Study on Blended Spinning Solution Composed of Chrome Shavings Extract and Polyvinyl Alcohol

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Abstract: The chrome shavings were dechromed with the method of oxidation, and the extract was attained in the conditions of acid or base respectively. The blended solution was obtained by blending chrome shavings extract with polyvinyl alcohol (PVA). The optimal proportion was acquired after comparing of the properties, including viscosity of the mixture, mechanical properties of the blended membranes. The optimal proportion of PVA : extract (prepared with acid method) is 2:8 while solid content is 10%. The results of degradation test indicated that the membranes developed with the extract and PVS could be degraded in soil, trypsin solution and AS1.398 solution.

Key words: composite fiber; chrome shavings extract; polyvinyl alcohol

With the increasingly global ecological problem and resource crisis, China's leather industry is facing the strategic challenges of "sustainable development". And the utilization of leather solid waste (especially the chrome shavings) has become one of the most important issues all over the world [1]. Biodegradable fiber was first developed in the 20th century 60's because of the request of medical application. Though the fiber was developed for over 40 years, the application of the fiber was mainly focus on medical and gardening fields because of its performance deficiencies or high cost [2-4]. Presently, it was reported that collagen which was extracted directly from animal skin was blended with other materials to produce composite fiber [5-11]. In this study, collagen and its hydrolyzate (summoned as extract) which was prepared from chrome shavings were utilized as the raw material of spinning. This kind of application can not only achieve the recycle use of tannery waste, but also be in line with the requirements of circular economy and so as to be beneficial to the sustainable development of China's leather industry. What's more, the fiber we produced will meet the requirements of "green fiber", and conform to the trend of the world's fiber and social development.

1 Materials and Methods

1.1 Materials and Equipments

Chrome shavings extract (acidic), Chrome shavings extract (basic), self-made; Polyvinyl alcohol(PVA), Chengdu Kelong Chemical Reagent Factory; trypsin, Chengdu Wenjiang Tianyuan Enzyme Factory; AS1.398 neutral protease, Yunnan Luliang Enzyme Factory; NXS-11A Rotary Viscometer, Chengdu Instrument Factory; GT-AI-7000S Electronic Mechanical Test Machine, Gaotie Technology Co., Ltd.; HZS-H Water Bath Oscillator, Harbin Donglian Electronic Technology Co., Ltd..

1.2 Experimental methods

1.2.1 Preparation of Blended Spinning Solution

After dechroming with H_2O_2, the basic extract was prepared from chrome shavings under the employ of alkaline protease, while the acidic extract was developed with the use of acidic protease (viz pepsin).

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PVA solution with certain concentration was blended with acidic and basic chrome shavings extract respectively. The total solid contents of blend solutions (mass percentage) were 8%, 10% and 12%, while the proportions of extract and PVA were 1:9, 2:8, 3:7 and 4:6.

1.2.2 Viscosity Test

The α value (instrument readings) of blended solutions was measured under different conditions of temperatures T and shear rate γ, then the apparent viscosity was calculated by the equal of η = Kα (K is the apparatus constant).

1.2.3 Mechanical Properties of Membranes

The membranes samples were air-conditioned in atmosphere of constant temperature and humidity for 24h [12], followed by sampling, measurement of thickness. The tensile strength and elongation at break of the samples were determined on the Mechanical Test Machine.

1.2.4 Degradation Test of Membranes

The optimal proportion of the blended solution was acquired after comparing the results of viscosity test of the solutions and mechanical test of the membranes. The membranes which were made from the optimal proportion were employed in degradation test. The samples were air-conditioned and dried at 80℃ for 3h to measure the moisture content. The dry weight of the samples = sample weight × moisture content.

1.2.4.1 Degradation in Soil

The membranes were prepared into the shape of rectangle by 5.5cm × 3.5cm, and were weighted (record as W0) and divided into groups. Subsequently, the membranes were buried in the soil and taken sampling every 7 days. The samples were cleaned and were dried at 80℃ for 3h before they were weighted (record as W1). Degradation percentage (%) = (W0-W1)/W0.

