CHEMICAL ENGINEERING TRANSACTIONS

VOL. 59, 2017

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Zhuo Yang, Junjie Ba, Jing Pan

ISBN 978-88-95608- 49-5; **ISSN** 2283-9216

DOI: 10.3303/CET1759054

Novel Thermoplastic Natural Down Powder Film with High Mechanical Properties

Ke Zhang, Kai Yang, Pei Lv, Wenbin Li

College of Textiles, Wuhan Textile University, Wuhan 430073, China
KeZhang@126.com

Superfine down powder was modified by formamide which acts as a plasticizer and then hot-pressed into thermoplastic down films. The influences of formamide content, hot-pressing time, pressure intensity and exposure to atmosphere on the mechanical properties of thermoplastic down films were investigated. The maximum tensile strength of thermoplastic down films can reach 28.74 Mpa after exposure to atmosphere for 40 days.

1. Introduction

Concern for the environment and shortage of oil is driving research into ways to reuse natural protein fibers, which are usually biodegradable, renewable and environmentally friendly compared with synthetic polymers. One important method of reusing protein fibers is to extract keratin from these protein fibers using complex chemical methods, the keratin was then blended with synthetic polymer to produce protein biomaterials. Unfortunately, keratin solution is unstable in the process of extruding and hot-pressing under high temperature due to the destruction of its super-molecular structure.

Consequently, various natural protein fibers such as feather fiber, wool fiber and silk fiber have been straightly applied as filler to produce composites (Barone, 2005; Barone et al., 2005; Barone and Schmidt, 2005; Bullions et al., 2006; Martínez-Hernández et al., 2007 ; Cheng et al., 2009 ; Conzatti et al., 2012 ; Li et al., 2007). Feather fibers have been thermally preceded into protein films by using convenient plasticizing agents, such as glycerol and soybean oil (Barone et al., 2005; Barone et al., 2006; Hong and Wool, 2005). However, the film modified by glycerol showed higher weight loss of glycerol, which limited its application. Furthermore, down feather dimensions (highly order, hierarchical branched structures) make it unsuitable for producing thermoplastic protein films. In this context, down feather was cut into small pieces of fiber and then ground into superfine down powder (SDP), which has the size distribution between 0.2-12 μm and the average particle size of 2.34μm (Xu et al., 2009). Based on our previous study, superfine down powder has the nearly 14 times the specific surface area of down feather and was blended with polypropylene and polyurethane respectively. (Liu et al., 2013; Guo et al., 2015; Chen et al., 2015; Liu et al., 2010; Liu et al., 2009; Liu et al., 2011). Therefore, more hydrogen bonds can form between superfine down powder and plasticizing agent resulting into higher mechanical properties of thermoplastic down films after hot-processing.

Formamide is one of the most important biochemical models and has two C=O and one N-H corresponding to the receptor and donor of hydrogen bond proton respectively. So there are many N-H······O=C bonds in the backbone of formamide, and can react with $–NH_2$ and -NH by forming various hydrogen bonds. Superfine down powder, which has a large amount of the amino acid, of which the cysteine is a sulfur-containing amino acid and can form sulfur-sulfur (S-S) cystine bonds with other intra- or intermolecular cysteine molecules. Therefore, this indicates that the formamide is an excellent plasticizing agent to prepare thermoplastic superfine down powder films.

In this paper, superfine down powder was blended with various amounts of formamide and then hot-pressed into thermoplastic down films. The influences of formamdie content, hot-pressing time, pressure intensity and exposure to atmosphere on the mechanical properties of thermoplastic down films were investigated. The weight loss of formamide as a function of exposure to atmosphere was investigated.

Please cite this article as: Ke Zhang, Kai Yang, Pei Lv, Wenbin Li, 2017, Novel thermoplastic natural down powder film with high mechanical properties, Chemical Engineering Transactions, 59, 319-324 DOI:10.3303/CET1759054

2. Experimental

2.1 Materials

Superfine down powder was produced from duck feather on a purpose-built machine (Xu et al., 2009). Acetone was supplied from Kedi Co. Ltd., Tianjin, China. Formamide (A.R.) and glycerol (A.R.) were supplied from Kedi Co. Ltd., Tianjin, China.

