The Effect of Weathering on the Flow, Microstructure and Physico-mechanical Properties of ABS

Dariush Salari[1*], Ali Olad[1], Aligoli Niaei[1], and Heidar Ranjbar[1,2]

(1) Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz,
Tabriz-5166616471, Iran
(2) Research & Development Center of Tabriz Petrochemical Complex,
National Petrochemical Complex, P.O. Box: 51745-354, Tabriz, Iran

A B S T R A C T

The effects of weathering on the flow, microstructure, and physico-mechanical properties of an unstabilized poly(acrylonitrile-butadiene-styrene) (ABS) were investigated by irradiating the ABS samples with a wavelength distribution comparable to solar light at 45ºC and relative humidity of 50 percent. A series of ABS samples were prepared by melt mixing of SAN and high rubber content g-ABS. All specimens were characterized by melt flow index (MFI) measurements, heat distortion temperature (HDT), Fourier transform infrared spectroscopy (FTIR), impact strength (Izod), tensile testing and measuring of CIEL*a*b* colour components (data of L*,a*,b* and YI). Alteration in the flow and physical properties was observed. The samples underwent extensive reduction in Izod impact strength, elongation-at-break, work-to-break, and turned yellow upon irradiation. The MFI, HDT, and FTIR results showed that upon weathering of ABS, cross-linking and chain scission of rubber phase were the governing degradation and yellowing mechanisms. The loss of unsaturation (disappearance of 1,4-polybutadiene) and alteration in carbonyl group as well as the hydroxyl group were observed. Significant amounts of photoproducts were detected in the directly irradiated surface layer. The colour difference of yellowing ΔYI exhibits a systematic tendency to higher values with increasing irradiation time.

(∗) To whom correspondence to be addressed.
E-mail: d.salari@yahoo.com

INTRODUCTION

Acrylonitrile-butadiene-styrene (ABS) polymers are one of the important engineering polymers in the world due to their attractive mechanical properties and convenient processing conditions. The polymers consist of an elastomeric component, usually polybutadiene (PB), dispersed in a copolymer of styrene (S) and acrylonitrile (AN); PB and the thermoplastic component (SAN) become compatible due to grafting of SAN on the elastomer chains. A rubber phase (PB), typically between 5 and 30%, is incorporated as a disperse phase in a rigid matrix to give a material with a significantly higher fracture resistance than the parent polymer. Toughening mechanisms include crazing, shear yielding, bridging and cavitations which involve localized deformation of the brittle matrix associated with stress concentrations initiated by the rubber inclusions. The physical properties of ABS strongly depend

on the nature and amount of elastomeric phase, the particle size of the dispersed phase, the extent of the grafting and the molecular weight of the continuous phase.

ABS polymers are susceptible to oxidative degradation when exposed to heat, mechanical stress and ionizing or UV irradiation in the presence of oxygen, due to the formation of reactive intermediates such as free radicals (for instance, R° and ROO°) and hydroperoxides, ROOH. Modification of the chemical structure of polymers due to degradation leads to changes in the molecular mass, degree of crystallinity, and mechanical properties. Numerous studies have addressed the challenge of understanding the complex degradation kinetics and mechanism [1-4].

The irradiation of polymers is important in a number of commercial applications including medical implant devices and packaging materials. Scott et al. [1] have shown that rubber-modified plastics undergo rapid loss of physical properties in outdoor weathering due to photo-oxidative degradation. This is because of the presence of unsaturation in the polymers which are highly susceptible to oxidation [1,2]. Photo-oxidation is also accompanied by loss in weight and yellowing [1,3,4].

Previous studies [5-9] have looked at the effect of both reprocessing and thermal ageing on the properties of recycled ABS. It was generally found that neither reprocessing nor thermal ageing had significant effect on the strength modulus of the material. However, both, and particular thermal ageing, have a detrimental effect on strain to failure and impact strength. Although heat stabilizers are commonly included in ABS to prevent thermal degradation in high temperature environments, stabilization against weathering and the effect of ultraviolet (UV) irradiation is sometimes overlooked. Exposure to UV-radiation can induce microstructural changes, which can in turn lead to polymer oxidation and degradation. Whilst photo-oxidative degradation of ABS has been reported to occur primarily in PB phase [10-15], degradation can also occur in the SAN phase [3]. Adeniyi [16] and Adam et al. [17,18], have shown that thermal and photo-degradation of unstabilized ABS are essentially those of its PB-

