Preparation of SiC Whisker and Application in Reinforce of Polystyrene Resin Composite Materials

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ABSTRACT: A simple approach to fabricate silicon carbide (SiC) whisker is reported via using cellulose nanocrystal (CNC) as templates. The CNC with a length between 2 and 4 μm and a width about 40 nm is prepared by hydrolysis of microcrystalline cellulose (MCC) in strong sulfuric acid condition. The sol–gel reaction of tetraethyl orthosilicate (TEOS) is employed to coat the CNC in the presence of acetic acid as acid catalyst. The SiC whisker is obtained by calcination of CNC/SiO$_2$ hybrid at 1200°C. The obtained SiC whisker is found to have uniform size and shape with a length of ca. 2–4 μm and a width of 40 $\pm$ 5 nm. XRD, SEM, TEM (HRTEM), SAED, EDX and FTIR are used to characterize the samples. The obtained SiC whisker is used in polystyrene (PS) resin toughened. And mechanical properties of SiC/PS composites are tested by tensile impact experiments. The test results show that the 5 wt. % SiC whisker particles can disperse homogeneously in the PS resins which use a silane coupling agent (KF9701) as compatibilizer. Our results also show that the SiC whisker is excellent reinforcing material, which the tensile strength of SiC/PS composites attains 110 MPa and the Izod notched impact strength attains 5.00 KJ/m^2. Comparing the pure PS resin, the tensile impact of SiC(5)/PS(94.5)/KF9701(0.5) composites can be increased by about 3 times and the Izod notched impact strength can be increased about 8 times. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 579–586, 2013

INTRODUCTION

Silicon carbide (SiC) whisker is excellent in characteristics such as specific strength, specific modulus, heat resistance, chemical stability, and so on.[1] The SiC whisker is useful and promising materials for the reinforcement of various composite materials due to its outstanding mechanical and chemical properties.[2] Many methods, including carbothermal reduction,[3] chemical vapor deposition (CVD),[4] laser ablation,[5] pyrolyzing,[6] and hydrothermal methods[7] have been developed to fabricate the SiC materials. Unfortunately, the common precursor gases (SiCl$_4$, CH$_3$SiCl$_3$) are toxic, corrosive, flammable, and explosive.[8] At present, composite materials are fabricated by combining more than two materials. For example, polymer/polymer, polymer/fiber, and polymer/mineral filler have excellent mechanical, thermal, and chemical properties. These composite materials have been successfully used as structural or packaging materials. However, the recent interest in nanotechnology has stimulated many researches and various efforts have been made to prepare functional materials. Using reactions on a solution of a soluble iron compound trapped within a polymer film, Sobon

et al.[9] produced polymethylmethacrylate (PMMA)/ferric oxide and PMMA/magnetite composites. Bianconi et al.[10] obtained poly (ethylene oxide) (PEO)/CdS and the crystal size, morphology and orientation of CdS were controlled by a polymer matrix. Pracella et al. synthesized glycidyl methacrylate-modified SEBS through using styrene-b-(ethylene-copropylene) (SEP) as a compatibilizer. It showed a remarkable effect on the reduction of phase domain and about two times enhancement in impact toughness.[11]

PS resin is one of the examples of polymer materials that have limited impact resistance. To improve the mechanical and transport properties of PS resins, attention was paid on the inclusion of doped manganite particles of general chemical formula A$_{1-x}$A$'_x$MnO$_3$, where A and A$'$ was a rare-earth metal and an alkali-earth metal, respectively.[12,13] El-Safty et al. prepared dental PS resin-composites through nano-mechanical method, which the mean values of the PS resin-composites ranged from 0.73 GPa to 1.60 GPa for nanohardness and from 14.44 GPa to 24.07 GPa for elastic modulus.[14] Polystyrene/styrene-ethylene-propylene-styrene/vinyl ester resin (PS/SEPS/VER) blends used

the ultra high molecular weight polyethylene (UHMWPE) fiber as reinforced composites.[15] In plastic engineering design application, the impact strength is one of the most critical properties to be studied. The ability of a material to withstand repeated impact and robustness of the design is essential. However, SiC whisker is attractive candidates for reinforced ceramic or polymer matrix composite this role, because of its high strength, high elastic modulus, and good thermal stability. The investigations of tensile impact of the SiC/PS composites have been little reported, which the composites are fabricated by using the SiC whisker as a reinforcing material.

In this article, we present a novel, easy prepared and cost-effective method to prepare the SiC whisker. This method is based on the use of CNC as templates, the TEOS as SiO_2 precursor and acetic acid as a catalyst. The SiC whisker is obtained through a high temperature calcination approach. And the preparation SiC whisker is used to polystyrene (PS) resin reinforcing. Comparing pure PS resin, the tensile impact of SiC(5)/PS(94.5)/KF9701(0.5) composites can be increased by about three times and the Izod notched impact strength can be increased about eight times.

