

THE EFFECTS OF HEAT AGING ON ACRYLONITRILE–BUTADIENE–STYRENE (ABS) BLENDS

Heat aging of ABS blends

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Abstract

Degradation of thick ABS materials at elevated temperatures is observed to be predominantly a surface effect which deteriorates the bulk mechanical properties under impact conditions. It is postulated that a critical level of surface degradation initiates polymer crazing in the rubbery butadiene phase, which propagates through the polymer, causing failure. A physico-mechanical study of the effects of heat aging on the rubbery phase in ABS reveals an increase in the loss modulus and $\tan \delta$, demonstrating a decrease in the free volume which may be due to cross-linking of free radicals formed by hydrogen abstraction and chain scission. Microscope FTIR spectroscopy of aged ABS surfaces shows that the degree of butadiene unsaturation decreases with time, and that carbonyl and hydroxyl absorbances increase as expected with thermo-oxidative degradation. Degradation of the rubbery polybutadiene phase in ABS may be initiated by hydrogen abstraction from the carbon α to unsaturated bonds, producing hydroperoxide radicals leading to carbonyl and hydroxyl products. Cross-linking is facilitated by the free radicals produced. Heat aging of ABS at elevated temperatures below the glass transition (T_g) of the SAN phase causes physical aging. This aging of the SAN phase provides thermal energy which allows for a structural reconfiguration of the glassy morphology towards an amorphous polymer. In this case, heat aging relaxes the intrinsic molecular stresses and causes a decrease in the initial rate of transition from the glass to the liquid when temperatures approach T_g . It is also possible that the physical aging of the SAN phase in ABS may contribute to the deterioration of the mechanical properties of the polymer.

Keywords: ABS, degradation, durability, heat aging, physical properties, pipe

1 Introduction

Durability prediction of acrylonitrile-butadiene–styrene (ABS) polymers is important in a wide range of polymer applications, including water pipeline systems. A number of factors influence ABS pipe durability, including material composition, processing conditions, operating conditions, environmental weathering, heat aging, installation and notch damage. The availability of a lifetime prediction model for ABS in pipe applications, would allow for accurate

selection of polymer material, according to the environmental and operating conditions the pipe will be required to perform in, thus decreasing the number of future pipe failures and maintenance costs.

In polymers such as polypropylene, low density polyethylene and ABS, specific aspects of the microstructure facilitate thermal oxidation. Tertiary substitution of carbon atoms allows hydrogen abstraction by oxygen to be more thermodynamically favourable. Thermal energy provides the activation energy required for the initiation of oxidation, thus accelerating the overall process of degradation. After periods of exposure to heat and oxygen, the mechanical properties of ABS such as impact strength and elongation to break, deteriorate, leading to polymer failure (Wolkowicz and Gaggar 1981). The literature cites various explanations for the degradation of ABS due to heat aging. Several papers state that the thermo-oxidative degradation of ABS is confined to the rubbery polybutadiene phase, while others claim that degradation of properties is due to a combination of physical aging in the SAN phase and oxidation of the polybutadiene phase (Gesner 1965; Shimada and Kabuki 1968; Wyzgoski 1976; Salman 1991). Shimada and Kabuki (1968) proposed a mechanism for the thermo-oxidative degradation of unstabilised ABS film, proposing that degradation occurred in the rubber phase and that the degradation mechanism leads to the formation of hydroperoxides. Degradation was said to occur by hydrogen abstraction from the carbon α next to trans-1,4 and 1,2 unsaturations in the polybutadiene phase producing hydroperoxide radicals. The rate of reaction follows Arrhenius-type kinetics, and the rate constants and reaction orders were determined from the rate of formation of carbonyl and hydroxyl products as monitored by Fourier transform infra-red (FTIR) spectroscopy.

In this study, thick stabilised ABS specimens were aged at elevated temperatures in order to study the effects of heat aging on ABS pipe. The presence of anti-oxidants and UV stabilisers in the ABS was expected to complicate the mechanism of oxidation due to the effects of stabiliser solubility and diffusion. The study does not consider environmental effects such as the migration and leaching of stabiliser in typical outdoor water pipes. Results and observations are based on accelerated heat aging experiments and it is likely that thermo-oxidation of ABS in real applications would be different. Also considered is the localised oxidation at the surface of the specimen due to the limited oxygen diffusion (DLO) in the polymer as discussed by Wise et al. (1997).