1.2.4.2 Degradation in Protease Solution

The membranes were prepared into the shape of rectangle by 5.5cm × 3.5cm, and were weighted (record as W0). Subsequently, the membranes were immersed in the culture disks, and trypsin or AS1.398 which was solved in phosphate buffer (pH=7.4) with the concentration of 2mg/ml was added. Changed the solution and took the sample every 2 days. The samples were cleaned and were dried at 80℃ for 3h before they were weighted.

2 Results and Discussion

2.1 Viscosity of Blend Solution

2.1.1 Viscosity of Extract-PVA Blend Solution

(1) Relevance between viscosity and shear rate

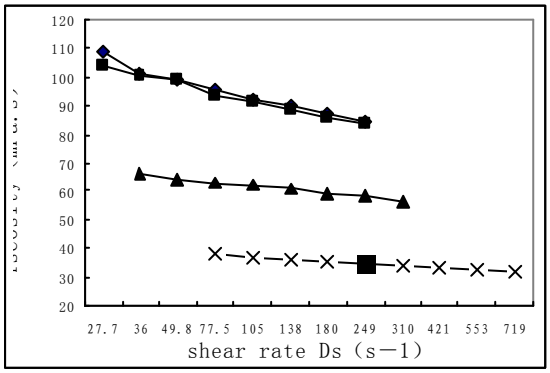

Fig.1 The viscosity of extract (basic)-PVA 8% blend solution at 30℃

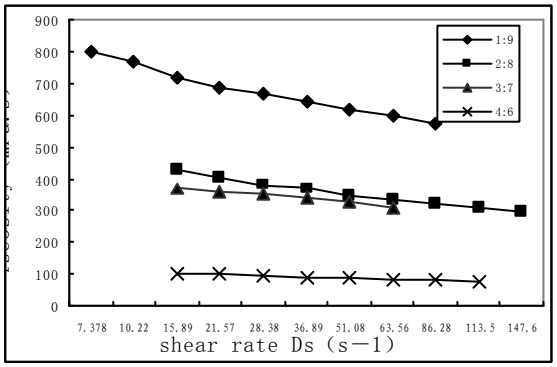

Fig.2 The viscosity of extract (basic)-PVA 10% blend solution at 30℃

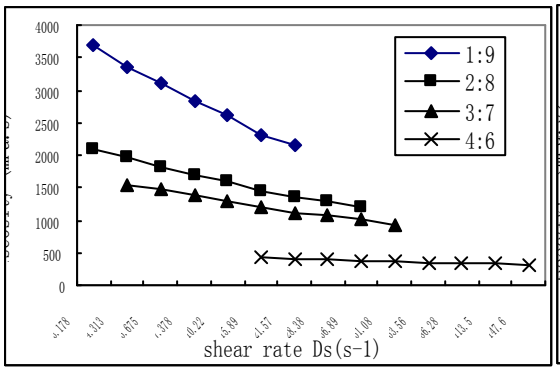

Fig.3 The viscosity of extract (basic)-PVA 12% blend solution at 30℃

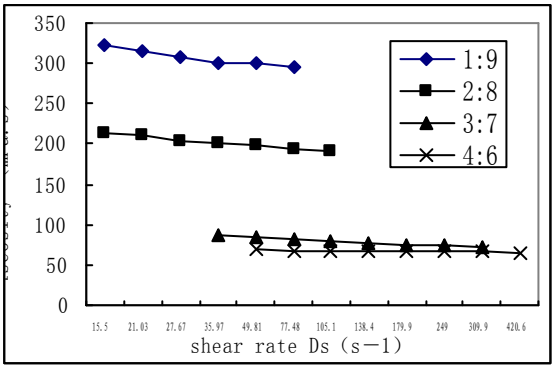

Fig. 4 The viscosity of extract (acidic)-PVA 8 % blend solution at 30℃

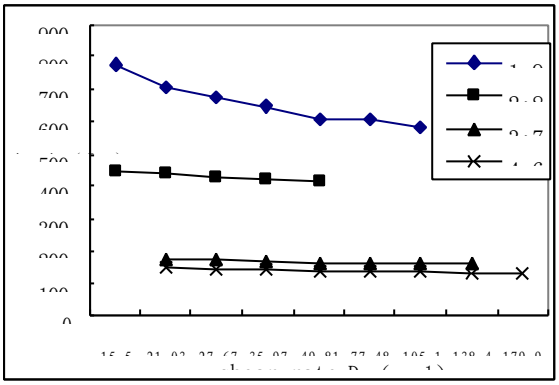

Fig. 5 The viscosity of extract (acidic)-PVA 10% blend solution at 30℃

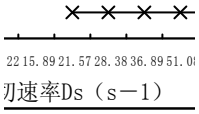

Fig.6 The viscosity of extract (acidic)-PVA 12% blend solution at 30℃

The extract (basic)-PVA blend solution obtained with different proportions was determined with viscometer, and the test results at 30℃ were shown in figure 1, 2 and 3. Simultaneously, the test results of the extract (acidic)-PVA were shown in Figure 4, 5 and 6.

