Bleaching and Dyeing of Superfine Wool Powder / Polypropylene Blend Film

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ABSTRACT

Fibers based regenerated protein draw much attention for recycling discarded protein resources and can produce biodegradable and environmental friendly polymers. In this study, superfine wool powder is blended with polypropylene (PP) to produce wool powder/PP blend film through extrusion and hot-pressing. Hydrogen peroxide is used to bleach the black colored surface of the blend films. The effects of peroxide concentration, bleaching time and powder content on the final whiteness and mechanical properties of the blend films are investigated.

The bleached films are dyed with acid red dyes and the dyed color is evaluated using a Computer Color Matching System. Color characters of dyed films, such as L^*, a^*, b^*, ΔE^*ab, C^*ab and K/S values are measured and analyzed. The study not only reuses discarded wool resources into organic powder, widens the application of superfine wool powder on polymers, but also improves the dyeing properties of PP through the addition of protein content.

Keywords: Wool Powder, Polypropylene, Blend, Bleaching, Dyeing

1. Introduction

There has been great interest in investigating fibers based on regenerated protein to develop new textile fibers and recycle redundant protein materials in recent years (Matsumoto et al., 1996; Yang et al., 1996; Cates & White, 1956; Barone et al., 2005; Barone et al., 2006; Katoh et al., 2004).

In most of these studies, keratin was extruded (Barone et al., 2006) from protein fibers using complicated chemical methods, or S-sulfo keratin (Katoh et al., 2004) and other polymers were blended to produce blend fibers through melt or wet spinning.

However, the protein was prone to decompose in the process of spinning and the inherent microstructure of protein was destroyed inevitably. Therefore, the protein biofibers might lose the original properties of the protein. On the other hand, protein powder could keep the original properties of materials without destroying the microstructure. Hence, it has been widely applied in modern industries and hi-tech related fields with various special properties (Novak et al., 2004; Zhang et al., 2001; Miyajima et al., 2001).

Silk powder is produced as one of the useful physical forms of silk fibroin protein with special properties, compared with fiber and silk films for biomaterial applications (Freddi et al., 1999; Tanaka et al., 1998).

It has been also applied to finish yarn-dyed cotton fabrics which offer good drape characteristics and moisture absorbing properties (Kawahara et al., 1996).

Previously, we developed wool and down powder (Xu et al., 2004; Xu et al., 2003) and applied them on modification of polymers (Xu et al., 2006).

With the purpose of producing protein/polymer blend fiber without losing its original properties, we produced down-powder/viscose blend films

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and characterized its dyeing properties (Wang et al., 2006).

Previously, we produced and characterized a type of superfine wool powder/PP blend pellets by extruding and hot-pressing the pellets into a type of blend film (Xu et al., 2007).

As the surface powder of the blend film degraded greatly during the hot-pressing which gave the blend film a black surface, we first bleached the blend film into a white surface and investigated the dyeing properties of the blend film. In this way, the compatibility of superfine wool powder and PP was investigated to produce superfine wool power/PP blend filaments. Furthermore, polypropylene (PP) was modified by superfine wool powder to improve its dyeing properties. It is meaningful to reuse the discarded wool fibers and widen the application of PP.

2. Experimental

2.1 Materials

Australian wool fibers (provided by Mayer Corporation of Hubei, China) were grounded into superfine wool powder on a specifically built machine (Xu et al., 2004; Xu et al., 2003), Figure 1 shows the particle size distribution of the wool powder. After calculation, 95% of the powder is less than 3.0μm in diameter and the average particle size is 1.7μm.

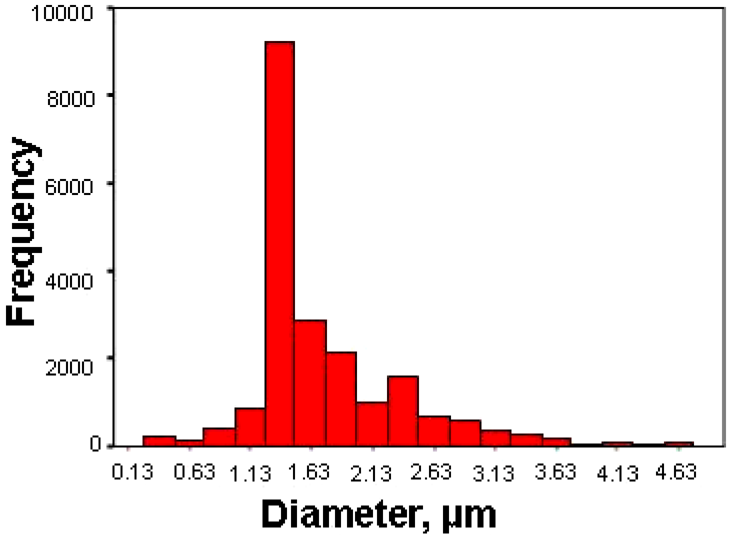
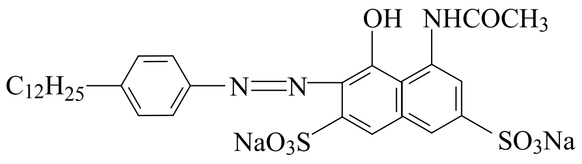


