

Preparation and Properties of Poly(ethylene terephthalate)/Inorganic Whiskers Composites

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ABSTRACT: To improve the crystallization and mechanical properties of poly(ethylene terephthalate) (PET), in this work, PET/SiO₂-MgO-CaO whiskers composites were prepared via *in situ* polymerization. The morphology, crystallization, and mechanical properties of the prepared composites were investigated. It was found that inorganic whiskers could be easily dispersed in PET matrix, as demonstrated by SEM and PLM. DSC and PLM observation indicated a strong nucleation capability of inorganic whiskers for PET. Mechanical analysis results showed that the glass transition temperature, tensile strength, and modulus of the composites were greatly improved. A pos-

sible chemical bonding between PET chains and the surface of whiskers was observed by FTIR, TGA, and sedimentation experiment. It could be the main reason for the good dispersion and improved properties of the prepared composites. This work is important for the application of PET due to the low cost but high reinforcing efficiency of this inorganic whisker. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 604–611, 2011

Key words: polymer-matrix composites (PMCs); mechanical properties; electron microscopy; thermal analysis

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a semicrystalline thermoplastic polyester with various excellent properties. Because of its low cost and high performance, PET is widely used in many applications such as fiber, films, bottle, packing, and engineering plastics in electronics. Thus, any enhancement of PET in crystallization, antistatic, mechanical, and other properties could lead to a great potential industrial application. In recent years, much effort has been made to prepare PET/inorganic nanocomposites.^{1–14} Karayannidis et al.¹ reported a new approach to prepare PET/silica nanocomposites with increased molecular weight and fully adjustable branching or crosslinking between silica and polymer molecule by solid-state polycondensation. Cui et al.² investigated the possibility of using the monomers of PET reacting with hydroxyl group on the attapulgite (not pre-modified) surface in the *in situ* preparation process. This improved the interfacial adhesion between the attapulgite and PET matrix. This leads to a uniform dispersion of attapulgite in PET matrix. Recently, a

modification approach involving direct silicon grafting reaction has been used to form covalent bonds with the hydroxyl group on the clay platelets.^{3–6} Yang et al.⁶ investigated PET/silane-grafted organoclay composites and achieved a covalent bond between clay platelets and polymer chains. The key for the preparation of high performance polymer nanocomposites is the good filler dispersion in the matrix and strong interaction between filler and matrix.^{7–9}

However, a strong surface energy of nanometer sized particles derived from the large specific surface area usually accelerates the nanoparticle reaggregation and results in a poor filler dispersion in polymer matrix. Comparing with nanoparticles, microscale particles could be relatively easier to disperse in the polymer matrix because of its lower surface energy. Whiskers are fiber-shaped single crystals with large length/radius ratio. Owing to their small diameters, whiskers are generally known to be free from the internal defects such as dislocations. Therefore, the strength of whiskers is close to the maximum theoretical value expected from the theory of elasticity.^{15,16} Previous researchers have demonstrated that whiskers exhibit much higher specific strength than short glass fibers and could reinforce thermoplastics more effectively.^{17–19} Therefore, whiskers are considered as alternative reinforcement fillers for thermoplastics and have attracted considerable amount of interests from scientists and engineers. These inorganic whiskers include silicon

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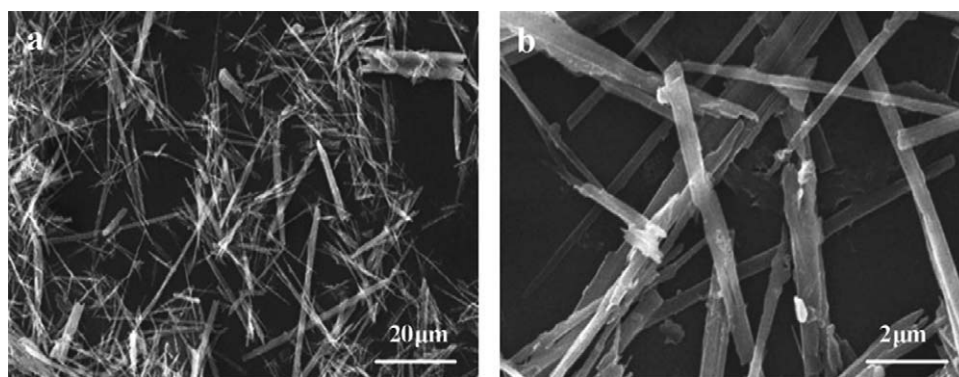


