

Study on the Photo Degradation of Pulp Mold Container

Yifang Ou, Qiulian Huang

Laboratory of Cellulose and Lignocellulose Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China

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ABSTRACT: The photodegradation of a pulp mold container was investigated with ultraviolet light. The results show that the degree of polymerization of samples decreased about 50%, tensile strength decreased 20–30%, sample weight lost 10–16%, and brightness decreased about 20%

after 8 weeks of UV irradiation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2052–2056, 2003

Key words: ultraviolet; photodegradation; pulp mold container

INTRODUCTION

The pulp mold container is a kind of new product, developed to substitute for foamed plastic containers, meeting the demands of environmental protection. The degradability of the pulp mold container is an important index used to evaluate its environment-friendly extent. There are many means to study the degradability of the pulp mold container such as photo degradation, thermal degradation, and biodegradation. To investigate the natural degradability of the pulp mold container, we adopted the method of photodegradation. When a pulp mold container is discarded in the natural environment, it is irradiated and degraded by sunlight. We used ultraviolet light to imitate sunlight, because ultraviolet light in sunlight plays a main role in the degradation of cellulose. The effects of ultraviolet irradiation on cellulose have been studied from different aspects. There are two kinds of reaction mechanisms undergone by cellulose during the course of photodegradation. One is direct photolysis, which only occurs at wavelengths < 310 nm: it will cause the bonds of C—C or C—H to cleave. Oxygen will promote this reaction and steam will retard it. The other is photosensitized degradation, which occurs at wavelengths ranging from 290 to 400 nm. The photons in this wavelength range cannot usually be absorbed by cellulose itself but are often absorbed by compounds mixed with the cellulose. The absorbed light energy causes cellulose to degrade. Both oxygen and steam can promote this reaction. A series of photolysis reactions will occur during the course of direct photolysis or photosensitization. This

brings about a decrease in the degree of polymerization (DP)¹ of cellulose, and its strength,² and causes yellowing³ and fragmentation of molecules to diverse volatile products.⁴ Although pulp mold containers are mainly made from plant cellulose, such as bagasse, straw, reed, and so on, there are also many additives in the container, of which the most important additives are antiwater and antioil agents.⁵ Colophony size and a kind of fluoride were used as antiwater and antioil agent, respectively, in this experiment. Colophony size is a kind of common emulsive agent for water resistance. The structure of the antioil agent is as follows: $(C_8F_{17}SO_2N(C_2H_5)-C_2H_4-O)_2PO_2NH_4$. It is a good agent for oil resistance. These additives would affect the photodegradation of cellulose, especially the photosensitization of cellulose.

EXPERIMENTAL

Preparation of samples

Reed pulp was acquired from the Nei Menggu Xi Shanzui Pulp and Papermaking Mill. It was obtained by alkaline sulfite pulping and hypochlorite bleaching and contains 0.47% ash and 1.25% lignin (72% vitriol method). The pulp was beaten to 30° SR in low viscosity, and then the concentration of pulp was adjusted to 1%. These agents were added to the pulp according to certain proportions, and then the mixed pulp was infused in a mold at certain temperatures and pressure controlled to about 320 g/m². Seven groups of samples were prepared. The first group contained no additives, which is called sample I in this article. Antioil agents amounting to 0.4, 0.7, and 1.0% (based on the dry pulp) were added into sample II, sample III, and sample IV, respectively, and 4, 5, and 6% of antiwater agent were added into sample V, sample VI, and sample VII, respectively. Twelve sam-

Correspondence to: Y. Ou (yifangou@mail.gic.ac.cn).

