Xin Wang,
Weilin Xu,
Wenbin Li,
*Xungai Wang

Thermoplastic Film from Superfine Wool Powder

Wuhan University of Science and Engineering,
Wuhan 430073, P. R. China
E-mail: weilin_xu@hotmail.com

***Centre for Material and Fibre Innovation,**
Deakin University,
Geelong 3217, Australia

Abstract
In this paper a research work is described in which superfine wool powder was plasticised by glycerol and hot-pressed into a kind of thermoplastic film. SEM photos show that the powder is moulded into a smooth surface and is conglutinated into a continuous phase in the cross-section of the film. The glycerol content, moulding pressure, temperature and moulding time were changed in the moulding process. The sizes and thickness aw well as tensile strength, modulus, breaking elongation and breaking energy of the films were also tested to investigate the thermoplasticity and mechanical properties of the films. The best moulding techniques included a glycerol content of 30%, a moulding pressure of 5 MPa, a temperature of 160 °C and a moulding time of 5 minutes.

Key words: *superfine wool powder, thermoplasticity, film, preparation, hot-pressing.*

Introduction

Synthetic films are widely used for different packaging purposes, which may create big environmental problems since their biodegradation is very slow. Some environmental friendly materials such as agricultural polymers and most carbohydrates could be used as package films, but they either can not be moulded or are soluble in water [1].

Keratins are fibrous proteins found in hair, wool, feathers, nails, horns and other epithelial coverings [5]. With the high concentration of half-cystine residues, the keratins in wool are regarded as three-dimensional polymers interlinked by S-S bonds between the reduced keratin-monomeric units [6]. Keratins are environmentally stable, biocompatible and have unique mechanical properties, therefore most of them have been used in biomedical applications in the form of solutions, powders, films, gels and filaments [15 - 18]. Recently there has been great interest in developing keratin films [1 - 4] that could be used as packaging in order to have more environmental stability. However, most of these films are cast from keratin solutions, and in order to dissolve keratins, complicated techniques such as purification, cleaning, dialysis, etc and a list of chemical salts or acid, such as sodium dodecyl sulfate, dimethylformamide (DMF), Na_2SO_3, thioglycolic acid, 2-mercaptoethanol, etc [5] are used in the processing, which makes the method of producing keratin too complicated and expensive to be applied in industry. Based on the thermoplasticity of protein fibre, plasticiser glycerol is widely used to treat protein fibre to make it ductile in hot environments; keratin can be extruded in these conditions [7, 8]. High crosslink like −S−S− bridges in wool keratin make it a kind of thermosetting polymer, and therefore it is not processable by conventional thermal techniques [1, 7]. However, producing wool keratin from superfine wool powder could break the high crosslink in it, which makes the powder thermally processable. Previously, we reported a novel method of producing keratins in superfine wool protein powder by grinding wool fibre on a purpose-built machine [10, 11]. It is feasible to produce keratin film from superfine wool powder as packaging or other uses.

In this paper, glycerol was used to change the thermoplasticity of superfine wool powder, which was then hot-pressed into thermoplastic film. Afterwards the effects of the glycerol content, moulding temperature, pressure and moulding time on the thermoplasticity and mechanical properties of the film were investigated. In this way, a new method was introduced to produce packaging film, and the thermoplasticity of superfine wool powder was studied, which was also a preparation of blend filament using superfine wool powder and other polymers on a melting spinning machine. The thermoplastic film could be applied for packaging purposes in industry.

Experimental

Materials

The wool fabric was provided by the Third Wool Factory of Lanzhou, China. The weight was 270 g/m. The Australian wool fibres were provided by the Mayer Corporation of Hubei, China. The superfine wool powder was produced from the wool fibres on a purpose-built grinding machine [10, 11]. The particle size distribution (***Figure 1***) gave an average particle size of 1.7 μm, with 95% of the wool powder being less than 3.0 μm in particle size.

