Liquefaction of Corn Stover and Preparation of Polyester From the Liquefied Polyol

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Abstract

This research investigated a novel process to prepare polyester from corn stover through liquefaction and crosslinking processes. First, corn stover was liquefied in organic solvents (90 wt% ethylene glycol and 10 wt% ethylene carbonate) with catalysts at moderate temperature under atmospheric pressure. The effect of liquefaction temperature, biomass content, and type of catalyst, such as H_2SO_4, HCl, H_3PO_4, and $ZnCl_2$, was evaluated. Higher liquefaction yield was achieved in 2 wt% sulfuric acid, 1/4 (w/w) stover to liquefying reagent ratio; 160°C temperature, in 2 h. The liquefied corn stover was rich in polyols, which can be directly used as feedstock for making polymers without further separation or purification. Second, polyester was made from the liquefied corn stover by crosslinking with multifunctional carboxylic acids and/or cyclic acid anhydrides. The tensile strength of polyester is about 5 MPa and the elongation is around 35%. The polyester is stable in cold water and organic solvents and readily biodegradable as indicated by 82% weight loss when buried in damp soil for 10 mo. The results indicate that this novel polyester could be used for the biodegradable garden mulch film production.

Index Entries: Biodegradability; liquefaction; polyester; strength; solubility.

Introduction

Most synthetic polymers used in daily life and industries are derived from petroleum. The main shortcomings are (1) dependence on the petroleum resource that is not renewable and (2) poor biodegradability and consequent negative impact on the environment. Numerous attempts have been made to develop biodegradable materials from renewable resource to replace petrochemical-based ones.

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Crop residues are naturally occurring polymers. For example, ligno-cellulosic materials are made up of mainly of cellulose, hemicellulose, and lignin, which are rich hydroxyl groups. It is the hydroxyl group that makes it possible to convert crop residues into biopolymers. Liquefaction is an effective way to convert lignocellulosic materials into intermediates rich in hydroxyl groups. Japanese researchers investigated liquefaction of wood with polyethylene glycol and phenols, and prepared polyurethane foams from liquefied materials *(1,2)*. Yamada and Ono *(3)* reported the production of phenol–formaldehyde resin from liquefied wood. Kurimoto and Doi synthesized polyurethane-like foams obtained by reacting liquefied wood with polyisocyanate *(4)*. New resin systems have also been illustrated by reacting with multifunctional epoxy compounds by Kobayashi and his colleagues *(5)*. However, no study of polyester synthesis from liquefied biomass has been reported.

This research was focused on the development of a novel process to convert crop residues such as corn stovers into bio-polyester. The process involves two steps: (1) converting corn stover to bio-polyols by means of chemical liquefaction, in which, the corn stover experienced partial degradation and chemical reactions, and becomes a homogeneous liquid. (2) Preparing biodegradable polyesters from the bio-polyols through crosslinking with carboxyl acids and acid anhydrides.

Material and Methods

Raw Materials and Procedures of Liquefaction

The biomass samples used was corn stover taken from Agricultural Utilization Research Institute in Minnesota. The dried samples were ground in a Wiley mill to pass a screen of 1 mm aperture. The ground sample and liquefaction reagent (90 wt% ethylene glycol and 10 wt% ethylene carbonate) containing the appropriate amount of catalyst were put into a round bottom distilling flask with three cylindrical standard ground joint necks. To one neck of the flask was attached a condenser. The temperature of liquefaction was measured with a thermometer (upper limit of 300°C), which was attached to one neck of the distilling flask. The required reaction time for the liquefaction, as determined, was about 2.5 h. A stirrer was attached to the top neck of the distilling flask. Liquefaction was completed with continuous stirring under atmospheric pressure. After reaction, the stirrer kept running until the mixture cooled down to room temperature. Collect the liquefied mixture for later use. All experiments and analysis were performed in five duplicates.