TABLE I
Weight of Samples Used to Test DP and the Weight of Filter and Insoluble Residue

Samples: Time/day	I		II		III		IV	
	M ₀ /g	m/g	m ₀ /g	M/g	m ₀ /g	m/g	m ₀ /g	m/g
0	0.2393	37.4734	0.1777	37.4718	0.2288	37.4729	0.2879	37.4720
7	0.2648	37.4739	0.2075	37.4716	0.2441	37.4732	0.2435	37.4726
14	0.2596	37.4737	0.2442	37.4733	0.1875	37.4716	0.2693	37.4734
21	0.2906	37.4747	0.2551	37.4741	0.1523	37.4714	0.2137	37.4728
28	0.2701	37.4742	0.2803	37.4744	0.2497	37.4738	0.1878	37.4719
35	0.3002	37.4748	0.2959	37.4750	0.1731	37.4722	0.1569	37.4710
42	0.2903	37.4744	0.2655	37.4746	0.2599	37.4740	0.2365	37.4706
49	0.2649	37.4740	0.3008	37.4749	0.2701	37.4742	0.1741	37.4732

ples were prepared in each group. In addition, another group with 0.8% of antioil agent added was also used to test tensile strength.

Photo-degradation

Samples were degraded in an ultraviolet light box that was designed according to the Chinese national test method for single-use degradable containers (GB/T 18006.2-1999). The sources of ultraviolet irradiation were high-pressure mercury lamps (wavelength, ~340 nm). The samples were fixed between two lamps and picked out every 1 or 2 weeks during photodegradation. The temperature in the box was kept at 46°C and the humidity was held constant at 80%.

Performance test

The performance changes of samples such as average DP, weight loss, and brightness were tested. Every value was obtained by three parallel tests. The value of tensile strength was obtained by 12 parallel tests.

Average DP

The sample was dried in an oven to constant weight and weighed. It was then dissolved in cupriethylenediamine solution. A dried filter was weighed and

the solution was filtered with it. The filter and insoluble residue were dried together and weighed. Therefore, the concentration of sample solution can be obtained from the equation,

$$C = [m_0 - (m - m')]/v$$

in which m' is the oven-dry weight of filter, equaling 37.4691 g, v is the volume of the solution, equaling 50 mL, m_0 is the oven-dry weight of samples before solution, and m is the oven-dry weight of the filter. The unsolvable residue, the data of m_0 , and m are shown in Tables I and II.

Relative viscosity values of cupriethylenediamine solution were tested by using a Ubbelohde viscometer in 25°C and the calculated intrinsic viscosity values were then tested by the Mark-Houwink formula

$$\lg[\eta] = \lg(\eta - \eta_0)/\eta_0 * C - K[\eta]^*C$$

in which $K = 0.13$, and C is the concentration of sample. The intrinsic viscosity was converted to average DP by the equation⁶: $DP^{0.905} = 0.75[\eta]$.

Sample weight

Weight loss was calculated from the initial and final weight dried at 105°C for 20 h.

TABLE II
Weight of Samples Used to Test DP and the Weight of Filter and Insoluble Residue

Samples: Time/day	I		V		VI		VII	
	M ₀ /g	m/g	m ₀ /g	m/g	m ₀ /g	m/g	m ₀ /g	m/g
0	0.2393	37.4734	0.2298	37.4739	0.2389	37.4730	0.1940	37.4730
7	0.2648	37.4739	0.2137	37.4728	0.2341	37.4732	0.2392	37.4733
21	0.2906	37.4747	0.2599	37.4740	0.2505	37.4746	0.2847	37.4738
35	0.3002	37.4748	0.2901	37.4750	0.2708	37.4749	0.2949	37.4740
49	0.2649	37.4740	0.2653	37.4744	0.3012	37.4753	0.2487	37.4728

TABLE III
Ranges of Data for Tensile Strength of Samples Containing Antioil Agent

Antioil agent /%		0	0.4	0.7	0.8	1.0
Before degradation	Strength ranges/KN/m	8.75–9.21	10.03–10.92	9.49–10.31	9.43–10.26	10.61–11.62
	Average strength/KN/m	9.00	10.47	9.91	9.86	11.15
After degradation	Strength ranges/KN/m	7.65–8.43	7.73–8.37	7.27–7.79	7.68–8.39	6.89–7.42
	Average strength/KN/m	8.05	8.02	7.56	8.03	7.17

Brightness

Brightness was tested with a Micro TB-IC photometer (Technidyne Co. USA). Blue light (main wavelength, 457 nm) was adopted as the light resource and the geometric condition was 45°/0.