The Glycerol was provided by Bodi Chemical Co. Ltd. Tianjian, China, analytical grade. The polyethylene glycol (PEG600) was produced by Guoyao Corporation Chemicals Co. Ltd. China, chemical grade.

Preparation of hot-pressed films

Various contents (10% ~ 50%) of the glycerol plasticiser were added to the superfine wool power, after which the mixture was stirred in a blender for 5 minutes, and then the blend was sandwiched between two pieces of PET films, which were placed on the armour plate of a hot-pressing machine (XLB-D350 × 350, provided by Huzhou Dongfang mechanical Co., Ltd. Zhejiang, China). After that the blend was hot-pressed for several minutes (1 ~ 9 min) at a moulding pressure of 1 ~ 9 MPa and moulding temperature of 100 ~ 200 °C. Finally, it was possible to extract the thermoplastic film from the PET films after they had cooled down in the air.

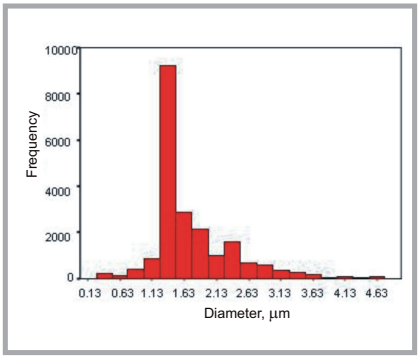

Figure 1. *Particle size distribution of superfine wool powder.*

Wang X., Xu W., Li W., Wang X.; Thermoplastic Film from Superfine Wool Powder.
FIBRES & TEXTILES in Eastern Europe 2009, Vol. 17, No. 2 (73) pp. 82-86.

Characterisations of hot-pressed films

A microscope (QUESTAR KH-1000, America) was used to take micrographs of the surface of the film. Scanning Electron Microscopy analysis of the thermoplastic films was also carried out with a Hitachi X-450 microscope, at an acceleration voltage of 20 KV, after gold coating.

Thermoplasticity was indirectly revealed by measuring the dimensions and thickness of the hot-pressed film under the same experimental conditions. The dimensions of the films were determined by testing the particle sizes of the round films. The thickness of the films was tested on a fabric thickness tester (YG(B) 141D, provided by Wenzhou Darong Textile Instrument Co. Ltd. China).

The mechanical properties were tested on an Instron 5566 Universal Testing Machine, at a gauge length of 30 mm and strain rate of 50 mm/min. The width of the samples was 20 mm, and each sample was tested 5 times and the results were averaged.

Results and discussion

Materials selection

In order to investigate the thermoplasticity of wool, different materials such as wool fabric, wool fibre and superfine wool powder were chosen to produce hot-pressed films on the hot-pressing machine. No plasticiser was added to the materials and experimental conditions were the following: a temperature of 160 °C, a pressure of 5 MPa and a moulding time of 5 min.

Figure 2 shows micrographs of the hot-pressed films. As for the fabric, there was no change after the hot-pressing, as photo (a) shows. Photo (b) shows that wool fibres could be hot-pressed into film; however the fibres are just compacted together without any connection; the film is fragile without any practical application.

Superfine wool powder (photo (c)) can also be hot-pressed into a film.Since the average particle size is 1.7 μm, powders can be conglutinated and piled up together, producing smoothed film, as in the micrographs in photo (d). Therefore superfine wool powder is the best material for producing hot-pressed film. However, the film is not viscoelastic enough to eliminate the possibility of cracks appearing in application. A plasticiser may change the thermoplasticity of wool

