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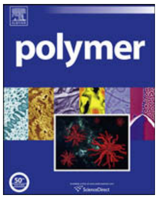

Interfacial enhancement by shish–calabash crystal structure in polypropylene/inorganic whisker composites

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ABSTRACT

The polymer matrix structure and the interface are strongly influenced by filler in semi-crystalline polymer composites because the fillers have the potential to nucleate the polymer crystallization. The structure of the nucleated crystalline polymer on filler is of particular interest and is a key to the interfacial enhancement. In this work, whiskers, with a large length/diameter ratio and with a diameter (0.2–2 μm) much larger than that of carbon nanotubes but much smaller than that of common fibers, were used to nucleate crystal morphology in polypropylene (PP)/whisker composites. The crystal morphology, interfacial adhesion and tensile properties of the composites were carefully investigated. A kind of peculiar shish–calabash crystallization morphology, with whisker serves as shish and PP spherulites serves as calabash, was observed for the first time in the thin film via PLM and in the injection molded bars by SEM. The formation mechanism of this shish–calabash structure was attributed to be that only a few nuclei could be induced on the whisker surface, which develop into large PP spherulites without hindrance, and finally stringed by the whisker, forming the shish–calabash structure. As a result, a significant improvement of interfacial interaction and tensile properties has been achieved.

1. Introduction

In recent years, polymer/filler composites have been intensively investigated in both industrial and academic fields, because they exhibit valuable mechanical and thermal properties when compared with pure polymers [1–3]. Good adhesion results in efficient stress transfers from the continuous polymer matrix to the dispersed filler and can increase the ability of the material to absorb energy, thus improving the mechanical properties of composites [4–7]. The polymer matrix structure and the interface are strongly influenced by filler in semi-crystalline polymer composites because the fillers have the potential to nucleate the polymer crystallization. The structure of the nucleated crystalline polymer layer on filler is of particular interest. Transcrystallization at interfaces, as a surface-induced crystallization, is an effective and economical method to improve the interfacial adhesion, and thus is attractive for many researchers in the past [8–13]. The prerequisite for transcrystallization is the presence of a high density of active nuclei on the substrate/fiber surface. The closely packed nuclei hinder the full extension of spherulites, which are then forced to grow in one direction, namely perpendicular to the substrate/fiber [9]. On the other hand, hybrid shish–kebab (HSK) structure, in which filler (carbon nanotubes or whisker) acts as shish and induces polymer (PE or nylon 6) crystal lamellae (kebab) periodically decorating on its surface and aligning approximately perpendicular to its long axis, has been recently reported, and shows great potential to enhance the interfacial interaction for polymer composites [14–22]. Between transcrystallization and HSK, if a fibrous-shaped filler can only initiate a few nuclei, one expects a formation of separated spherulites on the surface of filler, instead of transcrystal morphology. And if the diameter of the fiber is much smaller than that of formed spherulites, one expects a formation of peculiar shish–calabash structure, with fibrous filler serves as shish and polymer spherulites serves as calabash. This shish–calabash structure is different from the shish–kebab structure, for the polymer crystals in shish–kebab are lamellae, while they are spherulites in shish–calabash. Furthermore, the package density of crystal is much larger in shish–kebab structure than in shish–calabash structure. The schematic representation of the formation process of this shish–calabash crystallization morphology is represented in Fig. 1. Thus depending on the package density of crystallization on fibrous filler, there may be four types of crystal morphology, namely, randomly separated crystals, shish–calabash, shish–kebab, transcrystalline.