2 Experimental

Commercial ABS pipe resin and styrene-acrylonitrile copolymer (SAN), in the form of impact (notched and unnotched) and tensile specimens conforming to ASTM D256 (ASTM 1993) and AS 1145 (Standards Australia 1989), were heat aged at 90°C and 120°C in a Qualtex Solidsat Universal 2000 series cabinet oven. Oven-turbulence was minimal with wind speeds in the range of 1–2 m/s being measured by a hot wire anemometer. Oven heat distribution was measured by a platinum thermoresistor and found to be within a range of $\pm 2^\circ\text{C}$. Specimens were placed on talc-coated glass plates, occupying $\leq 10\%$ of the total oven space, and air circulation was maintained at 4 exchanges/hour, as required by ISO 188 (ISO 1982). Heat aging experiments were conducted for up to 672 hours (at 90°C and 120°C) for notched and at 120°C for unnotched ABS specimens, with samples removed for mechanical assessment every 168 hours. Heat aging of a different unnotched ABS resin was conducted at 100°C using the same procedure.

Instrumented impact analyses were performed using a Radmana impact tester, in accordance to ASTM D256. Modulus and elongation to break percentages were assessed on an Instron 5565 screw-driven tensile tester (5 kN) using pneumatic grips (70 psi grip pressure) according to AS 1145.

To enable analysis of physical properties such as T_g and loss modulus, specimens were sectioned prior to heat aging to the required dimensions for physico-mechanical property assessment. T_g and loss moduli were measured using a Rheometrics Scientific Solids Analyser RSA II DMTA, for both the rubber polybutadiene phase and the rigid SAN phase of ABS after heat aging at 120°C and 90°C.

To monitor the effects of aging on the characteristic infra-red absorptions of vinyl groups in ABS, and to detect the presence of carbonyl and hydroxyl species due to oxidation, a qualitative analysis of ABS aged at 120°C was conducted on a Perkin–Elmer FTIR 2000 with a microscope accessory. Complete microtome cross-sections (20 μm thick) of ABS aged for 672 hours were investigated using transmission mode, with microscope stage control and imaging, allowing for visual identification of the analysed polymer section.

Positron annihilation lifetime spectroscopy analyses were conducted on ABS aged at 90°C and 120°C to investigate the effects of heat aging on free volume.

3 Results and discussion

3.1 Mechanical property analyses

The impact strength of notched (notching occurred after heat aging) ABS as a function of the aging time at 90°C and 120°C is shown in Fig. 1. At 90°C, the loss of impact strength is not significant. At 120°C, a slight constant loss of impact strength is observed. Onset of a brown colouration occurs on the surface of ABS specimens aged at 120°C, which develops as a function of time (Fig. 2). However, for unnotched ABS aged at 120°C, the impact properties decrease rapidly from an initial value of 245 kJ/m^2 to a value of 30 kJ/m^2 , after which the rate of loss is minimal, as shown in Fig. 3. Aging of a second unnotched ABS resin at 100°C reveals a considerably smaller decrease in impact strength, initially from 148 kJ/m^2 to 122.3 kJ/m^2 after 600 hours. It is expected that impact properties of aged unnotched ABS at 90°C would not be significantly affected, although this will be proven in future work. Aging of SAN copolymer at 90°C did not cause any significant decrease in the unnotched impact strength.

The difference in impact strength for notched and unnotched ABS aged at 120°C and the discolouration observed on the ABS surface after aging, indicates that heat aging causes thermo-oxidative degradation at the surface of ABS, which influences the mode of polymer failure. It is suggested that diffusion of oxygen in the aging times considered is limited to the surface due to the polymer morphology, which leads to an increase in polymer density due to cross-linking caused by aging. Cross-linking at the polymer surface leads to surface stress hardening and an increase in modulus. Under impact conditions, micro-cracks initiate in the hardened layer, which propagate through the bulk of the polymer, causing failure. Wolkowicz and Gaggar (1981) state the loss of impact properties is controlled by a critical depth of degraded polymer and once this depth is reached, impact properties degrade rapidly, as is also seen in this work (Fig. 3). It can be seen that the impact properties show more than an 80% decrease at 168 hours for specimens aged at 120°C. At this time the coloured surface layer was approximately 0.06 mm deep. Further exposure did not reduce the impact

strength, even though the depth of the degraded layer continued to increase, it being 0.5 mm after 672 hours. These results are in agreement with Wolkowicz and Gaggar (1981), who found the critical depth to be between 0.07 and 0.2 mm.