component. By direct photolysis, the PB-component activates photo-oxidation. Loss of elastomeric properties is associated in the first instance with loss of PB unsaturation under mild conditions. Under more severe ageing, there is cross-linking and catastrophic disunification of the terpolymer matrix by means of scission of the PB/SAN grafts. Jouan et al. [19,20] and Piton et al. [21,22] investigated the photo-oxidation of PB and ABS in condition of long wavelength irradiation ($\lambda > 300$ nm). The main photoproducts including hydroperoxides, α-β unsaturated ketones and final carboxylic acid groups have been identified by using FTIR spectroscopy and chemical titrations. HPLC analysis of low molecular weight fragment obtained after irradiation of ABS, PB and PS films revealed the oxidation of PS component in terpolymer ABS while the homopolymer PS showed no oxidation. Pickett et al. [23-26] and Diepens et al. [27] investigated the effects of irradiation conditions on the weathering of engineering polymers. However, in spite of the widespread use of ABS, virtually a few works have been reported on its yellowing with solar light. Published degradation studies on ABS have suggested that structural changes depend on the irradiation wavelength. To the best of our knowledge, the effect of solar radiation at 45°C on the flow, microstructure and physico-mechanical properties on ABS polymers has not been investigated and the mechanism of yellowing reactions also remains essentially unresolved. The thin degradation layers on specimens are very effective in the loss of mechanical properties, but the reason for these phenomena has not yet been completed.

The present study, therefore, focuses on the oxidative degradation behaviour of ABS in which the PB constitutes the weak site for photo-oxidative degradation. A primary objective of the present study is to investigate in depth the changes of the flow and heat resistance behaviour of general purpose ABS which was produced by melt mixing of SAN and high rubber content g-ABS, to correlate these changes with FTIR and colour spectrophotometry results and to predict more specifically the mechanism of yellowing and loss in physico-mechanical properties of weathered ABS. In this work, the effects of weathering with full spectral solar irradiation at 45°C

and relative humidity of 50 percent on the microstructure and impact properties of ABS have been also studied.

EXPERIMENTAL

Materials
The materials used in this work were a polybutadiene-*graft*-styrene-acrylonitrile resin (PB-*g*-SAN) (*g*-ABS coded HRG), with a rubber content (PB) of 60% by weight, that was synthesized in our laboratory and a styrene acrylonitrile (SAN) copolymer (SAN coded APH), with an acrylonitrile content of 25% by weight, industrial products of Tabriz Petrochemical Complex (Tabriz, Iran). The content of PB in ABS was 15.1 wt%. The SAN is used for dilution of *g*-ABS. Magnesium stearate (acid scavenger) and ethylene-bis-stearamide (processing lubricant), were kindly supplied by Tabriz Petrochemical Complex (Tabriz, Iran). The sample, which contained processing antioxidants, was used without purification to avoid any change in the polymer composition.

Methods
Sample Preparation
The ABS compounds, used for this studies, were prepared via melt-mixing the SAN (75 phr), *g*-ABS (25 phr), acid scavenger (0.4 phr), and processing lubricant (0.4 phr) using SM twin-screw laboratory extruder set at 160 rpm (L/D = 36, co-rotating, intermeshing) (Korea). The six heating zones were set at 180, 190, 210, 210, 210, and 225ºC. The extruded strands were quenched immediately in water at room temperature and chopped into granules by using SM pelletizer (Korea). The obtained granules were dried at 80ºC for 2 h in an air oven before processing in order to avoid possible moisture degradation reactions. Some materials were kept for analysis whereas the remaining was introduced for injection moulding. The specimens for calculating tristimulus values and physico-mechanical tests were moulded using an LG injection moulding machine (Korea) at injection temperatures varying from 180 to 205ºC. Moulded parts consisted of both length: 90 mm; width: 50 mm; thickness: 2.5 mm flat plaques for the measurement of yellowness index, and length:

63.5 mm; width: 12.7 mm; thickness: 3.17 mm sheet for the measurement of Izod impact strength properties. For the evaluation of heat distortion temperature, specimens were prepared according to ASTM D-648 method. For the evaluation of tensile properties, Dogbone-shaped samples were prepared according to ASTM D-638 method. For the evaluation of the effects of photo-oxidation on materials, ABS granules and injection moulded parts were introduced into a weathering chamber. Photo-oxidation was performed in a Weathering Chamber (Atlas Weatherometer, Germany). This instrument was characterized by (1) an ultraviolet (UV) source supplying full spectrum solar radiation, (2) a careful control of the temperature at 45ºC directly on the sample, (3) a rotation of 26 samples at constant speed and at constant distance from the sources, and (4) relative humidity of 50%. Injection moulded parts were continuously irradiated, with one side exposed to radiation, and granules exposed to radiation without covering. The specimens were removed for analysis after exposure times of 0, 25, 50, 100, 200, and 400 h.

