

Preparation and Characterization Keratin-based Bio-degradable Mulching Film

Li Wen-xin, Chen Zong-liang, Ouyang Yan-ying, Xu Ji-jun*

College of Resources & Environment, Shaanxi University of Science & Technology, Xi'an 710021, China

Abstract: It is necessary to develop utilization methods of recovered wool for the large amount of waste wool generated during goat leather making and the feasibility of hair-save unhairing process. To investigate a new method of utilization waste wool, the hydrolysate of wool and polyvinyl alcohol were blended, modified by glycerin and glutaraldehyde. Then the film was prepared with the method of solution molding. The tensile strength and elongation rate at the breaking point of the composite film were obtained under an optimized condition. The tensile strength, elongation rate at the break point of film were descending with the increment of the hydrolysate content. The dosage of glutaraldehyde and glycerin can improve the property of the film. The structure of mulching film was characterized by XRD, FT-IR, DSC-TG and AFM. After blending hydrolysate with the PVA, the IR absorption spectrum displayed strong protein characteristics, which showed that the keratin structure didn't change. And the red shift phenomenon of different degree displayed that the hydrolysate and PVA had a very strong hydrogen-bond function. The XRD spectrum displayed that the structure of the film was subjected to hydrolysate quality size, quality ratio, temperature and crosslinking agent and plasticizer. The DSC-TG displayed that the ultrasonic processing changed wool keratin molecule mass distribution, which can available improve the hot function of the film. AFM showed that the film surface was smooth and neat, which indicated that the keratin and PVA were good miscible fluid. The degraded status of the film was observed by burying it in soil, insulating it directly in atmosphere, cultivating edaphon experiment, respectively. Comparing with the market mulching plastic, the application performance of mulching film was studied. The result showed that the blend film was well degraded and can be used as mulching film in agriculture.

Key words: keratin; polyvinyl alcohol; bio-degradation; mulching film

1 Introduction

Consumption of the plastic mulching film in our country is recognized as the first in the world since introducing from Japan in 1978. The ultra-thin plastic film was successfully prepared in 1986, which is still used in large area today. The environmental pollution becomes serious because the non-degradability of this film, so that "white evolution" to "white harm" is increasingly evident. The research of degradable film began in the 1970s. There are more than 100 units engaged in the scientific research, production and the application trial. At present, it has been developed some degradable film, such as photodegradable,

* Corresponding author, Phone: +86-(0)13335401921. E-mail: liwx@sust.edu.cn

photo-biodegradable , biodegradable , fibrous and liquid film. According to the survey, the ordinary agriculture film farmers using can't meet the demand of scientific cultivation and culture today. We are eager to use the new green film in order to improve the overall efficiency of agriculture. In recent years, as sustainable natural biomass materials, protein becomes environmentally friendly polymer biological material because of its good mechanical and calorific stability and bio-degradability. In this paper, we prepared new environmental friendly film with waste wool and PVA, in order to find a new way for the development of the mulching film.

2 Experimental

2.1 Material and instruments

The hydrolysate of wool, Self-made; PVA (degree of polymeric 1750 ± 50), Tianjin Chemical Reagent wholesale company; Glycerin (analytically pure content $\geq 99\%$), Tianjin Jin North Fine Chemical Co. Ltd.; Glutaraldehyde (A.R. content $\geq 50\%$), Tianjin Jin-dong Tianzheng Fine Chemical Reagent factory; TS — 2000 — S tensile strength dollars, Gotech Testing Machines Co. Ltd.; D/max2200PC X-ray diffraction, Rigaku Co.; EQUINX-55 Fourier transform infared spectrometer, BRUCHER Co. (Germany); STA 409PC integrated thermal analyzer, NETZSCH Co. (Germany); 515-2414 GPC instrument, Waters Co.(USA).

2.2 Preparation of Keratin-based film

Dissolve PVA in the hydrolyzate of wool in 120°C oil bath completely, add glycerin and glutaraldehyde, after mixed, wipe film on the glass sheet, air dry at room temp, then strip the film, stand-by.

2.3 Analysis

2.3.1 Mechanical properties

Make air conditioning for 4 hours according to GB/T 2918-1998 standard choice of the environment, code named 23/50. Test mechanical properties immediately after air conditioning. The test of tensile strength and elongation at break carried out in the accordance with the rule of GB13022, choosing the sample III, at the speed of $500\pm 50\text{mm/min}$ (no-load). The test of right-angle tear strength carried out in the accordance with the rule of QB/T 1130, using a single sample, at the speed of $200\pm 20\text{mm/min}$ (no-load).

2.3.2 Characterization of structure

(1) IR spectroscopy (FT-IR)

Scan the film thinner than 0.025mm directly using infrared spectrometer.

(2) X-ray diffraction analysis (XRD)

Scan the film sample using X-Ray Diffractometer. Operating parameters are the line of Cu target $K\alpha$, pipe pressure is 40KV, pipe flow is 40mA, scanning point of view is $5\sim 50^{\circ}$.

