

THE FTIR STUDIES OF PHOTO-OXIDATIVE DEGRADATION OF POLYPROPYLENE

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ABSTRACT

The photo-oxidative degradation process of polypropylene film containing iron ions was investigated via FTIR and absorbance subtraction technique. It is shown that the iron ions play an important role in the decomposition of hydroperoxide and the increase of the degradation rate of polypropylene film. The amorphous region of PP film undergoes degradation prior to the crystalline one.

Extensive efforts have been made to investigate the photooxidative degradation of polypropylene^[1], but only a little attention has been paid to the study of the action of metal ions in polypropylene degradation. We have developed the controllable-degradation polypropylene film for agricultural purpose by using iron ions as sensitizer. Polypropylene film could be completely degraded into fine powder within certain period.

The FTIR is a powerful tool for studying polymer structure changes in the degradation process. With the help of on-line data processing techniques, one can obtain a great deal of useful information from it^[2]. In this work, the FTIR was used as a monitor to detect the structural changes of polypropylene during the degradation and to understand better the degradation mechanism of polypropylene in the presence of iron ions.

EXPERIMENTAL

1, Sample preparation

The isotactic polypropylene power was blended with iron stearate of 0.5% in weight and was pressed into film at 180°C in one minute. The film without iron stearate was prepared in the same way. The thickness of the film is about 70 μ . The isotactic polypropylene was supplied by Liaoyang Chemical Company. The iron stearate was synthesized by the method recommended in reference [3]. The melting point of the compound is 90.4°C.

2, Photo-oxidation of the film

The prepared film was put into a photo-oxidation instrument and underwent degradation at 50 + 1°C. The light source is a high pressure mercury lamp. The UV light shorter than 2900Å was filtered out via a glass cover. The film was radiated at preset time and taken out for FTIR measurement.

3, FTIR measurement

The FTIR instrument is a BRUKER IFS-113V vacuum type with MCT detector. The environment interference was essentially eliminated. The spectra were 64 scans to gain a high signal to noise ratio. The spectrum resolution was set at 2cm⁻¹. Scan velocity was 0.47cm/s. The spectra obtained were stored on disc and processed by the software on the computer.

RESULTS AND DISCUSSION

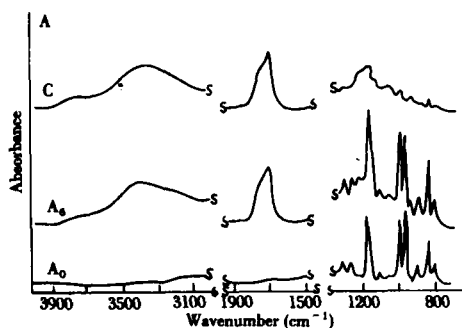


Fig.1 The subtraction spectrum of polypropylene film after photo-oxidation.

A_0 is the spectrum before photo-oxidation. A_6 is the one after 25hr photo-oxidation. C is the difference spectrum between A_0 and A_6 .

Fig 1 shows the spectrum changes before and after 25h of the photo-oxidation. Spectrum A_0 is the unphoto-oxidized film, A_6 is the one of photo-oxidized, and C is the difference between A_6 and A_0 . One can clearly see that there are bands in three regions on the spectrum which have been changed. At the range from 3600cm^{-1} to 3100cm^{-1} , it appeared a wide peak which is due to the hydrogen-bonded hydroperoxide. The new bands, in the range from 1850cm^{-1} to 1600cm^{-1} , are the carbonyl group. There is a rising of the spectrum background in the 1300cm^{-1} to 700cm^{-1} region. The carbonyl group appearing during degradation is very useful to characterize the mechanism of polypropylene degradation. Adams^[4] has used base and acid to convert the carbonyls to other compounds and assigned them in detail. The rising of the background is attributed to the absorption of those degraded polypropylene products which are difficult to be analysed.

There is another interesting change on the spectrum. The 998cm^{-1} and the 973cm^{-1} bands behave different during photo-oxidation, although both of them are conformational regular bands. The former represents longer helix chain segment which can be usually used to measure the crystallinity of polypropylene, the latter represents the shorter helix chain segment and has no relation to the crystallinity^[5]. It has usually been used as an internal reference band of thickness of film. One can see from spectrum A_6 that the 998cm^{-1} band increased intensity after 25h photo-

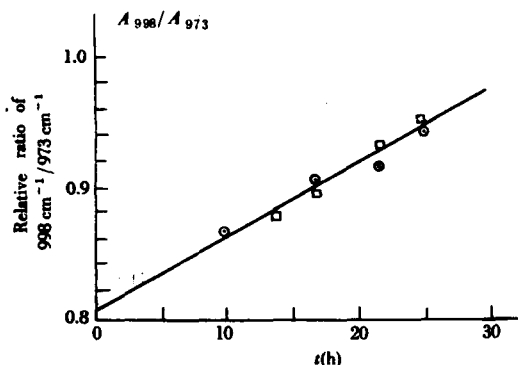


Fig 2 The relative ratio of $998\text{cm}^{-1}/973\text{cm}^{-1}$ changes with the increase of photo-oxidation time.

