

Characterization of Hot-Pressed Films from Superfine Wool Powder

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ABSTRACT: In this study, superfine wool powder was plasticized with glycerol and hot-pressed into a film. Scanning electron microscopy photos showed that the superfine wool powder could be molded into a smooth film and that the wool powder was distributed evenly in the cross section of the film. Fourier transform infrared analysis revealed no substantial changes in the chemical structure of the wool powder after hot pressing, but the absorbing peaks of glycerol were found in the spectrum. X-ray diffraction analysis showed that the overall crystallinity increased after the wool powder was hot-pressed

into film. Thermogravimetry (TG) analysis indicated that the thermal stability of the hot-pressed film decreased. A transition point appeared in the TG curve of the wool hot-pressed film as glycerol was added. The differential thermal analysis curve of the film showed sharp absorbing peaks similar to that of wool powder. With increasing glycerol content, the film showed increasing ductility and softness. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2852–2856, 2008

Key words: fibers; films; mixing; modification; strength

INTRODUCTION

Synthetic films are widely used as packaging materials nowadays; this creates a big environmental problem because of the films' poor biodegradation. Some environmentally friendly materials, such as agricultural polymers and most carbohydrates, can be used as package films, but they either cannot be easily molded or are soluble in water;¹ this limits their applications in packaging.

Keratins are fibrous proteins found in hair, wool, feathers, nail, horns, and other epithelial coverings;² with the high concentration of half-cystine residues, keratins in wool are regarded as three-dimensional polymers interlinked by S—S bonds between reduced keratin monomeric units.³ Keratins are stable and biocompatible, and most of them can be used in biomedical applications in the form of solutions, powders, films, gels, and filaments. There has been considerable interest in the development of keratin films,^{1,4–6} and these films could be used as high-value packaging materials for their environmental stability. However, these films have been cast from keratin solutions, which were obtained from complicated wet processes that involved purification, clean-

ing, and dialysis, and chemicals such as sodium dodecyl sulfate, dimethylformamide, Na₂SO₃, thioglycolic acid, and 2-mercaptoethanol were used in the processing.²

The plasticizer glycerol has been widely used in the modification of protein fibers to make them ductile in hot environments, and keratin could be extruded in these conditions.^{7,8} Previously, we reported a novel method to produce keratins by the grinding of wool and down fiber into a superfine powder on a purpose-built machine.^{9–11} In this study, glycerol was used to change the plasticity of superfine wool powder, and the powder was then hot-pressed into films. Scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction, and thermal analysis were used to characterize the hot-pressed films. These characterizations were necessary before the film could be used for different applications.

EXPERIMENTAL

Materials

Australian wool fibers (provided by Mayer Corp., Hubei, China) were ground into superfine wool powder with a purpose-built grinding machine.^{10,11} The number-based particle size distribution gave an average particle size of 1.7 μm, with 95% of the wool powder being less than 3.0 μm in diameter.

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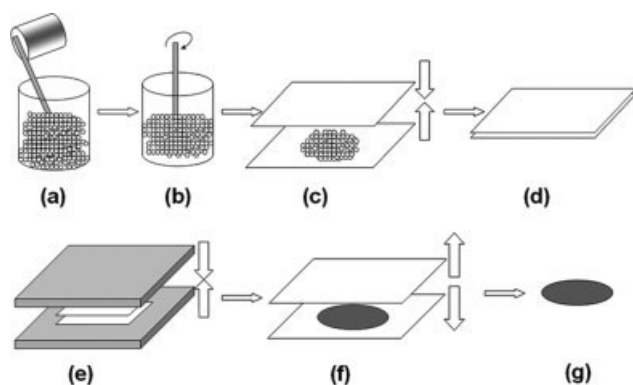


Figure 1 Schematic diagram of the hot-pressed film fabrication.