Cyclic carbonates, such as ethylene carbonate and propylene carbonate, have been found to be novel reagents that can liquefy lignocellulosic materials rapidly at medium temperature under atmospheric pressure, although reaction mechanisms involved have not been well established *(3)*.
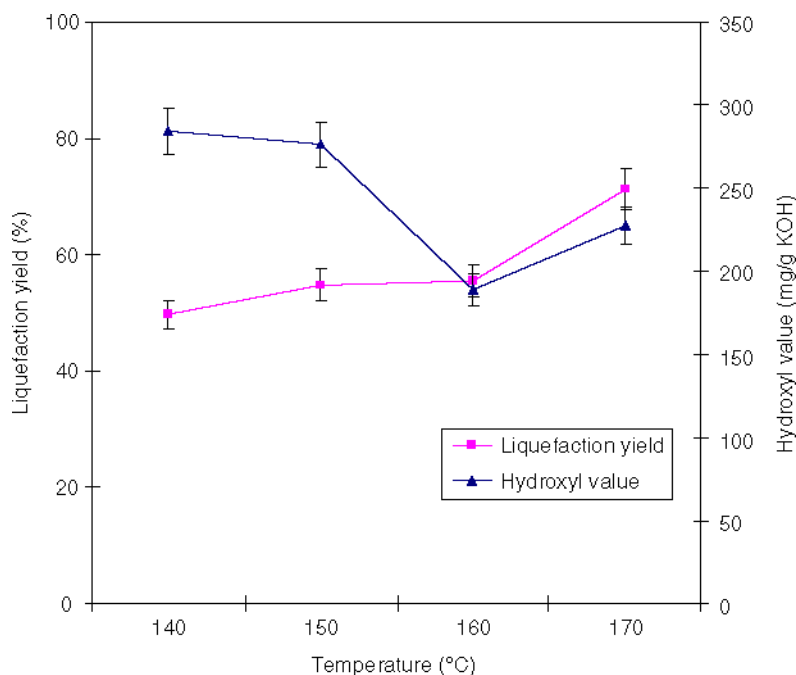
Fig. 1. Effect of temperature on liquefaction of corn stover. Liquefaction reagent/ corn stover ratio: 4; catalyst content: 2% (w/w, on liquefaction reagent); liquefaction time 2 h. Error bars represent standard deviations calculated from the data obtained from five duplicated experiments.

In this article, mixed solvents containing 90% of ethylene glycol and 10% of ethylene carbonate was used as liquefaction reagent. Figure 1 shows the effect of temperature on liquefaction yield and hydroxyl value. Liquefaction yield increased rapidly with increasing temperature. Temperatures higher than 160°C are required to achieve a high liquefaction yield. On the other hand, hydroxyl value decreased with increasing temperature. This could be considered that hydroxyl group-rich carbohydrate were decomposed and converted to low-molecular weight products, such as organic acids, at high temperature.

Corn stover meal is a porous and low-density material. Its liquid absorption capability is very high. To get a satisfactory liquefaction, it is very important to mix uniformly the stover meal with liquefying reagent. An effective stirring is definitely necessary. Otherwise, carbonization may occur because of incomplete heating. Table 1 shows the liquefaction results at various loading level of corn stover. When the ratio of stover to liquefaction reagent was below 30/100, liquefaction was smooth, and a uniform liquid was obtained. A mild stirring was enough. With increasing ratio, violent stirring became very important. The viscosity of the liquefied product increased significantly. For example, corn stover could be completely liquefied at a ratio of 40/100, but the viscosity was higher. When the ratio was over

Table 1
Possibility of Liquefaction at High Corn Stover Load

Stover/liquefying reagent	Stirring method	Result
30/100	Magnetic stirrer	Uniform liquefaction, thin liquid
40/100	Mechanical stirrer	Uniform liquefaction, thicker liquid
50/100	Mechanical stirrer	Partial carbonization

Conditions were liquefaction temperature 170°C, liquefaction time 4 h, catalyst content 5% (w/w, on liquefaction reagent).

50/100, the liquefaction was unable to complete because the liquefaction reagent was too little to maintain a uniform reaction. Carbonization occurred at this ratio.

