

Full Length Research Paper

Preparation and characterization of keratin-K₂Ti₆O₁₃ whisker composite film

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Wool is the most popular natural material. In the textile industries, a lot of waste wool fibres and their products induce actions which lead to the regeneration of wool keratin materials. However, the most significant limitations may be the poor fracture resistance of neat keratin materials. Traditionally, biopolymer was used to enhance the mechanical property of wool keratin material, but it limits the application of the keratin material as a biomaterial. In this article, it was firstly proposed that potassium hexatitanate (K₂Ti₆O₁₃) whiskers be used to reinforce keratin film. The effects of coupling agent, whisker content, distribution and orientation on properties of composite were investigated by microscope and tensile testing. It was found that K₂Ti₆O₁₃ whiskers can effectively improve the mechanical properties of keratin films.

Key words: Biomaterials, mechanical properties, microstructure.

INTRODUCTION

Recently, there has been an increasing demand for novel biocompatible materials with various properties and much attention is focused on regenerated protein material (Kato et al., 2004; Pavlath et al., 1999; Tonin et al., 2006). One group of promising candidates are the wool keratin materials, which have the biodegradability and biocompatibility to support cell growth (Yamauchi et al., 1996). It is worth noting that tons of non-spin wool fibres are discarded during wool weaving every year and an abundance of waste wool fibres are thrown away in our daily lives. In wool, about 50 wt% of wool fibres is made of keratin, a usable protein (Fraser and MacRae, 1980). Therefore, from an economic and environmental point of view, it is worthwhile developing a simpler process to use and reuse these resources.

The desirable forms of regenerated wool keratin can be solutions, powders, films, gels and filaments, depending on the preparation conditions and the application field (Nam and Park, 2001). Researchers have found that it is difficult to obtain regenerated keratin materials with high

molecular weight even when using the best chemical or physical methods (Aluigi et al., 2007; Liu and Yu, 2005; Tang and Yu, 2005). Studies in Japan were at the forefront and a silk-like fibre based on a protein/PAN copolymer, called Chinon, was introduced in the 1960s (Morimoto et al., 1962). The keratin in the copolymer was in the range of 10-60 wt% and the rest was polyacrylonitrile (PAN) together with minor amounts of vinyl or vinylidene chloride (C₂H₂C₁₂) (Tachibana et al., 2002; Tanabe et al., 2002). Hence, without enhancement with PAN or polymerlike polyvinylalcohol (PVA), the regenerated keratin films would be too fragile to handle.

However, in the field of composite materials, nanofibres/whiskers, such as K₂Ti₆O₁₃ whiskers, are usually applied as reinforcements to increase the mechanical properties of composites (Bunsell, 1986; Tjong and Jiang, 1999). In this paper, it was interesting to find that the K₂Ti₆O₁₃ whiskers could be used to reinforce wool keratin films. It is well known that the mechanical properties of composites are strongly influenced by the microstructure, as it provides important information about the internal structure of materials (Chen and Chung, 1996; Paul and Bucknall, 2000; Sorensen et al., 1995; Yih and Chung, 1996). So the effects of whisker content, distribution, orientation and coupling agent were discussed. This way

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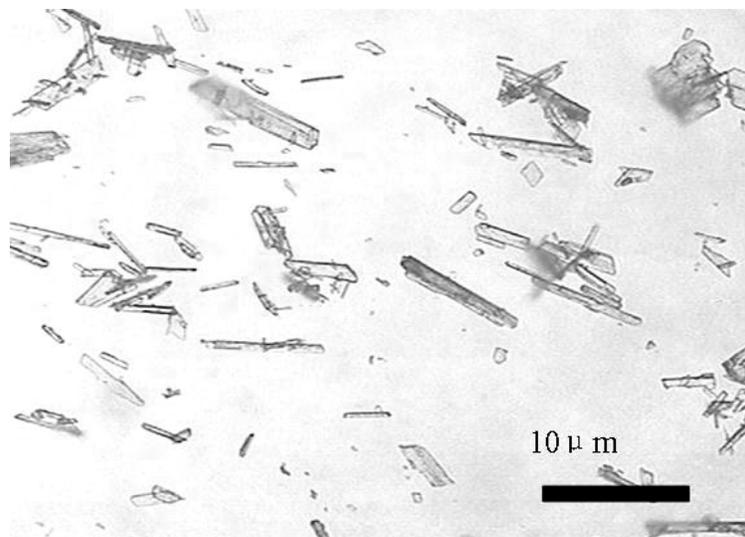


Figure 1. Optical micrograph of $K_2Ti_6O_{13}$ whiskers.