Fig. 1. Diameter distribution of superfine wool powder

Plasticizer glycerol (analytical grade) was provided by Bodi Chemical Co., Ltd. Tianjing. China. PP (F401, fiber grade) was provided by Panjing Polyethylene Co. Ltd.

Commercially available acid dyes were employed, C.I. Acid red 138, and its structure is as follows:



2.2 Preparation of Superfine Wool Powder/ PP Blend Film

Plasticizer glycerol was slowly added into the superfine wool powder with a content of 30%. The mixture was stirred in a blender for 5 minutes and then, the mixture was blended with PP with different powder content. In order to blend sufficiently, the blend was extruded in a screw extruder (SHJ-18, Dazhong Electrical Equipment Co. Ltd, Jiangsu, China) at 180 °C and cut into small pellets.

The particles were then sandwiched between two pieces of PET films which were placed on the armor 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 5 minutes under a molding pressure of 5 Mpa and molding temperature of 160 °C. Finally, the blend film was taken out from the PET films after they were air cooled.

2.3 SEM Analysis of the Blend Film

Scanning Electron Microscopy (SEM) analysis was carried out with a Hitachi X-450 microscope, at 20 KV acceleration voltages, after gold coating.

2.4 Bleaching of the Blend Film

Hydrogen peroxide was used in the bleaching of the blend film. The bleaching bath contained about 10% hydrogen peroxide with a bath ratio of 1:40 and some additives, such as Na_2CO_3 (0.2%) and $Na_2SiO_3{\cdot}9H_2O$ (0.7%). The bleaching temperature was set as 50 ^oC and bleaching time was about 1 h.

Whiteness of the bleached films were tested on a whiteness meter (WSB-Ⅱ, provided by Wenzhou Instruments and Apparatus Co. Ltd, China), and the weight of the blend films were also tested to calculate the weight loss rate of blend films after bleaching.

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, each sample was tested 5 times and the results were averaged.

2.5 Dyeing of the Blend Films

The dyeing of blend film follows a traditional exhaust dyeing procedure. The dye bath contained 5% (o.w.f.) acid dye with a bath ratio of 1:40. The films were immersed into the dyeing solution at 40^{o}C, heated up to 98 ^{o}C at a rate of 1.5 ^{o}C/min, and then maintained at 98^{o}C for 60 min. The pH of the dyeing bath was adjusted to 4 by sodium acetate. All the dyed samples were washed sufficiently in distilled water before the color measurement.

2.6 Color Measurement

Color characters of dyed films, such as L^*, a^*, b*, ΔE^*ab, C*ab and K/S values, were measured using a Computer Color Matching System (Datacolor International, SF600, Switzerland), using illuminant D_{65} and 10° standard observer condition. Relative colour strengths (K/S values) is measured based on the equation of Kubelka-Munk:

$$K/S = (1-R)^2/2R \tag{1}$$

where K refers to the coefficient of absorption, S is the coefficient of scattering and R is the reflectance of the dyed blend film.

3. Results and Discussion

3.1 SEM Photos

Figure 2 shows the surface morphology and cross-section of superfine wool powder/PP blend films with powder content of 20% and 60%. From Figure 2, the morphology of the blend film (a) and (b) show a smooth surface.

When the wool powder content increases from 20% to 60%, little wool powder can be found in the blend film. The cross-section of the blend films (c) and (d) show a smooth surface and there is no obvious wool powder in the SEM photos.

These SEM photos suggest that superfine wool powder has good compatibility with PP under the plasticizing of glycerol in the extrusion. The wool powder distributes uniformly in the film and almost no agglomerations occur. It is probably because PP melts in the extrusion and superfine wool powder disperses evenly into the melted PP during the process of extrusion.