In the presence of catalyst sulfuric acid, corn stover was subjected to a partial chemical degradation as well as reacted with ethylene carbonate and ethylene glycol to form a variety of glucosides. Bubbles were observed during the liquefaction, which could be attributed to the carbon dioxide produced during the reaction.

Preparation of Polyester From the Stover Polyols

The stover polyols used in this study for polyester were prepared under this condition: sulfuric acid (96%) at 2% on liquefying reagents; ratio of stover to liquefying reagent at 1/4 (w/w); temperature at 160°C; time in 2 h. The polyols had a hydroxyl value of 200 mg KOH/g and a viscosity of 2×10^5 MPa·s.

Polyester sheets were prepared by crosslinking the liquefied stover with carboxylic acids or anhydrides to form a network of polyester. First, the weighed liquefied stover, crosslinking chemicals, and other additives were mixed and heated together with stirring, and then the obtained homogeneous mixture was molded into a container or cast on a polished plate to form a uniform layer of the mixture (0.15–0.75 mm). The polyester sheet was obtained after curing by heating the mixture in an oven. Curing temperature and time varied (1–5 h, 140–180°C) depending on the formulation and thickness of the sheets.

Determination of Crosslinking Extent of Polyester

Because completely crosslinked network of polyester is almost insoluble in mixture of dioxane and water (4/1, v/v) (note: uncrosslinked polyol is soluble in the solvent), we used the percentage of insoluble residue in dioxane/water to evaluate, indirectly, the crosslinking extent of polyester. Weigh sample of crosslinked polyester, put it into a flask containing dioxane/water mixture (4/1, v/v) for 24 h at room temperature with stirring. After that, solvent was filtered out. The sample was

washed with the solvent until no visible black color, and then the insol-uble residue was dried overnight in an oven at 105°C to determine its weight. The crosslinking extent of polyester was calculated using the fol-lowing equation:

$$\text{Crosslinking extent (\%)} = (W_r / W_s) \times 100$$

where W_s is the weight of initial sample and W_r is the weight of insoluble residue.

Solubility of Polyester

Polyester sheets were cut into small pieces of about 3×3 mm^2. Weigh the polyester pieces, put them into flasks containing water or selected solvents, and keep for 8 d at room temperature. After that, water or solvent was filtrated out. The samples were washed with corresponding water or solvent, and then dried overnight in oven at 105°C to determine weight loss. For the solubility of polyester sheets in hot water, alkaline and acid solution, the samples were refluxed for 6 h in water, 2 M NaOH or 2 M H$_2$SO$_4$, and then washed with water, dried to determine weight loss. The solubility of polyester sheets was calculated using the following formula.

$$\text{Solubility (\%)} = [(W_i - W_f) / W_i] \times 100$$

where W_i is the initial weight of sample and W_f is the final weight of sample after treatment with water, solvents, alkali, and acid solution.

Tensile Strength of Polyester Sheets

Tensile strength of the polyester sheets was evaluated with a material testing system (Model APEX-T1000, Satec Systems, Inc., Grove City, Pennsylvania). Width of testing sample was 25 mm. Loading speed was 5 mm/min. Before testing, the thickness and width of the sample and ini-tial length of the sample between grippers were entered into the control system. After testing, the tensile strength, elongation and strain–stress curve of the sample were produced automatically by the computer.

