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EVALUATION OF PHOTODEGRADABILITY OF LOW DENSITY POLYETHYLENE BY THERMOANALYTICAL TECHNIQUE

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ABSTRACT

Accelerated photoageing of low density polyethylene film has been studied using high energy UV radiation in the presence of air. The change in molecular structure by chain scission and the formation of oxygenated and unsaturated groups due to photooxidative degradation is followed by a decrease in viscosity average molecular weight ($\overline{M}_v$) and an increase in density. The gel content is formed by recombination of macroalkyl and alkoxy radicals. Degradability of aged samples has been evaluated by TG and DSC measurements. Dynamic and isothermal thermogravimetric data show the destabilization behaviour of aged samples. DSC data show that the area of the melt endotherm increases with crystallinity increase due to the formation of a more ordered structure by rearrangement of smaller molecular chains and also due to chemicrystallization. Internal plasticization due to smaller molecules causes broadening of the endotherm towards lower temperatures. The change in exotherms at 503 and 565 K shows the increase in degradability of polyethylene during UV ageing.

INTRODUCTION

The enormous increase in the production of polyolefins has brought to the fore the waste disposal problem of such polymers in industrial and urban life. The use of plastic materials capable of transforming themselves into products which can re-enter the biological cycle appears as one of the most viable solutions to their disposal problem. Polyolefins have been found to degrade at a faster rate on exposure to terrestrial sunlight or at elevated temperatures in the presence of oxygen [1–8]. The initial process either during thermal or photodegradation of polymers is substantially affected by the presence of trace amounts of impurities such as hydroperoxy, carbonyl and unsaturated groups and contaminants such as catalyst residues and metallic compounds which are incorporated in trace amounts during processing. Few workers [4–6,9] have used thermal and photo techniques to make the polyolefins degradable and sensitive to photodegradation. Pozzi et al. [10] have investigated the photodegradability of polyethylene, introducing carbonyl groups in the molecular chain by oxidation of the aliphatic chain

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with photoactivated NOCl and hydrolysis of the oxime. Carlsson and Wiles [11,12] have also studied the photodegradability of oxidized polyolefins, i.e., having carbonyl and hydroperoxy groups. Studies have also been done on the degradability of polyolefins in the presence of photosensitizers [9,13,14]. Spectroscopic and chromatographic techniques have generally been used to follow the degradation of polymers. Very little work has been reported on the evaluation of the degradability of polyolefins by thermoanalytical techniques [7,15–17].

In this investigation additive free low density polyethylene (LDPE) film samples were irradiated by UV radiation for different periods of time and the photodegradability of these samples has been evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The changes in molecular structure and properties during photooxidative degradation have also been followed by spectroscopy, determination of gel content, viscosity average molecular weight ($\overline{M}_v$), and density.

EXPERIMENTAL

Low density polyethylene obtained from IPCL, Baroda, was extruded in the form of thin films of 0.05 and 0.025 mm thickness after the removal of stabilizers. These film samples were exposed to high intensity UV radiation for different time periods in the presence of air. UV ageing was achieved using UVS 500 arc tubes and the samples were placed on a rotating disc for uniform exposure of samples at a distance of 42 cm.

The molecular structural change of aged samples was studied using a Perkin-Elmer 599B IR spectrophotometer. The viscosity average molecular weight ($\overline{M}_v$) was determined by measuring the intrinsic viscosity (η) of dilute solutions of polyethylene in xylene at 75 ± 0.1°C using an Ostwald viscometer. The Mark Houwink equation was applied with K and α values of 135×10^{-5} and 0.63, respectively [18]. The gel content was removed using a Soxhlet extractor before measuring the intrinsic viscosity (η). Density measurements were determined using the floatation method in a methanol–water mixture.

The thermal stability of UV aged 0.05 mm thick samples was evaluated by thermogravimetry and differential scanning calorimetry. Dynamic thermogravimetric traces (TG) were determined using a Stanton Redcroft TG 750 thermobalance at a constant heating rate of 10°C min^{-1} in a constant flow of oxygen (10 ml min^{-1}). Isothermal thermogravimetric data on aged and unaged samples were determined at 505 K in a constant flow of oxygen. The temperature (505 K) for the isothermal run was attained by rapid heating at 100°C min^{-1}. Dynamic differential scanning calorimetry of the samples was measured using a Du Pont 990 system with a heating rate of 10°C min^{-1}. About 5 mg of sample were used for each TG and DSC run. The melting behaviour and the initial thermal degradation of photoaged and unaged samples were studied by DSC curves.

