

# Synergistic Interaction of Treatment and Blending on the Stability of High-Density Polyethylene

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**ABSTRACT:** Degradation of high-density polyethylene (HDPE) films blended with 0.5, 1.0, and 2.0% metal ions (MIs; chromium = 36%, silicon = 8%, aluminum = 4%, and chlorine = 2%) and 5, 10, and 20% potato starch were studied under two different abiotic treatment conditions (they were either heated to 70°C or exposed to UV at 300–400 nm) for a period of 100 days. The addition of metals did not affect the mechanical strength of the polymer, whereas starch blending did. The latter turned the polymer yellow. HDPE with MIs exhibited higher levels of oxidation than the other samples. UV treatment affected the mechanical strength of the MI-blended HDPE more than the other additive or the thermal treatment. The formation of extractable oxygenated

compounds and unoxidized low-molecular-weight hydrocarbons increased with increasing concentration of additives in HDPE. The surface energy in all cases increased; this indicated that the polymers turned hydrophilic. The maximum weight loss (28%) was seen in the 2% MI-blended HDPE exposed to UV followed by the 20% starch-blended polymer exposed to heat (24%). These results indicate a synergy between blending and the treatment strategy; this also suggests an optimal waste-disposal strategy. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2790–2798, 2012

**Key words:** mass spectrometry; mechanical properties; metal–polymer complexes; polyethylene (PE); star polymers

## INTRODUCTION

The durable properties of polyolefins make them an ideal material for a large number of applications. An increase in their use has resulted in an increase in the amount of waste generated. So, the ever-increasing use of these polymers has led to their accumulation in the environment at a rate of 25 million tons per year.<sup>1</sup> This alarming scale has led to global concern and has become a social issue.<sup>2</sup> As a result, the development of environmentally friendly polyolefins has become an urgent need.

The majority of plastic products are made from petroleum-based polyolefins that do not degrade in landfills or in compostlike environments. They contain predominantly C–C bonds, which are generally resistant to biodegradation because microbial enzymes cannot access them because of their hydrophobic nature. Among the three polyolefins polypropylene (PP), low-density polyethylene, and high-density polyethylene (HDPE), the last is more highly resistant to biodegradation than the other two.

Several approaches for solving these pollution problems caused by polyolefins were developed in the 1970s.<sup>3</sup> These included blending with biopolymers, biodegradable polymers, or additives that induced biodegradability.<sup>4</sup> The mixture of conventional plastic and a biodegradable polymer produces a material with different mechanical properties.<sup>5–7</sup> There is great interest in incorporating starch into conventional plastics because the latter is a polysaccharide and is environmentally friendly.<sup>8–11</sup> The rate of degradation of polyethylene (PE) could be increased by the introduction of other naturally derived polymers.<sup>12</sup>

The addition of metal ions (MIs) to a polymer enhances its rate of degradation. These metal additives include Co, Mn, Cr, Ni, Mo, and Fe on an Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> support.<sup>13–15</sup> Such products are called photodegradable polymers. PE that has been oxidized by MIs is more susceptible to microbial degradation than normal PE because of its increased hydrophilicity and the presence of low-molecular-weight fragments.<sup>16</sup>

The mechanism of biodegradation here (known as *oxobiodegradation*) involves two stages,<sup>17</sup> (1) abiotic (photo or thermal) oxidation, and (2) microbial degradation. The initial abiotic oxidation is an important stage, as it determines the rate of the entire process. The reduction in the molecular weight of the polymer in this stage could be significant. Lower molecular

Additional Supporting Information may be found in the online version of this article.

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weight hydrocarbons are more susceptible to attack by microorganisms than high-molecular-weight polymers, so thermal or UV pretreatments of the polymer to enhance abiotic degradation are being vigorously researched.

The thermal and photolytic oxidation of prooxidants and starch-blended PE and PP have been reported.<sup>18,19</sup> Among the two different abiotic processes, the UV-exposed prooxidant blended sample underwent a more efficient oxidation than the thermally pretreated sample.<sup>20</sup> The mechanism of photocatalytic (MIs) degradation was reported.<sup>21</sup> Photodegradable (or oxo-biodegradable) polymers have invited major interest compared to starch-blended polymers<sup>22</sup> because the amount of polymer visibly left behind in the environment in the former is much less compared to the latter. Also, the polymer can completely degrade or deteriorate even in the absence of microbes. This can then be easily digested by the enzymes produced by microorganisms in the biotic environment. A balanced mixture of both antioxidant and prooxidant additives could lead to the desired rate of degradation. Iron ( $\text{Fe}^{3+}$ ) plays a role in the photooxidation process by initiating the radical reaction.<sup>23</sup>

In this study, an attempt was made to understand the synergistic effect of treatment and blending on the stability of HDPE over a period of 100 days. Different concentrations of MIs and starch were blended with HDPE, and their performance after pretreatment with UV radiation or thermal energy were studied. The changes in the physiochemical properties of the polymer and the formation of different oxidation products were analyzed. Such a detailed study on HDPE has not been reported so far, and this knowledge could be used to select the concentration level of starch or MIs required in a blend and the oxidation conditions necessary for environmental degradation of this polymer. This results of this study can help in the planning of waste disposal, depending on the type of blend.

## EXPERIMENTAL

### Materials

Film-grade, high-molecular-weight HDPE granules were supplied by Seven Seas Polymer Pvt., Ltd. (Madurai, India). Potato starch powder with 3% moisture was supplied by Sisco Research Laboratories Pvt., Ltd. (Mumbai, Maharashtra, India), and the MI-blended HDPE masterbatch was procured from by Bio Bags, India.

