

# The Oxidative Degradation of Styrenic Copolymers: A Comparison of Photoproducts Formation Under Natural and Accelerated Conditions

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**ABSTRACT:** Natural and accelerated weathering of polystyrene and high-impact polystyrene were carried out in the present investigation. The structural changes in the polymer samples were characterized by using FTIR spectroscopy, tensile strength testing, and SEM spectroscopy. The natural exposure was conducted throughout the year. Rates of photooxidation were determined by measuring the evaluation in hydroxyl and carbonyl regions. The surface deterioration was revealed from SEM micrographs. The drop in tensile strength was also monitored. A correlation between natural and artificial weathering was considered for lifetime prediction in a short exposure time. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1676–1682, 2002

**Key words:** HIPS; oxidative degradation; natural weathering; accelerated weathering; photooxidation; degradation; radiation; FTIR

## INTRODUCTION

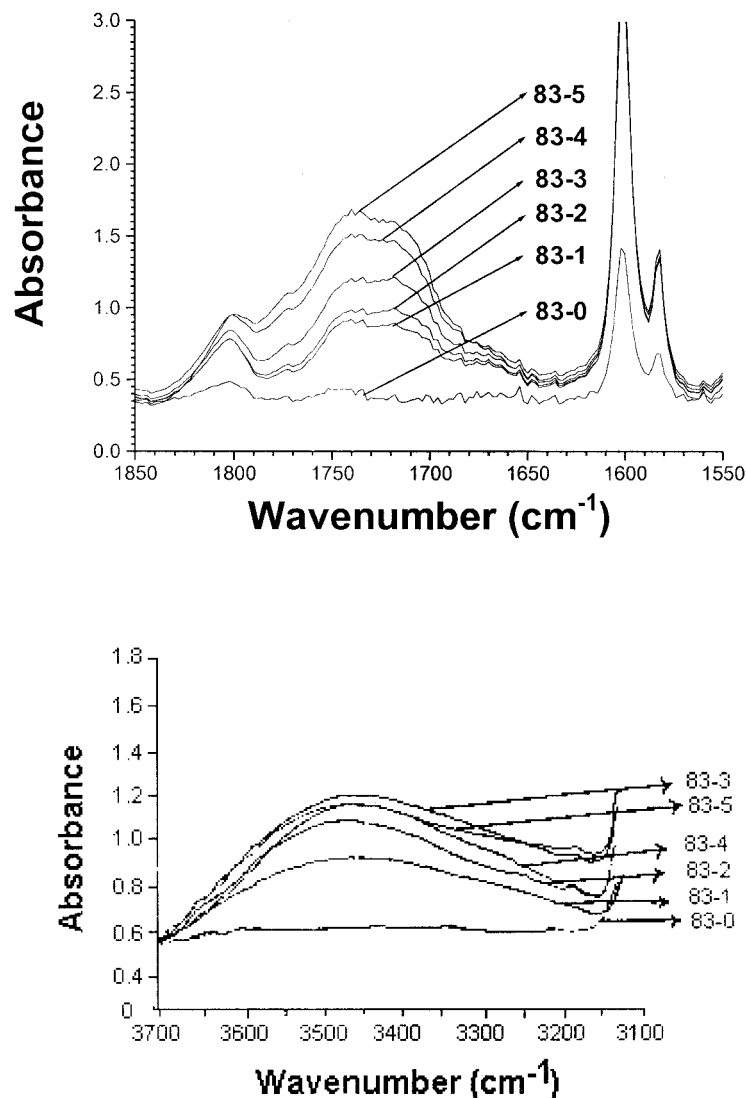
Natural weathering of plastics refers to the adverse response of plastics to climate. Upon exposure of polymers to environmental conditions, the physical or chemical attack leads to their degradation. The UV light and heating effects of solar radiation play major roles and the polymer leads to chain scissions. The solar UV light (295–400 nm) generally contains < 5% of solar energy but it is sufficient to break the bonds of polymers. As a consequence of degradative reactions, the polymer loses properties such as mechanical, rheological, thermal, electrical, and changes in color, and finally leads to embrittlement. Thus, the service life becomes limited, due to weathering<sup>1</sup> of polymers. The deterioration of a material depends on how and to what extent it interacts with its surroundings. Weathering implies the action of an individual or a combination of various environmental factors on polymers (i.e., heat, light, ion-

