Photostability of Isotactic Polypropylene Containing Monoazo Pigment

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ABSTRACT: The photodegradation of isotactic polypropylene (PP) films containing a monoazo pigment and hindered amine light stabilizers (HALS) has been undertaken. PP films were exposed to medium pressure mercury lamp radiation in the laboratory for periods of up to 8 weeks and the degree of degradation (oxidation/deterioration) was examined using FTIR spectroscopy and differential scanning calorimetry (DSC) as well as by measuring changes in the mechanical properties, contact angle, and density. The results of these measurements indicate that unstabilized PP films degraded after only 240-h irradiation. By adding an organic pigment to PP films along with antioxidant and HALS, the photostability of PP films increased to the 1500-h level. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2950–2957, 2008

Key words: photodegradation; polypropylene; organic pigment; photostabilizer; antioxidant

INTRODUCTION

With the increasing use of isotactic polypropylene (PP) in exterior applications, there is a growing need for stabilizers to protect this polymer against photodegradation.[1–6] While the introduction of hindered amine photostabilizers (HALS) has provided enhanced UV stabilization, there continues to be an interest in making further improvements.[7–9] The optimum MW for HALS changes with end use application or the polymer type. HALS with MW of 500–600 is used in thick polyolefin products. In thin products of high surface to volume ratios, such as films and fibers, HALS are required to be less volatile and more persistent in the polymer. Mixtures of low and high molecular weight HALS are known to have a synergistic effect on polymer stability.[10–12] With the latter point in mind, most colored PP products are fibers that have been made by adding pigments to the polymer matrix prior to extrusion. In the early days of PP, stabilizers did not provide sufficient stability for the polymer itself to outlast the pigment. Almost any pigment of sufficient thermal stability at melt-spinning temperatures is acceptable in terms of color stability. Because of the wide variety of end uses there is a need for pigments exhibiting different cost as well as color stability (photostability or lightstability) characteristics.[13–15]

Ideally, the pigments used should be heat stable at polymer processing conditions, photostable for extended periods, and migration resistant. Light absorbing characteristics, photochemical behavior, and the nature of the degradation products determine whether a pigment will not only be stable to UV radiation but also avoid sensitizing the degradation of the polymer host.[2,16–21] Also the purity and complexity of the surface chemistry and the behavior and particle size of the pigments are important. Those pigments with pure aromatic character and no surface activity were more likely to behave as effective triplet energy quenchers for TiO_2 pigment. For instance, anatas was a photosensitizer whereas rutile was a photostabilizer.[18,20,22]

From a previous review[23] it is known that organic pigments can have a negative effect on UV stability, including certain white, yellow, orange and red pigments that exhibit sensitizing properties in the presence of UV radiation. While others (e.g., phthalocyanine pigments) have a favorable effect and prevent harmful UV radiation from reaching the deeper layers of a plastic substrate. In addition, pigments can have synergistic or antagonistic effects when combined with other additives. They can also increase a sample's surface temperature via strong absorption across the full spectrum of solar radiation.[10,14,16]

Allen and coworkers[2,14] used IR spectroscopy to examine the effects of three pigments (copper phtha-

locyanine, chromium green, and cadmium yellow), a primary antioxidant, and a hindered amine on the photostabilization of PP. They concluded that pigments alone offered little photostability. A combination of pigments and an antioxidant provided modest improvement over pigment alone. However, a combination of pigment and HALS gave a significant improvement in PP photostability. Interestingly, the addition of antioxidant to HALS/pigment combinations reduced PP photostability considerably below the level obtained using cadmium yellow and chrome green but enhanced photostability when copper phthalocyanine was used. The latter results are consistent with outcomes from another study involving copper phthalocyanine and HALS.[24]

The photodegradation of PP containing $CaCO_3$ or talc and either carbon black or TiO_2 has been examined,[19] by determining the depth of degradation in the polymer substrate. The goal of this study was to compare the protective effects of carbon black or TiO_2 and to determine the influence of filler concentration on PP. The results showed that the limiting depth of the upper, completely degraded layer significantly depended on the concentration of additives—including fillers. The efficiency of carbon black pigment was higher than TiO_2. HALS alone offered only a limited UV protection effect in the filled PP.

