

Investigation of the Photodegradation Behaviors of an Ethylene/Vinyl Acetate Copolymer Solar Cell Encapsulant and Effects of Antioxidants on the Photostability of the Material

S. Isarankura Na Ayutthaya, J. Wootthikanokkhan

Division of Materials Technology, School of Energy Environment and Materials, King Mongkut's University of Technology, Thonburi, Bangkok 10140, Thailand

Received 8 March 2007; accepted 16 September 2007

DOI 10.1002/app.27428

Published online 7 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This study concerns the photodegradation and stabilization of a solar cell encapsulating material made from ethylene/vinyl acetate copolymer (EVA). EVA was compounded with various additives in a twin-screw extruder. After that, the extruded film was cured in a hydraulic compression mold before being exposed to ultraviolet (UV) radiation at an ambient temperature for 800 h. The thermal stability of the material was also studied through the aging of the sample at 90°C for 2000 h. The tensile strength of the unstabilized EVA decreased only slightly after the thermal aging. On the other hand, the strength of the material decreased noticeably after the UV irradiation. Fourier transform infrared spectra of various EVA films revealed that there was no deacetylation occur-

ring after the UV irradiation. However, results from the swelling test and swollen-state NMR suggested that the polymer degraded via a chain-scission mechanism. After compounding with some antioxidants, most of the EVA films scarcely degraded after the UV irradiation, with the exception of the EVA compounded with a combination of the aromatic phosphate compound (0.1 phr) and hindered amine light stabilizer (0.1 phr). The results are discussed in light of an antagonism effect that occurred because of the aforementioned combination. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3853–3863, 2008

Key words: antioxidants; elastomers; stabilization; swelling

INTRODUCTION

An encapsulant, also known as an encapsulating material, is considered to be one of the most important components in the fabrication of a solar cell module (Fig. 1). The main function of the encapsulating material is to serve as an adhesive or sealant, protecting the silicon solar cell from moisture. In addition, this material helps to provide and maintain physical isolation of the solar cells and circuit components from exposure to hazardous or degrading environmental factors such as reactive elements, soiling of covers, hail, salty spray, and birds.¹

Table I shows the specifications of materials to be used as solar encapsulants. The specifications are rather general, especially for some properties such as ultraviolet (UV) resistance and thermal resistance. For some more specific details, information concern-

ing the testing methods, conditions, and tested values being regularly used in industry for quality control of commercial ethylene/vinyl acetate copolymer (EVA) solar encapsulants² (Table II) should also be considered and used as a reference. For example, the photostability of the material is determined from the retention of mechanical strength after UV irradiation for 800 h, whereas the thermal stability of the material is determined from the retention of mechanical strength after thermal aging in the air at 90°C for 2000 h.

Because of these demanding requirements, only a few polymers are suitable for this purpose. These include silicone, poly(butyl acrylate), polyurethane, and EVA. The silicone polymer may possibly satisfy the technical requirements, but the price of the material is considerable. Poly(butyl acrylate) is inherently resistant to severe weathering conditions. However, fabrication of a solar cell module with this polymer is usually carried out by the use of the raw material in the form of a butyl acrylate syrup followed by *in situ* polymerization of the monomer on the glass substrate.^{3,4} In this respect, the pungent odor and toxicity of the butyl acrylate monomer are considered to be drawbacks of the material. A two-part aliphatic polyurethane system has also been developed

Correspondence to: J. Wootthikanokkhan (jatuphorn.woo@kmutt.ac.th).

Contract grant sponsor: National Science and Technology Center of Thailand; contract grant number: CO-B-22-1H-20-4701.

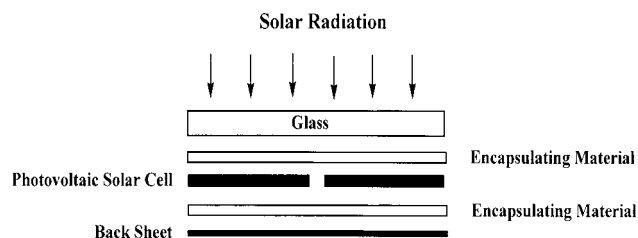


Figure 1 Solar cell module.

for this application. However, poor interfacial bonding strength between the polymer and glass substrate and the limited pot life of the two-part urethane prepolymers are considered to be drawbacks of the material.

An EVA film, on the other hand, can be produced from an extrusion process before lamination with the silicon solar cell and the glass superstrate in a vacuum bag⁵ typically at a temperature of less than 170°C. Other advantages of EVA include the inherently transparent and hydrophobic properties of the material; this means that the light transmittance and water absorbance of the EVA film could meet the specifications. Besides this, the gel content and tensile modulus of EVA can also be controlled by adjustment of the compounding formulation. More importantly, the cost of the EVA raw material is relatively cheap and commercially viable.

By contrast, the use of an encapsulating material made from EVA still has some limitations; that is, the polymer tends to be degraded after being exposed to a high temperature and/or UV radiation for a certain time. According to the relevant literature,¹ it has been reported that the EVA encapsulating material starts to degrade after an exposure period of 4–10 years, depending on the geographical location and climate. Degradation of the EVA solar encapsulating material is a serious issue and deserves consideration because the degradation is usually accompanied by some changes in the color of the polymer film, from colorless (transparent) to yellow and/or brown. As a result of the aforementioned EVA browning effect, performance and/or power conversion efficiency of the solar cell declines. Consequently, the service life of the solar cell module, which is normally targeted for 10–20 years, might be shorter than expected. Generally, degradation of EVA after exposure to heat and/or UV radiation involves many chemical reaction mechanisms, including Norrish type I and Norrish type II. The latter type is basically a deacetylation mechanism in which the acetate side groups are eliminated from the poly(vinyl acetate) repeating units in the EVA molecules. This reaction results in the formation of polyene molecules and acetic acid byproduct (Fig. 2). In this respect, the conjugated double bonds in the

polyene molecules are considered to be the chromophore, which is attributable to the EVA browning effect.⁶

In addition, the EVA browning effect might be attributed to other factors, including the presence of some new UV-excitable chromophores produced from the reaction between residuals of some curing agents and the α , β -unsaturated carbonyl groups inherently existing in the EVA molecules.⁷ Furthermore, the interactions between some compounding additives and the curing agent might generate chromophores, resulting in a discoloring effect. For example, Klemchuk et al.⁸ investigated the discoloration of an EVA-based encapsulating material and found that the discoloration is due to interactions between a peroxide curing agent and some stabilizing additives (e.g., UV absorbers or phosphate compounds). Another important factor affecting the net EVA discoloration is the photobleaching reaction in the presence of air (oxygen). For example, Pern⁷ reported that EVA browning of the Carrisa Plains photo voltaic modules usually appears in the central regions of the solar cells, typically with a 3–10-nm clear band around the cell perimeter. No discoloration was observed in EVA between adjacent solar cells. It was believed that the clarity at the edges resulted from the diffusion of oxygen from between adjoining cells and from the spaces between the modules and the Tedlar backing foil. This means that photoinduced discoloration reactions are competing with the photobleaching (photooxidation reaction).