RESULTS AND DISCUSSION

Figures 1 and 2 illustrate the changes in IR spectra of 0.05 mm thick film samples as a function of time after UV ageing. It has been found that with the increase in ageing time, carbonyl group concentration (band in the region 1830–1650 cm^{-1}) increases, centreing mainly at 1720 cm^{-1} showing the formation of ketonic groups. Other small bands at 1730, 1745, 1780, and 1795 cm^{-1} have also been identified and have been found to increase in intensity during ageing, due to the formation of aldehydic, ester and perester groups. The increase in the band intensity at 1645 cm^{-1} may be due to the formation of conjugated unsaturated groups during UV ageing. The band at 910 cm^{-1} also increases with the time of UV ageing, showing the increase in the concentration of terminal unsaturated groups (vinyl group, $-CH{=}CH_2$). The increase in the band intensity in 3600–3260 cm^{-1} may be due to the formation of hydroxyl and conjugated hydroperoxy groups. Similar changes have also been observed in the carbonyl, hydroxyl and unsaturated regions of IR spectra of 0.025 mm thick film (Fig. 3), and using the $-CH_2-$ group band as standard, the relative increase in the absorption at 1720, 3440 and

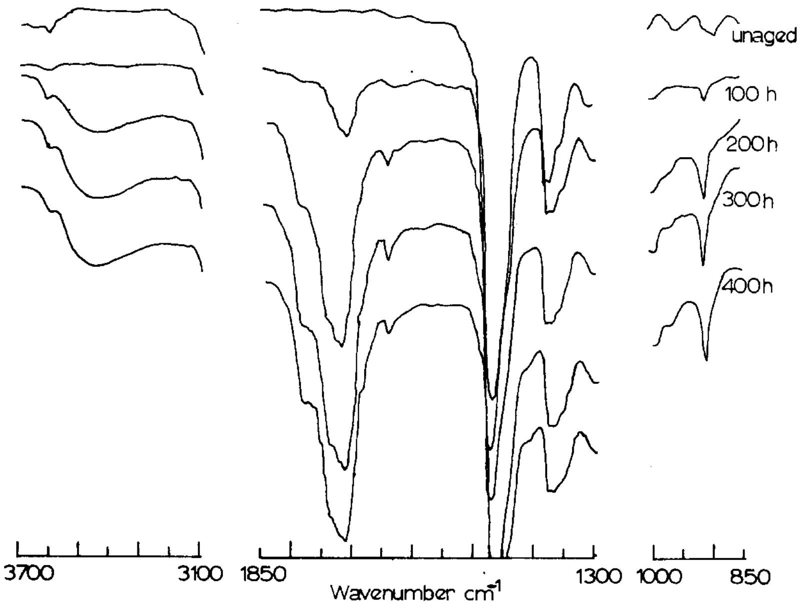

Fig. 1. Change in IR spectra of 0.05 mm thick LDPE film samples during UV ageing (3700–3100 cm^{-1}, 1850–1300 cm^{-1}, and 1000–850 cm^{-1}).

910 cm^{-1} has been observed to be the same in both 0.025 and 0.05 mm thick film. The appearance of a broad band in the region 920–870 cm^{-1} in the spectra of unaged sample shows the presence of both vinyl and vinylidene groups, and on UV ageing the band narrows down centreing at 910 cm^{-1} (Fig. 1), showing that vinylidene groups are taking part in the photoinitiated reaction. The increase in the intensity at 910 cm^{-1}, followed by a decrease at

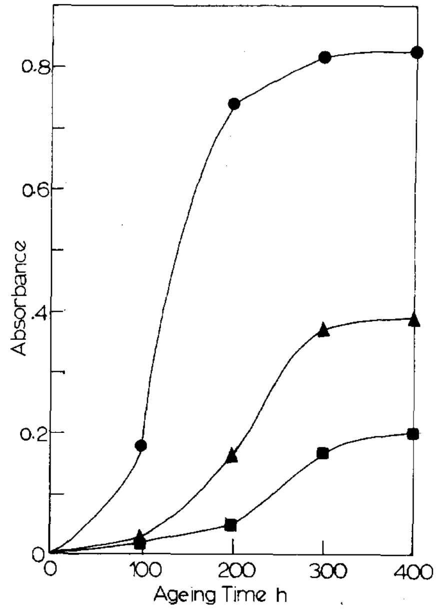

Fig. 2. Change in absorbance at ▲, 3440 cm^{-1} (–OOH), ●, 1720 cm^{-1} (>CO) and ■, 910 cm^{-1} (vinyl) during UV ageing of 0.05 mm thick film.

