Physical Aging of Poly(acrylonitrile-Butadiene-Styrene). I. Dynamic Mechanical Measurements

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Synopsis

Injection- and compression-molded poly(acrylonitrile–butadiene–styrene) (ABS) samples were aged at 40 to 90°C in a nitrogen atmosphere. Dynamic mechanical measurements show that aging restricts molecular mobility in the glassy poly(styrene–acrylonitrile) matrix of ABS. The α, or glass transition, of the matrix is affected only by aging at higher temperatures such as 90°C. On the other hand, the β transition is suppressed to some extent by aging at all temperatures from 40 to 90°C. The rate of decrease in intensity of the β transition loss peak after aging at 60 to 90°C parallels the loss of tensile elongation previously reported. These results indicate that the effects of aging on the glassy phase are unique for different aging temperatures. Therefore, a simple time temperature superposition may not exist for the effects of physical aging on ABS.

INTRODUCTION

A previous study of the effects of oven aging on poly(acrylonitrile–butadiene–styrene) (ABS) has shown that aging at 50 to 90°C causes significant decreases in tensile elongation even in the absence of oxidative degradation.[1] Based upon the combined results of infrared spectroscopy, electron microscopy, differential scanning calorimetry (DSC), and the recoverable nature of the embrittlement, it was suggested that the changes in tensile elongation were due to physical aging of the glassy poly(styrene–acrylonitrile) (SAN) matrix of ABS. Physical aging of unmodified glassy polymers has been investigated by Petrie[2] and, more recently, by extensive studies by Struik.[3] The present study describes the effects of physical aging on the glassy SAN matrix of ABS as revealed by dynamic mechanical measurements. In particular, the influence of aging temperature from 40 to 90°C is described and the relation of the physical aging phenomenon to the β transition in ABS is discussed.

EXPERIMENTAL

Commercially available Marbon Cycolac L ABS and SAN were used in this study. Samples were examined as received. Cycloac E ABS used in previous studies[1] is no longer commercially available and therefore dynamic mechanical measurements were made using the Cycolac L. These materials have similar polybutadiene contents, exhibit similar initial mechanical properties and evidence similar tensile elongation decreases after aging.

Injection-molded bars were prepared with a cross section of 3.2 by 3.8 mm with a length of 62.0 mm. Also compression-molded sheets 3.2 mm thick were prepared and samples 3.2 mm wide by 62.0 mm long were cut and polished from the sheets.

Dynamic mechanical properties of both injection- and compression-molded bars were measured directly using a Rheovibron DDV-III-C dynamic visco-elastometer. An oscillating strain of 0.07% was employed at a frequency of 3.5 Hz. Temperature was raised at 1–2°C/min. It should be noted that the large force capacity of the Rheovibron allowed measurements to be made on thick injection-molded bars such as were previously used for tensile elongation measurements.[1]

Samples were aged in an oven purged with dry nitrogen at temperatures ranging from 50 to 90°C. In addition, samples were aged at 40°C in nitrogen-purged test tubes immersed in a constant temperature water bath. Temperatures were controlled to within 1°C.

