Degradation of Polyethylene Containing Ferric Salt and Starch

Jianping Gao*, Shaomin Wang, Jiugao Yu, Tong Lin, Xiaodong Wang
Tianjin University, Tianjin 300072, P.R.China

SUMMARY: The degradation of polyethylene containing four different ferric salts was compared, using remaining percentage elongation at break as a parameter; and the degradation process was also evaluated with carbonyl index, or with the formation and concentration of hydroperoxide groups. Starch can act as a synergist during the photodegradation of ferric contained PE film. X-ray photoelectroscopy analysis shows that part of ferric ions turned into ferrous ions during the degradation process because of the redox reaction of ferric ions with oxygen. When stabilizer was added, the changes from ferric ions to ferrous ions decreased. If the PE samples were exposed to high pressure mercury lamp in the atmosphere of nitrogen gas, the absorption peaks of carbonyl group was not found in IR spectra after several days exposure.

Keywords, Polyethylene, degradation, starch, ferric ions, synergism

Introduction

Interest in degradable plastics has been increasing enormously as a result of the increasing volume discarded plastics litter, and the decreasing landfill capacity for disposing of it. This bring about a pressure for the development of degradable plastics. Photodegradation is the process by which UV photosensitizer absorbs sunlight to cause the reduction in the molecular weight of polymer materials so that plastics articles become brittle and disintegrate. The photodegradable polymers and their degradability have been studied in the last two decades[1-2], and the results were reviewed or summarized in books[3-6]. Thus far, the application of photodegradable plastics is limited to agricultural mulch, beverage can loop and plastics bag [7].

Polysaccharides , such as starch and chitosan, are biodegradable natural polymers. A major approach has been starch-filled polymers. The starch biodegrades relatively rapid but leaves biodisintegrated PE that biodegrades very slowly[8-11] . Some approaches for the improvement has been investigated, including the incorporation of UV photosensitizers in the starch plastics. In this system, photodegradation and biodegradation mutually stimulate during the degradation process[12].

Experimental

Preparation of UV sensitizers

ferric salt, including iron stearate(S), octanoyl ferrocene(O), ferric triacetylacetonate(T) and ferric tris-dibutyl carbamodit-hioate (D) were prepared in the lab[13].

Carbonyl index and hydroperoxide group

 CCC 1022-1360/99/$ 17.50+.50/0

Carbonyl index of the degraded polymer film was determined with Nicolet 50X FTIR, and the concentration of hydroperoxide group formed during the degradation process was analyzed with iodometric potentiometric titration.

Results and discussion

Comparation of different ferric salts in the degradation of polymer filmsAdding transition metallic ions with high valence such as ferric salts in polyethylene can initiate PE film to degrade in environments, especially under the sun. Using remainingpercentage elongation at break (RP)as a parameter, the photo-degradation levels of PE films with different ferric salts, including iron stearate(S), octanoyl ferrocene(O), ferric triacetylacetonate(T) and ferric tris-dibutyl carbamodithioate(D), were compared; and the results show that the degradation of PE film, as shown in figure 1, is in the decreasing order: T > O > S >D . The control sample does not show any apparent change in RP at the same conditions.

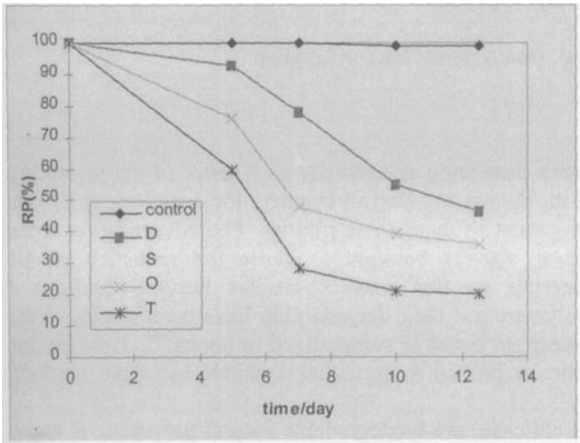

Figure 1 Degradation of PE with different ferric salts

The photo-degradation of PE film was also evaluated with carbonyl index (determined by IR technique). As the degradation reaction went in simulating environment, the carbonyl index increased steadily as shown in figure 2, because hydroperoxide group was formed during the photo-degradation and its' concentration became higher and higher in the first degradation stage(see figure 3).