### Methods

Preparation of starch and prooxidant-based masterbatches

The potato starch was dried until its moisture content was reduced to 0.3% (w/w). The potato masterbatch

was prepared by the mixture of HDPE and this starch (1 : 1 w/w) with a kneader (Haake Rheomex 3000, Dieselstr, Karlsruhe, Germany) at 150°C and a speed of 50 rpm. This mixture was then placed in a Haake Rheocord 90, which was equipped with a single-screw extruder (Rheomex 254). It had an extruder barrel, which had four temperature-controlled consecutive heating zones with temperatures of 150, 145, 150, and 150°C. A strand (diameter = 0.25 cm) of this compounded mixture was extruded through the die nozzle at 20 rpm and then pelletized into 0.5-cm chips. These granules were used as the starch-blended HDPE masterbatch (ST-HDPE).

### Film preparation

ST-HDPE masterbatches (5, 10, and 20%) were mixed with synthetic HDPE granules and then extruded into films 35  $\mu$  thick with an extruder (Postex Haake Fisions) with the barrel maintained sequentially at temperatures of 120, 140, 150, and 150°C at a screw speed of 55 rpm. The temperature settings on the first and fourth heating zones were altered, depending on the concentration of the blended additives (see Table I). MI masterbatches (0.5, 1, and 2%) were mixed with synthetic HDPE granules to produce prooxidant HDPE films (MI-HDPE), as mentioned previously.

### Abiotic degradation deterioration

Polymer films were cut into 20  $\times$  120 mm<sup>2</sup> pieces, placed in a holder, and then subjected to treatment. Heat treatment was performed for 100 days in an oven (Sigma Instruments, Chennai, India) maintained at 70°C. UV treatment was carried out in a UV chamber (Sigma Instruments) for 100 days. The wavelength of radiation was 400–315 nm (3.10–3.94 eV). The rate of oxidation of these aging samples was studied once every 7 days with the help of a Fourier transform infrared (FTIR) spectrometer.

### Characterization

#### Mechanical properties

The samples before testing were equilibrated to 50% relative humidity with H<sub>2</sub>O for 40 h at 25°C. Both the tensile and flexural properties of the films were measured with the help of a tensile testing instrument (DXLL-5000, Shanghai D&G Instruments Co., Ltd., Pudongxinqu, Shanghai, China) at a crosshead speed of 5 mm/min.

#### Spectroscopic analysis

FTIR measurements were carried out on the virgin sample and the samples retrieved after treatment with a Jasco N4200 spectrometer (Hachioji, Tokyo, Japan) at

**TABLE I**  
**Details of the Formulation and Sample Designations**

Film designation	HDPE concentration (g)	Metal-ion masterbatch concentration (g)	Starch masterbatch concentration (g)	Temperature of the extruder barrel (°C)				Color of the product
				Zone 1	Zone 2	Zone 3	Zone 4	
HDPE	100	0	0	150	145	150	150	Transparent
MI-HDPE-L	99.5	0.5	0	150	145	150	150	Transparent
MI-HDPE-M	99	1	0	150	145	150	150	Transparent
MI-HDPE-H	98	2	0	145	145	150	145	Transparent
ST-HDPE-L	95	0	5	145	145	150	140	Transparent
ST-HDPE-M	90	0	10	130	135	120	120	Light yellow
ST-HDPE-H	80	0	20	120	135	120	120	Light yellow

Each gram of the metal-ion masterbatch contained 36% chromium, 8% silicon, 4% aluminum, 2% chlorine, and 50% HDPE.

a resolution of 4 cm<sup>-1</sup> in the frequency range 4000–500 cm<sup>-1</sup>. The carbonyl index (Co<sub>i</sub>) of the polymer was calculated by division of the intensity at 1740 cm<sup>-1</sup> with that at 1465 cm<sup>-1</sup>, which corresponded to that of the methylene band.<sup>24</sup>

#### Gas chromatography–mass spectroscopy (GC–MS)

The extraction of the degradation products resulting from the photooxidation (UV) of samples (MI–HDPE and ST–HDPE) was performed as per a reported method.<sup>25</sup> A total of 0.5 g of sample was cut into small pieces, mixed with 10 mL of chloroform in a glass vial, and sonicated in a Branson 2210 apparatus (San Diego, California, USA), for 2 h in a hot-water bath held at 55°C. The extract obtained was concentrated by evaporation of the solvent at room temperature. Then, 2 mL of chloroform was added, and the solvent layer was filtered through a 0.2-mm filter before analysis.

This extract was analyzed by GC–MS (Bruker EM640S, Billerica, Massachusetts, USA) with helium as the carrier gas. The gas chromatograph was equipped with an HP 5MS (Jasola, New Delhi, India) capillary column of medium polarity. The oven temperature was programmed from 40°C for 4 min and then increased to 250°C at a heating rate of 5°C/min; it was held at this temperature for 20 min. Samples were introduced in

the spill-less injection mode at 250°C. All of the degradation products were identified by comparison of the mass spectrum with the data available in the National Institute of Standards and Technology (NIST) database (<http://webbook.nist.gov/chemistry/>).

#### Surface changes

The surface topography and deterioration of the treated and untreated HDPE samples were analyzed with scanning electron microscopy (SEM) with a Nanoscope IV digital instrument (Veeco Technologies, Chiyoda-ku, Tokyo, Japan) equipped with an automatic defect classification system (ADCS) controller.

#### Weight loss

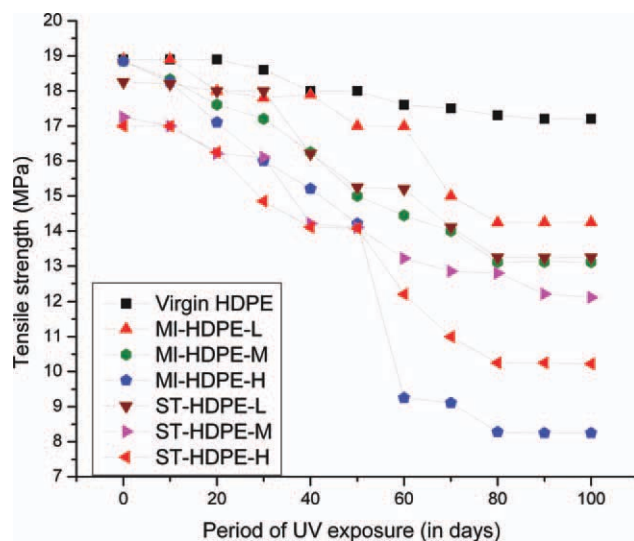
Gravimetric weight loss is an indication of degradation. The samples were weighed before treatment and at the end of 100 days with an accurate five-digit weighing balance. The percentage weight losses with standard error were estimated from three samples<sup>26,27</sup> and compared with the initial values.

