Accelerated and Environmental Weathering Studies on Polyethylene–Starch Blend Films

P. KRISHNA SASTRY,* D. SATYANARAYANA,[†] D. V. MOHAN RAO

Organic Coatings & Polymer Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India

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ABSTRACT: Biodegradable polymers are desirable for a variety of applications, such as in packaging, agriculture, and medicine. Polyethylene (PE) blended with starch is already found to be a potential candidate to replace nondegradable thermoplastics in the areas of packaging. Films of polyethylene (PE)—starch blends with and without vegetable oil as a compatibilizer were prepared. The degradation of the films under thermooxidative treatment, ultraviolet light exposure, high temperature, high humidity, and natural ambience (soil burial) were monitored. It is seen that vegetable oil as an additive has a dual role: as a plasticizer, it improves the film quality; as a prooxidant, it accelerates degradation of the film. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2251–2257, 1998

Key words: biodegradable; polyethylene-starch; vegetable oil; prooxidant

INTRODUCTION

The organic matter in municipal waste is systematically fragmented by microorganisms into CO_2 , H_2O , NH_3 or similar low-molecular-weight compounds, imparting fertility to the soil. The plastic component is resistant to microbial attack and, hence, accumulates. The plastic waste can neither add to the fertility of the soil nor improve its firmness in landfill operations.

Many solutions have been proposed¹ for soil waste management of plastics, like recycling, incineration, landfill disposal, and degradable plastics. Recycling will not yield quality products due to the heterogeneous nature of the plastics. Incineration of plastics will release toxic gases and vapors, which could prove to be a serious health hazard. Use of plastic in landfill operations is least preferred because of space constraints.

It is increasingly felt that the best alternative would be making the plastics degradable. Natural polymers, such as starch and proteins, are biodegradable, whereas most synthetic polymers are not as the organisms lack the necessary enzymes for the transformation of these materials to metabolic intermediates. Hence, the effort is towards imparting biodegradability to synthetic polymers. The progress made in the synthesis of biodegradable polymers has been reviewed by several others.^{2–5}

Low-molecular-weight plastic additives like plasticizers and fillers are usually susceptible to microbial attack. This leads to physical embrittlement of the polymer, leaving a porous and mechanically weakened polymer. The microbes, in turn, release nonspecific oxidative enzymes that could attack the synthetic polymer. Also, the gradual degradation of the natural polymer leads to increased surface area by erosion and pitting. This will accelerate the degradation of the synthetic polymer by diffusion of O_2 , moisture, and enzymes into the porous polymer matrix.

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Correspondence to: D. V. Mohan Rao.

 $[\]ast$ Present address: Bureau of Police (R&D), Hyderabad, India.

[†] Present address: R & D Bakelite Hylam Ltd., Hyderabad, India.

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S.No.	Code Name	Compositional Details
1	TSM-5	PE, 5% starch
2	TSM-10	PE, 10% starch
3	TSC-10	PE, 10% starch
4	TSC-VO-10	PE, 10% starch and 0.1% sunflower oil
5	CF (control film)	PE

Table I Coding of Different Samples

Polyethylene (PE)–starch composites come under this category.⁶⁻¹² These are mixtures of a readily degradable starch component within a PE matrix. The starch content could be as high as 50% by weight. Poly(vinyl chloride) compositions filled with starch¹³ or with starch graft copolymers¹⁴ are also readily attacked by microorganisms.

An extensive search of potential biodegradable fillers for thermoplastics has disclosed that only raw starch satisfies the requirements for adequate thermal stability and minimum interference with melt flow properties and product quality.⁶ The use of starch as a filler in plastics has been of interest for the past 30 years because it is available at low cost and in abundance.

EXPERIMENTAL

Industrial grade starch was purchased from Laxmi Starch Company, Hyderabad and LDPE granules from IPCL, Gujarat. Low-density polyethylene (LDPE) films containing 5 and 10% starch with or without vegetable oil were fabricated in a Windsor blow film extrusion machine at Hindli Industries, Hyderabad. These films were coded as in Table I. TSM-5 and TSM-10 were prepared by mixing starch with PE mechanically for 1 h. TSC-10 films were fabricated from a compounded mixture of starch and PE. TSC-VO-10 films were made from a compounded mixture of starch, PE, and 0.1% of sunflower oil.^{8,15,16} Compounding in the cases of TSC-10 and TSC-VO-10 and extrusion of all the films were carried out at 120°C.

