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(6) Physical Aging Studies of Styrene-Butadiene and Carbonate-Siloxane Block Copolymers

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Abstract

The physical aging process in styrene-butadiene and carbonate-siloxane block copolymers has been studied by monitoring the time dependent changes in mechanical and thermal properties. Specifically, stress-strain, stress relaxation and differential scanning calorimetry experiments were utilized. For the styrene-butadiene systems, it was found that the rate of physical aging increases with decreasing glassy content between 50 and 100% glass. However, the rate must decrease to zero when the percent glass reaches zero. The occurrence of physical aging was also noted in the polycarbonate siloxane block copolymer investigated. The data are discussed in light of the practical ramification of utilizing these block copolymers in material applications.

Introduction

The physical aging phenomenon in glassy polymers has drawn considerable interest within the polymer science area during recent years. When a polymer material is cooled at a finite rate through the glass transition, it is not generally in thermodynamic equilibrium. The observed aging behavior of glassy polymers is, in fact, due to the inherent nonequilibrium nature of the glassy state. During the cooling process the molecules are not able to reach their equilibrium conformation with respect to temperature due to the rapid increase in viscosity and associated decrease in molecular mobility as the glass transition is approached. As the polymer material is cooled through the glass transition, the molecules are essentially "frozen" into a nonequilibrium state relative to the corresponding equilibrium state at that same temperature. There is thus a thermodynamic potential for the molecules to approach the equilibrium state by undergoing further packing and conformational changes. The molecular mobility below the glass transition, although greatly reduced, remains finite, thus allowing the polymer molecules to approach the equilibrium state corresponding to normal liquidlike packing. The measurable thermodynamic state functions, enthalpy and volume, have been found to decrease with sub-Tg annealing as the excess enthalpy and volume originally quenched into the system decrease.

Practical interest in the aging behavior of glassy polymers has arisen due to the rather significant mechanical property changes which have been observed to occur as a result of the approach toward the equilibrium state (1-4). Typical of these changes are an increase in tensile and flexural yield stresses, a decrease in impact strength, fracture energy, ultimate elongation, and creep rate, and a transition from ductile behavior to brittle fracture. The utilization of polymers as engineering materials requires that

the nature and extent of these property changes be fully understood for all types of systems. However, almost all experimental work reported in the literature has been conducted on purely glassy linear homopolymers. Although it had been previously established that network glassy epoxies undergo physical aging (2), it was only recently that the first systematic studies of physical aging in these network systems and rubber-modified derivatives were completed (5,6). The fact that physical aging, or nonequilibrium behavior, has been observed to occur in covalently crosslinked systems inspires one to question whether similar behavior occurs in "pseudo" network systems such as semicrystalline polymers, where the crystalline regions serve as physical crosslinks, and in partially glassy domain-forming block copolymers, where the glassy regions may also serve as physical crosslinks. The glassy phase in these materials would obviously be expected to undergo the same changes it would experience if isolated. However, the important questions from an engineering viewpoint are whether or not the property changes in the glassy phase result in observable property changes in the two-phase materials, and, if so, to what extent do these changes occur and how do they relate to the fraction of glassy polymer.

In this paper we report results of an investigation of the physical aging process in styrene-butadiene and carbonate-siloxane block copolymers. The current widespread and expanding application of block copolymers as engineering materials underscores the importance of these results. The results of a similar study on semicrystalline poly(ethylene terephthalate) are reported elsewhere (7,8).

Materials

Styrene-butadiene-styrene (SBS) triblock copolymers used in the investigation were prepared and supplied through the courtesy of Dr. K. Udipi of Phillips Petroleum Company. These linear block copolymers had a weight percent styrene of 55, 78, and 93. In addition, pure polystyrene (PS), also supplied by Phillips Petroleum, and a radial block copolymer of 76 weight percent styrene were included in the study. Thin films of the block copolymers were cast from toluene to obtain good phase separation (9), care being taken to remove all solvent. The pure PS and the 93% styrene linear block copolymer were also compression molded at 160°C, in addition to being cast, to allow comparison of properties with those of the toluene-cast materials.

A carbonate-siloxane multiblock copolymer was supplied by Dr. A.K. Banthia of the Department of Chemistry at VPI&SU. This multiblock copolymer was synthesized by first forming a dimethylamine terminated polysiloxane (PSX) oligomer and a hydroxy terminated bisphenol-A-polycarbonate (PC) oligomer, and then reacting these oligomers to form the PC-PSX multiblock copolymer. The copolymer used for this study was 10% PSX, as determined by NMR. Films of the PC-PSX block copolymer were cast from chloroform, care being taken to remove all solvent. In addition, pure PC supplied by Dr. R. Kambour of General Electric Co. was also utilized for the investigation.

