Physical Aging of Poly(acrylonitrile-Butadiene-Styrene). II. Differential Scanning Calorimetry Measurements

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Synopsis

Thermal analysis has been employed to study the effects of physical aging on poly(acrylonitrile–butadiene–styrene) (ABS). Physical aging refers to the thermoreversible molecular rearrangements which occur in the glassy poly(styrene–acrylonitrile) phase of ABS. Results demonstrate that the effect of aging on the glassy phase is dependent on the aging temperature. The extent of physical aging can be measured quantitatively by enthalpy changes in the glassy phase. However, aging is seen to occur even at room temperature and this must be taken into account in making enthalpy change measurements. The physical state of the aged ABS depends upon the specific time and temperature path taken during aging. This implies that a simple time–temperature equivalence does not exist for physical aging. Quantitative correlations between enthalpy changes and mechanical property changes are not observed for properties measured at low speed. However, preliminary data suggest that a correlation does exist for properties measured at high speeds such as impact strength.

INTRODUCTION

A previous study of the effects of oven aging on ABS has shown that aging at 50–90°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, and differential scanning calorimetry (DSC) data it was suggested that the changes in tensile elongation were due to physical aging. The term physical aging refers to the thermoreversible molecular rearrangements which occur in the glassy poly(styrene–acrylonitrile) (SAN) matrix of poly(acrylonitrile-butadiene-styrene) (ABS). The preceding article[2] has shown how aging affects the dynamic mechanical properties of ABS. It provided further evidence that the loss of elongation was related to rearrangements in the glassy phase. The present study describes in greater detail the effects of aging on the glassy SAN matrix of ABS as revealed by DSC measurements. In particular, the influence of aging temperatures from 20 to 90°C is described and the relation of mechanical property changes to enthalpy measurements obtained by DSC is discussed.

EXPERIMENTAL

Commercially available ABS and polystyrene copolymers were used in this study. These included Marbon Cycolac E and L ABS, Dow San 100 poly(styrene–acrylonitrile), and Arco Dylark 232 poly(styrene–maleic anhydride) (SMA). Samples were examined as received and after purification. The latter was done

by dissolving in toluene and reprecipitating with methanol to remove processing lubricants or other low molecular weight contaminants. Precipitated samples were allowed to dry at room temperature for 24 hr, vacuum dried at 75°C for 24 hr, and compression molded into thin films at 190°C. Cycolac E ABS is no longer commercially available and therefore certain mechanical measurements were made using Cycolac L. The two materials have similar polybutadiene contents, exhibit similar initial mechanical properties, and evidence similar tensile elongation decreases after aging.

Tensile property measurements were described previously.[1] Izod impact tests were conducted using unnotched ABS Cycolac E samples in accordance with ASTM 256 E. The samples used were cut from the narrow portion of injection-molded ASTM D638 type I tensile bars. For high-speed testing, injection-molded bars of Cycolac L were prepared with a cross section of 3.2 by 3.8 mm and a length of 62.0 mm. A Plastechon model 581 was used to measure elongation to break at 89,000 mm/min.

DSC measurements were conducted at 10°C/min on shavings cut from the test bars and on thin films (0.1 mm thick). The latter were compression molded from the purified glassy polymers. A duPont 990 thermal analyzer was employed for these measurements. Although the operation of the DSC is relatively straightforward, it was found necessary to control strictly the details of cutting and placing samples in the DSC pans in order to obtain reproducible results. In addition, spurious results were sometimes observed when samples distorted and lifted off the DSC pan during heating presumably because of the release of molded-in stresses.

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

Differential Scanning Calorimetry

The typical DSC trace for an amorphous glassy polymer exhibits a step change at the glass transition temperature T_g. This occurs because of the difference of specific heat of the glassy and rubbery states of the material. An important point of this study is that commonly used procedures for molding glassy polymers employ rapid quenching to the glassy state. Such quenched samples, after storage at room temperature, can exhibit changes in the slope of the DSC trace at temperatures below the usually observed glass transition T_g. For example, Figure 1 shows the DSC traces of injection-molded and compression-molded ABS. In addition to the glass transition in the vicinity of 100°C, the DSC traces reveal slight changes in slope between 50°C and T_g.