#### Surface energy

The contact angle and surface energy of the films were measured at room temperature with a

**TABLE II**  
**Various Physicomechanical Properties at the End of 100 Days of Treatment**

Sample	Contact angle (°)			Surface energy (N/m)			Tensile strength (MPa)			Elongation		
	Initial	After		Initial	After		Initial	After		Initial	After	
		UV treatment	thermal treatment		UV treatment	thermal treatment		UV treatment	thermal treatment		UV treatment	thermal treatment
HDPE	73	71	71.5	35.7	39.2	38	18.9	17.2	17.2	201.12	225.25	235
MI-HDPE-L	73.1	70	71	35.7	41.1	41.25	18.9	14.25	14	202.1	285.25	275
MI-HDPE-M	72.1	69.2	71.85	35.8	48	47.23	18.85	13.11	13.25	202.25	253.5	265
MI-HDPE-H	72	68.2	67	35.8	56.25	54.68	18.85	8.25	9	202.22	175.25	200
ST-HDPE-L	71	65	65	35.8	42.5	41	18.25	13.25	14	201.1	256.25	222
ST-HDPE-M	71	65.25	67.15	36	48	45.25	17.25	12.12	12	198	200.25	215
ST-HDPE-H	70	64.85	64.99	37	51	49.25	17	10.22	9.99	185.76	185.25	200



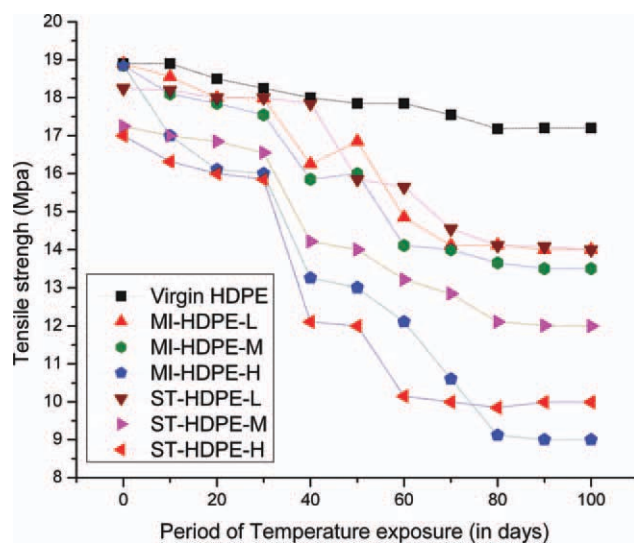
**Figure 1** Tensile strength profile of the UV-exposed virgin and blended HDPEs over a period of 100 days. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

goniometer easy drop instrument (KRUSS, DSA II GmbH, Hamburg, Germany) by Fowkes's method. Millipore-grade distilled water was used as the wetting liquid. The calculations were averaged from 10 measurements.<sup>28</sup>

## RESULTS

### Changes in the mechanical properties

Starch affected the transparency of the polymer, and at a concentration of 10%, the polymer turned yellow (Table I). The addition of MI up to 2% did not



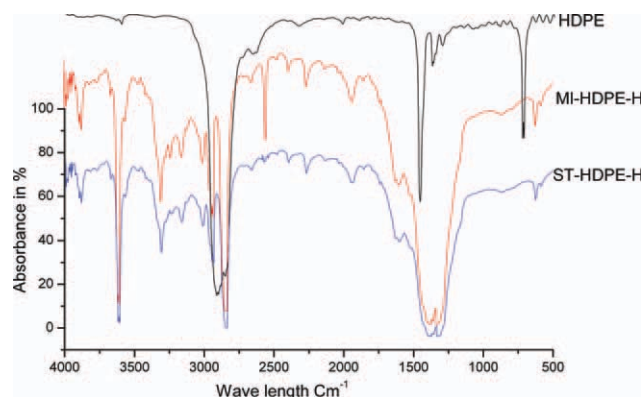
**Figure 2** Tensile strength profile of the thermally treated virgin and blended HDPEs over a period of 100 days. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

affect the tensile strength of HDPE. The addition of 10% starch decreased the tensile strength of the untreated polymer from 18.9 to 17.2 MPa (Table II). Figures 1 and 2 show the changes in the tensile strength of various polymers exposed to UV and heat, respectively, as a function of time. Table II lists the tensile strength and percentage elongation of these polymers at the beginning of the treatment and at end of 100 days. The maximum decrease in tensile strength was observed in the UV-treated 2% MI mixed polymer (MI-HDPE-H; from 17.2 to 8.25 MPa), followed by the same polymer thermally treated for 100 days (from 17.2 to 9 MPa). The tensile strength of 20% starch-blended HDPE decreased to about 10 MPa after 100 days of UV or thermal treatment. These results indicate that a small amount of MIs was more effective than starch in decreasing the mechanical integrity of the treated HDPE.

