggest that there are three regions within the crazes^[3-7], (1) the craze-bulk interface, a thin strain softened polymer layer approximately 5 nm thick from where craze fibrils extend in length by drawing fresh polymer and hence craze widens, (2) the craze mid rib, a thin polymer ribbon about 50–100 nm wide lying in the center of the craze^[8,9], which forms in craze initiating process, and (3) the craze fibrils other than the craze mid rib. Craze fibrils are made of polymeric material. But fibrillar material has some different characteristics from bulk material^[10], the surface to volume ratio of the craze fibrils is extremely high, and the molecular chains are probably highly oriented. Both features contribute to the increase of the molecular mobility in the fibrils, which may relax faster than ordinary bulk material.

Several previously published papers have shown the mechanical properties of the craze as means to determine its structure^[9-11]. Kambour found that craze material shows strong non-linear elastic-plastic behaviour

and rather low stiffness, comparable to that of rubber. Schirrer pointed out that crazes produced at high temperature are stiffer than those produced at low temperature. These results imply that the craze material has lower glass transition temperature (T_g) than the bulk material, and the crazes produced under different conditions have different T_g and structures.

Dynamic mechanical analysis is a very useful method to study the polymer morphology and its relaxation behavior. The present work is related to the measurement of the dynamic mechanical properties of craze material produced in polystyrene under various conditions using dynamic viscoelastometer and to the explanation of the results in terms of the fibril's structure in crazes. Other recent investigation techniques such as transmission electron microscopy (TEM)^[1], low-angle electron diffraction (LAED)^[12,13], and small-angle X-ray scattering (SAXS)^[14] may give more direct information on the craze structure. Nevertheless, these techniques are effective only to limited number of crazes produced under restricted conditions, such as crazing temperature and sample thickness, etc. . Whereas dynamic mechanical analysis is a technique which can be easily used to investigate various crazes developed under different conditions.

EXPERIMENTAL

A monodispersed polystyrene with a molecular weight 3×10^5 was used. A uniform film was obtained by spreading the solution of PS in chloroform onto a glass slide. The film was dried under vacuum at 60°C for 12 hrs, then was annealed at 120°C for 24 hrs. Film thickness was about 0.1mm. Experimental strips were cut from the film with 4 mm wide and 50 mm long.

Uniform multiple crazes in a specimen were initiated by bending a strip around a steel rod with diameter of 0.5mm. The crazes were grown in width by elongating the strip to a designed extension ratio at a speed of 0.2mm/min. The methanol crazes were initiated and grown in width in methanol by a similar process as air crazes. The specimens were dried in vacuum at room temperature under load. Maintaining the extension at the designed value, the crazed specimens were annealed at a controlled temperature under load. After the annealing treatment, the extension (λ , listed in Table 1) of the specimens was measured under unload, and dynamic mechanical measurement was performed immediately.

Table 1 Craze production and dynamic mechanical properties

Sample No.	Producing Temp. (°C)	Annealing		λ (%)	T (°C)	d (nm)
		T (°C)	t (hr)			
1						
2	20			5	81.5	5.8
3	20			0.5	57.9	3.7
4	20			3	78.7	5.5
5	20			10	82.0	5.9
6	20	20	12	5	81.0	5.7
7	20	20	24	5	78.2	5.4
8	20	20	48	5	76.4	5.2
9	20	70	1	3	82.6	6.0
10	20	70	6	3	89.8	7.2
11	70			5	84.9	6.3
12	80			5	90.0	7.2
13 *	20			5	63.9/102	4.1/10.7
14 *	20	70	1	5	80.1/104	5.6/11.6
15 *	20	70	6	5	92.6/106	7.7/12.7

* Methanol crazed specimen.

Dynamic mechanical measurement was performed by using a Rheovibron DDV-II-EA dynamic viscoelastometer in nitrogen atmosphere at a heating rate of 2°C/min. The test frequency is 110Hz. Since the neat stress which was applied to the specimen was very low during the measurement, this process can be recognized as an unloaded measurement^[15-16].