To demonstrate that this feature is characteristic of the glassy phase of ABS, styrene polymers having no rubber reinforcement were investigated. Figure 2 shows the DSC traces for two polystyrene copolymers after they were purified and remolded with similar heating and quenching conditions. Each trace in Figure 2 clearly reveals the glass transition as well as slope changes at temperatures below T_g. Thus, the DSC response observed for ABS below T_g can be
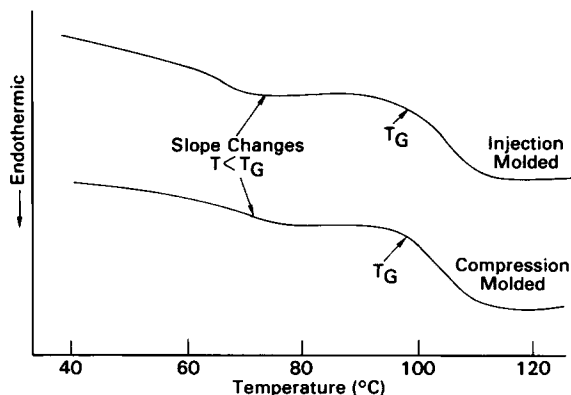
Fig. 1. DSC traces of injection- and compression-molded ABS.

attributed to the glassy styrene acrylonitrile phase and is a general phenomenon for all the glassy polymers investigated and cannot be attributed to the presence of processing lubricants.

Previous investigators have reported that isothermal aging of glassy materials at temperatures just below T_g causes an endotherm to appear coincident with the glass transition.[3] This was observed for ABS after aging at 90°C.[1] Figure 3 demonstrates how the DSC response changes with aging temperature for an aging time of 100 hr. For aging temperatures below 80°C the DSC endotherm no longer occurs coincident with the glass transition, but occurs at temperatures below it. In addition, the endotherm decreases in intensity and becomes broader as aging temperature decreases.

The effects shown in Figure 3 for injection-molded ABS were also observed for the pure poly(styrene–acrylonitrile) copolymer. Figure 4 shows the DSC traces for compression-molded SAN before and after aging at 40 and 60°C. The similarity of the DSC traces in Figures 3 and 4 again demonstrates that the response of the ABS is due to the glassy matrix. A repeated run of any previously aged sample after cooling at 10°C/min in the DSC cell shows only the step change at T_g.

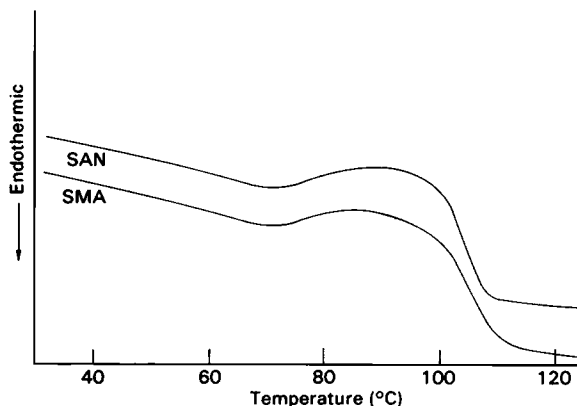The influence of aging time at 40°C on ABS is shown in Figure 5. The aging

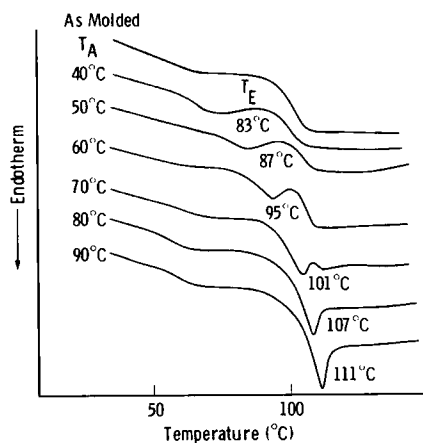Fig. 2. DSC traces of purified compression-molded films of SMA.