Whiskers, with large length/diameter ratio, are fiber-shaped single crystals. Its diameter (0.2–2 μm) is much larger than carbon nanotubes (CNTs) but much smaller than common fibers. Because

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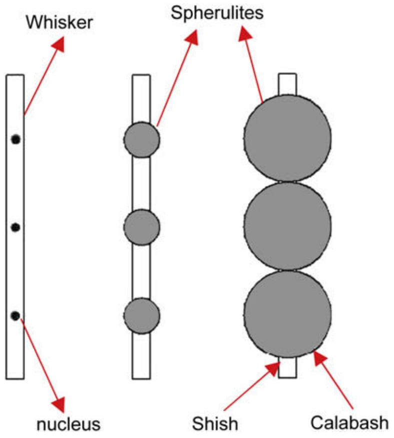

Fig. 1. The schematic representation of formation process of shish–calabash crystallization morphology.

whiskers could have much higher specific strength than short glass or carbon fibers, a lot of works have been focused on the preparation of various polymer/inorganic whiskers (such as aluminium borate whisker and potassium titanate whisker) composites and it was found that whiskers could reinforce thermoplastics more effectively. Therefore, whiskers are considered to be an attractive alternative to short glass or carbon fibers for reinforcing thermoplastics and have attracted considerable interests of scientists and engineers [23–30]. In our previous work, a new type of SiO_2–MgO–CaO whisker (SMCW) and HDPE composites were prepared and the crystal morphology was investigated. A hybrid shish–kebab (HSK) structure has been observed in the injection molded bar of PE/SMCW composites. In this HSK structure, SMCW acted as shish and induced PE crystal lamellae (kebab) periodically decorating on its surface and aligning approximately perpendicular to its long axis under the function of shear [21,22].

Due to the scientific importance and technical significance, in this paper, we will explore the possibility of formation of shish–calabash structure using whisker as the fibrous filler. To do this, whisker was first melt blended with polypropylene (PP) with various compositions. Then the isothermal crystallization of PP at the presence of whisker was carried out via Polarized light microscope (PLM). It was shown that only a few nuclei could be induced on the whisker surface, which develop into large PP spherulites without hindrance, and finally stringed by the whisker, forming the shish–calabash structure. More importantly, the shish–calabash structure was also observed in the injection molded bar of PP/whisker composites. As a result of interfacial enhancement via formation of shish–calabash structure, the prepared composites showed a significantly improved tensile property compared with pure PP.

2. Experimental section

2.1. Materials

A commercially available isotactic PP was manufactured by Dushanzi Petroleum Chemical Incorporation (Xinjiang, China), with a melt flow index of 0.96 g/10 min (190 °C, 2.16 kg). The whisker (SMCW) with a density of 3.0 g/cm^3 was produced in Mianyang Guangda Company (Sichuan, China). Its diameter ranges from 0.2 to 2 μm (mainly from 0.2 to 0.5 μm), and its length is in the range of 5–50 μm. Silicohydride (KH-550), supplied by Chenguang Research Institute of Chemical Industry (Chengdu, China), was used as the coupling agent for SMCW treatment. Its density is 0.945 g/cm^3 and its molecular structure is shown as follow:

$$H_2N{-}CH_2{-}CH_2{-}CH_2{-}Si{-}(OC_2H_5)_3$$

2.2. Modification of SMCW and preparation of the sample

SMCW was first treated with 10 wt% KH-550 solution for 8 min in a high-speed mixer (the rotation speed was 800–1000 rpm). After that the mixture was exposed in air for 4 h and then was dried at 90 °C for 4 h. The ultimate powder was used as inorganic filler for PP.

Melt blending of PP and SMCW was conducted using a TSSJ-25 co-rotating twin-screw extruder. The temperature of the extruder was maintained at 150 °C, 190 °C, 190 °C, 200 °C, 200 °C and 190 °C from hopper to die, and the screw speed was 110 rpm. Pure PP was also passed through extruder under the same conditions to serve as a reference. The palletized granules were dried for 20 h under 80 °C and then injection molded under the temperature of 200 °C. The ultimate PP/SMCW (with different modified SMCW content of 5–30 wt%) samples were termed as 5WPP, 10WPP, 20WPP, 30WPP respectively.

2.3. Scanning electron microscope

The specimens were mainly characterized via SEM. They first cryogenically fractured in liquid nitrogen (−170 °C). After the surface was coated with a thin layer of gold, the dispersion of SMCW in PP matrix was examined by an X-650 Hitachi scanning electron microscope at 20 kV. For the observation of crystal morphology, the specimens were also etched by 1% solution of potassium permanganate in a 10:4:1 (by volume) mixture, of concentrated sulphuric acid, 85% orthophosphoric acid and water, to remove the amorphous part of PP [31].