Tensile strength

Tensile strength was tested with a tensile-strength testing instrument (Alwetron thi, Sweden). Before measurement, the samples were put in an oven for 2 days, where both temperature and humidity were maintained constant at 46°C and 80%, respectively. The ranges for data are shown in Tables III and IV.

RESULTS AND DISCUSSION

Change of average DP

Figure 1 shows the change of average DP of samples with the amount of antioil agent and degradation time. The trend of the curves in the figure is to lower DPs. The average DP of sample II decreased slower and samples III and IV decreased faster than that of sample I in the initial stage of degradation. Perhaps the two opposite effects of the antioil agent on the degradation caused the different results. The antioil agent can also prevent steam absorption, which would promote photosensitization, and hence, hold back the degradation. At the same time, the agent can absorb ultraviolet so that it can promote the degradation. We also notice that there are small increases in some of the curves, for example, from the points of 27 days of sample II, 16 days of sample III, and 7 days of sample IV. Crosslinking of cellulose during the course of photodegradation may cause this. Absorbed photo energy

causes cellulose to produce long-chain free radicals. When two long-chain free radicals meet, crosslinking reaction occurs.

Figure 2 shows the change of average DP of samples with different amounts of the antiwater agents and time. The antiwater agent has an obvious protecting effect on the degradation of cellulose. All of the average DPs of samples V, VI, and VII decreased slower than did sample I. This may be because the steam-promoting effect plays a main role during the course of degradation. The antiwater agent prevented steam from entering into the impregnated samples so that the degradation became slower.

Weight loss

Figures 3 and 4 show the change of weight loss of samples with the amount of agents and irradiation time. The curves in Figure 3 show the samples with different antioil agent contents and those in Figure 4 stand for samples with different antiwater agent contents. Previous research showed that cellulose could be photolyzed and produced gaseous products such as H₂, CO, CO₂, and H₂O.⁷ A continuous increase in the weight loss was observed during the course of irradiation. The weight of samples lost about 10–16% after 8 weeks of irradiation. The entire weight loss was small and the effect of agents on the weight loss was also slight.

Brightness

The change of brightness with the amount of agents and degradation time is shown in Figures 5 and 6. It was found that the brightness increased slightly in the initial stage and then decreased. The level of chro-

TABLE IV
Ranges of Data for Tensile Strength of Samples Containing Antiwater Agent

Antiwater agent /%		0	4	5	6
Before degradation	Strength ranges/KN/m	8.75–9.21	13.31–14.28	13.67–14.82	13.18–14.25
	Average strength/KN/m	9.00	13.77	14.27	13.77
After degradation	Strength ranges/KN/m	7.65–8.43	10.98–11.93	10.21–12.15	9.38–10.12
	Average strength/KN/m	8.05	11.42	10.66	9.74

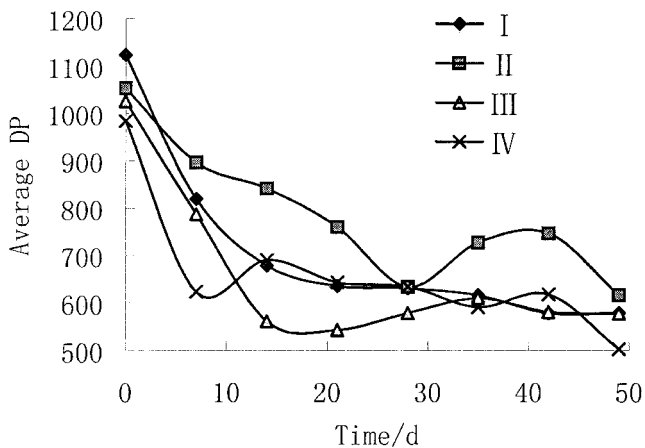


Figure 1 Change of average DP with time and the amount of antioil agent.

mophoric group affects the brightness of the sample. There were lots of chromophoric groups in the sample before degradation, which were formed during the course of pulping. These chromophoric groups are easily oxidized to carboxyl so that the level of chromophoric group decreased in the initial stage of irradiation and samples became bright. With longer degradation times, cellulose chains ruptured and aldehyde groups were formed so that the sample became yellower. The effect of antioil agent on the change of brightness is slight in the initial stage but it held back the change of brightness in the later stage. When the additives for antiwater was added into the sample, the change of brightness became slight and slow.

