Thermal Aging of Bisphenol-A Polycarbonate/Acrylonitrile–Butadiene–Styrene Blends

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SYNOPSIS

Thermal aging of immiscible bisphenol-A polycarbonate/acrylonitrile–butadiene–styrene (PC/ABS) blends containing 25, 60, and 75% PC and the PC and ABS blend components have been studied. Changes in Izod impact properties and dynamic mechanical spectra are reported following aging at 90, 110, and 130°C for times up to 1500 h. PC/ABS blends containing 60 and 75% PC were found to retain high impact performance following aging at elevated temperatures, compared to the PC blend component. Dynamic mechanical spectroscopy is an effective probe for investigating the structure–property changes occurring and the mechanisms of aging. For PC and ABS, the changes were mainly due to physical aging of the amorphous polymers when aged below the glass-transition temperature. For the PC/ABS blends, oxidative degradation additionally contributes to loss of toughness. Although structure–property changes are related to the behavior of the blend components, additional factors of potential importance for multiphase polymer–polymer systems have been identified, including a redistribution of stabilizers during the blend manufacture. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

All polymers show changes of internal structure with time via a range of aging processes, and produce an associated effect on the physical and mechanical properties. Such aging effects are, of course, extremely important for engineering polymers that are expected to show durability in a range of service environments depending upon the application. Common environments include, for example, mechanical stress, elevated temperature, chemicals, and their combinations.

Polymer–polymer blends form an increasingly important class of materials, with many commercially available systems being utilized for engineering applications. To date, however, there is only a limited amount of information available addressing the performance characteristics of blends, such as thermal aging behavior.

Stress relaxation studies on polymer blends have been reported that help develop an understanding of long-term performance, and also include the effects of thermal aging on structure and properties. Back in 1968, Rusch[1] reported stress relaxation data for an acrylonitrile–butadiene–styrene (ABS) copolymer and a bisphenol-A polycarbonate (PC)/ABS blend. It was concluded that the relaxation behavior was dominated by the continuous phase in the blend with the longest relaxation time. Two studies[2,3] provided an analysis of the relaxation moduli for two phase polymer blends by generation of a so-called master curve via time–temperature superposition procedures. A later communication by Maurer et al.[4] on the stress relaxation of PC/ABS blends has taken physical aging, and its effects on the relaxation behavior of the blend components, into account in the data analysis via superposition theories. Morphology was identified as an important feature of the blends in terms of understanding and modeling their overall response. Stress relaxation studies have also been described for miscible blends[5,6] that include sample aging time and temperature in the data analysis.

This communication presents a practical study of the effects of thermal aging on the toughness of PC/ABS blends and blend components, utilizing

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dynamic mechanical spectroscopy (DMS) as a probe for structure–property changes. Background information to the study discusses the blend system characteristics and the aging behavior of the PC and ABS blend components. These interrelated aspects are taken into account for both the design of the aging experiment and the data interpretation, helping to identify the additional features specific to the aging behavior of immiscible blend systems.

CHARACTERISTICS OF BLEND SYSTEM

PC is an amorphous polymer with a unique combination of transparency, toughness, stiffness, and high softening temperature. The high ductility of PC can be negatively influenced by many environmental factors, resulting in unexpectedly brittle failure. Impact properties are determined by a range of factors including the PC molecular weight, the sample history (including aging) and a range of test related parameters such as notch size, thickness, and temperature.

PC/ABS blends, as produced by common melt processing operations, are immiscible systems. Reported observations of shifts in glass transitions in the blends of the PC and the styrene-co-acrylonitrile (SAN) phase, which forms the matrix phase in ABS, are not due to partial miscibility between phases, but can be attributed to a redistribution or transfer of plasticizing lower molecular weight species between phases.[7] The blends have an attractive balance of processibility and mechanical properties including toughness.

Blend morphology is accepted as having a major influence on physical properties, and depends to a great extent on component composition ratios. Information on PC/styrenic copolymer blend systems from DMS studies[8,9] provides some evidence that blends having composition ratios in the range 30–70% PC content tend to show solid-state morphologies with co-continuity of the phases when produced via melt processing operations. The shear environment and rapid cooling rates associated with injection molding may result in intermediate structure between fully co-continuous and occluded systems, with the outside skin layer retaining co-continuity of phases outside this range.

POLYMER/BLENDS AGING PROCESSES

In the context of this study, physical aging and thermooxidative degradation are the more important

processes associated with changes in structure and properties at temperatures below the glass transition temperature, T_g.

Rapid cooling of an amorphous material from above to below T_g can result in the freezing-in of a nonequilibrium solid-state structure, for example after a melt processing operation. Over certain temperature ranges, there is sufficient internal molecular or segmental mobility to allow a continuation of restructuring, termed physical aging, as the amorphous (polymer) structure attempts to move toward thermodynamic equilibrium.

Physical aging can occur up to temperatures where ordering effects just dominate disordering effects, i.e., just below the temperature range associated with the T_g process for the amorphous phase. Aging rates are generally most rapid in the temperature range 10–20°C below T_g as determined via dilatometry. A thermal cycle to above T_g essentially removes the sample history by introducing molecular or segmental mobility on a much larger scale than attributed to the aging process.

There is an increasing amount of literature addressing the subject, not the least because of the potential influence on the prediction of the long-term performance of polymeric materials. Many studies have attempted to derive relationships between internal free volume and physical properties. A decrease or redistribution of the polymer internal free volume with aging can result in lower chain segmental mobility. The consequence is that properties that have an underlying link to internal mobility are most dependent on sample history. Typically, modulus and density increases are observed, and decreased practical toughness and slower creep rates can be anticipated.

Following from the early work of Kovacs,[10] Struik[11,12] has provided a comprehensive background to the subject of physical aging and its interrelationship with internal free volume and property changes for amorphous materials, including styrenic polymers such as PS, SAN, and ABS. Wyzgoski[13] investigated the effects of physical aging on the dynamic mechanical behavior of ABS and SAN. A decreased intensity of the so-called β transition reflected lower molecular mobility in the glassy polymer, this being concurrent with a monitored loss of tensile elongation.

There is extensive literature available from the last 30 years covering the effects of sample history on the physical properties of PC, with a comprehensive review of the subject beyond the scope of this current communication. It has been long recognized[14,15] that exposure to elevated tempera-

tures below T_g can result in significant increases for tensile and flexural yield strength and decreased ductility. The major decrease in PC impact values following even short-term aging at temperatures of 90°C and above is well-documented.[16] With many engineering applications making use of the toughness performance, there have been significant efforts[17,18] to develop a fundamental understanding of the physical aging process for PC.

Other physical processes, i.e., those not significantly resulting in structural changes to the polymer chain structure/molecular weight, which are broadly related to aging, can be identified. These include loss or uptake of low molecular weight species such as plasticizer. Specifically regarding blend systems, Bertilsson et al.[19,20] described the aging of PC/ polybutylene terephthalate (PBT) blends in which secondary crystallization and morphological changes were considered to contribute to property changes.

