

The Mechanism Of Photo-Oxidative Degradation Of Acrylonitrile-Butadiene-Styrene (Abs) Resins Used In Pipes

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Summary: This paper investigates the mechanism of ultraviolet (UV) degradation in ABS resins. ABS specimens were subjected to accelerated natural weathering at an ambient temperature to separate thermal effects from the mechanism of UV degradation. Degradation primarily occurs in the polybutadiene (PB) phase of ABS due to the polymer microstructure. Fourier transform infrared (FTIR) shows that degradation of the PB phase is predominantly located at the surface of the polymer and that bulk degradation does not occur. Changes in chemical structure observed by FTIR are associated with oxidation and the formation of photoproducts, corresponding to a carbonyl peak at 1721 cm^{-1} and hydroxyl peak at $\sim 3465\text{ cm}^{-1}$. The absorbance bands at 966.92 cm^{-1} and 911.43 cm^{-1} corresponding to the trans C=C unsaturation (vinyl) in polybutadiene, and the 1,2-butadiene terminal vinyl C-H band respectively, were distorted indicating bond un-saturation. The oxidation induction time (as determined by chemiluminescence) was significantly lower at the surface of weathered ABS compared to the bulk polymer. Dynamic Mechanical Thermal Analysis (DMTA) showed an increase in the glass transition temperature for UV-exposed specimens, reflecting an increase in Young's modulus due to crosslinking in the PB phase. Under plane strain loading conditions, brittle fracture occurs when surface degradation reaches a critical depth. To develop a technique for lifetime prediction after weathering, fracture mechanics theory was used to relate UV exposure time to an equivalent surface notch depth. Assuming that this relationship is geometry-independent, it was used to estimate the reduction in critical hoop stress for ABS pipelines under hydrostatic pressure

Keywords: ABS, weathering, degradation, fracture mechanics

1 INTRODUCTION

Acrylonitrile Butadiene Styrene (ABS) pipes are often used above ground in exposed applications. Although heat stabilisers are commonly included in ABS to prevent thermal degradation during processing and subsequent use in high temperature environments, stabilisation against weathering and the effect of ultraviolet (UV) radiation is often overlooked. Exposure to UV radiation induces changes in the polymer microstructure, which lead to polymer oxidation and eventual degradation.

Whilst photo-oxidative degradation of ABS resin is reported to primarily occur in the polybutadiene (PB) phase (Gesner 1965, Heaps 1968, Salman and Al-Shama'a 1991, Jouan and Gardette 1992), degradation can also occur in the Styrene Acrylonitrile (SAN) phase (Davis and Sims 1983, Jouan and Gardette 1992). According to Jouan and Gardette, degradation of the PB phase induces degradation of the SAN phase (Jouan and Gardette 1992). Photo-product species formed by photo-oxidation of the PB phase are strongly dependent on irradiation wavelength (Jouan and Gardette 1992). Photo-oxidative degradation of the polystyrene component of the styrene-acrylonitrile (SAN) copolymer also yields chromophores (Davis and Sims 1983, Jouan and Gardette 1992). Kulich and Gaggar conclude that initial colour fading is due to oxidation in the SAN phase, and subsequent yellowing discolouration is due to oxidation of the PB phase (Kulich and Gaggar, 1996). The level of SAN copolymer in an ABS blend is known to affect mechanical properties by altering the rate of oxygen permeation. Increasing the level of SAN copolymer decreases oxygen permeability and retards degradation of the dispersed PB phase.

Photo-oxidation of the PB phase is considered to be the major cause of mechanical property deterioration in ABS. For ABS exposed to ultraviolet radiation, photolysis of the methylene bond in the trans-1, 4-polybutadiene structure occurs, yielding an allylic radical polymer chain. The radical may undergo several reaction paths to yield further radicals together with oxygenated species such as hydroperoxides, ketones and esters (Shimada and Kabuki 1968, Shimada et al 1972). The rate of photo-oxidation is proportional to the intensity of irradiation and the log of the irradiation wavenumber (Shimada and Kabuki 1968).

With further UV exposure, stable oxygenated photoproducts decompose to yield oxygenated radical species. Photo-oxidation is accelerated by the presence of residual hydroperoxides formed during thermal processing, which may also decompose to produce other degradation products and radical chains. Crosslinking of the PB phase after radical formation is thought to contribute to the embrittlement of the PB phase (Scott and Tahan 1977). Several approaches exist to prevent photo-oxidation, including the use of UV stabiliser additives (Kulich and Gaggar 1996, Zahn 1997 Shimada and Kabuki 1972). Additives absorb the energy of irradiation and transfer it to the ABS resin by lattice vibration excitation. However since they are not able to completely absorb UV energy, bond disassociation of the methylene-methylene structure remains possible. The inclusion of pigments or additives intended for UV stabilisation may also reduce the impact resistance of the resin (Kelleher *et al.* 1967, Davis and Gordon, 1974).