Biodegradability of Polyester

To evaluate the biodegradability of polyester, natural degradation of polymers in soil was simulated in our laboratory. The soil used in this research was a merchandised potting soil. To guarantee the existence of desired microorganisms, about twofold garden soil collected from yard was mixed with the potting soil. The test samples were buried in the potting soil in flowerpots. The flowerpots were kept at 25°C in a cultivating room. The samples were watered twice a week. Every month, three samples were taken out, washed with water, dried in oven at 105°C to determine weight loss of the samples. The rate of biodegradation was indicated by the weight loss.
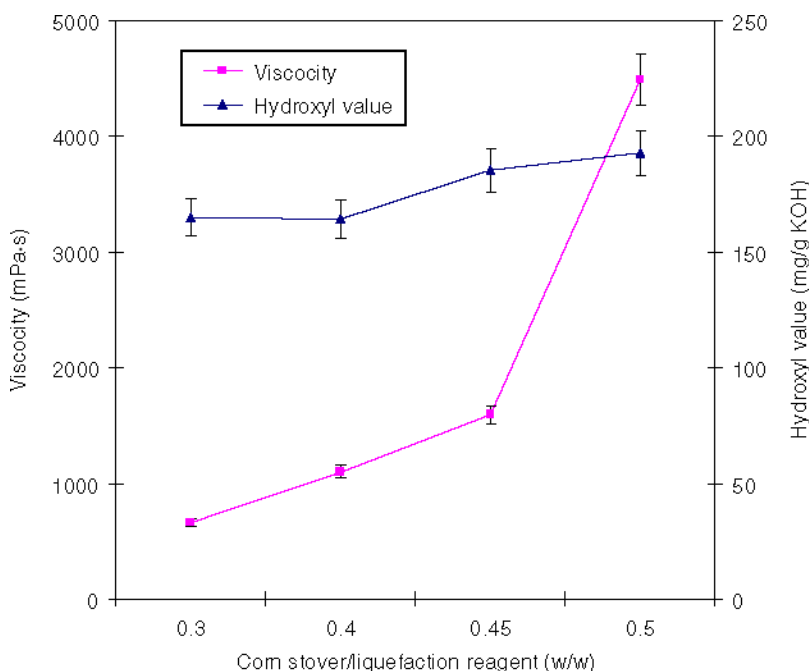
Fig. 2. Effect of the corn stover/liquefaction reagent ratio on the liquefaction of corn stover. Liquefaction temperature: 160°C; liquefaction time: 2 h; catalyst content: 2% (w/w, on liquefaction reagent). Error bars represent standard deviations calculated from the data obtained from five duplicated experiments.

Results and Discussion

Preparation of Bio-Polyols From Crop Residues

Figure 2 shows the liquefaction result of corn stover under various ratio of corn stover to liquefying reagent. With increasing solid content, the viscosity of liquefaction product increased sharply. The ratio of 45/100 was a critical point. A ratio higher than 45/100 will result in a very high viscosity, even a failure of liquefaction. The slight increase in hydroxyl value was because of high corn stover content.

Sulfuric acid is an ideal catalyst for the liquefaction. Usually, 1–3% of sulfuric acid on corn stover can make a good liquefaction. We also investigated other catalyst, such as hydrochloric acid, phosphoric acid, and zinc chloride. As shown in Table 2, these catalysts did not work for the liquefaction of corn stover. After 4-h reaction at 170°C with these catalysts, corn stover still maintained their original state (particles).

Preparation of Polyester From Polyol

The liquefied corn stover consisted of degraded stover fragments (oligosaccharides), glucosides, and residual and decomposed liquefying reagents, all of which contained two or more hydroxyl groups. Therefore,

Table 2
Liquefaction of Corn Stover With Different Catalysts

Catalyst	Dosage of catalyst % on straw	Straw/liquefaction reagent	Result
H_2SO_4	1.5	30/100	Completely liquefied
HCl	2.0	20/100	Unable to liquefy
H_3PO_4	6.0	20/100	Unable to liquefy
$ZnCl_2$	3.0	30/100	Unable to liquefy

Conditions were liquefaction temperature 170°C, liquefaction time 4 h.

Table 3
Crosslinking Chemicals for Stover-Based Polyols

Crosslinking chemicals	Formula	Result and observation
Adipic acid	$HOOC(CH_2)_4COOH$	Fair sheet, bubbles
Sebacid acid	$HOOC(CH_2)_8COOH$	Not well crosslinked, sticky, bubbles
Terephthalic acid	$HOOC(C_6H_4)COOH$	Weak sheet, brittle, bubbles
Terephthaloyl chloride	$ClOC(C_6H_4)COCl$	Many bubbles, like foam; brittle
Citric acid	$HOOCCH_2(HOOC)C(OH)CH_2COOH$	Brittle, bubbles
Maleic anhydride	$C_4H_2O_3$	Fair sheet, stiff
Succinic anhydride	$C_4H_4O_3$	Good sheet, flexible

Condition was OH/COOH = 1/1, sheets were cured at 140°C for 4 h.

it is feasible to crosslink the polyols into a network of polyester through esterification reaction between the hydroxyl groups of the polyols and carboxyl groups in crosslinking chemicals having two or more functional groups, such as dicarboxylic acids or cyclic acid anhydrides. Meanwhile, residual ethylene carbonate underwent ester interchange reaction with diacids (or anhydrides) to become polymer.