Fig. 3. Differential scanning calorimetry traces of Cycolac E ABS aged 100 hr in nitrogen. The aging temperature T_A and endotherm location T_E are indicated for each curve.

endotherm shifts to a higher temperature with a slight increase in magnitude. Aging at 60°C for several hundred hours also causes only slight additional changes in the DSC response compared to samples aged for only 24–48 hr. The use of higher heating rates in the DSC also tended to shift the shallow endotherms to higher temperatures.

The trend observed in Figure 3 suggests that the slight changes in slope near 70°C for the as-molded ABS might also be interpreted as an extremely shallow endotherm representing a sample "aged" at room temperature. To clarify this point, ABS samples were heated to 180°C and rapidly quenched with liquid nitrogen in the DSC to −120°C. Upon reheating at 20°C/min (higher heating rates enhance the intensity of secondary transitions) the previously observed slope changes below T_g were not detected. However, after "aging" 24 hr at room temperature, the DSC trace clearly revealed the typical slope change near 70°C, as shown in Figure 6. However, it is also apparent from Figure 6 that the slope change near 70°C is itself part of a very shallow endotherm which initiates just above room temperature. Thus, as suggested by Figure 3, the slope change
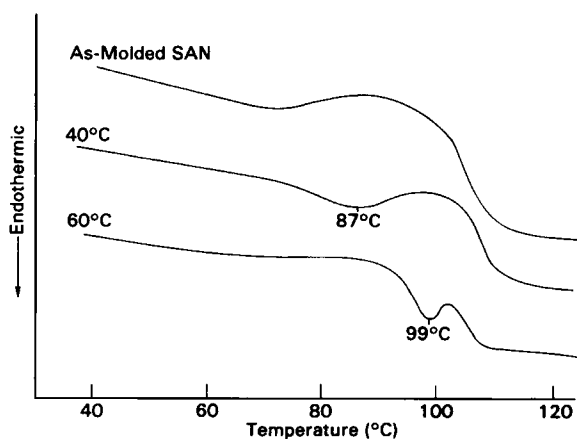

Fig. 4. DSC traces for purified SAN as-molded and after aging at 40 and 60°C for 100 hr.
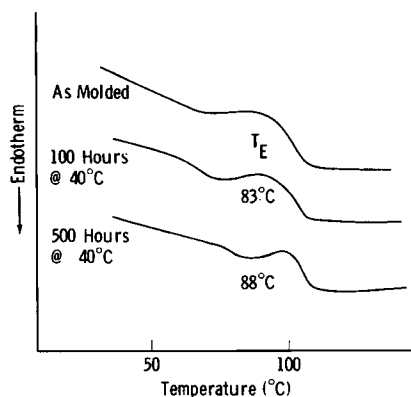
Fig. 5. Effect of aging time at 40°C on the differential scanning calorimetry traces of Cycolac E ABS. The endotyerm location T_E is indicated for each curve.

generally observed in a DSC trace between room temperature and T_g is due to room temperature aging and is not observed in rapidly quenched samples reheated immediately without room temperature storage.

Figure 6 also demonstrates the existence of additional slope changes at -5 and $-40°C$ for ABS. Also, the polybutadiene rubbery phase T_g is evident at $-90°C$. The origin of the slope changes at -5 and $-40°C$ is not presently known. It is possible that the events at -5 and $-40°C$ taken together represent a step change resulting from the onset of the secondary β transition in ABS. Similarly treated and purified SAN exhibits less intense indications of the events at -5 and $-40°C$ but clearly shows the shallow endotherm above room temperature.