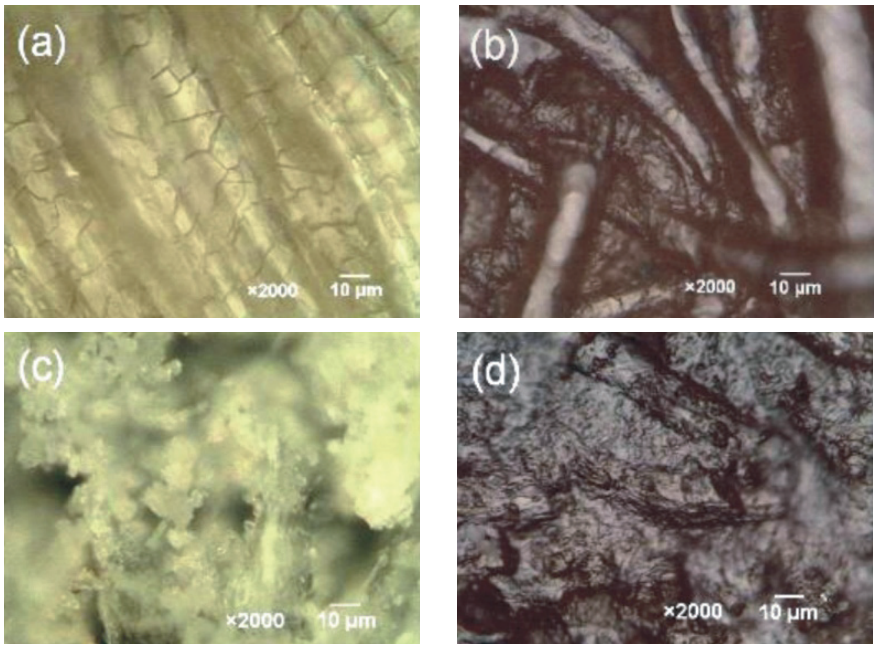

Figure 2. *Micrographs of hot-pressed films from (a) wool fabric, (b) wool fibres and (d) superfine wool powder, (c) Micrograph of superfine wool powder without hot-pressing.*

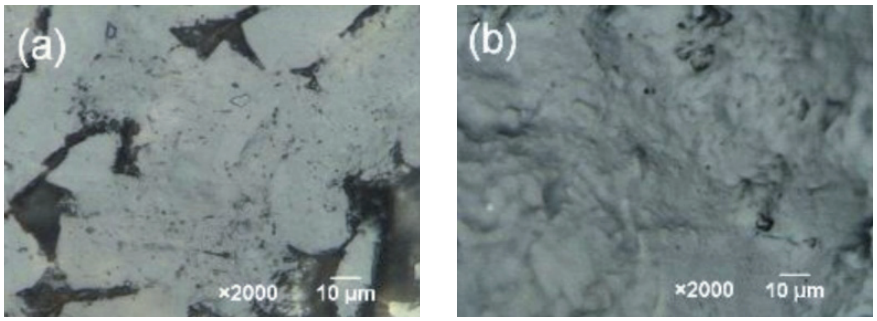

Figure 3. *Thermoplastic films from superfine wool powder plasticised by (a) PEG and (b) glycerol.*

powder in hot-pressing so that the hot-pressed film would be more applicable.

Selection of plasticiser

PEG and glycerol are the most widely used plasticisers for protein materials [8]. Both of them were added to the superfine wool powder to produce hot-pressed films with better thermoplasticity. Experimental conditions were the following: a temperature of 160 °C, a pressure of 5 MPa and a moulding time of 5 min.

Micrographs of hot-pressed films plasticised by PEG and glycerol are shown in ***Figure 3***. Photo (a) indicates that superfine wool powder is pressed into the film, but there are many cracks in it, and the film is still fragile, making it impossible to test its mechanical properties. The film plasticised by glycerol shows a smooth and plane surface in photo (b), the film being soft and able to be bent, which shows its viscoelasticity. The film can also be tested for its mechanical properties, which will be analysed later in this paper.

Since the high crosslinks in the keratins of wool fibre were largely broken during the grounding of the superfine wool powder, the latter was thermally processed and became ductile at a high temperature. It is reported that glycerol associated with the −OH containing hydrophilic amino acids in keratin, replaced water in the native keratin structure and acted as a plasticizer for the protein [7]. Therefore the superfine wool powder was successfully hot-pressed into the thermoplastic film at a high temperature.