RESULTS

Dynamic viscoelasticity plots of the uncrazed and the crazed specimens versus temperature are shown in Fig. 1. Crazes in Sample 2 were produced in air at 20°C. As usual, the storage modulus (E') decreases and the loss tangent ($\tan\delta$) increases with increasing temperature for the uncrazed specimen (Sample 1) in the range from -50°C to T_g , which is 128°C at 110 Hz^[17], whereas the dynamic mechanical behavior of the crazed specimen (Sample 2) has great variation, its $\tan\delta$ values are much higher than Sample 1. And a new loss peak appears at 81.5°C, which is named as α' . On the low

temperature side of the peak, the E' of the crazed sample decreased more obviously than the uncrazed sample with increasing temperature, whereas it increased when temperature was higher than the α' -peak.

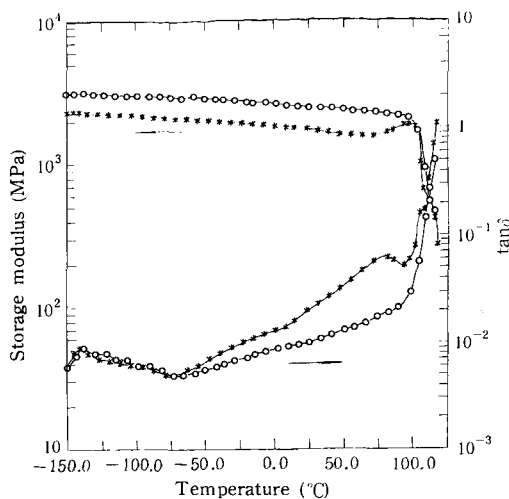


Fig. 1 Comparison of dynamic mechanical properties of crazed PS (*) with that of uncrazed PS (○)

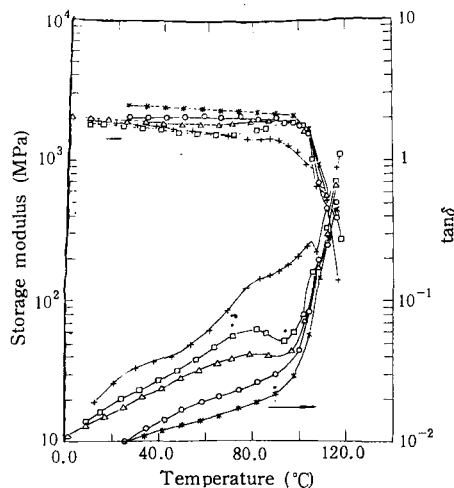


Fig. 2 Effect of different extension on dynamic mechanical properties of crazed PS. Extension: (*) 0.0%; (○) 0.5%; (△) 3.0%; (□) 5.0% and (+) 10.0%

Specimens were elongated to different extension ratio during craze growing in width. Fig. 2 shows that they have different dynamic mechanical properties. Sample 3 in which crazes were only initiated by bending showed a small α' -peak at 57.9°C which was much lower than that of Sample 2. For the specimens in which crazes were thickened by elongating the strips in excess of its yield point (strain is more than 2%)^[11,18], the temperature of α' -peak rose to about 82°C, and it was approximately unvaried with increasing crazes thickness, only the $\tan\delta$ value increased gradually. Fig. 2 also shows that values of E' of the specimens decreased with increasing extension, and only when the temperature was higher than their peak positions, they increased gradually and reached uniformity.

Fig. 3 shows the variations in E' and $\tan\delta$ of the crazed specimen which were annealed at room temperature with extension ratio of 5% under load. It is obvious that α' -peak temperature decreased gradually and E' increased with increasing annealing time, whereas the crazed specimens which were annealed at high temperature (70°C) displayed a very different property. For these specimens, Fig. 4 shows that the α' -peak shifted toward high

temperature with the increasing annealing time and tended to merger in the glass transition peak of the polymer.