Preparation of hot-pressed films from the superfine wool powder

The film preparation process is outlined in Figure 1. The plasticizer glycerol (analytical grade, provided by Bodi Chemical Co., Ltd., Tianjin, China) was added to the superfine wool powder [Fig. 1(a)], and the mixture was stirred in a blender for 5 min [Fig. 1(b)]. The blend was then sandwiched between two pieces of polyethylene terephthalate (PET) film [Fig. 1(c,d)]; these were placed on the armor plate of a hot presser [XLB-D350 \times 350, Huzhou Dongfang Mechanical Co., Ltd., Zhejiang, China; Fig. 1(e)]. After that, the blend was hot-pressed for 5 min under a molding pressure of 5 MPa and at a molding temperature of 160°C. After cooling [Fig. 1(f)], the hot-pressed film was removed from the sandwiching PET films for analysis [Fig. 1(g)].

Sample analyses

SEM analysis of the hot-pressed film was carried out with a Hitachi X-450 microscope (Tokyo, Japan) at

an acceleration voltage of 20 kV; after gold coating, both the surface and cross section of the film were tested.

The hot-pressed film and the superfine wool powder were both analyzed on a FTIR tester (Nicolet Avtar 360, Waltham, MA) with attenuated total reflectance and a scanning range from 600 to 4000 cm^{-1} .

In the X-ray diffraction analysis, the samples were dispersed onto a stub and placed within the chamber of an analytical X-ray powder diffractometer (Damax-rA, Rigaku Corp., Tokyo, Japan, wavelength = 1.54 Å, Cu K α radiation) with a generator intensity of 40 kV and a generator current of 50 mA. The samples were then scanned from $2\theta = 3\text{--}45^\circ$ in steps of 0.02° .

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on a Diamond DSC TG-DTA 6300 (PerkinElmer, Waltham, MA), nitrogen protected, at a heating rate of 20°C/min within the temperature range 30–600°C.

The mechanical properties were tested on an Instron 5566 universal testing machine (Datapoint Labs, Ithaca, NY), at a gauge length of 30 mm and a strain rate of 50 mm/min; the width of the samples was 20 mm, and each sample was tested five times, and the results were averaged.

The diameters of the films were measured with a ruler. The thicknesses of the films were measured with a fabric thickness tester [YG(B) 141D, provided by Wenzhou Darong Textile Instrument Co., Ltd., Wenzhou, China].

RESULTS AND DISCUSSION

SEM photos

Figure 2 shows the SEM photos of the hot-pressed film. Figure 2(a) shows the surface morphology of

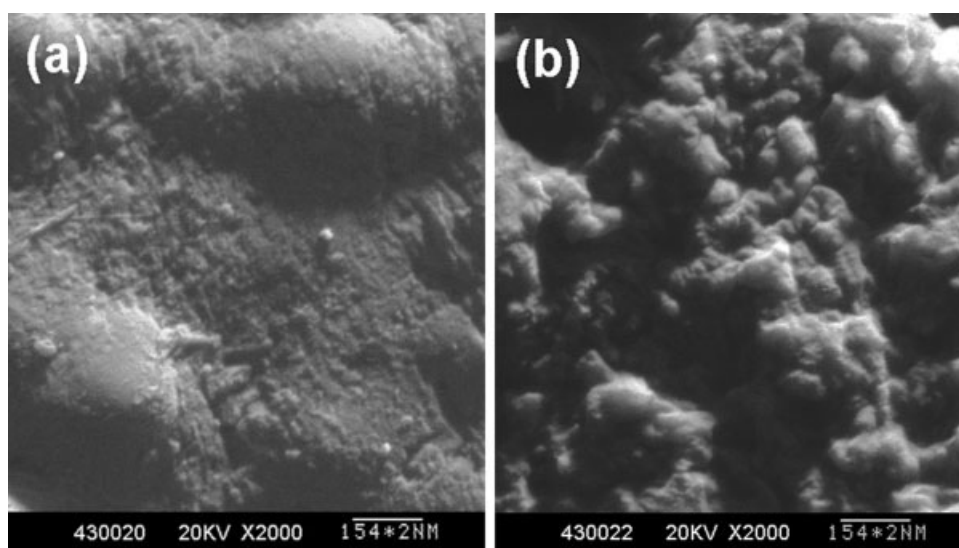


Figure 2 SEM photos of the hot-pressed films from superfine wool powder: (a) surface morphology and (b) cross section.

