Preparation and Characterization of a Biodegradable Mulch: Paper Coated with Polymerized Vegetable Oils

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ABSTRACT: Kraft paper was coated with resins based on vegetable oils and then tested for mechanical properties, rate of biodegradation in soil, and ability to inhibit weed growth. Resins included oxidatively polymerized linseed oil (LO) and a polyester formed by the reaction of epoxidized soybean oil and citric acid (ESO–CA). Tensile strength of LO-coated paper (82 MPa) was slightly higher than uncoated paper (68 MPa), while the tensile strength of ESO–CA coated paper was somewhat lower (45 MPa). Elongations to break (3–8%) were similar for all samples. The rates of weight loss and tensile strength during soil burial decreased as follows: uncoated paper > LO coated paper > ESO–CA coated paper. The polymerized oils acted as barriers to penetration of microorganisms to the cellulosic fibers. Resin-coated papers inhibited weed growth for > 10 weeks, while uncoated paper was highly degraded and ineffective by 6–9 weeks. © 1999 John Wiley & Sons, Inc.* J Appl Polym Sci 73: 2159–2167, 1999

Key words: mulch; paper; biodegradable; soybean oil; linseed oil

INTRODUCTION

Polyethylene films are used extensively in agriculture as greenhouse covers, forage covers, and agricultural mulch. Worldwide yearly consumption for polyethylene mulch film alone is currently over 1 billion pounds.[1] Plastic mulches and row covers help retain soil moisture, increase soil temperature, inhibit weed growth, and reduce insect damage, and thereby increase yields.[2–4] Most mulches are used for vegetable and fruit production due to their relatively high value. Disposal or recycling of polyethylene films, however, has become a daunting problem. Agricultural mulch, in particular, is very difficult to recycle due to contamination with dirt and debris as well as loss in mechanical properties from ultraviolet (UV)-catalyzed oxidation. Many landfills reject mulch film because of pesticide residues and, thus, it must be treated as hazardous waste.[5]

A biodegradable mulch would have the dual advantages of avoiding costs of removal and disposal as well as contributing humus to the soil. Several different types of degradable mulch have been considered, including polyethylene film containing prooxidants,[6] starch–polyvinyl (PVOH) alcohol films,[7] biodegradable polyester films,[8] and coated paper or fiber mats.[9,10] Although polyethylene films will disintegrate, the resulting fragments may require decades to completely biodegrade, and toxicity of degradation products is largely unknown.[11] Starch–PVOH films have rather poor resistance to water and, thus, would not be expected to maintain their integrity during rain. Progress is being made on laminating starch–PVOH films with different types of water-

resistant, biodegradable polyesters.[12] Although biodegradable polyesters, such as polylactic acid, polycaprolactone, and polybutylene succinate, have excellent mechanical properties,[8] their cost ($2–8/lb) is much higher than for polyethylene ($0.4/lb resin, $1–2/lb film).[2,13] Uncoated paper, although inexpensive ($0.28/lb for kraft paper),[14] degrades too rapidly to protect most crops adequately.[2]

Various types of coatings for paper have been developed to slow degradation and improve wet strength. Rivise,[15] Hutchins,[16] and Flint[17] have reviewed some of the early work on the use of paper mulches. In 1870, the first U.S. patent pertaining to utilization of paper as a mulch described the use of tarred paper to exclude insects from roots.[18] By the 1920s, chiefly through the work of Eckart in Hawaii on sugar cane and pineapple, the dramatic advantages of tar- or asphalt-coated paper for improving yields of fruits and vegetable became apparent. Paper impregnated with paraffin wax[19] and animal or vegetable oils[20] were also claimed for mulch use. With the advent of synthetic polymers in the 1940s and 1950s, polyethylene largely displaced paper in mulching applications, likely due to its low cost and excellent strength and flexibility.