2.2 Fabrication of superfine down powder thermoplastic film

Thermoplastic films with different contents of formamide were prepared according to the following procedures: superfine down powder was added into a beaker and then formamide was slowly added into the beaker. To avoid some aggregates of superfine down powder, the blend powder was mixed in an All-Purpose High-speed Smashing Machines. Then, the blend was sandwiched between two Teflon-coated compression molder and hot-pressed into thin films on a plate vulcanization machine (XLB-D350×350, china). After pressing, the film was removed from the molder and cooled until its temperature reached room temperature. This resulted in circular films with around 1.5 mm in thickness and different diameter. Amount of formamide were changed in experimental by 20 %, 25 %, 30 %, 35 %, 40 %, 45 % and 50 % to the weight of superfine down powder. In addition, thermoplastic films with different contents (20%) of glycerol were also prepared as the above procedure.

2.3 Measurements and characterizations

Morphologies of down feather and superfine down powder were examined on a Scanning Electron Microscope (JSM-5610LV), at 25 kV after gold coating.
Mechanical properties were tested on an Instron 5566 Universal Testing Machine, at a gauge length of 50 mm and strain rate of 50 mm/min. The length and width of samples respective was 60 mm and 20mm. Each sample was tested 5 times and the results were averaged.
The weight of the film was tested immediately after the film was cooled down, after that, the samples were weight every three days at room temperature. Weight loss was calculated according to the equation (1):

$$Weight\ loss(\%) = (W_1 - W_2)/W_1 \tag{1}$$

Where, W_1 is the original weight of the film, W_2 is the weight of film after different storage time.

3. Results and discussion

3.1 Characterizations of superfine down powder

The SEM microphotographs of down feather and down superfine down powder were shown in Figure 1. It was obvious that down feather was crushed into small pieces. After grinding, down feather was crushed into superfine down powder (Figure 1(b)), most of which had diameters of 1-15μm and aspect ratios (length-to-diameter ratios) of 30-100. The high aspect ratios of superfine down powder meant it could be a good reinforcement filler for composites.

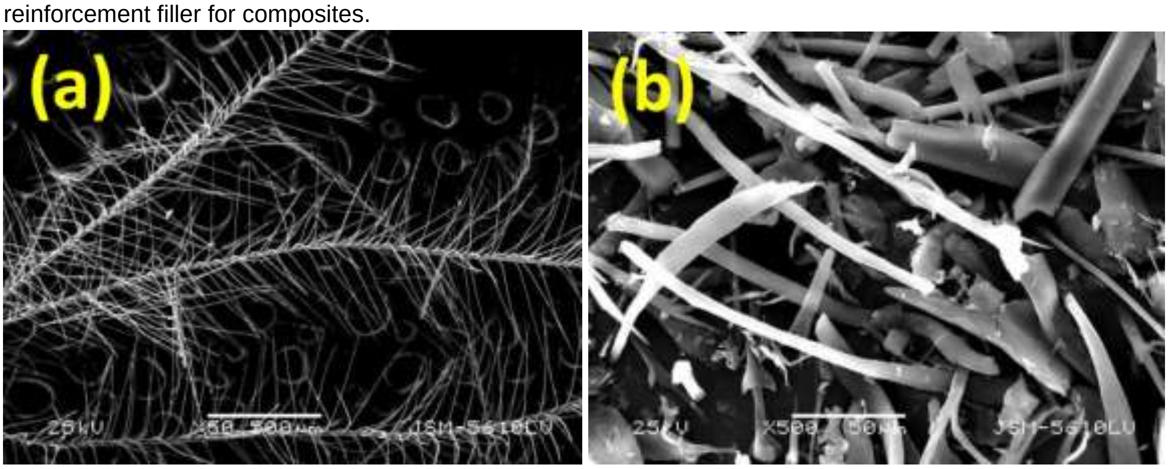

Figure 1: SEM of down feather (a) and superfine down powder (b).

3.2 Effect of formamdie content on the mechanical properties

Superfine down powder/formamide blends with different formamide contents were hot-pressed at 5Mpa and 150°C for 5min. The tensile strength, elongation at break and elongation at break of thermoplastic films with different formamide contents are shown in Figure 2. It was apparent that with the increase in formamide content, the tensile strength and Young’s modulus of thermoplastic films decreased steadily, but the elongation at break reached a maximum value when formamide content was around 35%. It is obvious that the superfine down powder films became more ductile with the increase in formamide content, which could be seen from Figure 3. With the increase in formamide content, the diameter of films increased and the thickness decreased at the same time. When the formamide content was lower than 20% the pressed films were too brittle to obtain good mechanical properties, and films with greater than 50% formamide were incomplete after hot-pressing. It is evidently that adding of formamide made the down powder film ductile and deformable.