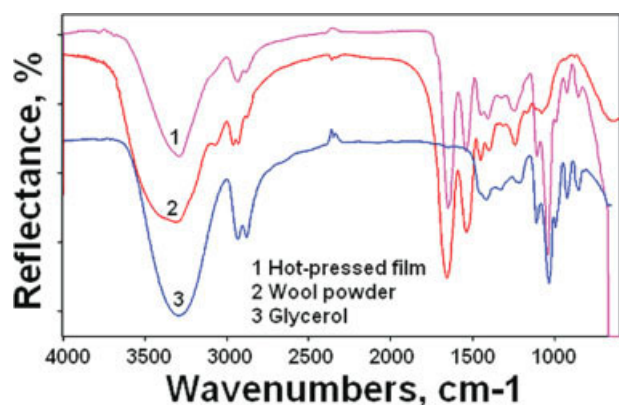


Figure 3 FTIR spectra of the hot-pressed film, wool powder, and glycerol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the hot-pressed film. It was obvious that the superfine wool powder was hot-pressed into a film with a relatively smooth surface, and almost no wool powder could be found on the surface. Figure 2(b) shows the cross section of the hot-pressed film, which indicated a relatively even distribution of the wool powder in the cross section. The powder was conglutinated into a continuous phase in the molding process, and a cohesive film was obtained.

FTIR analysis

The FTIR spectra from 600 to 4000 cm^{-1} of the hot-pressed films from superfine wool powder, wool powder, and glycerol are shown in Figure 3.

The spectra of wool powder and its hot-pressed film exhibited similar absorption bands around 3300 cm^{-1} (N—H and O—H), 2850 cm^{-1} ($-\text{CH}_2$), 1627 cm^{-1} (amide I), 1520 cm^{-1} (amide II), and 1233 cm^{-1} (amide III), which suggested that the main

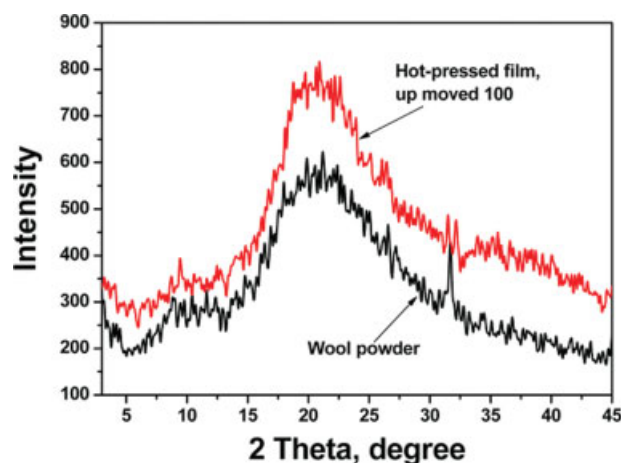


Figure 4 X-ray diffraction curves of the superfine wool powder and its hot-pressed film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

chemical structure was unchanged after the superfine wool powder was hot-pressed into film.

Compared with the FTIR spectrum of the superfine wool powder, the spectrum of the hot-pressed film also gave other absorption bands around 1109.7, 1013.48, 921.74, and 847.83 cm^{-1} , which were similar to the characteristic bands of glycerol, as shown in Figure 3. It is likely that these were the absorption bands of the alcoholic group as a result of the addition of glycerol to form the hot-pressed film.