MATERIALS AND METHODS

Materials

Tetracethyl orthosilicate (TEOS, 98%) was purchased from Sigma-Aldrich. Silane coupling agent KF9701 was produced by Japan Shin-Etsu Company. Polystyrene (PS, GPPS-123) was purchased from Shanghai Saike. Others solvents and reagents were purchased from Guangzhou Chemical Reagents Company. All chemicals were used as received without further purification. Double deionized water in this work was purified by using the PINE-TREE system (electric resistivity 18.2 MΩ cm^{-1}). All reactions involving air-and moisture-sensitive compounds were carried out under a dry argon atmosphere using standard Schlenk techniques and a glove box.

Preparation of Silicon Carbide Whisker

Cellulose nanocrystal (CNC) was prepared from degrading natural cellulose or microcrystalline cellulose (MCC) by using the method of acid hydrolysis.[16] In a typical experiment, 7 g of 4 wt % CNC were mixed with 300 g of distilled water and the mixture was stirred at 40°C for 30 min. Then, 3.0 mL acetic acid as acid catalyst was added to the above mixture, and stirring continued for 10 min. Totally, 6.5 mL of TEOS dissolved in 60 mL absolute ethanol and was added to the CNC mixture at a rate of 10 mL per hour under stirring. The products were filtrated and washed with absolute ethanol and distilled water in sequence. The as-prepared precursor of the CNC/SiO_2 hybrid were placed in a graphite crucible and calcinated at 1200°C for 12 h with a heating rate of 10°C min^{-1} under an argon atmosphere.[17,18]

Preparation of SiC/PS Composite Sheet

The preparation of SiC/PS composites sheet involved the following steps: First, surface treatment for the SiC whisker particles with the silane coupling agent, the KF9701 was dissolved in absolute ethanol. Second, the SiC whisker was added to the above solution then the mixture was stirred for 15 min. After that, the mixture was heated to 80°C for 20 min, then cooled it to room temperature and setting for 5 h. Thirdly, the mixture was rinsed with absolute ethanol and distilled water by filtration at least

Table I. Materials Composition of SiC/PS Composites

Sample	Material compositions wt. %		
	SiC	PS	KF970
PS	0	100	0
SiC/PS	2	98	0
SiC/PS/KF9701	2	97.5	0.5
SiC/PS/KF9701	5	94.5	0.5
SiC/PS/KF9701	10	89.5	0.5
SiC/PS/KF9701	10	89	1.0
SiC/PS/KF9701	14.8	83.7	1.5
SiC/PS/KF9701	15	84.5	0.5

three times and dried at 100°C for 8 h. Finally, the SiC/PS composites sheets were prepared by using mechano-chemical processes in an open mill machine at 160°C (type: 160 × 320 mm^2, Shanghai Rubber Machinery Factory, China). After that, the mixture was vulcanized (without any vulcanization additive) between two metallic sheets and pressed in a hot press machine (type: XL-D400×400×2, Changzhou Wujin Rubber Machinery Factory, China) annealing at 180°C under pressure 15 MPa for 8 min, and then cooled to room temperature. The compositions of the blends were listed in Table I.

Characterization

The crystalline structure of the SiC whisker was characterized by the X-ray diffraction (XRD) performed on a MSAL-XD2 with Cu Kα radiation (40 KV, 20 mA, $\lambda = 1.54051$ Å) at a scanning rate of 5°/min for 2θ ranging from 10 to 80°. For transmission electron microscopy (TEM) observation, the SiC/PS composites samples were ultramicrotomed with a diamond knife at -100°C with a Leica ultra cut. Then the ultrathin sections were stained by OsO_4 vapor for 1 h. And low-resolution TEM images were obtained using a Phillips Tecnai 12 microscope operated at 100 kV. The selected area electron diffraction (SAED) and high-solution transmission electron microscopy (HRTEM) pattern images were collected using a JEOL-2100F electron microscope with an accelerating voltage of 200 KV. Surface element analyses for the SiC whisker carried out with energy-dispersive X-ray spectrometry (EDX, JEOL-2010F). The morphologies of the SiC/PS sheets was performed on a scanning electron microscopy (SEM, LEO 1530 VP) at an accelerating voltage of 20 kV. The sheets were prepared by immersing the films in liquid nitrogen for 10 min before fracture. The fracture surfaces were coated with gold before analysis. The Fourier transform infra-red spectroscopy (FTIR) spectra were obtained with a spectrophotometer (EQUI-NOX-55, Thermo Electron Corporation) and the samples were prepared as KBr pellets. Thermogravimetry analysis was characterized by a Netzsch TG 209 F1 Iris®apparatus under a nitrogen environment (50 mL/min) at a heating rate 10°C/min from 60°C to 640°C.

A tensile test was conducted according to GB=T1040-2006 standards on a hydraulic universal testing machine (EMT, 2503, Shenzhen SANS Instruments). Notched Izod impact test was done at room temperature according to the GB 1943-2007 method with Zwick B5113 impact test device (Zwick GmbH & Co. KG Ulm, Germany).