TABLE I
Specifications and Requirements for Solar Cell Encapsulating Materials

Characteristic	Specification or requirement
Total hemispherical light transmission through 20 mL thick film integrated over the wavelength range of 400–1100 nm	> 90% of incident
Hydrolysis	None at 80°C, 100% relative humidity
Water absorption	< 0.5 wt % at 20°C, 100% relative humidity
Resistance to thermal oxidation	Stable up to 85°C
Mechanical creep	None at 90°C
Tensile modulus	< 20.7 MPa at 25°C
Fabrication temperature	No greater than 170°C
Fabrication pressure	No greater than 1 atm
UV absorption degradation	None at wavelength > 350 nm
Hazing or clouding	None at 80°C, 100% relative humidity
Odor, human hazard (toxicity)	None

TABLE II
Properties of a Commercial EVA Encapsulating Material

Property/characteristic	Testing method	Unit	Measured value	
			Standard cure type	Fast cure type
Vinyl acetate content	MDP method	%	28 or 33	33
Melt flow rate	JIS-K6730	g/10 min	15 or 30	30
Melting point (before crosslinking)	DSC	°C	61	61
Glass-transition temperature	HIS method	°C	-30	-30
Light transmittance	UV method	%	91	91
Tensile strength at break (after crosslinking)		MPa	25 or 22	18
Elongation at break (after crosslinking)		%	500 or 600	500
Tensile modulus (after crosslinking)		MPa	6	6
Water absorption	JIS K-7209	%	0.1	0.1
Crosslinking rate (150°C, 20 min)	HIS method	Gel %	85 or 80	90
Light resistance (800 h of UV irradiation)	JIS K-7113	% retention of strength	80 or above	80 or above
Heat resistance (90°C, 2000 h)	JIS K-7113	% retention of strength	85 or above	85 or above
Low-temperature resistance (-40°C, 2000 h)	JIS K-7113	% retention of strength	90 or above	90 or above

MDP, Mitsui-DuPont method; HIS, hi-sheet method.

Apart from the deacetylation, the polyethylene repeating units in the EVA copolymer molecules might also be degraded via other mechanisms, including chain scission or crosslinking. Consequently, the EVA formulation for use as an encapsulating material in solar cells is usually compounded with various additives, including a hindered amine light stabilizer (HALS; also known as a primary antioxidant), a peroxide decomposer (also known as a secondary antioxidant), and a peroxide curing agent. The use of a combination of the primary and secondary antioxidants is usually recommended because a synergistic effect can be expected. For example, a U.S. patent⁷ describes the composition of an EVA encapsulating material containing both kinds of antioxidants, which minimize the discoloration effect. In commercial applications, EVA-based encapsulating materials are available in two types, that is, the standard cure type (A9918) and the fast cure type (15295), and the stabilities of the two types of encapsulating materials are slightly different. A study by Pern⁹ found that standard-cure-type EVA discolors earlier and faster than fast-cure-type EVA.

It was believed that the type and content of the peroxide decomposer being used for compounding with EVA would have a significant effect on the photostability of the material. It was also believed that if a compounding formulation for the EVA solar encapsulant could be optimized, an encapsulating material with better stability and a longer service life might be expected. In this respect, the photodegradation behavior of the EVA solar encapsulant and effects of the type and content of the peroxide decomposer on the stability of the material deserve consideration. However, studies on the stability of EVA compounded with various kinds of peroxide decomposers are seldom reported in the open literature.¹⁰

Therefore, in this work, we first study the degradation behavior of EVA under UV irradiation. Sec-

ond, we investigate the effects of the type and content of the peroxide decomposer on the photostability of the EVA encapsulant. Two types of secondary antioxidants are considered herein, that is, the phosphate compound 2,4-bis(1,1-dimethylethyl)phosphate (Irgafos 168) and the sulfur compound dioctadecyl 3,3'-thiopropionate (Irganox 802). Changes in the mechanical properties of various EVA compounded films after aging have been determined, and the results are discussed in light of some changes in the chemical structures and swelling behaviors of the cured EVA encapsulating material.

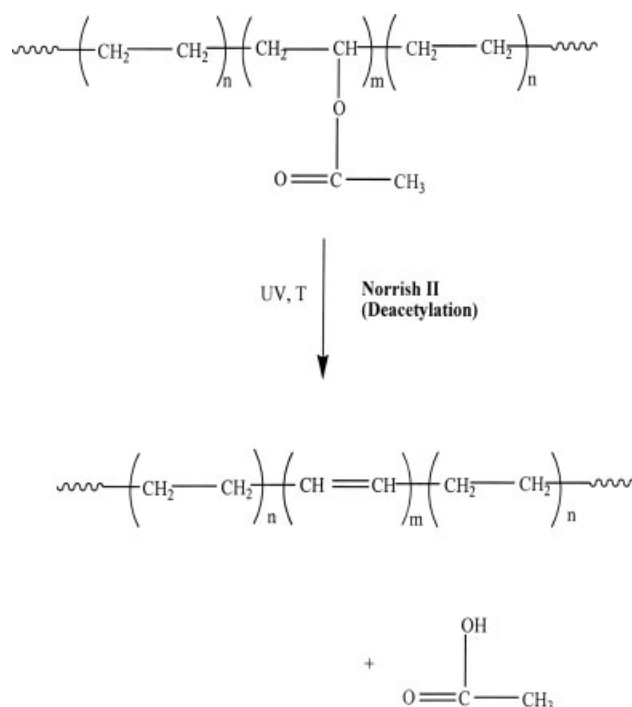


Figure 2 Degradation mechanisms of EVA via deacetylation.