Melt Flow Index
The melt flow index (MFI) measurements of the photo-irradiated ABS granules were performed on a modular melt flow series (Ceast, Italy). We followed the procedure, using ASTM D-1238. The test temperature was set at 200ºC and the nominal load was 5 kg. The measurements on each sample were repeated five times and the average values and standard deviations were calculated. The photo-irradiated granules were used without further treatment.

Heat Distortion Temperature
Heat distortion temperature (HDT) of photo-irradiated ABS was carried out using the heat distortion tester HD-PC (Yasuda, Japan) according to ASTM D648. This measured the temperature when the depth of deflection became 0.254 mm under a condition whose bath temperature could be raised at a constant speed and load was fixed in silicone oil bath.

Fourier Transform Infrared Spectroscopy
Fourier transform infrared (FTIR) spectroscopy

(Bruker, Germany) was used to monitor the alteration of surface layer of the photo-irradiated and un-irradiated ABS.

Impact Strength Measurement

The impact properties were carried out in Izod mode according to ASTM D256 standard on five rectangular specimens using a Resil impactor (Ceast, Italy).

Tensile tests were also carried out on a Shimadzu, 20 kN (Japan) testing machine according to ASTM D638 standard on five Dogbone-shaped samples. Average values and standard deviations were calculated from at least 5 samples. Work-to-break was calculated by integration of stress-strain curve.

Yellowness Measurement

Yellowness index (YI) was determined in accordance with ASTM E-313 by reflectance measurements using a Spectra flash SF450 data colour (Germany) together with a selected standard illuminant (D65) observer (10º) to determine the CIELAB colour coordinates (colour system defined by the International Commission on Illumination): L^* (measure of lightness/darkness), a^* (measure of redness/greenness), and b^* (measure of yellowness/blueness). The instrument is designed to give YI values. Several values of YI obtained from different parts of the samples were used to obtain an average value of the yellowness index.

RESULTS AND DISCUSSION

Melt Flow Index

The melt flow index (MFI) is a common property employed in industry for quality control of the final product in-order to guarantee its further processing capability and flowability for the manufacture of products. Figure 1 shows the slight decrease in the MFI of the photo-irradiated ABS subjected to 25 h. One reason for the decrease of MFI may be that, in the photo-degradation of ABS, the PB phase in which weaker bonds are present (the initial target of oxidation) simultaneously undergoes cross-linking and rupture, but the former predominates up to 25 h, whereas the latter predominates after this time. As
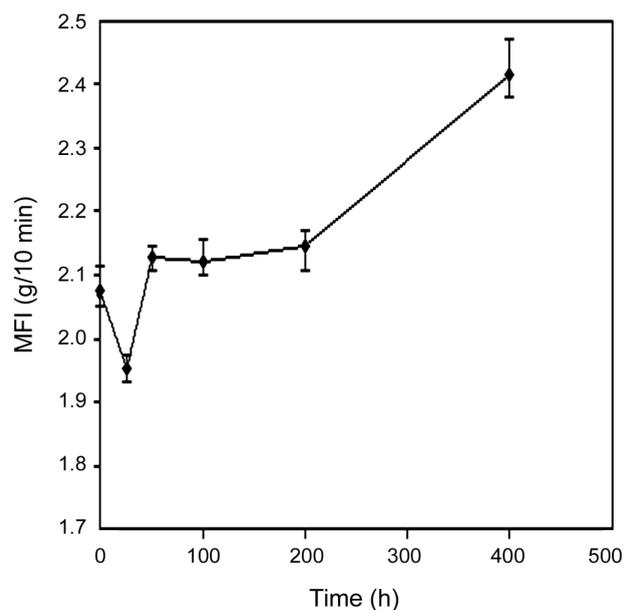

Figure 1. Influence of irradiation time on the melt flow index (MFI) of ABS specimens.

shown in Figure 1, there is a rapid increase in MFI until 50 h. The increase in MFI is due to the scission of weak links by attack of oxygen at weaker bonds, but it slows down later, indicating slight cross-linking again at longer irradiations until 100 h. The degradation of the grafted PB can lead to a de-grafting of SAN, which would be in line with the observed increase of MFI at longer irradiations after 200 h. As shown by Scott [1], PB grafting sites, containing tertiary allylic carbon atoms, are preferentially oxidized in the first stages of ABS photo-oxidation compared to secondary allylic carbon atoms. The thermal or photochemical homolysis of tertiary hydroperoxides leads to the formation of alkoxy macroradicals; β-scission of alkoxy macroradicals may occur. This leads to α,β-unsaturated ketones on PB component and induces the breaking of PB/SAN grafts [21].

