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Fabrication and characterization of polycaprolactone/calcium sulfate whisker composites

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Abstract. Polycaprolactone (PCL)/calcium sulfate (CS) whisker composites have been fabricated by melt blending and coprecipitation methods respectively. Scanning electron microscope (SEM) was used to observe the microstructure of the composites. The crystallization and thermal properties were characterized by polarized optical microscope (POM), X-ray diffractometry (XRD), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). For composites prepared by melt blending method, experiment results show that average length of the whiskers is shortened. The crystallization perfection of PCL in composites is improved by adding whiskers. The flexural strength increases whereas the impact strength decreases. For composites prepared by coprecipitation method, whisker addition worsens the crystallization perfection of PCL. An improvement of 21% in flexural strength and 22% in impact strength has been achieved for the composite with 15 wt% of whiskers.

Keywords: *biopolymers, biocomposites, polycaprolactone, calcium sulfate whisker, mechanical propertie*

1. Introduction

Polycaprolactone (PCL) is a type of synthetic, biodegradable polymer, applying in food packaging, tissue engineering, dressing for wound, and drug delivery [1–3]. So it becomes one of the most promising biodegradable polymers currently available on the market. However, some shortcomings such as high costs, low melting temperature and low mechanical properties restrict widespread industrial use of PCL [4]. In order to improve the physical properties of polymer, inorganic particles were usually used to improve some properties of the polymer. For instance, Wang *et al.* [5] used titania to enhance the mechanical properties of poly (lactic-co-glycolic acid). Their investigation indicated that the composite microsphere-sintered scaffold is a promising scaffold for bone repair. It is reported that PCL mixed with other biodegradable inorganic materials such as hydroxyapatite (HA) [6–10] and tricalcium phosphate (TCP) [11–13] could improve some properties so that the composites may offer attractive potential for bone tissue replacement and tissue regeneration.

Besides HA and TCP, CS as a biodegradable inorganic material is widely used in bone surgery as well. It was reported that CS was used for treating bone defects as early as 1892. Compared with HA and TCP, CS has a reasonable degradation rate [14–16] and has been widely used in bone treatment. As reported, CS can form calcium phosphate deposits when it is in contact with body fluids, which are finally responsible for conducting and accelerating bone formation [17]. La Gatta *et al.* [18] reported an injectable PCL/CS system for bone regeneration. They mixed calcium sulfate hemi-hydrate (CHS) with a photo-crosslinkable derivative of PCL, and

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the composite is proposed to be utilized in hard tissue repair particularly in the dental and orthopaedic field. Gao *et al.* [19] reported a composite fabricated with PLLA and CS power for bone repair. However, the mechanical property of this material, one of basic and important property for materials, has not been reported. Like most other inorganic powders, CS is a kind of brittle filler. It can reinforce polymer but untreated CS powder may damage the toughness of materials.

Being different from inorganic powder, whisker is considered to be an attractive alternative to short glass or carbon fibers for reinforcing and toughening thermoplastics and has attracted considerable interests of scientists and engineers [20]. A lot of work has been focused on the preparation of various polymer/inorganic whiskers composites [14, 21, 22]. It was reported that CS whisker was investigated to reinforce polyurethane elastomer [21], polypropylene [22] and non-metallic friction material [23]. These hybrid composites were generally produced by melt or solution blending method. However, the difference between two blending methods for the same material has not been reported. In addition, whiskers are often used to reinforce polymer, but calcium sulfate whisker is rarely reported to reinforce biopolymer materials.

Since PCL and calcium sulfate are well-known biocompatible and bioactive materials used in bone tissue engineering, the relevant composites with high mechanical properties should be promising materials for application in bone repair. It is also worth to note that all materials used for repairing bone tissue or other application need to have excellent mechanical properties. However, based on the literature review, it can be found that most efforts concentrated on preparation, bioactivity, and biodegradation of the PCL materials, and only a few works focused on the effect of whisker composition and preparation method on the mechanical properties. To improve mechanical properties of PCL and study the influence of blending method and CS whiskers on the crystallization, thermal behavior, and mechanical properties of the composites, PCL/CS whisker composites containing different CS contents (0, 5, 10, 15, and 20 wt %) were prepared by melting and coprecipitation blending methods respectively. The effects of whisker addition and different fabrication processes on the microstructure and properties of the composites such as the morphology, crystallization, thermal behavior, and mechanical properties have been investigated.

2. Experimental details

2.1. Materials and fabrication

Polycaprolactone (PCL) (W_η = 50 000) used in this experiment was purchased from Dow Chemical Co., Ltd, China and calcium sulfate (CS) whisker (length/diameter ratio: 40:1, and diameter: 1~6 µm) was supplied by Jian-kun Chemical Co., Ltd, China. The SEM photographs of the whiskers is shown in Figure 1.