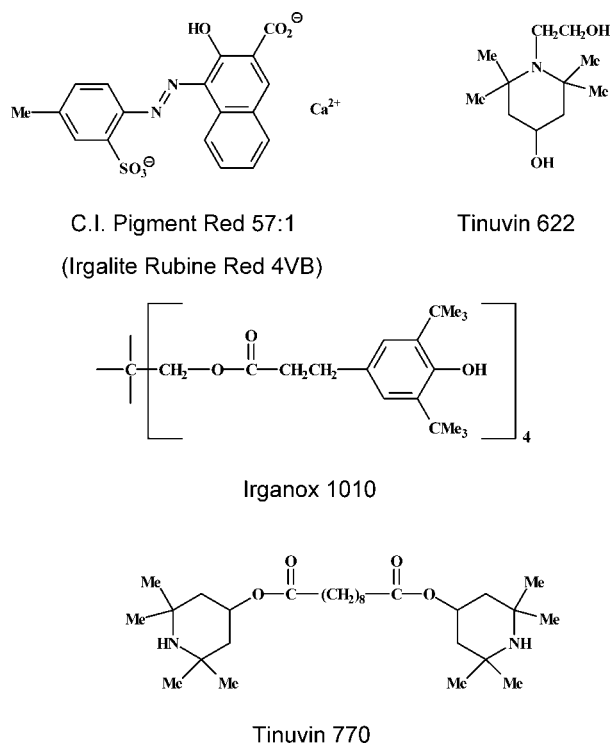Photodegradation depth profiles in 3-mm thick PP films containing HALS or TiO_2 pigment and HALS
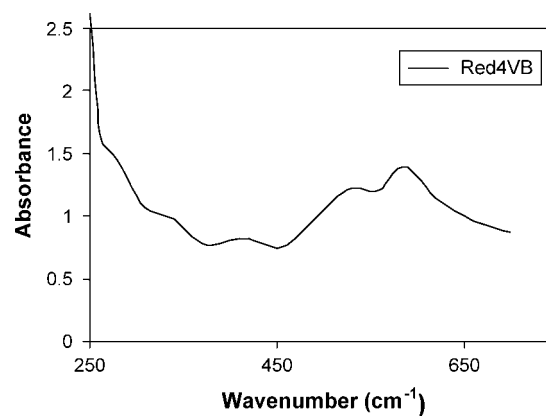

Figure 2 UV absorption spectrum of C.I. Pigment Red 57 : 1.

+ TiO_2 were compared with those obtained from the corresponding unstabilized films. In films stabilized by HALS, PP degradation was essentially uniform throughout the film cross section. At the surface, the level of degradation in the stabilized films was much lower than in unstabilized films. This was attributed to diffusion controlled oxidation. The presence of TiO_2 confined degradation to a thin region close to the exposed surface.[14,15]

A variety of analytical methods have been used to assess the physical and chemical changes of films and fibers following UV exposures. Methods used involve tensile strength, gravimetry, nuclear magnetic resonance (NMR), thermal analysis, infrared (IR) spectroscopy, staining, and iodometry. Among these methods, IR spectroscopy is used most often to determine the nature of the chemical changes. In the IR analysis of irradiated PP, generally, the regions involving hydro-peroxide (POOH) and carbonyl (C=O) groups have been considered.[25]

Although the contribution of HALS to the phtostabilization of pigmented PP substrates has been considered in a number of laboratories, it is not clear that the effects of additive (pigment, HALS) concentration on PP photodegradation have been examined. Simi-
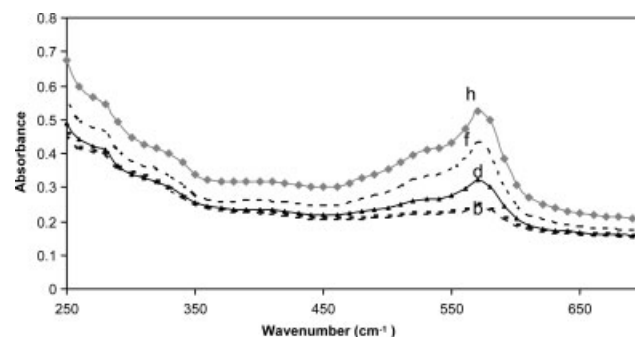

Figure 1 Chemical structures of additives used in this study.

Figure 3 UV absorption spectra of pigmented PP film samples b, d, f, and h.

TABLE I
Description of Film Samples used in this Study

Additive	Pigment Irgalite Rubine 4VB (%)	Tinuvin 622 (%)	Tinuvin 770 (%)
Sample			
a	0.025	0.05	0.05
b	0.025	0.1	0.1
c	0.05	0.05	0.05
d	0.05	0.1	0.1
e	0.075	0.05	0.1
f	0.075	0.1	0.05
g	0.1	0.05	0.1
h	0.1	0.1	0.05
i	–	0.1	0.1
j	–	–	–

All samples contain 35 g PP powder and 0.035 g Irganox 1010 antioxidant.

larly, the effects of additives on the mechanism and level of PP degradation merit further study. In the present study, the effects of organic pigment concentration on the photostability of isotactic PP in the presence and absence of HALS have been examined. The light source was a medium pressure mercury lamp having maximum intensity near the λ_{max} of the monoazo red organic pigment employed. The chemical structures of additives used in this study are shown in the Figure 1 and UV spectra of this pigment and pigmented PP films are shown in Figures 2 and 3.