RESULTS AND DISCUSSION

Morphology and Structure of CNC, SiC, and SiC/PS Composites

The obtained CNC crystal structure is supported by XRD result in Figure 1(a), where three strong peaks can be observed. There are three peaks at 12°, 20°, and 22°, respectively, of which 20° is a maximum value, in agreement with the typical XRD pattern of cellulose II. The XRD of CNC/silica hybrid is shown in Figure 1(b) and broad XRD reflection peak at 22° could be assigned to diffraction of the amorphous structures of the SiO_2. The SiC crystal structure is also supported by the XRD. As shown in Figure 1(c), the main peaks in the XRD pattern are assigned to the (111), (200), (220), (311), and (222) reflections of cubic β-SiC, in agreement with the standard JCPDS card (No. 65-0360). An additional diffraction peak at $2\theta = 35.654°$ is characteristic of stacking faults on the (111) plane in the SiC, which has also been observed in the literature.[19] The SiC whisker is successfully synthesized by using cellulose nanocrystal (CNC) as templates under calcination at high temperature.

The TEM image of obtaining the CNC is shown in Figure 2(a). The image shows that cellulose nanocrystals have a length between 2 and 4 μm and a width about 40 nm. The TEM image of SiC whisker is presented in Figure 2(b). It shows that SiC particles are rod-like nanoscaled whisker, with the length of around 2–4 μm and the surface of SiC becomes rougher. But it also shows that these particles are agglomerated to some extent, similar to the CNC. From the high magnification TEM images [Figure 2(c)], it could be clearly seen that the particles have an apparent rod-like structure.

The morphologies and microstructures of the SiC whisker are further characterized by the HRTEM and SAED (Figure 3). Figure 3(a) shows the HRTEM image of the SiC representative of the sample. This image illustrates that the SiC whisker has a homogeneous crystalline structure with adjacent fringes resolved at 0.25 nm, which fits well with the distance between the (111)
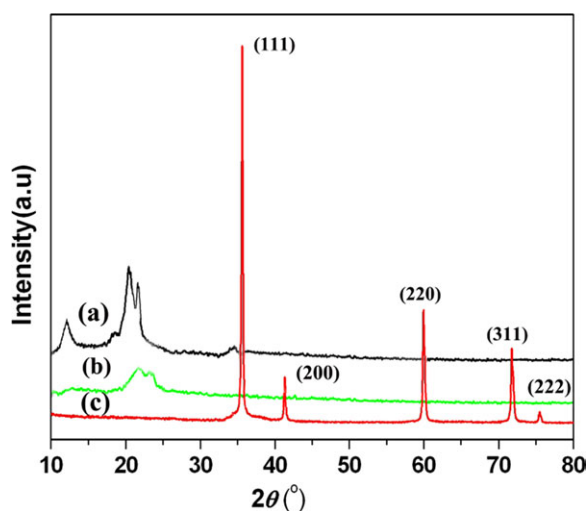

Figure 1. XRD patterns of CNC (a), CNC/SiO_2 hybrid (b) and SiC whisker (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
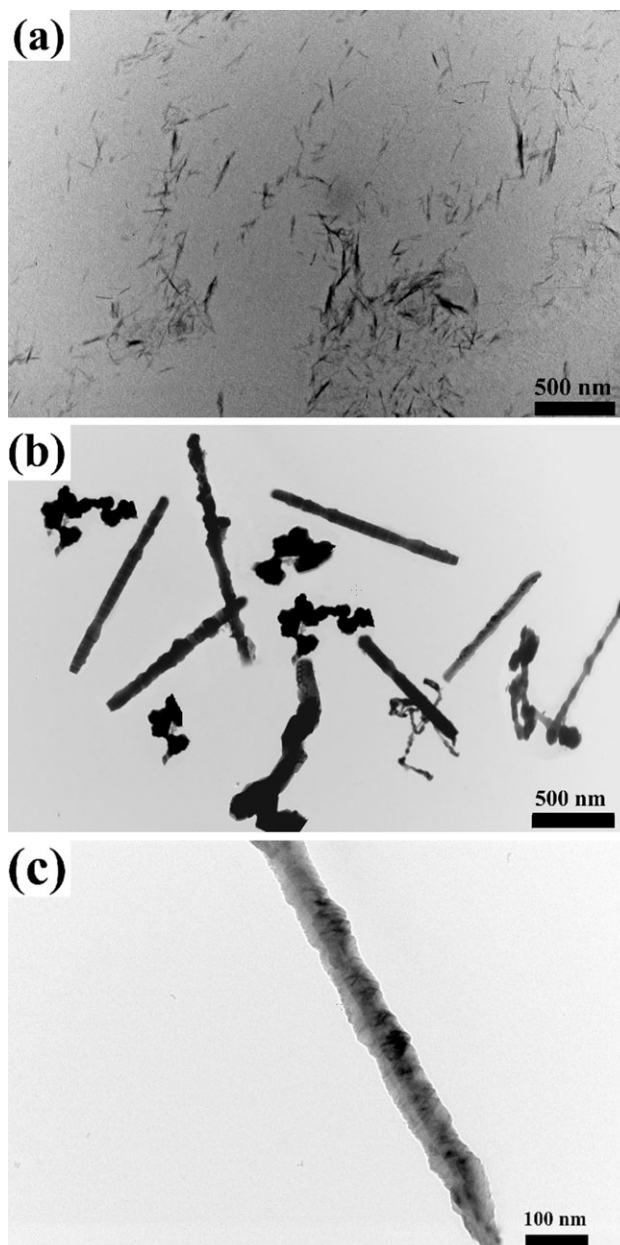