SEM photos

Figure 4 shows SEM photos of the thermoplastic film. Photos (a) and (b) show the surface morphology of the thermoplastic film at two different magnifications. It is obvious that the superfine wool powder was hot-pressed into the film, producing a relatively smooth sur-

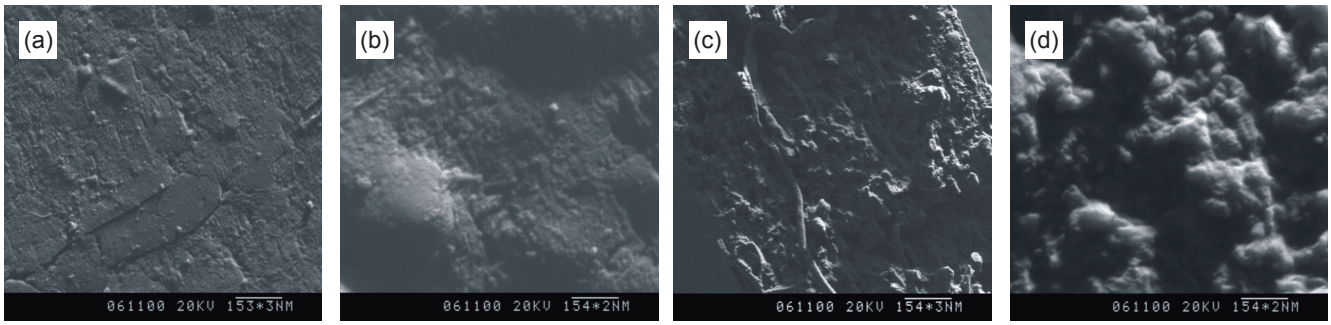

Figure 4. *SEM photos of thermoplastic films of superfine wool powder. (a), (b): surface morphology; (c), (d): cross-section.*

face, and almost no wool powder could be found on the surface. Thus the superfine wool powder became ductile in the hot-pressing process at a high temperature.

Photos (c) and (d) show the cross-section of the thermoplastic film, indicating a relatively even distribution of the wool powder in the cross-section. With the connection between glycerol and the –OH containing hydrophilic amino acids in keratin, the powder was conglutinated into a continuous phase in the moulding process.

Glycerol content

Glycerol played an important role in the moulding of wool powder thermoplastic film due to its plasticising effect. In the moulding process of the film, the glycerol content was changed from 10% to 50%, and the thermoplasticity and mechanical properties of the films were tested to investigate the effect of glycerol content on the properties of the thermoplastic films. The weights of the blend containing powder and glycerol were the same during the experiment, and other experimental conditions were the following: a temperature of 160 °C, a pressure of 5 MPa and a moulding time of 5 min.

Figure 5 shows the dimensions and thickness of films with different glycerol content. It is obviously that as the content of glycerol increases, the size of the film increases, wereas, the thickness the decreases quickly, the film becomes wider and thinner. This means that a higher content of glycerol may make superfine wool powder more ductile when hot-pressed into thinner thermoplastic film.

The mechanical properties of thermoplastic films with different glycerol contents are shown in ***Figure 6***; the percentages in the Figure indicate the content of glycerol used in the thermoplastic films.

From the Figure it is obvious that the modulus (the slope of the first linear part of the curves) and the breaking stress (the maximum values of force) of these films decrease with an increase in glycerol content, which means that the stiffness and tensile strength of the films weaken as the glycerol content rises.

At the same time, the elongation of these films increases greatly as the content of glycerol increases from 10% to 30%, fluctuating afterwards. Besides this, the breaking energy (the area under the curves) increases greatly and drops a little, with a maximum at a glycerol content of 30%. These suggest that the toughness, tenacity and ductility of the film are improves, to some extent, when the glycerol content is around 30%.

Hence a kind of soft and ductile film with good toughness could be produced by hot-pressing after the superfine wool powder was plasticised by glycerol.