In addition to the physical processes described above, chemical processes can also result in changes to the polymer structure during aging. In a general description, these could include a continuation of polymerization reactions, crosslinking, and a range of degradation reactions, with the latter often leading to molecular weight loss. Thermal aging in the presence of reactive chemicals can produce more severe structure/property changes.

Although the effects of degradation processes can be confined to the outermost layers of an aged material, the presence of such a brittle layer can result in drastic changes to ductility. So and Broutman[21,22] have described the effects that surface embrittlement can have on fracture behavior of polymers, including ABS. Thermooxidative aging is known[23] to decrease the ductility of ABS polymers and is a potential process for changes in the impact behavior of blend systems that include ABS as a component. For PC, any degradation processes leading to decreased molecular weight will clearly change ductility, but again these are not considered to be of significant importance in the context of this current study.

The study of thermal aging for impact modified PC reported by Cheng et al.[24] provides further information on the aging processes, with decreases in toughness being associated with structure changes via concurrent physical and degradative processes.

EXPERIMENTAL

In this study, the effects of thermal aging on Izod impact behavior of the blends and blend components

was monitored. DMS was selectively used to provide further information on structure–property changes during thermal aging.

The DMS spectra for the unaged blend components show that the values for the T_g, as given by the peak maximum in the G'' versus T scans, are 110°C for T_g (SAN) and 155°C for T_g (PC). There is an obvious relationship between the selection of aging temperatures and possibilities for physical aging in the amorphous phases in these immiscible blends. In addition, the rate and extent of chemical degradation processes can be affected because the diffusion rates and solubilities for reacting molecules are different above and below T_g.

The selected aging temperatures, T_a, for this study were:

1. 90°C, i.e., below T_g (SAN), T_g (PC);
2. 110°C, i.e., around T_g (SAN), below T_g (PC);
3. 130°C, i.e., above T_g (SAN), below T_g (PC).

Calibre® 300-4, a PC commercially available from The Dow Chemical Company, and an experimental ABS copolymer produced via mass polymerization techniques and containing 16% acrylonitrile and 12% polybutadiene (PBD) rubber were used as blend components. All the comonomer contents and blend composition ratios given refer to weight percentages.

PC/ABS blend compositions containing 25, 60, and 75% PC were chosen to provide systems having a variation of component ratio. The as-supplied blend components, available in pellet form, were weighed out in the desired weight ratios and tumble mixed for 10 min. The mixed pellet feedstock was melt compounded using a Buss MDK 46 Ko-Kneader machine (280°C heating zones, 220°C die; 15 kg/h; vacuum 0.8 bar), and the resulting blends pelletized for subsequent injection molding.

All blends and blend components were dried overnight at 90°C in an air circulating oven and injection molded with an Engel CC 90 ES 330/80 injection molding machine into multipurpose test bars [ISO 3167 : 1993(E) type A] with gauge dimensions of 80 × 10 × 4 mm and rectangular test bars (110 × 10 × 4 mm) for heat distortion (HDT) testing.

Test bars were laid on an aluminum sheet coated with polytetrafluoroethylene (PTFE) and then aged in air circulating ovens at three different temperatures (90, 110, and 130°C) and for times varying from 1.5 to about 1500 h.

After aging the HDT bars were cut in half and Izod impact properties were measured at temperatures of −20 and 23°C according to ASTM D256-84 (notch size 10 mil). Low temperature data were

generated on aged samples that were notched and then stored overnight in a refrigerator, and tested immediately on removal. Eight specimens were tested for each aging condition, and the data given in the figures represents the mean value for the notched Izod impact. Regarding the spread of impact values found, for samples with brittle failures (< 20 kJ/m^2) or ductile samples with a clean break (70–85 kJ/m^2) the standard deviation was $< 10\%$ of the value. Higher standard deviations were recorded either for some intermediate impact values where the test conditions corresponded to a ductile–brittle transition in the materials, or where only partial fracture of the test bar was observed.

For dynamic mechanical testing, samples (60 $\times$ 10 $\times$ 4 mm) were cut from tensile bars. Dynamic mechanical data were generated on a Rheometrics spectrometer RMS 800 using solid-state torsion rectangular geometry for samples taken from the gauge section of the tensile bars. Temperatures in the range -130 up to $+180°C$ were scanned in the cure mode with a heating rate of 2°C/min, forced constant amplitude torsional strain of 0.1%, and a fixed oscillation frequency of 10 rad/s. In the subsequent discussion of DMS data, it should be appreciated that the test geometry used biases the response of the outer or skin regions of a solid sample, as reported by Lewis and Nielsen[25] in their studies on the dynamic mechanical properties of particulate filled composites.

RESULTS AND DISCUSSION

Regarding the appearance after thermal aging, the PC test bars, which were colorless and transparent after molding, did not change in appearance during aging, even for the longest times at the highest temperature. The ABS and all PC/ABS blends, which were opaque and white after molding, did not change in appearance during aging at 90°C. Changes in appearance were observed during aging at 110 and 130°C, becoming more severe with time. The outside layer of test bars became progressively more yellowed and subsequently brown in appearance with time. The affected outside layer of the test bars was very sharply defined relative to the core regions, and reaching about 0.5 mm in depth after the longest aging times. Although the test bars were not turned during the aging period, there was no difference between the upper and bottom layer of the bars after aging.

Comparative molecular weight data were generated for PC via gel permeation chromatography (GPC) techniques, using tetrahydrofuran as solvent. Generated data confirmed that the molecular weight of the PC did not change significantly either on blending or during the aging experiments (e.g., PC unaged: $M_w = 36,400$; 144 h aged at 130°C: $M_w = 36,200$). Changes in PC molecular weight were not seen as a significant factor in the structure–property changes monitored in this current study, and it was
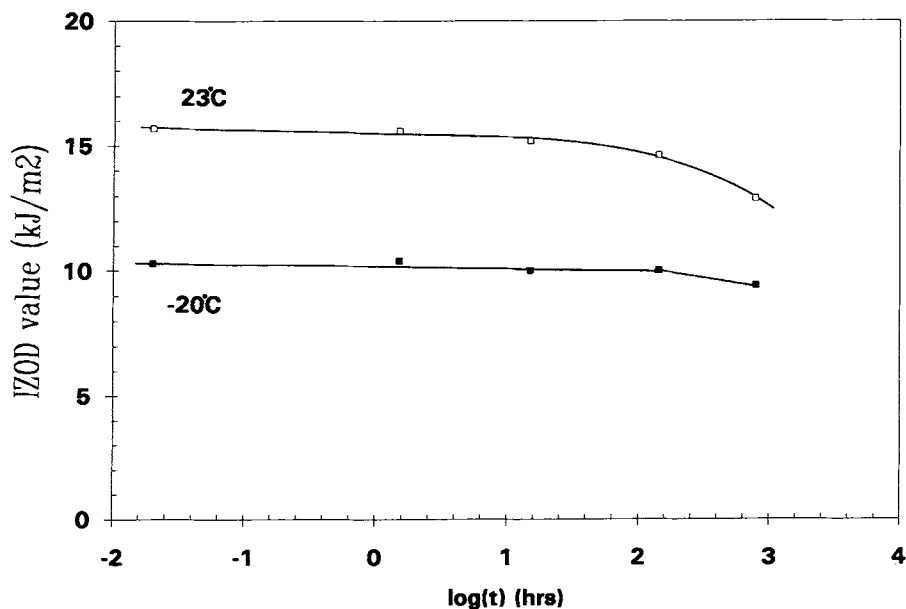