RESULTS

Figure 1 shows the loss factor tan δ versus temperature for injection-molded samples of ABS and SAN. The dashed line represents a hypothetical curve for a material evidencing only a single transition near 100°C. Above 35°C, increases in tan δ for both ABS and SAN indicate that some form of molecular motion occurs at these temperatures and increases in intensity with increasing temperature. From a review of the literature on polystyrene and its copolymers, it is clear that the rise in tan δ between 35°C and T_g is associated with the β transition.[4,5] Also the similarity between the ABS and SAN tan δ curves shows
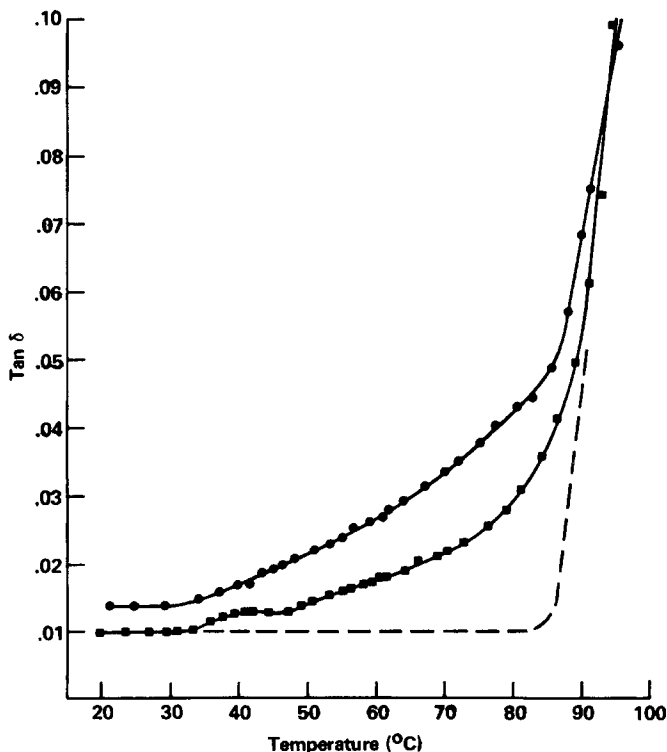

Fig. 1. Loss factor tan δ vs. temperature for injection-molded (●) ABS and (■) SAN. The dashed line represents a hypothetical glassy polymer exhibiting only a single transition near 100°C.

that the β transition in ABS can be attributed to molecular motion in the glassy SAN matrix of ABS. It appears that the intensity of the β transition is enhanced by the presence of the rubbery phase. However the dynamic stored modulus E' and the loss modulus E'' are both lower for ABS. This is observed for the injection-molded and the compression-molded samples. Figure 2 shows results for rapidly quenched compression-molded ABS and SAN. If a correction was made for the amount of rubbery phase material in ABS (about 25% based on infrared analysis) the value of E'' for ABS and SAN would be approximately the same. Thus the β transition is not enhanced in ABS. However, tan δ (= E''/E') values will be higher for ABS because of the tremendous lowering of the stored modulus E'.

The effect of cooling rate on the intensity of the β transition in ABS is shown in Figure 3 for compression-molded samples. Slow cooling was accomplished by simply turning off the molding press and allowing the sample to cool overnight. Quenching was done by immersion in an ice-water bath. Clearly, quenching enhances the β transition, as previously reported for pure polystyrene.[4] A similar enhancement is seen in E''. Comparing the results for injection (Fig. 1) and compression-molded samples (Fig. 3) of ABS it is noted that the former process provides a more severe quenching than even the ice-water quench of compression-molded samples, as judged by the tan δ values.

The effect of physical aging of ABS at 90°C is shown in Figure 4. The tan δ is decreased dramatically over the entire temperature range, and the steep rise in tan δ, corresponding to T_g, shifts to higher temperature with increased aging time Figure 4(a). The same effects of aging are observed in both tan δ and E''
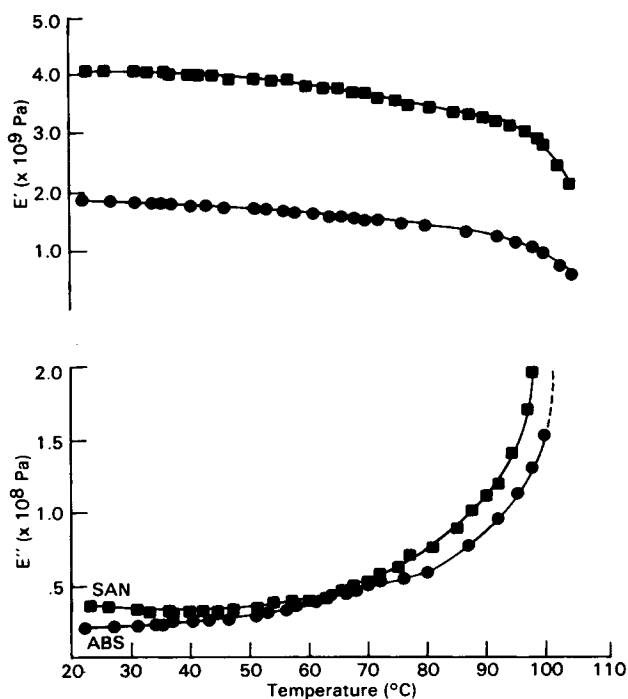