Further confirmation of the existence of room temperature aging is shown in Figure 7 for injection-molded ABS and purified compression-molded SAN after room temperature storage for two years. The DSC traces of both materials exhibit endotherms below T_g with SAN exhibiting somewhat more intense changes. In addition to the shallow endotherm above room temperature, which was previously observed after 24 hr aging, a relatively sharp endotherm is observed at
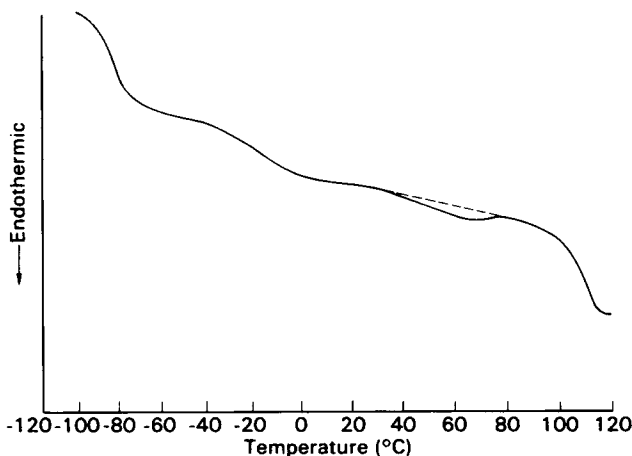

Fig. 6. DSC traces of injection-molded ABS reheated at 20°C/min immediately after quenching (- - -) and after 24 hr (——) at room temperature.
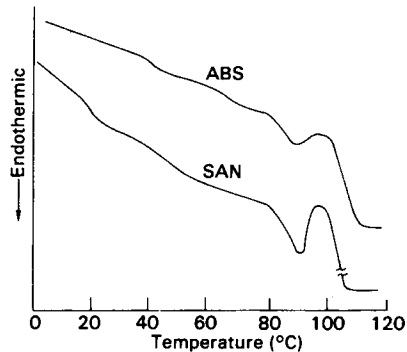
Fig. 7. DSC traces of ABS and SAN after room temperature aging for 2 years.

90°C, just below T_g. This endotherm is attributed to prolonged room temperature aging. It should be noted that the traces in Figure 7 were run at 20°C/min using larger amounts of material and higher sensitivity to intensify the DSC endothermic peaks compared to those shown in previous figures. The results of Figure 7 suggest that after sufficiently long aging times at room temperature the DSC endotherms may shift to higher temperatures and occur coincident with the step change at T_g. Further study is needed to clarify this.

These results demonstrate that aging is occurring at room temperature for ABS. Presently the kinetics of this aging process and its effect on mechanical properties have not been studied. For this report the important point is the finding that room temperature aging is in fact occurring for ABS materials and thus is causing the DSC response between 20°C and T_g to deviate from a flat baseline. For example, it becomes apparent that the DSC trace for as-molded ABS (Fig. 3) is actually a trace for ABS aged at room temperature. The storage or aging time for this sample is not known precisely but was likely to be two to three months.

Enthalpy Changes

Recognizing that aging is occurring even during storage at room temperature, there are two procedures which could be employed to quantitatively measure the peak areas of the DSC endotherms for ABS aged at higher temperatures. First, a flat baseline could be used and the combined effects of room temperature aging and high temperature (40 to 90°C) aging could be measured collectively. Second, the extent of aging over and above what occurs at room temperature could be measured by using the DSC trace for as-molded ABS as a baseline. The latter procedure was selected because of the desire to compare the endotherm areas with the corresponding changes in tensile elongation. As in the case of the DSC, the unaged control for tensile elongation measurements is representative not of unaged ABS but rather of ABS aged for a few months at room temperature.