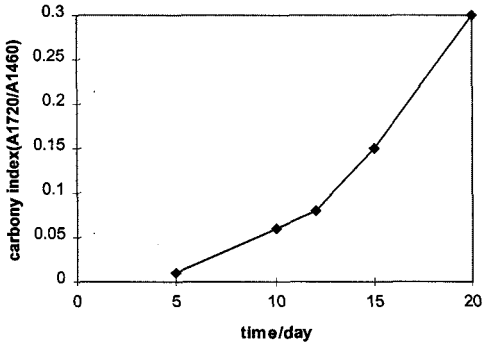

Figure 2 Changes in carbonyl index during the degradation

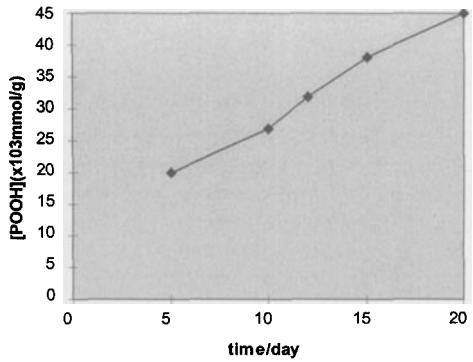

Figure 3 The formation of hydroperoxide groups

The synergism effect of starch on the degradation when starch was added into the ferric ion containing PE film, the degradation level of the film increased obviously as starch content was raised(see figure 4). The added starch granules can act as weak points on the PE film, especially in the interfacial areas, which can cause physical degradation of the PE film. Besides, starch has numerous hydroxide groups on the chains, these functional groups can cause the transfer of free radicals and form free radicals on the starch backbone. It is these free radicals that cause the further degradation of PE, and this the exact reason why transition metal ions with high valency , such as Ce^{4+} , Fe^{3+}/H_2O_2 or Mn^{7+} , were widely used to initiate the graft copolymerization of starch with various vinyl monomers[14].

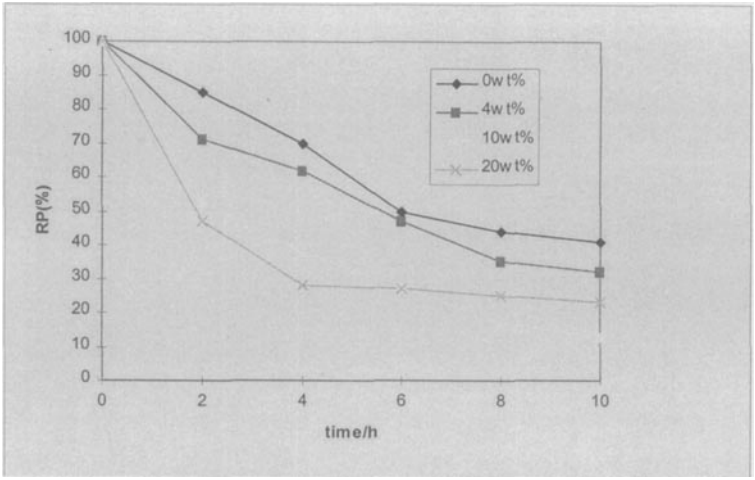

Figure 4 synergism effect of starch on the degradation

Using X-ray photoelectroscopy(XPS), the valency change of ferric ion in tris-dibutyl carbamodithioate was analyzed, the spectra of the samples (before and after photo-reaction)in figure 5 show that ferric peak became weak, while ferrous absorption turn strong, this means that part of ferric ions have changed into ferrous ion. When stabilizer was mixed with the ferric salt , we got the similar spectrum(not given) except that the peak height of the Fe^{2+} is lower than that without stabilizer (figure 5) at the same conditions . This means that the reaction from Fe^{3+} to Fe^{2+} slowed down.

