Thermo-oxidative degradation of isotactic polypropylene film: Structural changes and its correlation with properties

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Degradation of isotactic polypropylene has been studied by ageing the film samples at 70°, 80° and 90°C in air. Reactions involved in changing the molecular structure and formation of oxygenated and unsaturated groups, during thermo-oxidative degradation, are discussed. The increase in molecular weight ($\bar{M}_v$) suggests molecular enlargement mainly by recombination of alkyl and alkoxy radicals which produces non-radical products. Tensile strength has been found to increase initially and then decreases with ageing time. Increase in isotacticity and density of polypropylene may be due to the cleavage of the backbone chain in the amorphous intercrystalline region, facilitating poorly ordered molecular segments into a more ordered helical form.

Keywords Degradation; molecular structure; tensile strength; polypropylene; helical chain

INTRODUCTION

Polypropylene is susceptible to heat and light and, in the presence of oxygen, it undergoes thermo-oxidative and photo-oxidative degradation, which impairs some of its useful properties. The stability of polypropylene depends on trace amounts of impurities such as hydroperoxide, carbonyl and contaminations such as catalyst residues and metallic compounds[1-6]. A number of workers[2,3,7] have shown that the morphology of the molecules and the secondary bond forces in between them play an important role in the degradation of polypropylene. The radical mechanism of oxidative degradation of polypropylene and model compounds has been proposed by a few workers[1-4,8,9] and they have found that intramolecular hydrogen abstraction by peroxy radicals dominates over intermolecular abstraction due to the helical structure of polypropylene molecules and in this process various oxygenated groups, e.g. carbonyl and hydroperoxide are formed. Deterioration in physico–mechanical properties of polypropylene during thermo-oxidative degradation have also been studied by a few workers[2,10-12].

The present studies further investigate the changes in molecular structure and properties of polypropylene during thermo-oxidative degradation.

EXPERIMENTAL

Polypropylene resin was extruded in the form of 2 mil thick film for thermal ageing. Samples were aged at 70°, 80° and 90°C (±1°C) in an air oven for different time periods. The aged samples were kept in a dry and inert atmosphere at low temperature.

The spectra of the samples were recorded with a Perkin Elmer (model 577) infra-red spectrophotometer, to study the formation of oxygenated and unsaturated groups. Molecular weight ($\bar{M}_v$) was determined viscometrically at 135 ± 0.5°C in decalin. The Mark-Houwink equation was used with K and α values of 10×10^{-5} and 0.80 respectively[13]. Change in tensile strength was measured in an automatic tensile tester. Density measurements were done, using a methanol–water mixture. Isotacticity (Iso, %) was calculated by the equation[14,15]

$$\mathrm{Iso},\% = \left[1 - \frac{k-1}{0.853k - 0.113}\right] \times 100$$

where k is the optical density ratio ($D_{974\,\mathrm{cm}^{-1}}/D_{995\,\mathrm{cm}^{-1}}$).

RESULTS AND DISCUSSION

Infra-red spectra of unaged polypropylene film shows small bands in the 1800–1570 cm^{-1} region due to trace amounts of oxygenated and unsaturated groups and the intensity of the bands in this region changes with ageing time due to increase in concentration of these groups (*Figure 1*). Small change in intensity in the 3600–3300 cm^{-1} region has been observed with the time of ageing at 90°C due to the formation of hydroperoxide groups (*Figure 1*). Another small band has been observed at 888 cm^{-1} in the spectra of thermally aged polypropylene due to the formation of terminal vinyl groups. $\bar{M}_v$ has been found to increase slowly by 19.8% after 1200 h of ageing at 70°C, while at 80°C it increases by 43.6% after 720 h and then drifts slightly towards lower molecular weight and on further ageing it increases rapidly up to 1500 h by 188%. On ageing at 90°C, $\bar{M}_v$ increases up to 720 h and then decreases by 27% from the original value after 1500 h. The tensile strength of samples increases by 12.5% up to 600 h and then decreases at 70°C, while at 80°C it increases up to 84.5% after 300 h and on further ageing it decreases (*Figure 2*). The change in tensile strength of polypropylene on ageing at 90°C is different than that at 70°C and 80°C. On ageing the sample at 90°C, the tensile strength increases up to 81% after 300 h and then remains the same up to 1000 h. On further ageing it decreases slightly. The