2.4. Polarized light microscope (PLM)

A polarized light optical microscope equipped with a hot stage was used to study the crystallization morphology of neat PP and composites. The samples sandwiched between two microscope cover slips were first heated to 200 °C, pressed into thin film samples, and then maintained at 200 °C for 5 min. The temperature of the hot stage was then reduced to 130 °C at a rate of 100 °C/min. The crystallization process was observed and the morphologies were recorded by taking photographs at constant time intervals.

2.5. Tensile properties

Standard tensile tests were performed using an Instron universal tensile testing machine with a cross-head speed of 50 mm/min at room temperature (23 °C). The width and thickness of the dumbbell shaped specimens were about 10.20 mm and 4.24 mm. The tensile strength at yield was determined according to GB/T 1040-92 standard. The values of the tensile strength were calculated as averages over 5 specimens for each composition.

3. Results and discussion

3.1. Dispersion and orientation of whiskers in PP/SMCW composites

In this work, SEM was employed to assess the whisker orientation and dispersion because the dispersion and orientation of fibrous filler in polymer matrix are very important for the enhancement of mechanical properties of polymer composites. Fig. 2 represents the SEM fractured surface of injection molded bar of PP/SMCW composites viewed parallel to the flow direction. It can be observed that most of the whiskers are aligned parallel to the flow direction for all the composites with different SMCW content. One can also see a uniform dispersion of SMCW in PP matrix for all these samples, even at a high filler content of 30 wt%. This may be due to a good interfacial interaction between the modified SMCW and PP matrix. To see clearly the interfacial adhesion, SEM fractured surface of 20WPP and 30WPP with high magnification are also shown in Fig. 2. It can be clearly seen that almost all the whiskers are embedded in the matrix and the exposed part of the whisker is attached with a layer of PP matrix, suggesting a really good interfacial interaction between the modified whiskers and PP matrix. In a word, the modified SMCW can be well dispersed in PP matrix, most of the whiskers are aligned parallel to the flow direction and the interfacial adhesion in between is very strong.

3.2. Shish–calabash crystallization morphology by PLM observation

To see clearly the detailed nucleation mode of SMCW and the corresponding crystallization process of PP, the morphologies of 5WPP crystallized at 130 °C were recorded by taking photographs at constant time intervals (from 80 s to 160 s), as shown in Fig. 3. It can be found that some of the whiskers can preferentially induce the growth of PP spherulite as heterogeneous nucleating agent and a single whisker can only induce a limited crystal nucleation density on their surface, as can be seen in Fig. 3(a). It should be noted that due to the magnification of PLM experiment, only SMCW with larger diameter could be observed and investigated, though most of them are less than 1 μm in diameter, as indicated by Fig. 1. It is very