Figure 2. TEM images of CNC (a), SiC whisker (b) and magnification SiC whisker (c).

planes of the face-centered cubic SiC. It also indicates that the core stem of the nanostructure grows along the (111) direction. The crystalline nature of SiC is characterized by the SAED. The SAED pattern [Figure 3(b)] reveals that the SiC exhibits a single-crystalline nature. The corresponding selected area diffraction (SAED) pattern recorded along the (110) zone axis shows bright spots. And the EDX [Figure 3(c)] analysis of the SiC shows that the contents of the constituent weight are 90.02% (Si) and 9.98% (C). Therefore, the results further confirm that the prepared products are solely composed of SiC.

The infrared spectrum of the CNC is presented in Figure 4(a). The observed strong FTIR absorption bands at 3400, 2900, 1750, and 1061 cm^{-1} agree with cellulose standard. And the
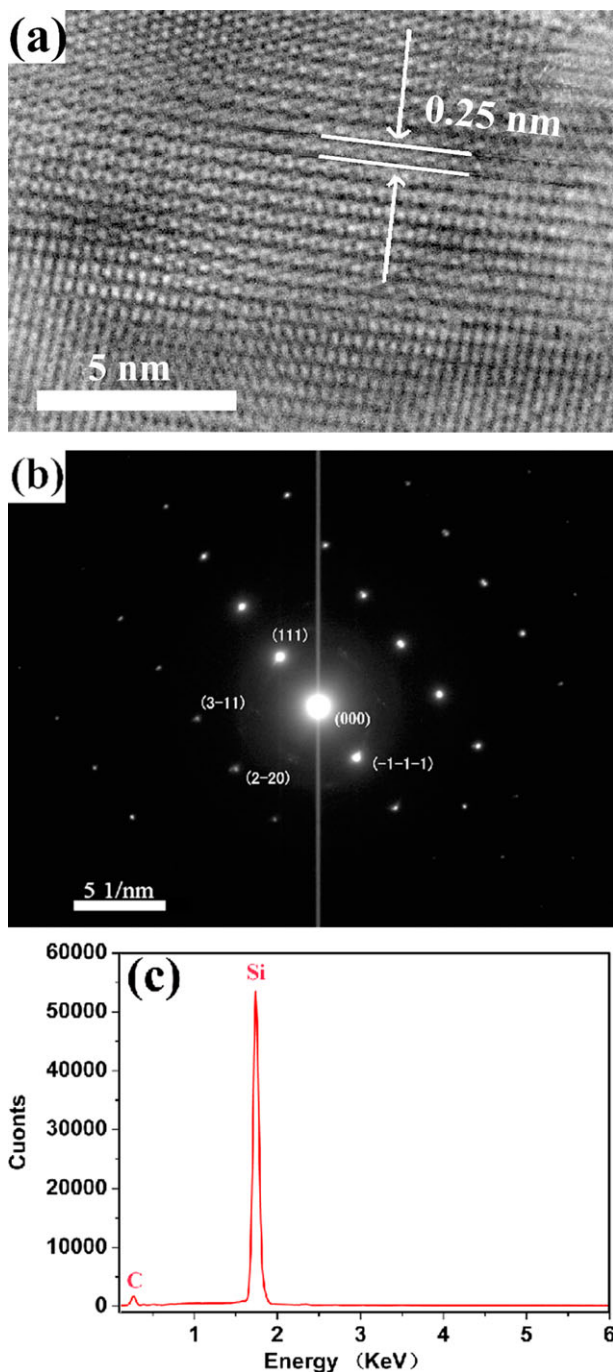
Figure 3. HRTEM image of SiC whisker (a), SAED analysis of SiC (b), and EDX spectra for SiC (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorption bands centered at 3400 and 1750 cm^{-1} are attributed to water. Figure 4(b) displays the infrared spectrum of CNC/SiO$_2$ hybrid and the strong and broad absorption band at 1119 cm^{-1} is the asymmetric stretching vibration of Si—O—Si.

After forming CNC/SiO$_2$ hybrid, the band of at 2900 and 1061 cm^{-1} gradually weaken. Figure 4(c) displays the characteristic FIIR spectrum of the SiC whisker. The intense band at 821 cm^{-1} is the TO phonons of SiC.[20] The sharp band of at 3400 and
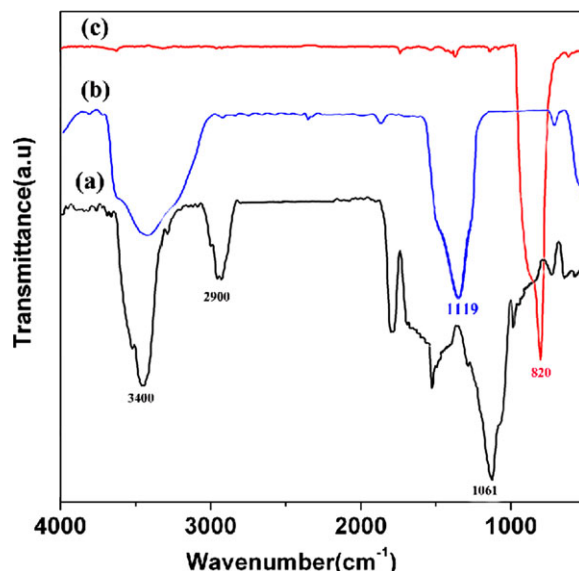

Figure 4. FTIR spectrum of CNC (a), CNC/SiO$_2$ hybrid (b) and SiC whisker (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1119 cm^{-1} in CNC/SiO$_2$ hybrid totally disappeared in SiC, indicating that organic cellulose core is completely removed due to high-temperature calcination.