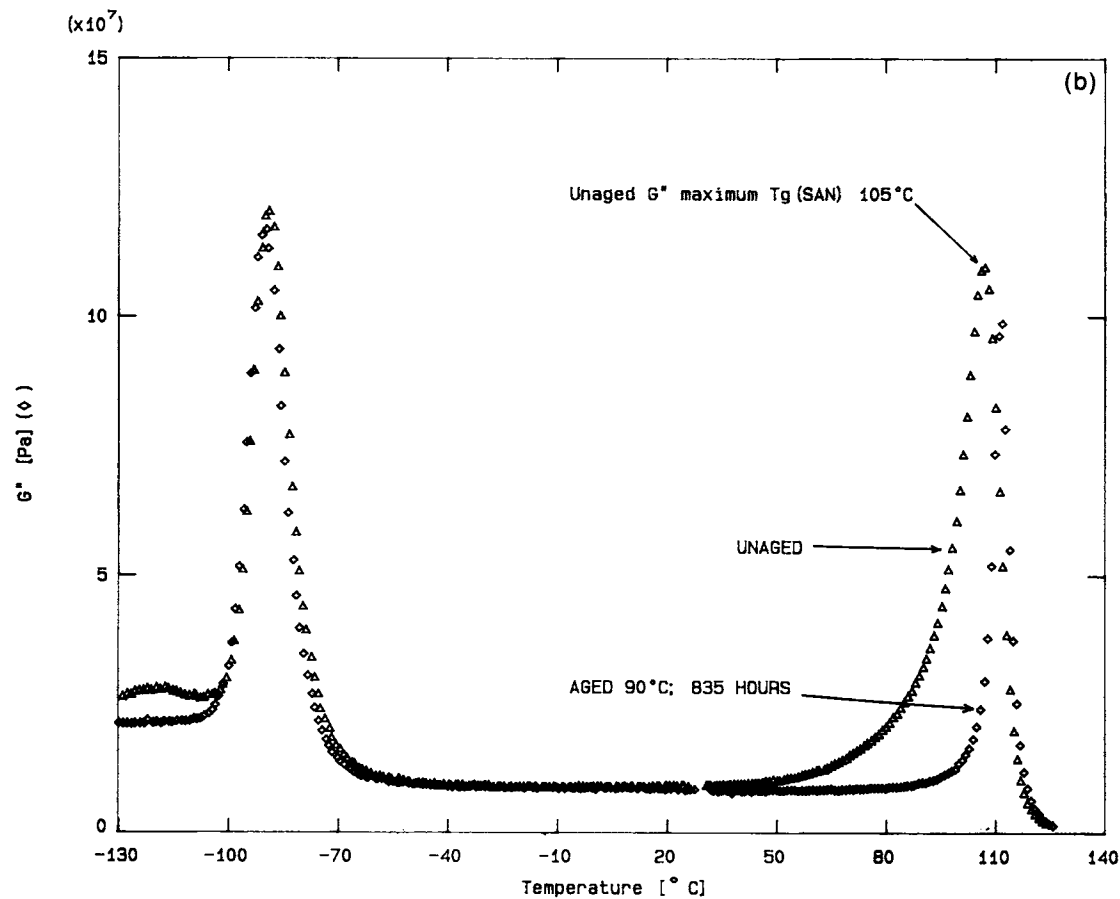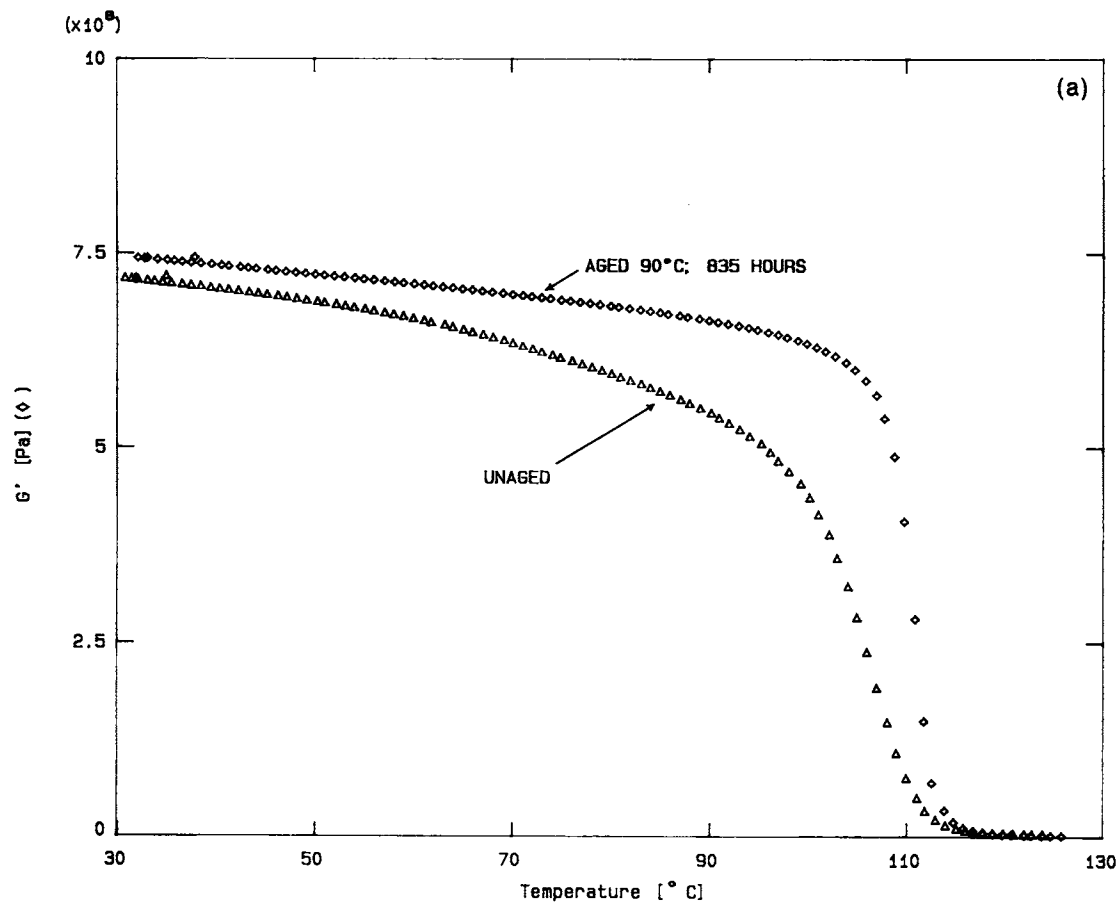**Figure 1** Izod impact data for ABS aged at 90°C.