(3) Analysis of the morphology (AFM)

Fix the film sample with double-sided adhesive on the mica sheet, then scan it with atomic force microscope by tapping mode with Si probe. The radius of curvature is less than 10nm, and the length of micro-cantilever is nm.

(4) Differential scanning calorimetry

In the protection of nitrogen, determine the endothermic curve of the sample directly on the Thermal generalization analysis. Weigh about 7.5mg sample, heating rate is 10 °C/min, scanning range is 20~500 °C.

2.3.3 Characterization of degradation

(1) Atmospheric exposure test

The GB3681-83[1]: put self-made film sample on the exposure plane, which is natural aging from solarization、blowing、drench and microbiological corrosion. Platform on the sixth floor in the college of Resource and Environment in Shaanxi University of science & technology is selected to be the test site. The platform is made of cement and the exposure plane is wooden which is 45° south-facing and 50cm away from the nearest point on the ground. The weather in Shaanxi belongs to subtropical climate. In Shaanxi, annual precipitation are 1000~1500 mm and annual total solar radiation are 90~120 kcal/cm². Natural exposure test began on April 21, 2008 while it is rainy season and the average temperature is 28 °C.

(2) Soil burial test

The garden in Shaanxi University of Science & Technology was selected to be test site. The samples were buried in 10~15 cm deep in the soil.

(3) Microbial culture test

The experimental[2,3] materials are as follows: ①plastics for test are self-made film、pure PVA film and merchant polyethylene agricultural film. ②microbial culture medium are nutrient agar and Czapek's medium (without carbon source). ③there are two inocula: sample in soil suspension I is fertile topsoil in vegetable plot, sample in soil suspension II is soil in compost (compost self-made film for half a year). Add 10g soil sample and 90mL sterile water respectively in conical flask with some glass beads, shake 15min for finished sample (hereinafter referred to as soil I and soil II).

Experimental procedure is as follows: ①cut the 3 films above to chips which is 12cm for use. ②Preparation of medium: prepare 500mL Czapek's medium and nutrient agar, sterilize them for 15min under pressure of 0.1MPa in the sterilizer, then take them out and cool down to about 50°C, pour into culture dishes respectively, there is 15mL in each dish, cooling and solidification for use. ③inoculating culture: add 0.1mL soil suspension I and II respectively into culture dish with Czapek's medium and with nutrient agar, daub in uniformity, then stick plastic chips on the surface of culture medium, three chips each. Put the culture dishes into incubator at 30 °C, cultivated for 10 days. ④test for bio-degradation: usually, samples for test are regarded as unique carbon source and energy, and the growth rate of specific

microbial is observed. It can be divided into 5 grade for abundance: grade 0 is that there isn't visible microbial growing on the surface of sample; grade 1, there are less than or equal to 10% sample surface which has growing microbial; grade 2, there are growing microbial on 10%~30% sample surface; grade 3, there are growing microbial on 30%~60% sample surface; grade 3, there are growing microbial on 60%~100% sample surface.

3 Results and discussion

3.1 The impact of modification on the mechanical properties of Keratin-based biodegradable mulching film

3.1.1 The impact of mass ratio of hydrolysate and PVA

Put wool into the mixed liquor of sodium sulfite and sodium hydroxide, then get the hydrolysate in which the mass fraction of solid is 7.8%. The test results of GPC are in the table 1, and the impact of mass ration of hydrolysate and PVA on the properties of films are on the fig 1 and fig 2.

Table 1 The test results of GPC

Title	Mn/Da	Mw/Da	M _p /Da	Mz/Da	Mz+1/Da	polydisperity	area%
Peak 1	13526	16764	13344	22641	33943	1.239432	34.65
Peak 2	3070	3806	4560	4546	5162	1.240080	47.23
Peak 3	940	980	1091	1013	1039	1.042406	14.93
Peak 4	417	420	412	423	427	1.007994	1.97
Peak 5	289	293	302	296	300	1.014130	1.22

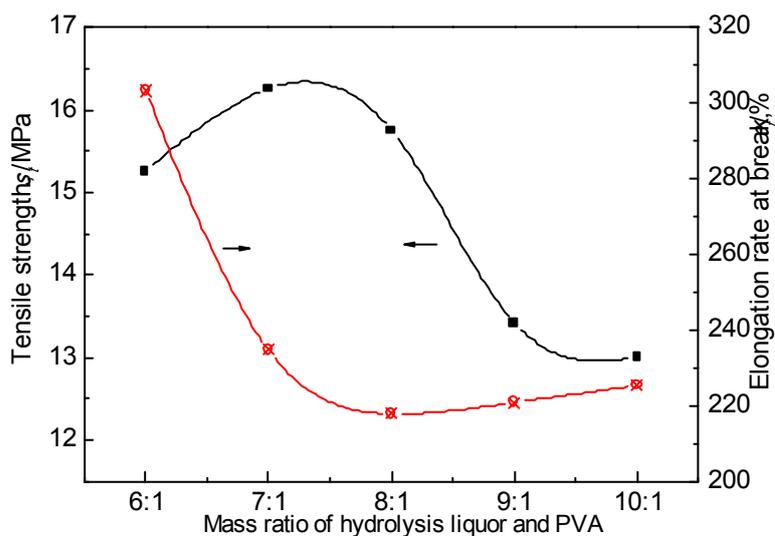


Fig.1 Influence of mass ratio of hydrolysis liquor and PVA on tensile strength and elongtion rate at break of film