Heat Distortion Temperature

Figure 2 shows variation of heat distortion temperature (HDT) as a function of irradiation time. The HDT of photo-irradiated ABS has rapidly increased up to 25 h, then the curve became flat until 50 h, after which HDT of irradiated specimens decreased. Possible explanations for this behaviour are given in MFI section.
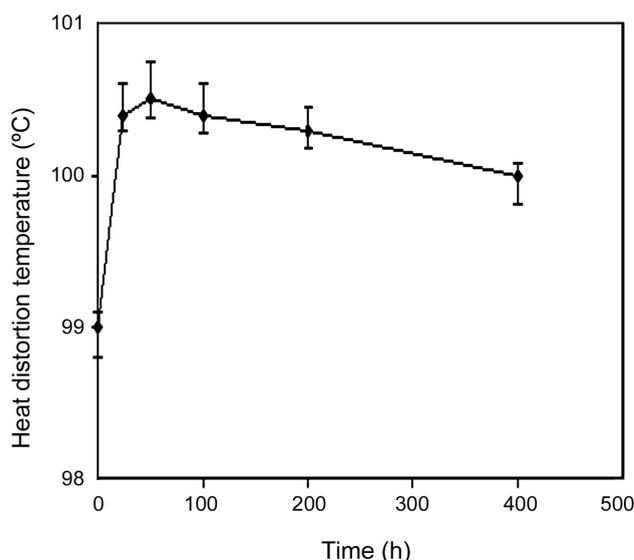
Figure 2. Influence of irradiation time on the heat distortion temperature (HDT) of ABS specimens.

Fourier Transform Infrared Spectroscopy

The absorbance spectra of the ABS samples subjected to photo-irradiation at 45°C in weathering chamber were studied. Figure 3 shows the Fourier transform infrared (FTIR) spectra of some selected virgin and photo-irradiated ABS samples. In order to obtain a quantitative picture of the structural changes caused by weathering, we determined the relative absorption ratios of the peaks corresponding to the maximum of the hydroxyl region (3296 cm^{-1}), carbonyl region (1723 cm^{-1}), *trans*-1,4 group (967 cm^{-1}), and vinyl-1,2 group (912 cm^{-1}) in relation to the height of a reference peak at 702 cm^{-1} absorption band corresponding to the out-of-phase bending vibration of the C-H bond of the aromatic ring, which remains unchanged during photo-irradiation [2,28]. The increase in the hydroxyl and carbonyl intensities on the irradiated side as well as a general increase of baseline in the fingerprint region could be clearly seen. The ester groups generated during degradation appear in the range of 1000-1300 cm^{-1} and could be seen as a general underlying increase, but the peak positions were not clearly visible [22,28].

The hydroxyl peak appeared as a broad signal with maximum at 3296 cm^{-1}, typical of an OH stretch. The tail of this band extended beyond 3000 cm^{-1}, suggesting the presence of OH groups from carboxylic acids. On the irradiated side, the carbonyl peak was broad with several shoulders. The various types of carbonyls formed during treatment (esters, acids, ketones, aldehydes, etc.) were responsible for the shoulders and peak width [16,28]. In the PB
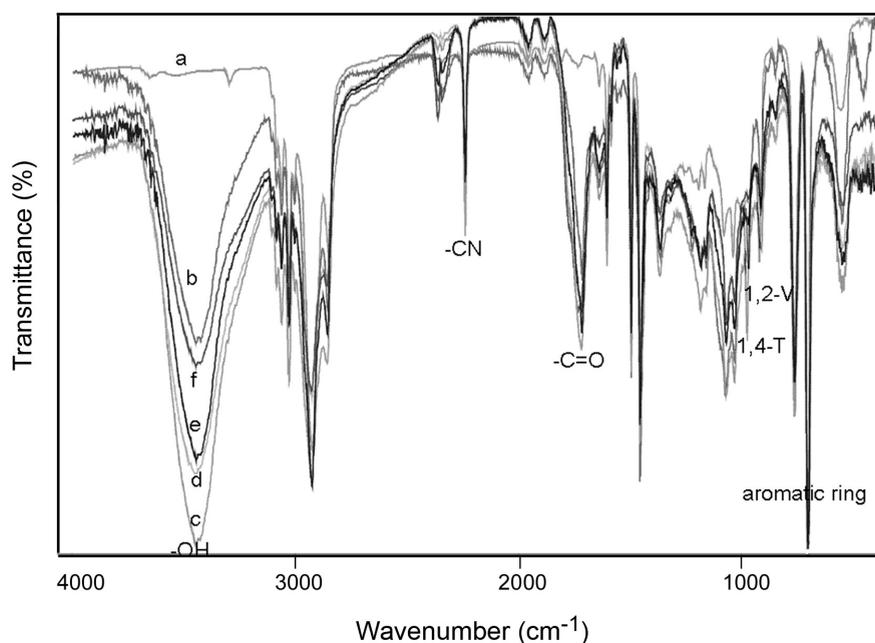

