

Thermal Degradation of Cellulose-Based Complex Material

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ABSTRACT: Thermal degradation of cellulose-based complex material was investigated by treating at 100, 140, and 160°C, respectively. The performance changes of the material such as average degree of polymerization (DP), weight loss, brightness, and tensile strength were tested during the thermal treatment. And the thermal analyses of the material was conducted to show the change in different heating stage from 27 to 700°C. The effect of anti water and anti oil agents in the complex material on the change of performances was investigated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2535–2539, 2002

Key words: thermal degradation; cellulose; complex material

INTRODUCTION

To solve so-called White Pollution, a serious environmental problem in China, scientists found some materials that can be degraded naturally to substitute for foamed plastic containers. Now these projects mainly focus on two ways: one is the degradable plastic containers, the other is pulp mold containers.¹ The former can be degraded to a certain extent due to the addition of starch. But they cannot be degraded completely because the plastic cannot be degraded in the end. The later can be degraded completely because cellulose can be degraded completely in the natural environment.² The cellulose-based complex material can be used to make pulp mold containers. The material consists of three layers. The middle layer is made from bagasse, straw, or other cheap plant cellulose to reduce the cost of material and increase strength. Outside layers are made from bright pulp to give good appearance. The multilayer material made from differ-

ent plant celluloses is stronger and cheaper than single-layer material only made from pulp. Cellulose is the most abundant naturally occurring polymer. Making this material is a good way to utilize cellulose. To explore the application of this material in different fields and investigate the influence of temperature on the material, it is necessary to study thermal degradation of this material under different temperatures.

EXPERIMENTAL

Preparation of Samples

The raw materials such as bagasse, reed pulp, anti-oil agent, and anti-water agent come from the Nei Menggu Xi Shanzui Pulp and Papermaking Mill. Colophony size and a kind of fluoride were used as anti-water and anti-oil agent, respectively. The samples of the complex material were prepared as follows: 2% content reed pulp was blended quantitatively with some anti-water and anti-oil agent; 50 mL reed pulp, 50 mL 5% content bagasse pulp, and 50 mL reed pulp were fed into a kind of special molding equipment in turn. Bagasse and reed can be separated and

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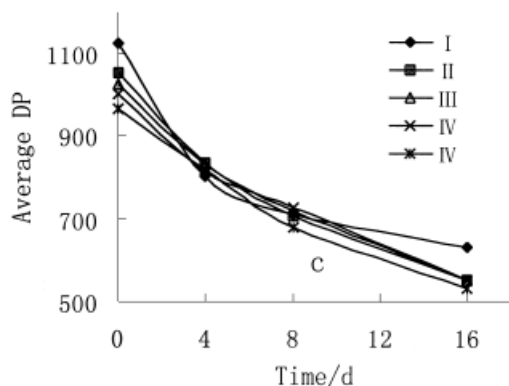


Figure 1 The decrease of average DP with time at 100°C.

formed different layers in the equipment. The up and under layers of sample were formed by reed pulp and bagasse formed a middle layer. Then the three-layer material was dried and cut into some pieces with a certain size for thermal degradation test. Six groups of samples were prepared with different amounts of anti-water and anti-oil agent. The first group contain none of the additives called sample I in this paper. Sample II and Sample III were added to 0.4 and 0.7% of anti-oil agent (based on the dry pulp) respectively. Sample IV and Sample V were added to 4 and 6% of anti-water agent respectively. Sample VI was added to 0.7% of anti-oil agent and 5% of anti-water agent.

Thermal Degradation

Referring to the Chinese national standard method of plastic aging in hot air, samples were put in an oven at 100, 140, and 160°C, respectively, and then blast once every 2 min to make sure samples were heated evenly. The degraded samples were picked out to test in a certain interval during heating time.

Performance Tests

Degree of Polymerization (DP)

According to Chinese national standard method of GB/T 1548-1989, the relative viscosity values in 25°C cupriethylenediamine solution were obtained by using a Ubbelohde viscometer. And then calculated the average DP of sample.