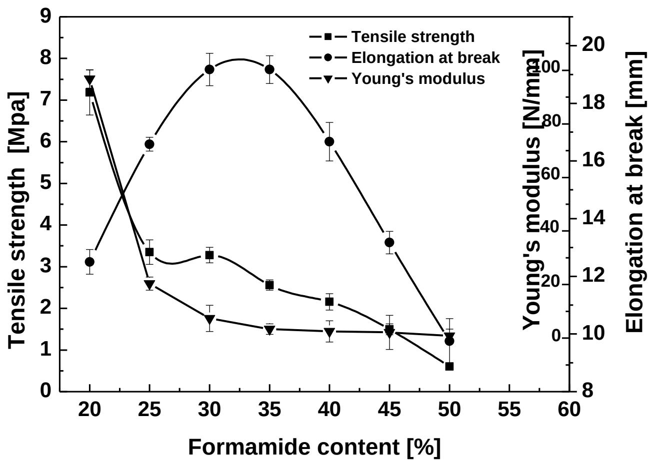

Figure 2: Tensile strength and elongation at break of superfine down powder thermoplastic films with different formamide content.

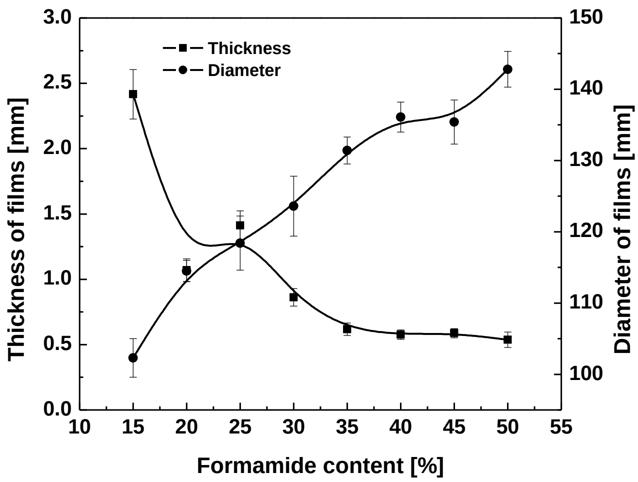

Figure 3: Thickness and diameter of powder thermoplastic films with different formamide content.

3.3 Effect of hot-pressing time on the mechanical properties

The effect of hot-pressing time on the mechanical properties of superfine down powder/formamide (65:35) thermoplastic film (pressed at 130 °C and 5 Mpa) is shown in Figure 4. The elongation at break of the film increased as the films were hot-pressed for longer time. The tensile strength and Young's modulus decreased slightly with the increase of hot-pressing time. The films pressed less than 3 min were too brittle to obtain good mechanical properties. This indicates that the mechanical properties of the thermoplastic film depend on the hot-pressing time. Furthermore, the films became more ductile when the films were pressed for longer periods of time.

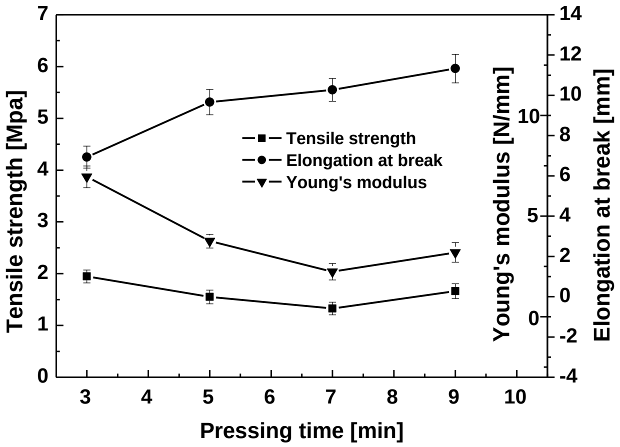

Figure 4: The effect of pressing time on the physical properties of down powder/formamide (65:35) thermoplastic films.

3.4 Effect of pressure intensity on the mechanical properties

The effect of pressure intensity on the mechanical properties of superfine down powder/formamide (65:35) thermoplastic film (pressed at 130 °C and 5 Mpa) is shown in Figure 5. With the increase in pressure intensity, the tensile strength and elongation at break of thermoplastic films increased steadily, while the Young's modulus decreased. This means that superfine down powder/formamide thermoplastic films became more flexible and tough when these films were pressed under high pressure intensity due to the structure of films were more compact and some small crystalline around surface of powder was more easily to be formed.
As we can see from above, formamide is a very good plasticizer to produce thermoplastic film from superfine down powder. Optimization of the preparation technique such as select properly increase the formamide content, hot-pressing time and pressing intensity can strengthen the plasticizing effect on the powder, thus a more ductile and deformable film was produced.