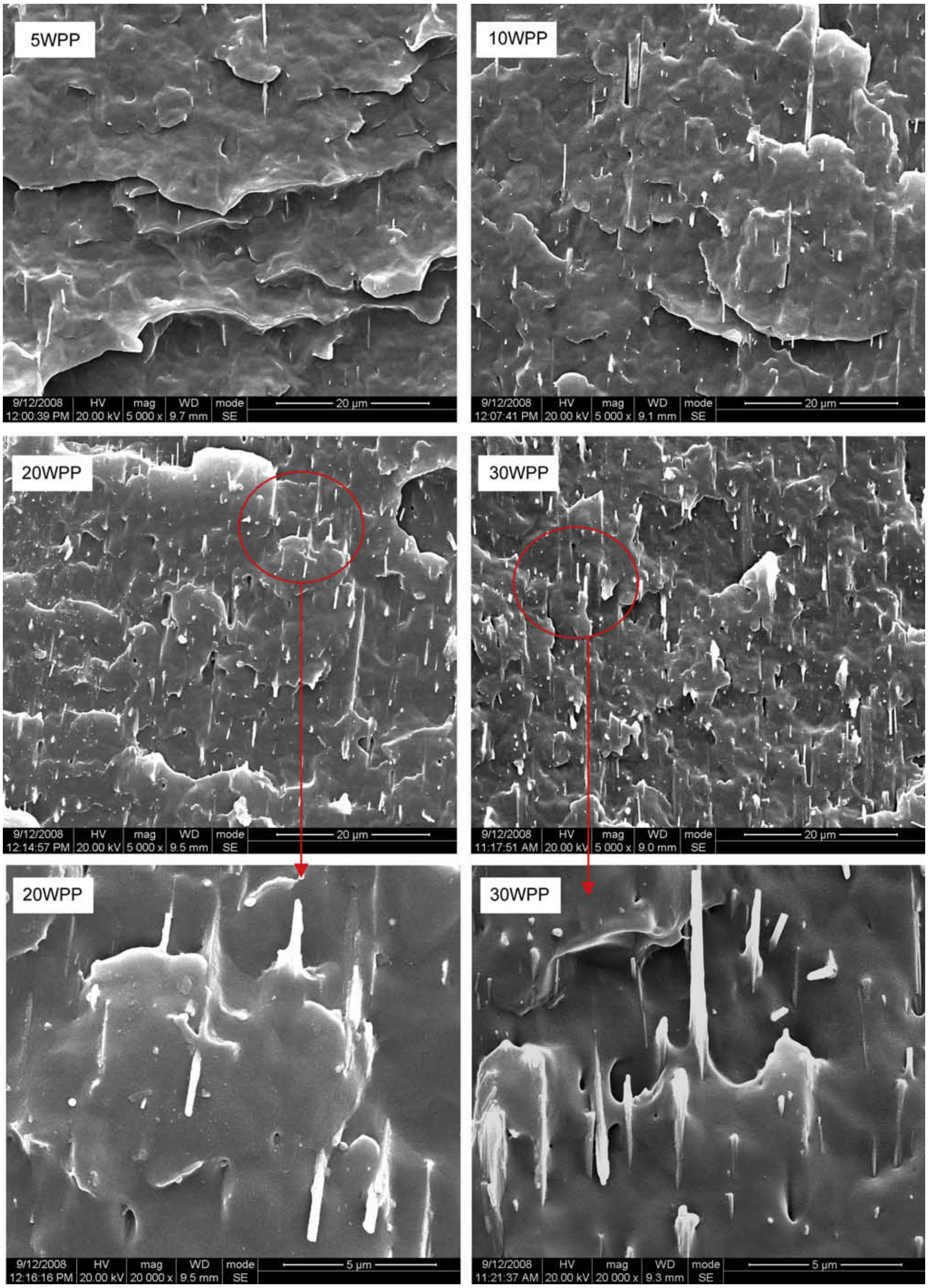

Fig. 2. SEM images to represent the dispersion and orientation of whiskers in PP/SMCW composites viewed parallel to the flow direction.