TABLE III
Typical Recipe for Compounding EVA

Chemical	Trade name	Amount (phr)
EVA	Evaflex 150	100
2,5-Bis(<i>tert</i> -butyldioxy)-2,5-dimethylhexane	Luperox 101	1.5
Bis(2,2,6,6-tetramethyl-4-piperidiny)sebacate	Tinuvin 770	0.1
Tris(2,4-di- <i>tert</i> -butylphenyl)phosphate and dioctadecyl 3,3'-thiopropionate	Irgafos 168 and Irganox 802FD	0.1, 0.2

EXPERIMENTAL

Materials

EVA (Evaflex 150, containing 33 wt % vinyl acetate) was purchased from Mitsu-Dupont Co., Ltd. (Tokyo, Japan). Bis(2,2,6,6-tetramethyl-4-piperidiny) sebacate (Tinuvin 770), used as a primary antioxidant, and 2,4-bis(1,1-dimethylethyl)phosphite (I) and dioctadecyl 3,3'-thiopropionate (Irganox 802 FD), used as secondary antioxidants, were obtained from Ciba Specialty Co., Ltd. (Basel, Switzerland). The peroxide curing agent used in this study was a standard curing type, 2,5-bis(*tert*-butyldioxy)-2,5-dimethylhexane (Luperox 101), which was supplied by Arkema Co., Ltd. (Philadelphia, PA). All chemicals were used as received.

EVA compounding

EVA was compounded through the mixing of the polymer pellets with various additives with a compounding recipe in accordance with Table III. The compounding was carried out in a Haake PolyLab (Karlsruhe, Germany) CTW100 twin-screw extruder equipped with a sheet die 0.5 mm thick. The screw rotating speed was 60 rpm, and the temperature profiles from the feed zone to the melting zone, the metering zone, and the die zone in the extruder were 105, 115, 125, and 135°C, respectively. The extrudate film was cooled and collected by passage through a take-off unit containing a chill roll and a winding roll. These rolls were rotated at speeds of 14 and 20 rpm, respectively.

Curing of the EVA film

The extruded EVA film was fabricated with a hydraulic compression mold (LabTech Engineering Co., Ltd., Bangkok, Thailand) at 160°C for a given time. Before the compression molding, an oscillating disk rheometer (Gotech, Taipei, Taiwan) was used to determine the time to reach 90% of the maximum torque by the rheometer (t_{90}) at 160°C. This was further used as the optimum cure time to vulcanize the EVA films. The use of an optimum cure time (t_{90}) for the lamination is important because if EVA had been undercured, the gel content (%) and creep resistance of the EVA encapsulant would have been

lower than the specifications. On the other hand, if the polymer had been overcured beyond t_{90} , the polymer might have degraded during the lamination.

UV stability test

Resistance to the degradation of EVA by UV radiation was determined with an accelerated weathering test machine equipped with fluorescent UV lamps of wavelengths between 280 and 330 nm. The UV light of this wavelength range is the most efficient portion of terrestrial sunlight that is damaging to plastics.¹¹ Experimentally, the test specimens were mounted in specimen racks with the test surface facing the lamp (see Fig. 3) and then exposed to a UV lamp for 800 h under air atmospheric conditions. During the test, the measured temperature of the film surface and the relative humidity were 50°C and 43%, respectively. Of special note is the fact that the exposure time and atmosphere used herein were based on conditions being regularly used in industry for quality control of commercial EVA encapsulants (Table II). Even though these testing conditions are not exactly identical to the service conditions of the solar cell module in a real application, the data obtained

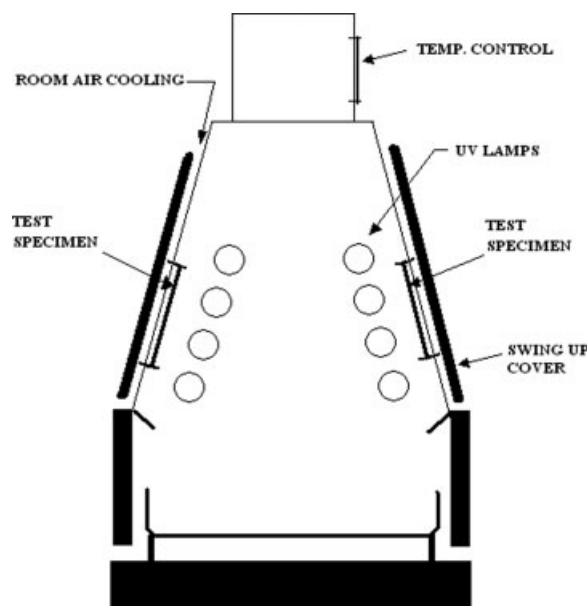


Figure 3 Schematic diagram of the UV-irradiation device.

from this test may be used as a guideline relating to the relative stability of various EVA films.

Thermal aging test

For the purpose of comparison, the thermal stability of the material deserves consideration. The cured EVA films were aged in a hot-air oven at 90°C for 2000 h. Again, the selected testing conditions were based on those being regularly used in industry for quality control of commercial EVA encapsulants (Table II).

Tensile strength test

After the UV aging and/or thermal aging was conducted for a given time, the samples were removed and cut into dumbbell-shaped specimens in accordance with the JIS K7113 (type 2) standard method. Finally, the stability of EVA, expressed in terms of the retention of the tensile strength after aging, was calculated by the comparison of the tensile strength value of the aged film with that of the EVA film before treatment (the aging).

Fourier transform infrared (FTIR) spectroscopy

Changes in the chemical structures of various EVA films were followed with a Bruker (Ettlinger, Germany) model Equinox-55 FTIR spectrophotometer. FTIR was scanned over wave numbers ranging from 600 to 4000 cm^{-1} . The spectrum was recorded with an attenuated total reflectance FTIR technique.