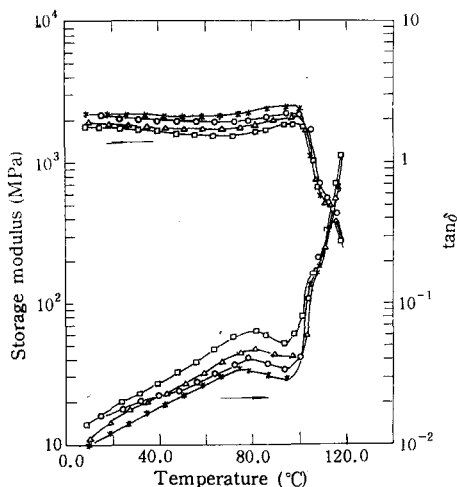


Fig. 3 Effect of annealing time on dynamic mechanical properties of crazed specimens which were annealed at 20°C with extension of 5% for 0.0 hr (□); 12 hrs (△); 24 hrs (○) or 48 hrs (*)

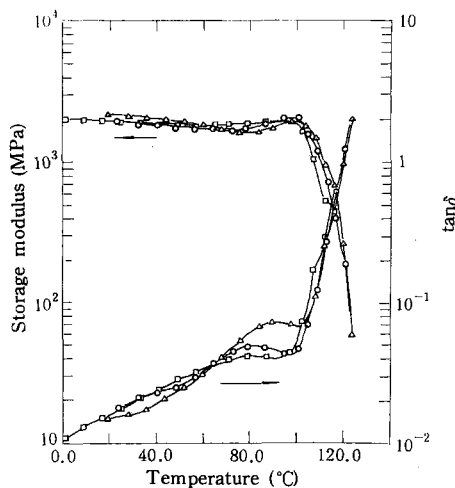


Fig. 4 Effect of high-temperature (70°C) annealing on dynamic mechanical properties of crazed specimen with extension of 3% for 0.0 hr (□); 1 hr (○) or 6 hrs (△)

This property of the high-temperature-annealed specimens are similar with that of high-temperature crazed specimen (i. e. , crazes in specimen were produced at high temperature). Fig. 5 shows that the high-temperature crazed specimen has a higher α' -peak temperature. It is imagined that the structure of the annealed crazes is analogous to that of high temperature crazes.

It is worth to point out that a shoulder peak was found at about 110°C for all air crazed specimens except high-temperature crazed ones. The peak position does not change with crazes thickening, and this peak disappeared when annealed the sample at high temperature. A hypothesis is that this peak is due to the strain softened craze-bulk interface.

Fig. 6 shows the dynamic mechanical properties of methanol crazed specimen (crazes were produced in methanol). This specimen (Sample 13) have two relaxation region in the range from 10°C to T_g . The peak positions are 63.9°C and 102°C respectively. When the specimen was annealed at 70°C, the temperature of both peak shifted toward high temperature.

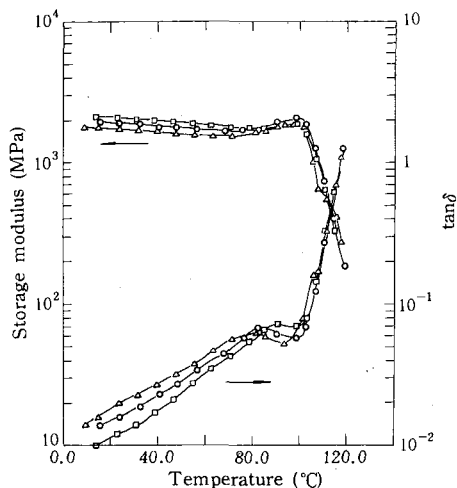


Fig. 5 Effect of producing temperature on dynamic mechanical properties of crazed specimen in which crazes were produced at 20°C (Δ); 70°C ($\circ$) or 80°C ($\square$)

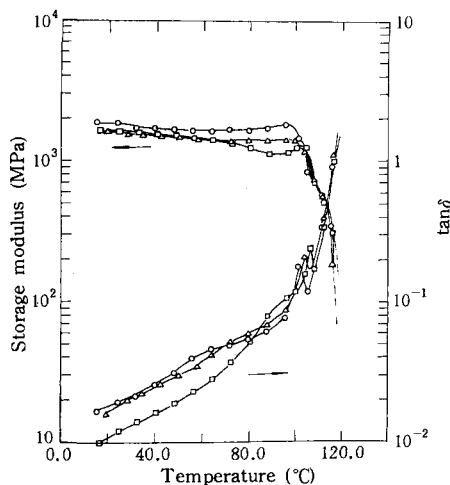


Fig. 6 Temperature dependence of storage modulus and loss tangent of methanol crazed specimen which was not annealed ($\circ$) or annealed at 70°C for 1 hr (Δ) and 6 hrs ($\square$). The extension of the specimens is 5.0%

The main results of dynamic mechanical analysis for all specimens are summarized in Table 1.

