

STUDIES ON TUNG OIL COATED REGENERATED CELLULOSE FILMS WITH WATER- RESISTANCE

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ABSTRACT

Regenerated cellulose films with water-resistance were obtained by an improved method of preparing cellulose cuoxam solution from pulps of agricultural wastes (linters, wheat straw, reed and Bamao). Experimental results showed that the mechanical properties of both the dry and wet films were excellent. Data from IR, SEM and tensile strength measurements implied that the significant improvement of water-resistance of the films was due to the cohesion between the thin Tung oil covers with hydrophobicity and the regenerated cellulose films. The films were completely biodegraded after being buried in soil for 100 days. The transmittance of the films derived from linter and reed in visible band range were 80-90%.

INTRODUCTION

The plant cellulose is the richest natural organic compound on the earth. Making use of agricultural wastes such as linters, wheat straw, reed and Bamao (a Chinese wild grass) to produce various biodegradable films can not only spare the oil resources but also protect our environment from pollution. Regenerated cellulose films obtained from cellulose cuoxam solution have been used for packing, separation etc., but soaking or exposing the films to moisture causes a rapid decrease in its mechanical strength. For that reason, we were interested in improving the water-resistance of the films by coating with cheap natural compounds. Tung oil is obtained from the seeds of the Tung tree (*Elaeococca vernicia*), indigenous to China. It is used widely as a component of coatings due to its property of quick drying and excellent water-resistance.

EXPERIMENTAL

Preparation of films

The raw materials used in this study were pulp of cotton linter (S), supplied by Chemical Fibre Manufacture of Hubei; wheat straw (J) by Jingan Co., reed (R) by Hanyang Paper Manufacture; Bamao (B) by Xianning Paper Manufacture. Their viscosity average molecular weights $\overline{M}_v$ were measured to be 1.91×10^5 , 2.11×10^5 , 1.21×10^5 and 8.9×10^4 respectively.

The 7wt. % cellulose solution in cuoxam was prepared according to the improved method as reported in our previous work^[1]. It was spread over a glass plate to a depth of 0.3mm with a glass tube at each end to provide the necessary gap, then was placed in coagulation and regeneration baths in order, each followed by a wash in running water, finally plasticized with 20wt. % glycerol, dried at 25°C. The dry films were treated with thin Tung oil, consisting of 3 parts of Tung oil, 7 parts of thinner and 0.01—0.03wt. % catalyst^[2] then stoved at 80—100°C for 3 minutes. The films derived from pulps of S, J, R and B were coded as RC-S01, RC-J01, RC-R01, RC-B01, while the ones not coated were coded as RC-S0, RC-J0, RC-R0, RC-B0. The films were prepared after a week of storing of the cellulose cuoxam solution in the air without adding any anti-oxidation agents.

Apparatus and procedures

Right-angled tearing strength (σ_{tr}), tensile strength (σ_b) and elongation at break (ϵ_b) of the dry and wet films were measured on the tensile testing machine (Model XLD-0.1, the Second Tensile Testing Machine Manufacture of Changchun, China) according to a Chinese standard method GB4456-84. The wet films were obtained by saturating the dry films in water for 10 minutes and then absorbing the water on the surfaces of the films with filter paper.

Scanning electron micrographs (SEM) of the films were taken with a SEM (ISI-SX-40). The films were coated with carbon and gold. Subsequently their surfaces were observed and photographed.

IR spectra of the films were recorded with Nicolet 170SX FT-IR spectrometer.

X-ray diffraction was measured with X-ray diffractometer (Rigaku 3015) by Mr. Yao at the Hubei Research Institute of Chemistry. The X-ray diffraction patterns with $\text{CuK}\alpha$ at 35kV and 25mA were recorded in the

region of $2\theta = 5-45^\circ$. Degrees of crystallinity (X_c) were calculated from X-ray data according to the usual method.

Viscosity average molecular weights ($\overline{M}_\eta$) of the films and the raw cellulose materials were determined from intrinsic viscosities $[\eta]$ in cadoxen at 25°C by the following equation^[3].

$$[\eta] = 3.85 \times 10^{-2} \overline{M}_\eta^{0.76}$$

Transparency of the films were measured on a visible spectrophotometer (Model 72, Shanghai Analytical Instrumental Manufacture) 500—700nm and a ultraviolet spectrophotometer (Model UV-240 Shimadzu, Japan) 190—500nm.

Test of cohesion between the Tung oil cover and the film was carried out as follows. The films were immersed in water and were wiped three times, then they were removed from the water and dried at 50°C . In order to observe the cohesion, the wiped films were analysed by SEM and IR, and were compared with the ones not wiped.

Biodegradability of the films was conducted by Prof. Wang at Agricultural University of Beijing. It was carried out by burying the films in the soil collected from a farm in Beijing, then calculated the weight loss. Temperature and water content of the soil were kept at 25°C and 20wt. % respectively.

RESULTS AND DISCUSSION

The experimental results of mechanical properties, molecular weights and degrees of crystallinity of the films are summarized in Table 1. It is clear that values of σ_b and σ_{tr} of the films treated with Tung oil were higher than the ones not treated. The tensile strength, toughness and elongation of the coated films are good, though molecular weights of the films became low because of the oxidative degradation. From Table 1 we can also notice that right-angled tearing strengths σ_{tr} and tensile strengths σ_b have the order: RC-S01 > RC-J01 > RC-R01 > RC-B01, which is well in agreement with that of molecular weights $\overline{M}_\eta$. The degrees of crystallinity of RC-R0 and RC-B0 are low, due to the presence of 20% hemi-cellulose. Table 1 shows that mechanical properties of both the dry and wet films are as excellent as polyethylene (PE) film. Significant improvement of water-resistance of the regenerated cellulose films is mainly attributed to the formation of the thin Tung oil covers with hydrophobicity.