Moulding pressure

In the formation of wool powder thermoplastic film, the moulding pressure may affect the dimensions and tensile strength of the film, which may reflect changes in the thermoplasticity and mechanical properties of thermoplastic films. The moulding pressure was changed in the production of the films, and other experimental conditions were the following: a glycerol content of 30%, a temperature of 160 °C and a moulding time of 5 min.

Figure 7 shows the thickness and sizes of the films under different moulding pressures. It is obvious that as the pressure increases, the sizes of the films increase almost linearly, while the thickness of the films decrease gradually, which indicates that the pressure greatly affects the dimensions and thickness of the films. At a higher pressure, wool powder may be forced to distribute widely and may

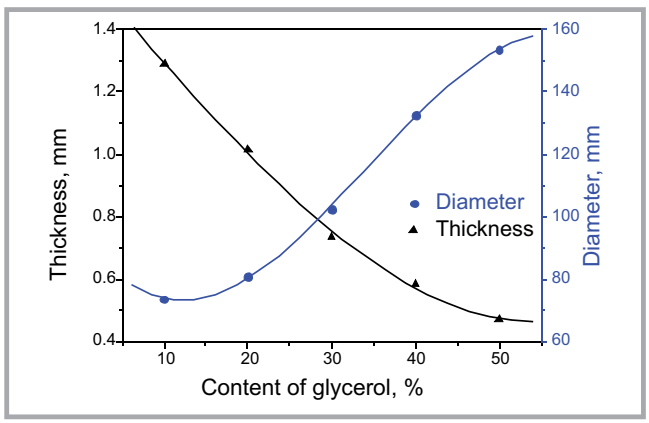

Figure 5. *Effect of glycerol content on the thermoplasticity of superfine wool powder film.*

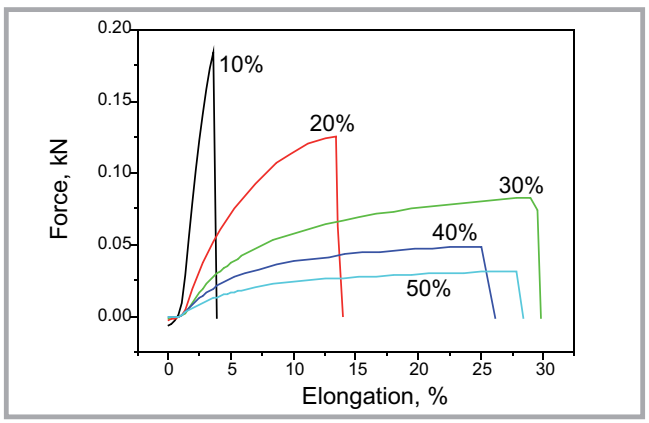

Figure 6. *Force-elongation curves of thermoplastic films from superfine wool powder with different glycerol contents.*

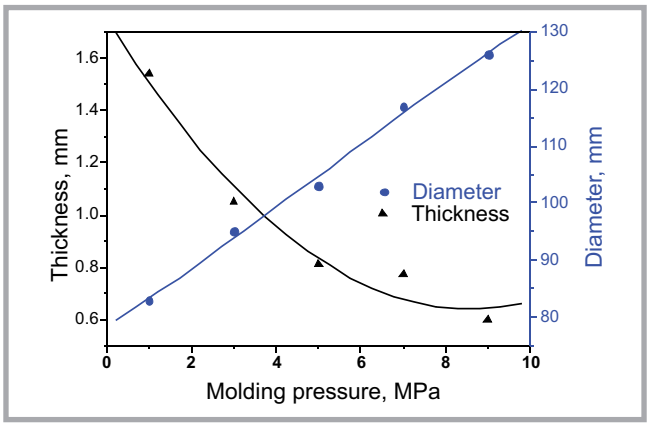

Figure 7. *Effect of moulding pressure on the plasticity of super-fine wool powder film.*