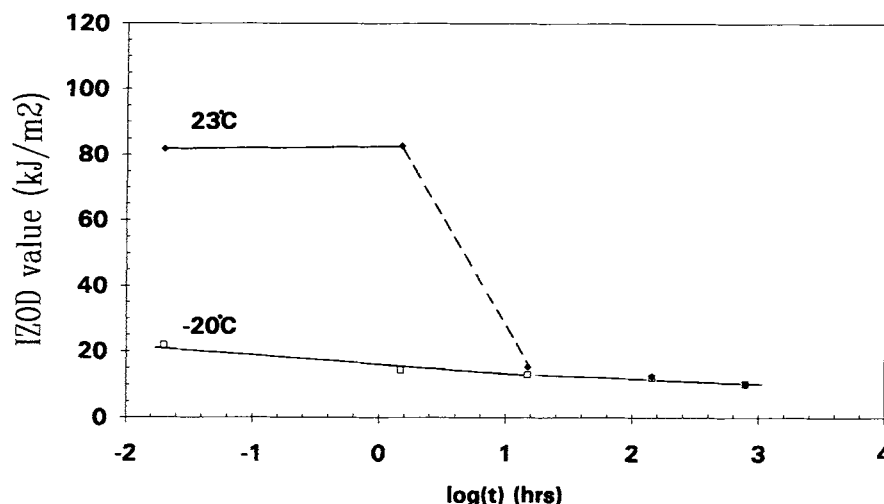**Figure 2** DMS data for ABS (a) G' versus T; (b) G'' versus T.

Figure 3 Izod impact data for PC aged at 90°C.

not felt appropriate to report these in any further detail.

Izod impact data for this ABS blend component is presented in Figure 1, showing only a small decrease in impact values for the longest aging times at 90°C.

DMS data for the ABS blend component unaged and following aging at 90°C are presented in Figure 2. Figure 2(a) quantifies the G' elastic modulus increases found over the temperature range 30°C to T_g (SAN) during aging. From the G'' loss modulus versus T data in Figure 2(b) it can be seen that the loss peak having a maximum at about −90°C and associated with T_g (PBD) shows little change in amplitude following aging. For the selected DMS test frequency, aging results in decreased loss in the temperature range 45–95°C, significant narrowing of the T_g (SAN) loss peak, and an increase of the G'' loss maximum from 107 to 112°C. Separate experiments have shown that the loss is recovered following a thermal cycle of the test bar to 120°C, i.e., above T_g (SAN), and that the changes in properties are thus mainly associated with physical aging processes in the amorphous SAN phase.

Figure 3 presents Izod impact data for the PC blend component following aging at 90°C. The unaged polymer has a high impact value, but after about 5 h of aging at 90°C, this decreases to the brittle fracture values found for low temperature impact testing. Similar low values are found for impact data of samples aged at 110 and 130°C. These data for the effects of aging on the impact behavior of PC are broadly in line with those reported by Broutman and Krishnakumar.[16]

DMS data for the PC blend component unaged

and following aging at 90, 110, and 130°C are presented in Figure 4. For scan temperatures above 100°C, the G' elastic modulus versus T data [Fig. 4(a)], show significant differences between the DMS spectra of the PC specimen aged at different temperatures. Figure 4(b) shows that aging results in lower tan δ values for temperatures above −10°C, with differences evident between the spectra of samples aged at the different temperatures. The loss peak associated with T_g (PC) is narrower after aging at 110 and 130°C, in contrast to aging at 90°C. For the so-called unaged sample, lower than expected tan δ values in the range 0–50°C reflect physical aging that occurred during sample storage (50 days, 23°C, 50% relative humidity) prior to testing.

Figure 5 presents Izod impact data for the PC/ABS blend having 25% PC content following aging at 90 and 110°C. The impact behavior is similar to the ABS blend component, also showing a slight decrease after aging at 90°C. Aging for the longest times at 110°C results in a significantly larger decrease in impact property than aging at 90°C.

Figures 6 and 7 present Izod impact data for the blends containing 60 and 75% PC following aging at 90 and 130°C. Data following aging at 110°C closely resembles the data for 130°C, and therefore has not been included.

The overall level of impact for both blends is of the same order as for unaged PC for the 23°C tests and significantly higher than PC for the −20°C tests. These two blend compositions show much better retention of impact properties after aging in comparison with the PC blend component.