Experimental

Three characterization techniques were used to follow changes in the mechanical and thermal properties of the various polymers. Stress-strain, stress relaxation, and differential scanning calorimetry experiments were performed as a function of sub-Tg annealing time.

All stress-strain experiments were performed on an Instron Model 1122, and stress relaxation experiments were performed on a Tensilon Model UTM-II

(Toyo Measuring Instruments Co. Ltd.). Dog-bone-shaped samples were cut from films of the various block copolymers prepared as described earlier (8). The dimensions of these samples were 10.00 mm (length) by 2.80 mm (width). The thickness ranged from 0.25 mm to 0.40 mm for the various polymers. The linear portion of the samples measured 5.75 mm. This was the initial sample length used to calculate percent elongation, since most of the strain occurs in this region.

The SBS and PC-PSX block copolymers, along with pure PS and pure PC, were heated to a temperature above the Tg of their respective glassy component and annealed to erase any previous aging. This annealing temperature was 122°C for the SBS and PS and 175°C for the PC-PSX and PC. The samples were then quenched in an ice water bath, the quench time being taken as time zero for subsequent sub-Tg annealing. The samples were quickly removed from the ice water bath and dried. The SBS and PS materials were stored at room temperature under atmospheric conditions and the PC-PSX and PC materials were stored at 100°C under vacuum. The PC-PSX and PC materials were aged at this higher temperature to reduce the temperature increment below Tg of the polycarbonate phase (149°C) and thus accelerate physical aging. Stress-strain and stress relaxation experiments were conducted as a function of sub-Tg annealing time. Stress-strain experiments were performed on the SBS and pure PS materials at a crosshead speed of 0.5 mm/min and on the PC-PSX and pure PC materials at a crosshead speed of 1 mm/min, and all experiments were performed at room temperature. For the stress relaxation experiments the samples were elongated to 0.95% at a crosshead speed of 2 mm/min. The percent relaxation of stress during the first five minutes of the experiment was calculated for each sample.

Differential scanning calorimetry experiments were performed on both the pure glassy polymers and the block copolymers to determine the basic qualitative

features of the enthalpy recovery process in these systems. A Perkin-Elmer DSC-2 instrument was used for these studies. DSC scans were made with a $10^{o}C\text{-}min^{-1}$ heating rate. Each sample was scanned through the glass transition of the glassy component, annealed at about $20^{o}C$ above the Tg for 5 minutes, cooled rapidly, and then scanned again. This second scan was taken as the DSC trace of a quenched, unannealed sample.

Results and Discussion

SBS Block Copolymers:

The degree of stress relaxation data occurring in five minutes after the applied strain for different SBS block copolymers of different composition cast from toluene are shown in Figures 1-4. It is evident that percent stress relaxation during this time period of the experiment decreases with sub-Tg annealing time, thus indicating an increase in the relaxation times. This behavior occurs due to the decrease in molecular mobility as free volume decreases during physical again. This reduced mobility causes molecular relaxations to become slower, thus shifting the relaxation spectrum to longer times as the physical aging process proceeds and the shorter time relaxations occur. Determining the percent relaxation of stress during the first five minutes of relaxation as a function of sub-Tg annealing time is only one method of monitoring this shift in the relaxation spectrum.

Figures 1-3, which give stress relaxation data for the linear SBS block copolymers, show that the decrease in percent stress relaxation is linear with respect to logarithmic sub-Tg annealing time until an apparent equilibrium value is reached for this experiment. From the data, it might be suspected that an actual equilibrium state has been reached and that physical aging has ceased, but this has been shown not to be the case as has been discussed in some detail in a previous paper for the authors (8). Specifically, the onset of this apparent equilibrium can be correlated to the increment of time over which the stress relaxation is monitored.

The initial slopes of the stress relaxation curves presented in Figures 1-4 may be related to the rate of recovery toward equilibrium or the rate of physical aging. For discussion purposes, the recovery rate is defined here as in an earlier paper (7,8) as being the negative of the slope for the percent

stress relaxation vs. logarithmic annealing time plot. The recovery rate, as defined here, is thus related to the rate of physical aging.

The stress relaxation data for the linear SBS block copolymers, shown in Figures 1-3, suggest that as the fraction of styrene is increased the rate of recovery decreases. The fact that these materials are glass-rubber systems at room temperature suggests two possible causes for the observed trend. First, the fraction of the total macroscopic strain imparted to the glassy component may vary both with percent glass and with morphology. Second, differences in the thermal expansion coefficient of the rubber and glass phases may, upon thermal treatment, result in stresses on the glass regions which may result in physical aging similar to that observed by Sternstein (10,11). These differences in thermal expansion coefficient are due to the fact that the rubber, since it is above its Tg, would generally have a higher thermal expansion coefficient than that of the glass phase, which is below Tg. When the block copolymer is quenched from above the Tg of the glass, the rubber exerts a tensile stress on the glass due to its greater tendency to contract.