Figure 3. FTIR spectra of ABS as a function of irradiation time: (a) 0 h, (b) 25 h, (c) 50 h, (d) 100 h, (e) 200 h, and (f) 300 h.

region, a major decrease in the range of 967 cm^{-1} and 912 cm^{-1} peaks could be clearly observed.

The spectral changes on the surface layer as a function of irradiation time were studied in detail. The peak at 1602 cm^{-1}, which was chosen to represent the styrene component, remained unaltered. No change was observed in the 3000-3200 cm^{-1} region of the aromatic C-H stretch, which provides further evidence that the aromatic component of the polymer was not affected by photo-irradiation. The spectra changed significantly with irradiation time in the hydroxyl, carbonyl, and butadiene regions. The increase in the hydroxyl region was considerable even in the early stages of the irradiation process (t = 25 and 50 h), and decreased gradually for longer exposures. The increase in the carbonyl band was also detected up to 50 h of exposure time. These results are reasonable, as hydroperoxide is expected to appear up to 50 h followed by their photolysis. Likewise, the increase, then plateau in the carbonyl region, could be due to ketone formation initially followed by photolysis.

The time dependency of the hydroxyl intensity with irradiation time was calculated by integrating the spectral region 3296 cm^{-1}. Figure 4 shows an initial accelerated increase in the first 50 h of irradiation, and a moderate decrease above 100 h of irradiation. The two regions were fitted well by straight lines whose slopes were proportional to the rate of hydroperoxide formation and were followed by photolysis. The rates were 0.0285 and -0.0012 h^{-1}, with correlation factors of 0.9901 and 0.9661, respectively. The large difference between the two rates indicated that the formation of hydroperoxide was a facile reaction that should occur in the initial stages of irradiation. The decrease of the hydroxyl intensity in the second stage was assigned to the hydroxyl consumption in degradation reactions, and/or to the decrease of the intensity from 1,4-PB as the degradation advanced. The limitation of BR photo-oxidation has been attributed to decrease of permeability to oxygen [22]. In the irradiated sample, oxygen was shown to no longer diffuse through the cross-linked surface layers: the concentration profiles of photoproducts and unsaturations reveal a heterogeneous reactor whose core is not oxidized.