The relatively high impact strength of some ABS resins can be attributed to an increase in the PB phase content, which is susceptible to photo-oxidation (Heaps, 1968, Kelleher *et al.* 1967). Zahn shows that the impact strength of high impact grade UV-stabilised ABS, decreases to ~ 70% of its original impact strength after UV exposure (Zahn 1997). In conditions of extreme UV exposure, it is recommended that the surface of ABS structures be painted to prevent photo-oxidative degradation (Shimada and Kabuki 1972, Gugumus 1979, Kurumada *et al* 1987). For thick ABS structures, degradation due to weathering is confined to the surface due to the formation of an initial degradation layer which prevents oxygen diffusion and further UV penetration. Subsequent oxidation of the bulk polymer is prevented and an embrittled surface layer forms, which eventually causes bulk failure under applied loading (Kulich and Gaggar 1996).

The critical performance requirement of thick-walled ABS pipe for outdoor water transport, is to withstand the internal hydrostatic pressure to which it is rated. A degraded surface layer on the pipe will contain numerous micro-cracks which may be sufficiently large to propagate into the pipe wall under an applied load (Kulich and Gaggar 1996, Tiganis *et al* 2001). In this study, thick ABS specimens (which was not UV stabilised), were weathered under accelerated conditions closely matching those of natural weathering. Changes in chemical and mechanical properties were assessed, and the influence of weathering on failure was analysed using fracture mechanics theory. An empirical relationship between UV-exposure time and an 'equivalent' surface notch depth is derived and used to estimate reduction in critical hoop stress for weathered ABS pipelines.

2 EXPERIMENTAL PROGRAM

2.1 Weathering

Specimens from a commercial ABS pipe resin comprising a SAN-graft-PB bimodal matrix with dispersed ungrafted PB polymer, in the form of impact (AS, 1146.1) and tensile (AS, 1145) specimens were weathered in an Atlas Ci 2000 weatherometer (Xenon Arc - 0.55 W/m²/nm @ 340 nm) at ambient temperature (30°C) such that the mechanism of degradation was not affected by heat (Tiganis *et al* 2001). Specimens were exposed using accelerated conditions for a 3-month duration with periodic removal for assessment. Table 1 shows the real accelerated weathering times and levels of UV exposure and the corresponding simulated times that are referred to in this paper. Simulated times were determined following Martin (Martin, 1977) and using an average of several years of total UV radiation data collected in Melbourne, Victoria and Allunga, North Queensland Australia, using an Eppley pyranometer. Based on the chosen accelerated conditions, a 3-month exposure period (1973 hours) approximates to a 1-year period of natural exposure.

Table 1: Accelerated weathering times and UV exposure levels with the corresponding simulated natural weathering times that are referred to in the text

Real Instrument time (hours)	UV exposure (MJ/m ²)	Simulated natural weathering time
41	7.5	1 week
82	15	2 weeks
164.5	33	1 month
329	66	2 months
493	100	3 months
658	133	4 months
986	200	6 months
1480	300	9 months
1973	400	12 months

2.2 Microstructural property assessment

Control and weathered ABS specimens were visually inspected using an Olympus optical microscope. To assess the effects of weathering on polymer microstructure, 20µm thick specimens of ABS were microtomed from both the surface and bulk of sample that had been weathered for 12 months. These specimens were assessed by Fourier Transform Infra-Red (FTIR)

spectroscopy to identify the carbonyl and hydroxyl absorptions formed due to the oxidation of weathered ABS and also to identify the characteristic infra-red absorptions of vinyl groups in control ABS specimens. The specimens were also analysed using an Atlas CL 400 chemiluminescence instrument to investigate the chemical stability of the surface of the weathered ABS. The samples were analysed at an isothermal temperature of 180°C in oxygen, after a nitrogen pre-phase. The onset of polymer degradation, or the oxidation induction time (OIT) was recorded for each sample.

2.3 Mechanical property assessment

The glass transition (T_g) temperature and loss moduli of the PB phase for ABS specimens before and after weathering were measured using a Rheometrics Scientific Solids Analyser RSA II DMTA. Instrumented impact analyses were performed on control and UV exposed ABS specimens, using a Radmana impact tester in accordance with AS 1146.1 (AS, 1146.1). To compare the effects of notching and UV exposure on the failure of ABS under static bending stresses, a hydraulically-driven Materials Testing System (MTS) 810 in a three point bending mode was also used. Notched (0.5 mm) control specimens were prepared according to AS 1146.1 and subjected to various nominal bending stresses. Exposed specimens (6, 9, 12 months) were also subjected to a static bending stress until failure and failure times were compared. Specimens were oriented such that tensile bending stresses acted on the UV-exposed or notched surfaces.

