New Biodegradable Films from Exploded Wood Solutions

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Synopsis

In this paper experimental results obtained with the exploded wood/tertiary amine oxide system are presented. The use of particular conditions leads to the formation of new biodegradable films. These films may have a natural color from brown to black. The mechanical properties are studied and a comparison with a black commercial synthetic film is made. The structure of the films is studied as well as the role of lignin as an antioxidant.

INTRODUCTION

Under the pressure of ecologists, industries in the western world should in the future tend to use biodegradable materials to avoid long-term pollution. However, in the last 10 years nonbiodegradable synthetic polymer films have superseded cellophane films which are biodegradable. Three main arguments can be advanced to explain this phenomenon: cellophane has a high price, its manufacturing process pollutes the environment, and its mechanical properties are poorer than synthetic polymer films.

Only a political decision could make the biodegradability of cellulose films a crucial property. If this becomes the case, the interest in cellulose film will markedly increase. Until now these films have been made with the viscose process, which is slowly being abandoned due to its complexity and pollution. Moreover, the viscose process does not allow the use of all kinds of cellulose as a raw material. Dissolving pulp must be used.

To avoid all these problems, research devoted to replacing the viscose process of making cellulose materials has occupied laboratories around the world for several years. For the most part, the research has been oriented towards a solvent system for cellulose.

Some patents have demonstrated the power of tertiary amine oxides to dissolve great amounts of cellulose.[1-4] This process is simple, fast, and nonpolluting, but it is difficult to commercialize because of solvent recovery problems and the cost-competitiveness of the viscose process. Nevertheless, the tertiary amine oxide system has been demonstrated to be advantageous for fibers, with a high recovery rate for the solvent.[5]

One means of decreasing the cost would be to use lignocellulosics of low price as raw materials. For this purpose, advantage may be taken of the steam-explosion process[6] which can convert lignocellulosic material (like wood chips) into a reactive and finely divided product soluble in organic solvents such as tertiary amine oxides.[7] The conditions for the preparation and spinning of

exploded wood solutions have been described.[8] The study of the structure of these fibers was taken up and the mechanical properties were presented.

It has already been mentioned that films could also be made from these solutions. Our paper deals with the fabrication of lignocellulosic films.

These films may have a natural color from brown to black according to the temperature of dissolution and yield in lignin. The mechanical properties have been studied and a comparison with a black commercial synthetic film has been made.

Experimental

Flash-hydrolyzed poplar wood is used throughout this paper to prepare the lignocellulosic material. Using the reactor located at the CERMAV, the chips of poplar wood are pressurized for 125 s in saturated steam at 27 bars (225°C) and are submitted to an explosive decompression. According to previous work, this treatment was the optimum to get fibers with good mechanical properties. This is why we chose this sample to make our films.

After washing with water and drying, the composition of the exploded wood was about cellulose 60%, lignin 37%, and hemicelluloses 3%. The exploded wood is then ground in a mechanical desintegrator (a Thomas type fitted with a 1 mm, mesh screen). The solution preparation in N-methylmorpholine N-oxide (MMNO) monohydrate was as described elsewhere.[7] The dissolution of the wood was monitored with an optical microscope.

It can be noted that roughly 80% of the lignin after steam explosion is soluble in a water–dioxane mixture and the remaining 20% can be extracted with soda and chlorite treatments. The steam-exploded lignin is easily soluble in a tertiary amine oxide in the same time as cellulose and hemicellulose.

The measured $\overline{DP}_v$ of the cellulose from the cupriethylene diamine method is 540. The solubility of the exploded wood was found to be up to 25%, but later on we used only concentrations of 17.5% in MMNO (w/w).

The films are made using a heating press and molded plates which allow us to cast films of 150–220 μm thickness. The pressure used is 5 bars for some seconds and 15 bars for 30 s.

Subsequently, the films are allowed to soak extensively in warm water for 24 h. The films are then immersed in a 30% glycerol solution at 60°C for 15 min. To avoid shrinkage, the drying is done between glass plates. The films are kept in a controlled humidified atmosphere (RH = 65%) for transmitted and scanning electron microscopy, optical microscopy, and measurements of the mechanical properties.

RESULTS AND DISCUSSION

Film Properties

Films regenerated from solutions of exploded wood in MMNO are shiny and always colored (from clear brown to black depending of the duration and the temperature of dissolution). All the films were air-dried after soaking in a 30% glycerol bath for 15 min. The films contain about 50% glycerol. The glycerol

retention in lignocellulosic films is no different from that in ordinary cellophane. The mechanical properties of the films are given in Tables I and II.

According to the method of fabrication of the films, tenacities from 10.5 MPa up to 17.7 MPa can be obtained. On the other hand, the elongation at break varies inversely from 206% down to 135%. From Table I we can conclude that the tenacity increases in all cases when we press or draw the films at high temperature (105 or 160°C). The highest effect (70% increase) is obtained by applying a bidirectional drawing for 30 mn. But, as a result, the elongation at break decreases remarkably by 30%; this effect is usually observed in fibers.