It is interesting to note that the stress relaxation behavior of the radial SBS block copolymer is very much different that that of the linear copolymers. For example, the percent stress relaxation after five minutes of relaxation is somewhat larger than that for the linear SBS block copolymer of comparable styrene content after 10 minutes of aging. Also, the recovery rate is slower, and an apparent equilibrium value of stress relaxation is not reached in the same time scale. The cause of this different behavior for this linear system can not as yet be explained.

Figures 6 and 7 show stress relaxation data for pure PS and the linear SBS block copolymer containing 93% styrene, both of which were compression

molded. Again it is observed that increasing styrene content decreases the recovery rate. Recovery rate is plotted as a function of percent styrene for the linear SBS block copolymers and pure PS in Figure 8. The general trend of decreasing recovery rate with increasing styrene content is clear. It is also evident that the apparent linear relationship between recovery rate and percent styrene at high percentages of styrene would not continue down to zero percent styrene. Indeed, as the percent styrene approaches zero the recovery rate must become zero, since it is only the glassy phase that undergoes physical aging. Hence, these data suggest that the rate of recovery may well be coupled to effects caused by a changing morphology as composition ratio changes.

Young's modulus data, obtained from stress-strain experiments on compression molded linear 93% styrene SBS material and pure PS, are plotted in Figure 9. It is clear that Young's modulus for both the pure polystyrene and block system increases in an approximately linear fashion with logarithmic sub-Tg annealing time. Again, the increase in Young's modulus is due to the shifting of the retardation spectrum to longer times, i.e. as free volume and molecular mobility decrease when the material is aged, retardation mechanisms become progressively longer due to the increased time required for molecular rearrangements to occur. Thus, when samples annealed below Tg for a short time are elongated, their high molecular mobility, as contrasted with longer annealed samples, allow more rapid rearrangement of the polymer molecules in reducing stress, and thus stress increases at a slower rate. When samples annealed below Tg for longer times are elongated at the same rate, reduction in stress by molecular rearrangement is slower, and thus stress increases at a faster rate.

DSC scans for pure PS (molded) at sub-Tg annealing times of zero and 16,800 minutes are shown in Figure 10, and scans for the 93% styrene linear SBS block copolymer (molded) at sub-Tg annealing times of zero and 15,500

minutes are shown in Figure 11. The traces labelled zero minutes were obtained after annealing above Tg for five minutes, quenching, and then scanning again. It is clear that from these heat capacity data and the earlier work of others (1,3,5) the enthalpy recovery behavior indeed occurs in these materials as expected. In addition, the enthalpy recovery peak is located well below Tg. This behavior has been observed in epoxy materials (5) and also in poly(ethylene terephthalate) (7,8,12).

PC-PSX Block Copolymers

As further proof of this general nonequilibrium behavior expected in related "glass" containing block copolymers, the stress relaxation data for the PC-PSX block copolymer containing 10% PSX and for pure PC aged at 100°C are shown in Figures 12 and 13, respectively. It is clear that both the absolute value of the percent stress relaxation and the recovery rate are greater for the PC-PSX block copolymer than for the pure PC. This is the same result as obtained for the SBS block copolymers. Again, as the fraction of glassy component is decreased, changes in morphology may result in changes in the distribution of strain between the glass and rubber regions. Also, the fact that the rubber has a higher thermal expansion coefficient causes the rubber to exert a tensile stress upon the glass, possibly resulting in mechanically enhanced aging. Further investigation of this point is now being made.

Stress-strain curves are shown in Figures 14 and 15 for both the PC-PSX block copolymer and pure PC, respectively, as a function of annealing time at 100°C. Behavior similar to that described previously for the linear SBS block copolymers and pure PS is observed. Again, this behavior is due to the decrease in molecular mobility as the material ages. The ability of the chains to rearrange and reduce the stress is impaired as mobility decreases with time.

Figure 16 shows DSC traces of pure PC as a function of annealing time at 100°C. It is seen that the enthalpy recovery peak becomes visible well below Tg and advances toward Tg with time. DSC traces of the PC-PSX block copolymer are shown in Figure 17. Again, it is clear that enthalpy recovery is occurring in this block copolymer, as was observed for the SBS block copolymers.

Conclusions

It was found that the physical aging process in the glassy regions of styrene-butadiene and carbonate-siloxane block copolymers result in time dependent changes in the mechanical and thermal properties of these two-phase materials. For the styrene-butadiene systems, the recovery rate was determined to increase as the glassy content decreases from 100 to 50%. It is clear, however, that the recovery rate must decrease to zero as the percent glass approaches zero. Enthalpy recovery behavior was also observed in the block copolymers, similar to that observed for the pure PS and PC.