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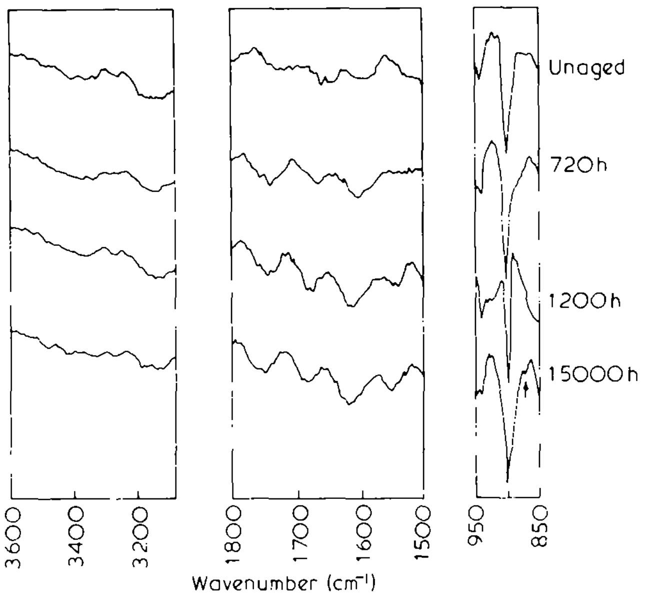


Figure 1 Change in the infra-red spectra of polypropylene film during ageing at 90°C

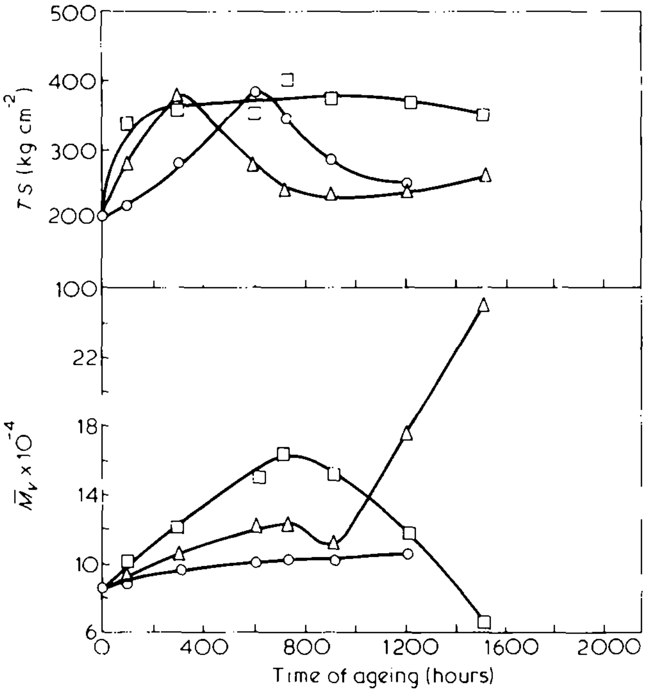
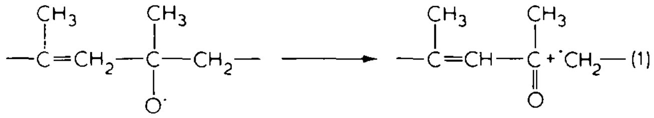


Figure 2 Change in viscosity average molecular weight ($\bar{M}_v$) and tensile strength (*TS*) of polypropylene with respect to time of ageing: ○, 70°C; △, 80°C; □, 90°C

shifting of the optima of tensile strength increase has been found to be inversely proportional to the temperature (*Figure 2*). An increase in density and iso-tacticity has been found with time and temperature of ageing of polypropylene (*Figure 3*).

The results of thermal ageing of polypropylene can be interpreted to correlate the structural changes with the properties during thermo-oxidative degradation. The preferential oxidation in isotactic polypropylene takes place in the amorphous region (low ordered region)[1-4]. Carlsson and Wiles[1] have stated that in primary process of oxidative degradation alkyl (R$^\cdot$) and peroxy (ROO$^\cdot$) radicals are formed where peroxy radical is formed by oxygen attack on the alkyl radical. The peroxy radicals may further abstract hydrogen atoms inter- or intramolecularly from the molecular chain preferably from tertiary C–H sites. The favourable geometric location (helical structure) of tertiary C–H sites helps the intramolecular hydrogen abstraction[1,4,16]. Chien *et al.*[16] have reported the sequence of tertiary hydroperoxy groups formed, which exist only in the hydrogen bonded form with each other or with carbonyl groups by their decomposition. The appearance of a small band at 3400 cm^{-1} shows the formation of hydroperoxide groups as reaction intermediates. Intramolecular hydrogen abstraction has also been observed in the oxidation studies of squalane[9]. Tertiary free and isolated hydroperoxide groups are very unstable, so they do not exist even at room temperature[1,16]. The possibility of the existence of isolated hydrogen bonded hydroperoxide groups is also remote. Such groups are mainly formed by intermolecular hydrogen abstraction at the peroxy radical site[1].