izing radiation, oxygen, ozone, humidity, rain, wind, dust, bacteria, and chemical pollutants). Apart from structural and morphological changes, the natural aging also depends on geographic locations (latitude, longitude, mountain, sea, desert, etc.), seasons, and environmental and atmospheric conditions. In India, Pakistan, or Saudi Arabia, where the radiation from the sun reaching to the earth is greater ( $250 \text{ kW cm}^{-2}$ ), the weathering life is only 2–5 years. Accelerated (artificial) weathering usually involves controlled conditions where exposure to various factors can be standardized and compared. In addition, it permits the isolation and control of particular environmental factors for detailed evaluation. The most important feature of artificial weathering is that it can accelerate degradation of the materials under known conditions. The service life of a polymer can be predicted with the formation of carbonyl and hydroxyl group absorption.

The natural and artificial weathering of polymers such as low-density polyethylene (LDPE),<sup>2</sup> polypropylene (PP),<sup>3</sup> LDPE-linear low-density polyethylene (LLDPE) blends,<sup>4</sup> and E-P copolymers<sup>5</sup> was discussed earlier, but the terrestrial (global

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**Figure 1** FTIR spectral changes in carbonyl and hydroxyl region for various times of natural exposed HIPS 8350 films (April to August). (83-0: Neat; 83-1: 30 days; 83-2: 60 days; 83-3: 90 days; 83-4: 120 days; 83-5: 150 days exposed naturally starting from April).

degradation of styrenic copolymers has not been studied widely.<sup>6-11</sup> In this article, the natural weathering behavior of styrenic copolymers with different polybutadiene content and its comparison with polystyrene is discussed. The carbonyl group formation in natural weathering is compared with corresponding accelerated weathering. A correlation between natural and accelerated weathering was considered for lifetime prediction in a short time.

## EXPERIMENTAL

### Materials

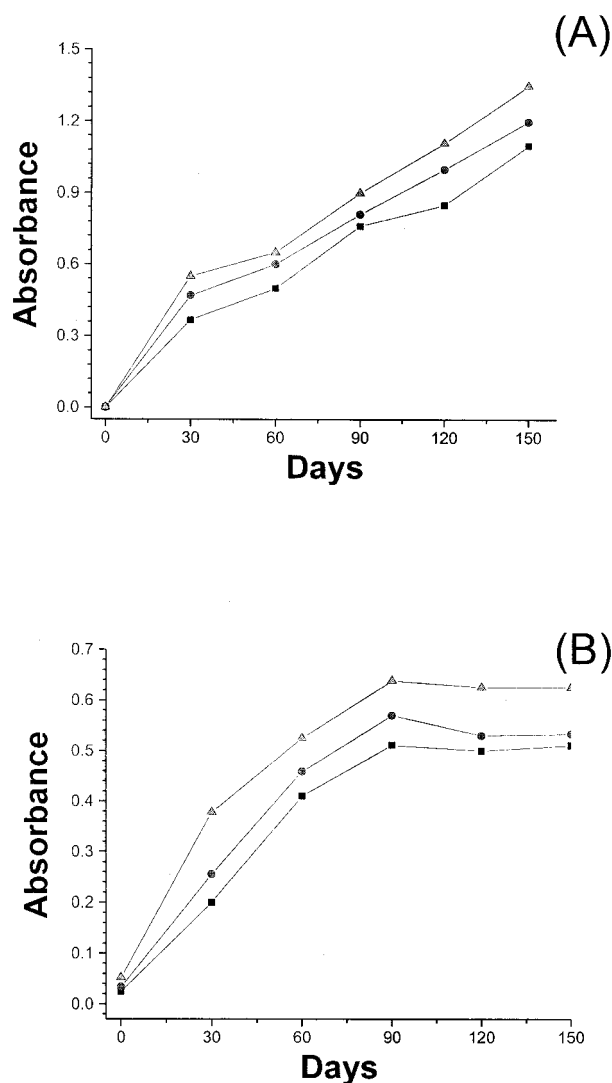
The materials investigated were high-impact polystyrene (HIPS) obtained from M/s. Polychem,