Recently, however, there has been a resurgence in research and practical interest in coated paper mulches, probably due to concerns about disposal of polyethylene, as well as the desire of organic farmers to have a natural, totally degradable mulch. Most of the coatings considered have been synthetic polymers such as polyethylene[3,9] or various polymer latexes.[21–25] Nonwoven mats of cellulosic fibers and polyesters have also been considered.[26,27] Anderson et al.[2] recently showed that the rate of loss of tensile strength of paper in soil can be slowed slightly by soaking it in soybean oil. Zhang et al.[28] found that coating a regenerated cellulose film with a thin layer of tung oil, followed by polymerization, slowed weight loss in soil (the half life increased from 30 to 37 days). No work, to our knowledge, has been conducted on the effect of polymerized vegetable oil coatings on the rate of biodegradation of paper and its effectiveness as a weed barrier.

As part of an ongoing project to develop biodegradable, water-resistant coatings for polysaccharide-based materials, we have studied the effect of coating paper with inexpensive vegetable oil-based polyesters on their mechanical, biodegradation, and weed inhibition properties. The polyesters chosen were an oxidatively polymerized unsaturated oil (linseed oil) and a poly(hydroxy-ester) formed by the reaction of epoxidized soybean oil with citric acid.

EXPERIMENTAL

Materials

Brown kraft paper was obtained from a local craft store and had a weight of 66 g/m^2. Raw linseed oil was obtained from Alnoroil Co., Valley Stream, NY, and had an iodine value of > 177 and a saponification value of 189–195. Cobalt octoate solution (6% Co in mineral spirits) was obtained from Pfaltz & Bauer. Epoxidized soybean oil was Paraplex G-62 from C. P. Hall Co., Bedford Park, IL, and had about 7% oxirane oxygen. Citric acid and tetrabutylammonium bromide were reagent grade and were purchased from Aldrich Chem. Co. Citric acid was ground with a mortar and pestle and passed through an 80-mesh screen prior to use.

Methods

Preparation of Coated Paper

Linseed oil (LO, 120 g) and cobalt octoate solution (0.40 g) were magnetically stirred for 10 min, then the mixture was applied to pieces of kraft paper (50.8 × 91.4 cm) using a paint brush. The oil penetrated quickly into the paper due to its low viscosity. The coated paper was hung from a rope and allowed to dry overnight. Coating weight was approximately 45 g/m^2.

Epoxidized soybean oil (ESO; 349 g, 1.5 mol epoxy), citric acid (CA; 99 g, 1.5 mol carboxyl), and tetrabutylammonium bromide (TBABr; 3.2 g) were first partially polymerized by heating in a 3-L beaker equipped with an air stirrer and hot plate. After the temperature of the mixture reached 110°C (about 10 min), the beaker was placed into a bucket of ice to stop the reaction. Prepolymerization was conducted in order to better disperse the CA in the ESO. The partially polymerized ESO resin was then spread onto paper sheets using glass rods. The ESO resin penetrated only partway into the paper due to its high viscosity. Polymerization was completed by placing the coated paper onto steel sheets covered with Teflon–aluminum foil (Bytac, Norton Performance Plastics, Akron, OH) and heating in an oven at 165°C for 3 min. A similar experiment was conducted without the TBABr catalyst to

evaluate possible effects of TBABr on biodegradation rates.

Testing for Biodegradation in Soil

Coated papers, as well as uncoated paper, were cut into 5.08 × 10.16 cm pieces, weighed, and sewn into nylon mesh bags having openings about 3 mm in size. Three replicates of each sample for each of four time points were then buried under 6 in. of soil in the NCAUR field plot starting June 30, 1997. During summer weeks, in which there was no rain, the plot was sprinkled with about 1.3 cm. of water. Samples were removed from the ground at 14, 42, 84, and 140 days. After removal, samples were brushed lightly, gently rinsed with deionized water, equilibrated for 7 days at 23°C and 50% relative humidity, weighed, and tested for tensile properties (see below). Average outdoor temperatures were about 21°C over the first 3 months of the experiment and then declined gradually to 0°C over the next 2 months. Rainfall was very light the first 6 weeks (<2 cm/week) and then increased (Fig. 1).