Figure 8 shows how a DSC baseline was constructed and also shows the endotherm peak area which was measured for various aging temperatures. From the endothermic peak areas, the corresponding enthalpy change which had occurred in the glassy phase during aging can be determined. Table I lists the calculated enthalpy changes for various aging times and temperatures based on
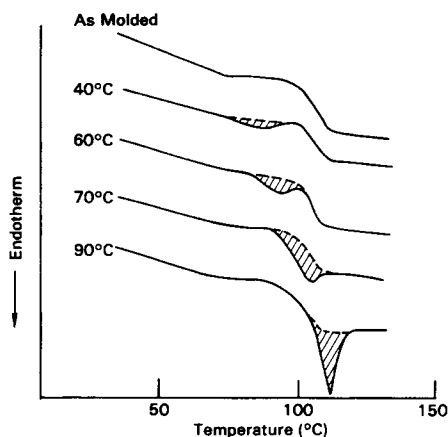
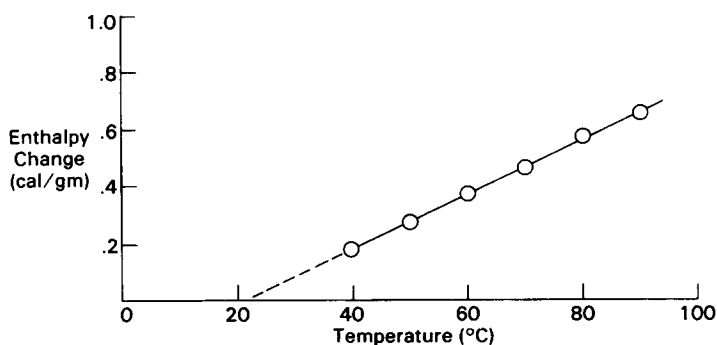Fig. 8. DSC traces for ABS showing areas used for enthalpy change calculations.

Fig. 9. Enthalpy change vs. aging temperature for ABS Cycolac E after 100 hr aging.

the equation $\Delta H = \text{A S } T/h\ m$ where ΔH is the enthalpy change (cal/g), A is the peak area (in.^{2}), S is the DSC sensitivity (mcal/sec in.), T is the temperature scale (°C/in.), h is the heating rate (°C/sec), and m is the mass of sample (mg).

Figure 9 shows the effect of aging temperature on the enthalpy change for ABS aged for 100 hr. A linear increase is observed from 40 to 90°C. At low tem-

TABLE I
Enthalpy Measurements for ABS[a] at Various Temperatures

Temperature (°C)	Time (hr)	Enthalpy (cal/g)
40	100	0.181
	500	0.225
50	100	0.279
60	100	0.374
70	100	0.458
80	100	0.573
90	24	0.380
	100	0.650
	308	0.724
	570	0.710

[a] Cycolac E.

peratures the enthalpy change extrapolates to zero at 21°C. A zero value is expected at room temperature since a zero area would obviously result from subtracting the DSC trace for as-molded ABS from itself.

The enthalpy change increases with both aging time and aging temperature and provides a convenient way of monitoring the kinetics of aging. However, caution must be exercised in the measurement of enthalpy change by use of the DSC trace. Obviously the baseline positioning and calibration of the instrument are important. In addition, the magnitude of the calculated enthalpy change depends on heating rate. Table II lists the values of enthalpy change calculated for Cycolac E ABS at various DSC heating rates. Above 10°C/min similar values are obtained, but at lower rates the enthalpy change decreases. This is to be expected since the endotherm is due to superheating in the DSC, and hypothetically a zero value of enthalpy change should occur for extremely low heating rates. In addition to heating rate effects, the sample weight might also be expected to influence the DSC response.[4] Table III lists values of enthalpy change for Cycolac L obtained by using different sample weights. It is noted that relatively constant values are obtained. Thus thermal lag in the sample does not provide ambiguous results for this range of sample weights. For the data in Table I, the samples used ranged from 11 to 13 mg.