In this research, PCL/calcium sulfate whisker composites were prepared by both melt and coprecipitation blending methods. For melt blending method, the pre-dried CS whiskers were premixed with PCL on a laboratory size two-roll mixing mill (Scientific Laboratory Bench Top Two-Roll Mill, LRM-M-100, China Vision Group CO., Limited) at 58ºC. The premixed composite was extruded using a Haake twin-screw extruder (Mini-lab II, Thermo Electron Corp., Hamburg, Germany) with a speed of 60 rpm at 100ºC. The composite was then injected using a Haake mini injection machine (Mini jet II, Thermo Electron Corp., Hamburg, Germany) under a pressure of 35 MPa. Before injection, the injection cylinder and the mold were preheated to the temperatures of 100 and 40ºC, respectively. The shape of molded samples is in accordance with ASTM D790 and ASTM D256 standards.

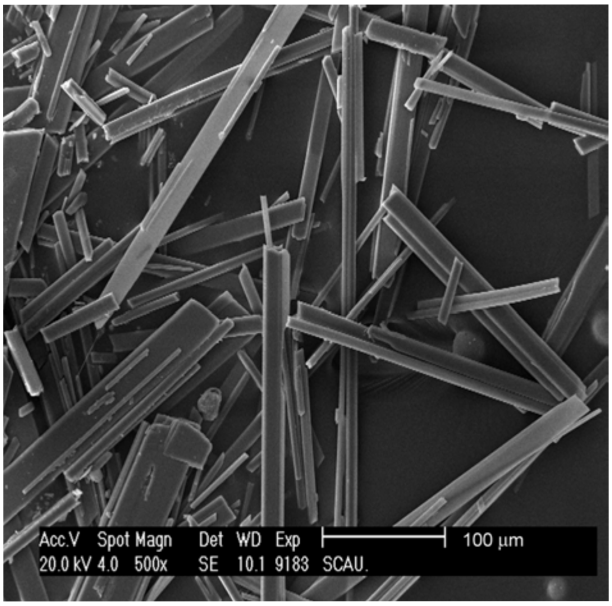

Figure 1. SEM micrograph of CS whiskers

For coprecipitation method, appropriate amount of PCL and CS whiskers were prepared to the desired weight fractions, and then separately, the PCL particles were dissolved in tetrahydrofuran (THF) (AR, Shengqiang Chemical Co., Ltd., Jiangsu, China) solvent and CS whiskers were dispersed in tetrahydrofuran (THF) solvent using a magnetic stirrer for about 120 min. Next, the PCL-THF solution and CS-THF dispersed liquid were mixed together and stirred for another 120 min. The mixture was then poured into ethanol (AR, Fuyu Chemical Co., Ltd., Tianjin, China) as nonsolvent to coprecipitate PCL/CS composite. After filtration, the recovered composite was washed using anhydrous ethanol to remove the residual THF. The flocculent composite was then vacuum-desiccated for about 12 hours at 45ºC, and finally the floc was hot-pressed for 5 min at 70ºC under a pressure of about 15 MPa to get samples.

2.2. Characterization

The flexural property was tested by an electronic universal testing machine (LR5K Plus, Lloyd instruments Ltd., England) according to the standard ASTM D790, and the rate of crosshead motion was set to be 2 mm/min. The notched impact test was performed by a pendulum-type impact test machine (Shenzhen Sans testing machine Co., Ltd., China) according to the standard ASTM D 256. Five samples were tested for each composition. The microstructure of the composites was observed by an environmental scanning electron microscopy (SEM, XL30, Phillips, Netherlands). Prior to the observation by SEM, the impact fractured cross-section of specimens was coated with Au by sputtering deposition. SEM micrographs were dealt with Image-Pro Plus software to measure the length of the whiskers in the composites. X-ray diffraction spectra were obtained by an X' Pert Pro diffractometer (PA Nalytical, Netherlands) with a Cu target and K_α radiation at a scanning rate of 2°C/min to study the changes of the crystal structure of PCL.

The thermal behavior and crystallization of the composites were examined by a differential scanning calorimeter (DSC, Netzsch 204, Germany) under N_2 flow (70 ml/min) and liquid nitrogen controlled cooling. In this study, the samples were firstly heated from room temperature to 100ºC, equilibrated for 2 min to eliminate thermal history, and then cooled at 10ºC/min to –120ºC, equilibrated at –120ºC for 2 min, and finally heated up again to 100ºC at 10ºC/min. Thermal decomposition studies were carried out using a thermogravimetric analysis (TGA, Netzsch TG 209, Germany) under inert flowing nitrogen (40 ml/min) from 50 to 700ºC at a heating rate of 10ºC/min.

The spherulite structure of PCL/CS whisker composites was studied by a polarized optical microscope (POM, BX51-P, Linkamthms600, Japan) equipped with a Linkam hot stage (THMS600/HFS91, Japan). In this experiment, the samples placed between two glass slides were heated up to 100°C, and then equilibrated at this temperature for 5 min to eliminate any residual PCL crystallization seeds, and finally crystallized for 30 min at room temperature. PCL spherulites were examined by POM and recorded by an attached digital camera.