EXPERIMENTAL

Materials and sample preparation

Isotactic polypropylene additive-free powder was obtained from Arak Petrochemical Company, Iran and was the commercial product polypropylene V30S. C.I. Pigment Red 57:1 (Irgalite Rubine 4VB) and hindered amine light stabilizers (HALS) Tinuvin 622, Tinuvin 77 and Irganox 1010 (an antioxidant) were obtained
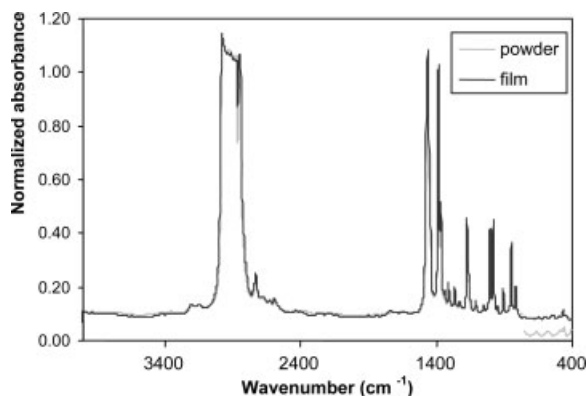
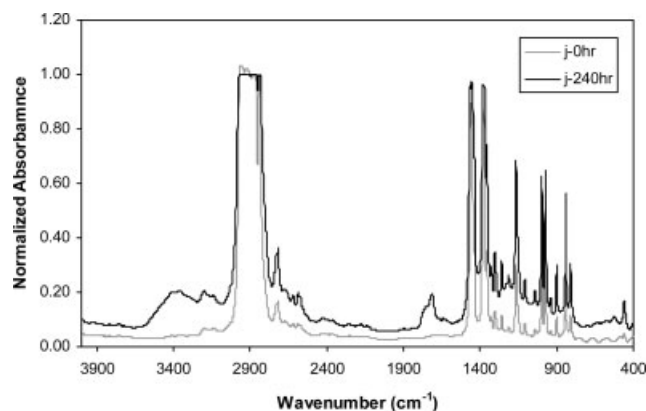**Figure 4** FTIR spectra of PP powder and corresponding film.

Figure 5 FTIR spectra of PP films irradiated for 0 and 240 h.

from Ciba Geigy Company. Films containing different stabilizers and azo pigment were prepared by extruding the corresponding powder blends at 210°C. The resultant polymer was converted to 150-μm thick films by hot pressing at 150°C and 150 bar pressure. The films were also cut into dumbbell-shaped samples for measuring changes in mechanical properties.

Photodegradation

Film samples were exposed to a mercury electric discharge lamp in an open-air covered chamber at 42°C ± 5°C and relative humidity of 35. The lamp was obtained from Crompton and Perkinson (England) and film samples were irradiated for periods of up to 8 weeks.

FTIR measurements

A Nicolet Nexus FTIR spectrophotometer was used to record spectra between 400 and 4000 cm^{-1} in a transmission mode. The nominal resolution of the spectrometer was 4 cm^{-1}, and the band at 2837 cm^{-1} was taken as the reference, for normalization of FTIR spec-
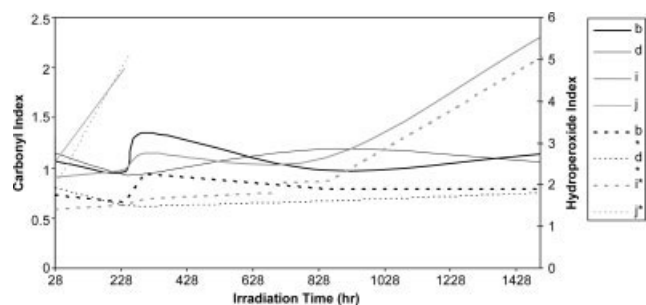
Figure 6 C=O index (left) and OOH index (right*) values obtained from FTIR spectra following irradiation of PP film samples b, d, i, and j.
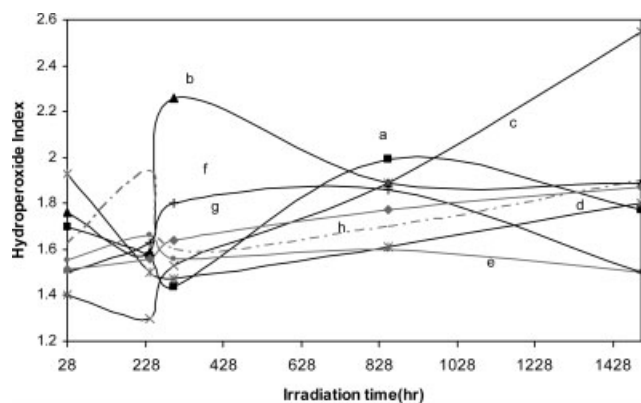
Figure 7 OOH index values from FTIR spectra following irradiation of PP film samples a–h.