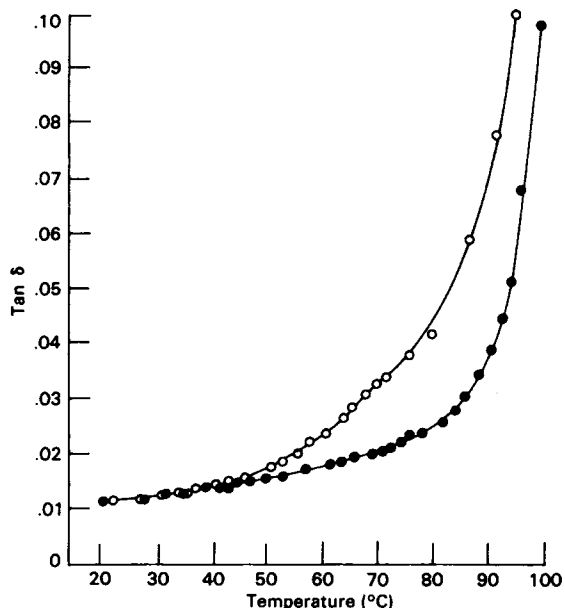Fig. 2. Stored modulus E' and loss modulus E'' for compression-molded (●) ABS and (■) SAN.

Fig. 3. Loss factor tan δ for ABS compression molded and then cooled at different rates; (O) quenched, (●) slowly cooled.

in the region of the β transition, as shown in Figure 4(b). Similar results were observed for pure SAN after aging at 90°C and this is shown in Figure 5. Previous investigators have observed a general suppression of tan δ for a variety of glassy polymers after aging near T_g.[6,7] It should be kept in mind that T_g does not shift to higher temperatures with aging, only the rise in tan δ corresponding to the onset of T_g is shifting. In theory the actual T_g, as measured from a volume or enthalpy versus temperature curve, should decrease with aging. This apparent conflict reflects in part the fact that the initially highly quenched sample begins to exhibit liquidlike properties at lower temperatures than a well-annealed glass. Also, annealing retards the kinetics of the transition thus delaying the apparent onset of T_g during a dynamic measurement.

To estimate the intensity of the β transition, the area enclosed by the tan δ temperature curve was measured using the dashed line in Figure 1 as a baseline. The baseline was shifted to follow the apparent shift in T_g so only the shoulder of tan δ peak at T_g was measured. From Table I it is seen that a large decrease occurs in the first 24 hr of aging at 90°C with no additional decrease after 312 hr. Thus prolonged aging (beyond 24 hr) primarily has the effect of shifting the T_g tan δ peak (or E'' peak) to higher temperatures without further decrease in the β peak. There is of course uncertainty in positioning the tan δ baseline so the absolute magnitude of the β-loss peak area is open to question.

Figure 6 shows the effect of aging at 60°C on tan δ. The decrease in tan δ owing to aging occurs only at lower temperatures with very little change near the glass transition. Again, similar results are seen for E'' plots. This provides direct evidence that the effects of aging at 60 and 90°C are not the same. Although aging at 60°C in part suppresses the rise in tan δ owing to the initiation of the β transition, it clearly does not suppress the larger scale segmental motions associated with the onset of the glass (or α) transition. In contrast, aging at 90°C