3. Results and discussion

3.1. Morphology of fracture surfaces

To study the dispersion of fillers and fracture surface, the impact-fractured cross-section of specimen was observed by SEM and the micrographs of the fracture surface of PCL/CS whisker composites are shown in Figure 2. The length of the whiskers in composites calculated by Image-Pro Plus software is listed in Table 1. For composites prepared by melting method, no obvious agglomeration of CS whiskers was observed. However, some whiskers were broken down so that the average length of whiskers become shorter, which could make the mechanical properties deteriorate [24]. For composites prepared by coprecipitation method, it could also be found that no obvious agglomeration of CS whiskers was observed. Figure 2d reveals that some of the whiskers were pulled out and broken down during impact test (X point), and the surfaces of CS whiskers and matrix do not closely adhere together (Y point), which indicates that the interfacial debonding between whiskers and matrix took place during the test. Additionally, plastic deformation of PCL at interface is observed clearly, which indicates the processes of pull-out and debonding dissipate a part of impact energy. The data in Table 1 show that the average length of the whisker for the composites prepared by melting method is shorter than that prepared by coprecipitation method. The possible reason is that, compared to the magnetic stirrer, the

Table 1. Length of CS whiskers in composites prepared by melting and coprecipitation methods

Fabrication method	Content of CS whisker [%]	Length [µm]			Standard deviation
		Min	Max	Mean	
Melting method	5	2.00	30.83	7.79	6.30
	15	5.99	55.69	17.00	12.96
	20	1.00	17.14	6.55	3.30
Coprecipitation method	5	16.84	43.46	32.64	10.81
	15	10.33	87.13	36.66	21.82
	20	5.78	91.89	26.01	20.30

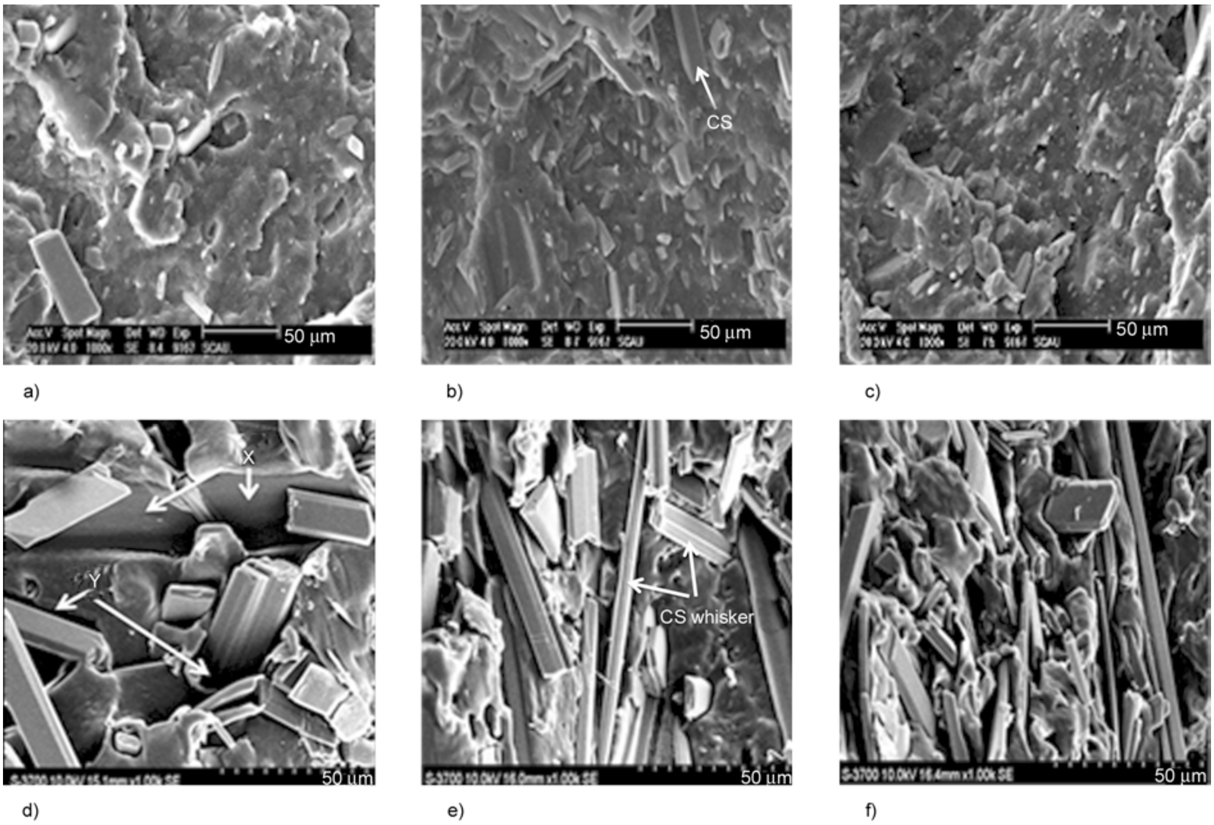

Figure 2. SEM micrographs of fracture surfaces for PCL/CS whisker composites prepared by melting method containing (a) 5 wt%, (b) 15 wt%, and (c) 20 wt% whisker, and prepared by coprecipitation method containing (d) 5 wt%, (e) 15 wt%, and (f) 20 wt% whisker.

shear stress of the screws in the extruder is so large for the CS whiskers that some of the whiskers are easily broken down during the process.