Figure 9 OOH absorbance values from FTIR spectra following irradiation of PP film samples a–c.

tra. The carbonyl index (C=O) of film samples was taken as the ratio of areas of the absorption bands at 1850–1654cm^{-1} and 2750–2696 cm^{-1}. The hydroperoxide (—OOH) index of film samples was the ratio of the areas of the absorption bands at 3250–3600 cm^{-1} and 2750–2696 cm^{-1}. The ratio of the absorption band at 998 cm^{-1} to the band at 974 cm^{-1} was taken as the percentage of helical content or crystallinity index. This ratio has been related to the percentage of isotactic polymer and to the crystalline fraction following adjustment.[21,25–27]

Density measurements

Film densities were measured according to ASTM Method D105-68[28] using a density gradient column filled with a mixture of ethanol and distilled water at 25°C. At least five separate measurements were made on each film.

Mechanical properties

An Instron tensile tester with 50-mm gauge lengths and the jaw speeds of 15 mm/min was employed to evaluate the mechanical properties of film samples.
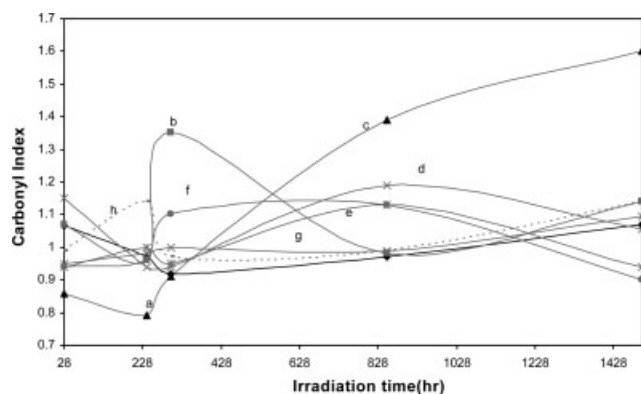
At least five samples were examined for each irradiation level and measurements were made according to ASTM Method D 882.[28]

Contact angle measurements

Contact angles for water on the surface of film samples were measured according to the ASTM method D 724-99.[28] Measurements were taken at multiple (5) spots on each film. Photographs of water drops on PP films were taken using a Karl Zeiss optical microscope.

Thermal properties

A Perkin–Elmer differential scanning colorimeter (Model DSC7), calibrated with indium, was used to study the thermal behavior of PP films. PP samples (3–5 mg) were encapsulated in aluminum pans, heated from −50 to 190°C at the rate of 10°C/min, and then cooled to room temperature. After measuring ΔH and T_m, the degree of crystallinity was calculated using the following equation, where ΔH_c is the fusion enthalpy of completely crystalline PP, and its value (210 J/g) was taken from the literature:[29]
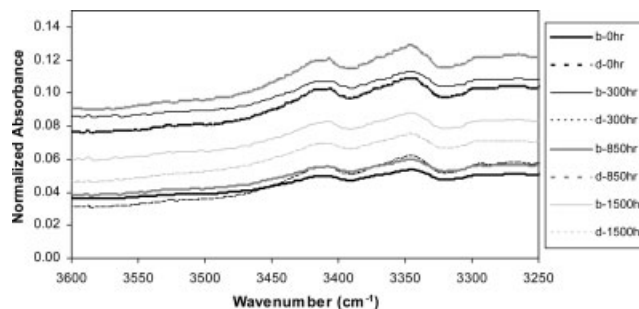
$$X = \frac{\Delta H}{\Delta H_c} 100\%$$

Figure 8 C=O index values from FTIR spectra following irradiation of PP film samples a–h.

Figure 10 OOH absorbance values from FTIR spectra following irradiation of PP film samples b and d.

Figure 11 OOH absorbance values from FTIR spectra following irradiation of PP film samples e and g.
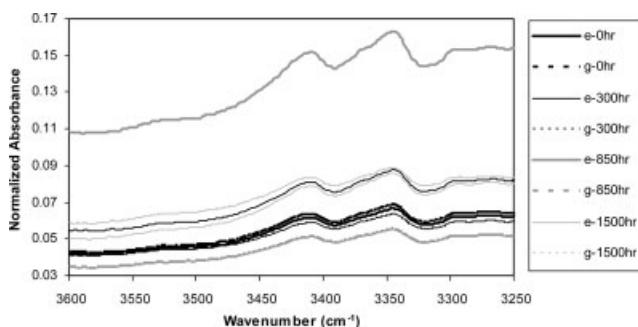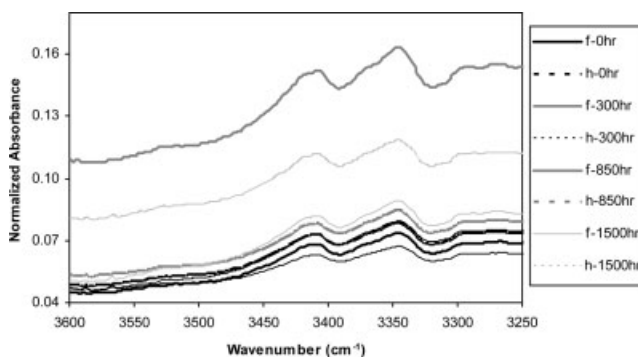

Figure 13 OOH absorbance values from FTIR spectra following irradiation of PP film samples a and c.