Figure 1 SEM images of SMCW (a) and (b).

carbide, potassium titanate ($K_2Ti_6O_{13}$), and aluminum borate ($Al_{18}B_4O_{33}$).^{15–20} SiO_2 -MgO-CaO whisker (SMCW) is a new type of filler and very cheap.^{20,21} Fibrous filler has been recognized as effective reinforcing additive in polymer matrix comparing with spherical filler.²² For example, it was reported that the SMCW whiskers can be dispersed homogeneously in polyolefin matrix, leading to an enhancement in the mechanical properties of the composites.²¹

In this work, this new type of inorganic whiskers (SMCW) was introduced into PET by *in situ* polymerization. There are some silicon hydroxyl groups on the surface of SMCW. Thus, it is possible to form chemical bonding between SMCW and PET chain during the preparation process of PET/SMCW composites. Our goal is to prepare PET/SMCW composites with good dispersion via the interaction between the hydroxyl groups on the whiskers' surface and PET chains. The morphology, crystallization, and mechanical properties of the prepared composites are also reported in this article.

EXPERIMENT PART

Materials and sample preparation

Ethylene glycol (EG), Sb_2O_3 , and triphenyl phosphite (TPP) were purchased from Chengdu Kelong Co. (Chengdu, China), and terephthalic acid (TPA) was purchased from Guanghan Resin Co. (Sichuan, China). All of these chemical agents were used as-received. The whisker (SMCW), as shown in Figure 1, was provided by Mianyang Guangda Co. (Sichuan, China). It is a kind of light yellow crystal material with a density of 3.0 g/cm^3 . Its diameter mainly ranges from 0.2 to 0.5 μm , and its length is in the range 5–50 μm . An appropriate amount of SMCW was first dispersed in EG with stirring. The mixture, including TPA, Sb_2O_3 , and TPP, was added into the autoclave. With vigorous stirring, the temperature was gradually increased to 230–250°C, and the air-pressure to 0.5 MPa by nitrogen. The reaction was

kept for 1.5–2 h until no more water was produced. Then, the temperature was increased gradually to 280°C and maintained at this temperature for polymerization. The vacuum of the reaction system was reduced gradually to less than 80 Pa. The reaction was stopped when the electric current reached the controlled value and the product was extruded from the reactor by compressed nitrogen and cut into pellets. The controlled value of electric current in this work was about 1.0 A, which corresponds to the value of intrinsic viscosity of about 0.75 dL/g (according to ISO1228-1975(E)). Those descriptions can be found in our previous literature. The similar reaction process can be found in our previous literature.²³ Then, the composites were extruded from the reactor by compressed nitrogen and cut into pellets. The contents of SMCW were 1, 3, and 5 wt %, respectively. For comparison, PET without whiskers was also prepared under the same conditions. We have confirmed that the addition of small amount (not more than 5 wt %) of SMCW (or clay) has just a little influence on the intrinsic viscosity of the synthesized PET, so the samples had similar molecular weight ($[\eta] \approx 0.73\text{--}0.77 \text{ d Lg}^{-1}$, ISO1228-1975(E)) in all the cases. After pelletizing, the as-prepared composites were dried under vacuum for 12 h at 110°C and then injection molded on a PS40E5ASE (Japan) injection machine between 265 and 280°C to obtain standard specimens for mechanical testing.

To investigate the interactions between PET and SMCW surface, SMCW was isolated from the PET/SMCW composites by successive centrifugation and dissolved cycles: the composites were dissolved in a mixture of phenol and tetrachloroethane (1/1, w/w); the suspension was centrifuged for 15 min (two times) to precipitate the whiskers completely; the precipitate was dissolved in the above mixed solvent again, stirred, and centrifuged to remove physically absorbed PET. The dissolving and subsequent centrifugation was performed five times until no precipitate formed when the supernatant liquid was dropped into methanol. The residual PET

enwrapped SMCW were washed twice with methanol and then dried. The original SMCW, the SMCW isolated from the PET/SMCW composite prepared by melt blending (by internal mixing at 265°C for 10 min, using the as-synthesized PET), and the SMCW prepared above were defined as original whiskers, melt blended whiskers, and *in situ* whiskers, respectively.

Characterizations

The FTIR spectra were recorded between 400 and 4000 cm^{-1} on a Nicolet-560 infrared spectrometer at a resolution of 4 cm^{-1} with an accumulation of 64 scans in transmission mode.