The time dependency of the carbonyl region (Figure 5), shows an initially accelerated increase up to 50 h of exposure time, and reached a plateau above 100 h of irradiation. The two regions were fitted fairly by straight lines whose slopes were proportional to the rate of carbonyl formation. The
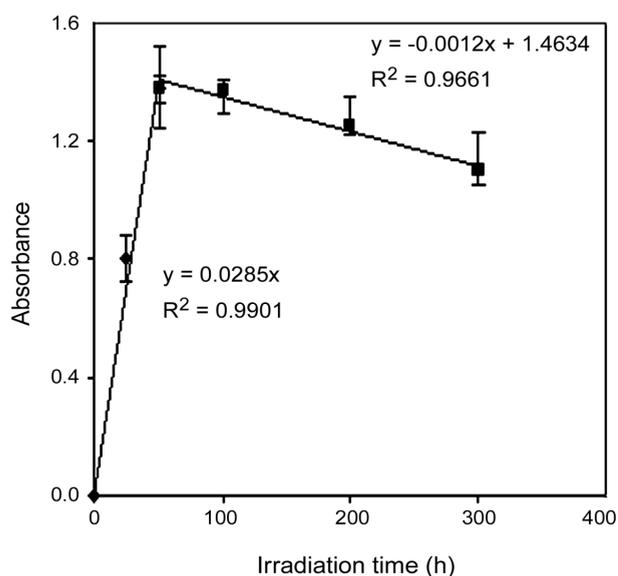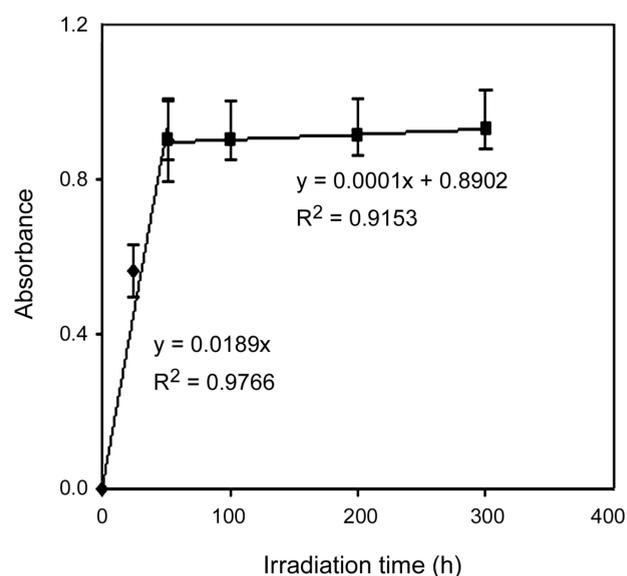

Figure 4. Evolution of the hydroxyl absorbance with the time for ABS subjected to polychromatic irradiation. The linear fits for the initial and final portions of the plot have slopes of 0.0285 and -0.0012 h^{-1}, respectively.

Figure 5. Evolution of the carbonyl absorbance, with the time for ABS subjected to polychromatic irradiation. The linear fits for the initial and final portions of the plot have slopes of 0.0189 and 0.0001 h^{-1}, respectively.

rates were 0.0189 and 0.0001 h^{-1}, with correlation factors of 0.9766 and 0.9153, respectively. This result was reasonable, as peroxides were expected to appear early in the degradation process and to initiate the degradation chain.

The time dependences of the PB intensity were also calculated, but their accuracy was limited because isomerization reactions could have occurred and fluctuations in the peak intensity of PB regions were observed [11]. The PB peak at 967 cm^{-1} decreased significantly during 50 h of irradiation, and the decrease was considerably slower for longer treatment times. As shown in Figure 3, the signal from 1,4-PB was not merely decreasing, but practically disappearing after 50 h of treatment. Unmistakably, the degradation of ABS seemed to be a direct result of the modification of chemical structure of 1,4-PB, not of 1,2-PB.