RESULTS AND DISCUSSION

Descriptions of film samples used in the experiments are given in Table I. In the samples used for experiments, one of them contained antioxidant alone (**j**) one contained photostabilizer and antioxidant (**i**) and the other eight film samples (**a–h**) contained a constant antioxidant level, two levels of photostabilizer, and four levels of pigment. Films **i** and **j** are control samples used to help assess the effects of pigment. To irradiate film samples, a medium pressure mercury lamp was chosen in preference to a low pressure lamp because of its widespread use in studies of this type and because its spectral output is closer to that of sunlight.[22]

FTIR analysis

To determine whether any chemical degradation occurred during polypropylene film formation, the FTIR spectrum of the PP powder was compared with that of the corresponding film (Fig. 4). The absence of spectral differences indicated that hot pressing (film formation) did not cause any polymer degradation. Figure 5 shows the FTIR spectrum of unpigmented and unstabilized PP film (sample **j**) after irradiation. Spectral changes occurred in the regions that are characteristic of carbonyl (1850–1650 cm^{-1})

and hydroperoxide (3250–3600 cm^{-1}) groups. These peaks are quite broad because they are the results of absorptions from multiple degradation products.[25] Figure 6 shows carbonyl and hydro peroxide index values for unpigmented and pigmented films before and after exposures up to 240 h. Sample **j** which did not contain any photostabilizer experienced degradation after just 240-h irradiation. Many conventional antioxidants such as the hindered phenols will reduce oxidation during the production stages but are ineffective as photostabilizers apparently because they themselves tend to undergo degradation. This problem was circumvented by adding HALS (sample **i**). The C=O and OOH levels in sample j were comparable to those in samples **i, b** and **d** following a 1500-h exposure.

Figures 6–8 show that as photodegradation took place in pigmented polypropylene films, oxidation (C=O, OOH) levels increased with increased exposure time and films containing more pigment had low oxidation levels (Figs. 7 and 8). The C=O and POOH builds-up are indicated by the carbonyl and POOH indices, respectively. As shown in Figures 9–16, changes in the amounts of pigment and additive correlated with POOH and C=O indexes. Unlike results from a previous study, it was found that the rate of hydroperoxide formation is higher than that for carbonyl compound formation in pigmented and unpigmented samples.
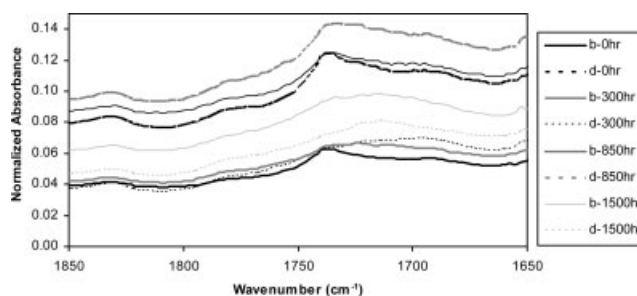

Figure 12 OOH absorbance values from FTIR spectra following irradiation of PP film samples f and h.

Figure 14 C=O absorbance values from FTIR spectra following irradiation of PP film samples b and d.
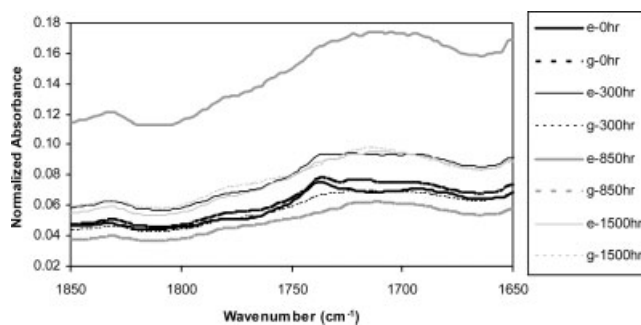
Figure 15 C=O absorbance values from FTIR spectra following irradiation of PP film samples e and g.