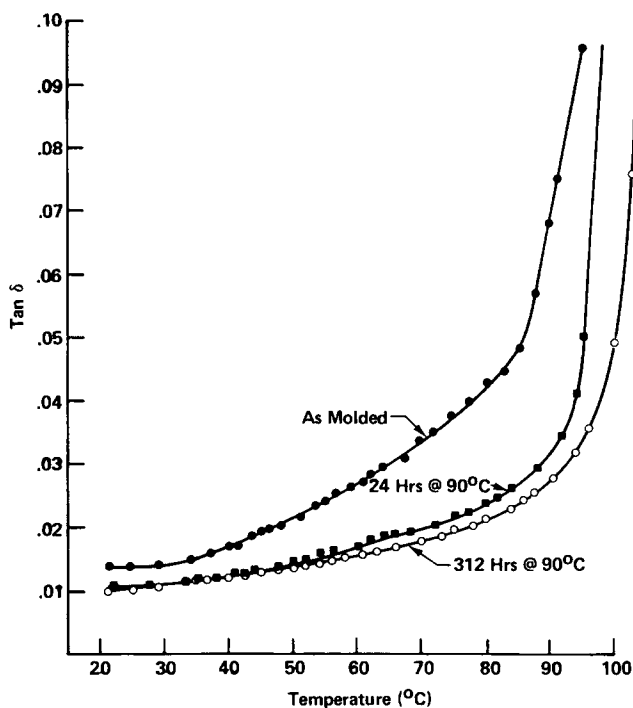Fig. 4. (a) Loss factor tan δ for injection-molded ABS before and after aging at 90°C. (b) Loss modulus E'' for the same samples.

TABLE I
Effect of Aging on the Relative Intensity of the β Transition of ABS

Sample	tan δ temperature area (10^3 mm^2)
As-molded	1.40
24 hr at 90°C	0.81
312 hr at 90°C	0.85
24 hr at 60°C	0.83
96 hr at 60°C	0.79

suppresses tan δ over the entire temperature interval of the β transition and in addition restricts the onset of the glass transition. Area measurements of the tan δ temperature curve (Table I) again suggest that the major decrease occurs after 24 hr of aging. Also it is noted that similar areas are measured after aging at 60 or 90°C. This serves to demonstrate that the effect of aging on the β transition is similar for the two aging temperatures even though their effect on the glass transition is not.

The effect of prolonged aging at 40°C on the β transition in injection-molded ABS is shown in Figure 7. Again it is observed that the tan δ is suppressed only at lower temperatures with no apparent change near the glass transition. Comparing Figures 6 and 7, it is seen that the rise in tan δ above 70°C occurs more abruptly for the sample aged at 60°C. Also a greater decrease in tan δ occurs after aging at 60°C. Thus there are distinct differences in the effects of aging at 40 and 60°C on the β transition.
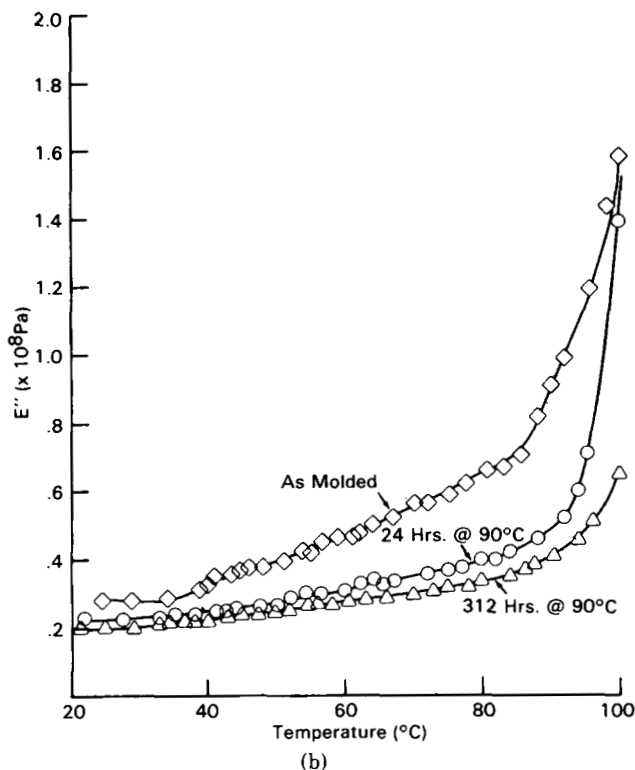
Fig. 4. (*Continued from previous page.*)