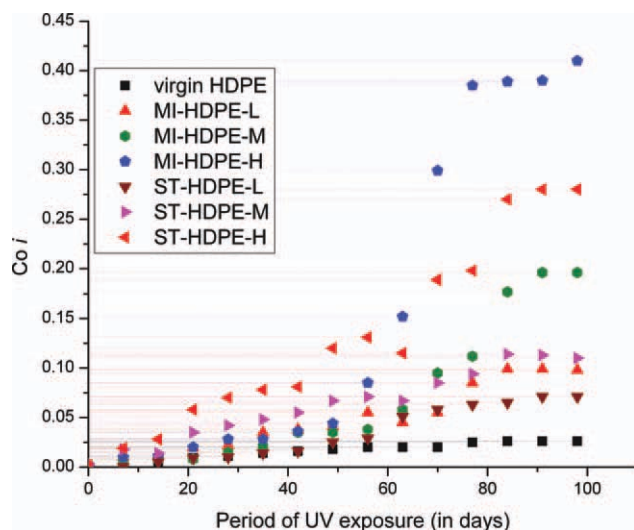
A large drop in the tensile strength in most of the samples happened between 30 and 50 days. The percentage elongation is an indication of the stiffness of a polymer, and the lower this value is, the stiffer the material is. The percentage elongation of 2% MI mixed HDPE decreased from 202 to 175% (the lowest value) after it was exposed to UV for 100 days. This indicated that the polymer became stiff and, thereby, brittle. The percentage elongation of the untreated virgin HDPE was 201%. In all other cases, the treatment increased the percentage elongation (which indicated that the polymer became supple).

### Spectroscopic analysis

The FTIR spectra of the native and metal- and starch-blended HDPEs exposed to UV are shown in Figure 3. The focus here is the peaks at 1715, 1740, 1640, and 3050–3550  $\text{cm}^{-1}$ , which corresponded to the ketone carbonyl ( $-\text{CO}-$ ), ester carbonyl ( $-\text{COO}-$ ), double bonds ( $-\text{C}=\text{C}-$ ), and hydroxyl ( $-\text{OH}-$ ), respectively. These peaks were formed



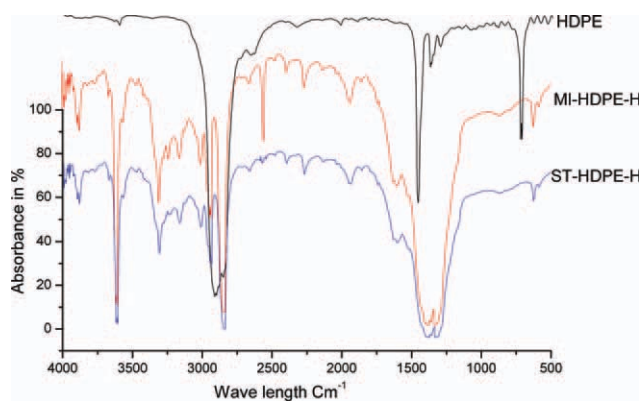
**Figure 3** FTIR spectrum of the UV-treated samples for a period of 100 days. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4**  $Co_i$  profile of the virgin HDPE and blended HDPEs on exposure to UV. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

during the oxidation of the polymer. Among the three polymers, MI-blended HDPE showed the maximum degradation. It had a strong broad peak at  $1710\text{ cm}^{-1}$ , corresponding to ketone. Broad peaks at  $3276$  and  $3360\text{ cm}^{-1}$  in the catalyst-blended HDPE and starch-blended HDPE, respectively, indicated the presence of an intermolecular hydroxyl group in the backbone of the polymers. This suggested that the backbone degraded with the formation of simpler functional groups, including COOH.<sup>21</sup>

Figure 4 shows the changes in the  $Co_i$  values of various HDPEs exposed to UV as a function of time. Generally,  $Co_i$  increases as a function of time. The highest oxidation was observed in 2% MI-blended HDPE followed by the 20% starch-blended HDPE and then the 1% MI-blended HDPE. Figure 5 shows the FTIR spectrum of the thermally treated HDPEs. Figure 6 shows



**Figure 5** FTIR spectrum of the temperature-treated samples for a period of 100 days. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

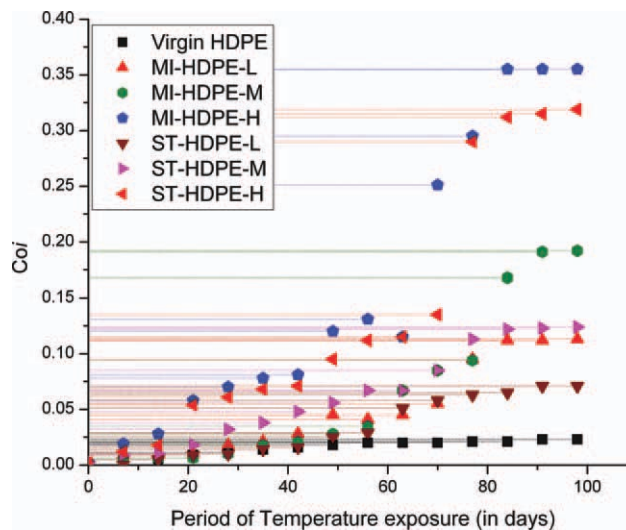
the  $Co_i$  values for all of the HDPEs exposed to heat as a function of time. The  $Co_i$  of the 2% MI-blended HDPE (MI-HDPE-H) reached values of 0.41 and 0.36 on the 100th day when it was exposed to UV and heat, respectively; this indicated that the former treatment oxidized the surface more effectively than the latter treatment. The  $Co_i$  of the 20% starch-blended HDPE (ST-HDPE-H) reached values of 0.27 and 0.32 on the 100th day after the UV and heat treatments, respectively. This indicated that MIIs as blending agents were more efficient in oxidizing the surface than starch. The carbonyl index was higher for MI-blended HDPE exposed to UV than those exposed to heat. Although the carbonyl index was higher for the starch-blended HDPE exposed to heat than that exposed to UV, this indicated that the treatment strategy required to oxidize the polymer depended on the types of blending used. Minimum oxidation was observed in unblended HDPE.