The degradation reaction may further propagate by the hydroperoxide group decomposition (O–O bond scission). The alkoxy radical, so formed, then plays a major role in thermo-oxidative degradation[1,4,9,10]. It has been reported that chain scission mainly takes place by β-scission reaction of macroalkoxy radical which results in the formation of carbonyl (1800–1650 cm^{-1}) and unsaturated (888 cm^{-1}, 1650–1570 cm^{-1}) groups (*Figure 1*). The appearance of a band at 1685 cm^{-1} may be due to the formation of α, β unsaturated ketonic groups (reaction 1).



$$-\overset{CH_3}{\overset{|}{C}}=CH_2-\underset{O^\cdot}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2- \longrightarrow -\overset{CH_3}{\overset{|}{C}}=CH-\underset{O}{\underset{\|}{\overset{CH_3}{\overset{|}{C}}}}+{}^\cdot CH_2- \quad (1)$$

Small bands at 1780, 1785, 1710 and 1745 cm^{-1} in carbonyl region of i.r. spectra (*Figure 1*) of the aged polypropylene sample may be due to the formation of γ-lactone, peracidic, carboxylic, and ester groups. The

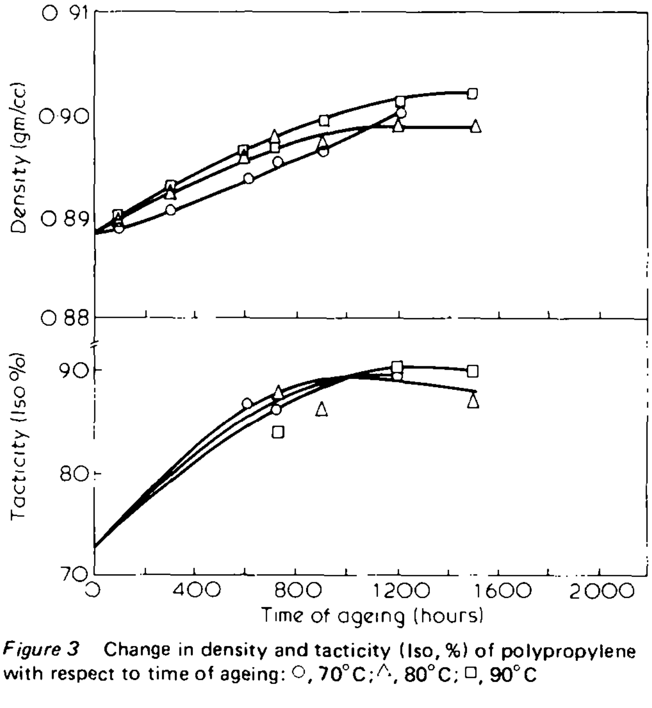
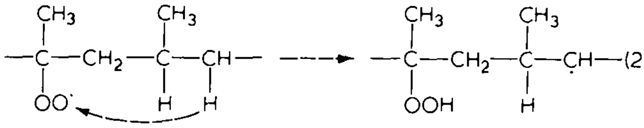


Figure 3 Change in density and tacticity (Iso, %) of polypropylene with respect to time of ageing: ○, 70°C; △, 80°C; □, 90°C

formation of these groups is initiated by reaction 2[17]. Adams[17] has reported that hydrogen atom abstraction by peroxy radical from secondary C–H site may also take place as in solid phase oxidation, H atom abstraction depends on its accessibility then C–H bond energy[4].



$$-\overset{CH_3}{\underset{OO^\bullet}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-\underset{H}{CH}- \longrightarrow -\overset{CH_3}{\underset{OOH}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-\underset{\cdot}{CH}- \qquad (2)$$

Reaction 2 may propagate at a faster rate due to oxygen attack at the free radical site. The termination reaction mainly effects the ultimate properties of polymer and macroalkoxy radical plays a central role in the deterioration of properties of polyolefins[1]. The continuous increase in $\bar{M}_v$ at 70°, 80°C and up to 720 h at 90°C shows that macroradical recombination takes place which may result in inactive product formation. It has been reported[3,4] that rigidity of matrix prevents the diffusion of alkoxy mcaroradicals (RO$^\bullet$) and cage recombination is expected to be the dominant process with the accessible radical (RO$^\bullet$). Boss and Chien[8] have reported that mainly alkyl (R$^\bullet$) and hydroperoxy (ROO$^\bullet$) radicals recombine by cage formation to form inactive products because oxygen saturation cannot be maintained in the solid phase. Long chain ester formation may also effect the increase in $\bar{M}_v$ of polypropylene[3]. $\bar{M}_v$ decreases at 90°C after 720 h, probably due to the faster rate of chain scission. Density and isotactic content increase (*Figure 3*) indicates that molecular ordering is taking place during thermo-oxidative degradation. The optical density (OD) ratio of the 974 and the 995 cm^{-1} bands in the i.r. spectra of unaged polypropylene indicates a helical content of 72.7%. Cleavage of the polymer backbone in amorphous intercrystalline region facilitates the relaxation of any non-helical poorly ordered molecular segments into the preferred helical form with the corresponding increase in local order and density[1,18]. The increase in crystallinity (Iso, % and density) and $\bar{M}_v$ at the same time could be explained by the fact that a considerable number of low molecular weight chains are formed which may attain more ordered form in the matrix[19,20]. The increase in tensile strength during ageing may be due to higher ordering in amorphous region and recombination of alkyl radical in ordered form while faster rate of chain scission decreases its value. The increase in oxygenated groups (polar groups) formation may also help in increasing the density (chemicrystallization) of polypropylene.

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