To crosslink the polyols, a variety of dicarboxylic acid, diacid chloride, and cyclic anhydride as crosslinking reagents were tested in this study, as shown in Table 3. The results show that although they all were able to react with the polyols to form polyester network, they varied in affecting the properties of formed polyester. A common problem of dicarboxylic acids is the bubbles caused by the water vapor, a byproduct of esterification. The chain length of diacid has an effect on crosslinking. It seems that a longer chain might result in a poorer crosslinking. Benzene ring makes terephthalic acid molecules stiff and bulky, which retarded the reaction between hydroxyl and carboxyl groups. Therefore, the formed polyesters were weak and brittle. Although diacid chloride is much more reactive than diacid, it did not give a good result. Because the

Table 4
Typical Formula of Polyester From BioPolyols

Carboxyl group/hydroxyl group	1.1–1.2/1

Carboxyl contributor
  (wt% in total carboxyl)
	Succinic anhydride, 95%
	  Citric acid, 5%

Hydroxyl contributor
  (wt% in total hydroxyl)
	Polyol, 90%
	  Polyethylene glycol 400, 5%
	  Hexanediol, 2%
	  Glycerol, 3%

reaction between diacid chloride and the polyols were so fast that many bubbles were formed in a short time, resulting from HCl gas produced as a byproduct during the esterification reaction. The results show that cyclic anhydrides, such as succinic and maleic anhydride, are ideal crosslinking reagent for the biopolyols. Because the amount of water produced by the anhydrides was only half of that by diacids, the polyester crosslinked by anhydrides had less and smaller bubbles. Compared with succinic anhydride, maleic anhydride produced stiffer and less flexible polyester, because the double bond in maleric anhydride makes its molecular not as flexible as succinic anhydride. Although citric acid has three carboxyl groups and one hydroxyl group, it is not a good crosslinker as expected. The polyester crosslinked by citric acid appears brittle and foamy *(6,7)*.

Effect of Additives

We found that a small amount of polyhydric alcohols, such as polyethylene glycol, hexanediol, and glycerol, can greatly improve the strength of the polyester. Succinic anhydride alone can react with the biopolyols into polyester, but it was weak and less flexible. The long-chain ones (polyethylene glycol and hexanediol) improve the flexibility of polyester, although glycerol (with more hydroxyl groups) is helpful to increase the crosslinking density. Glycerol also functions as a plasticizer to improve the flexibility of polyester. A small amount of citric acid is positive to the strength of the polyester owing to a higher crosslinking density.

Table 4 shows the formula tested in this study. The polyester samples used in next section to evaluate the properties of polyester sheet were prepared using this formula.