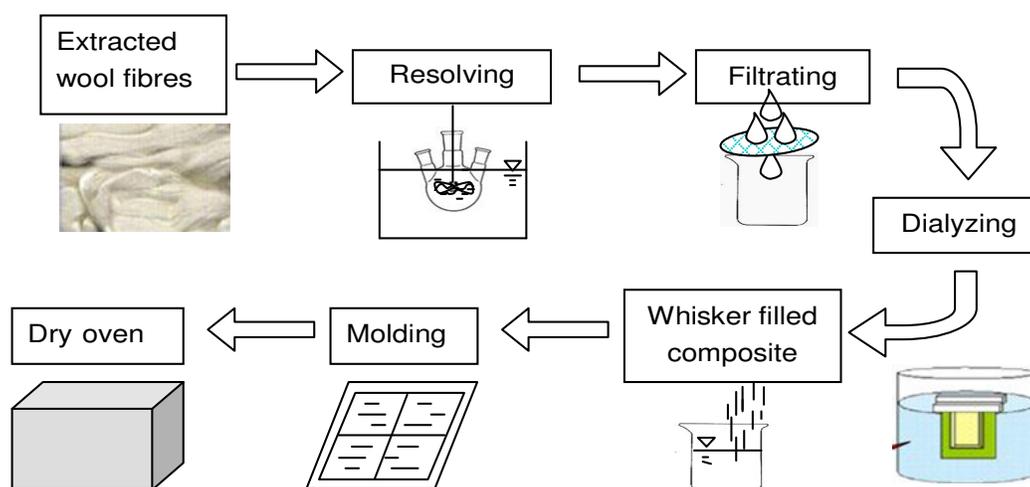


Figure 2. Schematic diagram of the whiskers reinforced membranes fabrication.

was regarded as a promising technique in improving mechanical properties of keratin materials.

MATERIALS AND METHODS

Urea, sodium disulfite ($Na_2S_2O_5$) and sodium dodecyl sulfate (SDS) (reagent grade, shanghai boer chemical reagent Co., Ltd), methyltrimethoxy silane ($C_4H_{12}O_3Si$) (reagent-grade, shanghai jjubang chemical Co., Ltd) were used without further purification. $K_2Ti_6O_{13}$ whiskers were purchased from Shanghai crystal whisker reinforced composite manufacturing Co., and the optical micrograph is shown in Figure 1. Tensile tests were carried out on an electrical single fibre strength tester (samples size $10 \times 4 \times 0.4$ mm, speed 20 mm/min) at RT ($20^\circ C$). The results were the averages of ten parallel measurements. Microstructural evaluations were conducted using the optical microscopy (OM) and scanning electronic microscopy (SEM).

Preparation of composites

Wool (5 g) was immersed in 500 ml of aqueous solution containing 8 M urea, 4 g of SDS and 10 wt% of $Na_2S_2O_5$. The mixture was heated to $80 - 90^\circ C$ for 5 h and cooled in a water bath at $30^\circ C$, and then the resulting mixture was filtered through a stainless steel mesh. The filtrate was dialyzed in distilled water using dialysis membranes for 72 h. The outer water was changed every day. The protein concentration of the dialysate measured on average was 300 mg/ml using a spectrophotometer. The protein concentration of the dispersion was standardized at 70 mg/ml and it was found that through this process, the molecular weight of keratin is around 30000 - 40000 daltons (Liu and Yu, 2008). The pretreated whiskers were dispersed in the keratin solution in a certain percentage. The resultant homogeneous keratin solution were cast onto a polyethylene mould and dried at $60^\circ C$ for 24 h. The microstructure of whisker reinforced composite was affected by the parameters in the ultrasonic and molding processing. The schematic diagram is shown in Figure 2.