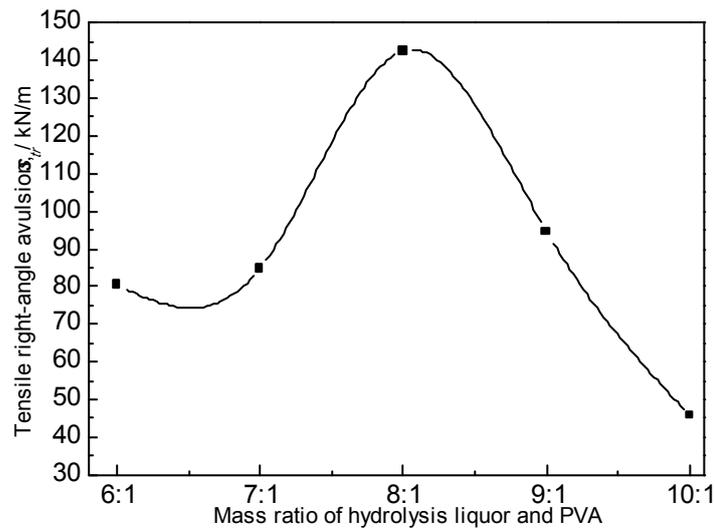


Fig.2 Influence of mass ratio of hydrolysis liquor and PVA on tensile right-angle avulsion of film

The composition of hydrolysate isn't unitary as shown in figure 1. There are 5 parts, thereinto, the area of the micromolecular hydrolysate whose number average molecular mass M_n is less than 500 is about 3%, polydispersion coefficient is about 1.0; macromolecular productions take up 35%, it's polydispersion coefficient is about 1.24. It shows that, in the productions the content of micromolecular amino acids is seldom. However, the majority is polypeptide, which is the production is a compound of polypeptide and bit of amino acids.

PVA blend directly with the protein. Although there is a certain combination of hydrogen between the two polymer, the compatibility between the two is poor, so, there is a degree of separation phenomenon. The research results of Zhang Youzhu and others[4] show that the best mass ratio of PVA and gelatin is 9:1 when there isn't phase separation between PVA and gelatin. At this time, the compatibility of two components is good, and surface of the film is uniform、smooth and flat; There is strong interaction between the two molecular, and the compatibility is improved so that the tensile strength and breaking strength of the film blends are increased.

We can see from the figures 1 and 2, when the mass ratio of wool hydrolysate and PVC is 7:1 to 9:1, both of them demonstrate good compatibility, and the right-angle tear strength (σ_{tr}) and the tensile strength (σ) of the film is higher than the standard of national quality parts and first-rate products ($\sigma \geq 12\text{MPa}$, $\sigma_{tr} \geq 60\text{kN/m}$). However, because of the poor film forming of the wool hydrolysate (mainly becomes to keratin), film shows more properties of keratin film along with the increasing of mass ratio of hydrolysate and PVA, its elongation at break (ϵ) reduced, lower than the standard of national qualified products, first-rate products ($\epsilon \geq 250\%$). We should properly do some cross-linking and plastification for modification, in order to improve the compatibility of wool hydrolysate and the PVA, to improve the mechanical properties of the film and to increase hydrolysate's content in the film.

3.1.2 The impact of the usage of glutaraldehyde and the mass ratio of hydrolysate and PVA

The impact of the usage of glutaraldehyde and the mass ratio of hydrolysate and PVA on the properties of the film is in figure 3 and figure 4.

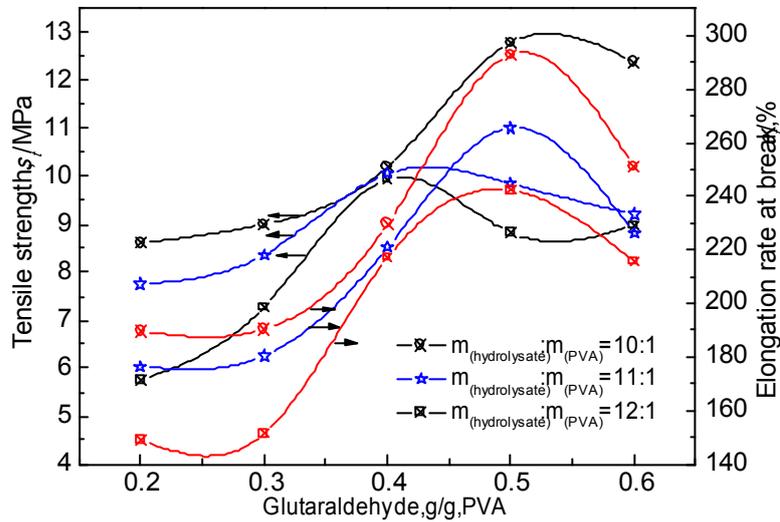


Fig.3 Influence of mass ratio of hydrolysis liquor and PVA and the dosage of glutaraldehyde on tensile strength and elongation rate at break of film