### Physical properties

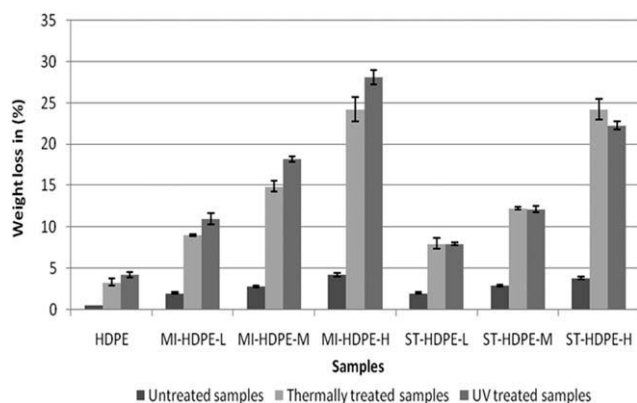
#### Contact angle and surface energy

HDPE is a hydrophobic polymer, and a minimum reduction in the contact angle was observed after treatment with the virgin polymer (Table II). As expected, the addition of starch to HDPE decreased the contact angle, which indicated that the surface turned hydrophilic. The lowest contact angle was observed ( $<65^\circ$ ) with the 20% starch-blended HDPE after it was exposed to heat or UV for 100 days. The contact angle decreased to  $65^\circ$  with 10 and 5% starch-blended HDPEs after treatment.

Decreases in the contact angle led to corresponding increases in the surface energy. The surface



**Figure 6**  $Co_i$  profile of the virgin HDPE and blended HDPEs on heating at  $70^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

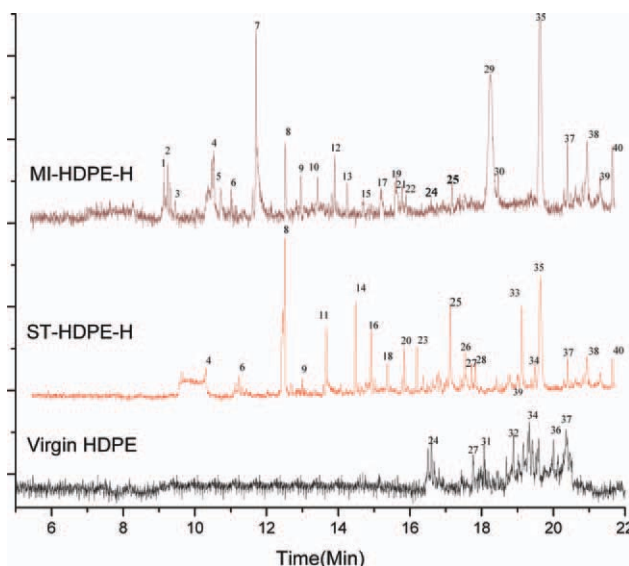


**Figure 7** Weight loss of the samples under both abiotic conditions.

energy of virgin HDPE was 35.7 N/m. The highest surface energy was observed in the 2%MI mixed HDPE (56.2 N/m) after it was exposed to UV for 100 days followed by the same polymer after thermal treatment (54.7 N/m). The increase in the surface energy after treatment was minimal in the case of virgin HDPE.

#### Weight loss

After 100 days of UV exposure, 28.1, 18.2, 11, 22.2, 12.1, 8, and 4.2% weight losses were observed in the MI-HDPE-H, MI-HDPE-M, MI-HDPE-L (high density polyethylene with low level concentration of additives among the three different concentration), ST-HDPE (high density polyethylene with medium level concentration of additives among the three different concentration), ST-HDPE-M, ST-HDPE-L, and virgin HDPE, respectively (Fig. 7). After thermal treatment, 24.2, 14.8, 9.0, 24.0, 21.2, 8.0, and 3.3% weight losses were observed in the same polymers, respectively. The maximum weight loss was observed in the 2% MI-blended HDPE exposed to UV (28%) followed by the 20% starch-blended HDPE exposed to heat (24%). This was followed by the 1% MI-blended polymer (18.2%). These results



**Figure 8** Chromatogram of chloroform-extracted degradation products of the UV-treated samples analyzed by GC-MS equipped with an HP 5MS column. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

indicate that the exposure of the MI-blended HDPE to UV and that of the starch-blended HDPE to heat achieved the best results. These findings were similar to the FTIR results; this indicated that there was a correlation between the oxidation of the polymer and the weight loss.

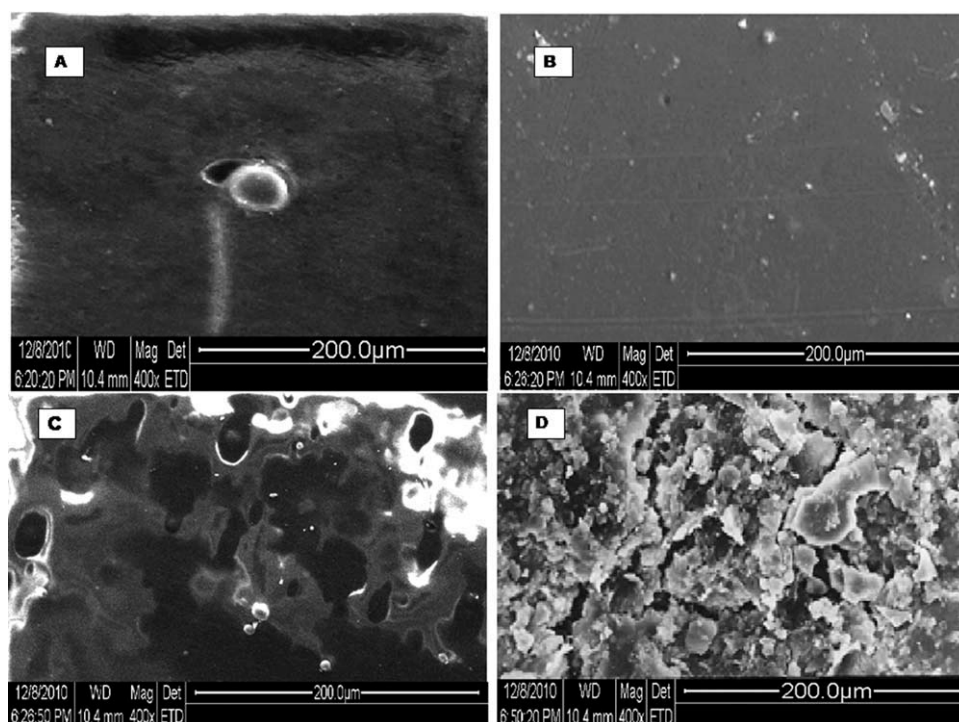
#### Degradation product and patterns (GC-MS study)

Qualitative analyses of the degradation products were made on the basis of the GC-MS results. The mass spectra were compared with the data from the NIST database. Figure 8 shows the GC-MS chromatogram of the volatile and semivolatile products extracted with chloroform from virgin HDPE and 2% MI-blended and 20% starch-blended HDPEs exposed to UV for 100 days.