The thermal stability was inspected on a WRT-2P thermo gravimetry (TGA) (Shanghai Scale Factory), from 50 to 700°C upon nitrogen atmosphere at a heating rate of 20°C/min.

For SEM investigation, the injection samples were cryo-fractured in liquid nitrogen. Then, the fractured surfaces were etched in NaOH/ethanol solution, coated with gold powder, and investigated on an Inspect F (FEI) SEM instrument with an acceleration voltage of 20 kV.

The thermal analysis of the samples was conducted using a Perkin-Elmer Pyris-1 DSC. The samples (4.5–5.5 mg) were heated to 280°C from room temperature at a rate of 100°C/min and held for 3 min to eliminate thermal history, then cooled down to 30°C at a rate of 10°C/min, and finally heated it again to 280°C under a rate of 10°C/min to measure the glass and melting temperatures of PET.

Polarized optical microphotographs were obtained by using a Leica DMIP microscope equipped with a Linkam THMS 600 hot stage. The samples were heated to 280°C to eliminate thermal history, and the samples were then cooled rapidly to 230°C. Subsequently, the *in situ* observation of crystallites growth was implemented under isothermal condition.

Standard tensile tests were implemented on an AG10TA tensile testing machine using the dumb-bell-shaped specimens at room temperature. The cross-head speed used was 5 mm/min, according to the ASTM D4812 standard.

For impact toughness, the injection-molded parts were tested with an I200XJU-2.75 izod impact tester at room temperature.

The dynamic mechanical properties were examined by a dynamic mechanical analyzer Q800 (TA Instruments) under dual cantilever mode using the rectangle specimens (length: 35 mm, width: 10 mm, and thickness: 4.2 mm). The dynamic mechanical properties were measured between 120 and 160°C upon a constant frequency of 1 Hz and a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Dispersion morphology of whiskers in PET matrix

The dispersion status of SMCW particles in the PET matrix are assessed by SEM and PLM. For SEM investigation, the injection samples were cryo-fractured in liquid nitrogen. Most of the SMCWs are coated with polymer matrix in the unetched samples even at the highest whiskers content of 5 wt % [see SEM images in Fig. 2(a)]. To investigate the dispersion of SMCW, the fractured surfaces were etched in NaOH/ethanol solution and the interface around the whiskers was etched, resulting in many holes around the whiskers. As shown in the SEM images of Figure 2(b–d), it can be identified clearly that the needles of SMCW are individually and homogeneously dispersed in PET, and this dispersion status can be preserved within the entire concentration range from 1 to 5 wt %. The same phenomenon of SMCW dispersion is also confirmed by PLM observation, as presented in Figure 3. It indicates that *in situ* polymerization is a good strategy for the preparation of homogeneous dispersed pristine inorganic whiskers in PET matrix.

Interfacial interaction between PET and SMCW

It is well known that the chemical bonding between polymer matrix and inorganic filler is favorable for the improvement of interfacial interaction in polymer/inorganic filler composites. In this study, the inorganic whiskers were introduced into PET via *in situ* polymerization. Possible interactions could exist between the hydroxyl groups on the surface of whiskers and the carboxyl groups of PET chains. This special interaction can be characterized by FTIR spectroscopy, TGA, and sedimentation experiment. Detail will be discussed in the following part.

The FTIR spectra of (a) original whiskers, (b) melt blended whiskers, and (c) *in situ* whiskers are shown in Figure 4. For clarity, the content of whisker in the two composites is 5 wt %, and the same below. The absorption peaks located from 850 to 1150 cm^{-1} and at 1630 cm^{-1} are the characteristics for the inorganic whiskers. While some differences in the (b) and (c) spectrums, such as the peaks of 1725 cm^{-1} and 1250 cm^{-1} are observed. The characteristic absorption bands at 1725 cm^{-1} and 1250 cm^{-1} are corresponding to C=O and C—O—C stretching vibration in the ester carbonyl group, respectively. It verifies that some PET chains are still kept on the whiskers surface after experiencing the repeated cycles of centrifugation and dissolving procedure. Comparing with the (b) spectrum, these two characteristic absorption bands in (c) spectrum are stronger, which demonstrates that there is a larger amount of PET chains kept on the surface of whiskers prepared via