Swelling behavior

Changes in the crosslink density of various cured EVA films were investigated through the monitoring of the weight fraction of the polymer in an equilibrium swollen gel. The EVA specimen was first cut and immersed in xylene for 5 days at room temperature. After that, the weight of the swollen gel (W_{gel}) was measured. Finally, the EVA swollen gel was dried to a constant weight (W_d). The value of the weight fraction of EVA in the swollen gel was determined with the following equation:

$$\text{Weight fraction (\%)} = (W_d/W_{\text{gel}}) \times 100 \quad (1)$$

Swollen-state $^1\text{H-NMR}$

Besides the aforementioned swelling test, a swollen-state $^1\text{H-NMR}$ technique was also used to obtain some information related to the crosslink density of the polymer. The concept of this technique is based on the assumption that the lower the mobility is of

the polymer chains, the broader the NMR peak width is.¹² In the experiment, a sample for the swollen-state NMR was carefully prepared by random sampling and cutting of the material from different areas throughout the cured EVA film. In addition, the sampling mass was controlled at 50 mg. This was to ensure that the only factor contributing to any change in the NMR peak width was the cross-link density change. After that, the sample was immersed in xylene for 5 days in the dark at 25°C to allow the sample to swell to an equilibrium state. A swollen-state $^1\text{H-NMR}$ analysis was conducted with an Advance DPX-400 instrument (Rheinstetten, Germany). The width of a particular peak [H (%)] was given as the signal strength at a reference point on the side of the peak (b) expressed as a percentage of the peak signal strength (a), as illustrated in eq. (2). The offset of the reference line (b) was 0.02 ppm:

$$H(\%) = (b/a) \times 100 \quad (2)$$

RESULTS AND DISCUSSION

After EVA was exposed to UV radiation, it was found that the tensile strength of the EVA film compounded without the use of any antioxidant declined remarkably (Fig. 4). However, by the addition of 0.1 phr of the primary antioxidant (Tinuvin 770), the tensile strength of the material decreased only slightly after the UV irradiation. This indicates that the EVA film became more stable against photo-degradation. More interestingly, by the addition of 0.1 phr of the secondary antioxidant, the tensile

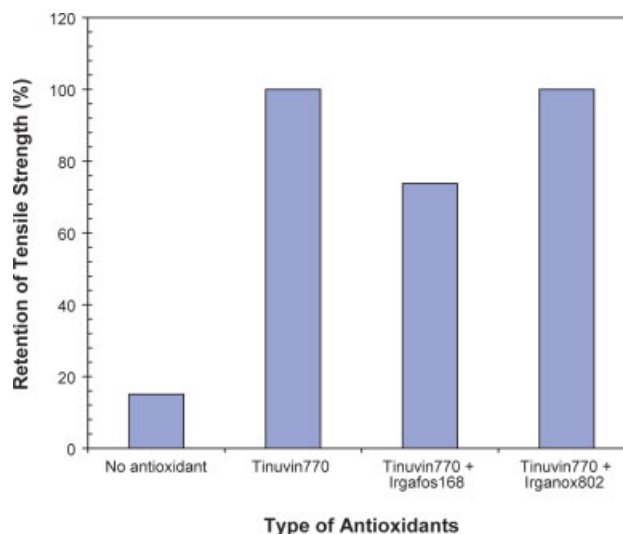


Figure 4 Retention of the tensile strength (after exposure to UV radiation) of various EVA films compounded with or without Tinuvin 770 (0.1 phr) and the secondary antioxidant (0.1 phr). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

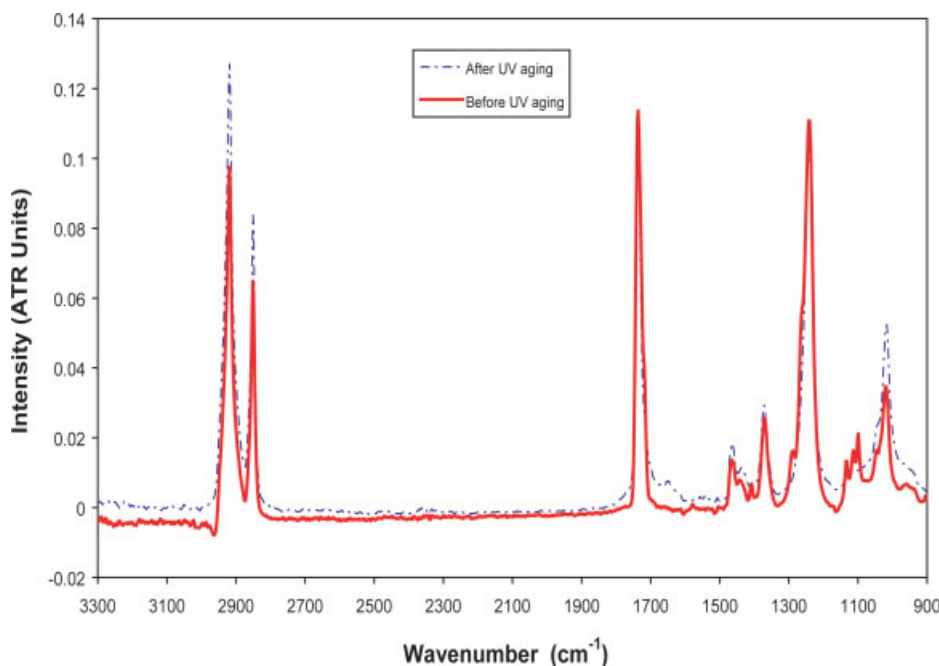


Figure 5 FTIR spectra of EVA films compounded without antioxidants before and after UV irradiation (ATR = attenuated total reflectance). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

strength either decreased or remained unchanged after UV aging, depending on the type of secondary antioxidant. In this respect, the use of 0.1 phr Irganox 802 is preferable because the tensile strength of EVA did not change significantly after it was exposed to UV radiation. On the other hand, the use of 0.1 phr Irgafos 168 led to a decrease in the tensile strength of the EVA film of about 25% after the UV irradiation.

Photodegradation behaviors of unstabilized EVA

To explain the aforementioned effects, some changes in the chemical structure of various EVA films after the UV irradiation should be considered. Figure 5 shows FTIR spectra of the EVA films that were prepared without the use of any antioxidants. Several infrared absorption peaks representing the characteristic chemical bonds in the EVA molecules can be seen, including the peaks at 2852 (C—H stretching), 1736 (C=O of ester), 1241 (C—O—C of ester ether), 1099 (C—O), and 1370 cm^{-1} (C—H). After the UV irradiation, some significant changes were noted. The peak at 1100 cm^{-1} , corresponding to C—O bonds, disappeared after the UV irradiation. Additionally, the ratio of the 1736 cm^{-1} /2852 cm^{-1} absorbance peaks decreased after the UV irradiation. Generally, this ratio could be used to provide a relative measure of the vinyl acetate content; that is, the lower the ratio is, the more deacetylation there is.¹³ In this respect, it seems that some acetate side groups in the EVA molecules were eliminated after

the UV irradiation. However, the FTIR spectrum of the EVA compounded with antioxidants (Fig. 6) shows that the aforementioned changes could be observed, even though the polymer was not exposed to UV radiation. In other words, it seems that the aforementioned FTIR spectral changes might not be a direct consequence of the Norrish type II mechanism only. More importantly, the FTIR spectrum in Figure 5 shows that the peak at a wave number of about 1600 cm^{-1} , related to carbon double bonds (C=C) in diene and polyene molecules, did not occur. These results suggest that the deacetylation of the UV-aged EVA films in this study was very small or seldom occurred.