In Figure 8 the tan δ-versus-temperature data for injection-molded ABS aged at 90°C is shown over a broader temperature range. The low-temperature loss peak associated with the glass transition of the rubbery polybutadiene phase shifts from −86 to −89°C. This slight shift for the aged ABS may be due to a release of molded-in stresses on the rubbery phase.[8] Prolonged aging (1000 hr) produced no additional change in the peak at −89°C. In addition to the suppression of the β transition previously shown in Figure 4 it is noted that the tan δ values are reduced at all temperatures above the polybutadiene glass transition. Thus, although aging clearly suppresses the β transition, it also suppresses molecular mobility at temperatures below the β tan δ peak. The results shown in Figure 8 also serve to emphasize that physical aging may affect a variety of changes in the rubbery as well as glassy phases of ABS. Such changes are not amenable to study by use of the Rheovibron alone.

DISCUSSION

Correlation with Tensile Elongation

Previously it was reported that the effect of aging on tensile elongation of ABS was highly dependent on aging temperature.[1] In particular the form of the elongation-versus-aging-time curves suggested that a simple time–temperature
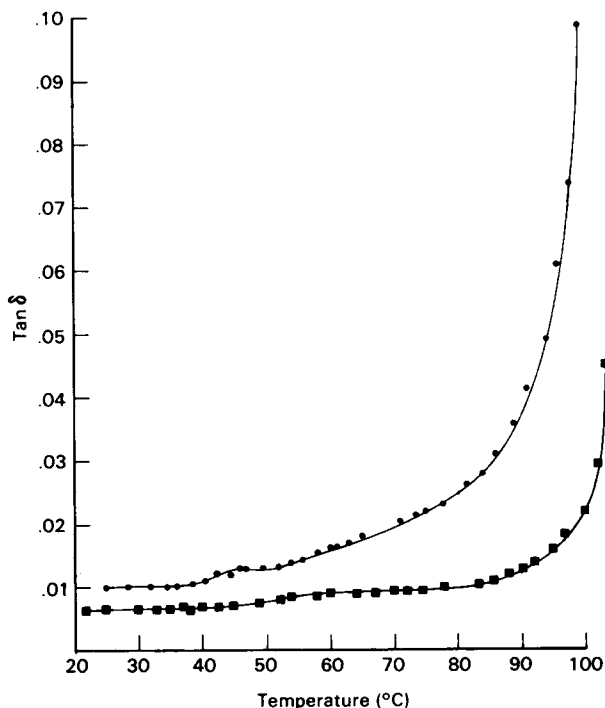
Fig. 5. Loss factor tan δ for injection-molded SAN before and after aging at 90°C. (●) As molded; (■) 312 hr at 90°C.

interrelationship did not exist. For example, aging at 40°C for over 500 hr produced no loss in tensile elongation, whereas aging only a few hours at 50 or 60°C reduced the elongation by 40%. Similarly prolonged aging at 50 or 60°C resulted in no additional decrease beyond 40%, whereas aging at 90°C for a few hours caused an 80% loss of elongation.

This investigation provides further evidence that the loss of elongation observed for aged ABS is related to molecular rearrangements in the glassy phase. These rearrangements, like the tensile elongation decreases, are unique for each aging temperature.

The dynamic mechanical measurements show that the material response after aging at 60°C is distinct from that observed after aging at 90°C. For example, tan δ values are suppressed only at lower temperatures (<70°C) by aging at 60°C, whereas aging at 90°C results in a suppression over the entire temperature interval up to T_g. Therefore, aging at 60°C even for prolonged times produces a different effect from aging at 90°C. Similarly, dynamic measurements demonstrate that the effects of aging at 40°C can be distinguished from the effects of aging at 60°C. Based on this data it can be understood how tensile properties are not affected in a similar manner by aging at different temperatures. The state of the aged structure, and its corresponding response to stress, are unique for each aging temperature.