It can be seen from fig.1~3 that the apparent viscosity of the solution declined when shear rate increased at 30℃. When the shear rate continues to increase, the fluid behaved as non-Newtonian, namely, the viscosity of the solution will gradually reduce, a phenomenon which is called "shear-thinning". At the same time, viscosity increased along with the increase of solid content. The solution is more homogeneous in 10% of solid content, and the viscosity is moderate for composite spinning. Fig. 4 ~ 6 showed the similar changes of extract (acid)- PVA.

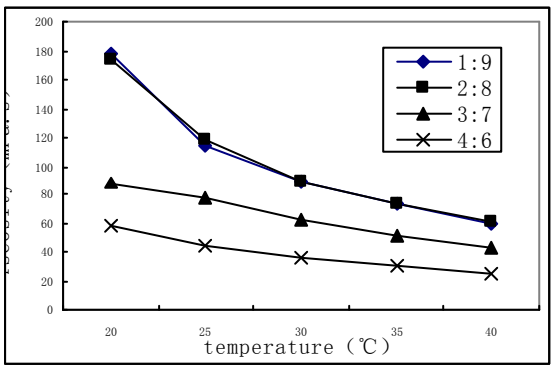

Fig.7 The viscosity of extract (basic)-PVA 8% blend solution in same Ds

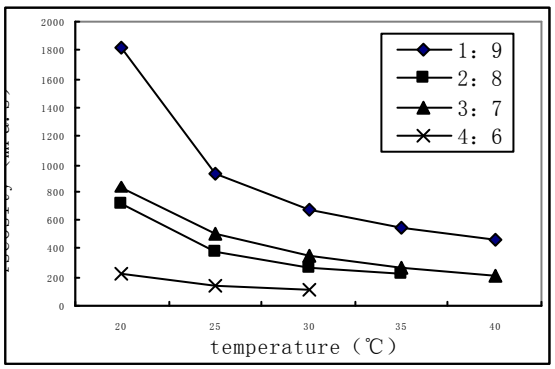

Fig.8 The viscosity of extract (basic)-PVA 10% blend solution in same Ds

2.1.2 Relevance between viscosity and temperature

The viscosity of extract (basic)-PVA with different proportion was tested under the same shearing rate (28 s-1) at the same temperature, and the results were shown in Fig 7~9. The corresponding curves of extract (acidic)-PVA were shown in Fig.10~12.

It can be seen from Fig.7~12 that the viscosity declined when the temperature increased under the same shearing rate, and the dropping range shrunk with the increasing temperature. The blend solutions with different proportions had almost the same viscosity at 40℃, and the viscosity increased while the solid content was higher. The temperature had a greater influence on the viscosity since the change of temperature led drastic change of viscosity. The results indicated that the viscosity of solution at 30℃ is suitable for spinning.