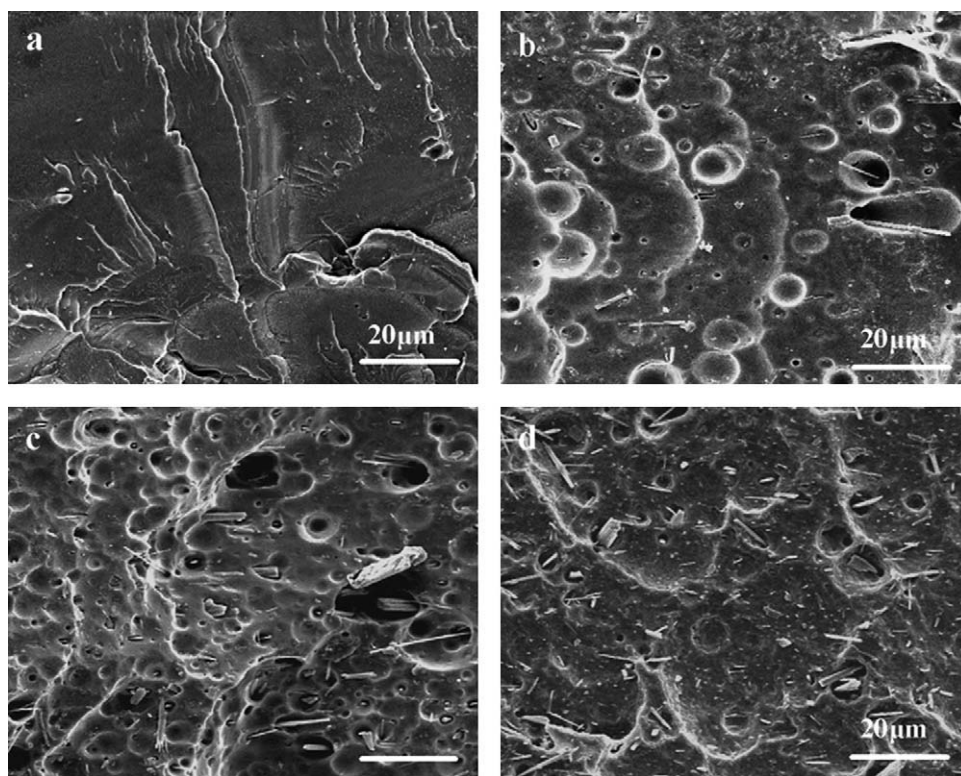


Figure 2 SEM images to represent the dispersion morphologies of SMCW in etched composites with the content of (a) 1 wt %, (b) 3 wt %, and (c) 5 wt %, and unetched surface with the content of (d) 5 wt %.

in situ polymerization than that via the melt blending method. A schematic illustration is proposed to discuss the possible mechanism of how PET chains can be linked on the whisker surface during *in situ* polymerization as shown in Scheme 1.

The amount of PET chains reserved on the surface of whiskers has been further characterized using TGA. The weight loss curves for different whiskers are presented in Figure 5. By extracting the mass loss of original SMCW, one can calculate the mass fraction of organic component (polymer) linked to the whisker. As indicated on the TGA curves, the mass fraction of PET reserved on the whiskers' surface are 2.6 wt % and 1.3 wt % for the *in situ*

whiskers and the melt blended whiskers, respectively. Obviously, the more PET chains reserved on the whisker surface, the stronger interfacial interaction between the polymer and filler can be achieved.

Subsequently, the dispersibility of the whiskers in organic solvent is assessed by sedimentation experiment. These three kinds of whiskers were dispersed in the phenol and tetrachloroethane (1/1, w/w) mixed solution by stirring for 5 min, and then precipitated for 30 min. The resulting photographs are presented in Figure 6. One can observe that the whiskers descended quickly in Figure 6 (a,b), which corresponds to the original whiskers and the melt blended whiskers, respectively. Whereas, the *in situ*