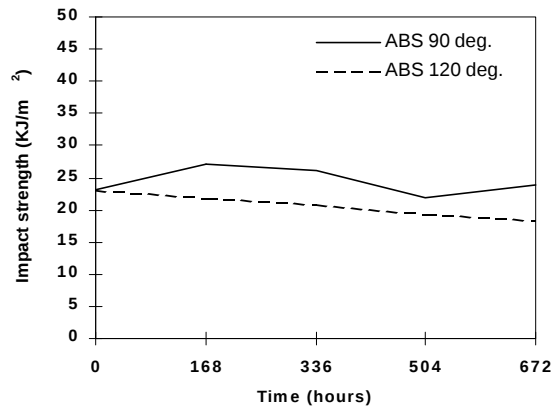


Fig. 1: Impact properties of notched ABS as a function of aging time at 90°C and 120°C

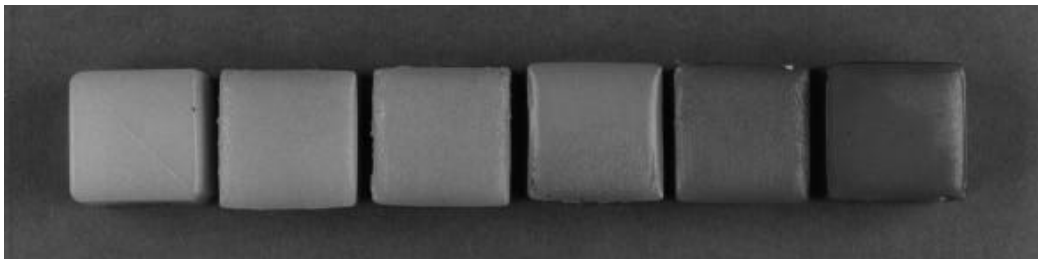


Fig. 2: Colouration of ABS as a function of aging time (left, 0 hours; far right, 168 hours) at 120°C

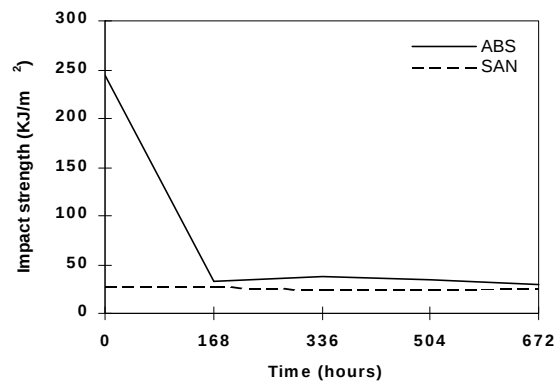


Fig. 3: Impact properties of unnotched ABS as a function of aging time at 120°C, and unnotched SAN copolymer as a function of aging time at 90°C

Examination of the cross-sections of impact specimens after aging at 120°C reveals that the colouration of the ABS was limited to the surface of the specimen, even after heat aging for several months. The literature has cited that colouration in the thermal aging of ABS is due to radical scavengers coupling with peroxy radicals formed during degradation (Faucitano et al. 1996). This would suggest

that the degradation and subsequent discolouration in ABS is confined to the surface of the specimen and is controlled by the rate of oxygen diffusion through the polymer. However, more work needs to be carried out to confirm this, as thermal degradation in the absence of oxygen may be occurring in the bulk polymer. Even so, Fig. 1 shows that notched specimens show a constant failure with time, whereas unnotched specimens show a rapid failure in the first 168 hours due to the effects of the oxidised surface layer. The results indicate that failure is critically dependent on the surface layer of the ABS where crack initiation occurs.

Figure 4 shows the tensile properties of ABS aged at 90°C. It can be seen that the energy to break and elongation to break decrease considerably in the first 168 hours. A slight increase in modulus is also observed. Aging of the SAN copolymer (SAN ratio as in ABS) reveals an increase in the Young's modulus and a slight initial increase in the energy to break and elongation to break, after which these properties are fairly constant (Fig. 4).