3.2 Bleaching of the Blend Films

Normally, wool fiber degrades at temperatures higher than 200 ^{o}C (Xu et al., 2004; Xu et al., 2003).

Wool powder in the blended pellets after extruding can keep its original properties as the time for the powder to pass through the groove of the extruder is less than 2 seconds and the extruding temperature is just 180 ^{o}C.

However, in the molding process of the blend film, the surface powder of the blend film adhere to the hot plate (over 160 °C) for 5 minutes which somewhat degrades the surface powder, so that the blend films show a black surface.

Since the superfine wool powder in the surface of the blend films degraded during the hot-pressing which made the films show black surfaces, the dyeing of the films may result in no obvious color which renders the film inapplicable in coloration. Bleaching of the films is necessary to make the powder in the blend film shows its original properties and then the film can be dyed with acid dyes.

Hydrogen peroxide was widely used in the bleaching of wool (Cegarra et al., 1978; Gacen & Cayuela, 1983; Cegerra et al., 2005; Liu et al., 2004; Liu et al., 2003).

Most researchers have investigated the influence of temperature, additives, peroxide content and bleaching time on the whiteness of bleached wool.

Since the film in this study is a type of blend film from wool powder and PP, the bleaching theory may be different from the bleaching of pure wool fibers. Moreover, bleaching causes damage to the wool powder in the blend films.

So in the experiment, peroxide content, bleaching time and the powder content may have different effluences on the whiteness of the film after bleaching than previous research.