DISCUSSION

1. The assignation of α' -peak

Investigations of dynamic mechanical and dielectric properties show that polystyrene has a β -relaxation peak due to phenyl ring rotation around the main chain or twisting of the main chain^[19-21]. The β -peak temperature is about 30°C when measured at 1 Hz^[22], and is 60°C at 20 Hz^[20]. The peak is suppressed by solvents and also by annealing, while it is enhanced by quenching^[19].

The new loss peak for the crazed polystyrene, named as the α' -peak in this work, is different from the β -relaxation peak. The β -relaxation of PS has a great frequency dependence, it could be only found at low test frequency. When the test frequency was 100 Hz or higher, it shifted toward higher temperature and merged with the glass transition peak^[21-23]. The test frequency used in the present work is 110 Hz, so the β -relaxation peak can

not be measured. In fact, previous works^[22-24] suggested that β -relaxation peak of PS is a very wide transition region from -50°C to T_g . Its feature is quite analogous with that of the uncrazed specimen (Sample 1) in this work. But α' -relaxation only appeared in crazed specimens and its behavior is quite different from that of uncrazed one. So, α' -peak found in the present work relates to the special structure of crazes.

For air crazes in PS, Brown and Kramer^[3] used SAXS to find that the craze fibrils have diameter of 6 nm and it appears to be approximately constant along the length of the craze. Such thin fibrils have extremely high surface to volume ratio, and hence have a very high sum of surface energy, which must reduce the molecular interaction energy and increase the molecular mobility in the fibrils, and make the T_g of fibrils decrease.

After studying scores of homopolymers and copolymers, Marcincin and Romanov^[25] give an empirical equation expressing T_g of polymer as a function of cohesive energy (E_{coh}) as follows, where V , V_s , and ρ are molar volume of monomer unit, additive parameter, and density of polymer respectively. For a designated polymer, they have constant values.

$$T_g = \frac{V}{V_s} 10^{0.1 E_{\text{coh}}/\rho V_s} \quad (1)$$

Since surface energy (γ) is the increment of inner energy of a system during a unit new surface formed, T_g of craze fibrils can be expressed as:

$$T_g' = \frac{V}{V_s} 10^{0.1(E_{\text{coh}} - \gamma A)/\rho V_s} \quad (2)$$

where A is surface area of a molar monomer unit crazes. The ratio of T_g of craze fibrils to that of bulk material can be obtained from the following equation,

$$\log \frac{T_g'}{T_g} = \frac{-0.1\gamma A}{\rho V_s} \quad (3)$$

The craze fibrils can be considered as a cylinder with certain diameter (d), so Equation 3 can be transformed as

$$\log \frac{T_g'}{T_g} = \frac{-0.4\gamma M}{\rho^2 V_s d} \quad (4)$$

where M is molar weight of monomer unit. After substituting relating parameters ($\gamma = 4.07 \times 10^{-2} \text{ N/m}$, $\rho = 1.05 \times 10^3 \text{ kg/m}^3$ ^[26], $V_s = 4.945$ ^[25], and $T_g = 401 \text{ K}$ ^[17]) to Equation 4, T_g' of the air craze fibrils with diameter of 6 nm^[3] is calculated to be 82.9°C . This value is coincident with the result of the crazed specimen in Fig. 1. So the α' -peak at about 81.5°C is due to the

glass transition relaxation of craze fibrils.