Applying a pressure (15 bars/cm^2) for a short time (30 s) at high temperature (160°C) gives a film with a high tenacity and a high elongation at break. Nevertheless, it has to be noted that using higher temperatures (185°C for example) decreases the mechanical properties. This is probably due to degradation of the cellulose and a change in the structure of the lignin. From Table I it can be seen that the roll process is very good since the tenacity is very high (not far from the maximum value) with a high elongation. Table II gives the mechanical properties for a polyethylene film and cellulose films. Our best lignocellulosic films (see Tables I and II) can have the same strength as polyethylene films but have a much lower elongation at break. The results are about the same for "exploded wood" films and pure cellulose films. Thus the presence of lignin (40%) in the film does not alter the mechanical properties which was also the case for fibers.[8]

Contrary to what happens with fibers (see Results and Discussion), increasing the cellulose $\overline{DP}_v$ [done by adding kraft cellulose ($\overline{DP}_v = 1200$)] seems (see Table I) to have no real effect on the mechanical properties.

Structure of the Films

Structural studies were undertaken. A cross section of a film viewed with an optical or a transmission electron microscope displays a homogeneous and compact structure (Fig. 1). The lignin domains were stained with permanganate. The size of these domains is roughly 20 nm.

Protecting Action of Lignin

It has been suggested that lignin may act as an antioxidant.[8] In tertiary amine oxides it is well known that at high temperatures some oxidizing reactions can happen and cause some degradation of the cellulose. This is why some chemicals like propylgallate or sodium hexametaphosphate[9,10] are added to the mixture to prevent these phenomena. It is also known that, at very high temperatures (above 150°C), some radical reactions can occur and give rise to explosion.

To understand the behavior of lignin in solutions of exploded wood in the tertiary amine oxide system, we have measured the DP of regenerated cellulose extracted from the lignocellulosic material. We made two solutions (with and without propylgallate) of exploded wood (15% w/w) in MMNO. Dissolution took place at 120°C and for 45 min. We observe (Table II) that films made with or without an antioxidant have the same mechanical properties. In the same experimental conditions, we also made two solutions in MMNO (with and without lignin added after extraction from exploded wood with the water–

TABLE I
Mechanical Properties of Different Films from Exploded Wood Solutions

Processing conditions of the films	Air-dried	Air-dried, then oven-dried and pressed for 30 min at 105°C	Air-dried, then pressed under 15 bar for 30 s at 160°C	Air-dried, then bidirectionally stretched at 105°C for 30 min	Air-dried, rolled at 105°C
Tenacity (GPa)	10.5 ± 1.2	11.8 ± 1.0	15.2 ± 1.5	17.7 ± 2.5	16.2 ± 1.5
Elongation at break (%)	198 ± 11	206 ± 13	170 ± 15	135 ± 20	150 ± 15

TABLE II
Mechanical Properties of a Commercial Polyethylene Film and of Films from Exploded Wood Solutions

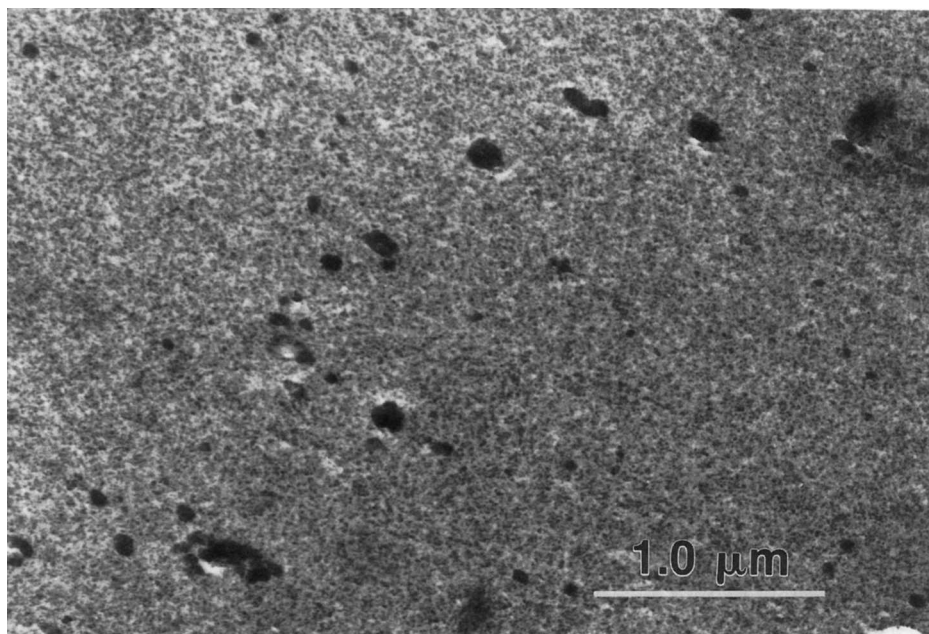| Processing conditions of the films	Polyethylene	Exploded wood, air-dried	Pure cellulose, air-dried, then oven-dried for 30 min at 105°C	80% exploded wood and 20% kraft pulp cellulose with antioxidant	80% exploded wood and 20% kraft pulp cellulose without antioxidant
Tenacity (GPa)	17.0 ± 1.2	10.5 ± 1.2	12.4 ± 1.0	9.3 ± 1.3	8.9 ± 1.1
Elongation at break (%)	1000 ± 200	198 ± 11	220 ± 20	185 ± 25	162 ± 20