It is clear that this nonequilibrium behavior observed within these pseudo network polymeric systems may well influence the mechanical response of these materials with aging or service time. Also, as has been discussed elsewhere, other important related properties such as transport (diffusion of penetrants) (13) and electric properties (14) may also be altered by this same phenomenon.

Figure Captions

Figure 1: Percent stress relaxation as a function of sub-Tg annealing time for toluene-cast linear SBS containing 55% PS.

Figure 2: Percent stress relaxation as a function of sub-Tg annealing time for toluene-cast linear SBS containing 78% PS.

Figure 3: Percent stress relaxation as a function of sub-Tg annealing time for toluene-cast linear SBS containing 93% PS.

Figure 4: Percent stress relaxation as a function of sub-Tg annealing time for radial SBS containing 76% PS.

Figure 5: Stress relaxation in PS with various thermal histories, but at the same strain and same temperature (Matsuoka et al. (4)).

Figure 6: Percent stress relaxation as a function of sub-Tg annealing time for molded linear PS.

Figure 7: Percent stress relaxation as a function of sub-Tg annealing time for molded linear SBS containing 93% PS.

Figure 8: Recovery rate ($-d\sigma$ relax/d log t) as a function of percent PS for linear SBS block copolymers and pure PS.

Figure 9: Young's modulus as a function of sub-Tg annealing time for a linear SBS block copolymer (93% PS) and pure PS.

Figure 10: Annealing time effects on the DSC traces of molded linear PS.

Figure 11: Annealing time effects on the DSC traces of molded linear SBS containing 93% PS.

Figure 12: Percent stress relaxation as a function of sub-Tg annealing time for PC-PSX containing 10% PSX.

Figure 13: Percent stress relaxation as a function of sub-Tg annealing time for pure PC.

Figure 14: Stress-strain curves obtained at various sub-Tg annealing times for the PC-PSX block copolymer containing 10% PSX.

Figure 15: Stress-strain curves obtained at various sub-Tg annealing times for pure PC.

Figure 16: Annealing time effects on the DSC traces of pure PC.

Figure 17: Annealing time effects on the DSC traces of the PC-PSX block copolymer containing 10% PSX.

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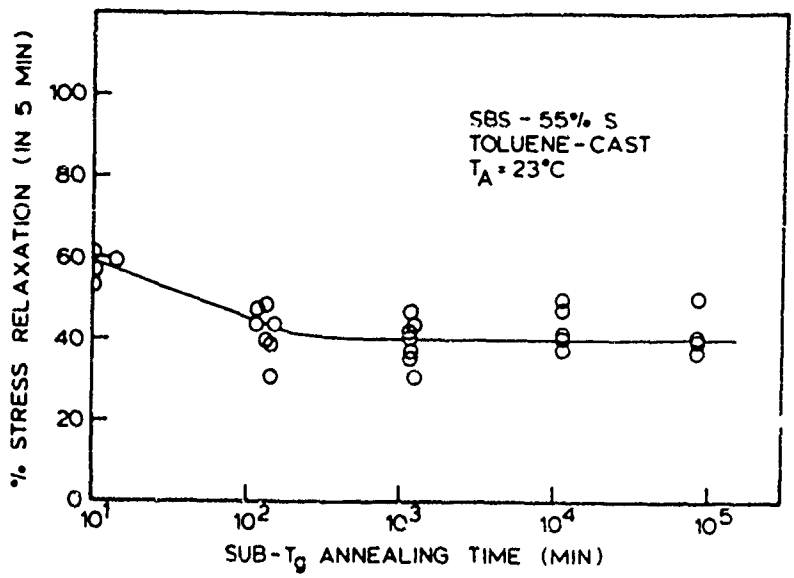

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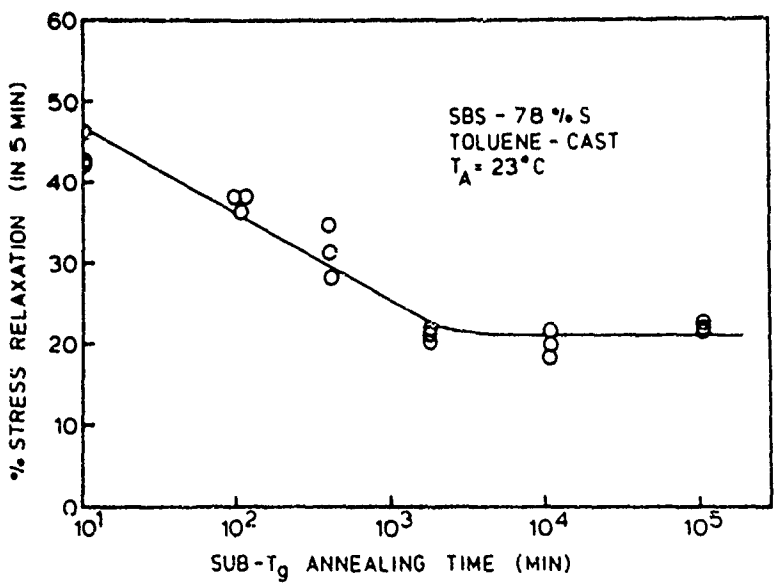