In addition to crosslinking reagents, the curing reaction of the polyol is dependent greatly on curing temperature and time. Figure 3 shows crosslinking results of biopolyols as a function of curing temperatures and time. It was noted that at the same temperature, crosslinking extend increased with increasing reaction time and high temperature enhanced the curing reaction. For example, when the sheet was cured at 140°C for
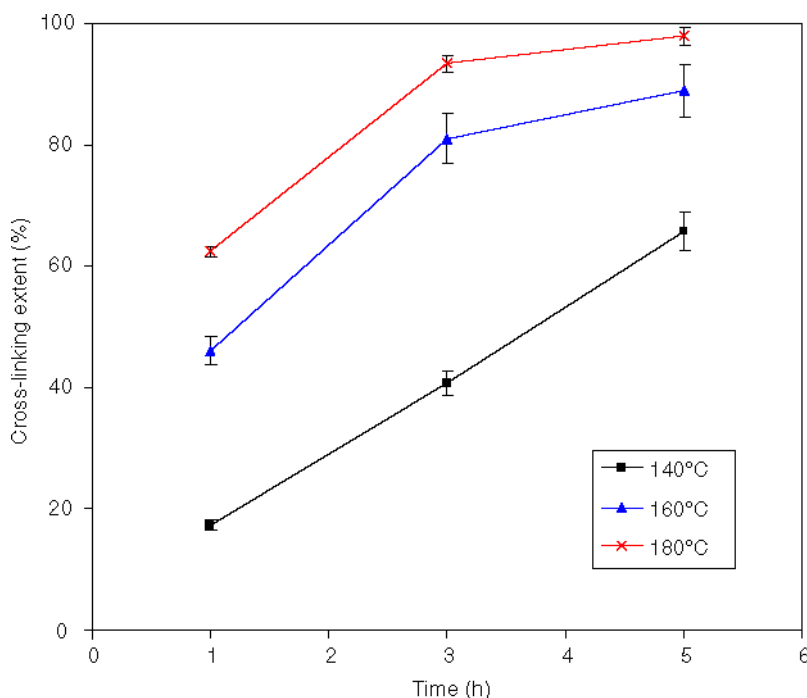
Fig. 3. Effect of curing temperature and time on the crosslinking of biopolyols. Error bars represent standard deviations calculated from the data obtained from five duplicated experiments.

5 h, the crosslinking extend was less than 65%, although if the sheet was cured at 180°C for 5 h, the curing extent was near 100%.

Properties of the Polyester Sheet

Solubility

Figure 4 shows that polyester was quite stable in cold organic solvents and cold water. Only about 8–13% was dissolved after 8 d soaking, depending on the solvents. The dissolved contents should represent those of unreacted crosslinking chemicals, residual liquefying reagents, and small pieces not completely crosslinked in the polyester. The solubility of polyester in hot water was 3–4 times higher than that in cold water. Because of the trace of sulfuric acid in the polyester, when it was refluxed in boiling water, the hydrolysis of the polyester was catalyzed by the sulfuric acid, which could be the main reason for the higher solubility of polyester in hot water than in cold water.

It is well known that ester can be catalytically hydrolyzed under either alkaline or acidic condition. Therefore, when the polyester was refluxed in 2 M NaOH and 2 M H$_2$SO$_4$ for 6 h, they were significantly soluble. The solubility was 66% in 2 M H$_2$SO$_4$ and 86% in 2 M NaOH, respectively. The polyester was more soluble in alkaline solution than in acidic one.
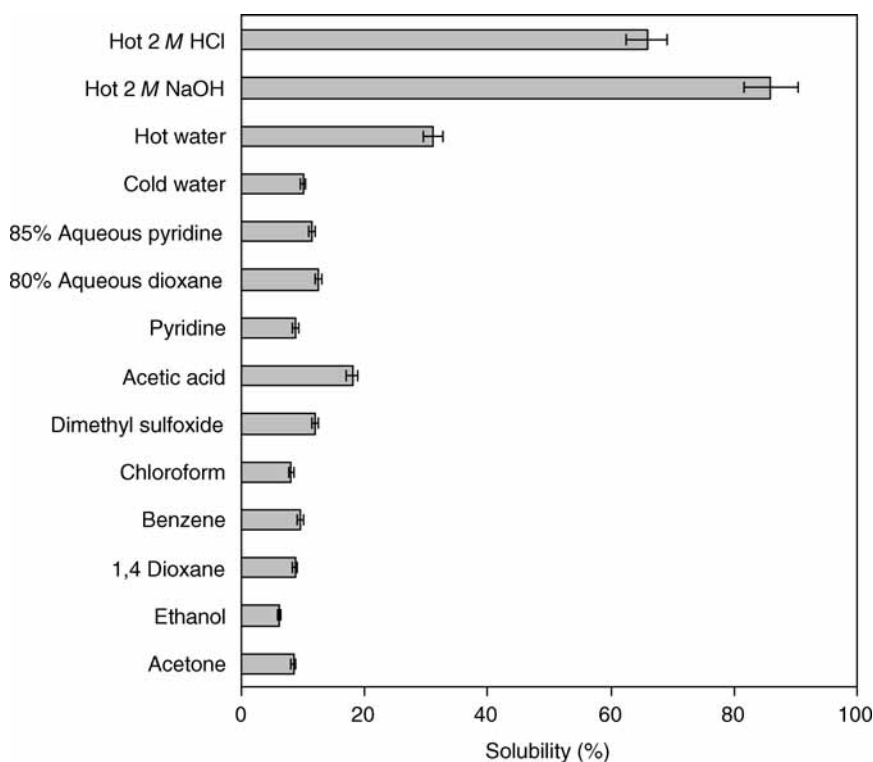
Fig. 4. Solubility of polyester sheet in organic solvents, water, alkaline, and acidic solutions. Sheets were cured at 140°C for 4 h. Error bars represent standard deviations calculated from the data obtained from five duplicated experiments.