3 RESULTS & DISCUSSION

3.1 The effect of weathering on the chemical properties of ABS

3.1.1 Optical microscopy and visual examination

A yellow-brown discolouration was observed to develop after 2 weeks of simulated natural weathering time under accelerated conditions, for the ABS polymer. Discolouration was localised at the surface and was of very minimal depth, with fading and slight yellowing occurring initially. The depth of discolouration increased with exposure time, reaching approximately 0.1 mm after 12 months of simulated natural weathering, at which point yellowing was prominent. Discolouration is often related to the coupling of radical scavengers with degradation peroxy radicals (Faucitano *et al.* 1996). However for ABS, discolouration is attributed to the formation of photoproduct chromophores during degradation. Chromophores absorb energy in the UV-visible spectrum and cause discolouration of the resin (Kulich and Gaggar 1996, Salman and Al-Shama'a 1991). According to the literature, both the PB and SAN phase are said to form chromophores upon oxidation which are responsible for fading and yellowing.

3.1.2 Chemical stability - Oxidation Induction Time

Degradation at the surface of ABS causes an increase in polymer density, limiting oxygen diffusion and thus decreasing the rate of degradation through a thick ABS specimen, such that degradation is absent in the bulk polymer (Lemaire *et al.*, 1996). If UV stabiliser is present in commercial grades of ABS, it must first be depleted at the surface for degradation to occur (Faucitano *et al.* 1996, Heaps 1968, Clough *et al.*, 1996). Figure 1 shows chemiluminescence traces for control polymer, and polymer at the surface and bulk of ABS weathered for 12 months. The voltage trace recorded in chemiluminescence assessment is directly related to light emitted by the decay of hydroperoxides, formed in the polymer due to photo-oxidation, upon heating. (Clough *et al.*, 1996).

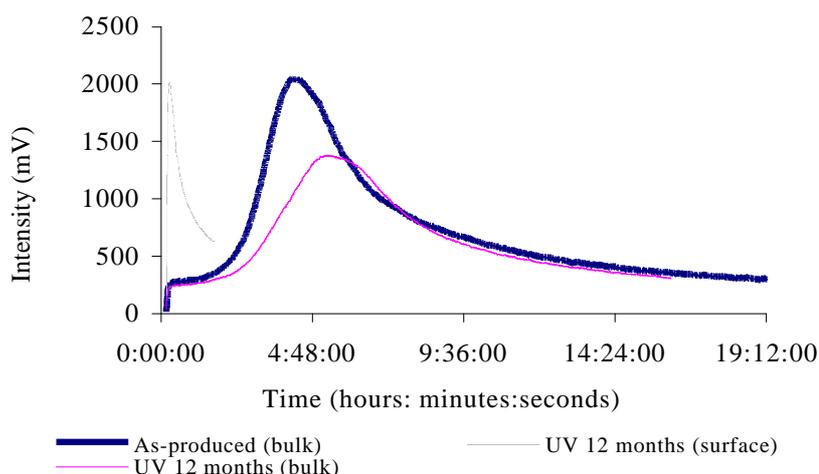


Figure 1: Chemiluminescence traces for control ABS polymer and polymer from the surface and the bulk regions of weathered ABS

As shown, the oxidation induction time (OIT) is almost instantaneous for the surface polymer of the weathered ABS specimen. This was expected as the resin was not UV stabilised and degradation occurred upon exposure. In contrast, the signal for the bulk polymer of the same specimen (OIT ~ 170 minutes) is similar to that obtained for control specimens (153 minutes), indicating that no degradation occurred in the bulk polymer.

3.1.3 FTIR analysis of polymer microstructure

FTIR spectroscopic analysis was used to study weathering-induced chemical changes in the microstructure of ABS. Results from control polymer specimens were compared to the surface and bulk polymer of ABS weathered for 12 months (simulated natural weathering time).

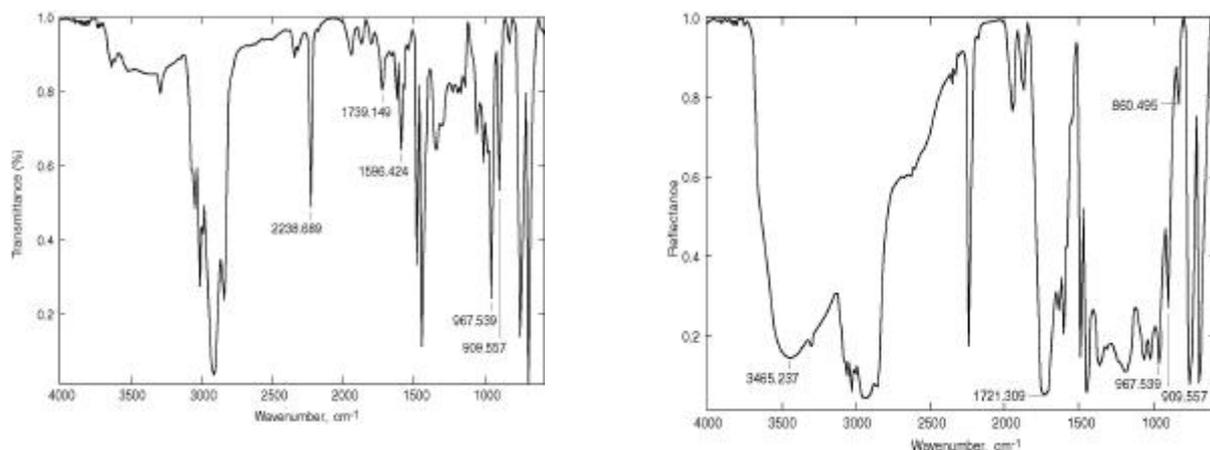


Figure 2. FTIR spectra of the bulk (left) and surface (right) polymer of a ABS weathered for 12 months