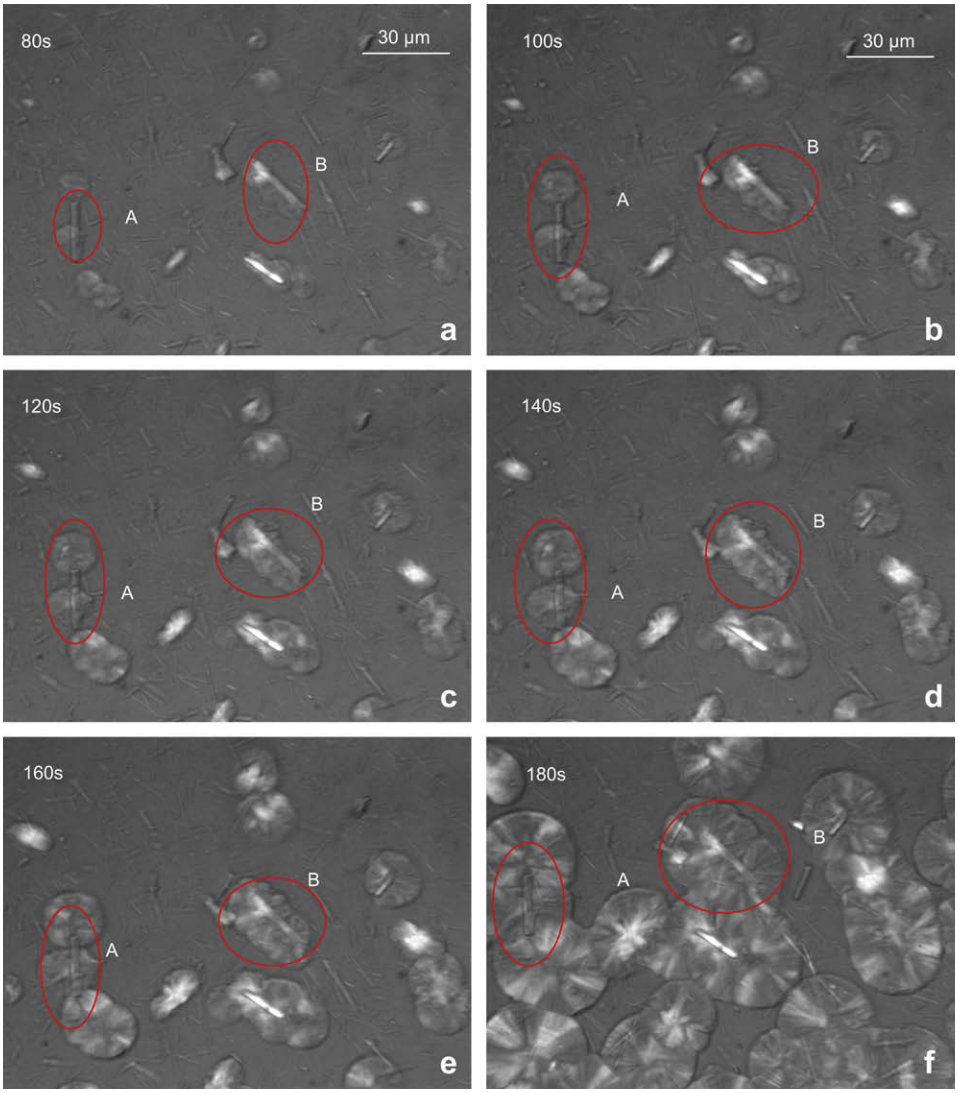

Fig. 3. PLM micrographs to represent the morphologies of 5WPP at different crystallization time crystallized at 130 °. (a): 80 s; (b):100 s; (c):120 s; (d):140 s; (e):160 s; (f):180 s.

interesting to see that the PP spherulite can grow through the whisker and the shish–calabash crystallization morphology (with PP spherulite as calabash and SMCW as shish) develops with the increase of crystallization time. For example, one can see that there is only one nucleus induced by the whisker *A* (with a diameter of about 2 μm) and the spherulite can grow through the whisker and fully develop into large spherulite. At the same time, the spherulites (induced by other whiskers) at both ends of the whisker *A* gradually grow and finally the both ends of the whiker A are embedded into the spherulites, thus forming the shish–calabash crystallization morphology, as can be clearly seen in Fig. 3(f). Furthermore, from Fig. 3(b), one also observes three spherulites induced by the whisker *B*. They are stringed by the whisker *B* and gradually develop into large spherulites, as can be seen in Fig. 3(c)–(f). Again, the shish–calabash crystallization morphology (with PP spherulite as calabash and SMCW as shish) are formed. It should be noted that this is different from the PP/glass fiber system in which the transcrystal structure is often formed because the relatively larger diameter of fibers (usually with a diameter of 10–30 μm) can induce a relatively high crystal nucleation density on their surface and the closely packed nuclei hinder the full extension of PP spherulites, which are then forced to grow in one direction and form transcrystallization morphology. In this case, whisker with a much smaller diameter can only initiate a few nuclei. Instead of forming transcrystal morphology, some separated spherulites are formed on the surface of the filler. They are finally stringed by the whisker, resulting in the formation of peculiar shish–calabash structure. However, except diameter and L/D of the filler, other factors, such as whisker content, surface properties (including shape, roughness, chemical properties, etc.), and crystallization conditions, may also influence the formation of shish–calabash structure, and this is under investigation in our group. Furthermore, to better understand the crystallization process of shish–calabash, AFM is also considered to characterize the details of crystal structure and interface.