For the 60/40 PC/ABS blend, extremely high impact values were recorded prior to aging. Inspection
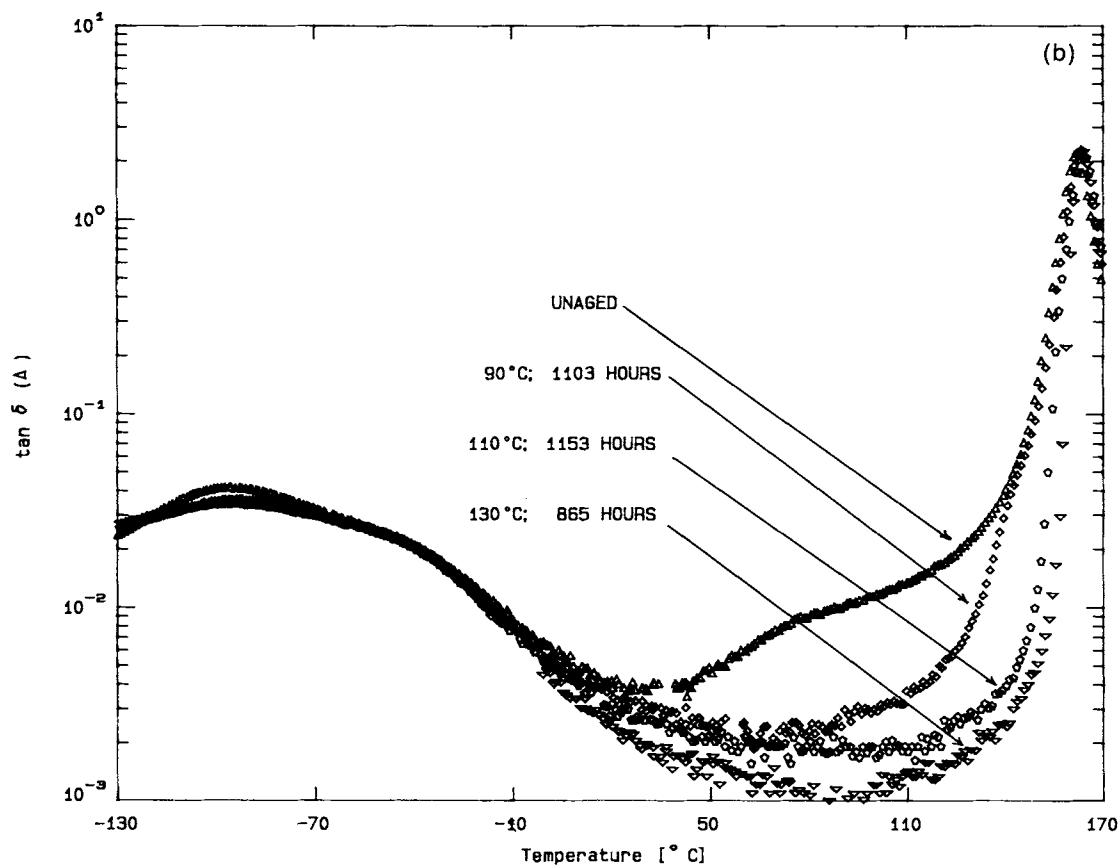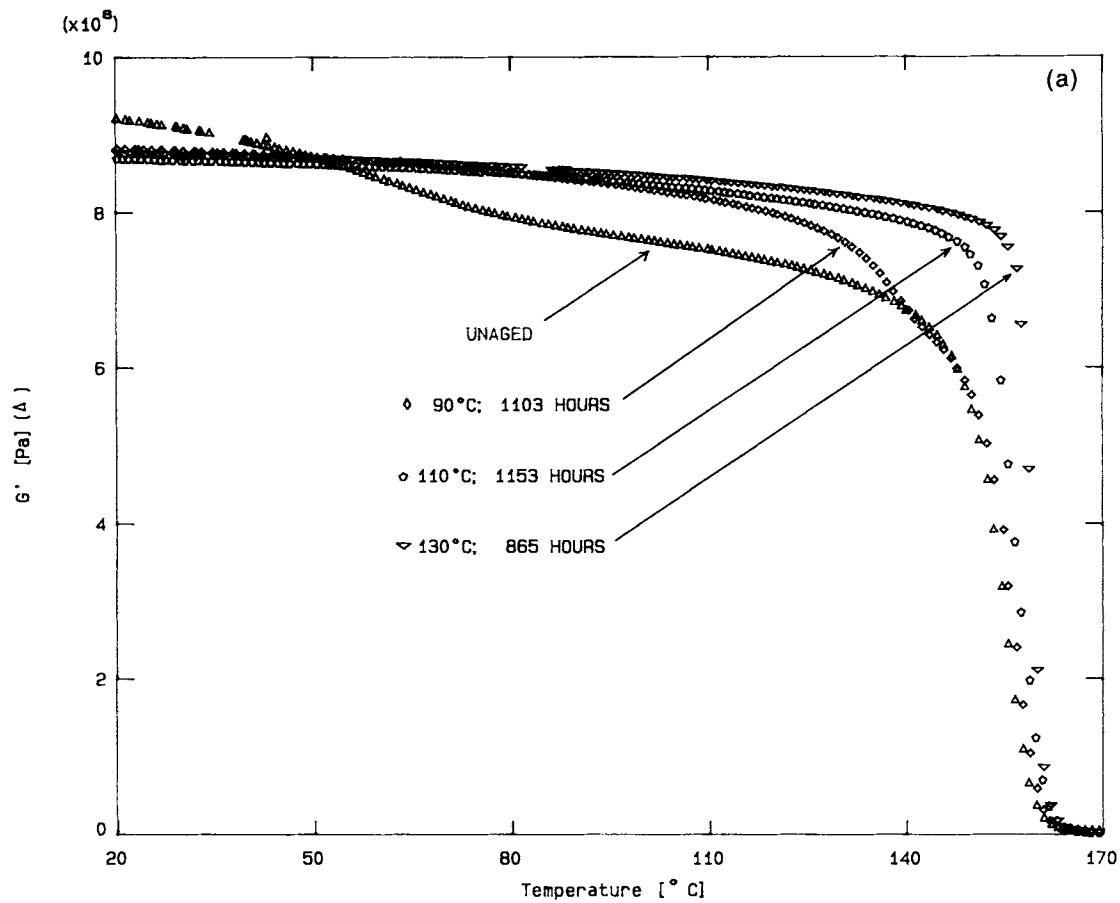
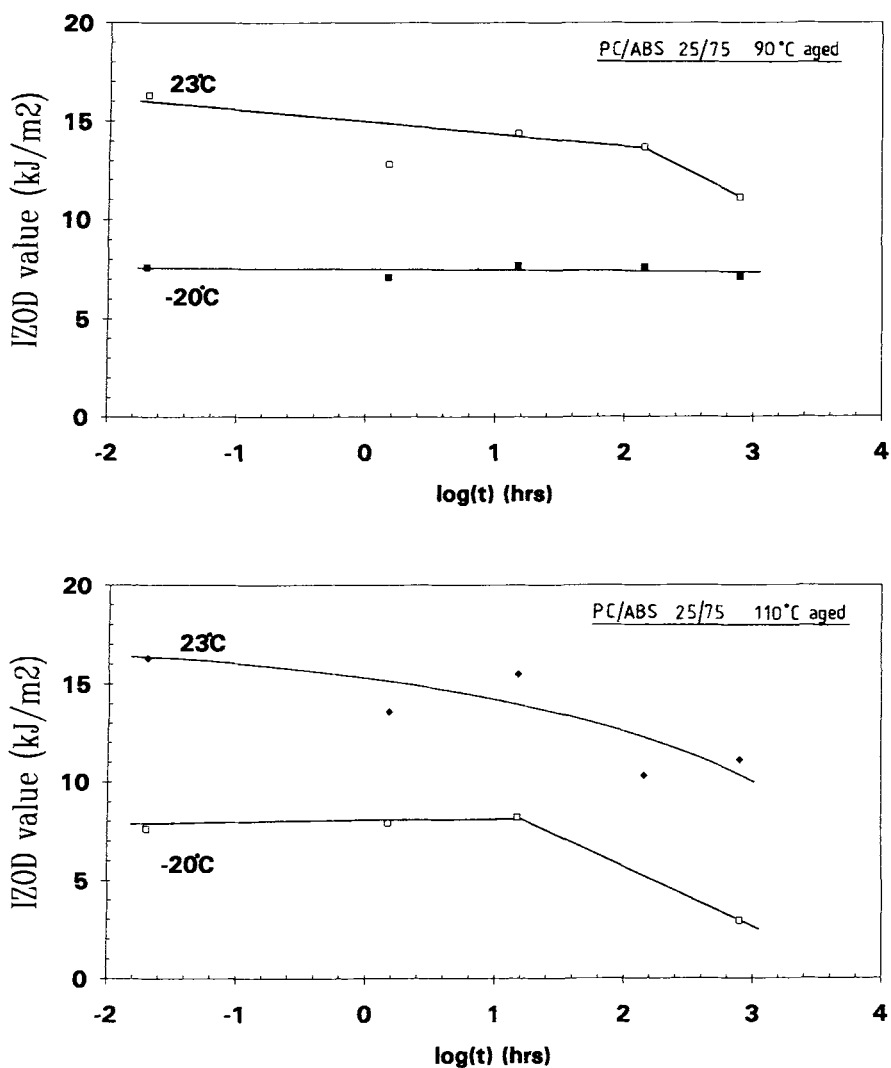**Figure 4** DMS data for PC (a) G' versus T; (b) G'' versus T.