Fig. 1. Transmission electron micrograph of a cross section of an exploded wood film stained with permanganate.

dioxane system) of bleached cellulose extracted from exploded wood. The $\overline{DP}_v$ of cellulose was measured in cupriethylene diamine according to the standard method.[11] For this purpose, to facilitate the dissolution of cellulose in cupriethylene diamine, the cellulose from MMNO solutions was regenerated in hot DMSO, then dialysed, filtrated, washed, and, if necessary, bleached (by a soda and chlorite treatment). The results are shown in Table III.

From this table we can draw several conclusions:

—Without an antioxidant and/or lignin, the cellulose is highly degraded (the $\overline{DP}_v$ goes down from 540 to 215). This result has been observed several times.[9,12]

—In the presence of lignin, the addition of propyl gallate to the solution makes only a very small difference to the degradation of the cellulose.

TABLE III
Viscosimetric Degree of Polymerization of the Cellulose for Various Samples[a]

Sample	Raw material exploded wood	Film of exploded wood with propylgallate	Film of exploded wood	Film of bleached cellulose	Film of bleached cellulose mixed with extracted lignin
$\overline{DP}_v$	540 ± 30	420 ± 25	410 ± 25	215 ± 10	315 ± 10

[a] Films were made using the same experimental conditions: concentration of 17.5% (w/w) in MMNO and temperature of dissolution, 120°C.

This demonstrates the protecting effect of lignin. This proves that it is not necessary to add an antioxidant in our solutions.

—The last experiment with the use of a mixture of bleached cellulose and extracted lignin shows that this lignin (partially degraded and perhaps not intimately attached to cellulose) gives only partial protection against degradation of the cellulose. Indeed this extracted lignin represented only 80% of the total lignin in the exploded wood, and in this experiment it is impossible to say if the partial protection is due to the change in the lignin composition or to the change in the interactions between the cellulose and the lignin.

Biodegradation of Exploded Wood Films

We have compared the biodegradation of a pure cellulose film and an exploded wood film. We used the Celluclast TM (Novo Industries) CLN 3004 enzyme (200 mg/mL). In 5 mL warm water (50°C) we degraded 67 mg of film using 6 mg of Celluclast. After 1 h, the pure cellulose film disintegrated into small pieces and the exploded wood film partly disintegrated. After 7 h both films disappeared and only dispersed lignin remained from the exploded wood film. Naturally, the use of lignolytic complexes would degrade the lignin too.

We have shown that exploded wood films are as biodegradable as pure cellulose films and this could be a very important advantage for the applications of these films. A measure of the permeability of exploded wood films and pure cellulose films gives roughly the same results. The presence of lignin in the film structure has no influence on this property as for the mechanical properties.

CONCLUSION

In this study, one of our objectives was to describe a fast and economical process to convert wood into biodegradable films using solutions in N-methylmorpholine-N-oxide. Indeed we could have used other tertiary amine oxides as described in a previous paper.[13] We could also use other exploded lignocellulosic materials such as straw, bagasse, etc.

We have shown that we are able to obtain quite strong films by this process. In the best cases the tenacity can reach (and maybe exceed) the tenacity of a synthetic film like polyethylene.

Exploded wood films are naturally colored from clear brown to black depending on the parameters used in the process. In these films the lignin and the cellulose are separated into microdomains. This is possibly the explanation for the insensitivity of the mechanical properties towards the value of cellulose DP. Indeed, even increasing the DP (i.e., the length of the cellulose chain), phase separation does not allow any chains of cellulose to go from one crystal in a microdomain to another. There would be no connections between the microdomains contrary to what occurs in fibers of pure cellulose. In this case the use of high DP allows the decrease of the cellulose concentration in the solution and increases the mechanical properties.

In this paper we have also proved that lignin acts as an antioxidant and prevents degradation of the cellulose in the MMNO system. It is hazardous to

predict possible uses for lignocellulosic films, but depending on their color and their mechanical properties one possibility could be to use them for agricultural applications. The main advantages of polyethylene films would be preserved, but these lignocellulosic films would be biodegradable.

When considering an industrial process, the experiments described previously are batch processes and would be inefficient. Whatever are our results, we note that these values could be improved if appropriate apparatus were used to make the films. It is sure that with the means we had in the lab, we have not obtained the optimal values. Nevertheless, our results can be compared with those obtained from other films.

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