As shown in Figure 2, the spectrum representing the bulk analysis from the exposed polymer replicates a trace that is typical for control ABS, with no observed changes in the characteristic infrared absorptions and no evidence of degradation products. In contrast however, spectral changes are clearly observed at the surface of the aged polymer, in particular the carbonyl peak at 1721 cm^{-1} and hydroxyl peak at $\sim 3465\text{ cm}^{-1}$ indicating changes in chemical structure associated with oxidation and the formation of photoproducts. The absorbance bands at 966.92 cm^{-1} and 911.43 cm^{-1} correspond to the trans C=C unsaturation (vinyl) in polybutadiene, and the 1,2 butadiene terminal vinyl C-H band respectively. The surface spectrum for weathered ABS shows a significant distortion in these bands, indicating changes in the PB microstructure, which are attributed to chain scission and cross-linking (Shimada and Kabuki 1968).

3.2 The effect of weathering on the mechanical properties of ABS

3.2.1 Effects of weathering on the glass transition of ABS

The effects of weathering on the microstructure and the thermo-mechanical response of the PB phase in ABS were investigated using dynamic rheology. For weathered specimens, increases in both the loss modulus (E'') and $\tan \delta$ parameters were observed, indicating an increase in the glass transition temperature (T_g) of the PB phase. These increases reflect an increase in modulus due to cross-linking of the PB phase (Kulich and Gaggar 1996). This will be confirmed in the future with further studies based on molecular weight distribution.

3.2.2 Effects of weathering on impact properties of ABS

Figure 3 shows the detrimental effect of weathering on the impact strength of ABS resin. The initial impact resistance of 214 kJ/m^2 decreases to approximately 60 kJ/m^2 within 1440 hours (2 months) of simulated natural weathering. Failure of exposed ABS is dependent on the extent of surface degradation and at a critical depth of degradation an abrupt failure occurs, as seen in Figure . Kulich and Gaggar (Kulich and Gaggar 1996) also observed a similar trend in the reduction of impact strength. Similar to thermo-oxidative degradation of ABS, photo-oxidation of ABS causes a sudden loss in impact strength that is critically dependent on the depth of surface degradation (Tiganis *et al* 2001). Zahn reports similar findings for ABS that is not UV stabilised, where impact strength falls to approximately 30% of the original value after 1500 hours of UV exposure (Zahn 1997).

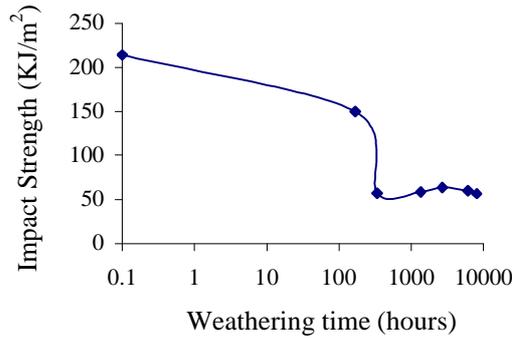


Figure 3: The effects of weathering on the impact strength of ABS resin

3.3 The effects of weathering on the failure mechanism of ABS

Results from the previous section suggest that weathering ABS creates a degraded surface layer that precipitates bulk mechanical failure similar to the action of a sharp surface notch. To investigate this hypothesis, the failure mechanism of UV-exposed specimens subjected to static bending stresses was examined. Figure shows the deflection/time curve for UV-exposed and virgin ABS specimens subjected to a static bending stress of 65 MPa.

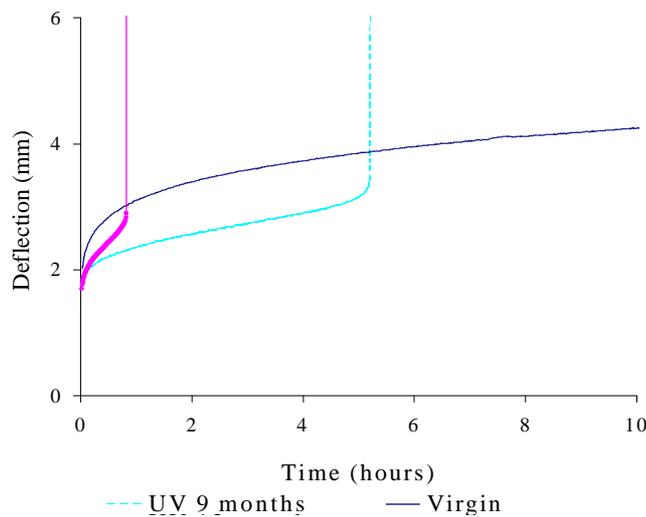


Figure 4: The variation of crosshead deflection with time for static load SENB tests on UV-exposed and un-notched virgin ABS specimens