Mechanical Property Measurements

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 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 resulted in no additional decrease beyond 40%, whereas aging at 90°C for

TABLE II
Effect of DSC Heating Rate on Enthalpy Change for Injection-Molded Cycolac E ABS Aged 308 hr at 90°C

Weight (mg)	Heating rate (°C/min)	Enthalpy change (cal/g)
11.215	1	0.439
10.867	5	0.585
11.739	10	0.716
11.950	20	0.718
12.415	50	0.732

TABLE III
Effect of Sample Weight on Enthalpy Change for Cycolac L ABS Aged 308 hr at 90°C

Weight (mg)	Enthalpy change (cal/g)
2.793	0.902
7.098	0.930
11.295	0.914
14.869	0.904

a few hours caused an 80% loss of elongation. Table IV shows the tensile elongation values for aged ABS measured at high crosshead speed (89,000 mm/min). For ABS the elongation to break in a high speed test has been shown to correlate with impact strength.[5] In the present case a loss of elongation is indicated after aging at 40°C. This was confirmed by additional measurements for samples aged for longer times at 40°C. Table IV also shows that a systematic decrease in elongation occurs with increasing aging temperature. This behavior parallels the change in enthalpy with aging temperature (Fig. 9). In addition, it has been found that for the same ABS material the loss of elongation measured at high speeds occurs more gradually with aging time at 90°C than the loss of elongation measured at low speeds. This is shown in Figure 10 for Cycolac L ABS. The more gradual loss of high-speed elongation parallels the rate of enthalpy change which is also shown in Figure 10 for the same ABS material.

The rate of loss of impact strength with aging also is observed to correlate closely with the enthalpy changes measured by DSC. For example, Figure 11 shows the concurrent changes in tensile elongation measured at 5 mm/min, Izod impact strength, and enthalpy change with aging time at 90°C for Cycolac E ABS. Tensile elongation falls rapidly to a low level within 24 hr in contrast to the observed enthalpy change which is more gradual. On the other hand, there is a parallel between the rate of loss of impact strength and the rate of increase of the enthalpy change after aging.

Similar rate effects have been observed for a variety of ABS resins and for compression-molded as well as injection-molded samples. It has also been observed that the maximum loss of Izod impact strength (assuming a leveling off after 300 hr at 90°C) is less for notched samples. In addition, compression-molded samples exhibit a greater loss of impact strength than injection-molded samples when the latter are tested in the flow direction. The values of high-speed tensile elongation or impact strength retained after extensive aging indicate that physical aging may ultimately not be as deleterious to ABS as other aging mechanisms such as oxidative degradation.

DISCUSSION

Endothermic Peaks at $T < T_g$

The DSC analysis of both as-molded and aged ABS demonstrates that endotherms occur below T_g rather than at T_g for samples annealed at 20–70°C. The endotherms observed below T_g are broader and less intense than the endotherms

TABLE IV
Effect of Aging Temperature on the Ultimate Elongation of ABS[a] Measured at 89,000 mm/min (3500 in./min)

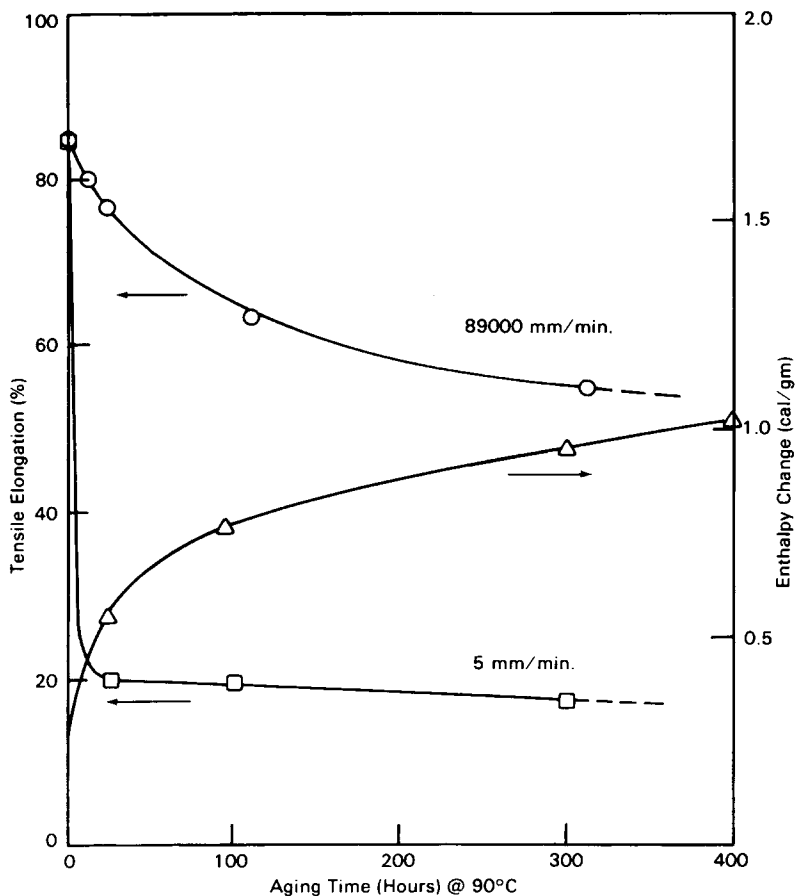| Treatment	Elongation (%)
None	86
24 hr at 40°C	67
24 hr at 60°C	56
24 hr at 90°C	49