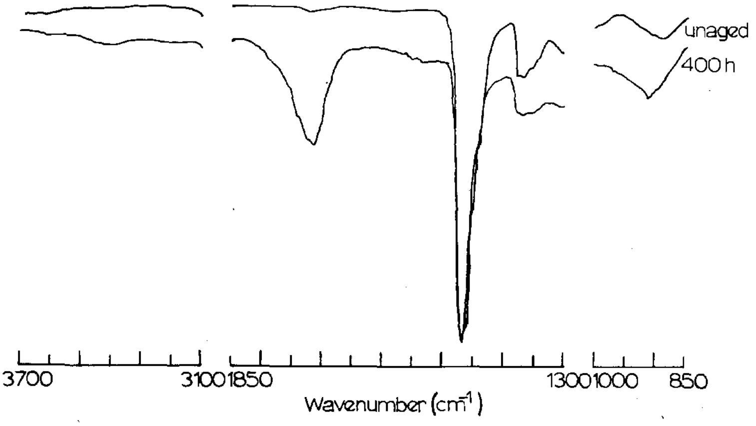

Fig. 3. Change in IR spectra of 0.025 mm thick LDPE film during UV ageing (3700–3100 cm^{-1}, 1850–1300 cm^{-1}, and 100 –850 cm^{-1}).

1378 cm^{-1} ($-CH_3$ groups) with the time of UV ageing shows that β-scission and Norrish type reactions are occurring in the molecular chain. The faster rate of chain scission results in the formation of smaller chain fragments, causing a rapid decrease in $\overline{M}_v$ (Table 1). The UV aged films also had a gel content which shows that the cage recombination reaction of macroalkyl and alkoxy free radicals [19,20] takes place with the molecular chain scission (Table 1). The increase in density with the time of UV ageing shows that chain scission and elimination of short chain branches results in the formation of smaller, more mobile molecular chains, resulting in an increased probability of a more ordered structure in the amorphous region [16,21]. The increase in the secondary bond forces by oxygenated (polar) groups also supports the formation of a more ordered structure [3]. The increase in absorbance ratio of the bands at 730 and 720 cm^{-1} has also been observed with the time of UV ageing, indicating the increase in crystallinity of polyethylene [22]. Polyethylene samples have been found to be brittle and their strength reduces to zero after UV ageing for 100 h, and on further ageing their brittleness increases and colour changes to light yellow, showing excessive degradation of polyethylene molecular chains.

Thermogravimetric studies of 0.05 mm thick film samples illustrate the decrease in thermal stability of photodegraded polyethylene with the time of UV ageing. TG data (Fig. 4) clearly show that the relative temperature of weight loss decreases and the rate of weight loss increases with the ageing time. The initial temperature of weight loss (T_i) and the temperature where steep weight loss starts (T_1) have been found to decrease with the ageing time, while the weight loss from T_i to $T_1 - W_1$, i.e. up to the first stage, may depend on the volatility of the smaller chain fragments as it increases up to 200 h and then decreases (Table 2). Derivative thermogravimetry (DTG) data also show the relative decrease in thermal stability of polyethylene with the time of UV ageing. Tmax (temperature where the rate of weight loss becomes maximum) has been found to decrease (Table 2) while the rate of

TABLE 1

Change in viscosity average molecular weight ($\overline{M}_v$), gel content and density with the time of UV ageing of 0.05 mm thick polyethylene film

Time of UV ageing (h)	$\overline{M}_v$	Gel content (%)	Density ($\mathrm{g\ cm}^{-3}$)
0	19690	nil	0.9124
100	14500	35.5	0.9248
200	12700	30.3	0.9291
300	10900	28.5	0.9300
400	8600	32.8	0.9320

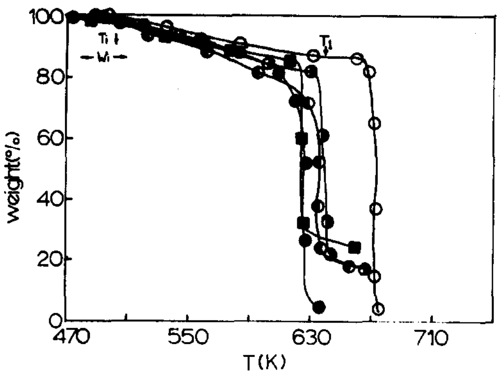

Fig. 4. TG curves of UV aged LDPE samples. ○, Unaged; ◑, 100 h; ◐, 200 h; ●, 300 h; ■, 400 h.

weight loss increases with the time of ageing.