Figure 5   Izod impact data for PC/ABS (25/75) aged at 90 and 110°C.

of the impacted test bars, some of which were only partially broken, showed a complex failure mechanism, with extensive deformation and drawing of the core regions. It is noted that this mode of fracture behavior results in a measured impact value determined, not only due to creating a new surface, but also an element due to bending the inner part of the bar. This observation provides some indirect evidence of morphological differences between the core and skin regions of the test bars that consequently have different contributions to the fracture behavior. The complexity of failure in injection molded blends across a wide range of composition ratios for PC/ABS blends is discussed in more detail by Lee et al.,[26,27] who also concluded that blends containing 60–70% PC were the most ductile compositions.

Following aging, inspection of the impacted test bars confirmed that the outside layers were affected by chemical aging processes, with the depth dependent upon aging time and temperature. The fracture surface of these degraded outer layers was completely smooth, with the removal of polybutadiene seen as a major contributor to the lower toughness following aging.

DMS data for the 60/40 PC/ABS blend as molded, and following extended aging at both 90 and 130°C illustrate a number of features relating to the resultant structure after aging. The G'' versus T data presented in Figure 8 show that the loss peak having a maximum at about $-90°C$ and associated with T_g (PBD) is almost removed after aging at 130°C. The peak amplitude is also significantly decreased after aging at 90°C, in contrast to the ABS blend component aged for similar times [Fig. 2(b)].
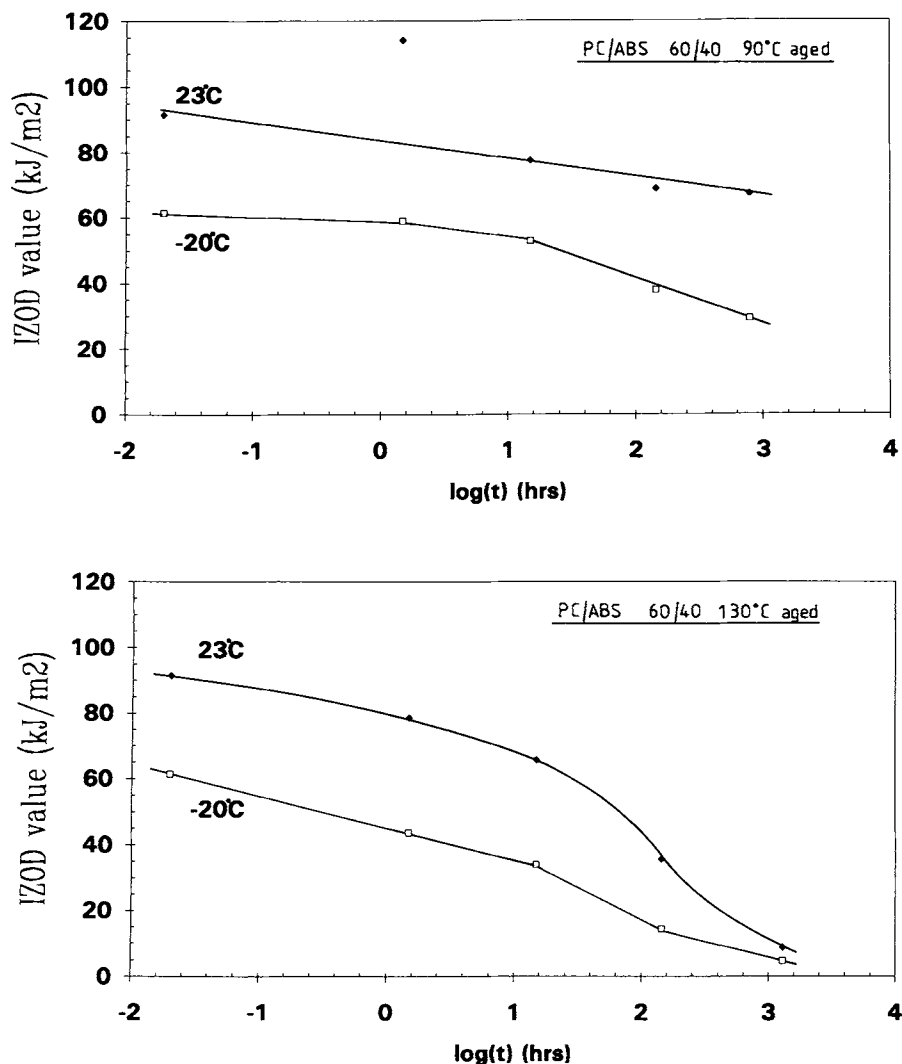
Figure 6   Izod impact data for PC/ABS (60/40) aged at 90 and 130°C.

The observation is associated with transfer of the antioxidant present in the ABS to the PC phase during the melt processing operations used to initially produce the blend.

The G' storage modulus versus T data for the 60/40 PC/ABS blend of Figure 9 show the moduli of the blend aged at 110 and 130°C to drop at lower temperatures, around T_g (SAN) compared to aging at 90°C. The higher plateau modulus in the temperature range between T_g (SAN) and T_g (PC) following aging at 110 and 130°C is associated with the physical aging of the PC phase in the blend.

Tan δ versus T data shown in Figure 10, in particular the form of the T_g (SAN) loss peak, also confirm the initial rationale behind the selection of the aging temperatures for this study. The SAN phase does not physically age at 130°C, i.e., above T_g

(SAN) in the blend, in contrast to aging at 90°C.

For the blend aged at 130°C, lower tan δ values are found in the temperature range between T_g (SAN) and T_g (PC) compared to data for the as-molded or 90°C aged blend. In this temperature range, tan δ (= G''/G') is influenced by the increased G' modulus of the PC phase for the blend aged at 130°C.

CONCLUSION

PC/ABS blends containing 60 and 75% PC were found to retain high impact performance following aging at elevated temperatures, compared to the PC blend component.