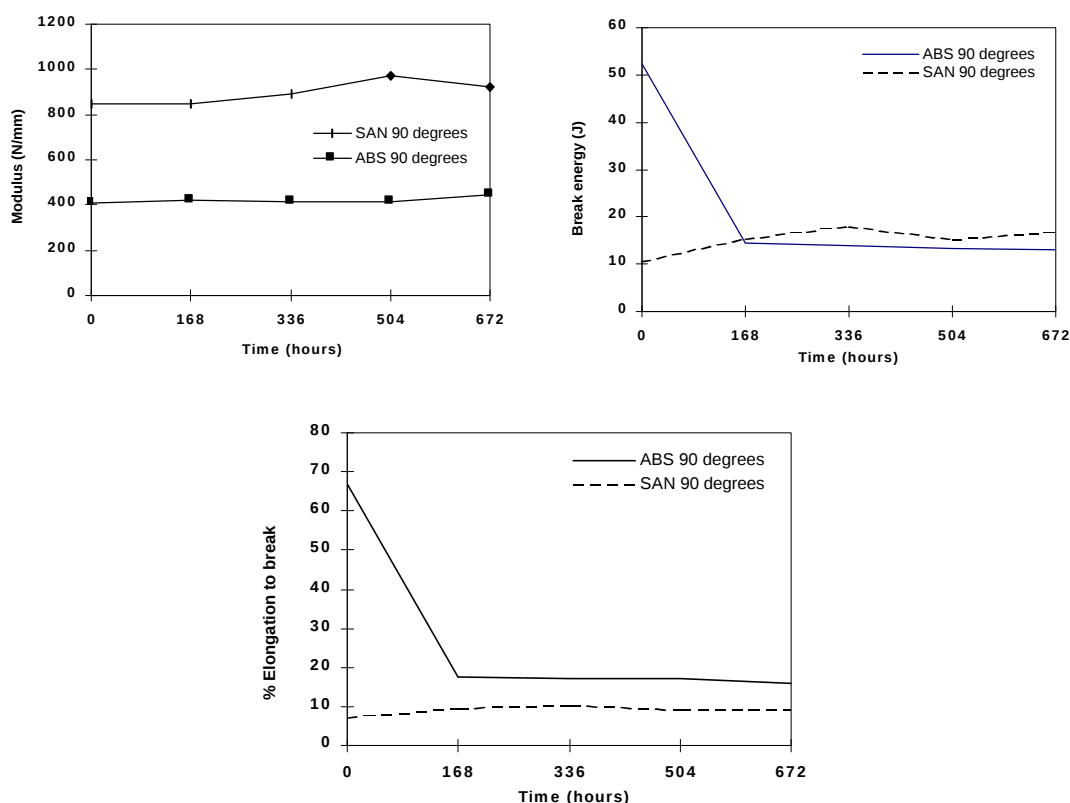


Fig. 4: Tensile properties of ABS and SAN copolymer aged at 90°C

In contrast, as shown in Figure 5, ABS aged at 120°C shows significant decrease in energy to break and elongation to break and an increase in the modulus. Similar decrease in tensile results were reported by Tavakioli (1994) who found a 30–70% reduction in tensile strength for ABS aged at 120°C.

Figure 6 shows a typical stress-strain curve for ABS after aging at 90°C. Although elongational properties decrease, the curve shows a ductile failure mode, indicating that thermal degradation is not severe. As the temperature of aging increases, the ABS shows an increase in modulus and a change in behaviour from ductile to brittle, as shown by the early failure at low elongation to break figures for the ABS aged at 120°C, compared to virgin polymer.