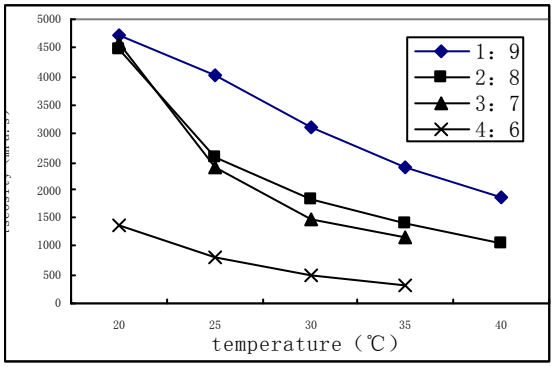

Fig.9 The viscosity of extract (basic)-PVA 12% blend solution in same Ds

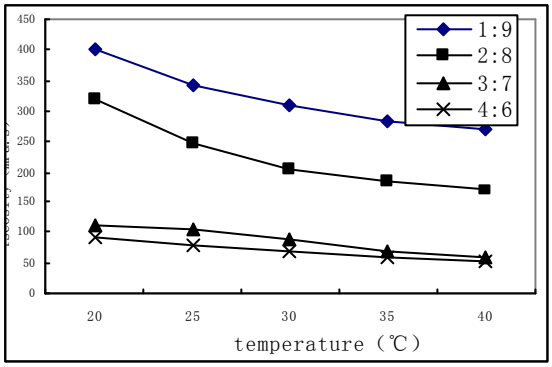

Fig.10 The viscosity of extract (acidic)-PVA 8% blend solution in same Ds

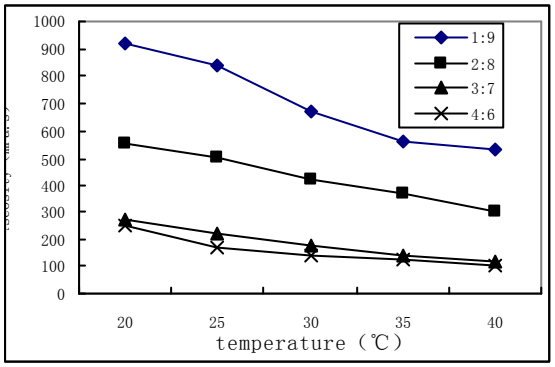

Fig.11 The viscosity of extract (acidic)-PVA 10% blend solution in same Ds

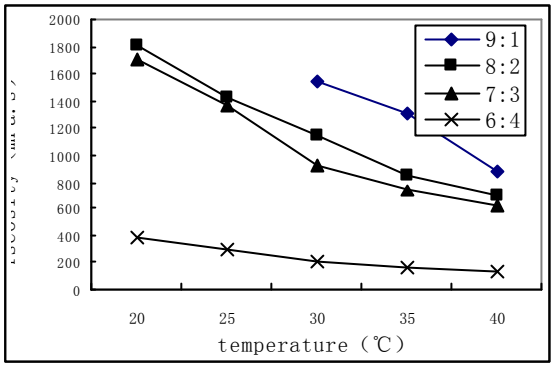

Fig.12 The viscosity of extract (acidic)-PVA 12% blend solution in same Ds

2.2 Performance of Membranes

2.2.1 Mechanical properties of extract-PVA membranes

The membranes were prepared by drying the blend solution PTFE molds, and they were evaluated by Mechanic Test Machine after the air-conditioning. The test results of tensile strength and elongation at break were shown in Table 1[7].

It can be found from Table 1 that the tensile strength of membranes declined along with the PVA reduced no matter when the total solid content were 8%, 10% or 14%. It illustrated that PVA made major contributions in tensile strength, and the intensity is the best in the proportion of 1:9 and 2:8. According to the rheological curves, the viscosity of the solutions was higher than 400mPa.s when the solid content

were 10% and 12%, and both of them were capable for spinning. It drew a result that the most appropriate ratio was 2:8 in 10% of solid content.

Compared the results of extract (basic)-PVA blend solution with extract (acid)-PVA blend solution, the tensile strength had no obvious difference. However, the basic blend solution was relatively much more unstable than the acidic ones. Therefore, the extract (acid)-PVA was chosen for spinning.

Table 1. The mechanical properties of extract-PVA membranes

Solid Content	proportions	Extract(basic)-PVA membranes Tensile strength（MPa）	elongation at break（%）	Extract(acid)-PVA membranes Tensile strength（MPa）	elongation at break（%）
8%	1:9	51.243	227.541	43.959	262.927
8%	2:8	45.730	192.404	42.494	273.947
8%	3:7	43.597	178.867	32.466	200.134
8%	4:6	33.373	181.330	25.081	196.526
10%	1:9	51.475	179.089	45.734	273.151
10%	2:8	46.200	166.301	44.897	220.149
10%	3:7	40.766	172.364	36.643	198.134
10%	4:6	37.798	201.426	30.125	209.689
12%	1:9	43.695	177.020	43.735	262.926
12%	2:8	45.339	249.422	44.595	219.543
12%	3:7	44.077	233.677	32.037	167.759
12%	4:6	39.293	223.667	36.602	158.528

2.3 Degradation Property of Membranes

2.3.1 Results of degradation in soil

With the 10% of solid content, the result of degradation in soil of extract (acidic)-PVA membranes (2:8) is shown in figure 13.