3.3. Shish–calabash crystallization morphology in injection molded bar of PP/SMCW composites

It is particular important to observe the shish–calabash structure in the injection molded bar of PP/SMCW composites. For this reason, the detailed crystalline morphology of injection molded bar (10WPP) was investigated via etching out the amorphous part of PP, and the result is shown in Fig. 4. It should be noted that the specimen is viewed in the direction parallel to flow direction. A kind of peculiar shish–calabash crystallization morphology is indeed observed which is similar to the above isothermal crystallization morphology observed by PLM, as shown in Fig. 3. One observes that one or two or several PP spherulites are stringed by the whisker with a relative small diameter, forming the shish–calabash crystallization morphology. To see clearly the novel shish–calabash morphology, the SEM photographs with high magnification are shown in Fig. 4b and c. It can be found that the spherulites are indeed stringed by the whisker like a string of calabash, the whisker indeed drill through the spherulites serving as shish, thus forming the shish–calabash morphology.

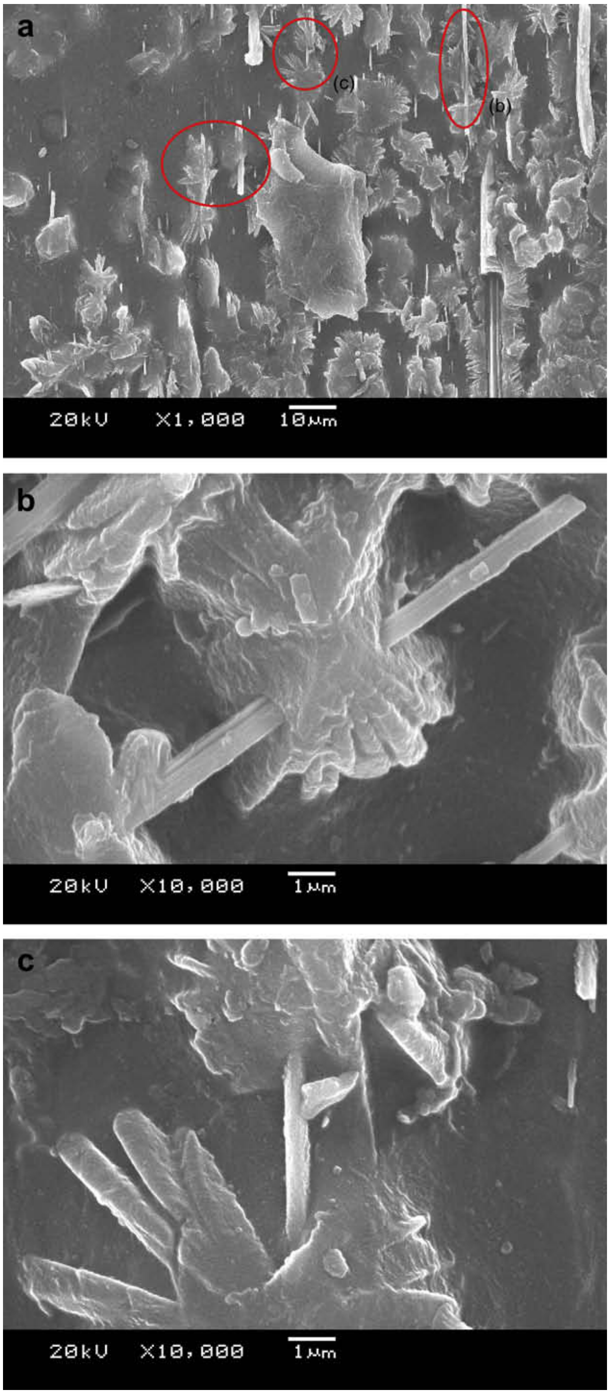

Fig. 4. SEM images to represent the crystallization morphology in injection molded bar of PP/SMCW composites (a): overview of the crystallization morphology; (b) and (c): Shish–calabash crystallization morphology observed in the composites.