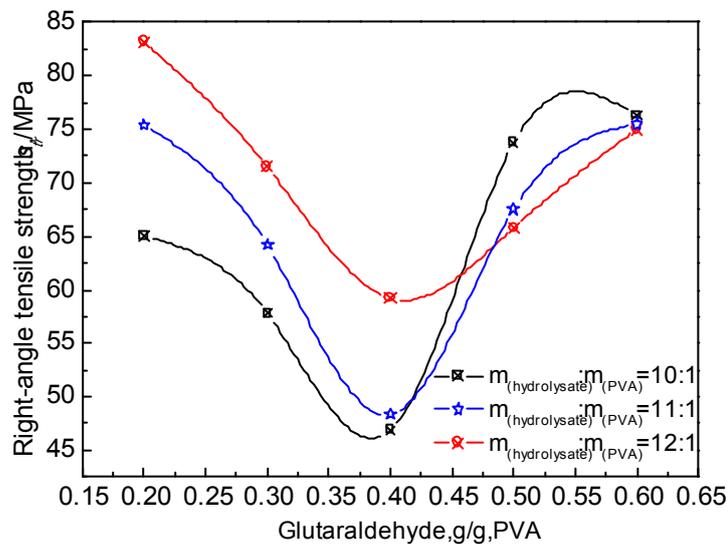
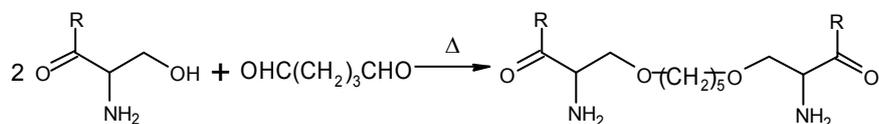
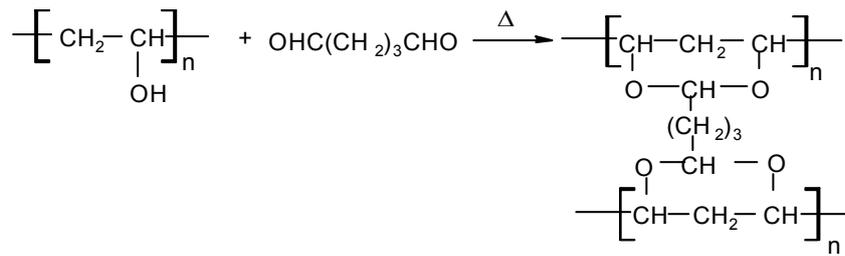


Fig.3 Influence of mass ratio of hydrolysis liquor and PVA and the dosage of glutaraldehyde on tensile right-angle avulsion of film

Glutaraldehyde can come into cross-linking with compounds which has reactive hydroxyl group (such as serine and PVA), the schematic formula is as follows:





Besides serine and PVA, reactive hydroxyl group on tyrosine and polypeptide chain also can come into cross-linking with glutaraldehyde. This cross-linking can form new chemical bond between hydrolysate and PVA, and increase the compatibility. The figure 3 and figure 4 show that the elongation at break and tensile strength of the films whose mass ratio is 10:1 and 11:1 can get the maximum by adding 0.05g/g PVA. Considering the right-angle tear strength, only the mechanical property of the film with the mass ratio of 10:1 can come up with the national standards. In order to increase the content of keratin in the film and improve the property of the film, we plan to plastify the films whose mass ratio is 10:1 and 11:1 with glycerin, and increase the elongation at break of these films.

3.1.3 The impact of the usage of glycerin and the mass ratio of hydrolysate and PVA

The impact of the usage of glycerin and the mass ratio of hydrolysate and PVA on the properties of the film is in figure 5 and figure 6.

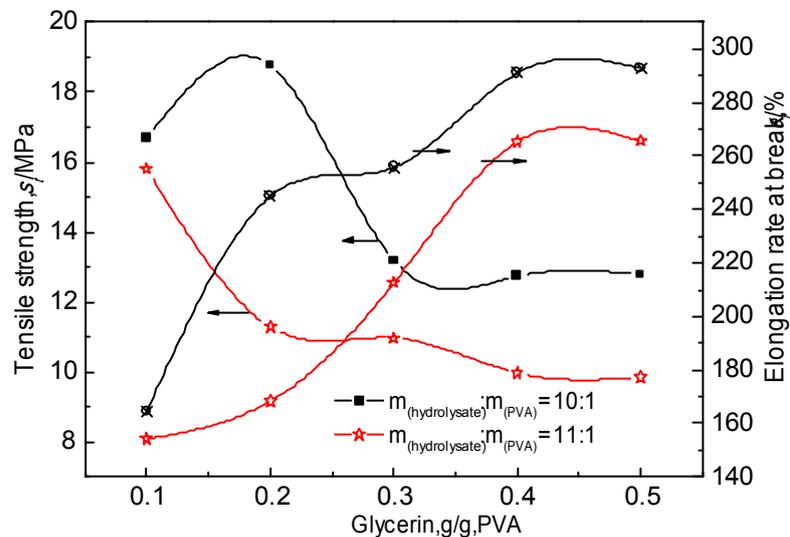


Fig5 Influence of mass ratio of hydrolysis liquor and PVA and the dosage of glycerin on tensile strength and elongation rate at break of film