As shown, the curve for un-notched virgin ABS is characteristic of creep deformation, an initial sharp increase in deflection, followed by relatively slow deformation. Failure eventually occurred by plastic collapse after three months. In contrast, whilst the initial sharp increase in deflection is observed in the UV-exposed specimens, the magnitude of deflection is reduced. This can be attributed to the increased stiffness of the degraded layer reported previously (Tiganis *et al* 2001). Furthermore, a transition is observed, after which deflection increases sharply. This typically indicates fracture failure with an increase in specimen compliance after crack initiation and subsequent propagation through the specimen thickness. Visual examination of failed specimens also suggested that brittle fracture occurred. Crack initiation was observed at UV-exposed surfaces, and separated surfaces appeared smooth with only limited stress whitening. Such features are typical of brittle failure from surface defects, with restricted plastic deformation in the bulk polymer.

Assuming that only limited plastic deformation occurs in the bulk polymer, Linear Elastic Fracture Mechanics (LEFM) theory can be used to relate UV exposure time to an 'equivalent' surface notch depth. For a single-edge-notched bend (SENB) specimen, an applied stress intensity factor (SIF) can be written as (Hashemi and Williams 1984)

$$K_I = Y \left(\frac{6M}{BW^2} \right) a^{1/2} \quad (2)$$

where M is the applied bending moment (Nm). B is the specimen thickness (m); W is the specimen width (m) and a is the surface notch depth (m). Y is a geometric correction factor which accounts for the influence specimen size and loading type

over K_I . At some stage during a test, a crack will initiate from the surface notch and slowly grow through the specimen thickness towards the free surface. Under plane strain conditions, the criterion for eventual brittle fracture can be written as

$$K_I = Y \left(\frac{6M}{BW^2} \right) a_c^{1/2} = K_{IC} \quad (3)$$

where a_c is the critical crack length, and K_{IC} is the material plane strain fracture toughness. By applying different static bending moments to SENB specimens, a range of failure times is produced and eq. (3) can be used to determine the variation of K_{IC} with time (Figure)

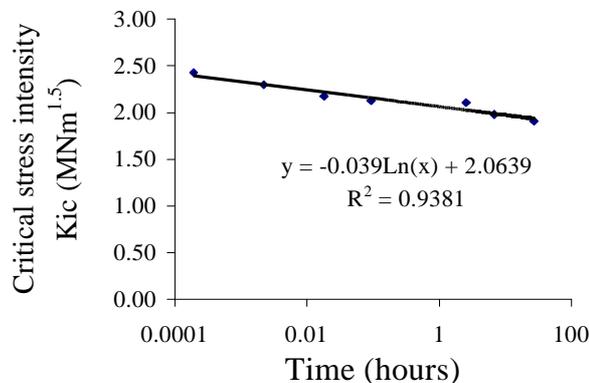


Figure 5: Critical stress intensity factor (K_{IC}) for un-exposed SENB specimens

As shown, the time-dependence of K_{IC} for *un-exposed* ABS specimens can be approximated as

$$K_{IC} = -0.04 \ln(t) + 2.06 \quad (4)$$

where K_{IC} is in $\text{MPa m}^{0.5}$ and t is in hours. If we assume that failure in UV-exposed specimens also occurs when $K_I = K_{IC}$, failure times for UV-exposed specimens can be used in equations (4) and (3) to obtain a relationship between UV exposure time and ‘equivalent’ notch depth (Figure).

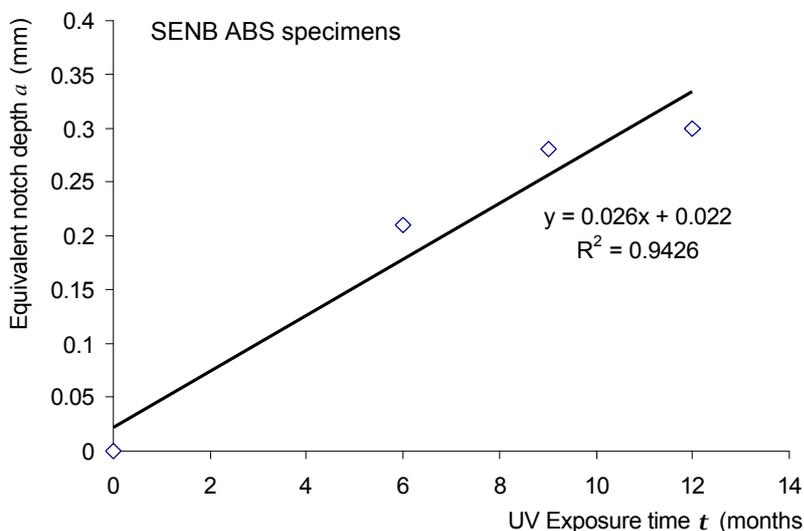


Figure 6: Equivalent notch depths determined from failure times in UV-exposed SENB specimens

As shown in figure 6, the resulting relationship from three-point bend tests is given by

$$a = 0.03t - 0.02 \quad (5)$$

where equivalent notch depth a is in mm and exposure time t is in months.