As shown in the first graph in Fig. 4, the increase in modulus for SAN after aging at 90°C is expected. This increase is due to physical aging, as the aging temperature was below T_g of the copolymer. Physical aging of a glassy polymer provides the thermal energy for structural reconfiguration towards an amorphous morphology with reduced free volume due to segmental motion. Aging thus causes a decrease in the initial rate of transition from the glass to liquid when the glass approaches T_g from sub- T_g temperatures. The decrease in free volume causes the actual glass transition temperature to increase, effectively increasing the mechanical modulus. The literature cites that physical aging of polymers causes an increase in polymer density and modulus, and a decrease in impact strength, fracture energy, elongation, creep and the rate of stress relaxation (Wyzgoski 1976; Qi et al. 1993). Initial increases observed for elongation and energy to break of the aged SAN copolymer are attributed to relaxation of intrinsic molecular stresses. Wyzgoski states that the high tensile elongation properties of ABS are also dependent on the deformation of the glassy matrix, so heat aging of the SAN phase would contribute towards embrittlement of the SAN phase and contribute to failure of the ABS polymer (Wyzgoski 1976). Aging of ABS at 90°C shows a decrease in the elongational property, as shown in the second graph of Fig. 5 and Fig. 6, yet as discussed above the SAN phase shows increases in this property when exposed at this temperature, consequently the reductions in elongation shown for ABS must be due to physical changes in the polybutadiene phase.

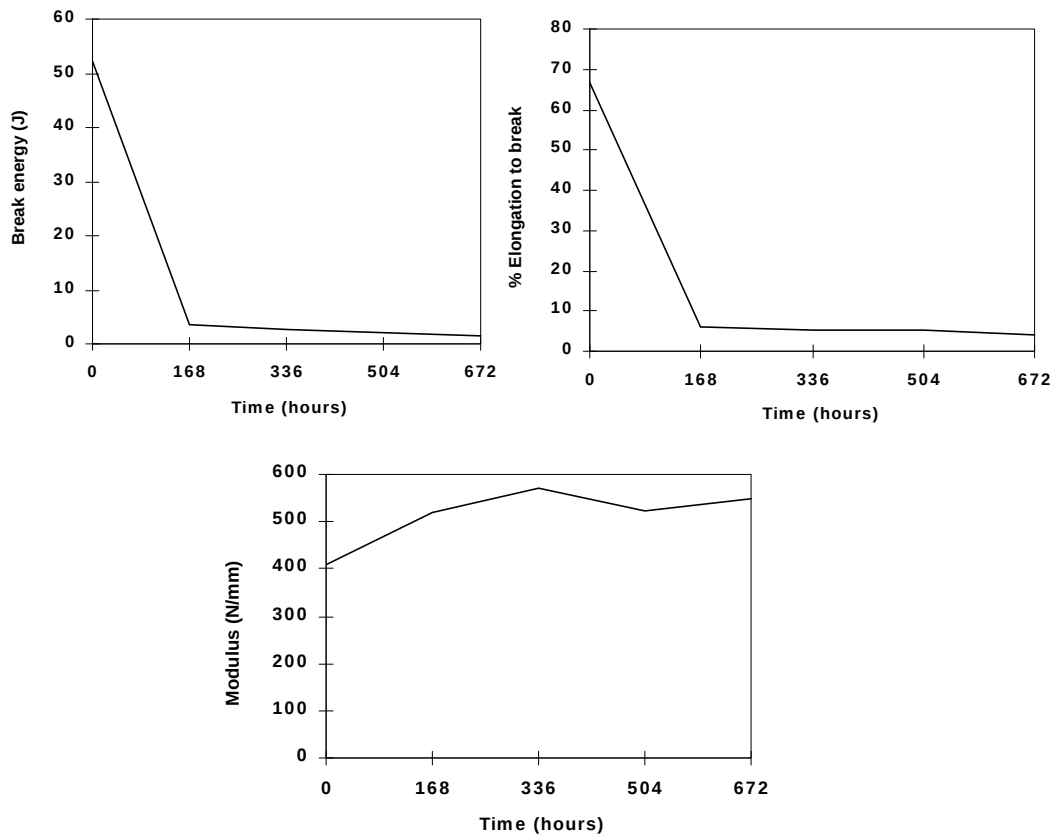


Fig. 5: Tensile properties of ABS aged at 120°C: break energy, elongation to break and modulus