Figure 5 shows the TG curve of the CNC, CNC/SiO$_2$ hybrid, and SiC whisker. The thermal stability of the CNC could be obtained in Figure 5(a). Between 130°C and 330°C, the weight loss is attributed to the oxidation and carbonization of the free polymer CNC. Figure 5(b) shows the TG curve of synthesized intermediate CNC/SiO$_2$ hybrid. Figure 5(a,b) of the absorption peak is similar, but the decomposition temperature of the CNC/SiO$_2$ hybrid is higher about 350°C. Figure 5(c) shows the TG curve of synthesized the SiC whisker. From the TG curve, the SiC whisker presents no any weight loss between 60°C and 640°C. It is clear that the SiC whisker have higher thermal stability than the CNC fibers and CNC/SiO$_2$ hybrid, which could
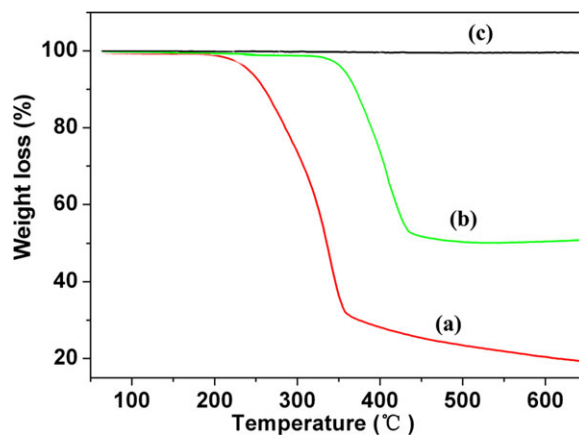

Figure 5. TG of the CNC (a), CNC/SiO$_2$ hybrid (b) and SiC whisker (b) between 75°C and 650°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
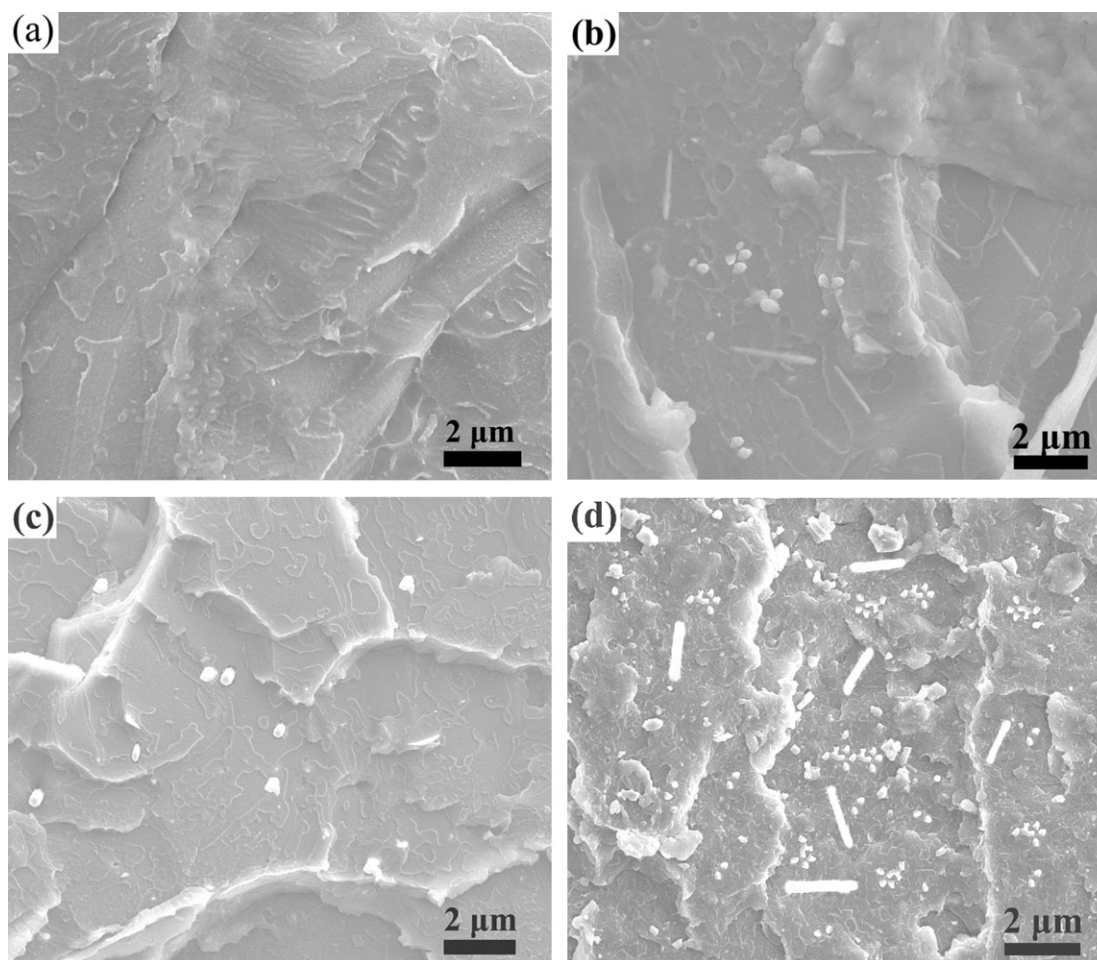
Figure 6. SEM micrograph of cross-section of SiC/PS composites with different wt % SiC and KF9701. (a) 0 wt %, (b) 2 wt % (KF970, 0%), (c) 2 wt % (KF970, 0.5%), (d) 5 wt % (KF970, 0.5%), (e) 10 wt % (KF970, 0.5%), (f) 10 wt % (KF9701, 1.0%), (g) 14.8 wt % (KF9701, 1.5) and 15 wt % (KF9701, 0.5%).