Tensile strength

The effect of additives on the change of tensile strength is shown in Figures 7 and 8. It was found that the addition of agents not only affect the change of tensile strength during the irradiation course but also

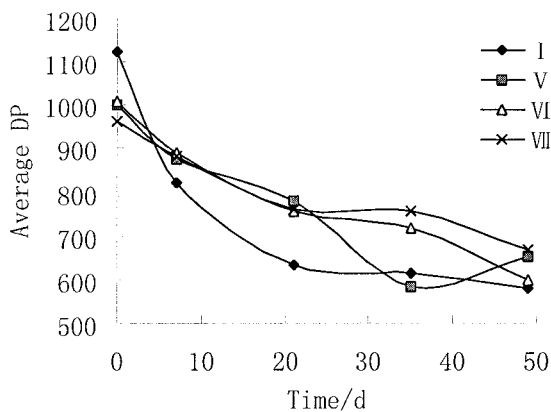


Figure 2 Change of average DP with time and the amount of antiwater agent.

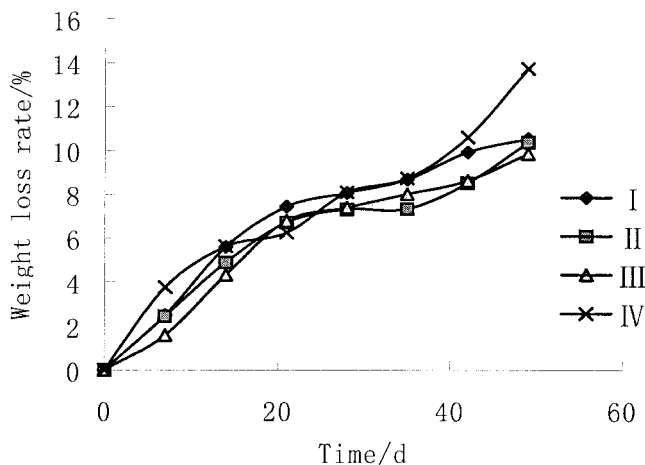


Figure 3 Change of weight loss with time and the amount of antioil agent.

the tensile strength before degradation. The tensile strength of samples before degradation increased with the amount of antiwater agent (see Fig. 8) and changed irregularly with the amount of antioil agent (see Fig. 7). This is probably related to the fact that the mechanical properties of the samples are strongly dependent on the equilibrium moisture content (EMC). The more the antiwater agent the sample contained, the less the EMC of the sample. The lower level of EMC would give higher tensile strength. The tensile strength of every sample decreased to a certain extent after degrading for 8 weeks. The decrease was about 10–30%.

CONCLUSIONS

1. Ultraviolet irradiation caused degradation of pulp mold container to a certain extent.
2. The DP of sample decreased with UV irradiation time in general and decreased about 50% after 8 weeks of irradiation

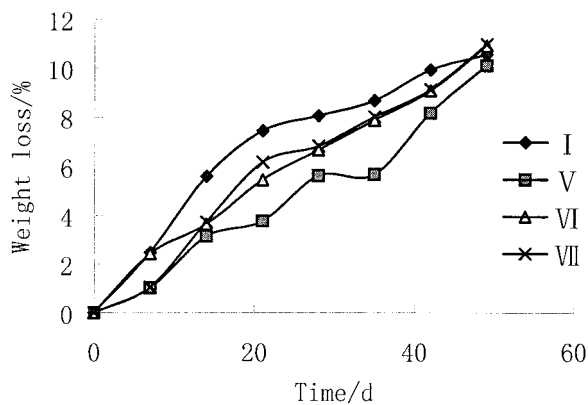


Figure 4 Change of weight loss with time and the amount of antiwater agent.