A variety of oxidation products were observed in the blended HDPE. Table III lists the groups of

**TABLE III**  
Possible Groups of Products Identified from GC-MS of the  $\text{CHCl}_3$  Extract of the UV-Treated Samples

Sample	Compound	Number of compounds in the virgin HDPE	Number of compounds in MI-HDPE	Number of compounds in ST-HDPE
1	Hydrocarbons	4	13	8
2	MIs	0	5	0
3	Ketones	3	9	5
4	Acids	0	0	6
5	Alcohols	0	7	4
6	Aldehydes	3	0	0
7	Esters	2	7	3



**Figure 9** SEM images of the polymers before and after UV treatment for a period of 100 days (A,C) starch-blended untreated and treated HDPE, respectively and (B,D) MI-blended untreated and treated HDPE, respectively.

products observed during the treatment, and the detailed list of the possible products are given in the Supporting Information. The number of hydrocarbons and ketones were highest in MI-HDPE. Among the 13 different compounds, 5 were not reported earlier (2,2-dimethyl nonane, 2-chlorobutane, 1,3-dichloropropene, 1,1-dichloro-1-pentene, and 5,6-benzo-1,1,4,4-tetraethyl-1,4-disilacyclohex-5-ene). Five different MI-based products were identified only in the MI-HDPE extract, including, dodecamethyl cyclohexasilane, 1,1,1,3,3,3-(hexamethyl)-2-(trimethylsilylmethyl)trisilane, 1,1,2,2-tetraethyldisilane, and dimethoxydimethylsilane.

Esters and alcohols are the next highest oxidation products in the MI-HDPE. 2,4-Dichlorophenyl acetate, pyridyl-methyl pentadecanoate 1,2-propanediol, 1,10-decanediol, and 1,12-dodecanediol were not reported before. Aldehyde and acids were not present in the MI-HDPE extract. Alcohol and acids were comparatively higher in ST-HDPE than in MI-HDPE. Acids groups were present only in the ST-HDPE extract; 1,2,3-propanetricarboxylic acid tris(trimethylsilyl) was not reported earlier. Aldehyde groups were present only in HDPE. The oxidation products of virgin HDPE was much lower.

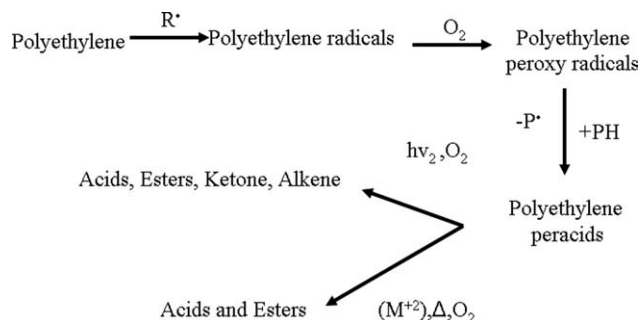
## SEM

The surfaces of the untreated ST-HDPE and MI-HDPE were smooth without cracks and free from any defects [Fig. 9(A,B)]. Starch globules were also observed

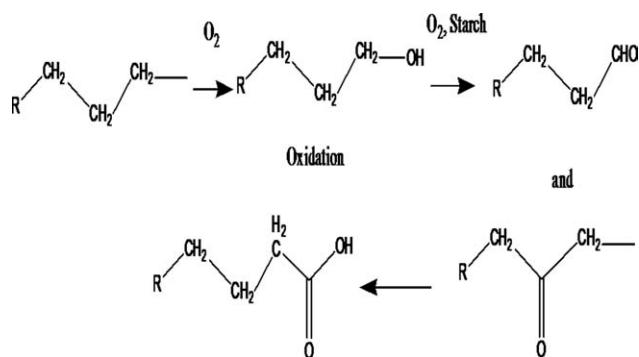
[Fig. 9(A)], whereas dispersed metal particles are evident in Figure 9(B). The SEM of the UV-treated ST-HDPE and MI-HDPE showed developed cracks and grooves due to the abiotic treatment [Fig. 9(C,D)]. However, the extent of the damage was much more profound in MI-HDPE than in the other.

## DISCUSSION

HDPE consists of repeating methylene units with an extremely high molecular weight, typically several hundreds or thousands of daltons. The size of this polymer molecule is large for it to be degraded by microorganisms, so it remains persistent in the environment. Additives used for the stabilization of the polymer further slow down the rate of degradation. The action of MIs or starch on the oxidation of



**Figure 10** Oxidation mechanism of polyolefin in the presence MIs (+PH, polymer chain; P<sup>•</sup>, polymer radicals).



**Figure 11** Oxidation mechanism of polyolefin in the presence of starch.

polyolefins has been discussed by others<sup>21</sup> (Figs. 10 and 11).