Table 1 Comparison of mechanical properties ,molecular weights ,degrees of crystallinity and water-resistance of the films

Membranes No.	σ_b (kg/cm ²)		σ_{tr} (kg/cm ²)		ϵ_b (%)		$\overline{M}_n \times 10^{-4}$	X_c (%)
	Dry	Wet	Dry	Wet	Dry	Wet		
RC-S01	280	263	135	114	146	157		
RC-S0	228	72	118	40	138	164	5.1	37
RC-J01	237	221	111	110	139	141		
RC-J0	209	124	71	32	125	154	3.5	39
RC-R01	189	177	79	73	66	71		
RC-R0	175	78	46	11	83	95	2.8	30
RC-B01	172	165	90	74	38	63		
RC-B0	68	29	31	10	56	70	1.8	29
PE	145		109		120			

Fig. 1 shows SEM of the films. Both RC-S01 and RC-S01-W (RC-S01 wiped in water) display smooth surfaces and have sausage-like homogeneous networks, while that of RC-S0 appears porous. It shows that the crosslinked Tung oil covers on the surfaces of regenerated cellulose films have not been wiped off.

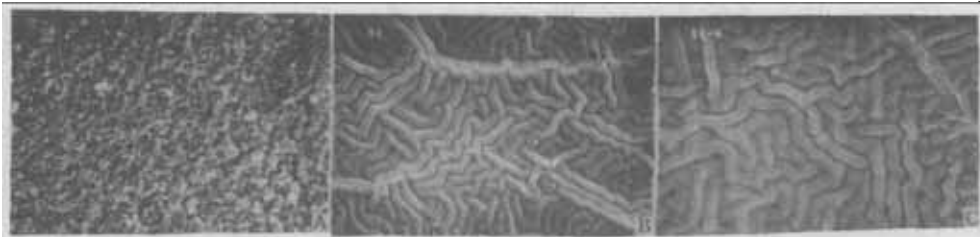


Fig. 1 SEM of the films of RC-S0(A); RC-S01(B); RC-S01-W(C)

Fig. 2 shows IR spectra of the films. The stretching vibration frequency at 2850 cm⁻¹ for crosslinked Tung oil and RC-S01 is attributed to the CH₂ group adjacent to carboxyl group in eleostearic acid. Because of superposition of =C—H, =C—O and C=O groups in Tung oil, the absorbance of RC-S01

film at 990,1167 and1743 cm^{-1} is larger than that of RC-S0. As seen in Figs. 1 and 2,the cohesion between Tung oil polymer and cellulose is very strong. The drying mechanism of Tung oil was assumed to be oxidation and addition polymerization^[4].

Fig. 3 shows the transmittances of PE and the films treated by Tung oil at wavelength region of 190—700nm. Depth of the samples is $0.02 \pm 0.005\text{mm}$. The values of the transmittance of the films derived from R and S fall between 80% and 90% similar to that of PE at 600—700nm.

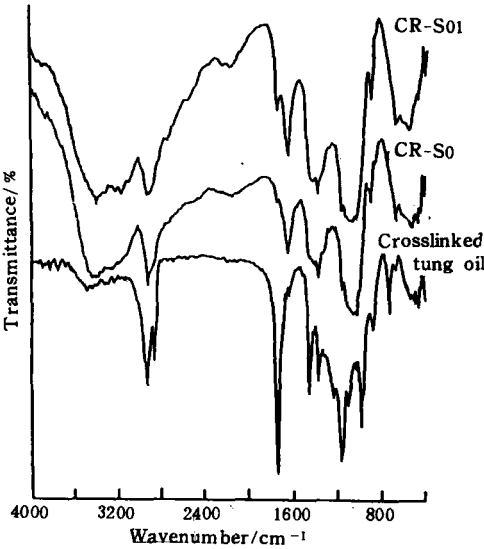


Fig. 2 IR spectra of the films

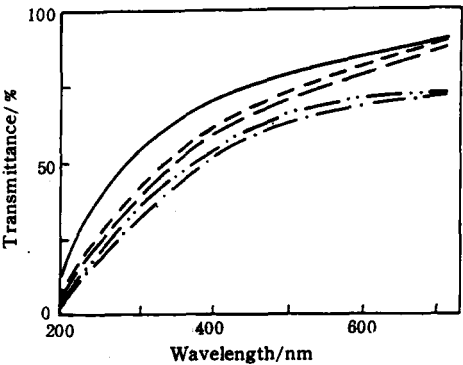


Fig. 3 Transmittances for the films of PE(—), RC-R01(---), RC-S01(— —), RC-B01(— · —) and RC-J01(— · · —)

The results of biodegradability of the films derived from pulps of linter and reed are listed in Table 2. The films had short half life of biodegradability,they were completely biodegraded after being buried in soil for 100 days,fragments of the films and crosslinked Tung oil covers were not found through microscope. Detailed studies on the products of biodegradation are in progress. It is clear that the biodegradability of the films treated with Tung oil is excellent.

Table 2 Experimental results of biodegradation for RC-S01 and RC-R01 in soil

Films No.	Degradation ratio (%)				Half-life (days)
	7 days	14 days	30 days	100 days	
RC-S01	29	55	82	100	14
RC-R01	39	60	—	100	12

CONCLUSIONS

Regenerated cellulose films were satisfactorily prepared from pulps of agricultural wastes. The films treated with thin Tung oil have good properties of mechanical strength, water-resistance, biodegradability and transmittance. The prospect of utilizing this material as a substitute of plastic film is promising.

Keywords:

Regenerated cellulose film; Cuoxam; Tong oil cover; Water-resistance; Biodegradability; Agricultural waste; Mechanical strength

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