X-ray diffraction

Figure 4 shows the X-ray diffraction curves of the superfine wool powder and its hot-pressed film. They showed the typical diffraction pattern of α -keratins with a prominent 2θ peak at 20.2° and a minor peak at 9° corresponding to crystalline spacing of 4.39 and 9.82 \AA , respectively.¹²

The peak around 9° was characteristic of the hydrated crystallinity of wool;¹³ however, no obvious peak around 9° was found in the X-ray diffraction curve of the hot-pressed film; this may have been caused by reduced hydrogen bonding within the wool powder after the powder was hot-pressed at an elevated temperature, which destroyed some crystals and amorphous regions in the wool powder. However, the intensity of the peak around 20.2° of the hot-pressed film was higher than that of the superfine wool powder. These results suggest that as a whole, the crystallinity of the hot-pressed film was slightly higher than that of the superfine wool powder.

Thermal analysis

Figure 5 shows the TG curves of the superfine wool powder and its hot-pressed film. The TG curve of

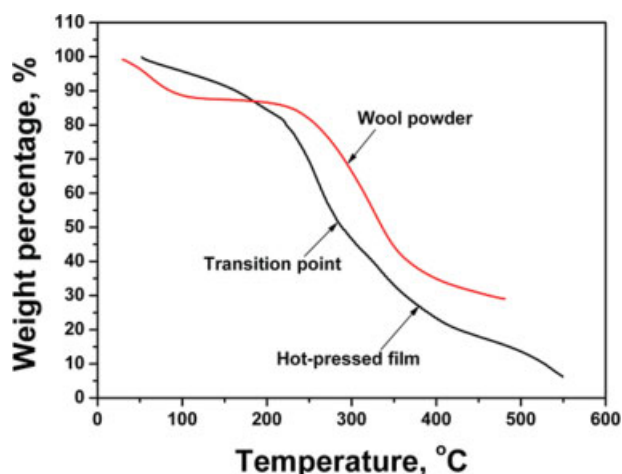


Figure 5 TG curves of the superfine wool powder and its hot-pressed film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the superfine wool powder showed two obvious weight loss steps. The first one corresponded to the evaporation of water, and the second one corresponded to the thermal decomposition and disintegration of the crystal region in the powder.¹⁴ However, the TG curve of the hot-pressed film showed just one weight loss step around 230°C, which corresponded to the thermal decomposition of the film. No obvious weight loss step was found below 100°C because water in the superfine wool powder would have largely evaporated in the hot-pressing process at a high temperature of 160°C. Also, there was an evident transition point in the TG curve of the hot-pressed film around 290°C. Because the boiling point of glycerol is around 290°C, it is likely that the evaporation of glycerol at 290°C affected the weight loss rate of the film.

The initial temperature of the thermal decomposition stage is usually used to compare the thermal stabilities of samples. As shown in Figure 5, the initial temperature of the hot-pressed film was lower than that of the superfine wool powder, so the thermal stability decreased after the superfine wool powder was hot-pressed into film.

The TG and DTA curves of the hot-pressed film are shown in Figure 6, and the DTA curves of the superfine wool powder and its hot-pressed film are shown in Figure 7. As shown in Figure 6, an evident endothermic peak existed around 230°C, which corresponded to the evident weight loss step in the TG curve. As shown in Figure 7, the DTA curve of the superfine wool powder showed two endothermic peaks around 80 and 230°C. According to previous studies,^{10,13} the first peak around 80°C corresponded to the evaporation of absorbed water, and the other peak around 230°C corresponded to the cleavage of linkages, such as $-S-S-$ bonds, hydrogen bonds, and salt links. However, there was no obvious endothermic peak around 80°C in the DTA curve of the