[a] Cycolac L.

Fig. 10. Tensile elongation measured at 5 and 8900 mm/min vs. aging time at 90°C for Cycolac L ABS. Concurrent changes in enthalpy are also shown.

usually reported, which occur coincident with T_g.[3] For a constant annealing time, the endotherm temperature is directly proportional to the prior aging temperature, and with increased aging time the endotherm shifts slightly toward higher temperatures with some increase in magnitude. The DSC results for ABS are similar to results for unmodified glassy copolymers such as poly(styrene–acrylonitrile), the matrix phase of ABS.

The magnitude of the DSC endotherms increases linearly with aging temperature from 40 to 90°C for a constant aging time. This is observed in spite of the differences in shape and temperature location for endotherms characteristic of different aging temperatures. Thus, it appears that DSC analysis can provide a valuable quantitative measure of the course of aging at 40°C as well as at 90°C. However, for precise quantitative measurements, the shape of the endotherms below T_g and the occurrence of room temperature aging demand strict control of sample history and proper baseline selection. In addition, the validity of using the DSC to make quantitative measurements of enthalpy change has been criticized by Richardson and Savill.[4] Robertson has also discussed
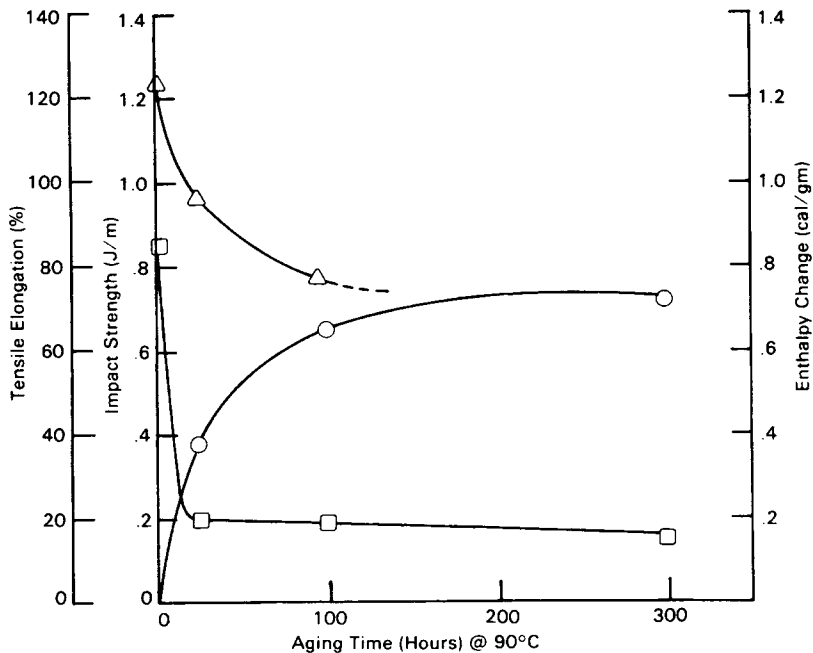
Fig. 11. Concurrent changes in tensile elongation, Izod impact strength, and enthalpy vs. aging time at 90°C for Cycolac E ABS.

possible limitations of this technique.[6] Thus in spite of the convenience of the method, its use should be approached with caution.