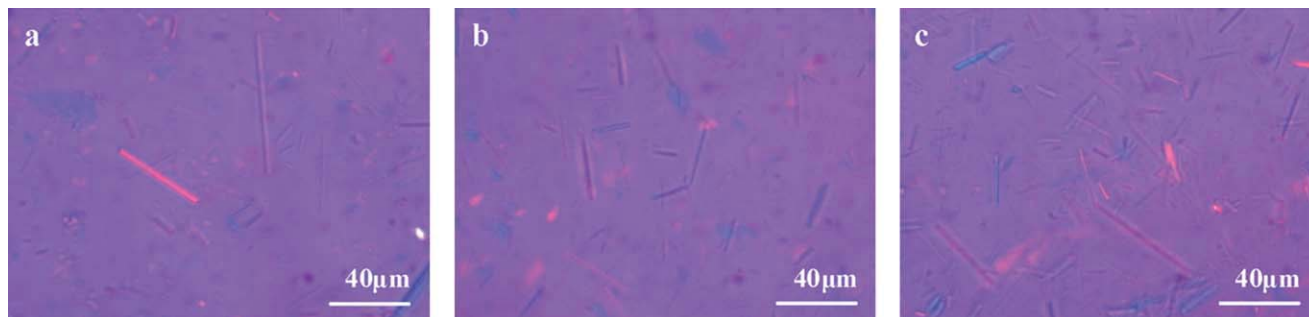


Figure 3 PLM photos of PET/SCMW composites with the whiskers content of (a) 1 wt %, (b) 3 wt %, and (c) 5 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

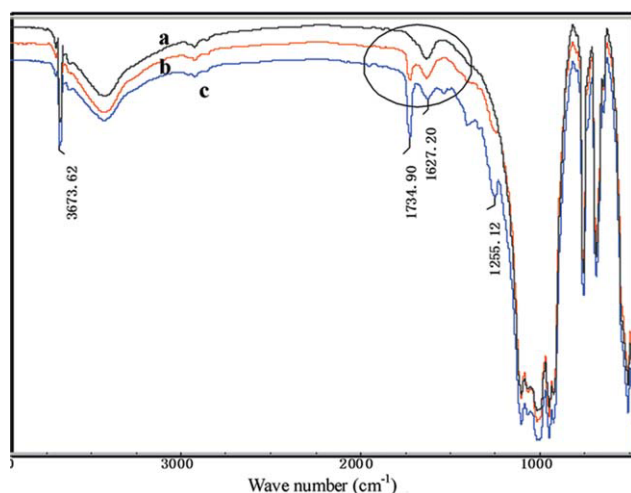
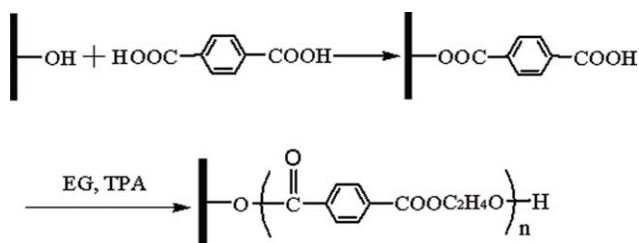


Figure 4 FTIR curves of (a) original whiskers, (b) melt blend whiskers, and (c) *in situ* whiskers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

whiskers have better dispersibility than the others, and stable dispersion can still be seen even after 30 min. However, the *in situ* whiskers would also descend after 1 h. The microscale SMCW is hardly suspended in the mixed solution because of its large density and dimension. The good dispersibility of *in situ* whiskers confirms that large amount of PET chains have been reserved on the surface of whiskers via *in situ* polymerization. More work regarding the direct evidence for the possible chemical bonding between PET and inorganic whiskers surface will be carried out in our future work.

Crystallization behaviors

As homogeneously dispersed fillers can act as good heterogeneous nucleating agent for semicrystalline polymers, a high efficiency of nucleated crystallization is important evidence for the good dispersion. The effects of SMCW on the crystallization and melting behavior of PET were investigated by DSC, and the resulting thermograms are shown in Figure 7. The cooling crystallization temperature (T_c) is increased remarkably from 175.2°C for the neat PET



Scheme 1 The reaction route between PET chains and the SMCW surface during *in situ* polymerization.