For the crazed samples which were elongated to different extension ratio, Fig. 2 shows the α' -peak intensity increases with the increasing extension. Because the value of extension of crazed specimen was measured in releasing stress, the extension was contributed by the thickness of crazes. the larger extension means the greater amount of craze material. So Fig. 2 indicates the α' -peak intensity has a relationship with the amount of craze material. If the specimen can be treated as a two-components system of craze material and bulk material, the weight fraction of craze material has a linear relation with λ as the following,

$$w' = \frac{V_f}{1 - V_f} \lambda \quad (5)$$

where V_f is the volume fraction of craze fibrils in craze material. Because the α' -peak was contributed by the glass transition relaxation of craze and α -peak was due to that of bulk material, and at the temperature near T_g of polymer, the crazes in specimen have been healed, the polymer in crazes also contribute to α' -peak. On the other hand, both peaks are due to the same molecular relaxation mechanism of a polymer. So the relative intensity of the α' -peak to mean transition peak $[(\tan\delta_{\alpha'} - \tan\delta_{un})/\tan\delta_{\alpha}]$ should equal to the weight fraction of craze material, where the value of $(\tan\delta_{\alpha'} - \tan\delta_{un})$ was used to express the α' -peak intensity which was only contributed by the glass transition of craze fibrils, because the effect to contribute the $\tan\delta$ value at the α' -peak was not only the glass transition of craze fibrils but also other reasons. The $\tan\delta_{un}$ is the mechanical loss value of the uncrazed specimen at the same temperature as the α' -peak position of the current specimen to represent the other reasons to affect the α' -peak intensity. If the value^[28,29] of volume fraction of fibrils of 0.3 was used in Equation 5. Fig. 7 confirms the relationship of the relative intensity of α' -peak with the weight fraction of craze fibrils. This result further indicates that the α' -peak is due to the glass transition of craze fibrils.

2. Effect on the fibril diameter

Fig. 8 shows the variation of the fibril's diameter with extension of specimens. It indicates that the fibrils have low diameter values at low extension and thicken rapidly with increasing extension. TEM investigation^[1] showed that crazes in PS had a thin (ca. 50–100 nm wide) brighter line in their middle zone, so called as "mid rib". It has been suggested that the fibrils in the mid rib region are subject to relatively high

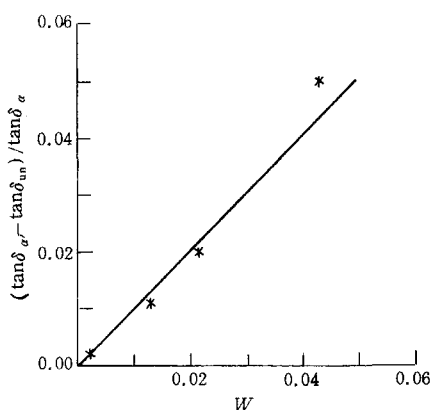


Fig. 7 The relationship of the relative intensity of α' -peak $[(\tan\delta_{\alpha'} - \tan\delta_{\alpha}) / \tan\delta_{\alpha}]$ and the weight fraction of craze material

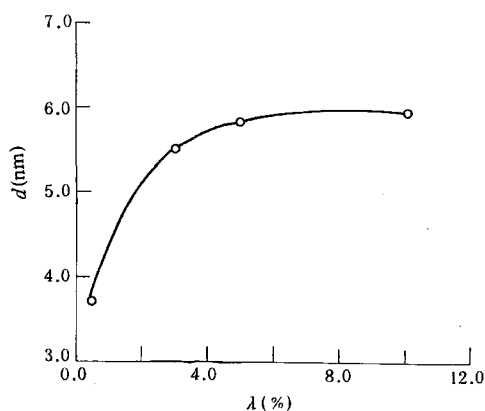


Fig. 8 The variation of the craze fibril's diameter with the extension (λ) of crazed specimens. The values of (d) were calculated from the T_g in Fig. 2 according to Equation 4

extension and hence possess a lower fibril volume fraction, because they are drawn from the craze surface in the high stress region^[27]. Crazes in Sample 3 were just created by bending and were not grown in thickness. The structure may coincide with that of mid rib. Figs. 2 and 8 show that the α' -peak of the specimen is at much lower temperature (57.9°C) and the craze fibrils are much thinner ($d = 3.7$ nm calculated from Equation (4), listed in Table 1). This result is in good agreement with the proposition of Lauterwasser and Kramer^[27] and indicates that the low density of the mid-rib is related to the thinner craze fibrils.