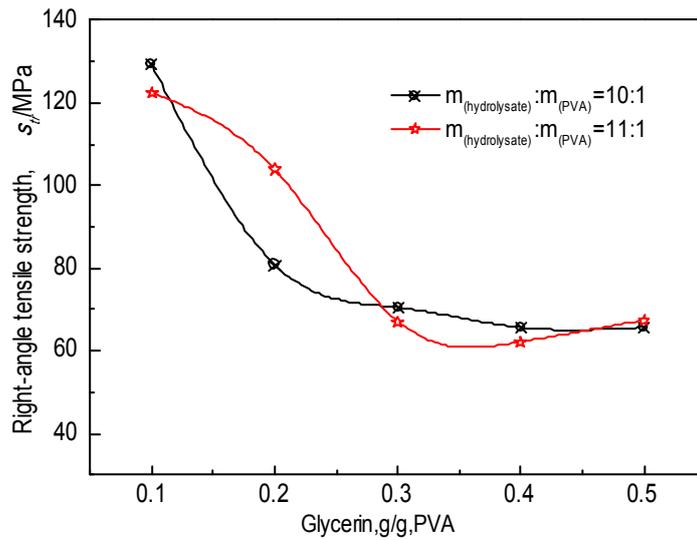


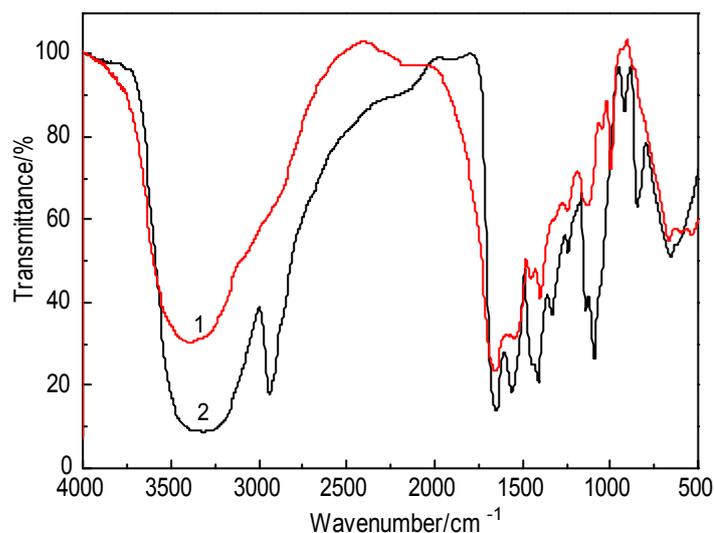
Fig.6 Influence of mass ratio of hydrolysis liquor and PVA and the dosage of glycerin on tensile right-angle avulsion of film

Polyhydric alcohols such as glycerin, glycol and so on have good plasticization to natural polymer like protein and starch. Adding plasticizer to proteinic compound can weaken the interaction of protein molecules, reduce tensile strength of the films, increase the elongation at break and conspicuously improve the processing characteristics of protein. From figure 5 and figure 6, we can see, after plastification, the mechanical property of films whose mass ratio of hydrolysate and PVA is 11:1 couldn't reach the national standard. However, it can reach the standard of national quality parts and first-rate products if its mass ratio is 10:1 and its usage is 0.3g glycerin/g PVA while the tensile strength is 13.19MPa, elongation at break is 255.81% and right-angle tear strength is 70.82kN/m. When increased the amount of glycerin, its elongation at break will continue to increase, but the tensile strength and tear strength of right-angle do not change enough. If the amount of glycerol is too much, after film formation, the free micro molecular glycerin would move to the surface of the film. Therefore, it's enough to add 0.3g glycerin / g PVA to the film after glutaraldehyde modified.

3.2 Characterization of the structure of keratin-based bio-degradable mulching film

3.2.1 The FT-IR characterization of mulching film

The FT-IR spectrogram of hydrolysate and the hydrolysate-PVA hybrid film are in the figure 7.



Tips: 1—wool hydrolysate; 2— wool hydrolysate-PVA hybrid film

Fig.7 FT-IR spectrum of hydrolysate and their blend films

In the figure 7, the absorption peak at 3420.36cm^{-1} in spectral line 1 is the vibratory absorption peak of imino group N-H in keratin molecule, the 1650.10 cm^{-1} and 1539.73cm^{-1} are stretching vibration absorption of amide I (C=O) and stretching vibration absorption (characteristic absorption band of anti-peptide bond structure) of amide II (mainly deformation vibration in NH-plane), respectively, and the 1394.45cm^{-1} is characteristic absorption band of cis-peptide bond. The absorption near 1120.23cm^{-1} is bending vibration peak of C-O-C bond, and the 680.17cm^{-1} is bending vibration peak of N-H bond. The absorption peak near 998.41cm^{-1} is S-O in the $-\text{SO}_3$ and near the 533.42cm^{-1} is characteristic absorption band of $-\text{S}-\text{S}-$. It's clear that disulfide bond in keratin was reverted to $-\text{S}-\text{SO}_3$. These indicate that the products are compound of polypeptide and amino acid.