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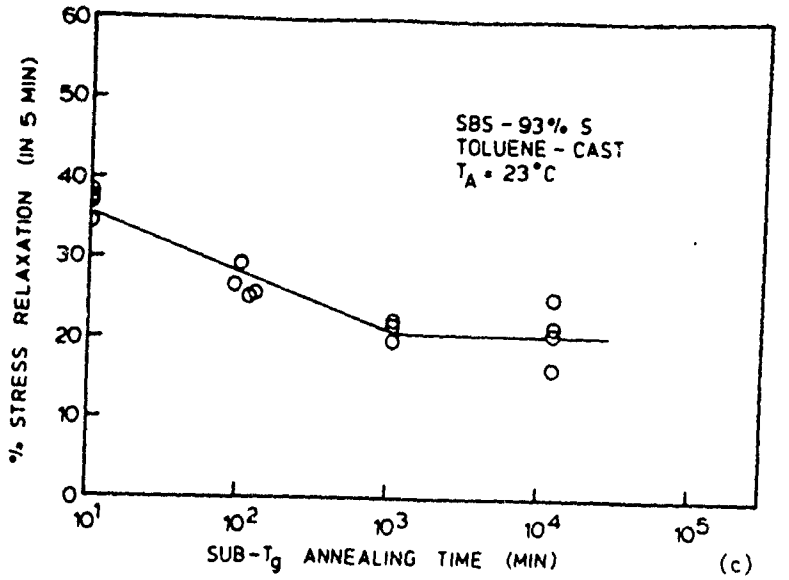

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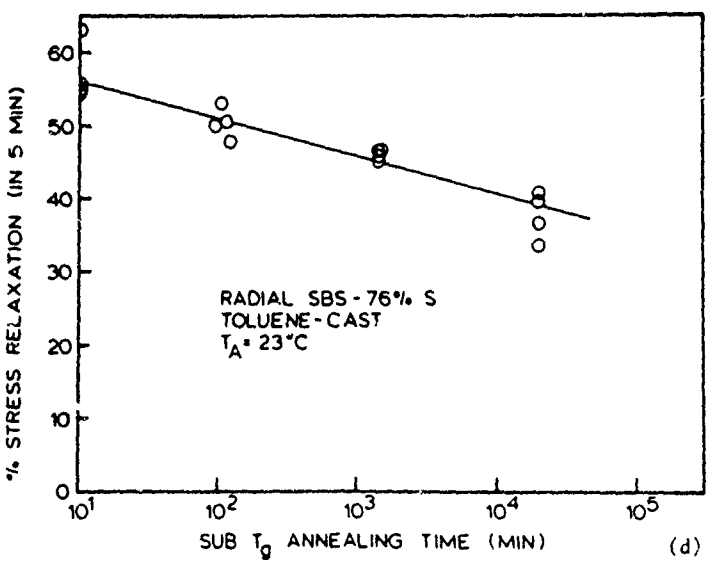

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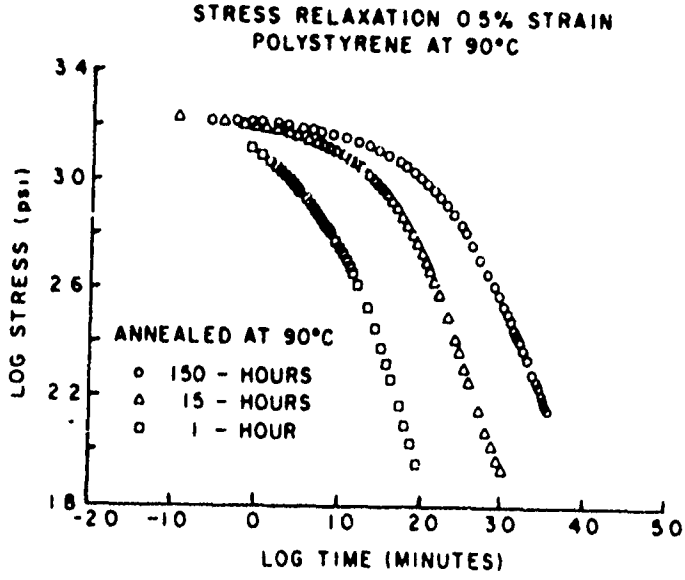