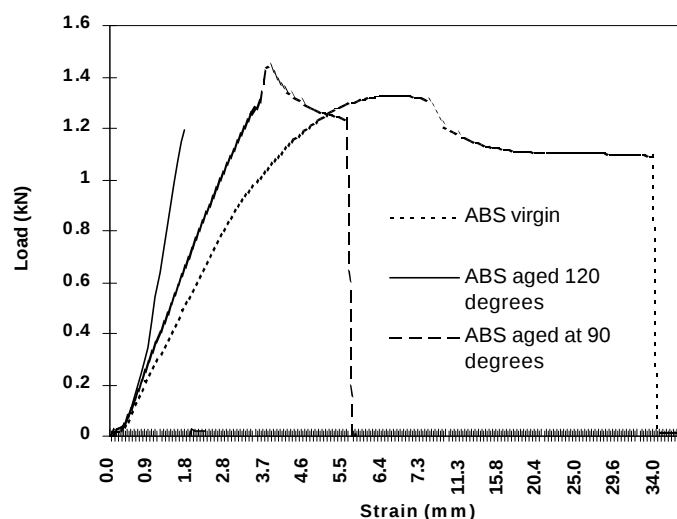


Fig. 6: Typical stress-strain curves for ABS aged at 120°C and 90°C

Brittle failure is observed for ABS aged at 120°C as compared to virgin polymer which shows a ductile failure mode upon tensile testing (Fig. 6). The deterioration of impact and tensile elongation, and the increase in modulus is attributed to thermal degradation of the polybutadiene phase. Colouration on the surface of the polymer indicates that a thermo-oxidative degradation mechanism has occurred causing chain scission and cross-linking of the rubber phase, leading to surface hardening of the aged ABS, which initiates crack formation. It is proposed that thermal degradation in the bulk region of the polymer in the absence of oxygen (surface discolouration is due to oxygen permeability and subsequent reaction with antioxidants) causes chain scission and cross-linking in the polybutadiene phase which deteriorates the bulk tensile properties of the polymer.

The increase in modulus and the decrease in elongation to break property of ABS aged at 120°C and 90°C demonstrate the effects of both surface oxidative and bulk degradation in the polybutadiene phase, which deteriorates the overall mechanical properties. At 90°C the physical aging of the SAN phase does not contribute to the loss of properties of the ABS. At 120°C the effect still has to be analysed for, as shown in Fig. 6, ABS at this temperature distinctly shows brittle failure, compared to a ductile failure for virgin ABS. Consequently the contribution to this behaviour from the SAN and butadiene phases has to be assessed. Future experiments will determine relative contributions as well as whether the thermo-oxidative degradation of ABS has an Arrhenius temperature dependence.

3.2 Physical property analyses

FTIR spectroscopy combined with transmission mode optical microscopy and image analysis, was carried out on a microtomed cross-section of the specimen. This allowed spectroscopic analysis within a localised region of the ABS microtome (100 × 100 µm area). Examination of the specimen surface compared to the bulk of the polymer (Fig. 7), indicates that for ABS exposed at 120°C for 672 hours, thermo-oxidative degradation of the ABS is occurring on the surface but not in the bulk polymer.