There are a lot of researches on the PVA film today. It's reported that the absorption peaks of PVA spectrum are at the 2944 cm^{-1} , 1330 cm^{-1} and 853 cm^{-1} , which are C-H symmetrical stretching vibration, bending vibration in C-H plane and carbochain characteristic peak caused by stretching vibration of C-C; strong absorption in 3325 cm^{-1} , 1420 cm^{-1} and 1096cm^{-1} are hydroxide radical characteristic peak caused by O-H stretching vibration, CH-OH bending vibration and C-O stretching vibration[4]. Compared to pure keratinous FT-IR, acidamide I、II、III and V peak of blend film all have some Einstein shift, the absorption peak becomes wide at 3300cm^{-1} , which is the result of the coabsorption of N-H in keratin molecule and a large of associating hydroxide radical in PVA in the blend film. And there is a stronger and narrow absorption peak at 2944cm^{-1} , which is vibration absorption peak of $-\text{CH}_2-$; The absorption peak at 920cm^{-1} is deformation absorption of PVA in the $-\text{OH}$ plane. It showed that films all performance the characteristic absorption of protein and PVA after blending, and these peaks also have some einstein shift.

These show that, after PVA blend with keratin, though the two didn't generate new chemical bonds, we can't ignore the strong action of hydrogen bond, which can improve acting force among the blend and the compatibility of PVA and keratin.

3.2.2 XRD characterization of mulching film

The XRD spectrogram of hydrolysate and its blends with the PVA are in the figure 8.

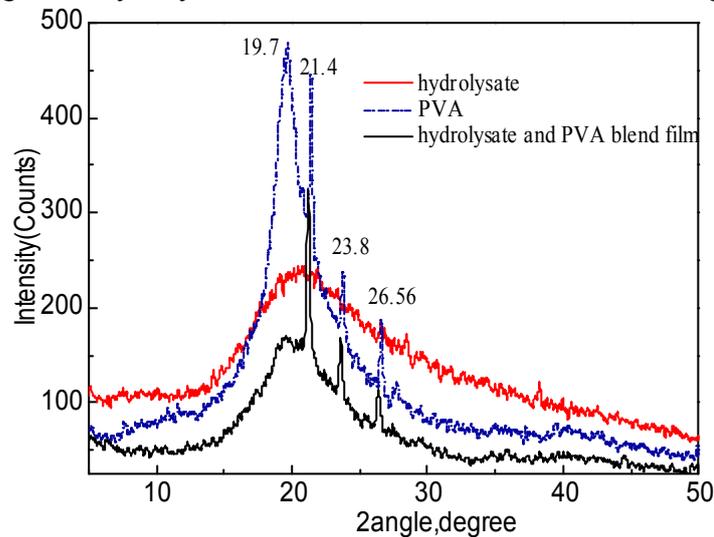


Fig.8 XRD spectrum of hydrolysate, PVA and their blend film

When the X-ray is diffracted by crystal, every crystalline material has its unique diffraction pattern, their characters can be represented by distance d between each diffraction crystal face and relative intensity I of diffracted ray. Interplanar spacing d is related to the shape and size of the crystal cell, however, relative intensity is related to the species of particles and its position in the crystal cell.

As shown in figure 8, pure powder of hydrolysate all are amorphous body, and its crystallinity is 0; there are some crystal in the pure PVA film, appearing strong absorption peak at 19.700、21.400、23.780 and 26.540, whose interplanar spacing d are 0.45137、0.41486、0.37390、0.33556nm and relative intensity I are 484、433、252、195, respectively, and its crystallinity after detection is 66.57%; blending PVA with hydrolysate at the mass ratio of 15:1, there are diffraction peak at 21.340、23.800 and 26.500, interplanar spacing d are 0.41549、0.37481 and 0.33626nm, and the relative intensity I are 380、194、125; compared with pure PVA film, interplanar spacing of crystal increased, the peak intensity reduced, and the absorption peak at 19.700 disappeared, which indicates that crystal cell in the blend films changed, its crystallinity after detection is 16.77%. All this shows that the main action of hydrolysate is filling, but the intermolecular force between hydrolysate and PVA can't be ignored, so crystal of blending films changes.

3.2.3 AFM characterization of mulching film

The AFM spectrogram of blending film of hydrolysate and PVA is in the figure 9.