Under the action of the additives and UV or heat, the polymer gets chemically transformed, as observed by others.<sup>29</sup> The catalytic degradation in the presence of transition metals in PE has been attributed to its ability to generate free radicals on its surface, which later react with oxygen to generate carbonyl groups (Fig. 10).<sup>30,31</sup> In contrast, starch-blended HDPE underwent direct oxidation, which led to the insertion of oxygen to form alcohols, aldehydes, and so on (Fig. 11). In our earlier article, the mechanism of photodegradation and thermal degradation of PE was proposed and verified (Figs. 10 and 11).<sup>16,32</sup>

It was reported that a reduction in the tensile strength and a loss of elongation are good indicators of oxidation.<sup>33</sup> The tensile strength of the virgin HDPE was greater than those of blended ones. Native starch has very low mechanical properties when compared to HDPE.<sup>34</sup> An increase in the starch concentration reduced the mechanical strength of the films.<sup>34</sup> This was due to the discontinuity created by the addition of starch granules to HDPE films and by the poor interfacial interaction between the starch and HDPE matrix because the former was hydrophobic and the latter was hydrophilic. Starch also imparted color to the films. On the contrary, MIs did not impart any color to the polymer. After 100 days of abiotic exposure, the tensile strength of the virgin HDPE exhibited a less significant change, whereas both the MI- and starch-blended films showed greater decreases in the tensile strength. The maximum decreases in the tensile strength were observed in MI-HDPE-H and ST-HDPE-H (56.23 and 52.25%, respectively) after UV exposure. The percentage elongation of MI-HDPE-H decreased after exposure to UV; this indicated that the sample had become brittle.

After 100 days, there was an appreciable increase in the carbonyl peaks in blended HDPE than in the control HDPE; this indicated higher levels of oxidation (Figs. 4 and 6). Similar findings have been

reported by others.<sup>35–37</sup> In the case of the starch-blended films, thermal treatment aided oxidation when compared to UV treatment. With the MI-blended polymer, however, UV treatment favored oxidation more than the thermal treatment. As reported, transition MIs are very effective prooxidants when compared to native starch, and they help to generate free radicals under UV.<sup>38,39</sup> Among the four polymers, MI-blended HDPE showed maximum degradation. It had a strong broad peak at  $1710\text{ cm}^{-1}$ , which was attributed to the carbonyl groups present in carboxylic acid. Broad peaks at  $3276$  and  $3360\text{ cm}^{-1}$  in the MI-blended and starch-blended HDPEs indicated the presence of hydroxyl groups in the backbones of the polymers. This suggests that the backbone was degrading with the formation of simple functional groups, including COOH. Similar observations have been made by others.<sup>40</sup> The starch-blended HDPE exhibited peaks at  $1730$  and  $3360\text{ cm}^{-1}$ , which corresponded to the carbonyl bond ( $\text{C}=\text{O}$ ) and intermolecular hydroxyl groups (OH), respectively.<sup>41</sup> All of the polymers exposed to heat and UV showed significant increases ( $p < 0.001$ ) in the carbonyl ( $1740\text{ cm}^{-1}$ ), ester ( $1715\text{ cm}^{-1}$ ), and vinyl ( $1640\text{ cm}^{-1}$ ) bands, which clearly showed that photooxidation had occurred.<sup>42</sup>

The low-molecular-weight degradation products that remained in the PE films after the different treatments were extracted with chloroform and analyzed by GC-MS. A wide variety of degradation products, including both oxygen-containing compounds, such as, ketones, carboxylic acids, alcohols, and esters, and unoxidized hydrocarbons, were detected. Among the degradation products, acids were present only in ST-HDPE-H. This may have been due the presence of starch ( $\text{C}_6\text{H}_{10}\text{O}_5$ ) in the sample. A few silicon-containing compounds were found in MI-HDPE-H because silicon was added as a prooxidant, which was oxidized during the treatment. The numbers of ketones, esters, and alcohols were relatively high in ST-HDPE-H when compared those in MI-HDPE-H. The degradation products in virgin HDPE were comparatively much lower. Other researchers have also identified similar products in thermally oxidized starch- and MI-based polymers<sup>43</sup> and thermally oxidized and UV-photooxidized degradable PEs.<sup>44–46</sup>

Changes in the contact angle and surface energy were indications of alterations in the hydrophobicity of the polymer surface. The surface after treatment turned relatively more hydrophilic, and FTIR spectroscopy indicated oxidation of the surface. Heating oxidized the surface more than did the UV treatment. A decrease in the hydrophobicity after treatment was reported by other researchers.<sup>47</sup>

## CONCLUSIONS

The effects of UV and thermal treatments on starch- and MI-blended HDPEs were reported here. A



higher rate of oxidation was observed with MI-blended HDPE under UV exposure when compared to the starch-blended and virgin HDPEs. That the weight loss of this polymer was the highest (28.1%) in these results indicates that MI-blended HDPE oxidized more quickly than the starch-blended HDPE, even though the percentage of MIs was comparatively much lower than the concentration of starch in HDPE. The numbers of oxidation products were much higher in the former than in the latter. Results from the FTIR spectroscopy and tensile strength and contact angle measurements were also positively correlated with these observations. SEM images indicated the deterioration of the polymer surface. In the case of the starch-blended HDPE, an increase in the concentration of starch imparted color to the polymer. MIs were a more effective degradant than starch under UV conditions, and because of their minimum concentration, they did not impact the final product adversely.