Isothermal thermogravimetric curves also show the destabilization behaviour, as comparative weight loss with time is more in aged polyethylene samples than unaged ones (Fig. 5).

DSC thermograms show that the melt endotherm (T_m) peak does not shift much towards the lower temperature but the peak area increases with the UV ageing of 0.05 mm thick polyethylene film (Fig. 6). The increase in the area of the melt endotherm shows the increase in crystallinity of polyethylene with the ageing time. The bimodal form of the melt endotherm increases up to 100 h of UV ageing which on further ageing decreases, and a sharp melt endotherm has been observed which shifts slightly towards lower temperatures, indicating internal plasticization in polyethylene due to the formation of smaller chain fragments. The more ordered structure due to the

TABLE 2

Thermogravimetric data (TG and DTG) for aged and unaged polyethylene

Time of UV ageing, (h)	T_i(K)	T_l(K)	W_l(%)	T_{max}(K)
0	484	664	13	668
100	490.5	632	18	640
200	488	626	27	635
300	487	618	25	626
400	483	622	16	625

T_i = Initial temperature of weight loss.
T_l = Temperature where steep weight loss starts.
W_l = Weight loss from T_i to T_l.
T_{max} = Temperature at maximum rate of weight loss.

short molecular chains formed during UV ageing increases the crystallinity and density of polyethylene [16,21]. The broad exotherms at 503 and 565 K show the oxidative degradation in unaged polyethylene while their area

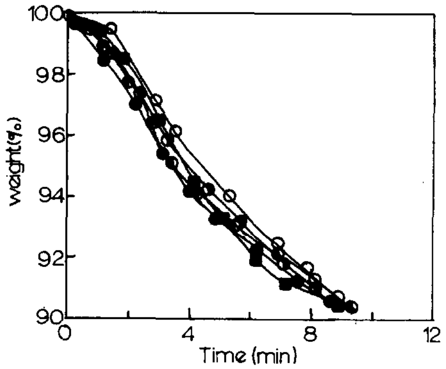

Fig. 5. Isothermal TG curves of UV aged samples at 505 K. O, Unaged; ◑, 100 h; ◐, 200 h; ●, 300 h; ■, 400 h.

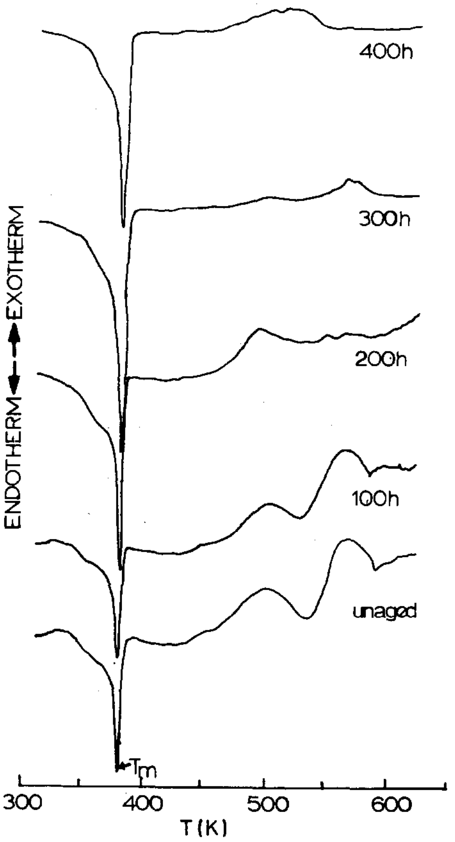

Fig. 6. DSC thermograms of UV aged LDPE film samples.

decreases with the time of UV ageing up to 300 h and a broad exotherm appears after 400 h of ageing, which shows that thermal stability decreases with the increase in photooxidative degradation of polyethylene.

This study can be helpful for making the polymeric material biodegradable by introducing carbonyl and other unstable groups, with the help of accelerated UV ageing, as these groups accelerate the degradability of polymers.

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