Tensile Strength and Elongation

The tensile strength and elongation of polyester was shown in Fig. 5. Two samples were evaluated. One was prepared from the biopolyols produced with ethylene carbonate/ethylene glycol (9/1) (sample 1), and to compare, another was made from the biopolyols produced with 100% ethylene glycol (sample 2). Two samples had similar strength and elongation. Although the sheets were not very strong (about 5 MPa), the strength is acceptable in some cases, such as garden mulch film. We are making more effort to improve the strength of the biopolyester *(8)*.

Biodegradability

The biodegradability of polyester films from corn stover biopolyols was shown in Fig. 6. It was found that the polyester films lost 82% of their initial weight during 10 mo. There is a certain amount of chemicals uncrosslinked or partially crosslinked remaining in the polyester films, which might be less resistant to microbial attacks than fully crosslinked materials, which may contribute to the great weight loss during the 10 mo. Microorganism spots or strains were observable on the surface of films
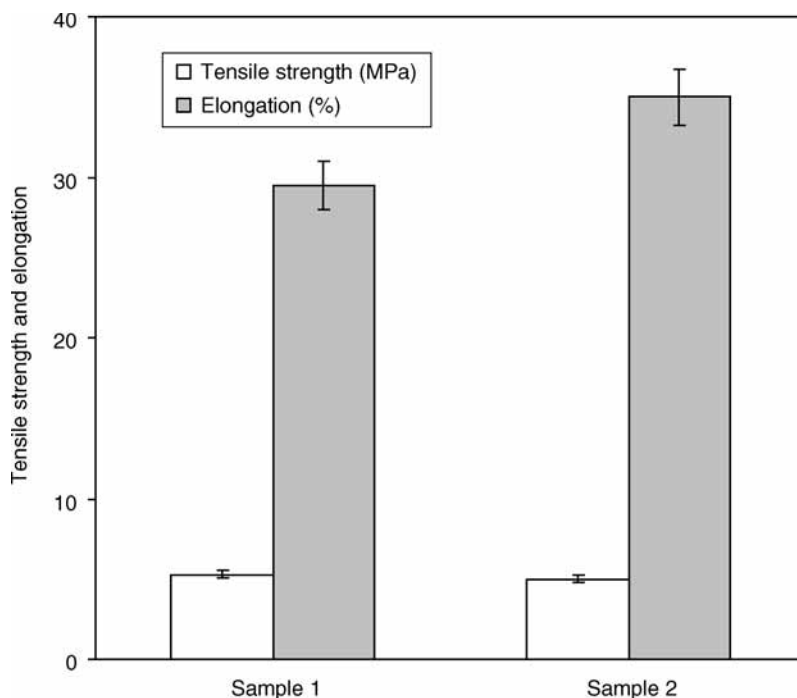
Fig. 5. Tensile strength and elongation of polyester sheets. Sheets were cured at 140°C for 4 h. Error bars represent standard deviations calculated from the data obtained from five duplicated experiments.

and in the surrounding soil, suggesting that there were nutrients for the microorganisms around the films, which were degraded chemicals from the bio-polyester films *(9,10)*.