3.2. Crystallization

Figure 3 shows the XRD spectra of CS whisker, pure PCL and the composites prepared by two methods. Results show that PCL contains three strong reflections at the angles (2θ) of about 21.4, 22.0 and 23.7°, corresponding to the (110), (111) and (200) planes of the orthorhombic crystal structure respectively [25]. XRD pattern of pure CS whisker indicates that the CS whisker in this experiment is $CaSO_4{\cdot}2H_2O$ [26]. Comparing the XRD pattern of the pure PCL with composite, it can be found that the strong reflections observed from PCL are also present in PCL/CS whisker composites. This indicates that the basic crystal structure of the PCL matrix in composites is still orthorhombic. For the composites, the reflection peaks at the angle of 20.8 and 11.5° are the characteristic peaks of $CaSO_4{\cdot}2H_2O$ whiskers [26]. Results also show that the reflection peaks of the composites at the angle of 21.4° move slightly to the larger angles compared to the pure PCL. It demonstrates that the d spacing of PCL in the composites decreases. This phenomenon may be caused by the fact that the whisker hampers the growth of the crystal grain, which would compress the cell. However, for the composites with 5 wt% whiskers prepared by melting method, the number

Table 2. Thermal and crystallization properties of PCL/CS whisker composites prepared by melting and coprecipitation methods

Crystallization and thermal parameters	Fabrication method	Content of CS whisker [%]			
		0	5	15	20
Crystallizaion temperature (T_c [ºC])	Coprecipitation	27.6	31.5	30.7	30.5
	Melting		30.4	33.0	33.1
Melting temperature (T_m [ºC])	Coprecipitation	57.9	58.7	58.3	58.5
	Melting		58	59	58.4
Glass transition temperature (T_g [ºC])	Coprecipitation	–62.0	–62.4	–61.5	–61.1
	Melting		–62.5	–63.2	–62.8
Undercooling (ΔT [ºC])	Coprecipitation	30.3	27.2	27.6	27.0
	Melting		27.6	26.0	25.3
Half peak width {$(\Delta T)_p$ [ºC]}	Coprecipitation	12.0	8.0	7.0	7.0
	Melting		5.0	5.5	5.0
Crystallinity (*Cr* [%])	Coprecipitation	54.6	46.1	47.4	54.6
	Melting		52.7	54.4	54.9

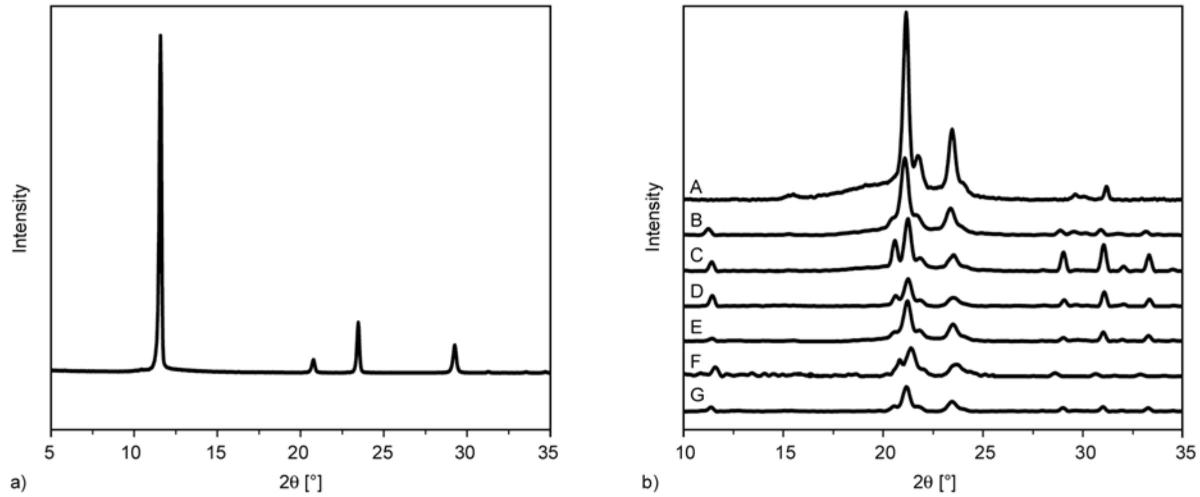

Figure 3. X-Ray spectra for (a) whiskers, (b) (A) pure PCL and composites prepared by melting method containing (B) 5 wt%, (C) 15 wt%, and (D) 20 wt% whisker, and prepared by coprecipitation method containing (E) 5% wt%, (F) 15 wt%, and (G) 20 wt% whisker

and scale of whiskers for the composites prepared by melt blending method are less than that of other composites, therefore the whiskers weakly hamper the growth of the grain and the d spacing and reflection peaks almost do not change.