Mumbai, India; HIPS 7240 and HIPS 8350 samples were obtained from M/s. Elf-Atochem, Paris, France. A commercial sample of polystyrene (Polychem) was also examined for comparison. The samples, which contained processing antioxidants, were used without purification to avoid any change in the polymer composition. The contents of polybutadiene in HIPS were determined<sup>12</sup> by <sup>13</sup>C-NMR and FTIR spectroscopy and were found to be 3.1, 6.3, and 7.9 mol %, respectively, for HIPS, HIPS 7240, and HIPS 8350.

### Procedure

Thin transparent films (~ 100 μm) were made in a hydraulic press at 200°C by applying 150 kg





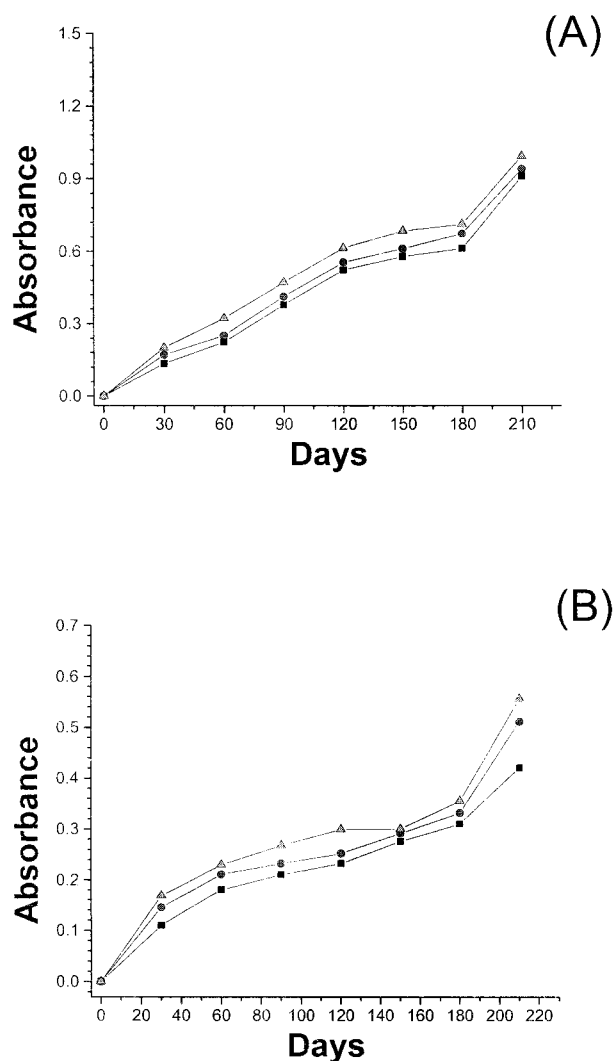
**Figure 2** Rate of carbonyl (A) and hydroxyl group (B) formation in HIPS (■), HIPS 7240 (●), and HIPS 8350 (▲) films in natural photooxidation during the months of April to August.

which clearly shows that initially polybutadiene phase is oxidized<sup>17</sup> because of unsaturation.