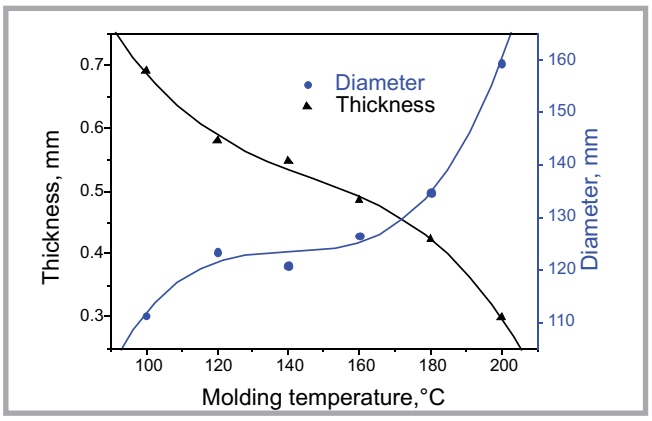

Figure 8. *Effect of moulding temperature on the plasticity of super-fine wool powder film.*

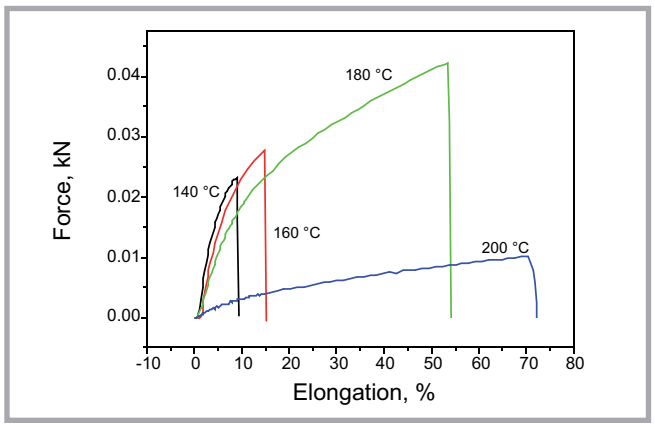

Figure 9. *Force-elongation curves of thermoplastic films at different moulding temperatures.*

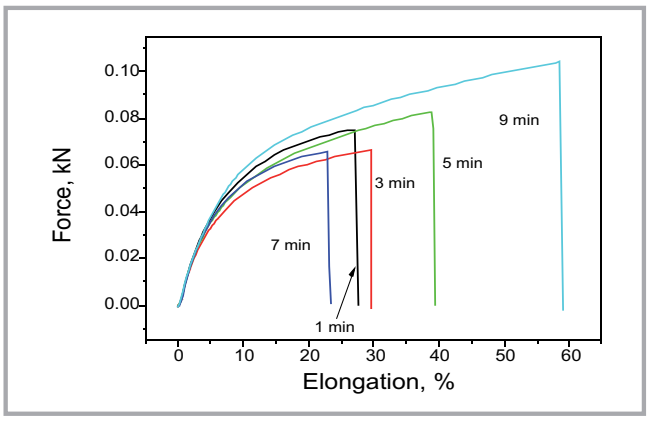

Figure 10. *Force-elongation curves of thermoplastic films after different moulding times.*

improve the plasticising of wool powder using glycerol at a high temperature, which makes the film more ductile and thermally processable.

Table 1 shows the mechanical properties of thermoplastic films at different moulding pressures. It is evident that the breaking stress and modulus decrease sharply with an increase in pressure, while the elongation and breaking energy fluctuate without big changes. This means that the pressure could not affected the thermoplasticity of the film; however, this physical compaction made the film stiffer and more fragile and only improved the plasticising of the wool powder to some extent; hence median pressure should be applied in the hot-pressing process.

Moulding temperature

The moulding temperature was changed during the hot-pressing of the wool powder thermoplastic films. Other experimental conditions were the following: a glycerol content of 30%, a moulding press of 5 MPa and a moulding time of 5 min.