○ film having iron stearate 0.5% in weight. □ film without iron stearate.

oxidation. Fig 2 shows the $998\text{cm}^{-1}/973\text{cm}^{-1}$ relative intensity ratio changes with the increase of photo-oxidation.

It might be considered that the crystalline part of polypropylene increased relatively after photo-oxidation and that the photo-oxidation is prior to taking place in amorphous area as in the case of photo-oxidation of polyethylene^[6]. The increase of conformational regular band can be attributed to oxidative crystallization arising from scission of the constrained chains in amorphous region and to the chemicrystallization in the replacement of nonpolar group such as $>\text{C}=\text{O}$, $-\text{COOH}$. Actually, there is no increase in crystallinity as such, but rather the ratio of crystalline part to unoxidized amorphous one increased.

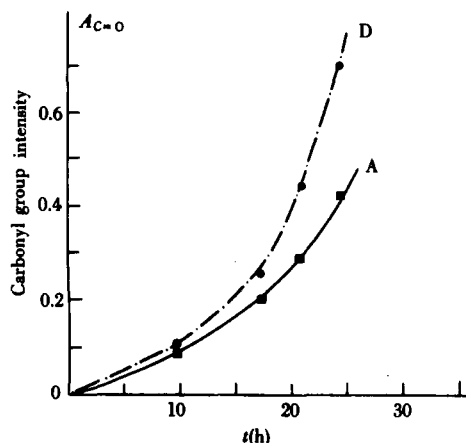
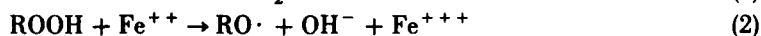
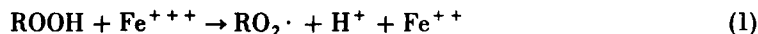


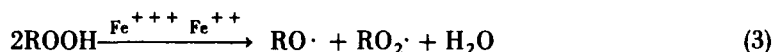
Fig 3 The carbonyl intensity increases with photo-oxidation time.

A, the film without iron stearate. D, the film containing iron stearate 0.5% in weight.

Fig 3 indicates the different changes of carbonyl groups with the increase of the degradation time between the film having the iron ions and the one without. It is evident that the presence of a few iron ions accelerates the degradation of polypropylene. The iron ions play an role of catalyst in photo-oxidation. The catalytic effects of metal ions are catalogued into two kinds. One kind is as sensitizer, the other is as stabilizer for photo-oxidation degradation of polyolefin depending on their ions nature. Many heavy metal ions having three valency states such as cobalt, manganese, chromium and iron, can accelerate the degradation process. However PbO , ZnO metal oxides stabilize the photo-oxidation degradation. The iron ions are believed to be sensitizer in photo-oxidation reaction. The catalytic action of iron ions in the degradation of polypropylene film might be interpreted as that, since the iron ions have relatively higher oxidation-reduction potential^[7], it would be expected to participate more readily in the following reaction to cause hydroperoxide to be decomposed into two radicals:



the overall reaction



the radicals are believed further to undergo β -scission reaction.

This assumption can be supported by comparing the relative ratio of carbonyl group to hydroperoxide one in two specimens. The relative band intensity of these two groups is a good

indicator of the relative concentration of these two groups in the film. The process of hydroperoxide decomposition into small molecular carbonyl compounds can be monitored by this ratio. Listed in Table 1 are the relative values for two specimens after 25h photo-oxidation at the same experimental condition. The specimen containing iron ions has a higher value than the one without. This means that much more hydroperoxide has been decomposed into small carbonyl compounds in sample D.

Table 1 The relative ratio of the carbonyl group to the hydroperoxide one in the film with or without iron ions after 25h photo-oxidation

	A(C=O)	A(OH)	A(C=O) / A(OH)
A 25h	0.42	0.32	1.3
D 25h	0.69	0.38	1.8

From the above discussion, one can conclude that the photo-oxidation of polypropylene can be accelerated by iron stearate. By using different content of iron in the film it would be possible to obtain controllable-degradation film. The amorphous of polypropylene film undergoes degradation prior to the crystalline one.

Keywords:

Polypropylene, photo-oxidation, FTIR.

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