Previous workers^[1-3] have suggested that crazes in PS increase in thickness by the surface drawing mechanism. Once craze fibrils are created, they extend in length by drawing new polymer from the craze bulk interface and the fibril diameter maintains a constant value which does not vary with the length of fibrils. Dynamic mechanical analysis in the present work have given a coincident result. Fig. 8 shows that once the crazes were grown in thickness by elongating the strip to extension of larger than 3%, the fibrils diameter approximately remain a constant values about 6 nm and was not varied with the increase in thickness of crazes.

From the α' -peak temperature shown in Figs. 3 and 4, Fig. 9 shows the variation of the craze fibrils diameter during the annealing process. It deduced that the fibrils diameter slightly decreased with increasing time

when the crazed specimens were annealed at room temperature. Because the annealing process was done under a fixed extension and under load, and the stress was concentrated at the fibrils in crazes. The craze fibrils must occur plastic deformation and become thin. This process make the α' -peak shift to low temperature with increasing annealing time at room temperature.

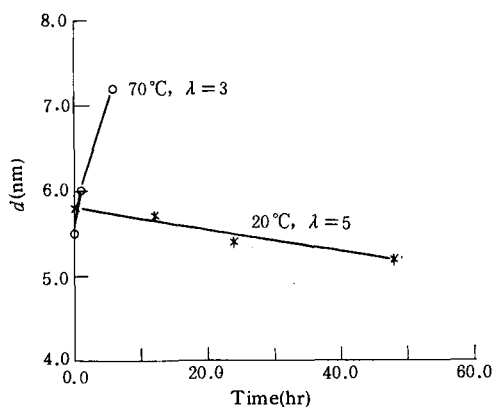


Fig. 9 The variation of the craze fibrils diameter during the annealing process at 20°C (*) or 70°C (○)

would explain why the fibrils is thicker in high-temperature-annealed crazes than in room-temperature-annealed crazes. For the crazes in poly (methyl methacrylate), Schirrer^[10] also found a similar result by using optical interferometry. He pointed out that re-entanglement occurred between the craze fibrils in high-temperature crazes.

Fig. 6 shows that the methanol-crazed sample has two peaks at 63.9°C and 102°C. It indicates that the methanol crazes have multiple structure. According to Equation 4, a hypothesis is that the craze material consists of two types of fibril with diameter of 4.1 nm and 11 nm respectively. Since the intensity of the peak at 63.9°C was relatively low, the amount of the thinner fibrils was very small. It could explain the results of SAXS that the fibril diameter in methanol crazes is 11 nm^[3]. Fig. 6 also shows that annealing methanol-crazed sample at 70°C can obtain the similar results as that of air crazed sample shown in Fig. 4. They both make craze fibrils thicken.

CONCLUSION

1. Dynamic viscoelasticity of crazed polystyrene has been measured at

Fig. 9 also shows that the fibril's diameter of the high-temperature annealed crazes increased with rising annealing time. This feature is similar to that of high-temperature crazes (produced at high temperature, shown in Fig. 5)^[6]. Because the annealing or producing temperature is near T_g of craze fibrils, a hypothesis is that fibrils can bundle together during the annealing or producing process through the polymer chain re-entanglement. So that many of them touched and a certain amount of fibril surface area was lost. This hypothesis

110 Hz. A new relaxation peak is found at about 82°C. This peak is assigned to glass transition relaxation of the craze fibrils.

2. The structure of the craze indicates that the difference between the T_g of craze fibrils and bulk material is mainly governed by the fibril diameter. From an empirical equation expressing T_g of polymer as a function of cohesive energy given by Marcincin and Romanov, an expression of the ratio of craze fibril T_g to bulk material T_g (T_g'/T_g) as a function of fibrils diameter (d) was obtained.

3. Dynamic mechanical analysis is a powerful technique for studying the microstructure of craze produced under a variety of conditions. The values of craze fibril's diameter determined by the technique are in good agreement with those values measured using SAXS and TEM.

4. Annealing the sample at room temperature under a constant extension ratio may lead craze fibrils to deform and decrease their diameter slightly, whereas annealing the craze sample at 70°C under a constant extension may lead polymer chain in fibrils to reentangle and make fibrils bundle together.

Keywords:

Polystyrene; Craze; Dynamic mechanical analysis

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