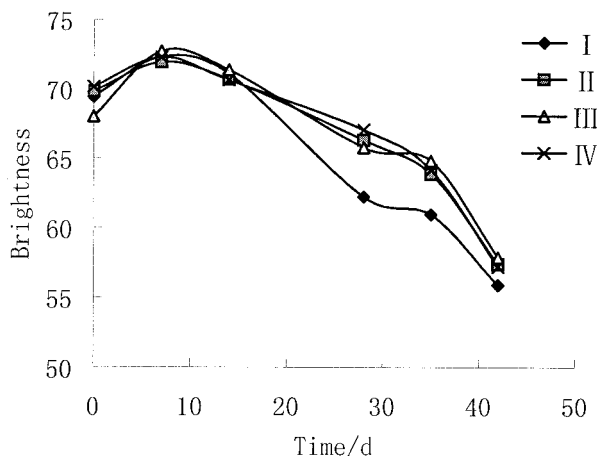


Figure 5 Change of brightness with time and the amount of antioil agent.

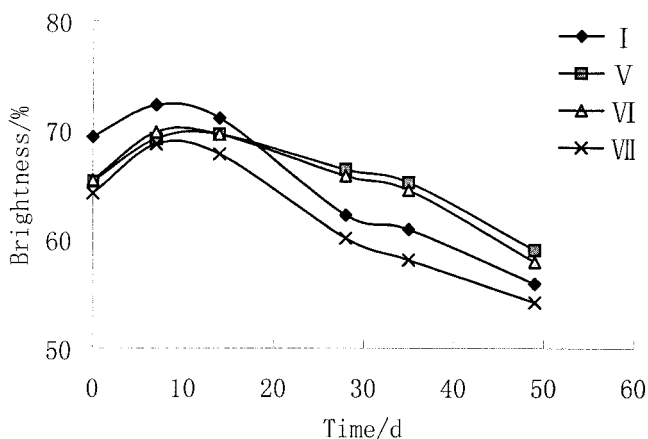


Figure 6 Change of brightness with time and the amount of antiwater agent.

- The sample weight decreased with UV irradiation time and the weight loss was 10–16% after 8 weeks of irradiation.
- Brightness increased initially then decreased later. The brightness decreased about 20% after 8 weeks of irradiation.
- Ultraviolet irradiation caused the tensile strength of samples to decrease. After 8 weeks of irradiation, the tensile strength decreased 10–30%.

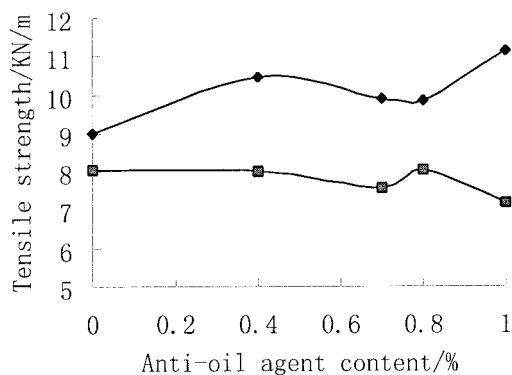


Figure 7 Effect of antioil agent on tensile strength.

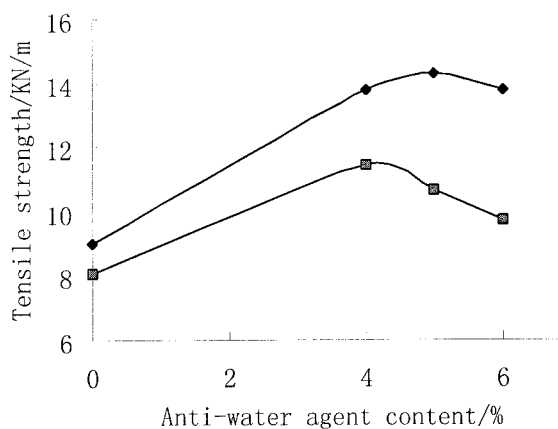


Figure 8 Effect of antiwater agent on tensile strength.

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