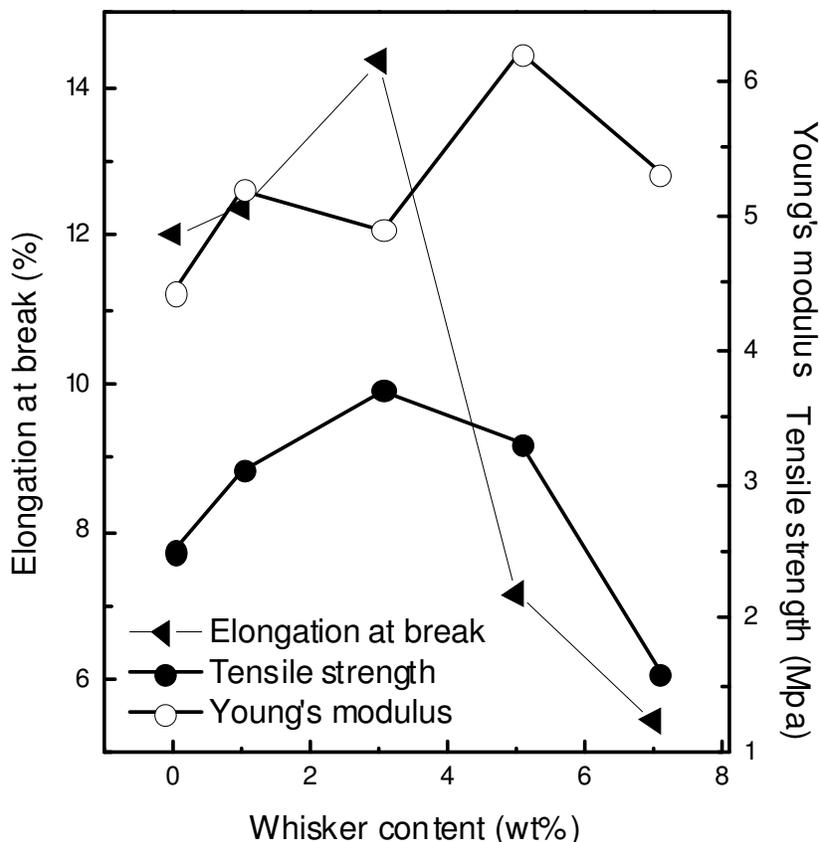


Figure 3. The elongation at break, tensile strength and Young's modulus of composites with various whisker contents.

RESULTS

Effect of whiskers content

The mechanical properties of keratin/whisker composites with various whisker contents are shown in Figure 3. When the whisker content increased from 0 to 3 wt%, the elongation at break and tensile strength of composites were increased from 12.0 to 14.4% and from 2.5 to 3.7 MPa, respectively. When the whisker content reached more than 3%, both elongation at break and tensile strength were decreased. On the contrary, Young's modulus was gradually increased. It was clear that composites of 3% whisker content displayed the best mechanical properties. So in the following researches, the whiskers content were all 3%.

Effect of whiskers distribution

The composites with different whisker distributions were prepared in ultrasonication step. In Figure 4a, condition at 59 kHz and 30 min ultrasonic offered the best distribution of whiskers in matrix; condition of 59 kHz and 15 min ultrasonic could gave partial clustering whiskers structure

(cluster 1, Figure 4b); no ultrasonic treatment led to the whiskers clustering severely (cluster 2, Figure 4c). Figure 5 showed the uniaxial stress-strain curves of keratin matrix (neat keratin film) and composites with random/cluster distributed whiskers. The mechanical property was much better in random microstructure than in whisker cluster microstructure.

Effect of whiskers orientation

Aiming at the study of whiskers orientation, it was found that the whiskers often exhibit anisotropy in composite due to the flow-induced alignment. Thus, the composites with different oriented whiskers were prepared, that is, random, normal and parallel whiskers orientation as seen in Figure 6. In Figure 7, the uniaxial stress-strain curves of composites presented the effects of whiskers orientation and coupling agent. Obviously, the composite with parallel whisker orientation provided the best mechanical properties.