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## References

- Trishul, A.; Doble, M. *Biomacromolecules* 2010, 11, 20.
- Muthukumar, T.; Aravinthan, A.; Lakshmia, K.; Venkatesan, R.; Vedaprakash, L.; Doble, M. *Int Biodeterioration Biodegrad* 2011, 65, 276.
- Arnaud, R.; Dabin, P.; Lemaire, J.; Al-Malaika, S.; Chohan, S.; Coker, M. *Polym Degrad Stab* 1994, 46, 211.
- Chandra, R.; Rustgi, R. *Polym Degrad Stab* 1997, 56, 185.
- Ratto, J. A.; Stenhouse, P. J.; Auerbach, M.; Mitchell, J.; Farrell, R. *Polymer* 1999, 40, 6777.
- Lima, S. M.; Estudo da Capacidade Biodegradadora de culturas de fungos em blendas poliméricas biodegradáveis; Tese de Mestrado, Universidade Federal de Pernambuco: Recife, Pernambuco, Brasil, 2005.
- Nakamura, E. M. L.; Cordi, G. S. G.; Almeida, N.; Duran, L. H. I. *J Mater Process Tech J Mater Process Technol* 2005, 162, 236.
- Kim, M. *Carbohydr Polym* 2003, 54, 173.
- Rodriguez-Gonzalez, F. J.; Ramsay, B. A.; Favis, B. D. *Polymer* 2003, 44, 1517.
- Matzinos, P.; Tserki, V.; Gianikouris, C.; Pavlidou, E.; Panayiotou, C. *Eur Polym J* 2002, 38, 1713.
- Baldev, R. V.; Annadurai, R.; Somashekar, M. R.; Siddaramaiah, S. *Eur Polym J* 2001, 37, 943.
- Artham, T.; Sudhakar, M.; Venkatesan, R.; Nair, M.; Krishnamurthy, K.; Doble, M. *Int Biodeterioration Biodegrad* 2009, 63, 884.
- Weiland, M.; Daro, D.; David, C. *Polym Degrad Stab* 1995, 48, 275.
- Jakubowicz, I. *Polym Degrad Stab* 2003, 80, 39.
- Williams, P. T.; Bagri, R. *Int J Energy Res* 2003, 28, 31.
- Sebaa, M.; Servens, C.; Pouyet, J. *J Appl Polym Sci* 1993, 47, 1897.
- Albertsson, A. C.; Andersson, S. O.; Karlsson, S. *Polym Degrad Stab* 1987, 18, 73.
- Erlandsson, B.; Karlsson, S.; Albertsson, A. C. *Polym Degrad Stab* 1997, 55, 237.
- Karlsson, S.; Hakkarainen, M.; Albertsson, A. C. *Macromolecules* 1997, 30, 7721.
- Muthukumar, T.; Aravinthan, A.; Mukesh, D. *Polym Degrad Stab* 1988, 95, 1988.
- Arkatkar, A.; Arutchelvi, J.; Sudhakar, M.; Bhaduri, S.; Uppara, P. V.; Doble, M. *Open Environ Eng J* 2009, 2, 68.
- Kolybaba, M.; Tabil, L. G.; Panigrahi, S.; Crerar, W. J.; Powell, T.; Wang, B. *Biodegradation* 2003, 300(3), 1.
- Koutny, M.; Lemaire, J.; Delort, A. M. *Chemosphere* 2006, 64, 1243.
- Sudhakar, M.; Artham, T.; Doble, M.; Sureshkumar, K.; Syed, J.; Inbakandan, S. *Polym Degrad Stab* 2007, 92, 1743.
- Rodrigo, L. C.; Haider, N.; Greus, A. R.; Karlsson, S. *J Appl Polym Sci* 2006, 79, 1101.
- Girois, S.; Audouin, L.; Delprat, P.; Verdu, J. *Polym Degrad Stab* 1996, 51, 133.
- Sudhakar, M.; Doble, M.; Murthy, P. S.; Venkatesan, R. *Int Biodeterioration Biodegrad* 2008, 61, 203.
- Roy, P. K.; Titus, S.; Surekha, P.; Tulsii, E.; Deshmukh, C.; Rajagopal, C. *Polym Degrad Stab* 2008, 93, 1917.
- Bonhomme, S.; Cuer, A.; Delort, A. M.; Lemaire, J.; Sancelme, M.; Scott, G. *Polym Degrad Stab* 2003, 81, 441.
- Osawa, Z.; Kurisu, N.; Nagashima, K.; Nankano, K. *J Appl Polym Sci* 2003, 23, 3583.
- Osawam, Z. *Polym Degrad Stab* 1988, 20, 203.
- Arutchelvi, J.; Sudhakar, M.; Ambika, A.; Mukesh, D.; Sumit, B.; Parasu, V. U.; *Indian J Biotechnol* 2008, 7, 9.
- Qureshi, F. S.; Amin, M. B.; Maadhah, A. G.; Hamid, S. H. *J Polym Eng* 1990, 9, 67.
- Sathya, K.; Syed, S. H. *J Plast Film Sheeting* 2006, 22, 39.
- Chiellini, E.; Corti, A.; Swift, G. *Polym Degrad Stab* 2003, 81, 341.
- Chiellini, E.; Corti, A.; Antone, S. *Polym Degrad Stab* 2007, 92, 1378.
- Jakubowicz, I. *Polym Degrad Stab* 2003, 80, 39.
- Lee, B.; Pometto, A. L., III; Fratzke, A.; Bailey, T. B. *Appl Environ Microbiol* 1991, 57, 678.
- Khabbaz, F.; Albertsson, A. C.; Karlsson, S. *Polym Degrad Stab* 1999, 63, 127.
- Albertsson, A. C.; Barenstedt, C.; Lindberg, T.; Karlsson, S. *Polymer* 1995, 36, 3075.
- Wiles, D. M.; Scott, G. *Polym Degrad Stab* 2006, 91, 1581.
- Albertsson, A. C.; Karlsson, S. *Prog Polym Sci* 1990, 15, 177.
- Hakkarainen, M.; Albertsson, A. C.; Karlsson, S. *J Chromatogr A* 1996, 741, 251.
- Karlsson, S.; Hakkarainen, M.; Albertsson, A. C. *Macromolecules* 1997, 30, 7721.
- Khabbaz, F.; Albertsson, A.; Karlsson, S. *Polym Degrad Stab* 1998, 61, 329.
- Khabbaz, F.; Albertsson, A. C.; Karlsson, S. *Polym Degrad Stab* 1999, 63, 27.
- Trishul, A.; Sudhakar, M.; Umadevi, V. R.; Viduthalai, R. R.; Suresh Kuma, K.; Sriyutha Murthy, P.; Venkatesan, R.; Doble, M. *Open Macromol J* 2008, 2, 43.