Testing for Weed Growth Inhibition

Three pieces of each of the coated papers and control (uncoated paper) 50.8 × 91.4 cm in size were placed onto rototilled ground in the NCAUR field plot. The outer edges (about 10 cm) of the samples were buried in the dirt to keep the samples stationary. The number of weeds protruding through openings in the samples were recorded over time. Photographs were also taken.

Tensile Testing

Dog-bone-type V tensile bars (4–5 for each sample) were cut and tested according to ASTM D638-91 using an Instron model 4201 Universal Testing Machine. The crosshead speed was 20 mm/min, and the gage length was 25.4 mm.

Scanning Electron Microscopy

Samples were mounted on aluminum stubs with graphite-filled tape and vacuum-coated with gold–palladium. Specimens were then examined with a JEOL JSM 6400V scanning electron microscope.

Fourier Transform Infrared Spectroscopy

Samples for Fourier transform infrared (FTIR) analysis were pulverized in liquid nitrogen using

Figure 1 Ambient average temperatures and precipitation in Peoria during field trials. Triangles indicate high and low temperatures. Data from Midwest Climate Center (Champaign, IL).

a Wig-L-Bug Amalgamator, mixed with KBr, and pressed into pellets. Spectra were obtained using a Nicolet Impact 410 spectrometer.

RESULTS AND DISCUSSION

Polymerization of Oils

Figure 2 shows FTIR spectra of paper coated with polymerized linseed oil (LO-coated paper) and epoxidized soybean oil–citric acid polyester (ESO–CA-coated paper). For LO-coated paper, no absorbance corresponding to C—H stretching adjacent to carbon—carbon double bonds of LO (3010

Figure 2 FTIR spectra of (A) kraft paper, (B) LO-coated paper, (C) ESO–CA–TBABr-coated paper, and (D) ESO–CA-coated paper. Top spectra are 0 time, and bottom spectra are after 12 weeks burial [6 weeks for (A)].

cm^{-1}; data not shown) is seen, indicating that most of the double bonds have reacted. Similarly for ESO–CA-coated paper, absorbances corresponding to citric acid carboxyl carbonyl stretch (1701 cm^{-1}) and epoxide ring vibration (822 cm^{-1}) have disappeared, indicating that essentially all ESO and CA have reacted. Interestingly, the reaction seems to occur with or without the TBABr catalyst (Fig. 2(C) and (D); respectively). Spectral assignments were from Bellamy.[29]

Highly unsaturated "drying" oils, such as linseed oil, are known to polymerize by reacting with oxygen to form hydroperoxides, followed by decomposition of the hydroperoxides to various types of free radicals.[30] The latter reaction is catalyzed by metal ions, such as cobalt, manganese, iron, and calcium. The radicals then combine to form carbon—oxygen or carbon—carbon crosslinks.

Epoxidized vegetable oils, as well as the more commonly used bisphenol A diglycidyl ether, are known to react with polyfunctional carboxylic acids.[31–34] When acidic catalysts, such as quaternary ammonium halides, are used as catalysts, the primary reaction product is a polyester containing a secondary hydroxyl group β to the carboxyl carbon. CA was chosen for this study because preliminary experiments showed that it reacted with ESO much faster and at lower temperatures than dicarboxylic acids, such as adipic and sebacic acids.

Effect of Coatings on Mechanical Properties

Figure 3 shows the initial (at 0 time) weights in $g/51.6$ cm^2 for coated and uncoated kraft papers. The higher weight–area values of the coated papers reflect the added weight of the coating. Figure 4 shows that the initial tensile strength of LO-coated paper (82 MPa) is slightly higher than for uncoated paper (68 MPa). Since the LO pene-

Figure 3 Weights/51 cm^2 of coated papers as a function of burial time in soil: (▼) Uncoated kraft paper; (●) LO-coated paper; (▲) ESO–CA-coated paper; (■) ESO–CA–TBABr-coated paper.

Figure 4 Tensile strengths of coated papers as a function of burial time in soil: (▼) Uncoated kraft paper; (●) LO-coated paper; (▲) ESO–CA-coated paper; (■) ESO–CA–TBABr-coated paper.