In this respect, it is believed that the aforementioned changes in the tensile strength of EVA after UV irradiation (Fig. 4) could be attributed to some other degradation mechanisms, including the chain-scission mechanism and/or crosslinking mechanism. In general, polyolefins can be degraded via either chain-scission or crosslinking mechanisms, depending on the chemical structure of the polymers. For example, polypropylene is degraded via a chain-scission mechanism, whereas high-density polyethylene is predominantly degraded via the crosslinking mechanism.¹⁴ In relation to this study, the weight fractions of various EVAs in a swollen gel needed to be investigated to obtain data related to the changes in the crosslink density of the material after UV irradiation. By carrying out a swelling test on various EVA films in xylene, we found that the weight fraction in a swollen gel of unstabilized EVA decreased

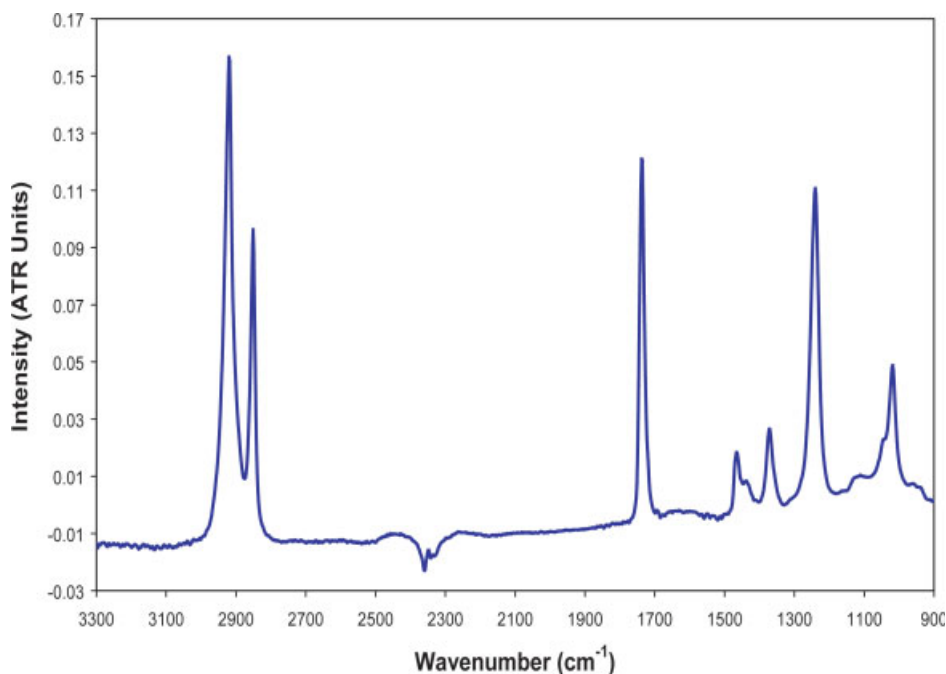


Figure 6 FTIR spectrum of an EVA film compounded with Tinuvin 770 (0.1 phr), Irgafos 168 (0.2 phr), and Luperox 101 (ATR = attenuated total reflectance). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

by 63% after UV irradiation (Table IV). This result implies that the network density of the crosslinked EVA decreased after curing. The result is in good agreement with the modulus values of the unstabilized EVA film, which decreased by 61% after UV irradiation.

In addition to the aforementioned swelling test, some changes in the molecular mobility of EVA were followed with the swollen-state $^1\text{H-NMR}$ technique. Figure 7 shows typical $^1\text{H-NMR}$ spectra of EVA before UV irradiation. The peak at 2.08 ppm represents a signal of the protons from the $-(\text{C}=\text{O})\text{CH}_3$ group. In addition, the peak at 4.90 ppm is attributed to the signal from the protons in the $>\text{CH}-$ group of the EVA molecule. After EVA was exposed to UV radiation, no major spectral change was observed, with the exception that the NMR peak width decreased significantly. By further

enlargement of the spectra (Fig. 8), it was possible to calculate the width of the peak, which is expressed in terms of the H (%) value. It was found that the H (%) value of the peak at 2.08 ppm decreased from 63 to 38% after EVA was irradiated. This result suggests that the mobility of the cured EVA molecules increased and/or the network density of the crosslinked polymer decreased after the UV irradiation.

TABLE IV
Effects of the Antioxidants on Changes in the Weight Fraction of the Polymer in a Swollen Gel and Changes in the 100% Modulus Values of Various EVA Films After UV Irradiation

Antioxidant	Change in the weight fraction (%)	Change in the modulus (%)
No antioxidant	-63	60.6
Tinuvin 770	0	0
Tinuvin 770 + Irgafos 168	0	0
Tinuvin 770 + Irganox 802FD	0	0

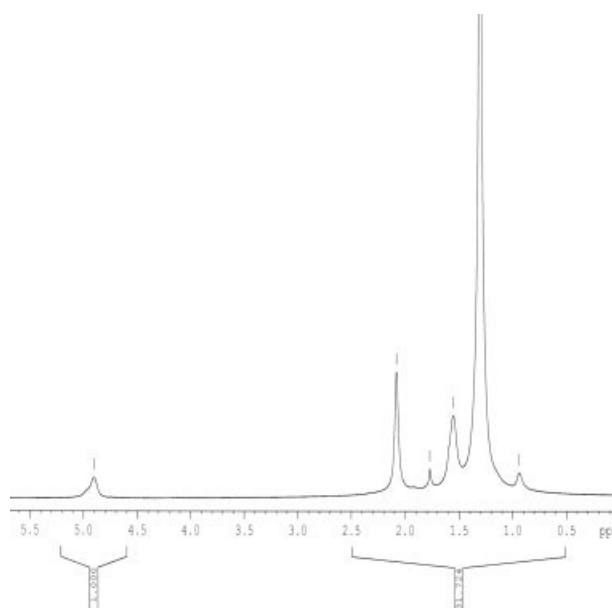


Figure 7 Typical $^1\text{H-NMR}$ spectrum of EVA before UV irradiation.