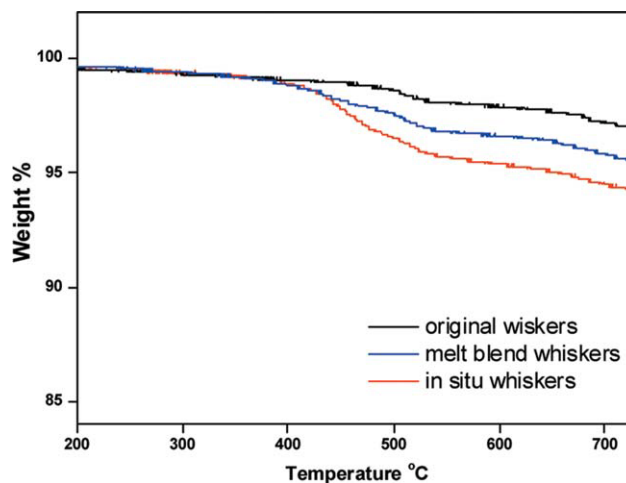


Figure 5 TGA curves for three kinds of SMCW isolated from the matrix: original whiskers, melt blend whiskers, and *in situ* whiskers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to 197.4°C, 201°C, and 201.2°C for the composites containing 1, 3, and 5 wt % SMCW, respectively. It is obvious that inorganic whiskers can serve as a good nucleating agent for PE and accelerate the crystallization rate greatly at relative low whiskers content (1 wt %). With further increasing SMCW content, the elevated rate of nucleating efficiency is not increased significantly, as the difference in T_c among 1, 3, and 5 wt % SMCW content is very small, due to saturation phenomenon in case of excessive nucleating agent. Similar results can be found in other studies in literatures.^{24,25} As to the melting behavior, the melt temperature of the composites is higher than that of pure PET, which is in agreement with the cooling crystallization behaviors of pure PET and the composites, because of the strong heterogeneous nucleating effect of SMCW.

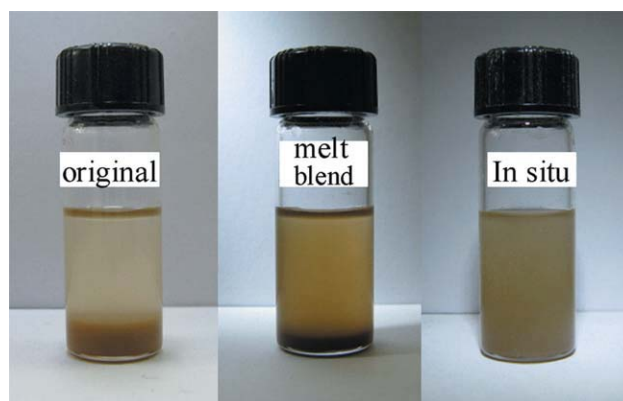


Figure 6 Precipitation experiment of the three kinds of isolated whiskers in mixed solution (a) original whiskers, (b) melt blend whiskers, and (c) *in situ* whiskers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

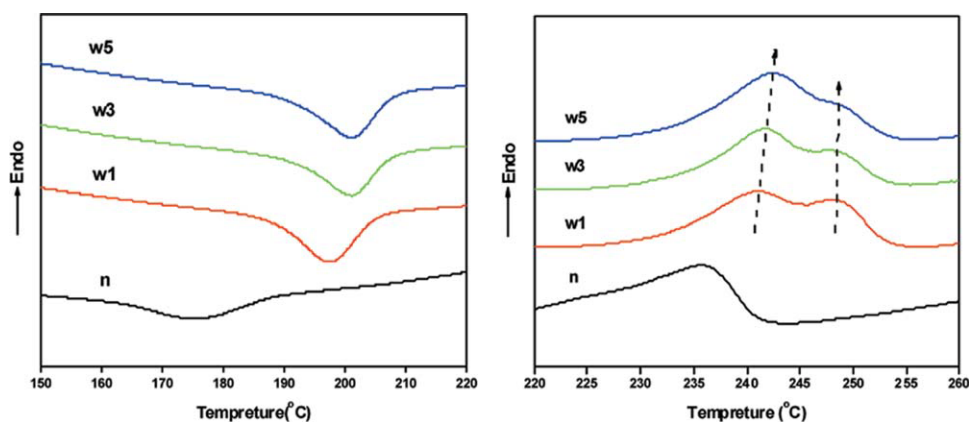


Figure 7 DSC curves for neat PET and PET/SMCW composites: the cooling scan after first heating and the second heating scan. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Furthermore, two melting peaks are observed for each composite. The lower one represents the melting of imperfect or smaller crystals, and the higher one might be related to the recrystallization process. The melting peak located at lower temperature becomes more distinct and increases slightly with increasing SMCW content (an arrow indicates this tendency directly on the thermogram).

PLM was used to observe the isothermal crystallization of the composites at 230°C. As shown in Figure 8, an interesting phenomenon is observed that many nucleating sites have been generated on the surface of SMCW needle, which induces obvious

transcrystalline growth of PET as the PET lamellae are perpendicular to the longitudinal direction of SMCW needle. This trans-crystallization regime coated around the SMCW needle can prominently promote the interaction between filler and matrix and thus reinforce the composites.