Figure 8 shows the size and thickness of the thermoplastic films at different moulding temperatures. It is evident that when the temperature is 100 °C, the film is very thick and small in size, after which, from 120 °C to 180 °C, the film gradually becomes wider and thinner as the temperature increases. When the temperature is 200 °C, the size of the film jumps from about 135 mm to 160 mm, at the same time the thickness clearly drops from 0.42 mm to 0.30 mm. It is obvious that the temperature greatly affects the dimensions and thickness of the films, therefore an increase in temperature may improve the thermoplasticity of the film.

Figure 9 shows force-elongation curves of the thermoplastic films at different moulding temperatures. When the temperature is below 140 °C, the film is too fragile to be tested for its mechanical properties, which makes it impossible to obtain their force-elongation curves. From the Figure we can see that when the moulding temperature rises, the breaking stress, elongation and breaking energy increase greatly, while the modulus decreases slightly. Thus the increase in temperature improved the mechanical properties of the thermoplastic film, which suggests that a high temperature may help the plasticising of wool powder using glycerol. However, when the temperature is 200 °C, the modulus, breaking stress and breaking energy of the film drop sharply from the peak (180 °C), and the elongation of the film increases to almost 75%. It is possible that when the temperature reaches 200 °C, wool powder may decompose to a degree that the mechanical properties deteriorate. To sum up, a high temperature in the moulding process can improve the thermoplasticity of hot-pressed films from superfine wool powder, but when the temperature reaches 200 °C, the film may degrade, and the mechanical properties will deteriorate.

Moulding time

The moulding time was changed during the hot-pressing of the wool powder thermoplastic films. Other experimental conditions were the following: a glycerol of content 30%, a moulding pressure of

Table 1. *Effect of moulding pressures on the mechanical properties of the thermoplastic film.*

Molding pressure, MPa	Mechanical properties			
	Elongation at break, mm	Breaking stress, N	Breaking energy, J	Modulus, N/mm^2
1	7.833	157.4	0.9247	74.9
3	7.580	104.1	0.5667	40.9
5	8.500	89.8	0.5727	36.2
7	13.97	95.8	1.0117	33.5
9	9.39	63.0	0.4424	25.4

Table 2. *Effect of moulding time on the plasticity of superfine wool powder film.*

Items	Molding time, min				
	1	3	5	7	9
Thickness, mm	0.76	0.67	0.70	0.66	0.78
Diameter, mm	101.5	102.5	109.4	93.9	98.5

5 MPa and a moulding temperature of 160 °C.

Table 2 shows the thickness and size of the thermoplastic films from wool powder after different moulding times. From the table we can observe that the thickness and size of the thermoplastic films show no discernable changes with an increase in the moulding time: they fluctuate at around 0.70 mm and 100 mm, respectively. This suggests that the moulding time barely affects the thermoplasticity of the films.

Force-elongation curves of the thermoplastic films after different moulding times are shown in Figure 10. It is obvious that the breaking energy, breaking stress and elongation increase with an increase in the moulding time. At the same time, the modulus shows little change. It seems that a longer moulding time can help the plasticising of superfine wool powder using glycerol, hence the mechanical properties of the film are improved. It can be seen that the curve of 7 min is irregular compared with others. The data for 7 min in ***Table 2*** is also irregular, which is probably due to an error in the experiments.

Although the moulding time barely affects the thermoplasticity of the films, a longer moulding time could improve the mechanical properties of the film; hence the moulding time must be a little longer.

Conclusions

Superfine wool powder can be hot-pressed into thermoplastic film after plasticising. Glycerol is the best plasticiser as it makes the film soft and thermally processable. SEM photos show that the powder is moulded into a smooth surface, and the powder is conglutinated into a continuous phase in the cross-section of the film. The toughness, tenacity and ductility of thermoplastic films are improved to some extent when the glycerol content is increased. An increase in the molding pressure makes the film wider and thinner, but it becomes stiffer and more fragile at the same time according to the force-elongation curves, it may only improve the plasticising of wool powder to some extent. A high temperature in the molding process greatly improves the thermoplasticity of hot-pressed films, but when the temperature reaches 200 °C, the film may degrade and the mechanical properties can deteriorate. The moulding time barely affects the thermoplasticity of the films, but a longer moulding time could improve the mechanical properties of the film. The best moulding techniques contain the following: a glycerol content of 30%, a moulding pressure of 5 MPa, a temperature of 160 °C and a moulding time of 5 minutes.