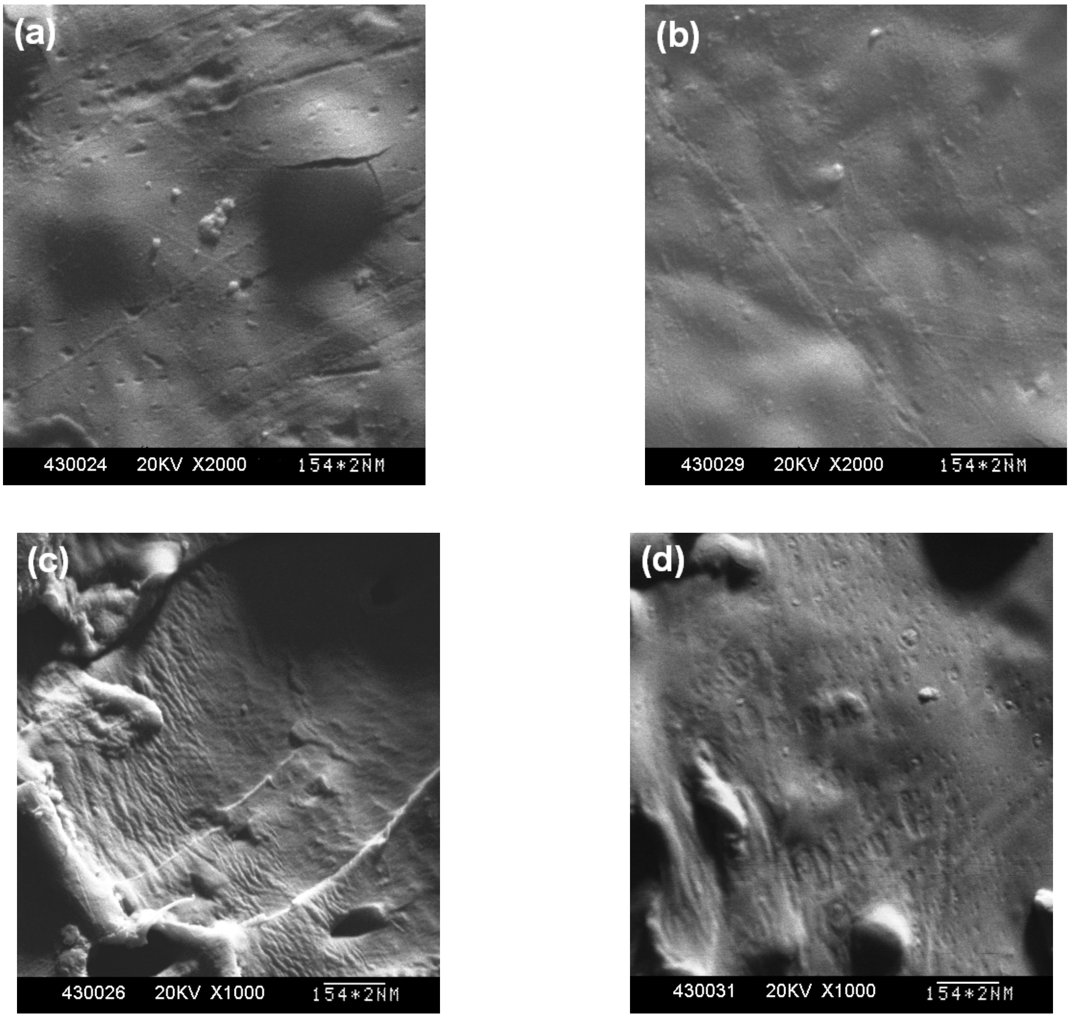


Fig. 2. SEM photos of surface morphology of superfine wool powder/PP blend films with blend ratio (a) 20/80 and (b) 60/40, and cross-section of the blend film with blend ratio (c) 20/80 and (d) 60/40.

Concentration of hydrogen peroxide

Figure 3 shows the effect of peroxide concentration on the whiteness and weight loss rate of the blend films (blend ratio 50/50). It is obvious that higher concentration of peroxide in the bleaching solution can improve the whiteness of the blend film greatly. Higher concentration of peroxide makes bleaching more sufficient in the bleaching process.

However, since hydrogen peroxide may react with wool powder and dissolve some of it into the solution, the weight loss of the blend film increases greatly when the concentration of peroxide changes from 0 to 20%. After that, the weight loss does not change much. There cannot be too much loss of wool powder in order to maintain the original properties of protein in the blend film, so higher concentrations of peroxide in the bleaching solution is not applicable. A 10% peroxide in the bleaching bath might be appropriate.

Bleaching time

Figure 4 indicates the effect of bleaching time on the whiteness and weight loss rate of blend film (blend ratio 50/50) in the process of bleaching. Although wool powder in the blend film dissolves into the bleach solution with an increase of bleaching time (the powder content changes from 50% to about 17% in Figure 4), it is obvious the whiteness of the blend film increases gradually. Evidently, a longer bleaching time can create a reaction in peroxide and wool in the blend film so that the film becomes whiter and the weight loss rate increases.

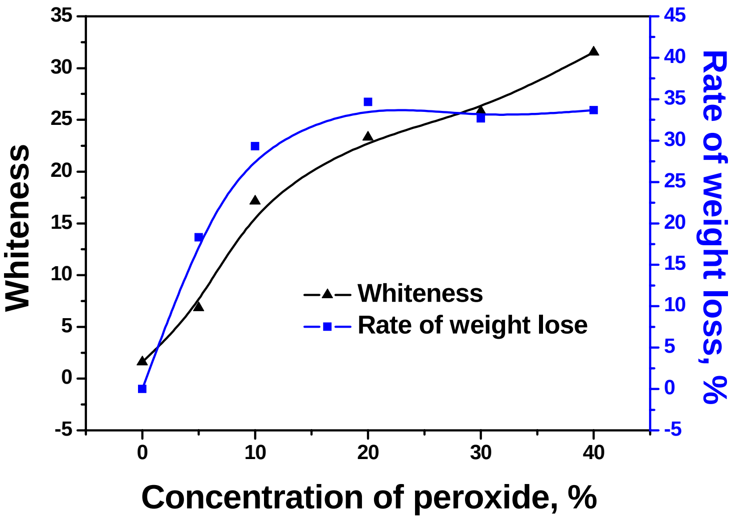


Fig. 3. Effect of concentration of peroxide on the whiteness and weight loss rate of blend films.

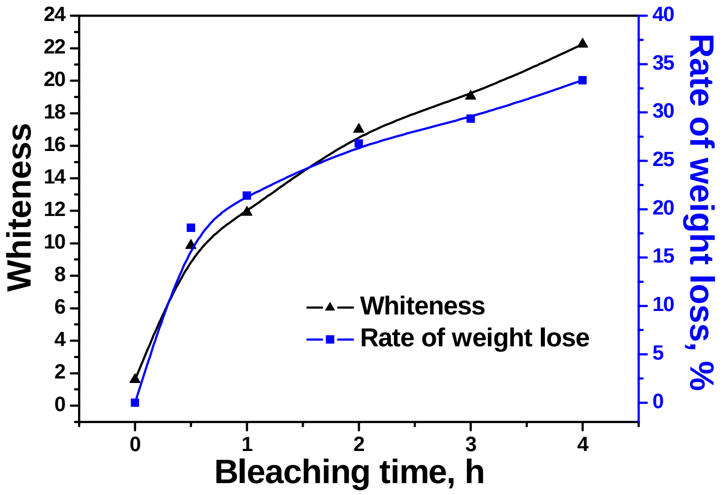


Fig. 4. Effect of bleaching time on the whiteness and weight loss rate of blend films