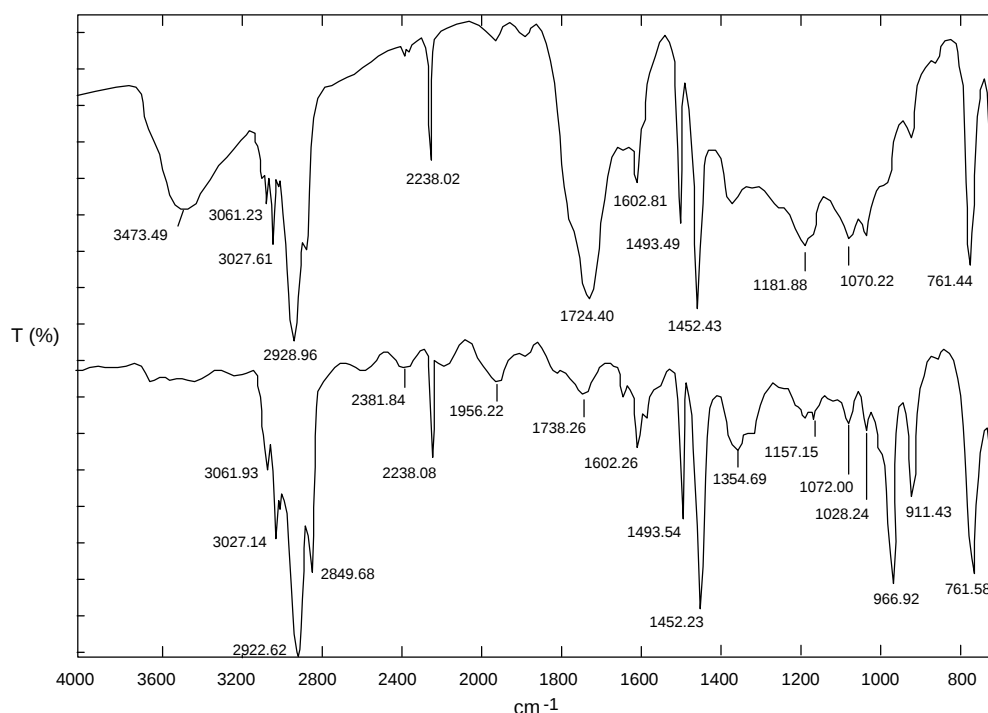


Fig. 7: Transmission FTIR spectra of ABS aged at 120°C. Upper spectrum at the surface and the lower spectrum the bulk ABS polymer

As shown in Fig. 7, this can be explained by thermo-oxidative degradation in the polybutadiene phase of ABS, which causes increases in carbonyl and hydroxyl absorbances and decreases in the absorptions caused by vinyl unsaturations (Gesner 1965; Shimada and Kabuki 1968; Salman 1991). The top spectrum taken from the edge of the sample shows a broad carbonyl band at 1724.4 cm^{-1} and a broad band for the hydroxyl group at 3473.49 cm^{-1} . As discussed, the absorbance bands in virgin ABS corresponding to the trans C=C unsaturation (vinyl) at 966.92 cm^{-1} and the 1,2 butadiene terminal vinyl C-H band being 911.43 cm^{-1} , decrease considerably for the aged ABS specimen.

Dynamic mechanical thermal analyses of ABS specimens heat aged at 90°C and 120°C , and SAN copolymer heat aged at 90°C , were conducted to investigate the effects of aging on the glass transition of the polymer both in the rubber phase and in the rigid SAN phase.

Polymers below their T_g at room temperature are labelled as being glasses and may be annealed or physically aged at temperatures below their T_g . The process of physical aging causes relaxation of intrinsic stresses. This can be seen in a reduced rate of transition from the glassy state to the liquid state, which occurs concurrently with an increase in the glass transition temperature and also an increase in the modulus. Such effects on the SAN phase have been stated to cause embrittlement of ABS polymers. Wyzgoski (1976) showed that physical aging of the SAN phase and embrittlement of the ABS is reversible by heating above the T_g of ABS, indicating that cross-linking is not occurring. The $\tan \delta$ and loss modulus (E'') parameters obtained by DMTA can be used to describe the glass transition of polymers. Figure 8 shows a reduced initial rate of glass transition represented by the $\tan \delta$ parameter, for ABS as the aging time at 90°C increases. Table 1 shows the E'' and $\tan \delta$ values of the SAN phase of virgin ABS and ABS aged at 90°C . Both parameters increase with aging time, which correlates with the increase in Young's modulus measured by tensile assessment.