Change in Izod and Impact Strength
Figure 6 shows variation of Izod impact strength as a function of exposure time. The Izod impact strength rapidly decreases initially with exposure time. Because of photo-irradiation, thin layer of photo-irradiated tensile and impact specimens was degraded, and cross-linking occurred on the rubber phase. The main reason for this conclusion was the very fact that, unsaturation (due to PB phase) as
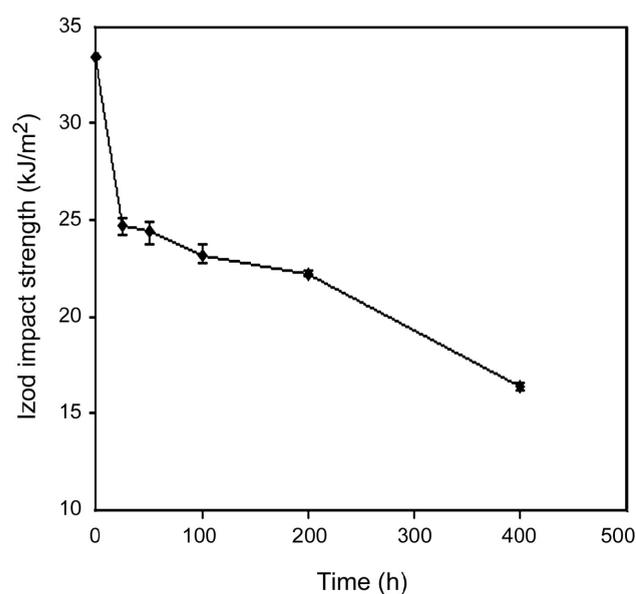
detected by FTIR, disappeared after these exposure times (Figure 3). Photochemical yields for scission and cross-linking for various polymer segments found in ABS indicate that cross-linking will occur in the rubber phase, while the SAN-based matrix will remain relatively unaffected at the irradiated levels used here. However, assuming that the principal effect of irradiation is to increase the cross-linking density within the rubbery domains a reduction in the relative difference between the modulus of two phases will result. Because of uneven physical characteristics of two phases, the result was a different fracture behaviour. The irradiated side became more brittle and posed a high modulus which resulted in a behaviour form known as "ductile to brittle transition" [12,29,30]. The loss of Izod impact strength was reduced and it was flat between 25 and 50 h, then the loss of Izod impact strength was increased after 200 h. Since the main reason for strength failure was due to impact, longitudinal crack and fracture manner, and even after 25 h of cross-linking and breakage of the chain, this method of fracture did not show any specific modification, thus the curve became flat. In addition, it is given that the sample has been irradiated for 400 h; that is one side irradiated for 100 h and the other side for 300 h, fracture behaviour was changed and longitudinal crack was developed within sample's both sides.
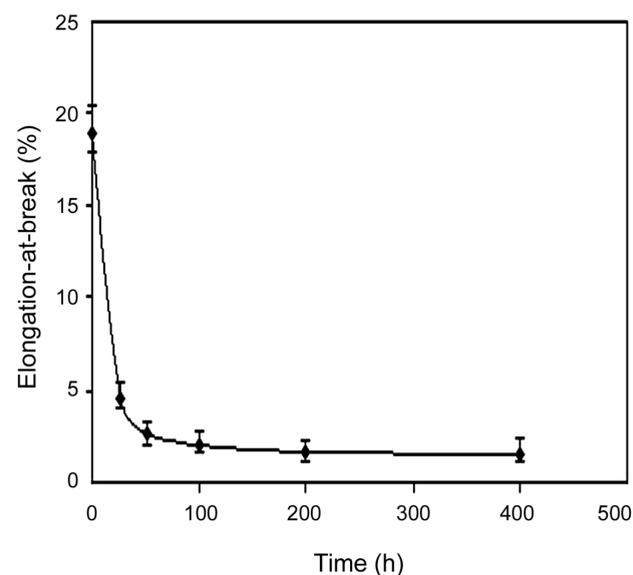

Figure 6. Influence of irradiation time on the impact strength of notched ABS specimens.

Figure 7. Influence of irradiation time on the elongation-at-break of ABS specimens.
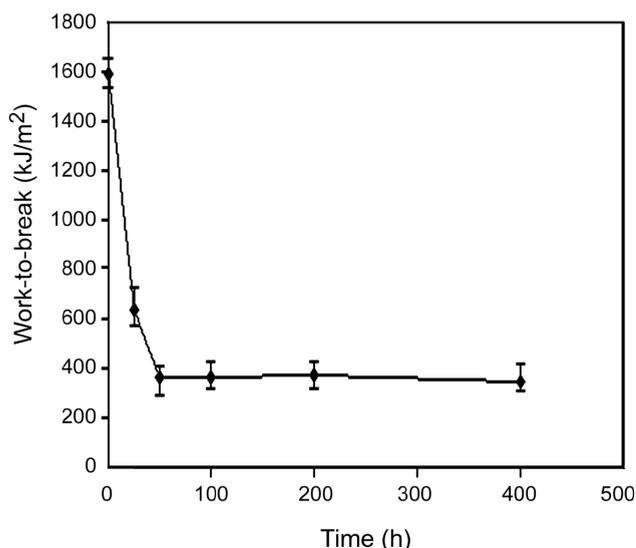
Figure 8. Influence of irradiation time on the work-to-break of ABS specimens.

Because of this modification in fracture behaviour, impact's failure was developed cumulatively.

Figure 7 shows the variation of elongation-at-break as a function of irradiation time. The elongation-at-break rapidly decreased initially with exposure time and then the curve became almost parallel to the x-axis after 50 h irradiation. The final elongation-at-break value approached that of SAN copolymer. The shape of the elongation-at-break curve versus exposure time (Figure 7) is very similar to Figure 6, suggesting that the same type of mechanism operates, that is, the PB phase is completely degraded after 50 h exposure.