Figure 5 Elongations to break of coated papers as a function of burial time in soil: (▼) Uncoated kraft paper; (●) LO-coated paper; (▼) ESO–CA-coated paper; (■) ESO–CA–TBABr-coated paper.

trated into the paper (the overall thickness was 85 μm for both LO-coated paper and uncoated paper), overall strength per unit area is higher for LO-coated paper since the polymerized oil replaces air. Likewise, tensile strengths of the ESO–CA and ESO–CA–TBABr-coated papers (45 MPa) are lower than the uncoated paper because much of the weaker resin did not penetrate the paper (thickness 180 μm). If it is assumed that the tensile strength (σ_t) of the composite can be expressed as the weighted sum of the components, as follows:

$$\sigma_t = \phi_a\sigma_a + \phi_b\sigma_b \qquad (1)$$

where ϕ is the volume fraction, and tensile strengths of approximately 23 and 16 MPa are calculated for LO and ESO–CA resins, respectively. These are rather high values for such soft resins and may imply some improvement in interfiber adhesion. Previous work has shown that strength of bonds between cellulose fibrils in paper is important in determining ultimate strength.[35] Also, a linear model for elastic modulus, similar to that of eq. (1) for strength, was found to fit experimental data for mats of polystyrene grafted kraft pulp fibers.[36]

Elongations to break of coated and uncoated paper (Fig. 5) were 3 ± 1% at 0 time. Interestingly, elongation values for coated papers increased to 7 ± 1% after 2 weeks of soil exposure, while those for uncoated paper remained unchanged. The reason for this unknown but could result from a decrease in fiber cohesion from rain

Figure 6 Photographs of (A) LO-coated paper, (B) ESO–CA–TBABr-coated paper, (C) ESO–CA-coated paper, and (D) uncoated paper after burial in soil for 2, 6, and 12 weeks.

or starch binder degradation, such that more of the load is transfered to the flexible resin.

Degradation in Soil

Rates of weight loss during soil burial (Fig. 3), as a percentage of initial weight, were most rapid in uncoated paper, followed by LO-coated paper and, finally, ESO–CA-coated paper. Rates of decrease in tensile strength with time (Fig. 4) also decreased in the following order: uncoated paper > LO-coated paper > ESO–CA-coated paper. Rates of decrease in weight and strength were similar for ESO–CA- and ESO–CA–TBABr-coated papers, suggesting that TBABr does not significantly impede biodegradation. Photographs of the buried samples (Fig. 6) show that uncoated paper had torn or disintegrated into small pieces by 6 weeks while the coated papers remained whole. After 12 weeks, LO-coated paper has also

disintegrated while the ESO–CA-coated paper has begun to tear. There were no significant changes in the measured thicknesses with time up to 6 weeks, so losses in weight were due to decreases in density and focal losses in area. Scanning electron microscopy (SEM) photographs (Fig. 7) show that, by 6 weeks, fungal cells and hyphae have extensively colonized the surface and interior of uncoated paper. Fibrillar breakage and defibrillation are evident. Fungal growth was also widespread on the surface of LO-coated paper at 6 weeks, but there was little penetration to the interior. The LO coating covers and fills the spaces between cellulose fibrils, so less surface area is available for microorganism growth. In contrast, the surface of ESO–CA-coated paper showed only focal areas of microbial colonization after 6 weeks, suggesting that the ESO-based resin may be more resistant to biodegradation than LO. However, the greater thickness of the ESO–CA-coated paper or the greater ratio of resin to paper may also influence biodegradation rates.

Figure 2 shows FTIR spectra of coated papers before and after exposure to soil for 12 weeks. It is apparent that for LO-coated paper, absorbances from the LO component (2929 and 2856 cm^{-1} from C—H stretching and 1741 cm^{-1} from C=O stretching) are greatly diminished relative to the cellulosic component (1163, 1059, and 1034 cm^{-1} from C—O stretching) after soil exposure. The ESO–CA-coated paper likewise shows a smaller preferential loss of the oil component. These data suggest that the polymerized oil coatings protect the cellulosic fibers from microbial attack by acting as a sacrificial barrier.