The starch content of test samples (TSM-5, TSM-10, TSC-10, and TSC-VO-10) was determined spectrophotochemically by the phenol sulphuric acid color reaction developed by Duboi et al.¹⁷

DEGRADATION STUDIES

Thermooxidative Degradation

Strips of test samples of 10×2 cm were cut along the extrusion axis and placed in an air oven at 70°C. The extent of degradation after 1, 2, 3, and 4 weeks was monitored.^{18,19}

High-Temperature, High-Humidity Treatment

Strips of test samples of 10×2 cm were cut in the machine direction and placed in a steam chamber. The samples were taken out at the end of 2, 4, 6, and 8 days, washed with 70% ethanol, and dried at room temperature before assessing the progress of degradation.

Ultraviolet Light Treatment

Ultraviolet (UV) lamps of long wavelength (~ 400 nm) were used to evaluate the photodegradability of the test samples (TSM-5, TSM-10, TSC-10, and TSC-VO-10). Films of 10×2 cm were cut and placed in a closed wooden box of $65 \times 30 \times 30$ cm size at a distance of 20 cm from the lamps. The films were removed after 1, 2, 4, and 7 weeks. The films were turned every other day to ensure even exposure.^{18,19}

Environmental Degradation

Strips of test samples of 10×2 cm were cut along the extrusion axis and buried in soil. The films were taken out after 15, 30, and 45 days, washed with 70% ethanol, and dried at room temperature.²⁰

EVALUATION OF DEGRADATION

Scanning Electron Microscopy

Test samples were examined with 5520 Hitachi model Scanning Electron Microscope. The films were gold-coated in the usual manner prior to examination of optical micrographs. The optical micrographs of the films were taken in polyvar wide-field photomicroscope from Richet Jong Australia, Type 300 002.

FTIR

The extent of PE oxidation was monitored by measuring the levels of keto carbonyl (1713 cm⁻¹) absorption by Fourier transform infrared (FTIR) spectroscopy. Absorbency at a given wave number was measured with a Nicolet FTIR. PE films subjected to various models of degradative treatment were mounted on standard FTIR sample plates. Carbonyl Index (CI) was calculated from following equation:

$$CI = \frac{absorption at 1713 cm^{-1}}{absorption at 1465 cm^{-1}}$$

CI was used as an index to monitor the extent of PE oxidation. 16,21

MECHANICAL PROPERTIES

Tensile strength and the percentage of elongation were determined on a Instron model 1026 Universal Testing Machine, which was operated at a speed of 2 cm/min with a 5 cm gauge length equipped with 5 kg load cell.

RESULTS AND DISCUSSION

Starch and PE are thermodynamically incompatible, which precludes generating a truly homogeneous blend through simple mixing. This is very explicit from the nature of films (TSM-5 and TSM-10) obtained by extruding simple mixtures of the two. Desired degree of dispersion of starch could not be achieved. Consequently, the films TSM-5 and TSM-10 were poor in clarity, and large-scale stratification could be observed, even with naked eye. The poor dispersion and adhesion resulted in inferior mechanical properties.

Melt blending, the second approach to a homogeneous blend, did bring in lot of improvements. Even though the distribution of starch in the PE matrix was uniform, the main problem here was that the granules lost their smooth spherical shape and got distorted. One possibility is the moisture content in the starch, which was not



Figure 1 SEM photographs of (1) TSM-5, (2) TSM-10, (3) TSC-10, and (4) TSC-VO-10.

predried, which makes it sensitive to thermomechanical shear.

It has been well established that the dispersion of one polymer in another and mutual adhesion can be promoted by adding compatibilizers. Compatibilizers are mediator molecules, which can interact equally well with both components. These could be small molecules or even block or graft copolymers of the component polymers. For example, the PE-polystyrene (PS) blend performs very poorly, but addition of a small amount $(\sim 1\%)$ of a PE-block-PS coerces the blend to behave as a single material with a single glass transition temperature (T_g) . The general view is that a properly chosen compatibilizer preferentially locates itself at the interface and reduces the interfacial energy between the phases, permits finer dispersion during blending, and improves interfacial adhesion.

Our attempts to improve the dispersion of starch in the PE matrix by adding vegetable oil falls into this category. The vegetable oil also acts as an autooxidant to promote oxidative degradation of the poly(olefin) according to Griffin.²² Figure 1 presents a comparative compilation of the scanning electron microscopy (SEM) photographs of the different samples at uniform magnification.