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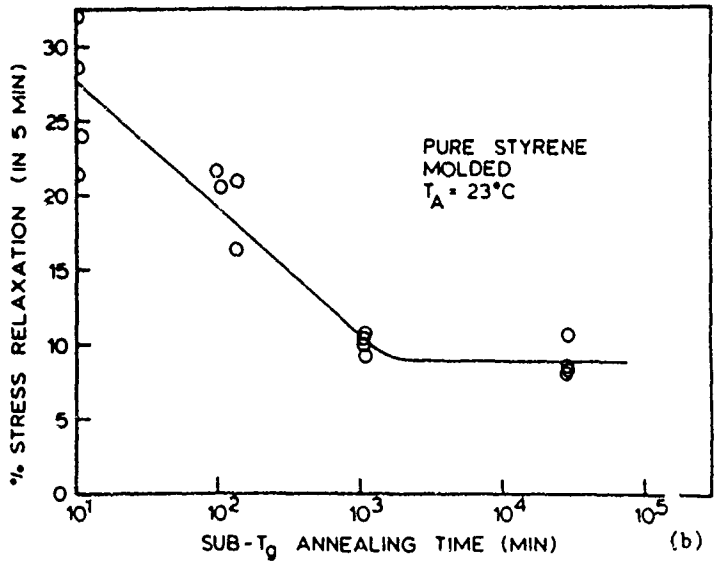

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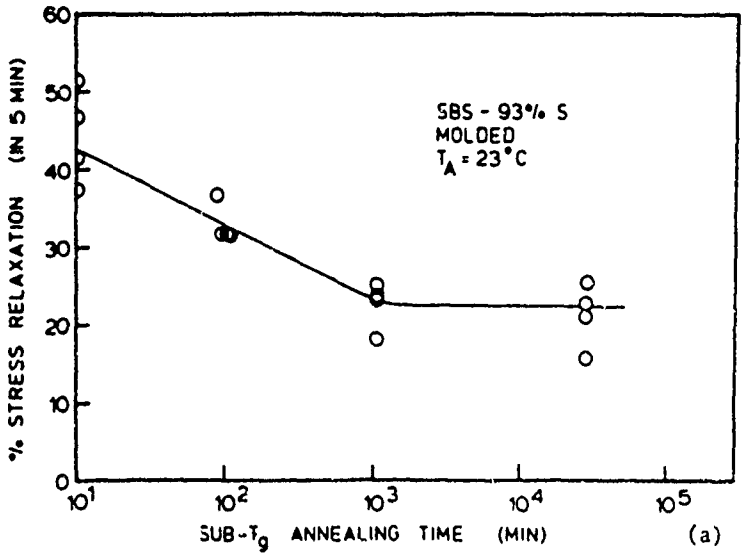

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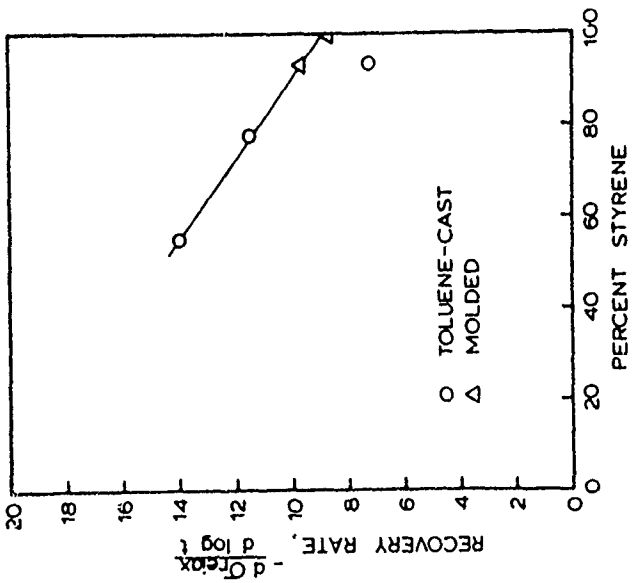