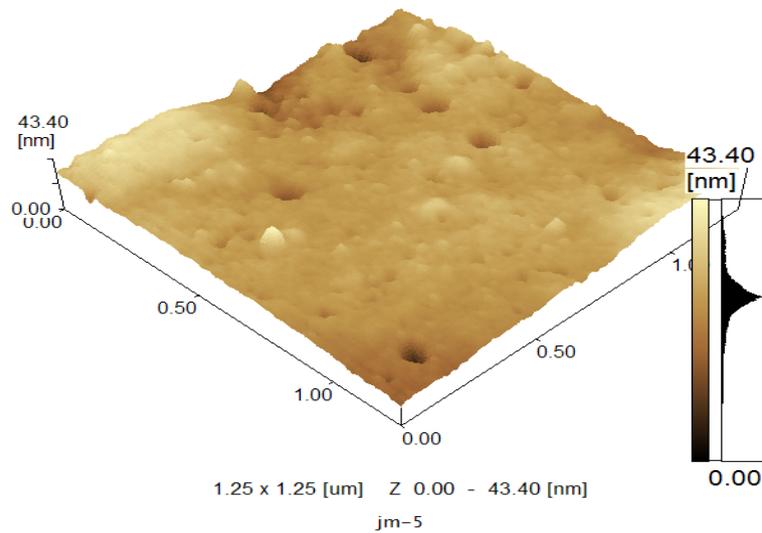


Fig.9 AFM picture of three-dimensional film

We can see from figure 9, the surface of film is dense、smooth and uniform, we can't see phase separation or delamination on the film, which shows that the compatibility of hydrolysate and PVA is good.

3.2.4 DSC-TG characterization of mulching film

The DSC-TG spectrogram of mulching film is in the figure 10.

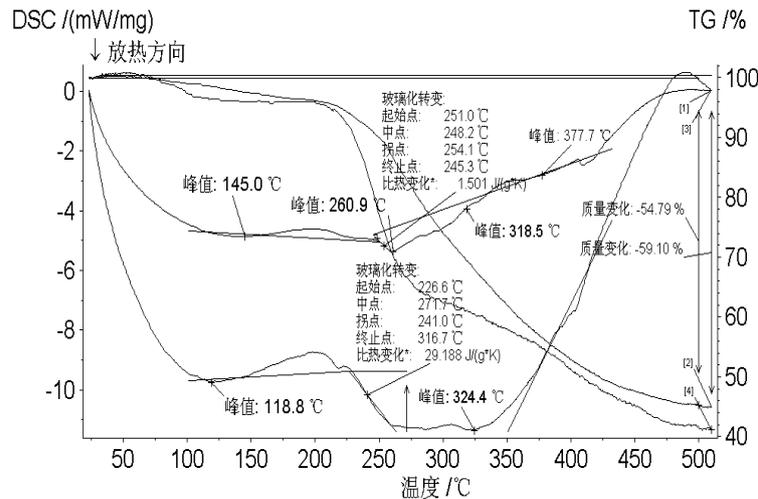


Fig.10 DSC-TG spectrum of mulch film

The spectral line 1 in the figure 10 is the DSC curve of hydrolysate, the maximum endothermic peak appear at 145.0, 260.9, 318.5, 377.7°C, decalescence lower than 145.0°C is generated by resolve of small molecule from products, such as amino acid. The one at 260.9°C is generated by cross linking and break of disulfide bond, 318.5°C is generated by peptide bond decomposition of micromolecular polypeptide and 377.7°C is generated by decomposition of macromolecular polypeptide; according to the figure, we can also see that the starting temperature, inflection temperature and final temperature of hydrolysate's glass transition are 251.0, 254.1 and 245.3°C, respectively. The spectral line 2 is the TG curve of hydrolysate, decomposition of the sample reach a basic balance at 450°C, mass loss ratio is 54.79%. The spectral line 3

is the DSC curve of mulching film, the maximum of heat liberation is at 118.8 °C, it is because hydrone in the film escaped, hydrolysate and PVA cure and cross link further to release energy[5]; the maximum of heat liberation at 324.4 °C is caused by decomposition of chemical bond[6-7]. Analyzing from spectral line, there are only one glass transition temperature of the film, the glass transition temperature of hydrolysate and PVA is inexistence. This shows that hydrolysate and PVA are compatible at the molecular level, its starting temperature, inflection temperature and final temperature are 225.6、241.0、316.7 °C; The spectral line 4 is the TG curve of mulching film, decomposition of the sample reach a basic balance at 500 °C, mass loss ratio is 59.10%.

We can know from above, hydrolysate blend with PVA at the molecular level, the compatibility is good, glass transition temperature of products increased, and the thermal stability improved.

3.3 Characterization of degradation properties of keratin-based biodegradable mulching film

3.3.1 Results and soil burial test analysis

In figure 11, there are the photos of sample which is buried for 3 months and 5 months.