The measurement of the intensity of the loss peak cannot be performed accurately because of the shifting of the glass transition and the general decrease in tan δ at all temperatures. However, the estimates of peak area presented here do serve to emphasize that the rate of change of tan δ occurs rapidly in the first
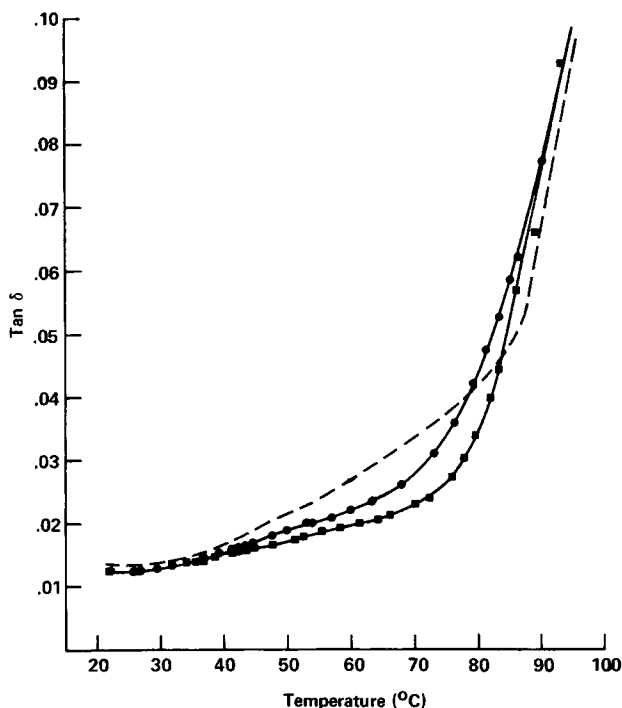
Fig. 6. Loss factor tan δ for injection-molded ABS after aging at 60°C. Dashed line represents unaged ABS; (●) 24 hr at 60°C; (■) 96 hr at 60°C.

24 hr of aging and then later at a reduced rate if at all. This pattern parallels the rate of loss of tensile elongation with time, which also decreased rapidly and then leveled off. A more accurate monitor of the extent of physical aging should be possible by use of DSC measurements as shown by Petrie.[2] A subsequent report will present the DSC analysis of the aged ABS samples used in this study.[9] The loss of tensile elongation was also shown previously to be thermoreversible in the sense that it is recoverable by reprocessing of ABS.[1] The thermoreversible nature of the dynamic mechanical properties has not been investigated at this time. The study of this aspect of physical aging would be most helpful in conjunction with an alternative and a more precise technique for measuring the β transition intensity.

Relation of Aging to the β Transition

The effect of aging on the β transition was demonstrated by the results of this study. It is equally important to consider the reverse question: What effect does the β transition have on aging? Struik[7] has indicated that physical aging occurs primarily in the temperature interval between T_β and T_g. The results presented here and also previous results[1] on ABS are compatible with this suggestion. Moreover, it appears that the intensity of the β transition (magnitude of tan δ) is to a first approximation a good measure of the relative propensity for physical aging to occur. For example, at 40°C where tan δ remains low, there is very little segmental molecular mobility in the glassy state and the effect of physical aging is also small. The higher tan δ at 50 and 60°C reflects a greater

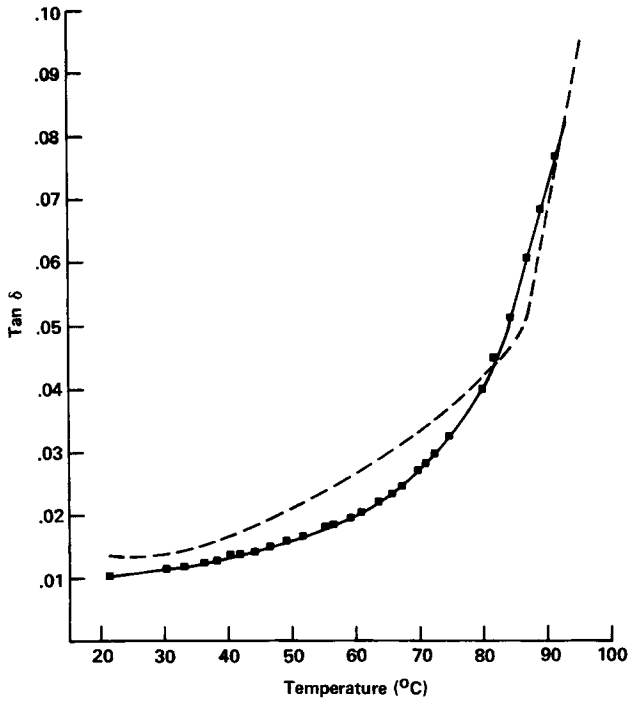Fig. 7. Loss factor tan δ for injection-molded ABS after aging at 40°C. The dashed line represents unaged ABS; (■) 296 hr at 40°C.