Table 2 shows the thermal and crystallization properties parameters of pure PCL and PCL/CS whisker composites determined by DSC measurement. The undercooling ΔT in Table 2 is defined using Equation (1) [27]:

$$\Delta T = T_m - T_c \quad (1)$$

where T_m and T_c are the melting temperature and crystallization temperature determined by DSC respectively. It can be observed from Table 2 that the T_c of the PCL in composites gradually goes up with the increase in weight fraction of the CS whisker, which indicates that the whisker has an excellent nucleating effect on the crystallization of PCL [28]. Results also show that the crystallization temperature of the composites prepared by melt blending method is higher than that prepared by coprecipitation method. This phenomenon might be caused by the change in size and number of the whiskers. As discussed above, some of the whiskers were broken down by shear stress of the screw during processing for melt blending method and the number of the whisker increased. This change could lead to the increase in the nucleation rate and hence enhance the crystallization rate. Additionally, a part of the molecular chain of PCL could be also broken down and became shorter during processing. The short molecular chain also has a nucleation effect, resulting in the increase of the nucleation rate of composites.

Undercooling can be used to characterize the crystallization rate of the polymer in the non-isothermal process. Generally, it is inversely proportional to the crystallization rate [29]. Results in Table 2 show that the undercooling ΔT of the composites decreases from 30.3 to 25.3ºC with increase in whisker composition by 20 wt%, and the ΔT of the composites prepared by melt blending method is lower than that prepared by coprecipitation method. These results further illustrate that whiskers have nucleation effect to PCL and the effect is relevant to the size of the whiskers. Although the number of the whiskers for the composites with 5% CS whiskers is less, it is enough to influence the nucleation of PCL so that ΔT is also lower than that of the pure PCL.

Generally, the crystallization perfection can be characterized by half peak width $(\Delta T)_p$ of the crystallization curve [29]. It can be seen from Table 2 that the half peak width $(\Delta T)_p$ of composites prepared by melt blending method is narrower about 7ºC than that of the pure PCL, and narrower about 2ºC than the composites prepared by coprecipitation method, which demonstrates that the crystallization perfection of the composites prepared by melt blending method is superior to that of both the pure PCL and the composites prepared by coprecipitation method. This phenomenon is associated to the shape of fillers. The fillers restrain the mobility of grain boundaries and eventually inhibit gain growth. It can be inferred from this result that the fillers with higher aspect ratio have a stronger restraining effect. The similar phenomenon was also reported by Vanherpe *et al.* [30] but the fillers were fibers. In this experiment, the aspect ratio of whiskers in composites prepared by coprecipitation method is higher than melt blending method, which leads to the stronger inhibiting effect. Therefore, the crystallization perfection of the composites prepared by melt blending method is better than that prepared by coprecipitation method.

To further illuminate the changes of crystallization properties, the crystallinity is calculated by using Equation (2) [31] and also listed in Table 2:

$$C_r = \frac{\Delta H_m}{\Delta H_m^0 \cdot X_n} \cdot 100\% \qquad (2)$$

where ΔH_m is the melting enthalpy for composite samples, ΔH_m^0 is the melting enthalpy of the matrix when it infinitely crystallizes and it is 136.08 J/g for PCL [32], and X_n is the weight percentage of PCL in composites. Results show that the crystallinity of composites almost remains constant compared to pure PCL. However, the crystallinity of composites prepared by melting method is slightly higher than that prepared by coprecipitation method. This is accordance with the conclusion that the nucleation effect of the whisker for the composites prepared by melting method is stronger than that prepared by coprecipitation method.

3.3. Thermal behavior

The test data listed in Table 2 show that the melting temperature (T_m) and the glass transition temperature (T_g) of the samples exhibit a small change by adding CS whisker. To find the relationship among the thermal degradation property, composition of the CS whisker and preparing method, thermogravimetric analysis was conducted. Figure 4 illustrates TGA curves for pure PCL and its composites prepared by both methods with different compositions of CS whiskers. Thermal degradation parameters obtained from TGA curves are listed in Table 3. When 50% weight loss is selected as the point of comparison, the thermal decomposition temperature ($T_{0.5}$) for the pure PCL is 423ºC, and the $T_{0.5}$ for composites prepared by both methods changes slightly compared to the pure PCL. The mass loss at 150–200ºC for the composites is due to the loss of the crystal water in $CaSO_4 \cdot 2H_2O$ whiskers at low temperature. Previous studies found that there are different changes of the thermal decomposition for PCL/inorganic filler composites [33, 34]. For this experiment, the $T_{0.5}$ of composites is slightly lower