Enhancement of properties

To characterize the thermal stabilities of pure PET and composites, TGA is carried out (see Fig. 9). The initial decomposition temperature and the weight loss of composites are dependent on the whisker

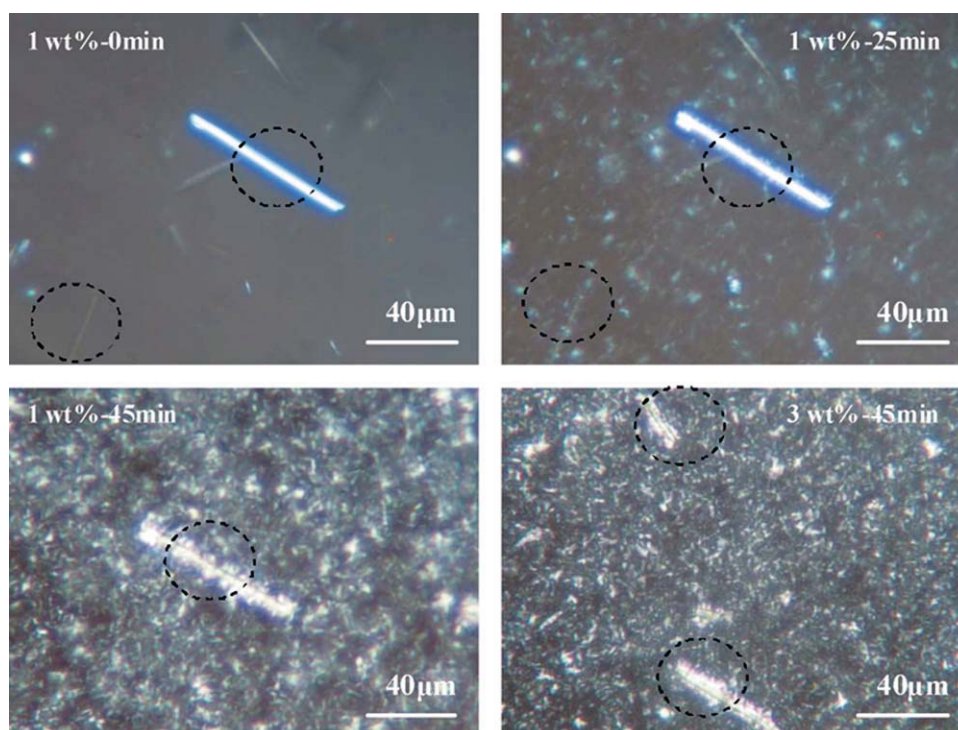


Figure 8 PLM photos of the isothermal crystallization of PET/SMCW composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

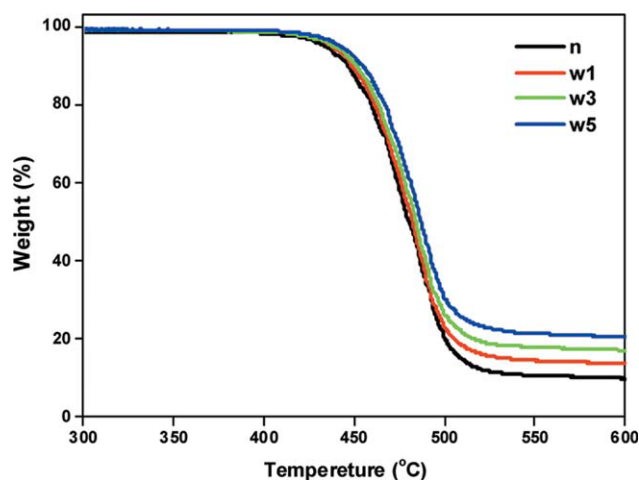


Figure 9 TGA curves for neat PET and PET/SMCW composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

content, though there is no obvious change of the slope. The degradation temperature for 10% weight loss on the TGA curve is improved for 8°C when 5 wt % whiskers is added into PET matrix. The additional inorganic whiskers can enhance the thermal stability performance by acting as a superior insulator and a mass-transport barrier during PET matrix decomposition. This improvement in thermal stability has been reported in many polymer/inorganic fillers systems.^{26–28}

The dependence of storage modulus on temperature for the neat PET and composites with 1, 3, and 5% SMCW are plotted in Figure 10. An obvious increase in glass transition temperature (7°C) and the modulus of composites after addition of SMCW into PET are significantly larger than that of neat PET within the entire measured temperature range,