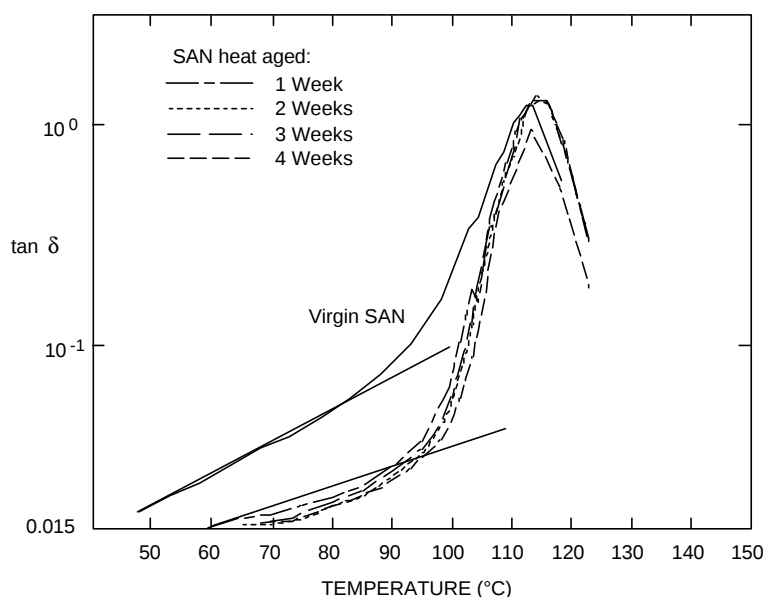


Fig. 8: $\tan \delta$ parameters of the SAN phase of ABS aged at 90°C. Tangents indicate a decrease in the initial rate of transition for aged SAN copolymer

Table 1: E'' and $\tan \delta$ values of the SAN phase of ABS aged at 90°C

Aging period (hours)	$\tan \delta$	Loss modulus (E'')
0	113.02	103.13
168	114.18	108.36
336	114.26	106.77
504	114.26	106.31
672	113.2	107.31

It can be seen in Table 2 that the T_g of the polybutadiene phase at approximately -85°C , does not change as a function of aging time at 90°C . This, together with the data from the mechanical assessment, suggests that significant changes in the morphology and free volume of the polybutadiene phase did not occur, and that the degree of chain scission and cross-linking at 90°C for the aging times considered (672 hours) are minimal. Thus, an explanation for the reduced elongation properties for the ABS aged at 90°C cannot be obtained from this data and further work will have to be carried out to explain this phenomenon.

However, for ABS aged at 120°C , significant differences occur in the glass transition of the polybutadiene phase, reflected by changes in E'' and $\tan \delta$ values as shown in Table 2. Both parameters show an increase with exposure time, indicating a decrease in free volume, possibly due to cross-linking reactions occurring during thermal degradation. This is in agreement with an increase in moduli, and decrease in elongation properties as measured by mechanical property assessments.

Table 2: E'' and $\tan \delta$ values of the polybutadiene phase as a function of aging time at 90°C

Aging period (hours)	90°C		120°C	
	$\tan \delta$	Loss modulus (E'')	$\tan \delta$	Loss modulus (E'')
0	-86.02	-85.09	-86.02	-85.09
168			- 78.74	- 77.27
336	-85.27	-85.82	-75.64	-72.31
504			- 80.91	- 80.91
672	-85.22	-85.78	-80.87	-80.87

Initial assessment of ABS aged at 90°C and 120°C by positron annihilation spectroscopy (PALS) supports the results obtained by both physical and mechanical assessments. PALS enables non-destructive measurement of the free volume in a polymer, by discharging positrons into the material and monitoring their lifetimes (Ramani et al. 1995). PALS indicates that for ABS aged at 120°C, the number of free volume sites (I_3) and their mean radius (τ_3) decreases as a function of aging time (most likely in both phases), whereas for ABS aged at 90°C, free volume parameters do not significantly change with time.

4 Conclusions

The thermo-oxidative degradation of ABS at 120°C is a surface effect which forms a hard surface layer which allows initiation of cracks under impact and tensile loads. Thermal degradation of the bulk polymer in the absence of oxygen, deteriorates the bulk mechanical properties of the polymer, allowing propagation of the initial crazes from the surface of the polymer into the bulk, thus reducing the overall properties. Physical and mechanical assessment shows that polymer failure is greatly dependent on the thermo-oxidative degradation at the surface. Oxidation of the polybutadiene phase at the surface of ABS causes stress hardening, which in turn crazes the polymer surface. The critical depth of surface oxidation is measured to be approximately 0.06 mm. For greater depths of surface oxidation, impact or tension causes craze propagation through the bulk material, causing premature polymer failure. This effect is temperature dependent because, for exposures at 90°C and 100°C for the same periods of time, thermo-oxidative degradation in the form of mechanical property deterioration was significantly less. Further heat aging trials are being conducted to establish an Arrhenius temperature dependence for the thermo-oxidative degradation of ABS.

Degradation of ABS due to heat aging also occurs in the rigid SAN phase by physical aging. This physical aging is in the form of enthalpic relaxation which occurs due to heat aging of the SAN phase at sub- T_g temperatures. Physical aging causes an increase in the modulus of the SAN glassy phase, but in this case is not the controlling factor in the embrittlement of ABS.

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