For the PC and ABS blend components, decreases in toughness following aging below T_g are primarily
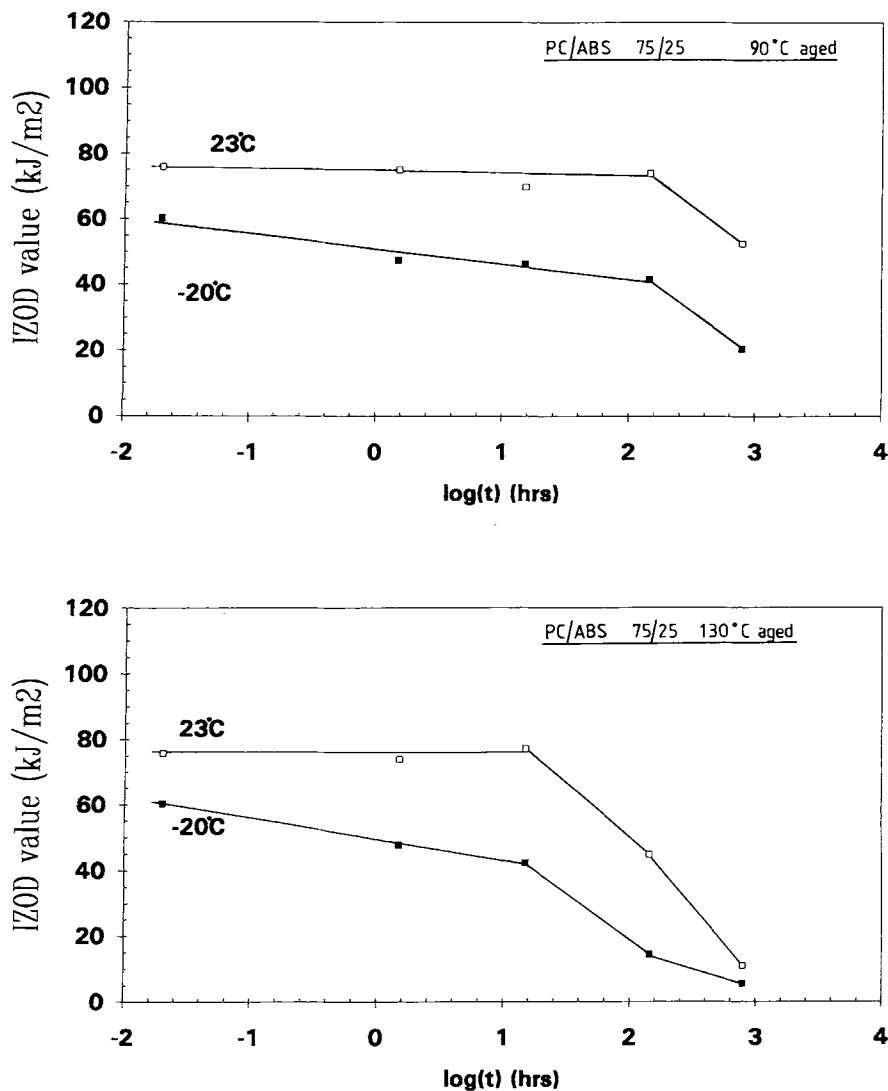
Figure 7   Izod impact data for PC/ABS (75/25) aged at 90 and 130°C.

associated with physical aging of the amorphous polymers.

For the PC/ABS blends, the decreasing toughness upon aging additionally results from oxidation of the butadiene rubber, which can be more severe than for the ABS component alone. The physical aging processes that can occur in the blend are shown to depend on the selection of aging temperatures in relation to glass transitions of the amorphous phases in the immiscible blends.

DMS is an effective probe for investigating structure–property changes occurring on aging, and helps to identify aging mechanisms. The test geometry used in this study biases the response of the outer layers, which is where the oxidative processes were evident.

The thermal aging behavior of immiscible polymer blends is related to the behavior of the blend components. This study has helped to identify that there are, however, some additional factors for multiphase polymer–polymer systems that should be appreciated when exposing the materials to long-term service at elevated temperatures. These include:

1. the removal, restructuring, or plasticization of a minor component can result in an unexpectedly large mechanical or physical property change;

2. during melt compounding, a redistribution of stabilizers can occur, leaving a particular phase unprotected;
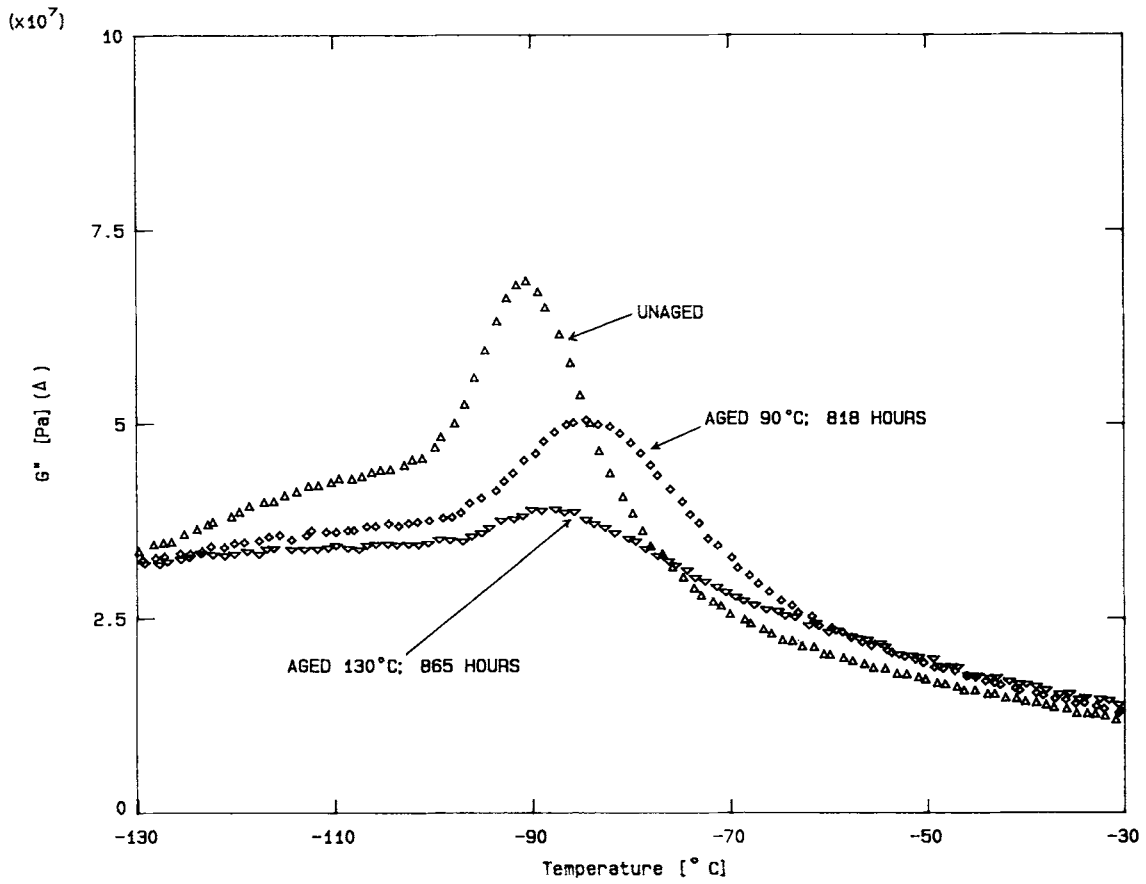
Figure 8 DMS G'' versus T data for PC/ABS (60/40); polybutadiene T_g loss peak.
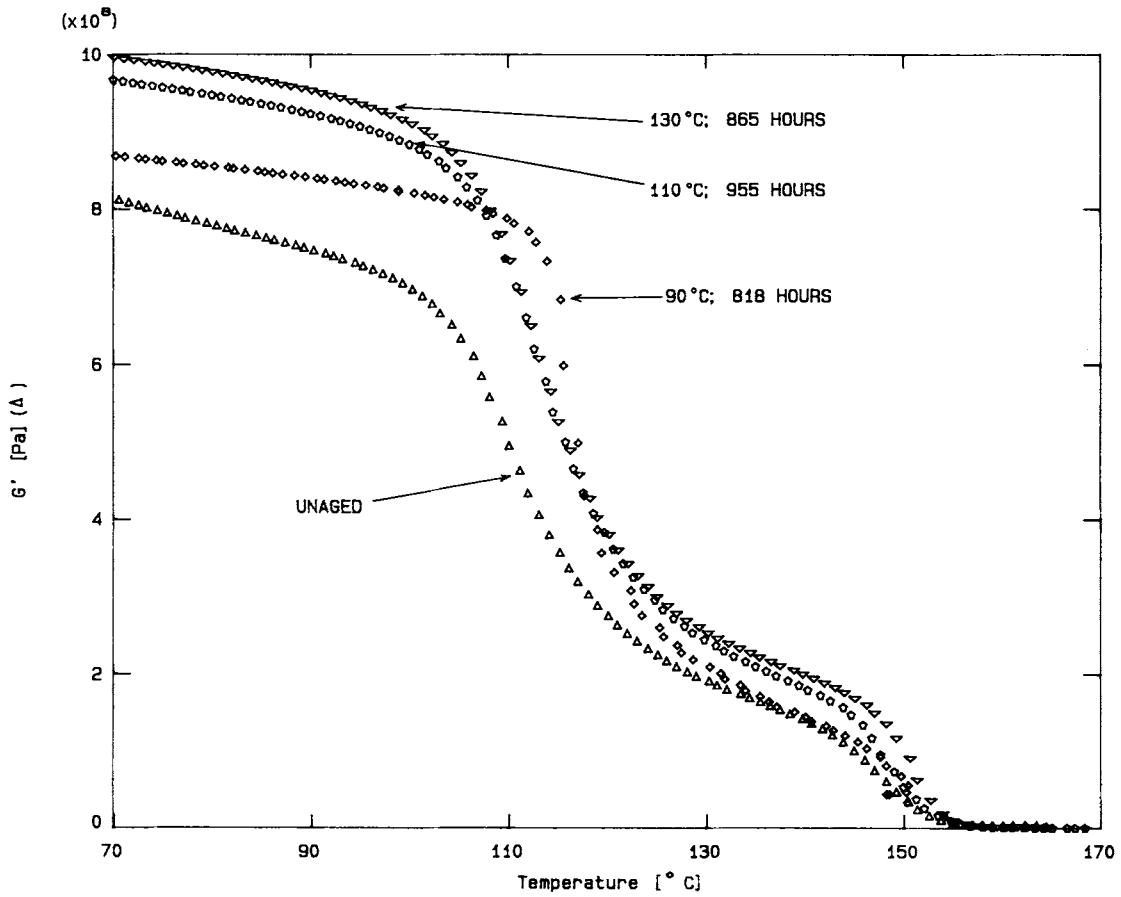