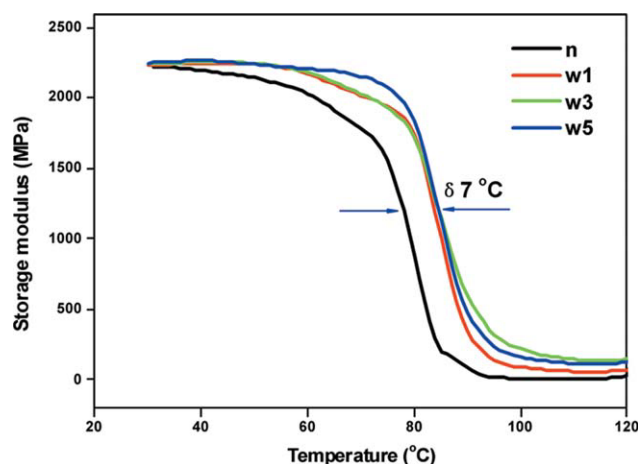


Figure 10 DMA curves for the dynamic mechanical behavior of neat PET and PET/SMCW composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

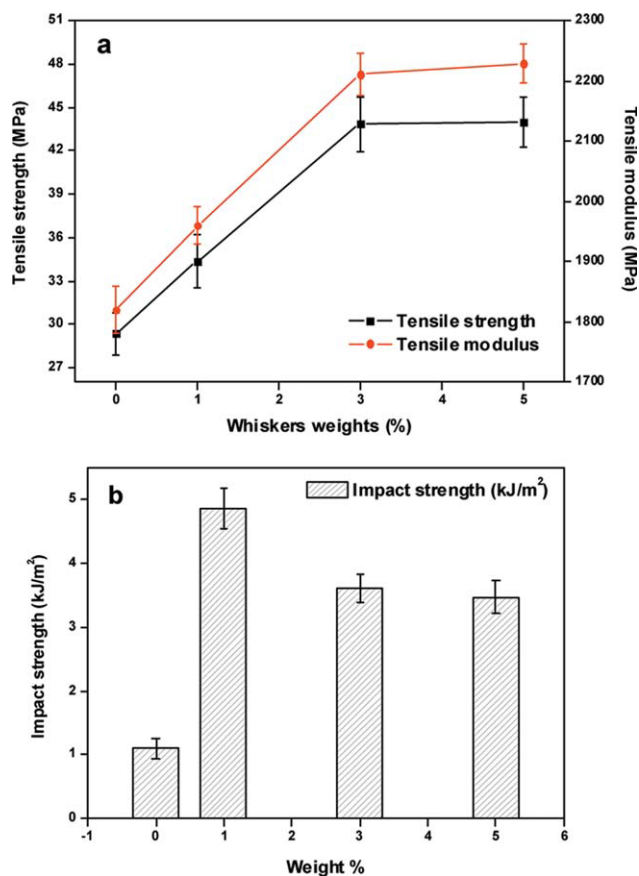


Figure 11 Stress–strain curves (a) and impact strength curves (b) for neat PET and PET/SMCW composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

implying that the mobility of the amorphous fraction of PET is strongly confined in the presence of whiskers. The reinforcement effect of SMCW is also obvious for the tensile properties. As illustrated in Figure 11(a), the tensile strength is increased by 50% for composites containing 3 wt % SMCW and no further increase is obtained while SMCW content is increased to 5 wt %. A similar property–filler content relation is also observed for tensile modulus. Moreover, the impact toughness of the composite is higher than that of the neat PET [Fig. 11(b)]. A maximum of five folds increase has been observed in impact toughness after adding 1 wt % of SMCW. Although the toughness decreases a little when the SMCW content is increased to 3 and 5 wt %, the impact strength of the two composites is still twice that of neat PET. Therefore, simultaneously strengthening and toughening can be achieved for the PET/SMCW composites prepared via *in situ* polymerization.

CONCLUSIONS

In this study, we have developed *in situ* polymerization strategy to fabricate novel PET/inorganic

whisker composites. Through *in situ* polymerization process, the whisker needles are homogeneously dispersed in PET matrix; and importantly, an amount of PET chains may be chemically linked to the surface of whiskers. The latter enhances the interaction between polymer and inorganic filler. The good dispersion of whiskers and strong polymer/fillers interaction substantially alter the crystallization behavior of PET, such as faster crystallization rate and the formation of trans-crystallization, and prominently improve the thermal stability and mechanical properties of composites. This new PET/inorganic whiskers composite exhibits good potential for industrial applications.

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