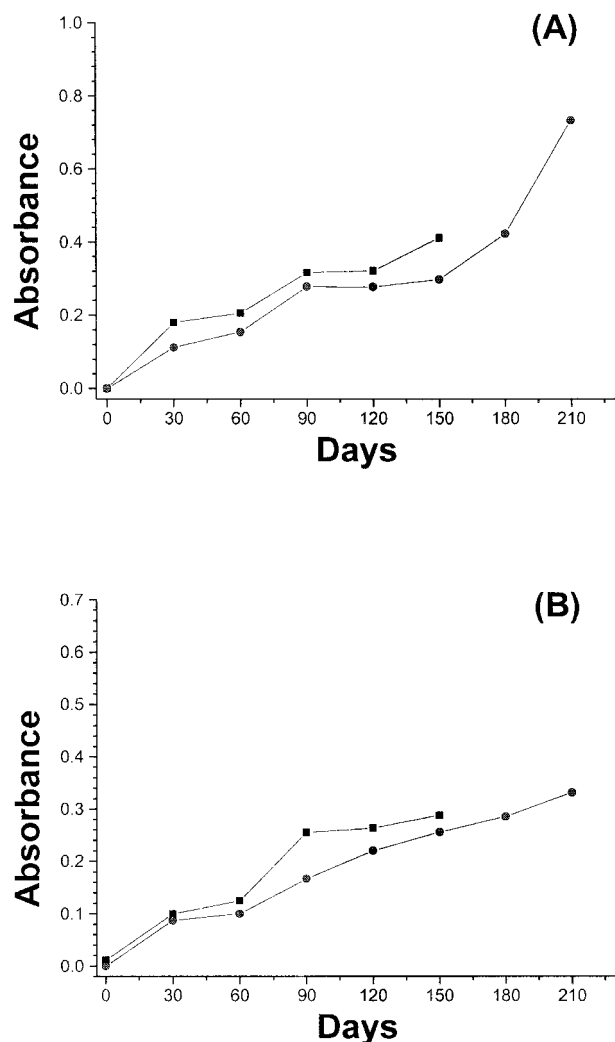
#### Kinetic Aspects of the Natural Photooxidation of Styrenic Copolymers

The rate of natural photooxidation of HIPS, HIPS 7240, HIPS 8350, and polystyrene (PS) films showed an increase in the formation of carbonyl and hydroxyl groups formation from April to August (Figs. 2 and 4). In April, the formation of the carbonyl groups are greater than the other months. During this time, the temperature was 40–44°C and the humidity in the environment

was 40–50%. The rainy season starts in India in the month of June, which shows that the hydroxyl absorption is greater in this period. The rate of natural photooxidation also depends on the polybutadiene content (Figs. 2 and 3). Figures 3 and 4 show that the rate of natural photooxidation in HIPS 8350 is minimum from October to January and maximum in March. During this period, the temperature is 30–35°C. HIPS 7240 and HIPS also showed the same behavior. In the photooxidation process, the polybutadiene oxidizes via the formation of unstable alkyl/peroxy radicals and unstable intermediate hydroperoxides lead to the formation of carbonyl groups. The natural photooxidation of PS is minimum as compared to



**Figure 3** Rate of carbonyl (A) and hydroxyl group (B) formation in HIPS (■), HIPS 7240 (●), and HIPS 8350 (▲) films with natural exposure during the months of September to March.



**Figure 4** Rate of carbonyl (A) and hydroxyl group (B) formation in PS films with natural exposure during the months of April to August (■) and September to March (●).

HIPS films. This result shows that polybutadiene phase is oxidized initially and suggests that the modification of the infrared absorption in the carbonyl and hydroxyl ranges could result from the oxidation of polybutadiene.

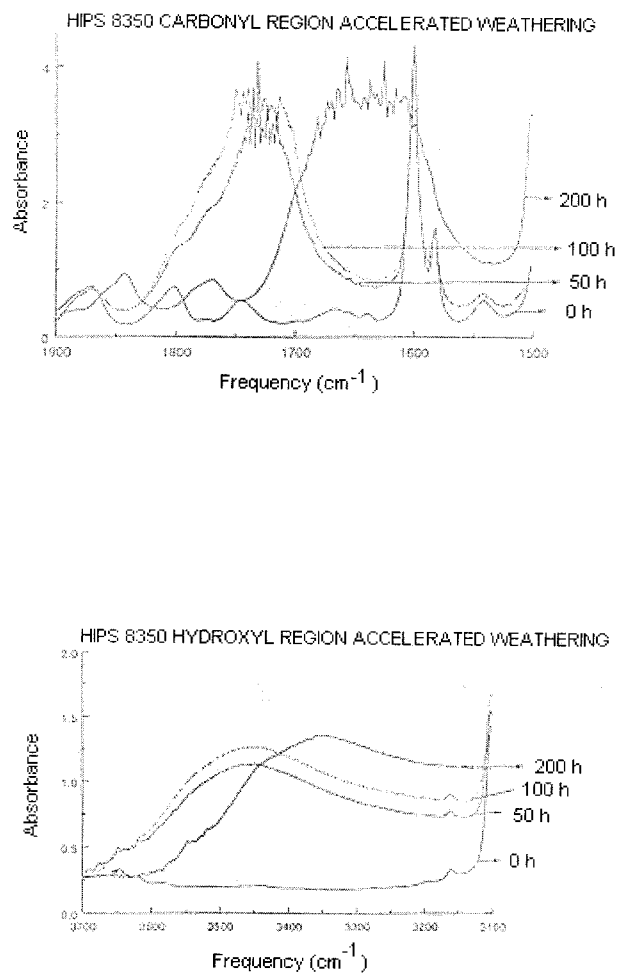
#### Comparison of Photoproducts Formation Under Natural and Accelerated Weathering Exposure