be attributed to the fact that the carbonization can improve thermal stability.

The characteristic morphologies of the fracture surface of PS matrix and SiC/PS composites are visible in Figure 6. The SEM images show PS/SiC composites with the different weight percent of SiC whisker and KF9701. Figure 6(a) shows the pure PS resin micrograph and there isn't any SiC whisker in PS matrix. Figure 6(b) shows SiC(2)/PS(98) composites sample without the KF9701. The SiC particle forms inhomogeneous distribution phase and two distinct phases are clearly observed. In the SiC(2)/PS(97.5)/KF9701(0.5) composites, the compatibility of SiC and PS could be improved through adding silane coupling agent [Figure 6(c)]. When the weight of SiC whisker continues to increase up to 5 wt %, there are more SiC whisker in PS resins and the SiC forms homogeneous distribution phase [Figure 6(d)]. While the weight percent of the SiC whisker and KF9701 is SiC(10)/KF9701(0.5), SiC(10)/KF9701(1.0), SiC(14.8)/KF9701(1.5), and SiC(15)/KF9701(0.5), respectively, it shows that SiC whisker is aggregated and uneven distribution of the dispersed PS phase [Figure 6(e–h)]. Miscibility of the SiC and polymers are clearly shown by the presence of a small quantity of silane coupling

agent which indicates an interfacial interaction between PS matrix and dispersed phase. Generally, immiscible and incompatible blends possess a high interfacial tension, which results in coarser morphology than corresponding adequately the compatibilized blends.[21] There are, however, some differences of surface coarseness, which are apparently due to the multiphase character of these blends. This implies that the role of SiC whisker in energy dissipation mechanism in these blends.