Many types of microorganisms are known to degrade cellulose, lignin, and polyesters; thus, it is not surprising that kraft paper coated with vegetable-oil-based polyesters is biodegradable. Endo- and exocellulases are secreted by many types of bacteria and fungi.[37,38] Lignin is also degraded by fungi via peroxidases and hydrogen peroxide.[39] There are naturally occurring polyesters, such as polyhydroxybutyrate (PHB)[8] and cutin, a crosslinked polyester of hydroxylated fatty acids found in leaf surfaces, which are biodegradable. It is somewhat surprising that LO-coated paper appears to degrade faster than ESO–CA-coated paper considering that the double bonds in LO are polymerized to single C—C or C—O bonds. The latter are normally thought to be more resistant to biodegradation than the ester linkages found in ESO–CA. Certainly, the glycerol–fatty acid ester bonds in polymerized LO could be

Figure 7 Scanning electron micrographs of (A) uncoated kraft paper, (B) LO-coated paper, and (C) ESO–CA-coated paper at 0 time and after burial for 6 weeks in soil (D)–(F).

cleaved by easterases, and the fragments might be washed away or further digested. Preliminary work has shown that poly(hydroxy-ester-ethers) made from Bisphenol A diepoxides and various dicarboxylic acids are biodegradable over several months.[40]

Inhibition of Weed Growth

Figure 8 shows the number of weeds growing through the paper as a function of time. These data show that weed growth is most rapid for uncoated paper, followed by LO-coated paper, then ESO–CA-coated paper. This is consistent with the degradation data. By 6 weeks, the uncoated paper had several tears or holes and weed growth through the paper began. As shown in photographs in Figure 9, most of the uncoated paper has disappeared (biodegraded and/or blown away) by 9 weeks on top of the soil. Loss of strength of uncoated paper during rain may also have contributed to its disintegration. In contrast, the coated papers remain mostly intact, albeit with some cracks and holes, up to 14 weeks. In conclusion, coating with vegetable oil resins extends the useful life of paper mulches to a length of time close to that required for many crops ($\sim$ 10 weeks).

Anderson et al.[2] have discussed the economics of using paper versus polyethylene as mulch. For black polyethylene film having an 0.8 mil thickness, about 126 kg is needed per hectare at a cost of \$533. For 40-lb kraft paper (65 g/m^2) made from recycled fibers, about 434 kg is required per hectare at a cost of \$268. In the case of the LO-coated paper used in our experiments, the weight of oil relative to paper was 0.69. Thus, 300 kg of LO

Figure 8 Number of weeds penetrating coated papers as a function of time for (▼) uncoated kraft paper, (●) LO-coated paper, (▲) ESO–CA-coated paper, and (■) ESO–CA–TBABr-coated paper.

Figure 9 Photographs of field trial of (A) LO-coated paper, (B) ESO–CA–TBABr-coated paper, (C) ESO–CA-coated paper, and (D) uncoated paper after 9 weeks in field.

would be required per hectare at a cost of $230. This brings the total cost to $498 per hectare for LO-coated paper, which is still cheaper than the polyethylene film. One must, of course, add some cost for the coating process, as well as higher costs for transportation, since the paper weighs more than the polyethylene. Offsetting these costs would be the approximately $200 per hectare cost of removing and disposing of the polyethylene at the end of the season. Thus, the costs of using polyethylene film and the LO-coated paper described here would be similar.

Further work is needed to determine if less LO might be sufficient to give paper adequate resistance to biodegradation. Alternatively, only the edges of the paper that are buried in the soil might need to be coated since paper mulches usually fail at the soil line.[2] Semidrying oils, such as soybean oil, which are less expensive than LO, also need to be examined as coatings. Since ESO ($0.60/lb) and CA ($0.70/lb) are even more expensive than LO, studies of area or thickness reduction would be especially important for the ESO–

CA-coated paper. Finally, field trials using polymerized vegetable-oil-coated papers as mulchs for different vegetable and fruit crops would ultimately be required to confirm the efficacy of coated papers as mulches.

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