DEGRADATION STUDIES

PE-starch polymers are susceptible to three main types of degradation: chemical, photo, and biolog-



Figure 2 Percentage elongation versus time (thermooxidative degradation).

ical. Chemical degradation occurs when the oxidants like transition metals or vegetable oils catalyze the formation of free radicals in PE, which react with O_2 to enhance the deterioration of the PE matrix.²¹ Heat and O_2 accelerate this chain scission of the PE.²³ UV light induces photodegradation within the PE matrix by generation of free radicals.^{20,24,25} Biological degradation of these PE films has been reported in a pure culture medium with streptomyces species after chemical degradation was initiated.^{18,26,27} Preirradiated samples biodegraded faster than nonirradiated samples.²⁸

In the laboratory, we monitored the degradation of (PE-starch) films under the following four different conditions:

- thermooxidative treatment,
- UV light exposure,
- high temperature and high humidity, and
- natural ambience (soil burial).

In all the experiments along with test samples, we included the control film (CF) as a control for comparative evaluation.

THERMOOXIDATIVE DEGRADATION

These studies were conducted in an air oven maintained at 70°C for a total span of 4 weeks. Weekly assessment of the mechanical properties and CI were carried out. Figures 2 and 3 show the variations in percentage elongation and the tensile strength with time. Initially, there is great disparity in the initial values of the percentage



Figure 3 Tensile strength versus time (thermooxidative degradation).

elongation of untreated films. They could be ranked as CF > TSC-VO-10 > TSC-10.

The deterioration of the samples is not so dramatic. The extent of loss in elastic properties suffered by the materials is in the following order: TSC-VO-10 > TSC-10 > CF.

The variation of tensile strength with time, however, shows fluctuations. We are not sure at this stage whether these are real or artifacts of experiments. Hence, we consider only the general trend for discussion.

All the films show deterioration in tensile strength with increased periods of oven treatment. However, the decrease in TSC-10 and CF films was lesser than TSC-VO-10 films in 4 weeks.

To summarize, TSC-VO-10 films suffered greater deterioration in mechanical properties than CF and TSC-10 films.

HIGH-TEMPERATURE, HIGH-HUMIDITY TREATMENT

The films were subjected to high-temperature, high-humidity treatment for 8 days. In this case,



Figure 4 Percentage elongation versus time (high-temperature, high-humidity treatment).



Figure 5 Tensile strength (high-temperature, high-humidity treatment).

the mechanical properties were assessed for every 2 days. Figures 4 and 5 show the variation in percentage of elongation and tensile strength with time.

All the films registered a decrease in their percentage elongation to varying extents, and CF suffered the minimum loss. In this context, the films could be ranked as follows: TSC-VO-10 \geq TSC-10 > CF. Likewise, there was corresponding loss in the tensile strength of the films. Disregarding the minor fluctuations, the films deteriorated in the following order: TSC-VO-10 > TSC-10 > CF.

UV TREATMENT

UV light treatment spanned 4 weeks. Weekly assessment of the mechanical properties was carried out. Figures 6 and 7 show the variation in the percentage of elongation and tensile strength with time.



Figure 6 Percentage elongation versus time (UV treatment).



Figure 7 Tensile strength versus time (UV treatment).

Though individual values vary, in terms of percentage variation, here again, we observe the same trend. TSC-VO-10 films are more sensitive to UV light than CF and TSC-10 films.

ENVIRONMENTAL DEGRADATION

Several samples of all the films were buried in the soil for 45 days. Assessment of the mechanical properties was carried out every 15 days. Figures 8 and 9 show the variations in the percentage elongation and tensile strength with time.

TSC-VO-1 films suffered more deterioration in their elastic response than TSC-10 and CF films. The percentage of elongation of TSC-VO-10 films decreased to a large extent in the first 30 days, and, thereafter, the decrease is steady.

TSC-10 and CF films were more resistant to environmental degradation. The percentage elongation recorded at the end of the fourth week was



Figure 8 Percentage elongation versus time (environmental degradation).



Figure 9 Tensile strength versus time (environmental degradation).



Figure 11 Carbonyl index versus time (thermooxidative treatment).

reduced to 20% of the initial value. The tensile strength of all the films decreased steadily.

Figure 10 shows the SEM of the samples TSC-10 (1-4) & TSC-VO-10 (5-8) at various stages of degradation. The micrographs are specially focused on the starch granules. In all cases, thermooxidative treatment seems to cause more drastic damage than either the high-temperature,

high-humidity treatment, or soil burial. This could be due to dry heat during thermooxidative treatment, which distorts the starch granules and ruptures them, while in the high humidity treatment the granules are dissolved away. During the soil burial, the process of degradation is also slow and smooth.