The loss in such elastomeric properties of ABS including Izod impact strength and elongation-at-break has been explained in terms of scission reactions of the graft of PB with the rest of the polymeric matrix [21]. Work-to-break was calculated by integrating stress-strain curve that was carried out at a cross-head speed of 500 mm/min. As shown in Figure 8, work-to-break rapidly decreased initially with time and then the curve became plateau. This observation suggests that the PB is completely degraded after 50 h irradiation period. The degradation of photo-irradiated layer, alteration in ductile to brittle transition behaviour and initiation of crack perpendicular to the applied force were main reasons for loss of toughness.
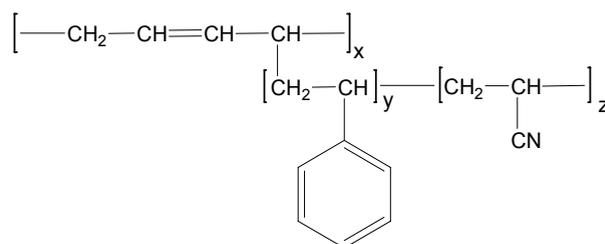
Scheme I. Proposed structure of ABS.

Yellowing

In photo-oxidative degradation, it was noticed that each sample turned opaque and developed yellowness shortly after irradiation. The proposed ABS structure is shown in Scheme I.

The C-H bond of polystyrene and polyacrylonitrile in SAN copolymer was more stable than that of the allyl group of PB due to the induction effect and steric hindrance of the phenyl group as well as delocalization of radicals by the allyl group.

Therefore, oxidation naturally began in the rubbery phase (allyl group) of PB. One of the most popular methods for investigating the changes in optical properties by photo-oxidation is the measurement of the L^*, a^*, b^*, and yellowness index.

The L^*, a^*, b^* (tristimulus values) of photo-oxidative ABS samples are given in Table 1. The samples underwent rapid photo-yellowing upon irradiation, yielding a measurable increase within 25 h which became more severe at longer periods. A study of the tristimulus values indicated that the observed changes in yellowing were due to variations in lightness as well as chromaticity. The L^* parameter calculated from tristimulus values was a direct

Table 1. Yellowness index (YI) of ABS specimens upon irradiation.

Irradiation time (h)	Tristimulus values			YI
	L^*	a^*	b^*	
0	71.3	-2.6	8.7	19.5
25	71.1	-3.0	9.1	20.1
50	71.2	-3.1	9.3	20.4
100	70.6	-3.4	10.4	23.2
200	69.9	-3.6	13.1	30.1
300	68.9	-3.5	15.5	36.9

measure of lightness of the surface colour varying between 0 (black) and 100 (white). The colorimetric data showed a relatively small change in L^* but significant changes in a^* and b^* values, indicating that discoloration was not a mere change in lightness. The positive value of b^* indicated yellowness while the negative a^* value corresponded to greenness. The starting material itself with $L^* = 71.3$, $a^* = -2.6$, and $b^* = 8.7$ might be described as having a light yellow-green surface. The value of a^* decreased while that of b^* increased with YI. This indicated an increase of yellow-green colour with irradiation. Table 1 shows the variations of yellowness index (YI) of ABS samples with irradiation time. The YI of the irradiated samples increased approximately linearly with time (up to 300 h).

CONCLUSION

Poly(acrylonitrile-butadiene-styrene) (ABS) was studied by melt flow index (MFI), heat distortion temperature (HDT), Izod impact strength, elongation-at-break, work-to-break and colour change upon exposure to polychromatic irradiation.

The MFI and HDT results suggest that the most important factors affecting the photo-oxidation of ABS are degradation (cross-linking and chain scission) of the rubber phase (g-ABS). Rubber phase simultaneously underwent cross-linking and chain scission, the former was predominant until 25 h, but after that, the latter was predominant.

The FTIR spectroscopic studies showed that the degradation of ABS by photo-irradiation was due to the disappearance of double bonds in 967 cm^{-1} peak from the *trans*-1,4-PB functional group and formation of hydroxyl and carbonyl groups.

Photo-degradation of ABS was heterogeneous; FTIR, Izod impact strength, elongation-at-break, and work-to-break profiling indicated that the major effects occurred in the thin surface layer of ABS materials. The irradiated side became more brittle and posed a high modulus which resulted in a behaviour form of "ductile to brittle transition" and a two-way notch was formed and consequently decreased the strength.

The results of yellowness index indicated that all

the samples suffered yellowing as result of photo-oxidative degradation and a systematic tendency to higher values with increasing irradiation time. Our results show that the photo-yellowing correlates very well with ABS degradation (FTIR detection).

ACKNOWLEDGEMENTS

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