The increasing trend in carbonyl/hydroxyl absorbance is obvious in accelerated weathering also. The natural and accelerated weathering of HIPS 8350 and PS showed the carbonyl band centered at  $1725\text{ cm}^{-1}$  and hydroxyl absorptions at  $3450\text{ cm}^{-1}$ ; however, maximum growth is expected for accelerated weathering, as shown in Figure 6.

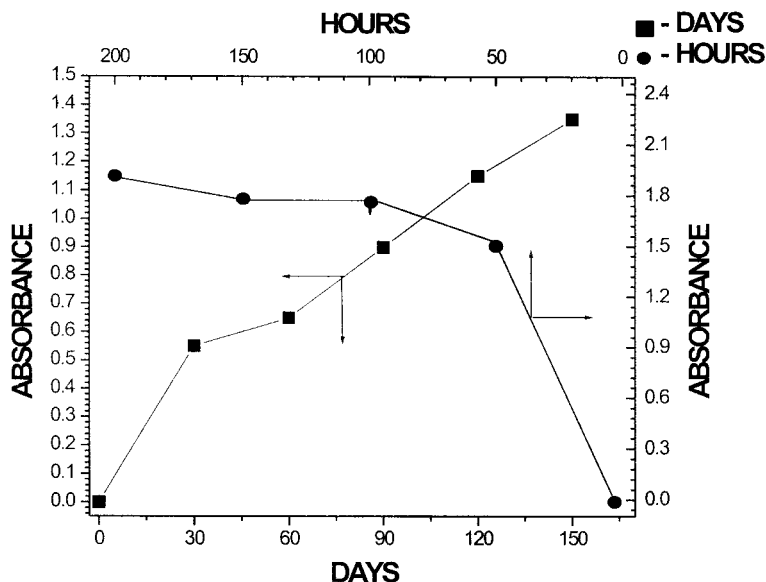
This can be attributed to the enhanced irradiations in artificial weathering. Figures 5–7 show that with the irradiation time, there is an increase in the carbonyl and hydroxyl group formation.

The structural modifications of exposed samples were noted in the SEM micrographs. The SEM micrographs of unexposed HIPS 8350 and those exposed for 6 months at Pune are presented in Figure 8. The comparison of these two micrographs indicated the breaking up of small particles on the sample surface and microcracks are apparent on the exposed films. The cracks propagated through the rubber particles. This surface behavior indicates that the degradation reactions initiate from the surface and then move into the bulk, thereby damaging the bulk properties, mainly the mechanical strength.

Almost all the changes in polymer sample detected by characterization techniques (spectro-