It was also found that incorporation of hydroxybenzophenone UV absorber into PP film containing HALS or antioxidant enhanced photostability. Hydroxyl groups in the α-position of the UV absorber undergo intramolecular proton transfer as a mechanism for dissipating the energy of absorbed or transferred (from excited polymer) UV light.[9,13]

Oxidation kinetics in thick films can be described as a three step process: the induction/auto-acceleration of POOH levels at the beginning, an intermediate slower POOH content increase, and finally a much slower POOH increase. It is believed that this behavior is related to the progression of oxidation from the film's surface to its interior.[28] In the hydroperoxide index chart there are maximum and minimum points in the amount of the hydroperoxide versus time. It is believed that oxidation moves to the virgin zones close to those already degraded. Therefore, the peroxyl radicals readily promote oxidation in a virgin aliphatic environment, where adjacent hydrogen atoms either within or adjacent to a given polymer chain are abstracted to generate POOH groups. The low rate of degradation can be a consequence of a "cage effect" arising from crosslink formation, which makes it difficult for photodegradation products to move away and radicals produced by scission at the side groups may tend to recombine.[30]
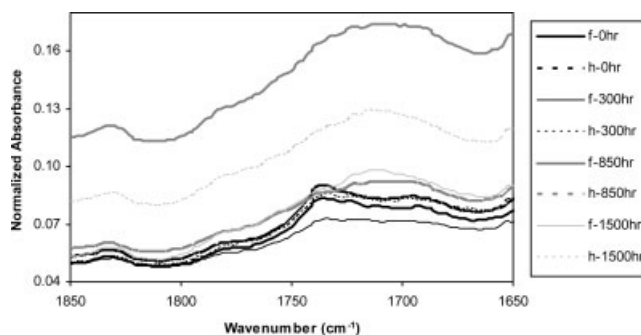

Figure 16 C=O absorbance values from FTIR spectra following irradiation of PP film samples f and h.
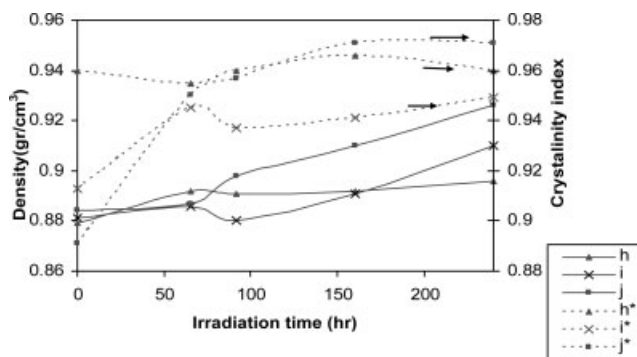

Figure 17 Density and crystallinity index (helical content) values obtained from gradient column and FTIR measurements on PP films h–j. * = helical content.

Density and 998/974 cm^{-1} FTIR absorption ratio

Figures 17–19 show the changes of helical content (crystallinity index; 998/974cm^{-1} ratio) during photodegradation and the density of PP films measured using a gradient column. The observed density values of irradiated films indicated an increase in film order during degradation period. These results are different from previous studies in which the densities of PP films were found to increase with irradiation time.[25,31]

Degree of crystallinity

UV exposure caused an increase in PP crystallinity during the irradiation period. Increased crystallinity can be attributed to chain rearrangements arising from chain scission in the amorphous region. The degradation is limited to the amorphous region and leaves the crystalline region, with higher density, intact.[31] Comparison of results in Figure 20 for film samples **a** and **h** shows that increasing the amount of pigment led to lower PP crystallinity, which suggests that pigment does not have nucleating effects.

Mechanical properties

Elongation at break of PP films irradiated for different times was measured. Results from pigmented
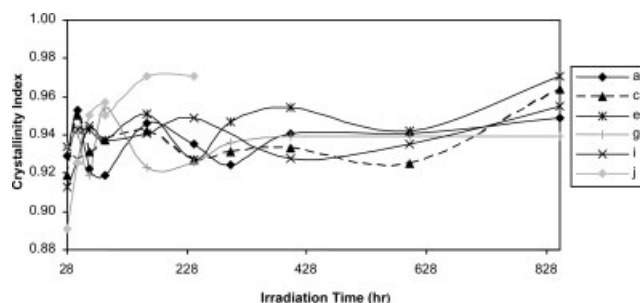

Figure 18 Crystallinity index (helical content) values obtained from FTIR measurements on PP films with (a, c, e, g) and without (i and j) pigment.
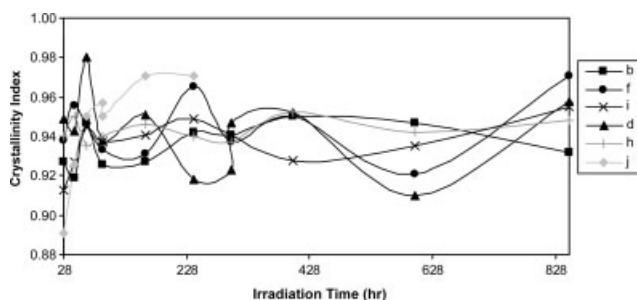
Figure 19 Crystallinity index (helical content) values obtained from FTIR measurements on PP films with (b, d, f, h) and without (i and j) pigment.
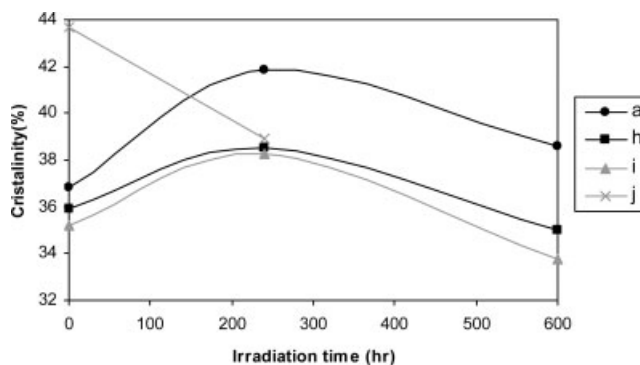