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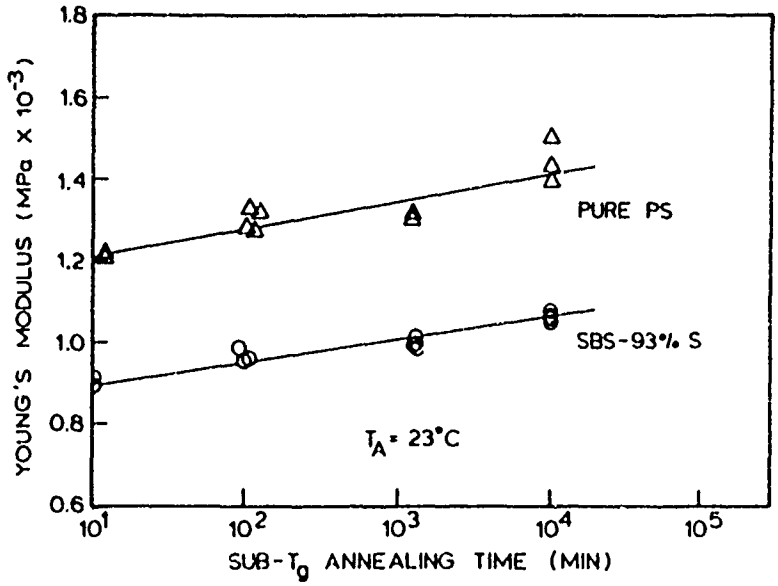

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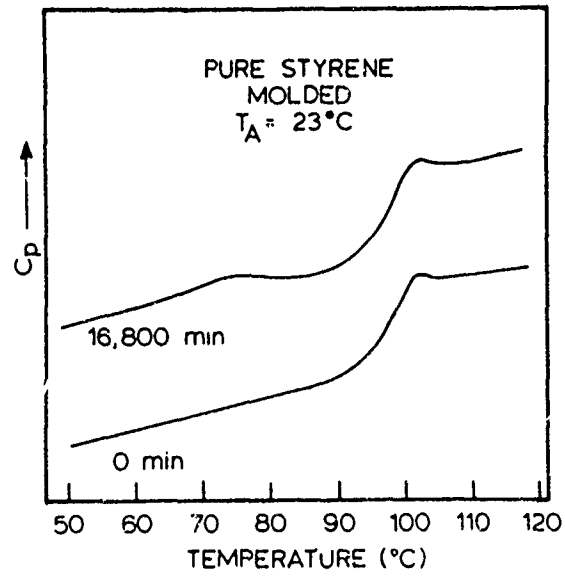

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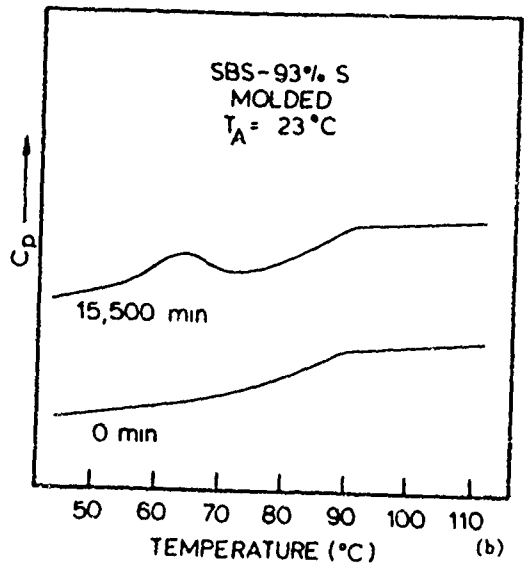

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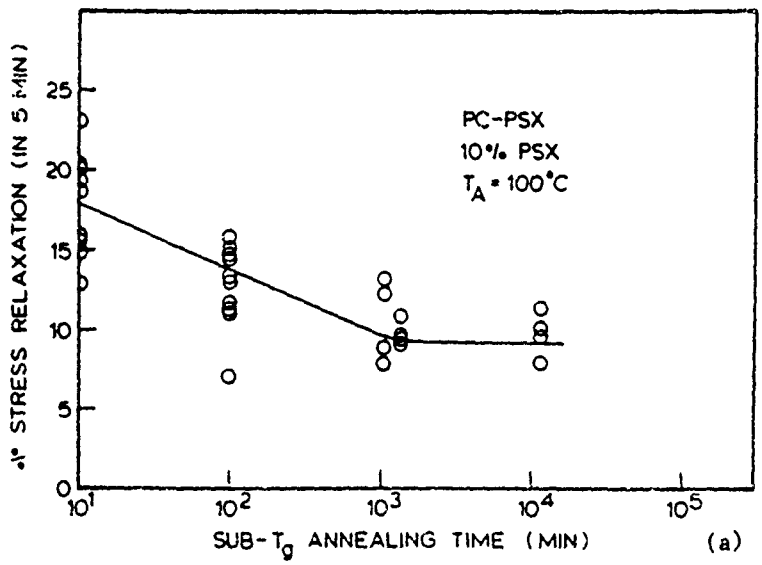