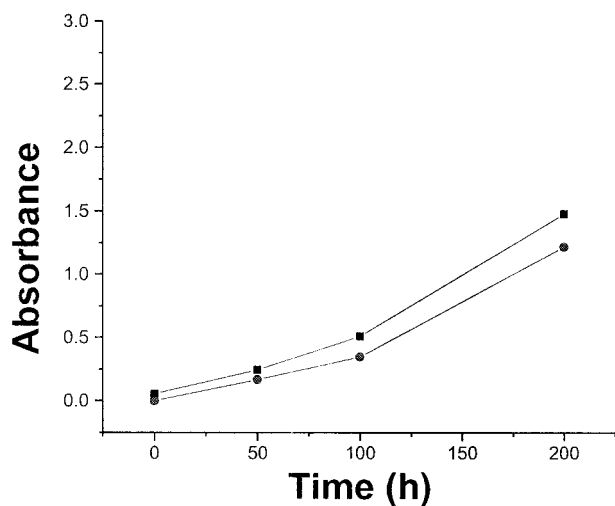
**Figure 5** FTIR spectral changes of HIPS 8350 films in the carbonyl and hydroxyl region for various time intervals exposed in accelerated condition.



**Figure 6** FTIR carbonyl group absorbance at  $1725\text{ cm}^{-1}$  under accelerated and natural exposure of HIPS 8350 films at various times (natural weathering from April to August).

scopic and micrographs) have an effect on changes in mechanical properties. Changes in tensile strength at break are presented in Figure 9 for the sample of PS, HIPS, HIPS 7240, and HIPS 8350 exposed at Pune region (April–August). The plots indicate a slight increase in tensile strength ( $\sim 5\%$  of the initial value) during the early stages of exposure ( $\sim 25$  h) and thereafter a continuous drop was observed. The increase can be attributed to the dominance of crosslinking

reactions over chain scission during the early stages.<sup>16</sup> The tensile strength of virgin sample at time zero is  $254\text{ kg cm}^{-2}$  for HIPS 8350. The deviation of 50% in tensile strength occurred after 180 days because of chain scission from April to August. The greater loss in tensile strength is exhibited for accelerated weathering because of enhanced acceleration of the irradiation. The increase in tensile strength is only in HIPS samples, which clearly indicate two-phase oxidation behavior of HIPS. The weaker bonds of polybutadiene in HIPS undergo simultaneous rupture and crosslinking but later predominate at  $\sim 25$  days exposure and thereafter only chain scission was observed on longer exposure and all polybutadiene samples were oxidized. The generated unstable functional groups (carbonyl/hydroxyl and hydroperoxides) of polybutadiene act as photoinitiators/photosensitizers for PS upon further exposure, and therefore the behavior of polystyrene oxidation is completely different from a pure polystyrene homopolymer.



**Figure 7** Rate of carbonyl (■) and hydroxyl (●) groups formation in PS films under accelerated photooxidation.

## CONCLUSION

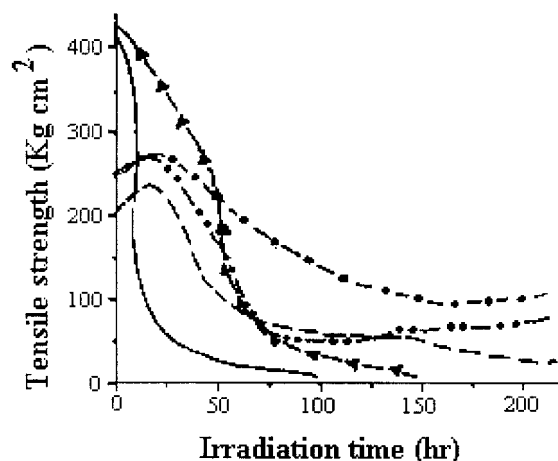
The degradation of polymers during natural and accelerated weathering is the direct consequence of changes in the structural and molecular characteristics. The deterioration of surface charac-

teristics as indicated by SEM micrographs confirms that the degradation reaction starts from the surface and then migrates to the bulk. This, in turn, affects the bulk properties of the polymer, which are primarily reflected in the mechanical strength. The artificially accelerated weathering can be considered a quick means of predicting the polymer's lifetime.

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**Figure 8** SEM micrographs of unexposed and exposed HIPS 8350 for 6 months at Pune: (a) unexposed; (b) after 90 days; and (c) after 180 days.



**Figure 9** Changes in tensile strength versus exposure time at break of PS (—▲—), HIPS (—), HIPS 7240 (—●—), and HIPS 8350 (—●●—) in accelerated weathering and April–August at Pune region in HIPS (—●—).

(a)

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(b)

(c)