Correlation of DSC and Dynamic Mechanical Measurements

The endothermic peaks observed by DSC at $T < T_g$ after aging are related to the onset of the β transition in the glassy state in an inverse manner. That is, the intensity of the β transition as previously reported[2] decreases as the magnitude of the endothermic peaks increases. For example, highly quenched samples exhibit an intense β-loss peak (tan δ) with no detectable endotherm at $T < T_g$. Upon aging at 60°C the β-loss peak is partially suppressed and corresponding endothermic peaks are observed by DSC. Upon aging at 90°C not only is the β-loss peak suppressed, but the onset of the glass transition is also suppressed and shifted to higher temperatures. Sharp endotherms occur corresponding to the more abrupt and rapid rise in tan δ at T_g.[2] The endotherms observed for aged samples do not reflect a first-order transition such as a crystal melting point. Rather, they occur because the heating rate in the DSC is faster than the kinetic response of the material as it undergoes the transition from a glass to a liquid. Presumably after aging below 70°C the DSC endotherms which occur at $T < T_g$ reflect the transition from a glass having limited segmental motion to a glass having more extensive segmental motion. The latter motion is associated with the onset of the glass transition which is clearly shown by dynamic mechanical measurements to initiate at about 70°C even though the T_g measured by DSC occurs at 100°C.

Relation of Enthalpy Measurements to Mechanical Properties

It is interesting to compare the magnitude of the enthalpy change (sometimes referred to as enthalpy relaxation[3]) to the observed tensile elongation decreases previously reported[1] after aging. The following points are noted: (1) aging occurs at 40°C with small, but measurable, changes in enthalpy, yet tensile elongation measured at conventional rates does not change; (2) the magnitude of the enthalpy change measured after 24 hr at 90°C (0.380 cal/g) is similar to that measured after 100 hr at 60°C (0.374 cal/g), yet tensile elongation decreases are different for these conditions (80% decrease versus 40%). These results indicate that enthalpy magnitude alone may not necessarily provide a correlation with mechanical property changes after aging. This is believed to be due to the fact that the state of the aged glassy phase is path dependent. That is, aging at 60°C does not produce the same state as aging at 90°C no matter what aging times are considered. In other words, a simple time–temperature superposition does not hold.

On a more positive note, the enthalpy changes appear to correlate with tensile elongation measurements made at an extremely high speed (89,000 mm/min). For example, the latter shows a decrease after aging at 40°C, a systematic decrease with increased aging temperature, and a more gradual rate of decrease after aging at 90°C. Thus, changes in high-speed tensile elongation after aging are seen to more closely parallel the enthalpy changes (Table I and Fig. 10). The rate of loss of impact strength also correlates with the changes in enthalpy after aging, as shown in Figure 11. All of these observations suggest that useful correlations between high-speed mechanical properties after aging and enthalpies measured by thermal analysis may be possible. In general, however, the state of the aged ABS glassy phase will depend on the specific time–temperature path taken during aging and it appears that the magnitude of the enthalpy change (as measured in this study) does not completely describe this state for a broad range of aging temperatures.

CONCLUSIONS

(1) Differential scanning calorimetry measurements of ABS aged at 20 to 70°C show endothermic peaks occurring at temperatures below T_g.

(2) Quantitative measurements of enthalpy change for these broad peaks require proper baseline selection to account for room temperature aging. However, enthalpy change alone does not completely specify the state of the aged glassy structure.

(3) Differential scanning calorimetry measurements support previous tensile elongation and dynamic mechanical measurements in showing that a simple time–temperature equivalence does not exist for the effects of aging at 20°C to T_g (100°C).

(4) The magnitude and rate of change of enthalpy with aging time correlates more directly with high-speed mechanical property measurements for ABS.

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