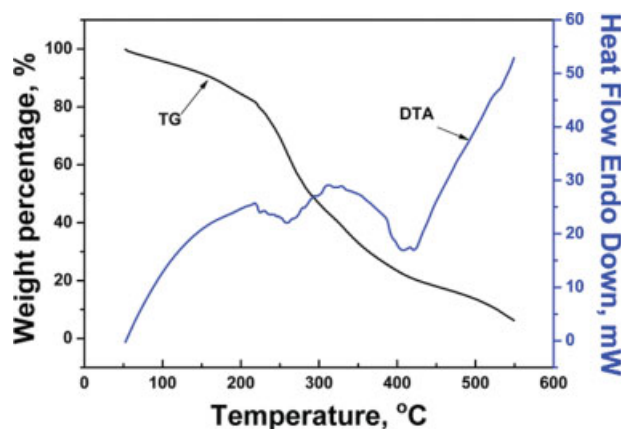


Figure 6 TG and DTA curves of the hot-pressed film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

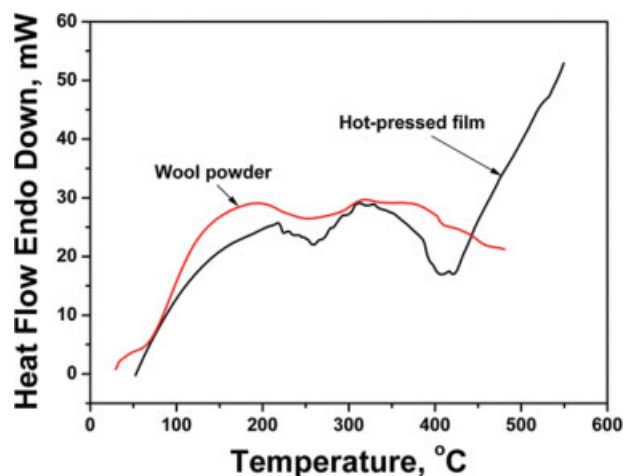


Figure 7 DTA curves of the superfine wool powder and its hot-pressed film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hot-pressed film; this was largely due to the absence of water in the film after hot pressing. As already mentioned, there was no weight loss step around 80°C in the TG curve of the film. Figure 6 shows that after 400°C, the DTA curve of the film became irregular. At this temperature, the film would have already decomposed, so any peaks there were meaningless.

Mechanical properties and dimensions

The glycerol content was changed in the preparation of the hot-pressed films, and the film mechanical properties were tested. The stress-strain curves are shown in Figure 8. It was obvious that the modulus and breaking stress of these films decreased sharply

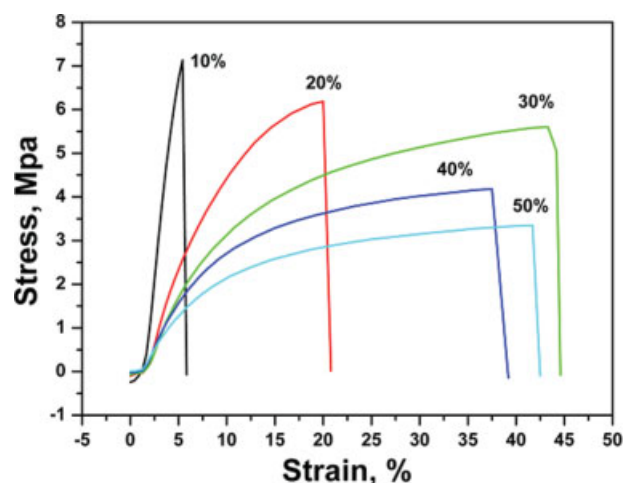


Figure 8 Stress-strain curves of the hot-pressed films from superfine wool powder with different glycerol contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Effects of the Glycerol Content on the Dimensions of the Hot-Pressed Films from Superfine Wool Powder

Dimensions	Glycerol content				
	10%	20%	30%	40%	50%
Diameter (mm)	73.5	81.0	102.5	132.8	153.5
Thickness (mm)	1.290	1.015	0.735	0.585	0.470

with increasing glycerol content. At the same time, a higher stain was observed when the content of glycerol increased from 10 to 30%, and the strain fluctuated slightly with glycerol content from 30 to 50%. Besides, the breaking energy increased greatly and then dropped a little with a peak at a glycerol content of 30%. These suggest that the toughness, tenacity, and ductility of the film were improved to some extent when the glycerol content was around 30%. However, when the glycerol content was higher than 30%, the films became very weak, so the strain at break decreased, and the breaking energy decreased. As glycerol associates with the —OH-containing hydrophilic amino acid in keratin and replaces water in the native keratin structure, glycerol acted as a plasticizer in the process and introduced free volume into the polymer,⁸ which resulted in a thermally processable and ductile film.