Effect of coupling agent

Coupled whisker/keratin composites had stronger mechani-

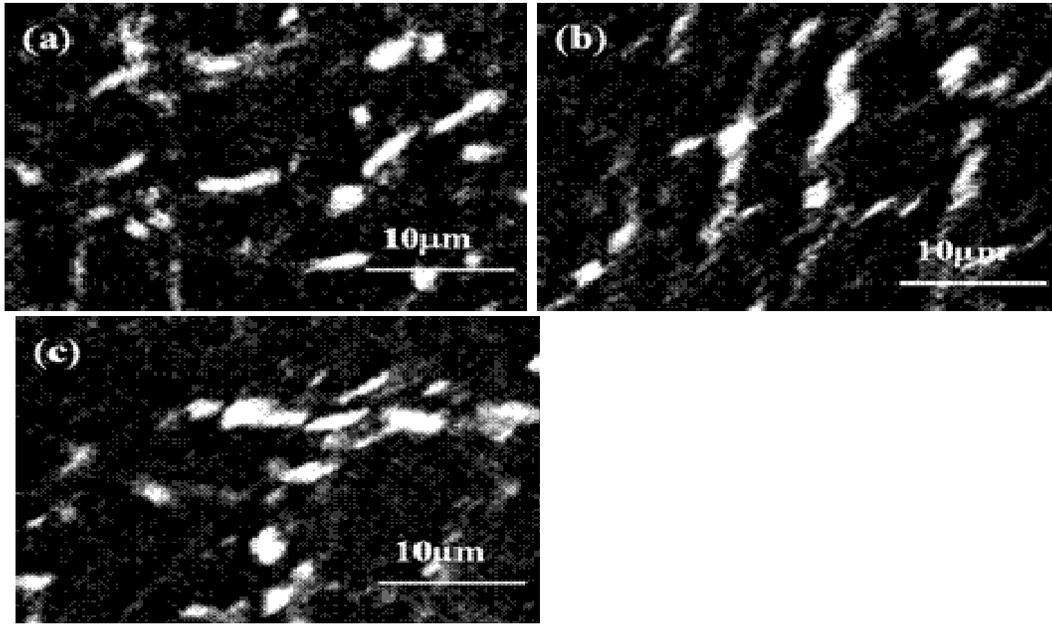


Figure 4. Micrographs of whiskers reinforced keratin films: (a) random whiskers distribution, (b) whiskers cluster microstructure (cluster 1) and (c) whiskers cluster microstructure (cluster 2).

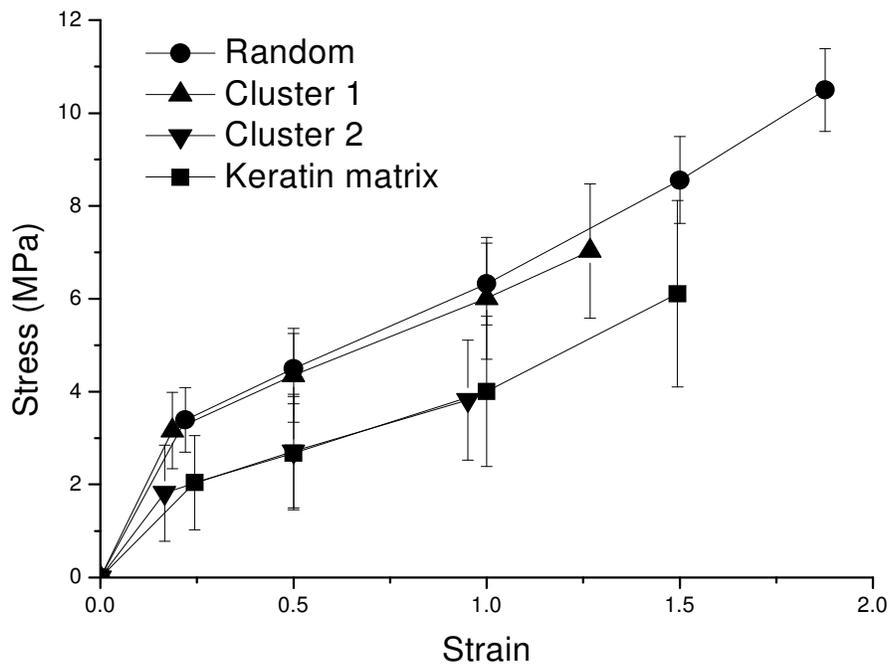


Figure 5. Tensile responses of neat keratin and composites.

cal properties than uncoupled ones (Figure 7) and it could be further explained by SEM images (Figure 8). Figure 8a showed that the neat keratin had ductile shear belt; in Figure 8b the unmodified whiskers were pull out from the matrix; in Figure 8c the coupling agent provided good interface bondages between whisker and matrix.

DISCUSSION

It has been found that the reinforcement content in composite plays an important role in molding processes (Bledzki and Gassan, 1999). From this investigation it was clear that the composition at 3% whisker was taken