Figure 20 Degree of crystallinity values obtained from DSC measurements on PP films with (a–h) and without (i, j) pigment.

and unpigmented samples are shown in Figures 21 and 22. Film **j**, which is free of photostabilizer and pigment, degraded fastest and was brittle after only 160-h irradiation. Results in Figure 21 show a decrease in elongation at break after up to ~200-h exposures for most film samples, and after the 200-h exposure level there was an increase in elongation at break, followed by a decrease in elongation at break at significantly longer exposure times. The partial recovery in mechanical properties of PP at the intermediate exposure levels was attributed to the formation of a very fragile degraded layer that became partially detached. This type of behavior was observed
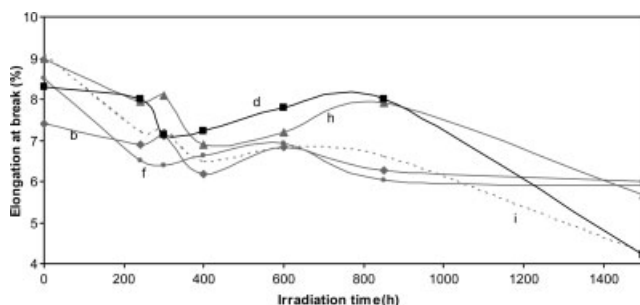

Figure 21 Elongation at break (%) values for PP films irradiated in the presence and absence of pigment and HALS.
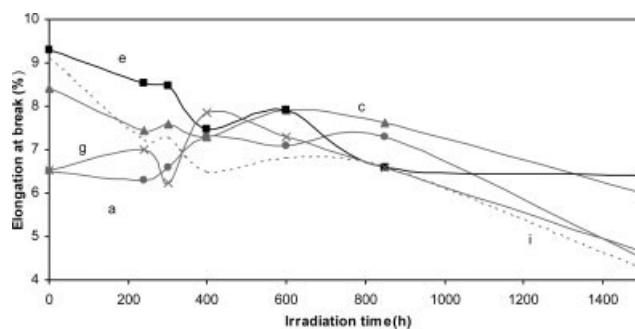
Figure 22 Elongation at break (%) values for PP films irradiated in the presence and absence of pigment and HALS.

by others following PP photodegradation.[31] The cracks formed on the surface of pigmented polypropylene during photodegradation may be able to propagate during subsequent tensile testing.[31] Allen and coworkers[14] reported similar changes in the mechanical properties of PP films.

Contact angle results

When a polymeric substrate is exposure to UV light in the presence of atmospheric gases, new functional groups may be produced on its surface. The resultant groups change the surface energy of the substrate, which is reflected in changes in the contact angles of liquids applied to the surface. Figure 23 shows the typical changes in contact angle of water with increasing exposure time for the unpigmented film. In Figure 24, it can be seen that the water drop expanded on the surface of film **h** after a 1500-h exposure, giving a lower contact angle than before exposure.

CONCLUSIONS

FTIR was used to show that the level of oxidation in unstabilized and unpigmented PP is greater than the levels in pigmented and HALS stabilized
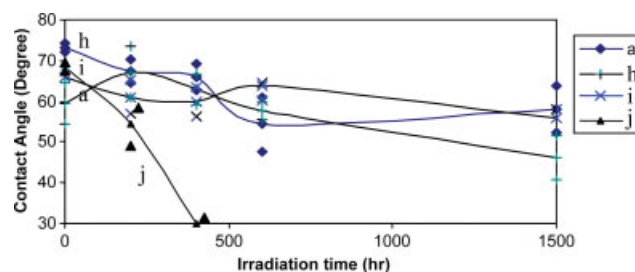