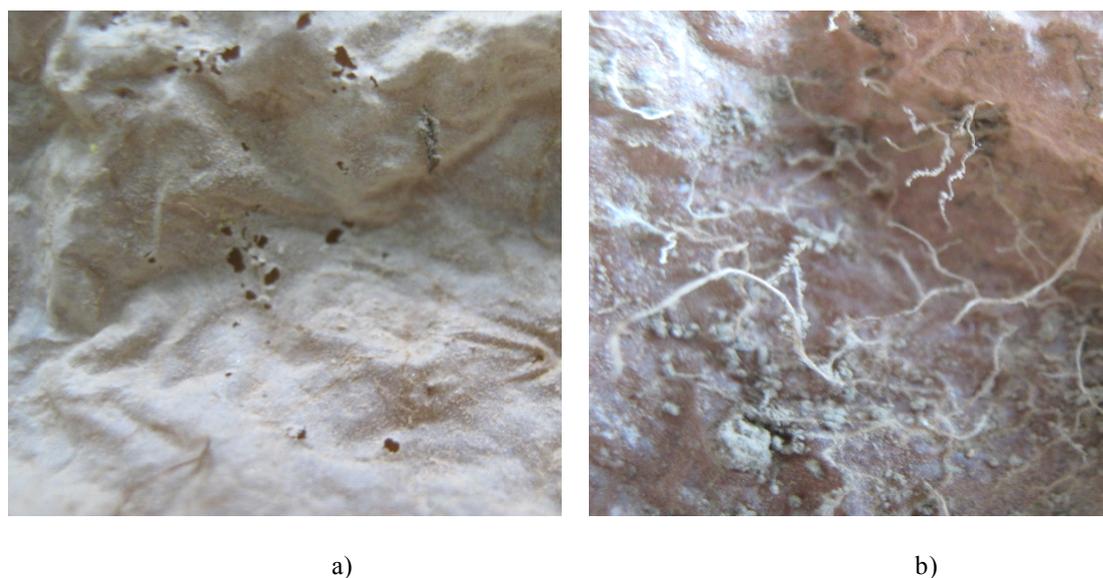


Fig.11 Picture of burying film (a, buried for 3 months; b. buried for 5 months)

It can be seen from figure 11, many small cavern, which are cause by the degradation of film by microorganisms in the soil, and rootlet of plants will after some time's soil burial; the products of film degradation are amino acids, so plant roots grow on the film, absorbing organic fertilizer. As the burial time goes on, roots grow more and more, and thicker, and the degradation becomes more quickly. It will be seen from it that mulching film has good degradation property.

3.3.2 Results and atmospheric exposure test analysis

The table 2 and figure 12 show the effect of the film property by the time of direct exposure to the atmosphere.

Tab.2 Influence of directly exposition time on film

time /day	tensile strength σ_t /MPa	elongation at break /%	Die C tear strength σ_{tr} /kN·m ⁻¹	remarks
0	13.19	255.81	70.82	The film spreaded out uniform;
10	11.37	203.26	60.53	The film shrink, harden;
20	9.46	168.47	52.17	The film shrink, harden obciously
30	7.61	86.48	43.10	Shrink, hard, embrittled;
40	5.49	43.67	38.54	Shrink, hard, more brittle;



Fig.12 Picture of directly exposition film

It indicates from table 2 and figure 12 that, the sample is homogeneous spreading, as the insolation time goes on, the sample became smaller and smaller. It because that when insolation, most moisture in the film ran away, which caused that the spacing between PVA and keratin molecular lessening continuously, so sample shrank; at the same time, because of intermolecular excessive cohesion, the film became harder and harder, more and more fragile. On the other hand, shrink of the film can focus the degradation by microorganism in the soil, and improve its degradation efficiency. However, the application experiment shows that when the membrane surrounding fixed, regardless of weather, the film won't shrink, and can keep warm and preserve the soil moisture as merchant shed film. Consequently, we'd better loose the soil fixed around film, which can help film shrink and degrade.

3.3.3 Results and microbial culture test analysis

The growth level of microorganisms on the surface of the film and the results of microscopic observation is in the table 3.

Tab.3 Result of animalcule developing grade and observing of film surface

Culture medium	inoculum	Pure PVA film			Homemade film			Merchant PVC film		
		microorganism growth rate level	microscopic observation		microorganism growth rate level	microscopic observation		microorganism growth rate level	microscopic observation	
Czapek's medium	Soil I	3	there are holes on the film	4	breach on the edge, hole in the center	0	No change			
	Soil II	3	there are holes on the film	4	breach on the edge, hole in the center	0	No change			
nutrient agar	Soil I	3	breach on the edge, hole in the center	4	breach on the edge, hole in the center	0	No change			
	Soil II	3	breach on the edge, hole in the center	4	breach on the edge, hole in the center	0	No change			

There are abundant bacteria、actinomycetes and epiphyte in the soil. There are many differences on the type and content of the bacteria in the soil at the different sampling place. In order to acquire more culture which can degrade keratin-based film, we selected the soil where film composting for half an year as sample. We can see from table 4-7, merchant PVC is difficult to be degraded by microorganism in the soil, but PVA and homemade film have good biodegradability, furthermore, the degradation of homemade film is superior to PVA film, this shows keratin contained in the film accelerate the degradation of the blending film.

4 Conclusion

When the mass ratio of hydrolysate and PVA is less than 10:1 (that is content of hydrolysate is 43.82%), after modified of glutaraldehyde and glycerin, mechanical property of blending film is superior to the GB4455-94 standard of agricultural polyethylene film. The main action of hydrolysate is filling, and

the degradation property of the film after fill the hydrolysate is superior to pure PVA or PVC film; because of the cross linking of strong hydrogen bond and glutaraldehyde, the film's structure is dense and its thermal property is steady. It has good thermal retentivity, water conservation and soil moisture preservation, and it can be used as agricultural mulching film.

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