We can learn from the Fig. 13 that extract-PVA membranes degraded rapidly in the previous 14 days, followed by a stable stage. However, the total degradation period is not so long mainly because of the existence of the hydroxyl which should be reacted in the later stage of the fiber development.

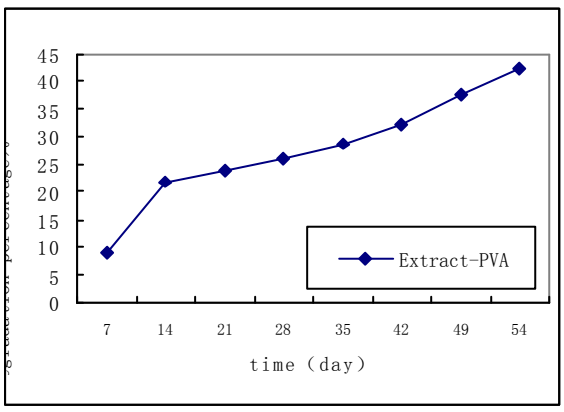

Fig. 13 Degradation property of membranes in soil

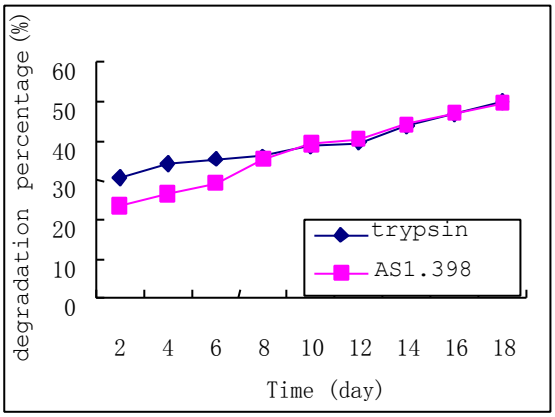

Fig. 14 Degradation properties of membranes in trypsin and AS1.398 solutions

2.3.2 Results of trypsin and AS1.398

With the 10% of the solid content, the results of degradation of extract (acidic)-PVA membranes (2:8) in the trypsin and AS1.398 solutions are shown in Fig.14. The degradation ratios of extract-PVA membranes are, respectively, 30.06% (trypsin) and 23.54% (AS1.398) in the first two days. The possible reason is that the collagen and PVA are hydrolyzed during the process. Generally, the degradation in the AS 1.398 solution is not as quick as the one in trypsin solution. As well known, collagen is a kind of structural protein with excellent performance of immunity and biodegradable, while PVA is one of the most easily degradable polymers [3]. Containing a large number of hydroxyl, PVA has good solubility in water and biodegradable, and it has been widely applied in medical fields. In this experiment, the hydroxyl is existent owing to the unemployment of acetalization which leading to the results of quick degradation.

3 Conclusion

(1) From the research of viscosity on different proportions and shearing rates at the same temperature, the viscosity of all kinds of proportions was decreasing when the shearing rates were increasing, which was according with the features of non-Newtonian fluid. Meanwhile, the decreasing degree was reduced as the increase of the extract content.

(2) From the research of viscosity on different proportions and temperature at the same shearing rate, the viscosity of all kinds of proportions was decreasing when the temperature was increasing. In the solutions with lower extract content, the viscosity changed drastically and the changing rate was reduced when the extract content was increasing. The temperature had the greatest influence among all the factors, and spinning at an appropriate temperature was crucial.

(3) The results of viscosity and mechanical tests indicated that PVA-extract (acidic) blended solutions had the best proprieties when the ratio was 2:8 at the solid content of 10%. The PVA-extract (acidic) was more suitable for spinning comparing with the PVA-extract (basic).

(4) The results of degradation experiments showed that the membranes degraded in different degrees in soil, trypsin or AS 1.398 solutions. It can finally conclude that the composite fibers based on extract are biodegradable, and they conform to the requests of "green fiber".

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