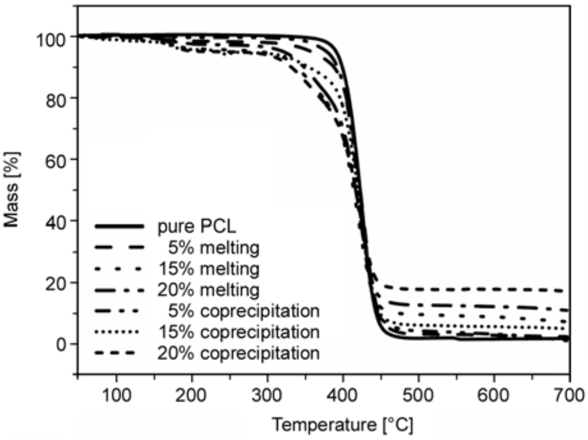

Figure 4. Thermogravimetric cureves for the pure PCL and composites prepared by both of melting and coprecipitation methods

Table 3. Thermal degradation properties of PCL/CS whisker composites prepared by melting and coprecipitation methods

Fabrication method		**Melting**				**Coprecipitation**		
Content of CS whisker [%]		0	5	15	20	5	15	20
Thermal degradation parameters	$T_{0.5}$ [ºC]	423	421	415	413	419	417	417
	Loss at 150–200ºC [%]	–	1.2	3.1	4.2	0.7	3.0	5.5

about 2–6ºC than that of the pure PCL. This may be due to the loss of the crystal water as well. The loss of the crystal water at low temperature may induce the decomposition of the PCL for the composites easily. As the PCL is decomposed, the residue should be the CS and a little chars of PCL, and the mass of residue is approximately equal to the mass of CS.

3.4. Spherulite morphology

The spherulite morphology of the pure PCL and the composites prepared by both methods is shown in Figure 5. It can be seen that the spherulite structure of pure PCL is imperfect, and there are some clear grain boundaries among the spherulites. Compared with the pure PCL, the spherulite size of all com-

