Modification of Polypropylene Composites Containing Potassium Titanate Whisker and Talcum

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ABSTRACT: Modified polypropylene was prepared by blending with potassium titanate whisker (PTW) and 10 w/w% talc via Haake extruder followed by injection molding. Reinforced with both PTW and talc, the PP composites exhibited better mechanical properties. The tensile modulus and flexural modulus of PP composites tend to increase with the increasing of whisker concentrations. The talc plays a synergistic role in improving the mechanical properties of composites and reducing cost. Torque measurement shows the PP composites has a good processing condition due to lubrication of PTW. TGA test shows PP composites containing 20 w/w% PTW and 10 w/w% talc is useful for improving PP composite's thermo oxidative stability. J Appl Polym Sci 116: 3455–3459, 2010

Key words: polypropylene; potassium titanate whisker(PTW); talc; chlorinated polyethylene(CPE)

INTRODUCTION

Isotactic polypropylene (PP) is widely used owing to its varieties of applications ranging from films, pipes, and even the matrix of the polymer alloys. However, PP exhibits relatively low modulus, dimensional instability, and any other disadvantages comparing to some engineering plastics. In recent years, various fiber and inorganic fillers reinforcements, such as glass–fiber, wood–fiber, and nano-$CaCO_3$ are commonly incorporated into PP matrix.[1–3]

Recently, whiskers are reckoned as a more effective reinforcement than traditional fiber like carbon fiber and glass fiber. They are nearly free from internal flaws such as dislocations because of their small diameter fiber. Furthermore, whisker like potassium titanate ($K_2Ti_6O_{13}$), one of the most promising whisker owing to its outstanding mechanical performance, hardness, and chemical stability, coupled with its price ranges from one-tenth to one-twentieth of the cost of the SiC whisker, is the most possible commercialized in the future. In this research, potassium titanate whisker (PTW) has been widely used to reinforce the themoplastic.[4–8]

Tjong and Meng[9,10] reported that adding PTW and liquid crystalline polymers (LCPs) into PP to investigate the microstructural and mechanical properties, finding an increase in mechanical properties due to whisker and a decrease in melt viscosity containing LCPs. They also have investigated the effect of PTWs on the thermal stability of polycarbonate (PC) using two different coupling agents. They mentioned the whiskers treated with coupling agents can degrade PC more easily and the tensile strength of coupling treated composites decreases rapidly with increasing whisker content.[11]

Talc is a kind of very cheap inorganic filler, which is helpful to reduce melt viscosity and plays a synergistic role in some composites. Considering the aforementioned research, PP/$K_2Ti_6O_{13}$/Talc composites were extrudered by Haake extruder and then injected to form specimens. Chlorinated polyethylene (CPE) and PP-*g*-MAH are also introduced into this composite to upgrade the PP composites. It is anticipated that such kind of composite has better process condition, dimensional stability, and thermal stability. Influence of talc on the properties of the composite is also studied.

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EXPERIMENTAL

Materials

The PP was from Dushanzi TianLi High & New Tech Co., China with the MFI (Melting Flow Index)

TABLE I
Properties of Potassium Titanate Whiskers and Polypropylene

Properties	Parameter (PP)	Parameter (PTW)
Specific density (g/cm^3)	–	3.3
Length (μm)	–	10–40
Diameter (μm)	–	0.5–1.0
Hardness	–	4 above
Tensile strength (GPa)	0.034	7
Tensile modulus (GPa)	0.345	280
Melting point (°C)	169.9	1350–1370
Melting Flow Index (g/10 min)	2.8	–
Heat resisting temperature (°C)	–	1200

of 2.8 g/10 min (GB/T 3682). The PTW was supplied by Shanghai Zuoda Composite Co., China, and the physical and mechanical properties are listed in Table I. The talc was supplied by Shanghai Shuosi Co., China. The maleic anhydride grafted PP with a graft ratio about 1% was purchased from Shanghai Sunny Co., China. Chlorinated polyethylene (CPE) was supplied by Dupont Dow Elastomers. Reagent-grade tetrabutyl orthotitanate here was used as the coupling agent for the whiskers.