Mechanical properties of the blend film (blend ratio 50/50) under different bleaching times are also tested and the results are listed in Table 1. From the table, as the bleaching time increases, the breaking elongation, breaking stress and breaking energy decrease greatly. This is probably due to the larger weight loss of powder in the blend film which deteriorates the strength of the film. The bleaching time was approximately 1 hour in the experiment to maintain the general mechanical properties of the majority of the wool powder in the blend film.

Table 1. Mechanical properties of blend film with different bleaching time.

Bleaching time, h	Mechanical properties			
	Break elongation, mm	Breaking stress, N	Breaking energy, J	Modulus, N/mm
0	1.940	53.1	0.0569	65.4
0.5	1.222	30.3	0.0236	49.9
1	1.577	39.0	0.0414	53.4
2	1.166	31.4	0.0222	50.8
3	1.566	40.8	0.0418	64.5
4	1.500	34.0	0.0332	61.7

Powder content

Blend films with different powder content were bleached and Figure 5 shows the whiteness and rate of weight loss of the film after bleaching. It is evident that the increase of powder content in the blend film can make the film whiter. When the powder content increases, more powder is distributed onto the surface of the blend film which makes the blend film more bleachable. However, at the same time, the weight loss rate increases and shows a similar trend for the increase of whiteness. This is probably because more powder in the blend film causes it to degrade and dissolve into the bleaching solution. From Figure 5, when the powder content is over than 40%, large amounts of powder are lost in the bleaching process which might severely affect the properties of the blend film.

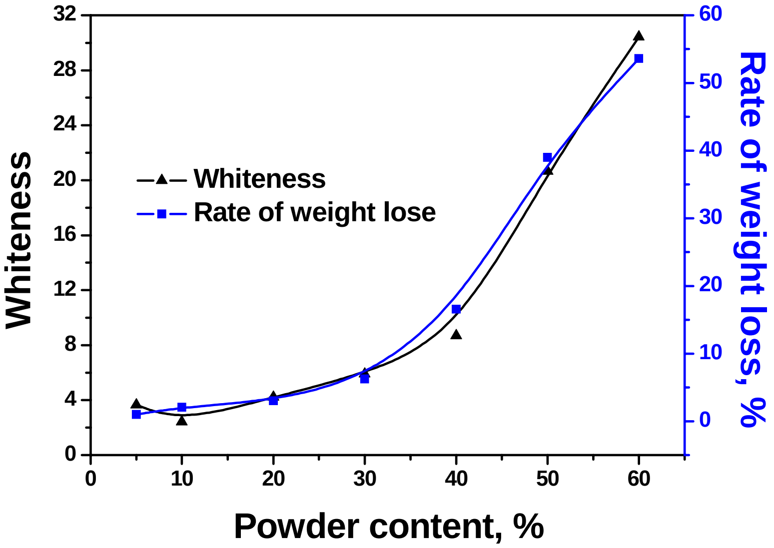


Fig. 5. Effect of powder content on the whiteness and weight loss rate of blend films

The mechanical properties of blend films with different powder content were tested before and after the bleaching. Figure 6 illustrates the breaking stress of the blend films with different powder content. Evidently, the breaking stress of the blend films drops greatly when the powder content increases from 0 to 20%. After that, the breaking strength fluctuates and shows no large changes.

However, when the powder content of the blend films is under 20%, the breaking strength after bleaching is lower than that of the unbleached blend films. Hence, bleaching deteriorates the mechanical properties when the wool powder content in the blend films is under 20%.

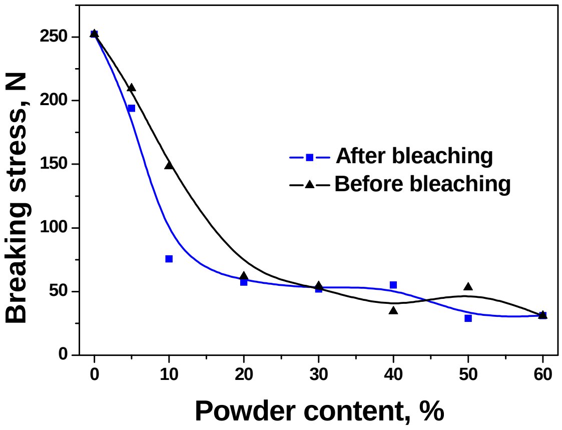


Fig. 6. Breaking stress of blend films with different powder contents before and after bleaching

3.3 Dyeing of the Blend Films

After bleaching, the surface color of the blend films changed from black to white. The bleached films with different powder content were dyed with acid red 138, and the K/S values were recorded and listed in Figure 7 to show the absorbing spectra of the dyed films. From Figure 7, the K/S value of pure PP film peaks at a wavelength of about 700 nm, and actually shows no visible color.