The diameters and thicknesses of the films with different glycerol contents are shown in Table I. It was evident that the diameter of the film increased and the thickness of the film decreased quickly with increasing glycerol content, so the films became wider and thinner. As free volume was added to the wool structure in the process of plasticizing, mobility in the keratin molecule allowed chain interdiffusion with other mobile chain parts,⁸ a higher glycerol content made the superfine wool powder more cohesive and ductile and, thus, allowed it to be hot-pressed into a thinner film.

CONCLUSIONS

With the addition of the plasticizer glycerol, superfine wool powder (with an average particle size of 1.7 μm) could be hot-pressed into a smooth film.

FTIR analysis showed that there were no substantial changes in the chemical structure of the wool powder after it was hot-pressed into film, but the absorption peaks of the alcoholic group from glycerol were found in the spectrum. X-ray diffraction showed that the hydrated crystallinity decreased, but the overall crystallinity increased after the powder was hot-pressed into film. Because most of the water in the powder was evaporated in the molding process, no obvious weight loss step around 80°C was found in the TG curve of the hot-pressed film. A transition point was found in the curve around 290°C which was perhaps due to the evaporation of glycerol. There was no obvious endothermic peak around 80°C in the DTA curve of the hot-pressed film due to the absence of water after hot pressing, and there was a broad endothermic peak around 230°C, which corresponded to the cleavage of linkages and the degradation of the film. With increasing glycerol content, the breaking stress and modulus of the film decreased and the strain increased; thus, the film became more ductile. Meanwhile, the film became wider and thinner with increasing glycerol content.

References

- Pavlat, A. E.; Houssard, C.; Camirand, W.; Robertson, G. H. *Text Res J* 1999, 69, 539.
- Iridag, Y.; Kazanci, M. *J Appl Polym Sci* 2006, 100, 4260.
- Yamauchi, K.; Yamauchi, A.; Kusunoki T.; Kohda A.; Konishi Y. *J Biomed Mater Res* 1996, 31, 439.
- Ichikawa, R.; Arai, K.; Kameda, T. *Jpn. Pat.* 9,291,138 (1992).
- Matsuda, H.; Takahashi, M.; Shinoda, K.; Kikyodani, S.; Inagaki, H. *Jpn. Pat.* 7,842,281 (1976).
- Schrooyen, P. M.; Dijkstra, P. J.; Oberthur, R. C.; Bantjes, A.; Feijen, J. *J Agric Food Chem* 2001, 49, 221.
- Barone, J. R.; Schmidt, W. F.; Gregoire, N. T. *J Appl Polym Sci* 2006, 100, 1432.
- Barone, J. R.; Schmidt, W. F.; Liebner, C. F. E. *J Appl Polym Sci* 2005, 97, 1644.
- Wang, X.; Xu, W.; Ke, G.; *Fiber Polym* 2006, 7, 250.
- Xu, W.; Guo, W.; Li, W. *J Appl Polym Sci* 2003, 87, 2372.
- Xu, W.; Cui, W.; Li, W.; Guo, W. *Powder Technol* 2003, 140, 136.
- Tsukada, M.; Shiozaki, H.; Freddi, G.; Grighton, J. S. *J Appl Polym Sci* 1997, 64, 343.
- Xu, W.; Ke, G.; Wu, J.; Wang, X. *Eur Polym J* 2006, 42, 2168.
- Xu, W.; Fang, J.; Cui, W.; Huang, J. *Polym Eng Sci* 2006, 46, 617.