Sample Weight

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

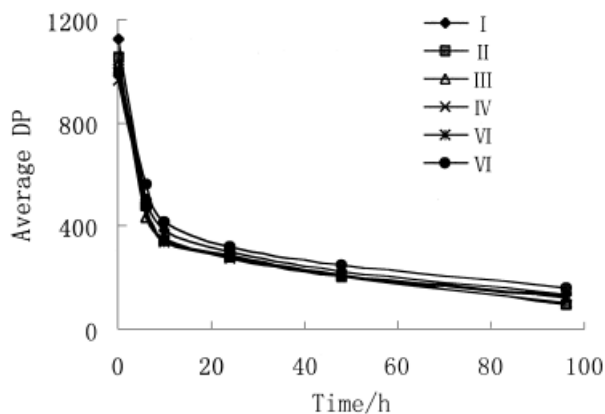


Figure 2 The decrease of average DP with time at 160°C.

Brightness

Brightness was tested with Micro TB-IC photometer (Technidyne Co. USA).

Tensile Strength

Tensile strength was tested with the instrument (Alwetron thi, Sweden).

Thermogravimetry (TG)

The TG analyses were carried out using a Netzsch TG 209 instrument. The samples were heated from 27 to 700°C with a heating rate of 10k/min under N₂ atmosphere.

RESULTS AND DISCUSSION

Average DP

Figure 1 shows the change of average DP with thermal degradation time at 100°C. The average

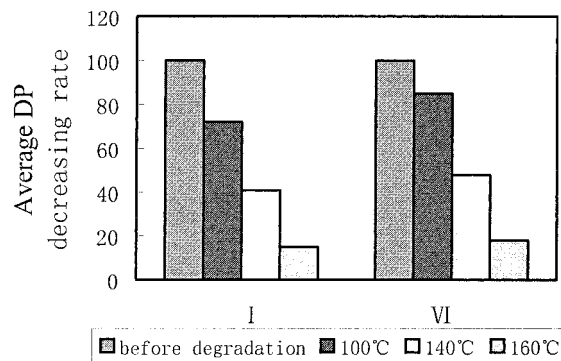


Figure 3 The effect of temperature on the decrease of average DP after degraded for 96 h.

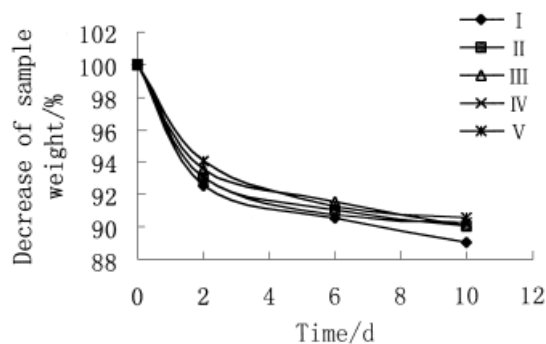


Figure 4 The change of sample weight with time at 100°C.

DP of sample decreased with time prolonging. The additives added for anti-water and anti-oil affect the decrease of average DP at a certain degree. They first made the rate of degradation become slow and then promoted the degradation. Colophony size formed a thin membrane to prevent water penetrating and so did the anti-oil agent to prevent oil penetrating. And the membrane held back the direct effect of heat on the inner cellulose so that the sample with agents degraded slowly. With time prolonging, the thin membrane was destroyed and formed many holes on the surface of sample, and the surface area contacting with the hot air increased, which would promote the degradation. Although the agents affect the degradation of the material, the effect is not great.

The change of average DP with time at 160°C is illustrated in Figure 2. It is apparent that the average DP of sample decreased very fast, especially in the first 20 h. In this condition the rate of degradation increased greatly and the effect of agents became so slight that it almost cannot be seen in the figure.

To investigate the effect of temperature on the degradation, Sample VI was treated for 96 h at 100, 140, and 160°C respectively. The results are given in Figure 3. The average DP decreased only 10 ~ 20% at 100°C, about 50% at 140°C, and

Table I Effect of Temperature on the Weight Loss Rate After Degraded for 48 h

	I	II	IV	VI
100°C	92.5%	93.3%	93.7%	95.3%
140°C	90.5%	92.0%	91.4%	92.0%
160°C	87.8%	88.5%	87.6%	89.0%

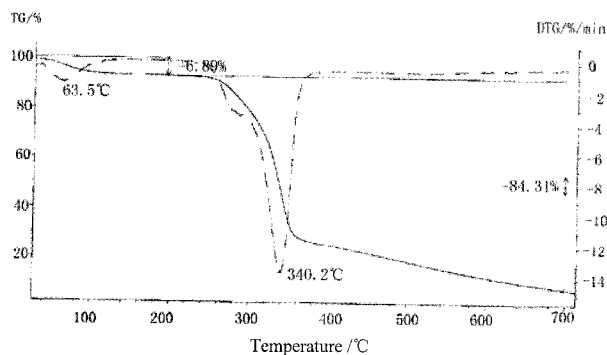


Figure 5 The thermal analysis of Sample I.

above 80% at 160°C. This may be due to the fact that cellulose is not stable when temperature is above 120°C.