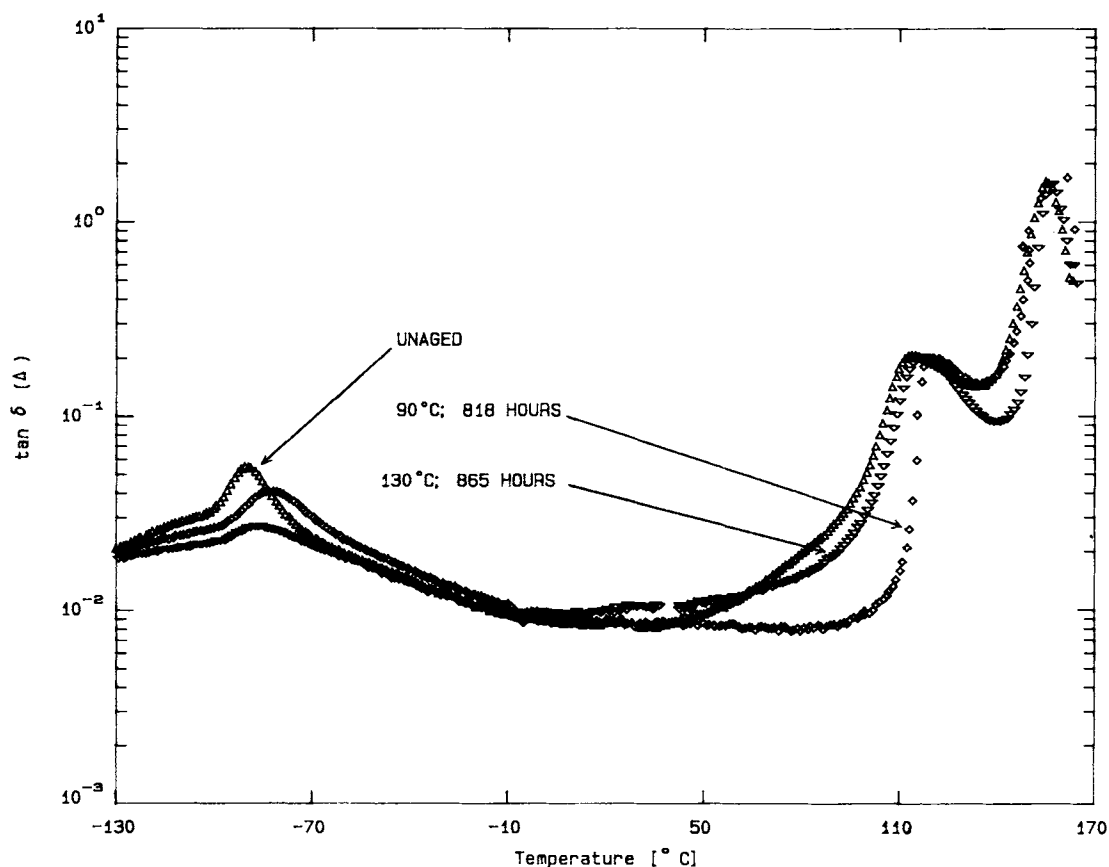
Figure 9 DMS G' versus T data for PC/ABS (60/40).

Figure 10 DMS tan δ versus T data for PC/ABS (60/40).

3. density changes can result during aging and these may alter the local stress at interfacial regions between phases and affect failure properties; this factor is particularly relevant regarding physical aging and the selection of aging temperatures.

Improved toughness retention in the blends can be engineered by controlling the location of additives present during the melt processing operations used to produce the blends and solid parts for final use.

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