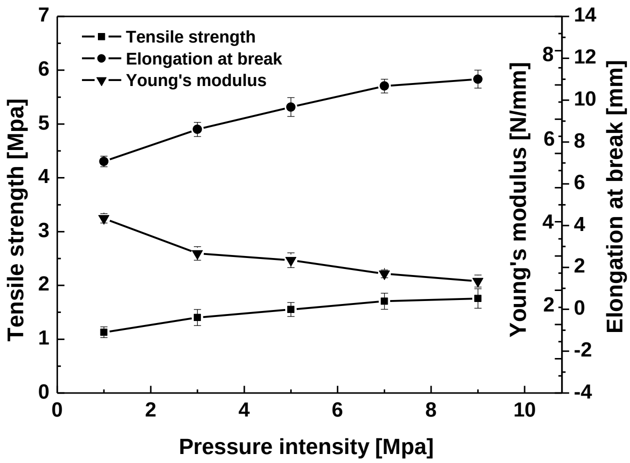

Figure 5: The effect of pressure intensity on the physical properties of down powder/formamide (65:35) thermoplastic films.

3.5 Loss of formamide of thermoplastic films from superfine down powder

The weight loss percentages of the thermoplastic films (pressed at 130 °C and 5 Mpa for 5min) under different storage time are shown in Figure 6. The curves of weight loss showed a sharp slop within 9days, and this showed the removal of formamide from the films. After 12 days, the weight of films became stable comparatively. It could be seen clearly that the formamide could not be found on the surface of formamide thermoplastic films after 1 day and 2 days. This indicates that formamide is a good plasticizer and can form more chemical bond with superfine down powder.
Furthermore, formamide thermoplastic films became tough when they were exposed to atmosphere for 40 days, as seen from Table 1. For formamide thermoplastic films after exposure to atmosphere for 40 days, the tensile strength and Young’s modulus increased greatly while the elongation at break decreased evidently. After a long time exposure to atmosphere, most formamide was removed from the microstructure of thermoplastic films, and then the films became more compact and adjust its formamide molecular and down powder to adopt new structure, which has fewer holes and more chemical bonds between powder and formamide.

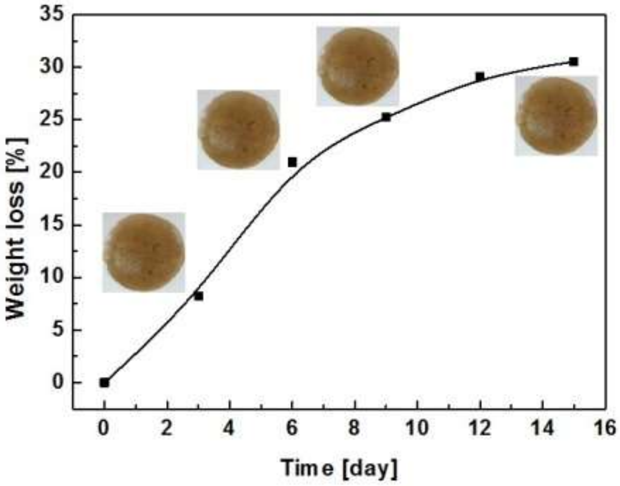

Figure 6: The weight loss of thermoplastic films exposed to atmosphere with different time periods.

Table 1: Mechanical properties of thermoplastic films after 40 days exposure.

Storage time [day]	Mechanical properties			
	Elongation at break [mm]	Young’s modulus [N/mm]	Fracture work [J]	Tensile strength [MPa]
0	12.83	3.898	0.1949	1.996
>40	1.867	198.3	0.1863	28.74

4. Conclusions

The results of this study indicate that the formamide is a good plasticizer, which not only improves the mechanical properties of superfine down powder thermoplastic films largely, but also sustains the excellent protein properties of down powder. With the increase in formamide content, the tensile strength and Young’s modulus decreased steadily. However, the elongation at break reached a maximum value when formamide content was around 35%. This suggests the more formamide content, the more ductile thermoplastic films we can obtained. Pressing time is another important fact to influence the mechanical properties of films. With long hot-pressing periods, thermoplastic films would become more ductile and thinner. After 12 days, the weight of formamide thermoplastic films became stable comparatively, and the formamide could not be found on the surface of the films. This indicates that formamide is a good plasticizer and can form more chemical bond with superfine down powder. It was worth noting that the tensile strength of formamide thermoplastic films could reach 28.74 Mpa after exposure to atmosphere for 40 days. Meanwhile, Young’s modulus of formamide thermoplastic films also increased greatly and the elongation at break decreased slightly.

Reference

Barone J.R., 2005, Polyethylene/keratin fiber composites with varying polyethylene crystallinity, Composites Part A Applied Science & Manufacturing, 2005, 36(11), 1518-1524, DOI: 10.1016/j.compositesa.2005.03.006.