Sample Weight

With the average DP decreasing the weight of sample decreased too. But the change of sample weight is not great and it decreased only about 10% after treated at 100°C for 10 days as shown in Figure 4. We can also see that the weight of sample with additives decreased less than that without agent according with the change of DP.

Table I gives the weight loss of four kinds of samples after treating for 48 h at 100, 140, and 160°C respectively. The samples weight lost 5 ~ 8% at 100°C and 11 ~ 13% at 160°C. The weight loss increased with the amount of additives decreasing and temperature increasing.

Figures 5 and 6 give the TG curves for the thermal degradation of Sample I and Sample VI. Both of the thermal degradations occurred in two stages. The sample weight lost a little in the initial stage. The weight loss rate (WLR) for Sample I was 6.89% and it increased up to the largest at

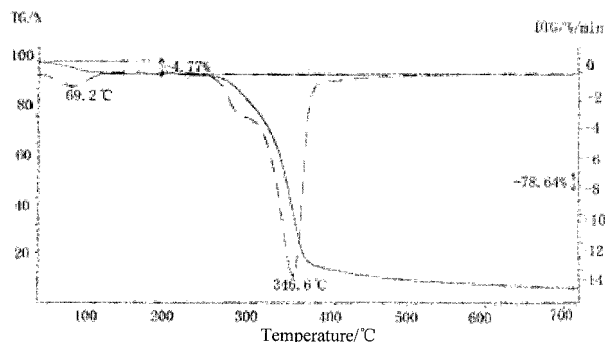


Figure 6 The thermal analysis of Sample VI.

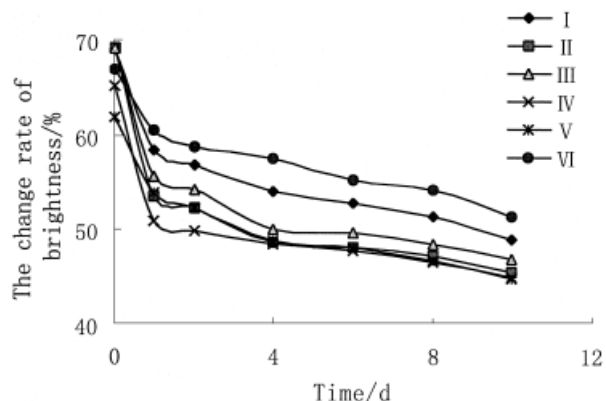


Figure 7 The change of brightness with time at 100°C.

63.5°C, and the WLR for Sample VI was 4.77% and it became the largest at 69.2°C in this stage. With temperature increasing to 200 ~ 230°C, both of the samples began to decompose into gases and their weight decreased largely. In this stage the WLR was 84.31% for Sample I, 78.64% for Sample VI and it became the largest at 340.2°C for Sample I, 346.6°C for Sample VI. That also indicated that the sample with additives degraded more slowly than that without agents.

Brightness

The brightness of the sample decreased obviously during thermal treatment. The results are shown in Figure 7. When Sample I was treated at 100°C for 10 days, its brightness decreased about 30%. When two kinds of agents were added together, the brightness decreased slowly. However, when they were added separately they promoted the decrease of brightness. We cannot explain the phenomena yet, but it indicated that the two agents could cooperate with each other to hold back the decrease of brightness.

Table II shows the change of brightness of Sample I and Sample VI with time at 160°C. From the table we can see the brightness de-

Table II Change of Brightness with Time at 160°C

	Time (h)					
	0	6	12	24	48	96
I	68.9	44.7	35	24.3	15.7	11.8
VI	66.9	40.2	33.1	24.8	18.9	12.7