molecular freedom at these temperatures, which allows more extensive rearrangements to occur. Finally, at 90°C it is seen that the significantly higher tan δ reflects considerable molecular mobility at this temperature where the effects of aging are pronounced. Assuming that significant aging does not occur below the β transition temperature the low-temperature limit for aging of ABS can be estimated at −30°C. This is estimated to be the T_β for pure polystyrene based on dilatometry or other slow measurement techniques.[4] However, since even the effects of 40°C aging are not seen to reduce tensile elongation, other means
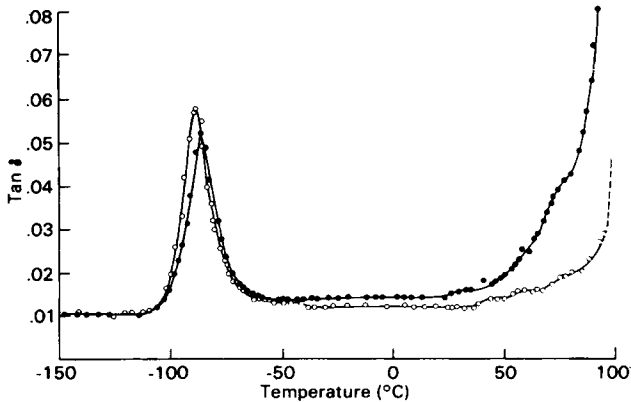

Fig. 8. Loss factor tan δ in the temperature range −150 to 0°C for injection-molded ABS before and after aging at 90°C. (●) As molded; (○) 500 hr at 90°C.

of characterizing physical property changes may be needed to detect effects of aging at these lower temperatures.

Crazing in ABS

The observation of physical aging in ABS and its relation to the β transition may provide an important clue to understanding ductility in rubber-modified glassy polymers. It is known that ABS deforms by crazing and shear banding of the glassy phase.[10] Also, Boyer has suggested initiation of crazing is related to the β transition.[4] In a similar vein others have related both the α and β transitions to deformation of polystyrene through Eyring analyses of yielding.[11]

Our studies of physical aging tend to support the Boyer hypothesis. For example, it is clear that the loss of elongation owing to aging occurs concurrently with a suppression of the β transition. The additional point to be made here is that the physical basis for a loss of elongation is the suppression of crazing. For example, during tensile testing, an aged compression-molded ABS sample exhibits very little stress whitening and fails at 10% elongation. The few crazes that do initiate in the aged sample propagate across the sample cross section and lead to failure by crack formation from one of the large crazes. This behavior is not unlike the sequence of events for failure of an unmodified glassy polymer. Aging must therefore neutralize the ability of the rubber particles to initiate extensive crazing even though no oxidation or morphological change occurs.[1] Thus it appears that the mutual interference of the numerous crazes and shear bands in the glassy matrix are the primary factors preventing the development of a catastrophic crack in unaged ABS—not the craze arresting ability of the rubber particles themselves. Clearly, additional studies on the rubbery phase and the rubber/glassy interface are needed.

CONCLUSIONS

(1) There is a close parallel between the changes in tensile elongation and the changes in the β transition as a result of physical aging at various times and temperatures.

(2) Physical aging results in a suppression of the β transition and the initiation of crazing in the glassy matrix of ABS. This occurs with no apparent degradation or change in morphology of the dispersed rubbery phase.

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