Conclusions

This study demonstrates that biopolyols produced from corn stover through an organ-solvent liquefaction procedure at moderate temperatures and atmosphere pressure can be directly used as chemical building blocks for making biodegradable polymers without separation and purification. The biopolyols are rich in hydroxyl groups that can react and form crosslink with carboxyl groups of some suitable chemicals to produce biopolyester. A variety of dicarboxylic acids, diacid chloride, and cyclic anhydrides as crosslinking reagents were tested in this study. Although they all were able to react with the stover biopolyols to form polyester, they varied in affecting the properties of the formed polyester. It was found that succinic anhydride combined with a small amount of citric acid, glycol, hexanediol, and polyethylene glycol is a good crosslinking reagent for making biopolyester from stover biopolyols. In general, the formed polyester were stable in cold water and solvents, had acceptable mechanical strength, and readily biodegradable. Biopolyesters made from
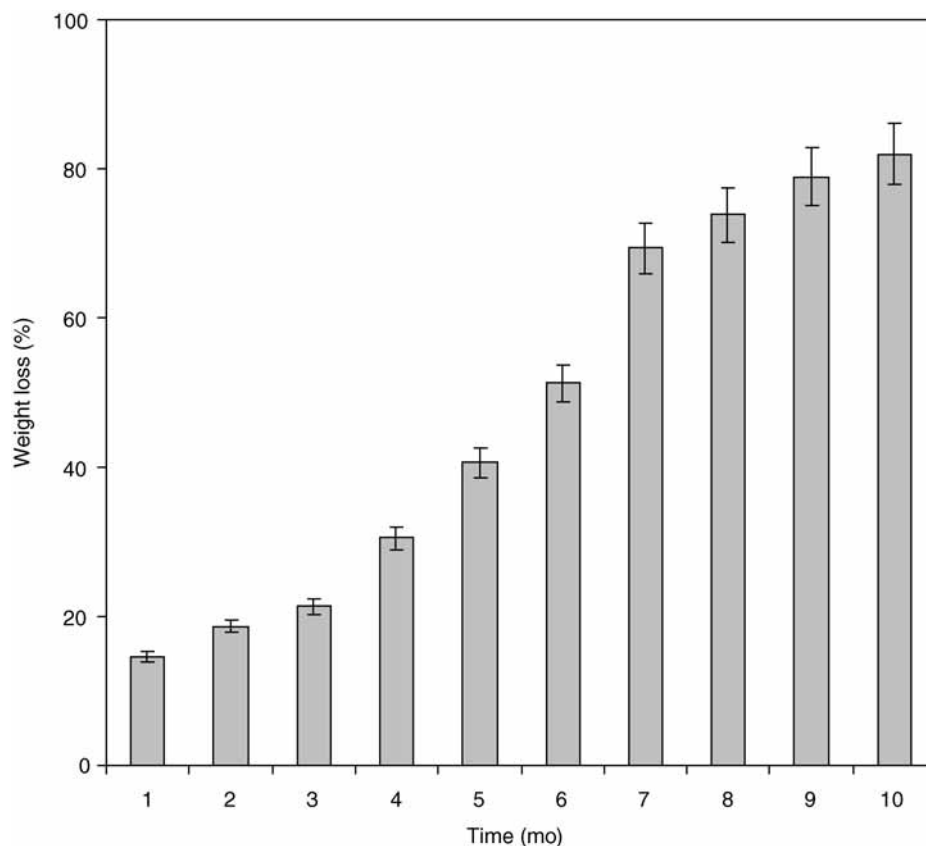
Fig. 6. Biodegradability of polyester films. Sheets were cured at 140°C for 4 h. Error bars represent standard deviations calculated from the data obtained from five duplicated experiments.

corn stover may be processed into sheets, films (e.g., mulching film), and fibers, which may be used in agriculture, gardens, and packaging and textile industries.

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