Sample preparation

Tetrabutyl orthotitanate was initially dissolved in acetone to form a 5 wt % solution, then poured whisker into this solution, mixed by hand thoroughly, and then dried in an oven at 80°C for 24 h. PP composite containing 10, 15, 20, 25, and 30 w/w% $K_2Ti_6O_{13}$ whiskers and also mixed with constant 10 w/w% talc, together with constant 10 w/w% PP-*g*-MAH and constant 10 w/w% CPE were prepared in Haake (model: Rheocord 300P + Rheomin 600P) at 180, 190, 190°C and 60 rpm, then the sheet were crushed into granule followed by injection molding. The mold temperature was maintained at 30°C whilst the barrel zone temperature were set at 185, 195, 200, 210, and 220°C. 20 w/w% PTW reinforced PP composite without 10 w/w%talc was also prepared for comparison.

Mechanical measurements

Tensile tests were carried out according to ASTM D638 on a universal testing machine with a crosshead speed of 50 mm/min. Flexural tests were carried out according to ASTM D790-2003 with a speed of 2 mm/min. Notched impact tests were carried out according to National Standard of China GB/T 1843-1996.

Torque measurements

Torque values for the PP composites and pure PP were measured using Haake mixer at 190°C and 100 rpm for 3.5 min. For each examination, 60 g sample was added into the batch.

Thermal analyses

Thermal analysis was carried out in NETZSCH (model: STA409C). The weight loss against temperature was measured at a rate of 10°C min^{-1} in an argon atmosphere from 35 to 650°C.

Morphological observations

The injection molded PP composites were cryofractured in liquid nitrogen(-170°C). The fracture surfaces were coated with a thin layer of gold. The morphologies were observed by Hitachi S-4700 scanning electron microscope at 15 kv.

RESULTS AND DISCUSSION

Mechanical properties

Figure 1 shows the variation of PP composite's tensile strength and Young's modulus with different whisker content. Evidently, the tensile strength of PP composites doesn't increase with the increasing the content of whisker while, on contrary even a slight decrease. However, the Young's modulus tends to increase apparently with increasing whisker content. The theoretical Young's modulus of PP composites can be also predicted by the Tsai-Halpin equation, which is frequently used to predict the elastic modulus of discontinuous short fiber reinforced composite. The equation assumes that the circular fibers are

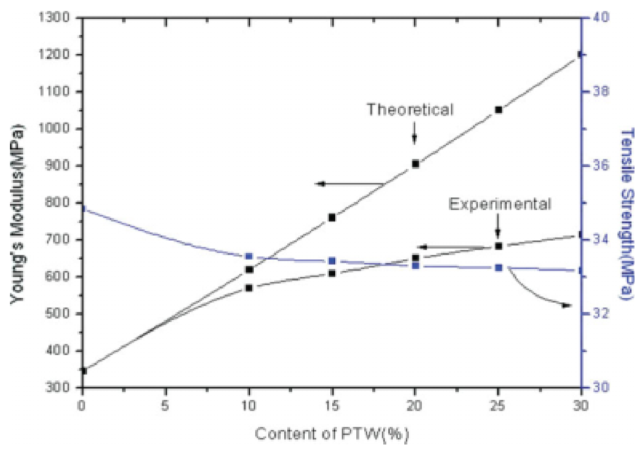

Figure 1 Tensile strength and Young's modulus versus PTW content for PP/PTW/Talc/CPE composites(Standard deviations are less than 5%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