Barone J.R., Schmidt W.F., 2005, Polyethylene reinforced with keratin fibers obtained from chicken feathers, Composites Science & Technology, 65(2), 173-181, DOI: 10.1016/j.compscitech.2004.06.011.

Barone J.R., Schmidt W.F., Liebner C.F.E., 2010, Thermally processed keratin films, Journal of Applied Polymer Science, 97(4), 1644-1651.

Barone J.R., Schmidt W.F., Gregoire N.T., 2010, Extrusion of feather keratin, Journal of Applied Polymer Science, 100(2), 1432-1442.

Barone J.R., Schmidt W.F., Liebner C.F.E., 2005, Compounding and molding of polyethylene composites reinforced with keratin feather fiber, Composites Science & Technology, 65(3–4), 683-692, DOI: 10.1016/j.compscitech.2004.09.030.

Bullions T.A., Hoffman D., Gillespie R.A., Price-O'Brien J., Loos A.C., 2006, Contributions of feather fibers and various cellulose fibers to the mechanical properties of polypropylene matrix composites, Composites Science & Technology, 66(1), 102-114, DOI: 10.1016/j.compscitech.2005.03.017.

Chen F., Xiong L., Cai M., Xu W., Liu X., 2015, Adsorption of direct fast scarlet 4BS dye from aqueous solution onto natural superfine down particle, Fibers and Polymers, 16(1), 73-78, DOI: 10.1007/s12221-015-0073-2.

Cheng S., Lau K., Liu T., Zhao Y., Lam P.M., Yin Y., 2009, Mechanical and thermal properties of chicken feather fiber/PLA green composites, Composites Part B Engineering, 40(7), 650-654, DOI: 10.1016/j.compositesb.2009.04.011.

Conzatti L., Giunco F., Stagnaro P., Capobianco M., Castellano M., Marsano E., 2012, Polyester-based biocomposites containing wool fibres, Composites Part A Applied Science & Manufacturing, 2012, 43(7):1113-1119, DOI: 10.1016/j.compositesa.2012.02.019.

Guo L., Chen F., Zhou Y., Liu X., Xu W., 2015, The influence of interface and thermal conductivity of filler on the nonisothermal crystallization kinetics of polypropylene/natural protein fiber composites, Composites Part B Engineering, 68, 300-309, DOI: 10.1016/j.compositesb.2014.09.004.

Hong C.K., Wool R.P., 2005, Development of a bio-based composite material from soybean oil and keratin fibers. Journal of Applied Polymer Science, 95(6), 1524–1538,

Li W., Qiao X., Sun K., Chen X., 2010, Mechanical and viscoelastic properties of novel silk fibroin fiber/poly(ε-caprolactone) biocomposites, Journal of Applied Polymer Science, 110(1), 134-139, DOI: 10.1002/app.28514.

Liu X., Gu S., Xu W., 2013, Thermal and structural characterization of superfine down powder, Journal of Thermal Analysis and Calorimetry, 111(1), 259-266, DOI: 10.1007/s10973-012-2202-0.

Liu X., Huang J., Huang J., Li W., Xu W., 2011, Coating superfine down powder on polypropylene for the production of dyeable fibers, Fibers and Polymers, 12(2), 220, DOI: 10.1007/s12221-011-0220-3

Liu X., Xu W., Li W., Chen Y., Rao J., 2010, Mechanical and water vapor transport properties of polyurethane/superfine down powder composite membranes, Polymer Engineering & Science, 50(12), 2400–2407, DOI: 10.1002/pen.21764.

Liu X., Xu W., Peng X., 2009, Effects of stearic acid on the interface and performance of polypropylene/superfine down powder composites, Polymer Composites, 30(12), 1854-1863.

Martínez-Hernández A.L., Velasco-Santos C., De-Icaza M., Castaño V.M., 2007, Dynamical–mechanical and thermal analysis of polymeric composites reinforced with keratin biofibers from chicken feathers, Composites Part B, 38(3), 405-410, DOI: 10.1016/j.compositesb.2006.06.013.

Xu W.L., Wang X., Cui W.G., Peng X.Q., Li W.B., Liu X., 2009, Characterization of superfine down powder, Journal of Applied Polymer Science, 2009, 111(5), 2204–2209.

Zanella K., Concentino V., Taranto O.P., 2017, Influence of the type of mixture and concentration of different binders on the mechanical properties of "green" charcoal briquettes, Chemical Engineering Transactions, 57, 199-204, DOI: 10.3303/CET1757034.