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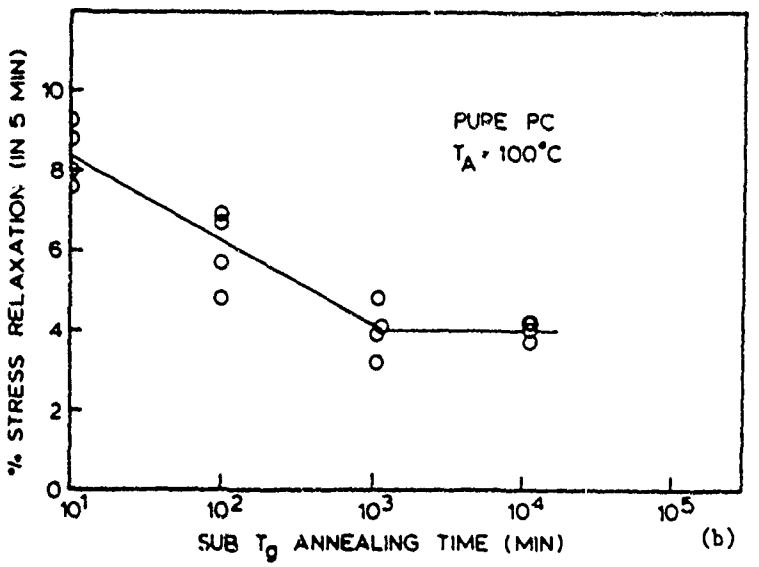

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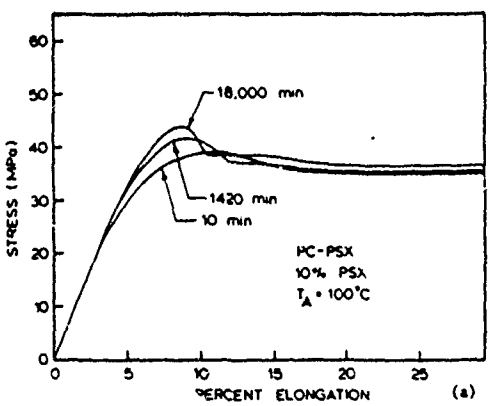

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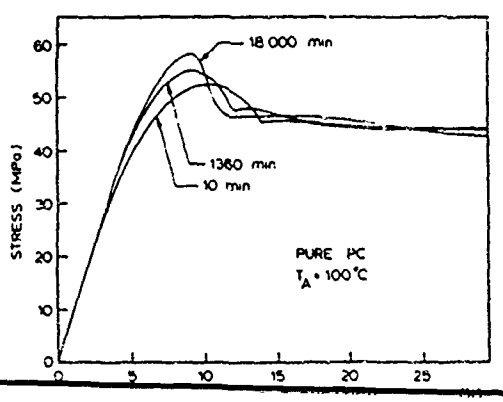

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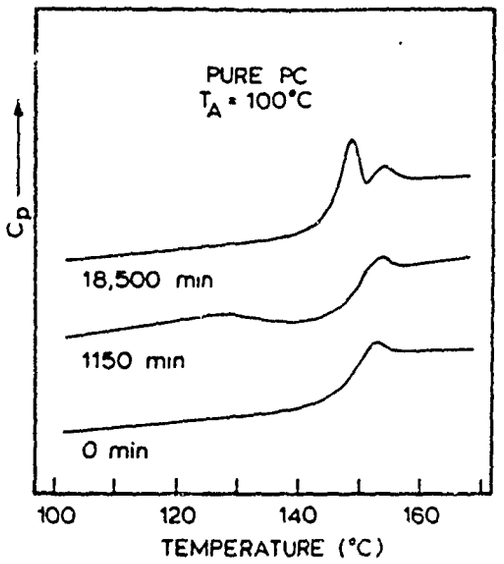

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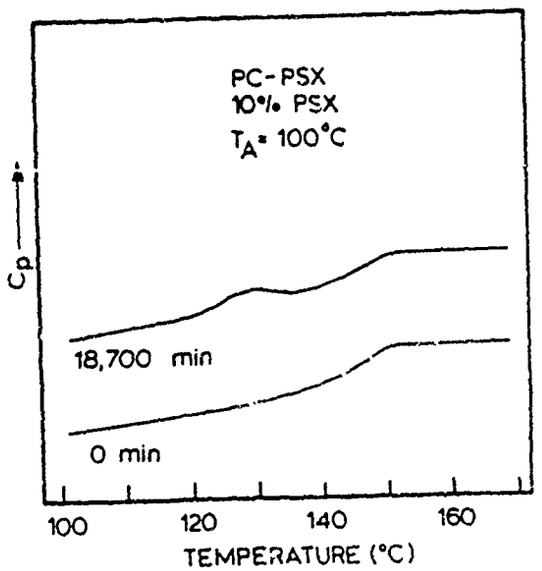

Figure 17