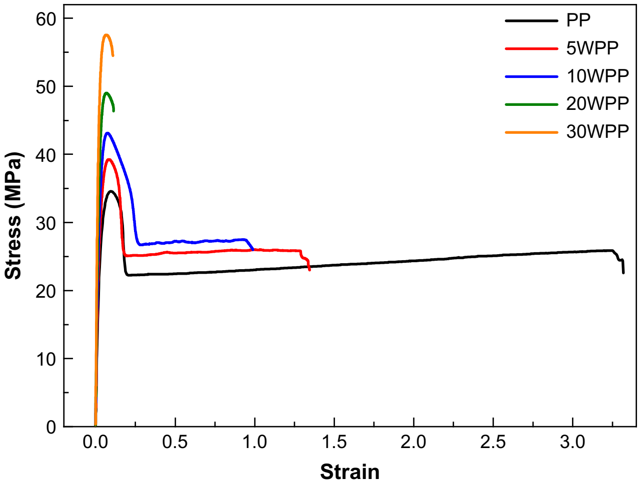

Fig. 5. The typical stress-strain curves of pure PP and PP/SMCW composites.

3.4. Tensile properties and interfacial interaction

The typical stress-strain curves of pure PP and PP/SMCW composites are shown in Fig. 5. And the detailed average values of tensile strength, tensile modulus and elongation at break of various composites are show in Table 1. It can be observed that the elongation at break decrease by the incorporation of SMCW. However, both the tensile strength and tensile modulus are obviously improved with the presence of 5 wt% SMCW and they further increase with the content of SMCW increasing. The tensile modulus of pure PP is 1.2 GPa and increased to 1.9 GPa and 3.4 GPa by adding 10 wt% and 30 wt% SMCW, respectively; correspondingly the tensile strength is enhanced from 34.8 MPa to 43.0 MPa and 57.6 MPa. It is well known that good adhesion can result in efficient stress transfers from the continuous polymer to the dispersed filler and can increase the ability of the material to absorb energy, thus improving the mechanical properties of composites. Therefore, most work has been focused on modifying the surface of filler and controlling the interfacial adhesion between the filler and the matrix. The interfacial control can be achieved with a silane coupling agent, such as an organofunctional silane compound, or with the addition of a binding agent or an additive agent, such as maleicanhydride, into the polymer matrix [32–35]. In recent years, it has been found that transcrystallization structure at interfaces can also effectively improve the interfacial adhesion and physical properties of composites. In this work, we show a good example that the interfacial adhesion can be also very much improved by the formation of shish–calabash morphology. To further confirm the interfacial interaction of the composites, the morphology of fractured surface of the samples (10WPP) along and perpendicular to the tensile direction is carefully examined, as shown in Fig. 6. Fig. 6a represents the fractured surface of the samples along the tensile direction. One can find that the whiskers firmly adhere to the PP matrix even after subjected to the tensile function. The fractured surface of the samples perpendicular to the tensile direction is presented in Fig. 6b. Again, it can be seen

Table 1
Mechanical properties of the prepared samples.