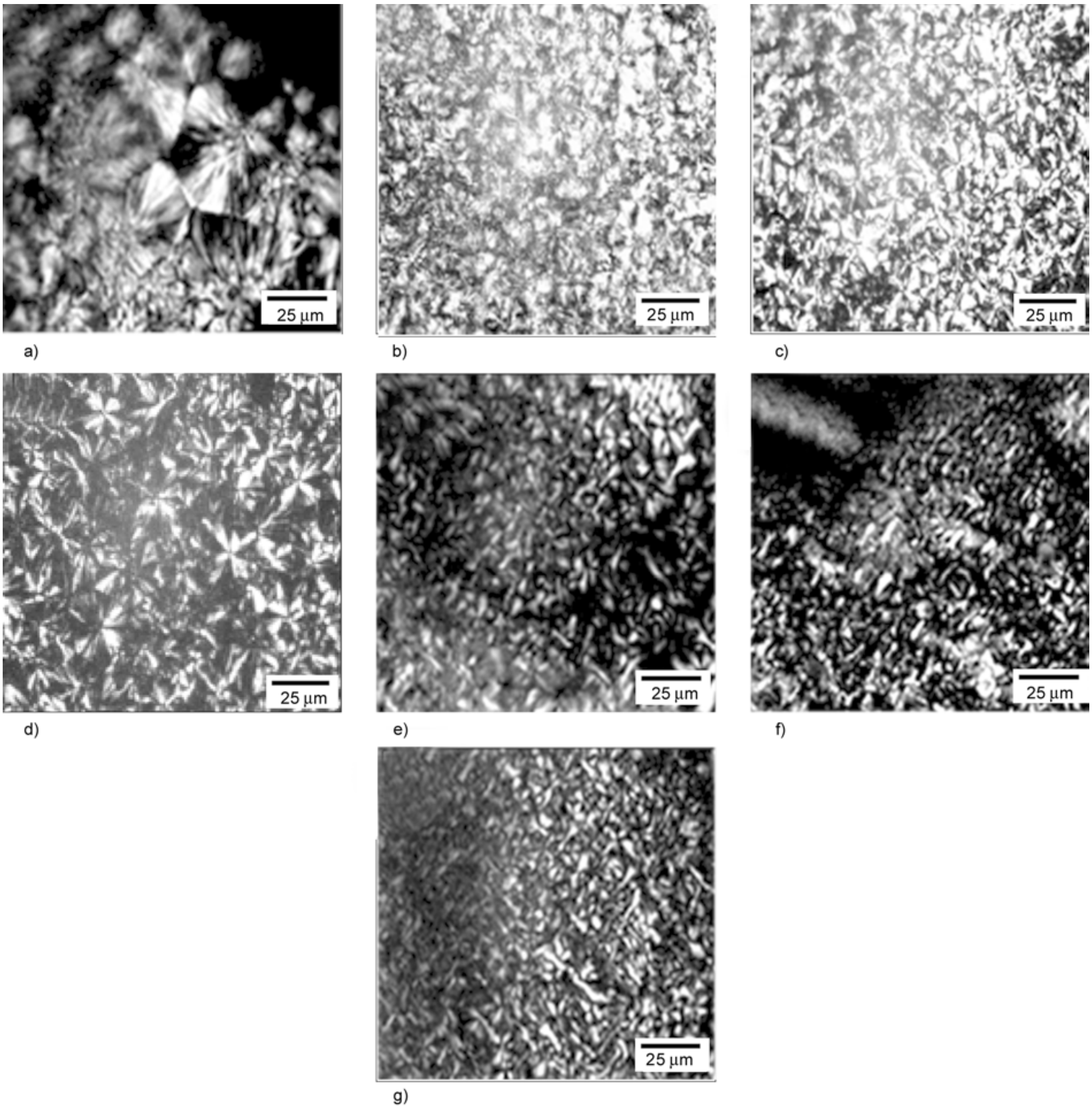

Figure 5. Spherulitic morphology (400×): (a) the pure PCL and composites prepared by melting method containing (b) 5 wt%, (c) 15 wt%, and (d) 20 wt% whisker, and by coprecipitation method containing (e) 5 wt%, (f) 15 wt%, and (g) 20 wt% whisker

posites significantly reduces, which illustrates that CS whiskers have grain refining effect to PCL. POM pictures in Figure 5 also reveal that the crystallization perfection of the composites prepared by melt blending method is better than that of the composites prepared by coprecipitation method, which is consistent with the result of DSC. However, it can be seen from Figure 5b–g that the spherulite size of the composites prepared by coprecipitation method is smaller than that of the composites prepared by melting method. It indicates that the grain refining effect of the long whiskers is stronger than that of the short whiskers.

3.5. Mechanical properties

Figure 6 and Figure 7 show the relationship between the composition of CS whisker and the flexural strength and modulus of composites. Results show that for the pure PCL sample prepared by melting method, the flexural strength and modulus are 22 and 30% higher than that prepared by coprecipitation method. A lot of researchers reported that for pure polymer, mechanical properties were improved by different fabrication method, such as solid extrusion, hydrostatic extrusion, and hot tension-drawing, which aimed at the orientation of the molecular chain or structure of polymer to reinforce the polymer [35]. In this experiment, the orientation of molecular chain for PCL may occur in the mold during injection process and not happen during the coprecipitation mold-pressure process. Consequently, the flexural strength and modulus of pure PCL sample prepared by melting injection are higher than those prepared by coprecipitation method.

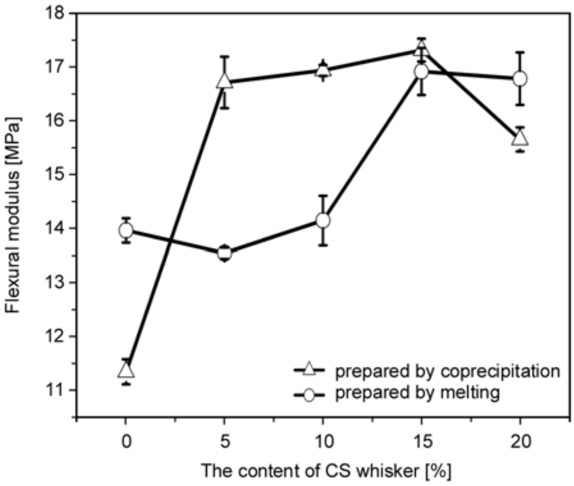

Figure 6. Relationship between the composition of CS whisker and the flexural strength of the composites

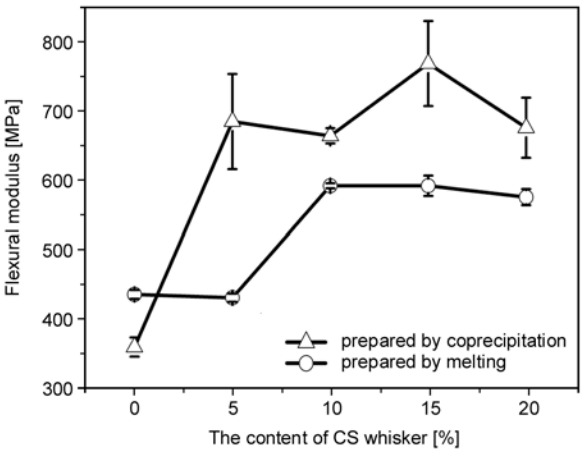

Figure 7. Relationship between the composition of CS whisker and flexural modulus of the composites

For composites prepared by coprecipitation method, the flexural strength and modulus of the samples containing 15 wt% CS whiskers are higher about 21% and 75% respectively than that of the pure PCL samples prepared by melting method. However, further increase in the composition of CS to 20 wt% leads to decrease of the flexural strength and modulus of the composites. Results also show that for the CS whiskers less than 20 wt%, the flexural strength and modulus of the composites prepared by melting method are lower than that of the composites prepared by coprecipitation method. This result can be explained by load-transfer theory [24]. Classical load-transfer theory suggests that the stress can transfer from polymer matrix to whiskers through the interfacial layer. Whiskers have higher modulus than the polymer matrix so that they can afford parts of stress to disperse the load in the matrix. Therefore, the strength of the whisker composites is improved by whisker addition. The load-transfer theory also suggests that the strength of the composites filled with long whisker should be higher than short whisker, which can explain why the flexural strength of CS whisker composites prepared by melt blending method is lower than that prepared by coprecipitation method.