Figure 23 Contact angles for water on PP films irradiated in the presence and absence of pigment. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
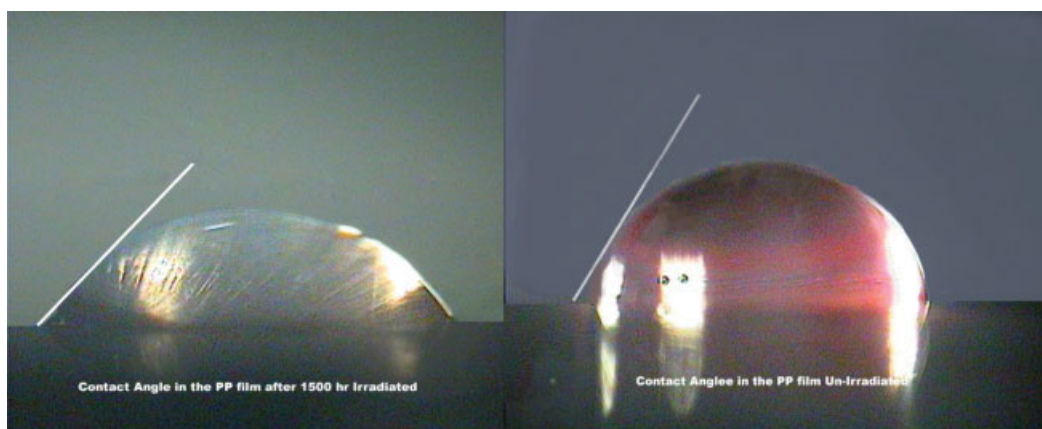
Figure 24 Water drop on the PP film h before (right) and after (left) a 1500-h light exposure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PP. In the presence of a monoazo red pigment, the photostabilizing effect of HALS is enhanced and it seems that the presence of pigment improves photostability. It was also found that increasing pigment levels affords better photostability than a UV absorber.

References

1. Ahmed, M. Polypropylene Fibers Science and Technology; Elsevier: New York, 1982.
2. Allen, N. S.; Edge, M. Fundamentals of Polymer Degradation and Stabilization; Elsevier Applied Science: London, 1992.
3. Kelen, T. Polymer Degradation; Van Nostrand Reinhold: New York, 1983.
4. Hamid, S. H.; Handbook of Polymer Degradation, Revised and Expanded, 2nd ed.; King Fahad Institute of Petroleum and Minerals: Dhahran Saudi Arabia, 2000.
5. Henman, T. J. World Index of Polyolefin Stabilizers; Imperial Chem Industries: England, PLC, 1982.
6. Lundberg, W. O. Auto-Oxidation and Antioxidants; Interscience: New York, 1961.
7. Allen, N. S. Degradation and Stabilization of Polyolefines; Applied Science: New York, 1983.
8. Gugumus, F. Polym Degrad Stabil 1993, 39, 117.
9. Kikkawa, K. Polym Degrad Stabil 1995, 74, 135.
10. Gugumus, F. Polym Degrad Stabil 1999, 66, 133.
11. Gugumus, F. Polym Degrad Stabil 2002, 75, 295.
12. Gugumus, F. Polym Degrad Stabil 2000, 67, 299.
13. Miraftab, J.; Horrocks, E. Polym Degrad Stabil 1994, 44, 351.
14. Allen, N. S.; Edge, M.; Corrales, T.; Catalina, F. Polym Degrad Stabil 1998, 61, 139.
15. Wiles, D. M. In Degradation and Stabilization of Polymers; Geuskens, G., Ed.; Applied Science: London, UK, 1975; p 137.
16. Turton, T. J.; White, J. R. Polym Degrad Stabil 2001, 74, 559.
17. Allen, N. S.; Chirions-Pardon, A.; Appleyard, J. H. Polym Degrad Stabil 1984, 9, 15.
18. Allen, N. S.; Parkinson, A. Polym Degrad Stabil 1983, 5, 189.
19. Rysavy, D.; Tkadleckova, H. Polym Degrad Stabil 1992, 37, 19.
20. Vaillant, D.; Lacoste, J.; Lemaire, J. J Appl Polym Sci 1997, 65, 609.
21. Stengrevics, E. Influence of Pigment on the Light Stability of Polypropylene; Ciba-Geigy Corp: Brookfield Center, 1986.
22. McNeill, C. I.; Zulfigar, S. Polym Degrad Stabil 1985, 10, 147.
23. Klemchuk, P. P. Polym Photochem 1983, 31, 1.
24. Lubs, H. A. The Chemistry of Synthetic Dyes and Pigments; Krieger: New York, 1972; p 583.
25. Aslanzade, S. Polym Degrad Stabil 2005, 90, 461.
26. Blais, P.; Carlsson, D. J.; Wiles, D. M. J Polym Sci Part A-1: Polym Chem 1972, 10, 1077.
27. Rjeb, A.; Tajounte, L.; Chafik El Dorissi, M.; Letarte, S.; Adnot, A.; Roy, D.; Claire, Y. J Appl Polym Sci 2000, 77, 1742.
28. Cstejon, M. L.; Tiemblo, P.; Gomez-Elvira, J. M. Polym Degrad Stabil 2000, 70, 357.
29. Annual Book of ASTM Standards, USA, Textiles, 2004.
30. Davidson, R. S.; Meek, R. R. Eur Polym J 1981, 17, 163.
31. Rabello, M. S.; White, J. R. J Appl Polym Sci 1997, 64, 2505.