3.4 The effect of weathering on ABS pipe under hydrostatic pressure

Having derived an empirical relationship between τ and a , it can be applied to pressure pipelines if we assume that eq. (5) is independent of specimen geometry. If this is true, then subjecting a pipe to the same UV exposure as a rectangular bar

specimen will result in the same equivalent external surface notch depth. Whilst current work investigates the validity of this theory, we now go on to suggest how UV exposure may influence the performance of ABS pipes under hydrostatic pressure.

Let us assume that a pipe has been weathered in service for a known period, τ , and we require the reduction in its hydrostatic pressure capacity. If an equivalent external surface notch depth can be determined from eq. (5), the corresponding applied SIF (K_I) associated with a pipe under internal pressure is given by (Rooke and Cartwright 1974)

$$K_I = y \left(\frac{2pR_i^2 \sqrt{pa}}{R_o^2 - R_i^2} \right) \quad (6)$$

y is a geometric correction factor, p is the internal pressure (Pa), R_i is the pipe inner radius (m), R_o is the pipe outer radius (m) and a is the equivalent notch depth determined from eq. (5). As before, failure will occur when $K_I = K_{IC}$ as given in eq. (4). Figure shows the predicted effects of weathering on ABS pipe. Equivalent notch depths between 1.6-1.9 mm, correspond to weathering periods of 4.5-5.3 years simulated natural exposure.

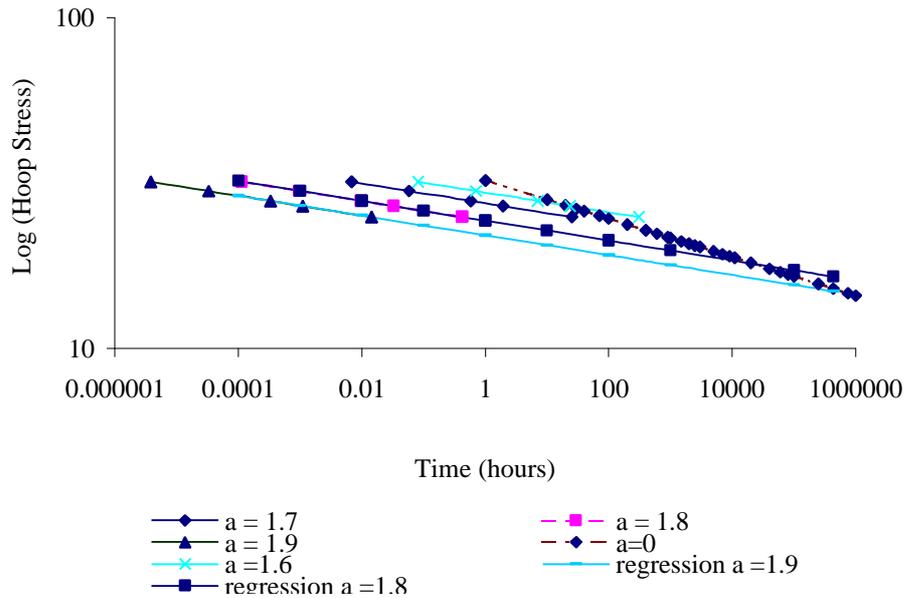


Figure 7 : The predicted effect of weathering (and the equivalent surface notch) on the long term hydrostatic performance of ABS

As shown, increasing UV exposure is predicted to reduce the time to failure for a given applied hoop stress. Whilst these predictions should be validated by experimental investigation, they may highlight the importance of UV-stabilisers in ABS pipes used in outdoor applications.

However, it should be noted that the results in figure 8 do not indicate *in-service* lifetimes. They indicate the performance of pipes that are *no longer* subjected to UV degradation *after* a period of exposure. In-service lifetime prediction can be idealised as a ‘competition’ between UV degradation at the pipe outer surface (which in turn produces an equivalent notch depth) and slow crack growth under the applied hydrostatic stress. During slow, stable crack growth, the applied SIF can be related to crack growth rate (da/dt) by a ‘power law’ relationship (Sandilands and Bowman 1986)

$$\frac{da}{dt} = AK_I^m \quad (7)$$

Where A and m are constants for a particular environment and are dependent on material visco-elasticity. Figure schematically illustrates the transition between UV-controlled degradation and slow crack growth for a pipe in service.