	PP	5WPP	10WPP	20WPP	30WPP
Tensile strength (Mpa)	34.8 ± 0.3	39.3 ± 0.5	43.0 ± 0.6	49.1 ± 0.5	57.6 ± 0.5
Tensile modulus (Gpa)	1.2 ± 0.05	1.5 ± 0.10	1.9 ± 0.05	2.5 ± 0.05	3.4 ± 0.10
Elongation at break (%)	3.32 ± 0.10	1.35 ± 0.10	0.99 ± 0.02	0.11 ± 0.01	0.10 ± 0.01

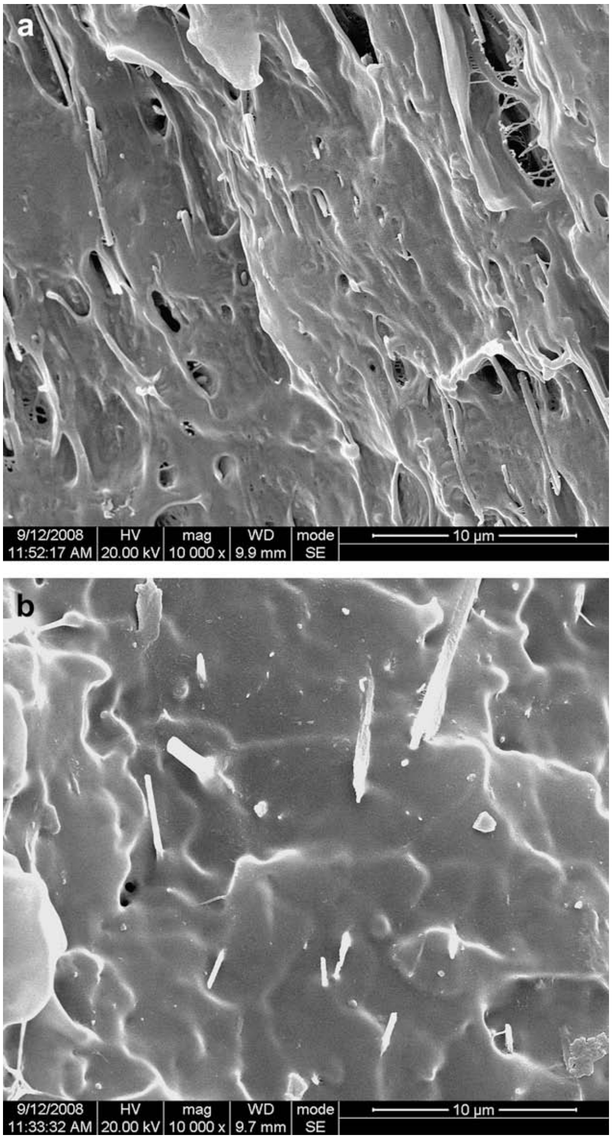

Fig. 6. The morphology of fractured surface of the as-prepared samples (a): along and (b): perpendicular to the tensile direction.

that almost all the whiskers are embedded in the matrix and even the exposed part of the whisker is attached with a layer of PP matrix, suggesting a really good interfacial interaction between the modified whiskers and PP matrix. This strong interfacial adhesion between the modified whiskers and the polymer matrix, which causes the successful stress transfer from PP matrix to whiskers, may be the main cause of the enhancement of the tensile properties. Concerning the cause of this strong interfacial interaction, the surface modification effect of SMCW with Silicohydride (KH-550) may be an important reason. However, the peculiar shish–calabash crystal morphology may be another key factor which contributes to the good interfacial adhesion between the whisker and the matrix. At this moment it is difficult to separate the contribution of the shish–calabash from the coupling agent, to the enhancement of tensile properties, since without coupling agent, it is difficult to disperse the whisker and cannot to obtain the shish–calabash structure.

4. Conclusion

In this work, whiskers, with a large length/diameter ratio and with a diameter (0.2–2 µm) much larger than that of carbon nanotubes but much smaller than that of common fibers, were used to nucleate crystal morphology in polypropylene (PP)/whisker composites. A kind of peculiar shish–calabash crystallization morphology, with whisker serves as shish and PP spherulites serves as calabash, was observed for the first time in the thin film via PLM and in the injection molded bars by SEM. The formation mechanism of this shish–calabash structure was attributed to be that only a few nuclei could be induced on the whisker surface, which develop into large PP spherulites without hindrance, and finally stringed by the whisker, forming the shish–calabash structure. As a result, a significant improvement of interfacial interaction and tensile properties has been achieved.

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