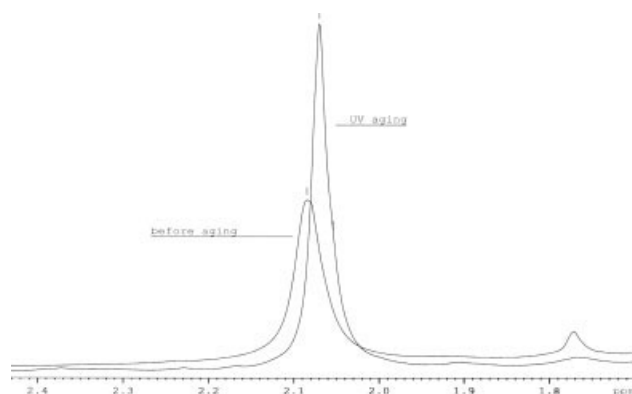


Figure 8 Overlaid $^1\text{H-NMR}$ spectra of EVA samples before and after UV irradiation.

All of the aforementioned results from the swelling test, the NMR spectra, and the tensile modulus suggest that, after the UV irradiation, the cured EVA molecules degraded via chain scission. Notably, the degradation mechanism of EVA is similar to that of polypropylene. In this study, it was proposed that the chain-scission degradation of EVA might occur via the formation of free radicals on the tertiary carbon in the EVA molecules (Fig. 9).

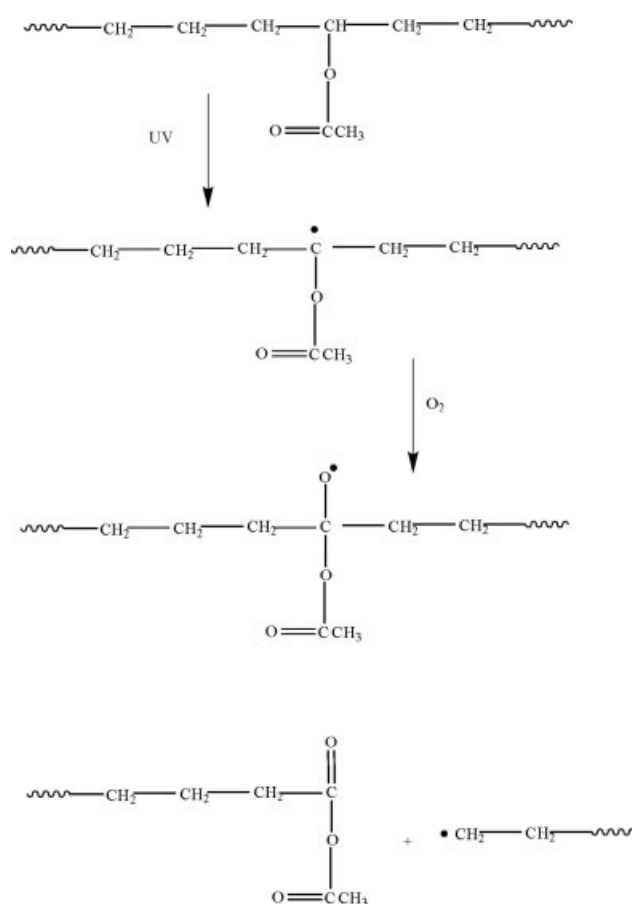


Figure 9 Proposed mechanism for UV degradation of EVA.

This tertiary carbon radical is rather stable because of a steric effect and an inductive effect provided by the acetate side groups. Consequently, this reaction pathway is thermodynamically favorable. Subsequently, monomolecular breakdown of the macroradical occurs, resulting in a shorter polymeric chain and primary radical species. Crosslinking is unlikely in this case because of the low reactivity of the tertiary carbon macroradical and a steric effect provided by the bulky acetate groups.

Effect of antioxidants on the photodegradation behavior of EVA

When the EVA film was compounded with some antioxidants, the weight fraction of EVA in a swollen gel of the material did not decrease after UV irradiation. It seems that the EVA films became more stable and degraded minimally after the compounding. However, it should be remembered that, for the EVA that was compounded with 0.1 phr Irgafos 168, the tensile strength of the material decreased after UV irradiation (Fig. 4). In this respect, it might be possible that some changes in the chemical structure (e.g., the chain scission) of the EVA compound might not be sufficiently large to cause the obvious changes in the swelling behavior or tensile modulus of the material. However, by the use of a swollen-state NMR technique that is more sensitive to changes in molecular mobility, it was found that the width of the NMR peak [H (%)] at 2.06 ppm decreased after the UV irradiation (Fig. 10). This result implies that the polymer experienced some small chain scission.

From all of the aforementioned results, it can be seen that the type of secondary antioxidant has a significant effect on the UV stability of EVA. Specifically, the use of 0.1 phr Irgafos 168 led to a decrease in the tensile strength of the EVA film of about 25% after the UV irradiation. This was not the case for the EVA encapsulant that was compounded with

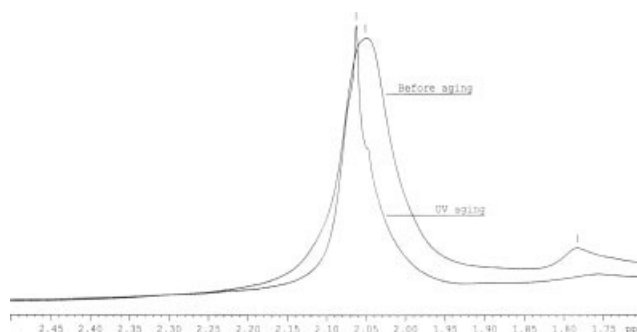
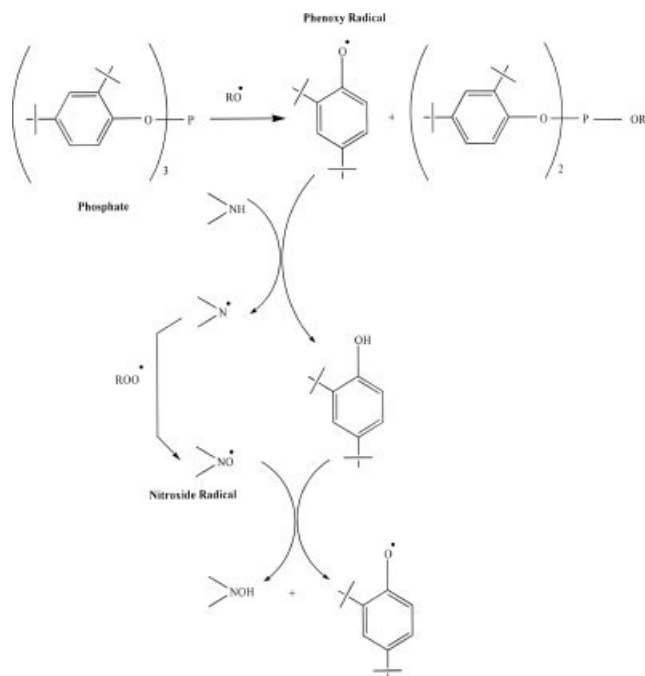


Figure 10 Overlaid $^1\text{H-NMR}$ spectra of an EVA film before and after UV irradiation (EVA was compounded with 0.1 phr Irgafos 168).