Acknowledgments

- *The authors are grateful to Ms. Jing Bai and Ms. Yanan He from Wuhan University of Science and Engineering for providing technical assistances.*
- *This project was financed by 'The Funding for Innovation-Team of the National Science Foundation of Hubei Province' and 'The Funding for Supporting the Elite of New Century of the Ministry of Education of China'.*

References

1. *Pavlath A. E., Houssard C., Camirand W., Robertson G. H.; Text. Res. J. Vol. 69 (1999), pp. 539-541..*
2. *Yamauchi K., Yamauchi H. Hojo, Y., Tanabe T.; Mat. Sci. Eng. C Vol. 23 (2003), pp. 467-472.*
3. *Schrooyen P. M. M., Dijkstra P. J., Oberthur R. C., Bantjes A., Feijen J.; J. Agric. Food Chem. Vol. 48 (2000) pp. 4326-4334.*
4. *Schrooyen P. M. M., Dijkstra P. J., Oberthur R. C., Bantjes A., Feijen J.; J. Agric. Food Chem. Vol. 49 (2001) pp. 221-230.*
5. *Iridag Y., Kazanci M.; J. Appl. Polym. Sci. Vol. 100 (2006) pp. 4260-4264.*
6. *Yamauchi K., Yamauchi A., Kusunoki T., Kohda A., Konishi Y.; J. Biomed. Mater. Res. Vol. 31 (1996) pp. 439-444.*
7. *Barone J. R., Schmidt W. F., Gregoire N. T.; J. Appl. Polym. Sci. Vol. 100 (2006) pp. 1432-1442.*
8. *Barone J. R., Schmidt W. F., Liebner C. F. E.; J. Appl. Polym. Sci. Vol. 97 (2005) pp. 1644-1651.*
9. *Koga J., Kawaguchi K., Nishio E., Joko K., Ikuta N., Abe I., Hirashima T.; J. Appl. Polym. Sci. Vol. 37 (1989) pp. 2131-2140.*
10. *Xu W., Guo W., Li W.; J. Appl. Polym. Sci. Vol. 87 (2003) pp. 2372-2376.*
11. *Xu W., Cui W., Li W., Guo W.; Powder Technol. Vol. 140 (2003) pp. 136-140.*
12. *Tsukada M., Shiozaki H., Freddi G., Grighton J. S.; J. Appl. Polym. Sci. Vol. 64 (1997) pp. 343-350.*
13. *Xu W., Ke G., Wu J., Wang X.; Eur. Polym. J. Vol. 42 (2006) pp. 2168-2173.*
14. *Xu W., Fang J., Cui W., Huang J.; Polym. Eng. Sci. Vol. 46 (2006) pp. 617-622.*
15. *Wrześniewska-Tosik K., Adamiec J.; 'Biocomposites with a Content of Keratin from Chicken Feathers';* ***FIBRES & TEXTILES*** *in Eastern Europe No 1(60) 2007, pp. 106-112.*
16. *Wrześniewska-Tosik K., Wawro D., Stęplewski W., Szadkowski M.; 'Fibrous Products with Keratin Content'; FIBRES & TEXTILES in Eastern Europe No 2(61) 2007, pp. 30-35.*
17. *Wrześniewska-Tosik K., Wawro D., Ratajska M., Stęplewski W.; 'Novel Biocomposites with Feather Keratin'; FIBRES & TEXTILES in Eastern Europe No 5-6(64-65) 2007, pp. 157-162.*
18. *Wrześniewska-Tosik K., Kucharska M., Wawro D.; 'Fibrous Keratin - containing composite'; FIBRES & TEXTILES in Eastern Europe No 6(71) 2008.*

Received 08.03.2007 Reviewed 18.09.2008