The XPS spectra of the PE film, containing tris-dibutyl carbamodithioate, indicated that oxygen peak became sharp and strong after photo-degradation. Meanwhile, the oxygen peak of the film side exposed to the high pressure mercury lamp was more strong than that of the opposite side.

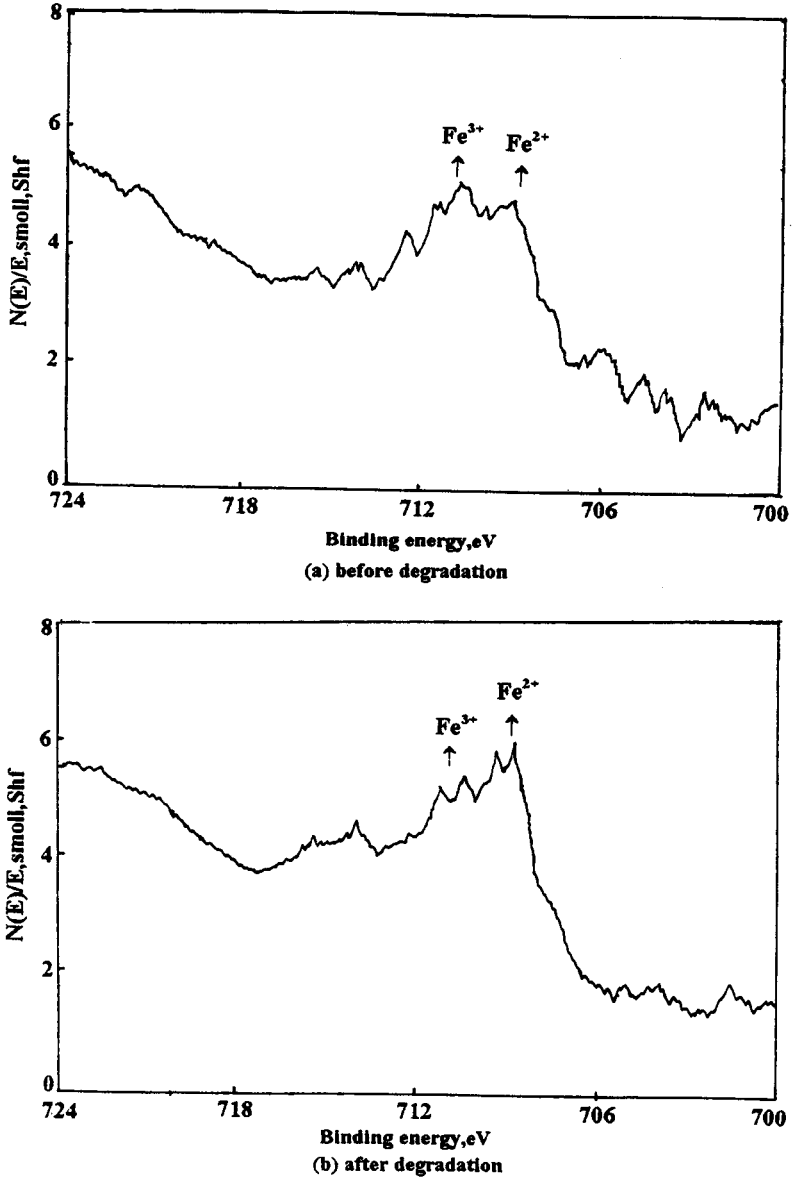

Figure 5 XPS spectra of the 2P orbit of iron element

The degradation of PE film exposed to air and nitrogen gas was compared, the results in figure 6 show that the IR spectrum of the degraded PE film in N2 atmosphere do not display the absorption peak corresponding to carbonyl group, which symbolize the degradation.