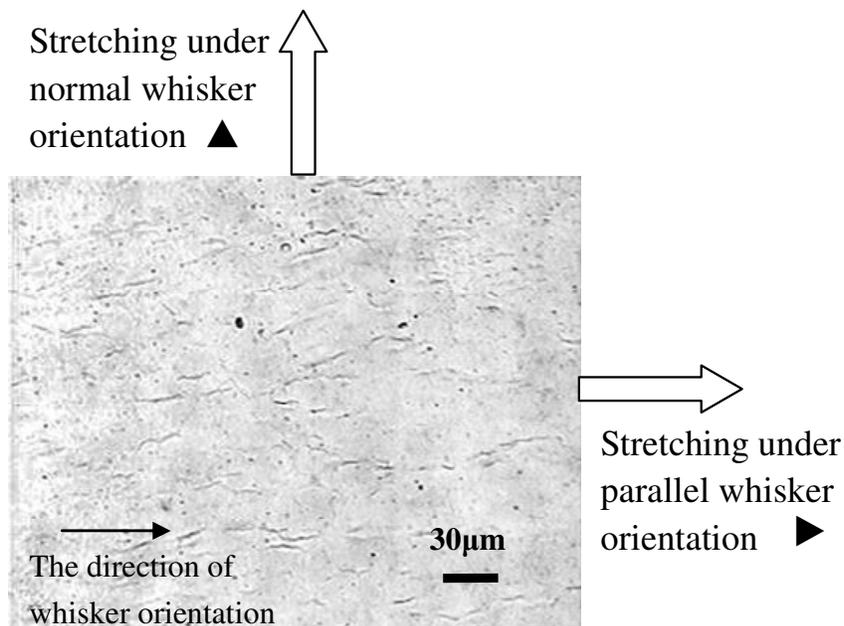


Figure 6. Sketch of whisker orientation in matrix.

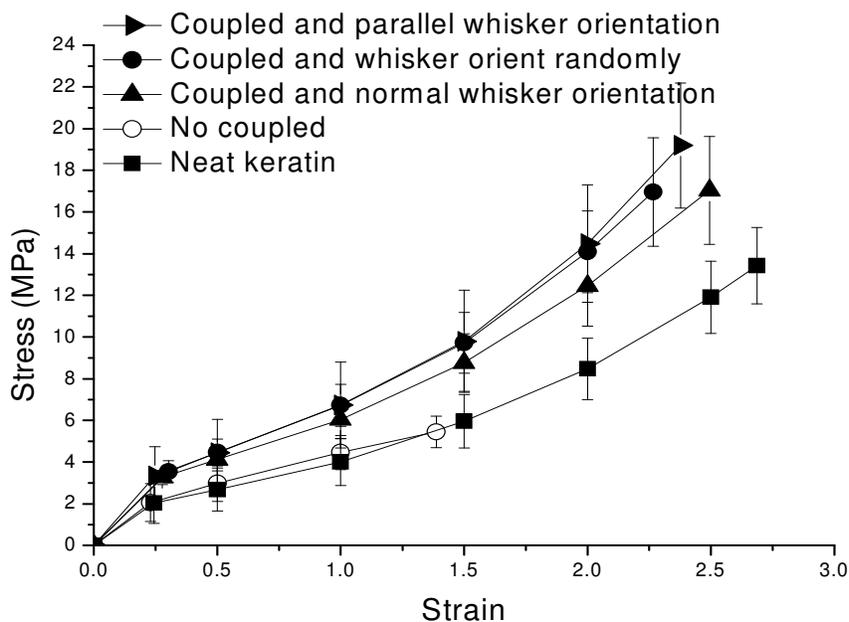


Figure 7. Tensile responses of neat keratin and composites.

to be the optimum composition. The optimized composition showed a 19.5% increase in elongation at break, 48% in tensile strength and 10.7% in Young's modulus compared to the matrix keratin. At a lower level of whisker content, the composite showed poor mechanical properties due to poor whisker population and low transfer capacity to one another (Haydaruzzaman et al., 2010). As a result, stress

got accumulated at certain points of the composites and highly localized strains occur in the matrix. At intermediate levels of whisker content (3%), the population of the whiskers actively participated in stress transfer. High levels of whisker content increased population of whiskers, which may lead to agglomeration and stress transfer, became blocked. As a result, composite property was again