Scheme 1 Proposed mechanism for the antagonistic effect resulting from interactions between the phosphite compound and HALS.

Irganox 802, where the tensile strength of the material did not significantly change after the photoaging. In this respect, the aforementioned effect might be attributed to an antagonism effect caused by an interaction between the aromatic phosphite (Irgafos 168) and the hindered amine stabilizer (Tinuvin 770) during the photoaging. This type of antagonistic effect was also observed by Bauer et al.¹⁵ in their study on the photooxidative stability of polypropylene. According to the mechanism proposed by Bauer et al. (Scheme 1), the phenoxyl radical (produced from the phosphate) and its further products might interact with the nitroxyl radical (produced from the parent HALS compounds), lowering the concentration of the nitroxyl radical, which is a light stabilizer. Consequently, the overall photostabilization effect of the HALS is lower, leading to the antagonism. In relation to this study, the aforementioned effect might be explained in a similar fashion.

It is noteworthy that, when the amount of the secondary antioxidant (I) used was increased from 0.1 to 0.2 phr, the tensile strength of EVA did not decrease after UV irradiation (Fig. 11). It seems that the aforementioned antagonistic effect disappeared. Again, a similar effect was observed by Bauer et al.¹⁵ in their study on the photostability of polypropylene. In that case, it was explained that when the amount of the aromatic phosphate (I) increased, the phenoxyl radicals might have experienced some other side reactions that did not necessarily involve the HALS or its derivative nitroxyl radical. For example, the phenoxy

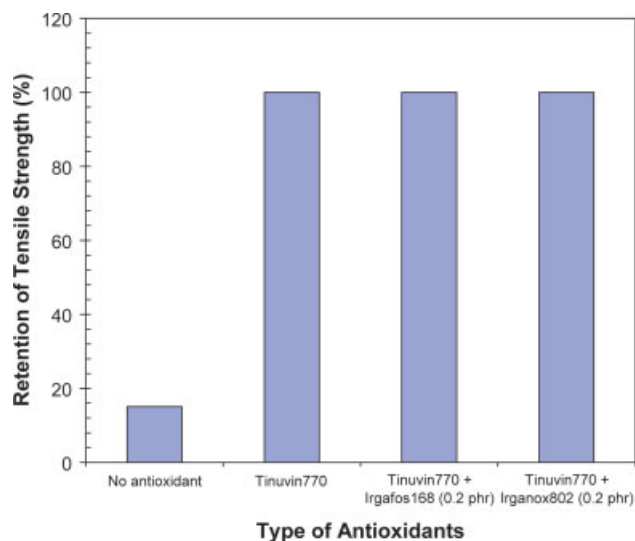
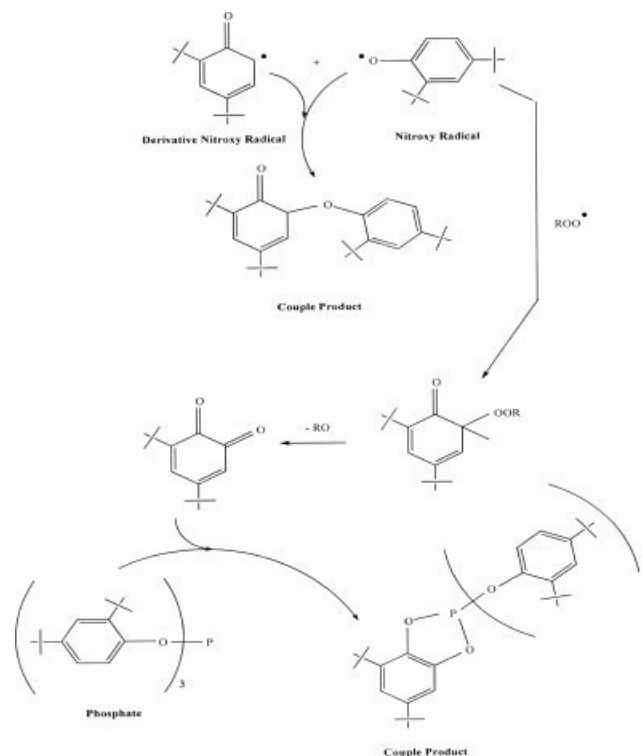


Figure 11 Retention of the tensile strength (after exposure to UV radiation) of various EVA films compounded with or without Tinuvin 770 (0.1 phr) and the secondary antioxidant (0.2 phr). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

radical can undergo a C—C coupling reaction with the phenoxy resonance to form the coupled product (Scheme 2). Furthermore, the *ortho*-quinone formed from the reaction between the phenoxy radical and peroxy radical might react with a phosphate molecule, giving rise to another kind of coupled product.



Scheme 2 Proposed mechanism for the interactions between the phosphite compound and HALS.

The aforementioned reactions do not lead to a depletion of the nitroxy radical produced from the HALS. Consequently, the level of the antagonism decreased, and thus the tensile strength of the EVA film hardly decreased after UV irradiation.

It is worth mentioning that the aforementioned antagonism was not the case for the EVA compounded with Irganox 802 as a secondary antioxidant. This is because Irganox 802 is a kind of sulfur compound and thus no phenoxy radical was generated from the decomposition of the chemical. Therefore, no antagonistic effect was observed for the EVA compounded with Irganox 802 in this study.

Thermal stability of EVA

Finally, it is worth considering thermal stabilities under an air atmosphere of the EVA encapsulating material. Figure 12 shows the retention of the tensile strength of various EVA films after thermal aging at 90°C for 2000 h under an air atmosphere. The tensile strength of the unstabilized EVA film decreased slightly (ca. 7.5%) after the thermal aging process. This change is very small compared to the 85% change in the same material after UV exposure (Fig. 4). Through the compounding of EVA with some antioxidants, the tensile properties of the materials decreased only slightly after the thermal aging, regardless of the type of antioxidant used. Similarly, the elongation values of the unstabilized EVA increased only a little (ca. 7.5%) after the thermal aging, whereas those of the EVA compounded with various antioxidants did not change (Fig. 13).