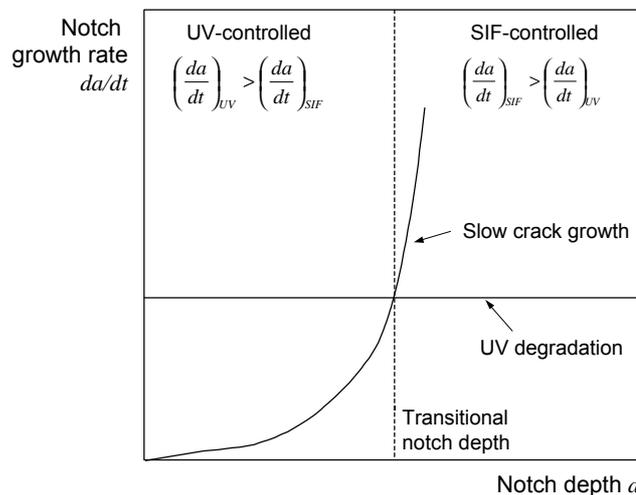


Figure 8: Schematic diagram of the transition between UV degradation and slow crack growth in service

As shown, the constant equivalent notch growth rate attributed to UV degradation is obtained by differentiating the linear relationship in eq. (5), and the ‘mechanical’ slow crack growth rate is described by eq. (7). Whilst notch growth is initially controlled by UV degradation, it becomes SIF-controlled above a transitional notch depth, which must be determined for in-service lifetime prediction. Although the initial results in this study suggest that equivalent notch growth under UV degradation proceeds at a constant rate, the effect of limited oxygen diffusion must be considered. For example, after extensive periods of UV exposure, the depth of the degradation in ABS will cease to grow with exposure time. Consequently, the empirical relationship between equivalent notch depth and exposure time may be misleading. Current work at CSIRO is progressing towards separate relationships between degradation depth/equivalent notch depth, and degradation depth/UV exposure time. It is anticipated that the growth of an equivalent notch can then be related more accurately to the kinetics of the UV degradation process.

4 CONCLUSIONS

Photo-oxidative degradation of the PB phase in ABS occurs in the absence or depletion of residual UV stabiliser, and ultimately precipitates mechanical failure of the polymer. Degradation of the elastomeric PB phase in ABS is initiated via photolysis of the methylene bond in the trans-1, 4-polybutadiene polymer structures, producing radicals that oxidise to produce carbonyl and hydroxyl products. Cross-linking of polymer chains, is also facilitated by free radicals. Degradation processes such as crosslinking cause an increase in polymer density at the polymer surface, preventing further penetration of UV light and oxygen into the bulk polymer. Thus degradation in thick ABS structures is localised at the surface. The mechanism of ABS photo-oxidative degradation in the PB phase is based on auto-oxidation and is strongly dependent on the wavelength and intensity of irradiation. The kinetics of degradation are not expected to be typically Arrhenius due to the limitation of oxygen diffusion.

In weathered ABS, the contribution from the dispersed PB phase to the overall ductility of the polymer, by particle cavitation, or localised shear yielding/crazing in the SAN matrix between PB particles, is greatly reduced due to degradation of that phase. Under impact loading, micro-cracks initiate from existing flaws in the degraded polymer surface layer. When the degraded layer reaches a critical depth, these cracks are sufficiently large to propagate into the bulk of the polymer causing abrupt mechanical failure.

Under static loading, the effect of UV degradation was compared to that of a sharp surface notch. Deflection/time curves and failure surface examination of degraded specimens indicated crack initiation and subsequent brittle propagation from the UV-exposed surface. Using plane strain fracture toughness measurements on un-exposed SENB specimens, an empirical relationship between UV-exposure time and an equivalent surface notch depth was determined. In the absence of experimental validation, it was assumed that this relationship was geometry independent and could be applied to pipelines under hydrostatic pressure. The variation of critical hoop stress with time was generated, indicating how a period of UV exposure may reduce failure times after subsequent UV protection. The in-service lifetimes of UV-exposed pipes was idealised as a competition between the growth rate of an equivalent notch under UV degradation, and the slow crack growth rate under an applied SIF. It was proposed that UV-controlled notch growth becomes SIF-controlled above a transitional notch depth.

Whilst the current study may suggest that weathering stabilisers or protective paints are required for ABS pipes that are under UV exposure, further investigation is required. The effect of degradation kinetics on equivalent notch growth must be considered, and the relationship between exposure time and notch depth must be validated for different test geometries.