Besides the length of whiskers, the dispersion of the whiskers in the matrix is also one of the important factors affecting the strength of the composites. It is well known that the agglomeration of the fillers can deteriorate the mechanical properties of the composites [22]. In this experiment, the decrease of the strength for the composite with higher CS whisker composition of 20 wt% prepared by coprecipitation method may be mainly influenced by the agglomeration of the whiskers. For composites with 20 wt% CS whiskers prepared by melting method, the strength increases continually because of the better dispersion of CS whiskers. It reveals that, for composites with less than 15 wt% CS whisker, the length of the whiskers is the main factor to affect the flexural strength. For composites with 20 wt% CS whiskers, the dispersion of the whiskers becomes a main factor to affect the flexural strength.

Our results also show that the change trend of flexural modulus for composites is similar to the change of flexural strength. It indicates that although CS whisker belongs to the rigid filler which can improve the rigidity of materials [19], but the rigidity will not be improved infinitely with the addition of whiskers. The effect of the whiskers on the flexural modulus is similar to the flexural strength.

Figure 8 shows the relationship between the composition of CS whisker and notched impact strength of the composites. It can be seen that for the pure PCL, the impact strength of the sample prepared by melt blending method is about 3 times higher than that prepared by coprecipitation method. For composites prepared by melt blending method, the impact strength decreases gradually with the increase in CS whiskers. For composites prepared by coprecipitation method, the impact strength increases when the composition of CS whisker is less than 15 wt%, and then decreases when more than 15 wt%. However, it is still higher than that prepared by melt blending method.

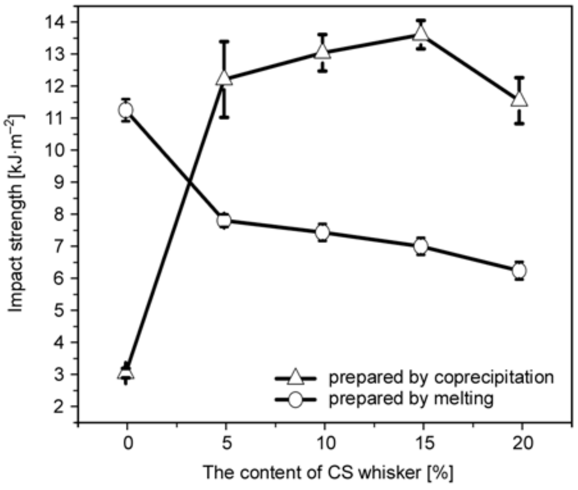

Figure 8. Relationship between the composition of CS whisker and notched impact strength of the composites

Generally, impact strength is sensitive to the defects of materials. In this study, defects such as small cavities could take place in the pure PCL samples prepared by coprecipitation method during the molding, whereas the small cavities rarely occur in pure PCL samples prepared by melt blending method. Therefore, the impact strength of the PCL samples prepared by melt blending method is higher than that prepared by coprecipitation method. The difference in impact strength between the composites prepared by two methods should be ascribed to several factors such as spherulite size, whisker debonding during impact test and whisker length. It is reported that the decrease of spherulite size will benefit the improvement of impact strength [27]. POM observation shows that the composites prepared by coprecipitation have smaller spherulite size. SEM pictures show that some CS whiskers debonded with PCL and were pulled out for the samples prepared by coprecipitation method, which could absorb a part of impact energy. Composites prepared by coprecipitation blend method have longer CS whiskers in average, which could absorb more impact energy and improve toughness of composites [24]. Therefore, the impact strength of whisker composites prepared by coprecipitation method is higher than that of both the pure PCL and the composites produced by melting method.

4. Conclusions

PCL/CS whisker composites have been prepared by both the melt blending and coprecipitation methods. Our experiment results have justified that the melting method benefits the crystallization of PCL and the flexural properties, but deteriorates the toughness of the PCL/CS whisker composites. Coprecipitation method harms the crystallization of the composites, but can improve mechanical properties. The thermal properties of PCL for composites are nearly unaffected by the presence of whiskers for two methods. For composites prepared by coprecipitation method, the spherulite size of the PCL is reduced by CS whisker addition, and the flexural and impact strength of composites with 15 wt% CS whisker are highest. Investigation shows that longer whiskers benefit the mechanical property of the composites. It is worth to mention that the biocompatibility of composites is important for the bone repair, and the biocompatibility for the composite system is under our investigation.

Acknowledgements

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