In order to determine the dispersion of composites blends and study their nature and interface, the same samples, stained with the OsO_4, were observed by TEM. Figure 7(a) shows the TEM image of the obtained the sample SiC(2)/PS(98) composites without the KF9701. Some of the black and larger aggregates show in the PS matrix. We believe that the formation of these aggregates is the origin that the SiC whisker is not well dispersed in the PS matrix without the KF9701. Figure 7(b) shows a TEM image of the sample SiC(5)/PS(94.5)/KF9701(0.5). It shows that the SiC whisker can be uniformly dispersed in the PS matrix slit. In other words, the silane coupling agent plays an important role in the dispersion of SiC whisker.
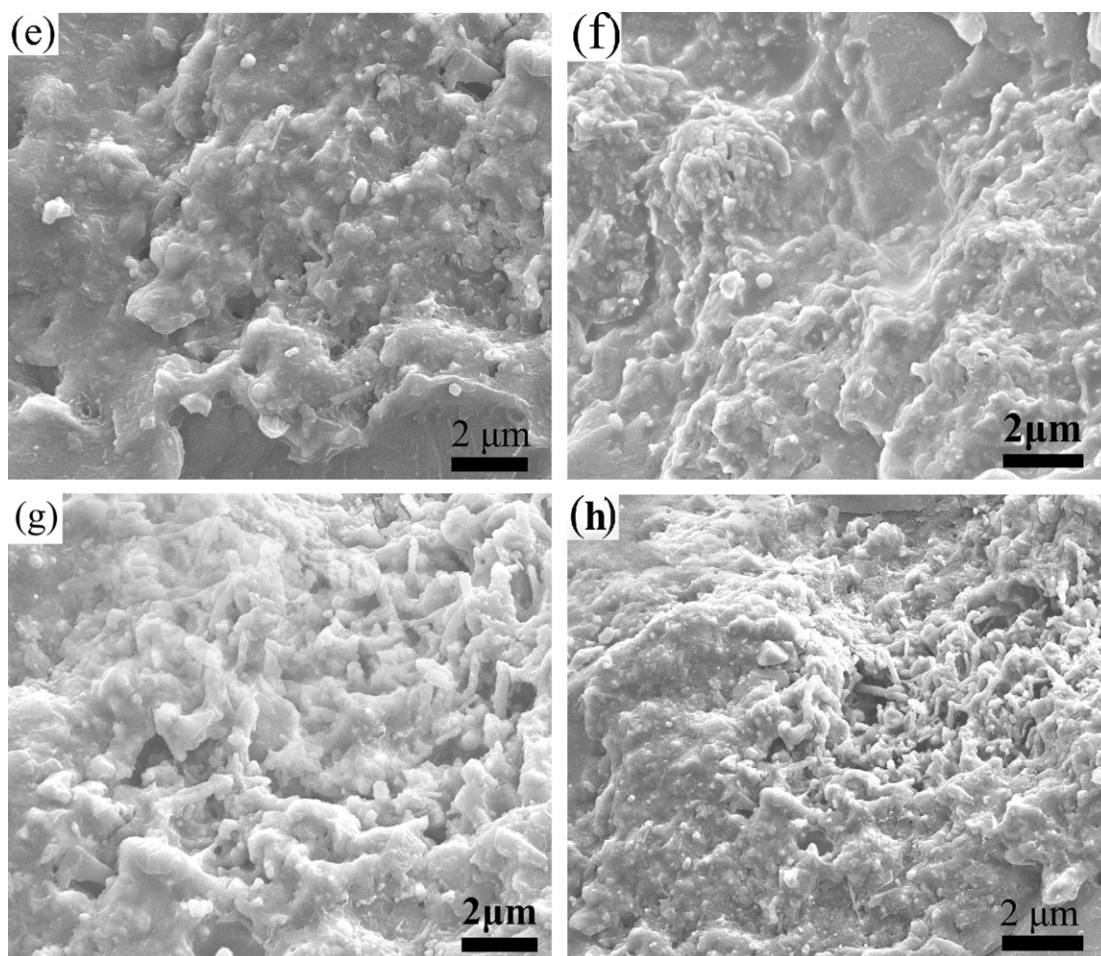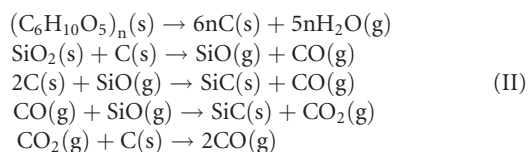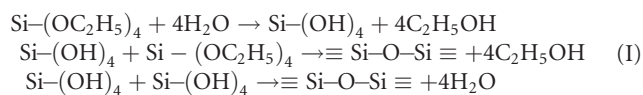
Figure 6. (Continued)

In this work, the tensile behavior and impact test are carried out in room temperature. In the SiC(0)/PS(100) composites, the tensile strength and impact strength of compounds are 37 MPa and 0.65 KJ/m^2, respectively. When the weight percent of the SiC whisker is ranged from 2 wt % to 15 wt %, the tensile strength and notched impact strength of the composites are shown in Table II. In the presence of silane coupling agent and 5 wt % SiC whisker, the tensile strength of the SiC(5)/PS(94.5)/KF9701(0.5) composites is about 3 times of that of the PS sample, and the notched impact strength of the composites is about eight times of that of the PS sample. When SiC whisker is 2 wt % with and without KF9701 as silane coupling agent in PS sample, the tensile strength is 50 Mpa and 60 Mpa, and impact strength measured ranges from 1.12 KJ/m^2 and 1.50 KJ/m^2, respectively. The test results show that the KF9701 have compatibility effect and the SiC whisker is excellent reinforce materials for polymer resins. The intermediate sample SiC(5)/PS(94.5)/KF9701(0.5) composites exhibit highest impact strength values at almost all studied compared to pure PS and other composite blends. The reason is that the SiC whisker can locate PS resin in the amorphous region and formed close contact with each other. The close contact SiC whisker enhances the PS matrix modulus, and increase the molecular chain movement of the amorphous region. The polystyrene resin slit is limited, but it will result in performance degradation when the coupling agent and silicon carbide excessive. The composites form some physical connection points, strengthened the intermolecular forces, and thus improved the tensile impact strength.[22]

Formation Mechanism of SiC Whisker

In our case, the CNC carries some negative charges, since the MCC are hydrolyzed in the sulfuric acids, and either reification may occur between sulfuric acid and the surface hydroxyl groups of the CNC.[23] TEOS is converted into the aqueous silanol sols and then the CNC gels are immersed in aqueous silanol sols. Absorbed silanol (Si—OH) in CNC gels are converted to the silica by poly-condensation reactions. In the CNC molecules, there are large amounts of hydrogen bond which can induce to form wire and rod-like structure.[24] After the solvent is evaporated, the CNC/SiO$_2$ hybrid is prepared by a sol–gel process. During the heat treatment, CNC/SiO$_2$ is carbonized on the silica fiber surface. The CNC acts as the template during the whole process for the SiO$_2$ decomposition and carbonization of the decomposed species.[25] The formation of SiC whisker involves in a solid-gas reaction between carbon and Si vapor generate from the Si solid powder under high temperature conditions. In this synthetic process, the main reactions could be illustrated by the reactions outlined in equations (I) and (II). The formation of the SiC is the

vapor-solid (VS) growth mechanism,[26] and V stands for vapor feed gases and S for growth carbon substrate. The carbon atoms in the vapor feed are accreted to the surface of SiO_2 at 1200°C, which soon becomes supersaturated, and SiC precipitates are synthesized through a vapor-solid (VS) mechanism without catalysts. In the synthesis process, the CNC fibers not only acts as the template and inducing effect but also acts as the carbon source during the conversion from carbon into SiC fibers. And the resulting SiC could well keep the original morphologies of the CNC fibers.