5 ACKNOWLEDGEMENTS

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6 REFERENCES

1. ASTM D638, (1996), Standard test method for Tensile Properties of Plastics.
2. Clough, N.C. Billingham, and K.T. Gillen, (1996), in Polymer durability; Degradation, stabilisation and lifetime prediction, Advances in Chemistry Series 249.
3. Davis, A. and Gordon, D., (1974), 'Rapid Assessment of Weathering Stability from Exposure of Polymer Films. I. Real and Simulated Weathering of Commercial ABS Terpolymers' *Journal of Applied Polymer Science*, (18), 1159-1171.
4. Davis, A. and Sims, D. (1983), 'Vinyl Polymers' in *Weathering of Polymers*, Applied Science Publishers, London, Chapter 8, pp. 213.
5. Davis, P. and Burn L.S., (2001), Incorporating Failure Models into Asset Management Strategies for Plastic Pipes, In press.
6. Faucitano, A., Buttafava, A., Camino, G. and Greci, L. (1996), *TRIP*, 4, (3), 92.
7. Gesner, B.D. (1965), 'Environmental Surface Effects on ABS Resins' *Journal of Applied Polymer Science*, 9, 3701-3706.
8. Gugumus, F. (1979), in *Developments in Polymer Stabilisation – I*, eds Scott, G., Applied Science, London, Chapter 8.
9. Hashemi, S. and Williams, J.G., (1984), 'Size and loading mode effects in fracture toughness testing of polymers', *Journal of Materials Science*, 19, pp.3746 –3759.
10. Heaps, J.M. (1968), 'Stabilisation of ABS' *Rubber and Plastics Age*, October, 967-970.
11. Hearn, E.J., (1985), 'Thick Cylinders' in *Mechanics of Materials*, 2nd edit., An Introduction to the Mechanics of Elastic and Plastic Deformation of Solids and Structural Components, Volume 1, Pergamon Press., England, Chapter 10.
12. Jouan, X. and Gardette, J.L. (1992), 'Photo-oxidation of ABS: Part 2 – Origin of the Photodiscoloration on Irradiation at Long Wavelengths' *Polymer Degradation and Stability*, 36, 91-96.
13. Kelleher, P.G., Boyle, D.J. and Gesner, B.D. (1967), 'Environmental Stability of ABS Plastics', *Journal of Applied Polymer Science*, (11), 1731-1735.
14. Kinloch, A.J. and Young R.J., (1983), in *Toughened Multiphase Plastics. Fracture behaviour of polymers*, Applied Science Publishers, London.
15. Kulich, D.M. and Gaggar, S.K. (1996), 'Weathering of Acrylonitrile-Butadiene-Styrene Plastics: Compositional Effects on Impact and Color' in *Polymer Durability Stabilisation, and Lifetime Prediction*, eds R.L. Clough, N.C. Billingham and K.T. Gillen, American Chemical Society, Washington, DC, pp. 483.
16. Kurumada, T., Ohsawa, H., Yamazaki, T., (1987), *Polymer Degradation and Stability*, 19, 263.
17. Lemaire, J., Gardette, J.L., Lacoste, J., Delprat, P. and Vaillant, D., (1996), 'Mechanisms of Photooxidation of Polyolefins: prediction of Lifetime in Weathering conditions', in *Polymer Durability Stabilisation, and Lifetime Prediction*, eds R.L. Clough, N.C. Billingham and K.T. Gillen, American Chemical Society, Washington, DC, pp. 610.
18. Lu, J.P., Davis, P., Burn, L.S., (2001), 'Lifetime Prediction For ABS Pipelines Under In-Service Loading Conditions' *Plas. Rubber Proc. Appl.*, in press
19. Martin, K.G., (1977), 'Solar Weathering Indices for Australian Sites', CSIRO Division of Building Construction and Engineering, Research Technical Paper, (18), Highett, Melbourne, Australia.
20. Rooke, D.P. and Cartwright, D.J., (1976) *Compendium of Stress Intensity Factors*. HMSO, London, UK,
21. Salman, R.S. and Al-Shama'a, N.D., (1991), 'Effect of Thermal Aging on the Optical Properties of ABS Plastics' *Polym.-Plast. Technolo. Eng.* 30(4), 343-349.
22. Scott, G. and Tahan, M., (1977), *European Polymer Journal*, 13, pp. 981.
23. Shimada, J. and Kabuki, K. (1968), 'The Mechanism of oxidative Degradation of ABS Resin. Part II. The Mechanism of Photo-oxidative Degradation' *Journal of Applied Polymer Science*, 12, 671-682.
24. Shimada, J., Kabuki, K. and Ando, M. (1972), 'Mechanism of Photo-oxidative Degradation and Stabilisation of ABS Resin' *Review of the Electrical Communication laboratories*, 20, (5-6), 553-563.
25. Standards Australia, AS 1146.1, (1990), Methods for impact tests on plastics - Part 1: Izod impact resistance.
26. Tiganis, B.E. and Burn, L.S. and Davis P. and Hill A., (2001), 'Thermal Degradation of Acrylonitrile-Butadiene-Styrene (ABS) Blends' *Polymer Degradation and Stability in press*.
27. Zahn, A. (1997), 'Comparison of ASA and ABS; Study of the Ageing Behaviour of Different Products' *Kunststoffe*, 87, (3), March, 314-318.