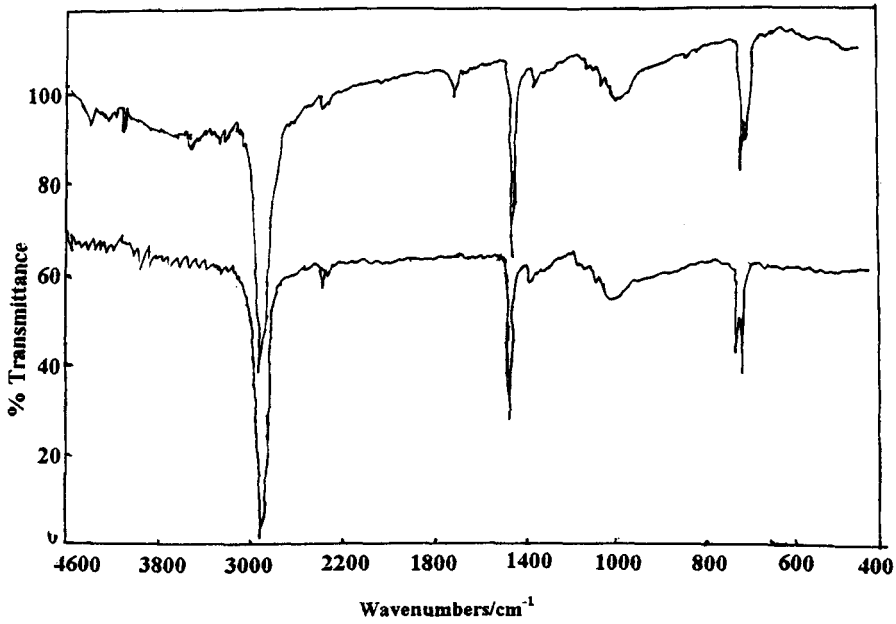

Figure6 IR spectra of the degraded samples in air(a) and N_2 gas atmosphere(b)

Conclusion

Ferric salt can cause the photo-degradation of PE film exposed to the highpressure Hg lump, but the degradation level depends on the structure of the salts and degradation conditions. Starch acts as synegist in the photodegradation because it contains nomerous -OH groups. Ferric ions turn into ferrous ions during the degradation; at the same time, hydroperoxide groups are formed. Stabalizer affects this change, so it can controll the degradation.

References

1) L.Jacques, A.Rene. Plast.Eng.,29,139(1995)
2) G.Yanai,A.Ram, J.Appl.Polym.Sci.,59(7),1145(1996)
3) F.Christa, Int.J.Mater.Prod.Technol.,9(4-6),482(1994)
4) B.Ranby, Photodegradable, Photo-oxidation and Photostabilization, Wiley Interscience, New York,1975
5) A.C. Albertsson, Degradable Polymers, Recycling, and Plastics Waste Management, M.Dekker, New York,1995

6) G.Scott, Degradable Polymer: Principles and Application, Chapman & Hall, London, 1995
7) P.P.Klemdauk, Polym.Degrad.Stab.,29,183(1990)
8) J.L.Willett, J.Appl.Polym.Sci.,54,1685(1994)
9) R.L.Shogren, Starch,4,276(1993)
10) J.P.Gao, R.C.Tian, J.Appl.Polym.Sci.,(1995)
11) W.M.Doane, Starch,44,293(1992)
12) B.S.Yoon, S.H.Lee, J.Appl.Polym.Sci.,60(10),1677(1996)
13) J.P.Gao, J.G.Yu, Chem. Indus. & Eng., 12(6), 26(1998)
14) J.P.Gao, J.G.Yu, W.Wang, J.Macromol.Sci.,A35(3),483(1998)