$$Si-(OC_2H_5)_4 + 4H_2O \rightarrow Si-(OH)_4 + 4C_2H_5OH$$
$$Si-(OH)_4 + Si-(OC_2H_5)_4 \rightarrow \equiv Si-O-Si \equiv +4C_2H_5OH \quad (I)$$
$$Si-(OH)_4 + Si-(OH)_4 \rightarrow \equiv Si-O-Si \equiv +4H_2O$$

$$(C_6H_{10}O_5)_n(s) \rightarrow 6nC(s) + 5nH_2O(g)$$
$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g)$$
$$2C(s) + SiO(g) \rightarrow SiC(s) + CO(g) \quad (II)$$
$$CO(g) + SiO(g) \rightarrow SiC(s) + CO_2(g)$$
$$CO_2(g) + C(s) \rightarrow 2CO(g)$$

CONCLUSIONS

In summary, a simple and cost-effective approach is reported for fabrication of the SiC whisker using the CNC as a template,
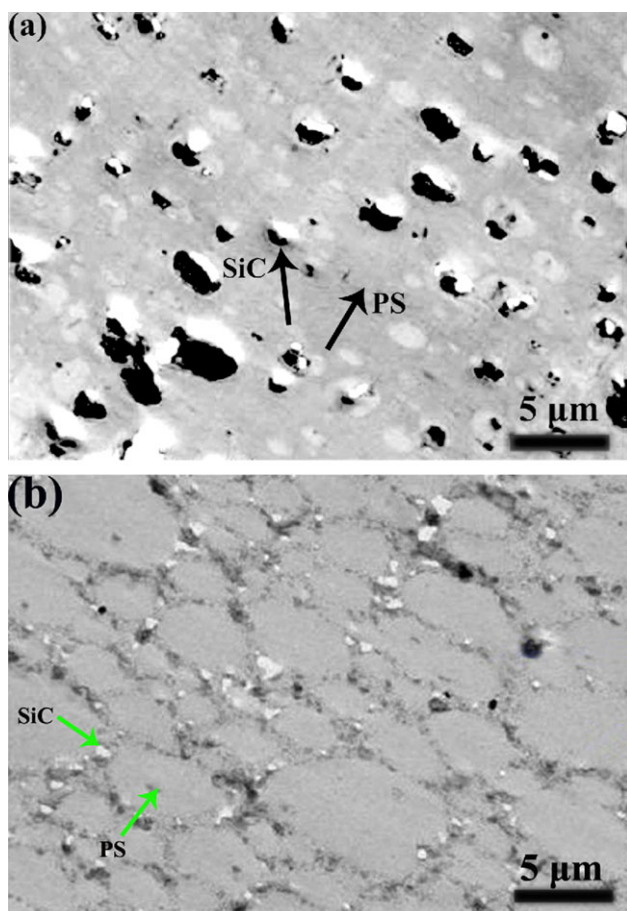

Figure 7. TEM images of SiC(2)/PS(98) composites (a) and SiC(5)/PS(94.5)/KF9701(0.5) composites (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Effect of SiC Whisker Content on Tensile Behavior and Impact Strength Constant of Composites

Filler content (wt %)	Tensile behavior (MPa)	Impact strength (KJ/m^2)
PS(100)	37	0.65
SiC(2)/PS(98)	50	1.12
SiC(2)/PS(97.5)/KF9701(0.5)	60	1.50
SiC(5)/PS(94.5)/KF9701(0.5)	110	5.20
SiC(10)/PS(89.5)/KF9701(0.5)	100	5.02
SiC(10)/PS(89)/KF9701(1.0)	102	5.15
SiC(14.8)/PS(83.7)/KF9701(1.5)	94	4.89
SiC(15)/PS(84.5)/KF9701(0.5)	92	4.78

taking advantage of negatively charged and hydrogen bond of CNC which are prepared by sulfuric acid hydrolysis. The obtained SiC whisker has a uniform shape with the length of ca. 2–4 μm and a width of 40 ± 5 nm. The results show that the CNC is an ideal template for manufacturing SiC whisker materials with uniform shape and size. Using the KF9701 as compatibilizers, the 5 wt %. SiC whisker particles can disperse homogeneously in the PS resins and the SiC/PS composites show significant improvement in Izod impact strength. A slight improvement is observed in the impact properties when SiC whisker is from 10 to 15 wt %. But the best result is obtained by using a combined compatibilizer system in intermediate blends SiC(5)/PS(94.5)/KF970(0.5). And the tensile strength of the intermediate blends is about three times of that the PS resin, and the notched impact strength of the intermediate blends was about eight times of that of the PS resin.

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