In general, when the powder content in the blend films increases from 0% to 60%, the peaks of K/S values change from 700 nm to around 510 nm, and the peaks at 510 nm become more and more obvious with the powder content increase.

However, the K/S values at the peaks of the spectra decrease when the powder content increases from 30% to 60%. This is probably due to the great weight loss of wool powder of the blend films in the process of bleaching.

On the other hand, more wool powder is distributed onto the surface of the blend films when the wool powder content is over 30%. Although most of the wool powder is lost in the bleaching process (from Figure 5, the powder content in the blend film after bleaching is around 10%-20%), the existing wool powder can even be dyed into a vivid color better than others. According to a previous study (Wang et al., 2006), the absorbing peaks of K/S value around 510 nm are ascribed to the absorbing of red color, so as the powder content increases, the absorbing peak of red in the spectra become more and more obvious.

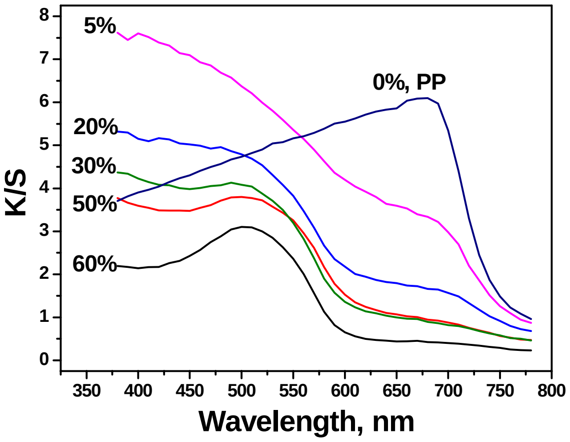


Fig. 7. K/S values of dyed blend films with different powder content, percentages in the figure indicate the powder content in the blend films

Table 2. Color values of blend films with different powder content

Powder content	Color values				
	L*	a*	b*	ΔE*ab	C*ab
0%	34.41	-0.7	-4.27	0	4.33
5%	34.31	4.77	7.35	12.83	8.76
20%	40.88	11.18	10.54	20.06	15.37
30%	45.16	17.06	12.48	26.68	21.14
50%	44.68	15.81	8.42	23.23	17.91
60%	52.04	25.19	11.88	35.26	27.86

The color values of all the dyed blend films are listed in Table 2. It is obvious that the lightness of color (L*) increases quickly when the powder content increases. The redness-greenness value (a*), color differences ΔE*ab and saturation C*ab increase at the same time. These characteristics indicate that with a powder content increase, the dye blend films show an obvious red color. Hence, the bleached blend films can be dyed with acid red dyes.

4. Conclusions

A blend of superfine wool powder and PP is extruded into pellets and then hot-pressed into a type of blend film. Superfine wool powder can be blended with PP and dyed with acid dyes. SEM photos showed that superfine wool powder has good compatibility with PP under the plasticizing of glycerol in the extrusion. The superfine wool powder distributed uniformly in the film and almost no agglomerations occurred.

Hydrogen peroxide can successfully bleach and remove the black colored surface of the blend films. Increase of hydrogen peroxide concentration, bleaching time and superfine wool powder content in the blend films in the bleaching process can increase the whiteness of the bleached films.

However, the weight loss rates increase at the same time, which might deteriorate the mechanical properties of the blend films and weaken the original properties of the superfine wool powder in the blend film.

Ideally, the blend film is bleached for 1 hour with 10% hydrogen peroxide. The bleached blend films can then be dyed with acid red dyes. The K/S values of the dyed films peak at around 510 nm which corresponds to the characteristics of red color. Lightness of color (L*) , redness-greenness value (a*), color differences ΔE*ab and saturation C*ab increase at the same time, which indicates that the dyed blend films show more obvious red color with the increase of superfine wool powder content.

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