Figure 11 displays the CI value as a function of



Figure 10 SEM photographs of (1-4) TSC-10 (5-8) TSC-VO-10 at various stages of degradation: (A) untreated; (B) thermooxidation; (C) high-temperature, high-humidity (8 days); (D) soil burial (45 days).

time. CF and TSC-10 films register very low CI values. On the other hand, the CI value of TSC-VO-10 increases steeply as a function of time.

CONCLUSIONS

The results of the various experiments conducted clearly establish that the films of TSC-VO-10 more susceptible to the degradative treatments than CF and TSC-10. All the three samples differ in their chemical makeup, which is the most important factor that determines the degradability. To illustrate, in TSC-VO-10, the vegetable oil with its unsaturated functionality acts as a good trigger for proliferation of free radicals, which deteriorated the TSC-VO-10 films faster than that the TSC-10 and CF films. Among TSC-10 and CF, while TSC-10 degrades albeit at a slow pace, CF is almost inert. Oxidants such as unsaturated vegetable oil indeed play a definite role.

REFERENCES

- F. Lo, J. Petchonka, and J. Hanly, *Chem. Eng.* Prog., 89, 55 (1993).
- 2. L. Taylor, Chem. Tech., 9, 542 (1979).
- 3. G. J. L. Griffin, Pure Appl. Chem., 52, 399 (1980).
- G. Sudesh Kumar, V. Kalpagam, and U. S. Nandi, JMS Rev. Macromol. Chem. Phys., C22, 225 (1982– 83).
- D. Satyanarayana and P. R. Chatterji, JMS Rev. Macromol. Chem. Phys., C33 349 (1993).
- 6. G. J. L. Griffin, Adv. Chem. Ser., 134, 159 (1974).
- G. J. L. Griffin, Am. Chem. Soc. Div. Org. Coat. Plast. Chem., 33, 88 (1973).
- R. L. Evangelista, W. Sung, J. Jane, R. J. Gelina, and Z. L. Nikolov, *Ind. Eng. Chem. Res.*, **30**, 1841 (1991).
- F. H. Otey, R. P. West Hoff, and W. M. Doane, *Ind. Eng. Chem. Prod. Res. Dev.*, **19**, 592 (1980).

- F. H. Otey, R. P. West Hoff, and W. M. Doane, *Ind. Eng. Chem. Res.*, 26, 1659 (1987).
- 11. G. J. L. Griffin, U.S. Pat. 4,016,117, 1977.
- 12. G. J. L. Griffin, U.S. Pat. 4,021,388, 1977.
- R. P. Westhoff, F. H. Otey, C. L. Mehltretter, and C. R. Russell, *Ind. Eng. Chem. Prod. Res. Dev.*, 13, 123 (1974).
- R. P. Westhoff, F. H. Otey, C. L. Mehltretter, and C. R. Russell, *Ind. Eng. Chem. Prod. Res. Dev.*, 15, 139 (1976).
- J. C. Johnson, Industrial Starch Technology: Recent Developments, Chemical Technology Review, Noyes Data Corporation, New Jersey, Vol. 142, 1979, p. 104.
- W. Sung and Z. L. Nikolov, *Ind. Eng. Chem. Res.*, 31, 2332 (1992).
- M. Duboi, K. A. Gilles, J. K. Hamilton, P. A. Rebers, and F. Smith, *Anal. Chem.*, 28, 350 (1956).
- B. Lee, A. L. Pometto III, A. FratZke, and T. B. Bailey Jr., Appl. Environ. Microbial., 57, 678 (1991).
- K. E. Johnson, A. L. Pometto III, and Z. L. Nikolov, Appl. Environ. Microbial., 59, 1155 (1993).
- S. M. Goheen and R. P. Wool, J. Appl. Polym. Sci., 42, 2691 (1991).
- A. C. Albertson, S. V. Anderson, and S. Karlson, *Polym. Degrad. Stab.*, **18**, 73 (1987).
- 22. G. J. L. Griffin, U.S. Pat. 4,983,651, 1991.
- A. Holmstorm and E. Sorvik, J. Polym. Sci., Polym. Chem. Ed., 16, 2555 (1978).
- C. David, M. Trojan, and A. Daro, *Polym. Degrad.* Stab., 37, 233 (1992).
- 25. A. C. Albertson and S. Karlson, J. Appl. Polym. Sci., 35, 1289 (1988).
- A. L. Pometto III, B. Lee, and K. V. Johnson, Appl. Environ. Microbiol., 58, 731 (1992).
- A. C. Albertson and Z. G. Banhidi, J. Appl. Polym. Sci., 25, 1655 (1980).
- P. H. Phones, D. Prasad, M. Heskins, M. H. Morgan, and J. E. Guillet, *Environ. Sci. Technol.*, 8, 919 (1974).