The aforementioned results indicate that, in this study, thermal oxidative aging was less damaging to

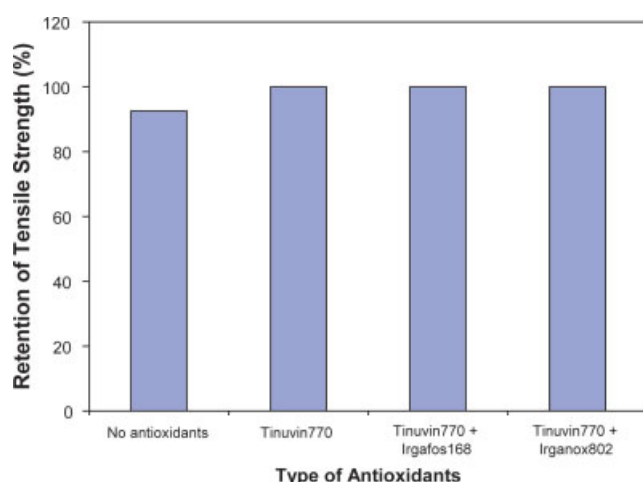


Figure 12 Retention of the tensile strength (after thermal aging) of various EVA films compounded with or without Tinuvin 770 (0.1 phr) and the secondary antioxidant (0.1 phr). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

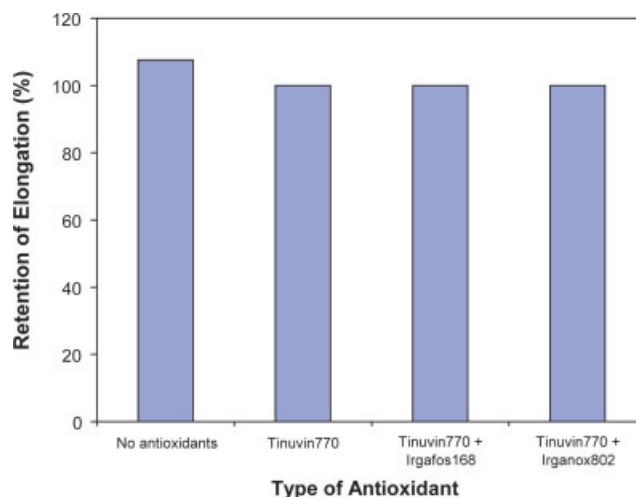


Figure 13 Retention of the elongation (after thermal aging) of various EVA films compounded with or without Tinuvin 770 (0.1 phr) and the secondary antioxidant (0.1 phr). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the EVA encapsulating material than UV exposure. It seems that the aforementioned degradation of EVA after UV irradiation (Fig. 4) was mainly caused by UV light, given the fact that the aging time and the actual temperature that the sample experienced during the UV-irradiation test were much lower than those during the thermal aging process. This finding is also consistent with the work of Pern,⁷ who reported that the damage caused by thermal stress is secondary to the UV-induced damage. It seems that the energy from the UV light is strong enough to induce some dissociation of covalent bonds in the EVA molecules, resulting in the formation of free-radical species. Subsequently, chain scission of the EVA macroradicals occurred and subsequently led to the degradation of the polymer.

CONCLUSIONS

From the aforementioned results, the following can be concluded:

1. In this study, the EVA-based encapsulating material predominately degraded under UV irradiation via the chain-scission mechanism.
2. The type and amount of the secondary antioxidants investigated in this study had a significant effect on the photostability of the EVA film. When the phosphate compound Irgafos 168 was used as a secondary antioxidant at a concentration of 0.1 phr, the tensile strength of EVA decreased after the UV irradiation. This was not the case for the EVA compounded with the thiopropionate (Irganox 802). The effect was explained in light of an antagonism between

the aromatic phosphate (Irgafos 168) and the HALS compound (Tinuvin 770).

3. When the amount of Irgafos 168 was increased from 0.1 to 0.2 phr, the antagonistic effect disappeared. This was probably due to some changes in the reaction pathways of Irgafos 168 after the amount of the antioxidant was increased.

Special thanks go to Arkema Pte., Ltd., and Global Connection, Ltd., for providing some chemicals to support this research work.

References

1. Czanderna, A. W.; Pern, F. J. *Sol Energy Mater Sol Cells* 1996, 43, 101.
2. Solar EVA Technical Information; Hi-Sheet Industries: Tokyo, 2004.
3. Gupta, A.; Ingham, J. D.; Yavrouian, A. H. (to California Institute of Technology). U.S. Pat. 4,383,129 (1983).
4. Gupta, A.; Ingham, J. D.; Yavrouian, A. H. (to California Institute of Technology). U.S. Pat. 4,374,955 (1983).
5. Pern, F. J.; Czanderna, A. W. *Sol Energy Mater Sol Cells* 1992, 3, 25.
6. Allen, N. S.; Edge, M.; Rodriguez, M.; Liauw, C. M.; Fontan, E. *Polym Degrad Stab* 2001, 71, 1.
7. Pern, F. J. (to Midwest Research Institute). U.S. Pat. 6,093,757 (2000).
8. Klemchuk, P.; Ezrin, M.; Lavigne, G.; Holley, W.; Galica, J.; Agro, S. *Polym Degrad Stab* 1997, 55, 347.
9. Pern, F. J. *Angew Makromol Chem* 1997, 252, 195.
10. Allen, N. S.; Edge, M.; Rodriguez, M.; Liauw, C. M.; Fontan, E. *Polym Degrad Stab* 2000, 68, 363.
11. Shah, V. In *Handbook of Plastics Testing Technology*, Shah, V., Ed.; Wiley: New York, 1984; Chapter 5.
12. Tinker, A. J. In *Blends of Natural Rubber*; Tinker, A. J.; Jones, K. P., Eds.; Chapman & Hall: London, 1998.
13. Vazquez, M. R.; Liauw, C. M.; Allen, N. S.; Edge, M.; Fontan, E. *Polym Degrad Stab* 2006, 91, 154.
14. Santos, A. S. F.; Agnelli, J. A. M.; Trevisan, D. W.; Manrich, S. *Polym Degrad Stab* 2002, 77, 441.
15. Bauer, I.; Habicher, W. D.; Koner, S.; Al-Malaika, S. *Polym Degrad Stab* 1997, 55, 217.