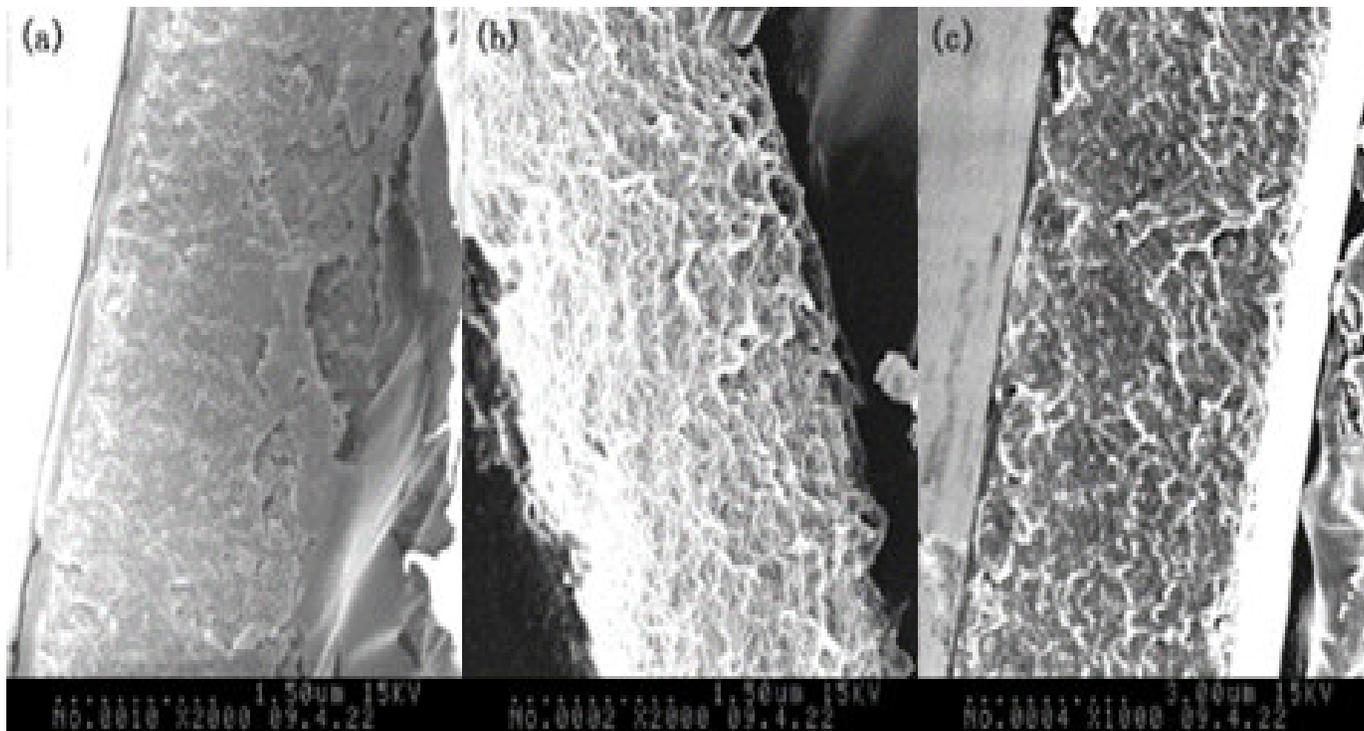


Figure 8. (a) SEM morphology of neat keratin, (b) no coupled composite reinforced by whiskers, and (c) coupled composite and whisker orient randomly.

decreased. The whiskers distribution in composite was detected by image analysis and then tensile responses were tested. It was found that the random microstructure whiskers showed a 72.1% increase in tensile strength, 25.3% in elongation at break and 84.3% in Young's modulus than the matrix keratin. However, the cluster microstructure weakens the performance of the composites. A possible cause for this might be that the clustering of whiskers had considerable effect on strength and plastic behaviour of composites (Prabu and Karunamoorthy, 2008). Clustering can initiate premature failure because of high plastic strain that occurred in the matrix material near the whisker cluster region. The parallel orientated whiskers could afford a large part of stress in matrix, so the composite showed good mechanical properties. The parallel orientated whiskers displayed a 42.9% increase in tensile strength, -11.5% in elongation at break and 61.6% in Young's modulus than the matrix keratin. The reason might be that the parallel oriented whiskers can increase the interaction region with each other and it was conducive for stress transfer in matrix (Cooper et al., 2002).

Coupling agent could help to improve tensile strength and Young's modulus of composite (Bledzki et al., 1996). Figure 8a showed that the neat keratin had ductile shear belt, which mean the keratin was tough fracture; in Figure 8b it was obvious that the unmodified whiskers were pulled out from the matrix without interfacial adhesion;

Figure 8c revealed that the coupling agent provided relatively good interface bondages between whisker and matrix. The improvement in the properties of composites might be ascribed to the stiffness of the whiskers and the strong interfacial bondage between the whisker and matrix. The coupling agent could effectively provided Van der Waals force, dipole-dipole interactions and hydrogen bonds, etc. to increase the interface bonding (Gassan and Bledzki, 1997). From the above analysis, it was concluded that $K_2Ti_6O_{13}$ whiskers can effectively improve the mechanical properties of keratin films.

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