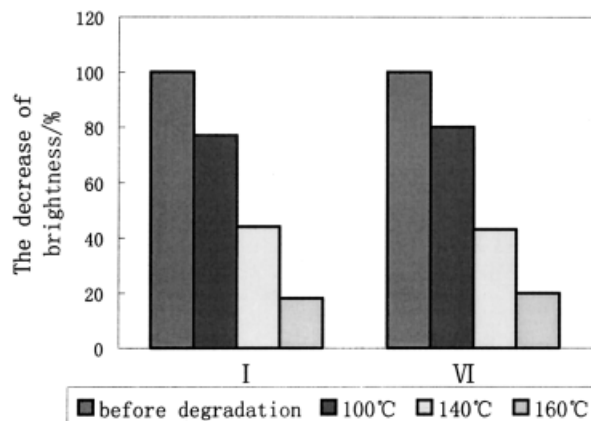


Figure 8 The effect of temperature on the decrease of brightness after degraded for 96 h.

creased greatly at a very high temperature. The effect of temperature on the brightness was remarkable. It is very clear in Figure 8 which shows the brightness change of Sample VI after degrading for 96 h at 100, 140, and 160°C respectively. The brightness decreased about 20% at 100°C, 50% at 140°C, and 85% at 160°C.

Tensile Strength (TS)

When cellulose, as main raw material, was degraded, the strength of samples had to decrease too. Table III shows the TS change of five groups of samples after degrading for 20 days at 100°C. The results showed that TS decreased very slowly at 100°C. The decreasing rate was 5.7 ~ 16.2%. We also can see the effect of amount of additives on the TS is not negligible.

The tensile strength of Sample I and Sample VI was tested during thermal degradation at 160°C as shown in Figure 9. The tensile strength decreased quickly in the initial stage, which is according with the change of average DP (see Fig. 2). The tensile strength of sample decreased above 70% at 160°C. The effect of temperature on

Table III Change of Tensile Strength (TS) After Degraded for 20 Days at 100°C

Sample	I	II	III	IV	V
TS before degradation	11.8	10.5	11.2	13.8	13.8
TS of degraded sample	11.2	10.2	10.0	11.9	11.5
Change rate (%)	94.3	96.9	90.1	86.8	83.8

TS is also great. TS decreased about 5% at 100°C, 35% at 140°C, and 75 ~ 80% at 160°C after degrading for 96 h as shown in Figure 10.

CONCLUSION

The complex material is easily degraded under high temperature. Sample weight decreased 11% after degrading at 160°C for 48 h and the brightness decreased about 90%, DP decreased above 80%, the tensile strength decreased 70 ~ 80% at 160°C for 96 h. And sample began to decompose at 230°C and the rate of decomposition came to the highest at 346°C.

The material degraded slowly under 100°C. Its weight decreased 5 ~ 7% after degrading at 100°C for 48 h and the brightness decreased

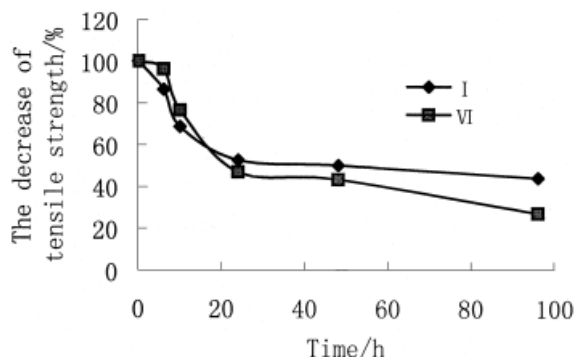


Figure 9 The change of tensile strength with time at 160°C.

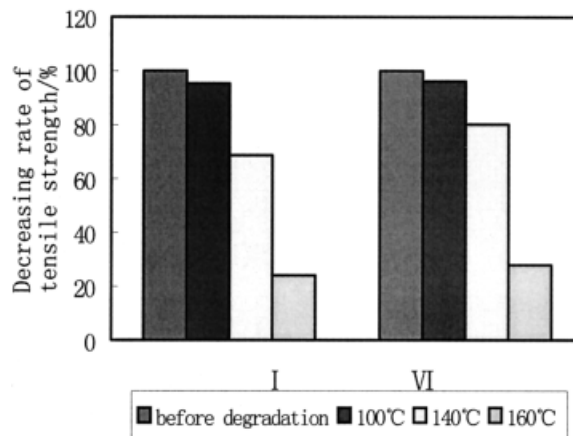


Figure 10 The effect of temperature on the decrease of tensile strength after degraded for 96 h.

about 20%. DP decreased about 20%, the tensile strength decreased about 5% at 100°C for 96 h. So the material should be used under 100°C.

Agents added for anti-water and anti-oil affected the degradation. On the whole the agents would reduce the change of parameters and hold back the thermal degradation. And the effect is obvious under low temperature and it becomes slight under high temperature.

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