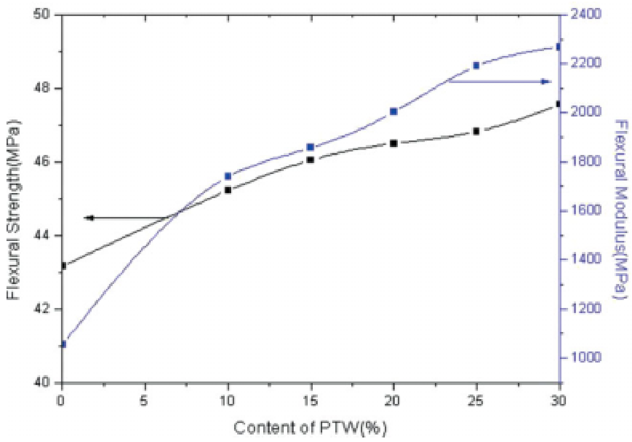

Figure 2 Flexural strength, flexural modulus against PTW content for PP/PTW/Talc/CPE composites(Standard deviations are less than 5%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

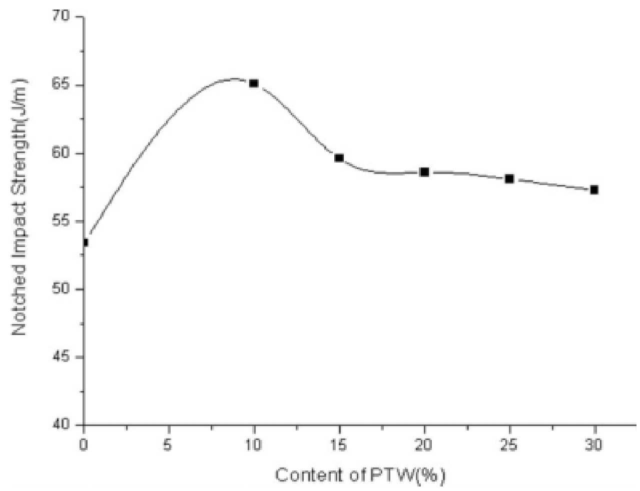

Figure 3 Notched impact strength against PTW content for PP/PTW/Talc/CPE composites(Standard deviations are less than 5%).

uniformly distributed throughout the matrix, and the continuity of stress and strain along the fiber/matrix.[9,12] Tsai-Halpin equation is given as follows:

$$\frac{E_c}{E_m} = \frac{1 + \varepsilon\eta\varphi_f}{1 - \eta\varphi_f f} \quad (1)$$

where E_c and E_m are the elastic modulus of composite and matrix, respectively; φ_f is the volume fraction of short fibers. The constants ε and η are given by

$$\varepsilon = 2(L/D) \quad (2)$$

$$\eta = \frac{E_f - E_m}{E_f + \varepsilon E_m} \quad (3)$$

where L/D is the aspect ratio(length/diameter) of reinforcing fibers, and E_f is the modulus of the fibers. The average value of L and D can be draw from Table I, then used to be for the calculation of ε and eq.(2). It can be seen from Figure 1 that the experimental data of PP composites are much lower than that the theoretical values. Tjong et al.[8–10] reported the same situation in PTW reinforced thermoplastic matrix. The reason can be as follows: (1) The length and diameter of whisker can be broken during mix and injection processing. This would cause the reduction of the whisker's aspect ratio (length/diameter), leading to decrease in whisker's enhancement. (2) The whisker may be more easily agglomerated in high content for its nanoscale in its diameter size and no longer distributed throughout the matrix uniformly, which will dramatically affect the PP composite's Young's Modulus. (3) The Tsai-Halpin equation is generally used to estimate the stiffness of composite with only a single reinforcing component, while here existing another 10 w/w% talc addition. The specific density of whisker is larger than talc, therefore the volume fraction of whisker is smaller compared to talc. Here the ignoring of volume fraction of talc will affect the final Tsai-Halpin equation calculation value.

Figure 2 shows the variations of flexural strength and flexural modulus with whisker content for PP composites. Apparently, the flexural strength tends to a slight increase, while the flexural modulus goes through a dramatic increase. The whisker with its diameter on nanoscale producing microreinforcing effect can be responsible for this increase.

The variation of impact properties of PP composites with whisker content is shown in Figure 3. The impact strength of PP composites reach the maximum value at the 10 w/w% whisker content, and then decrease with the increasing the content of PTW. The agglomerates of whiskers can still be considered as mechanical weak point leading to stress

TABLE II
Comparison of Mechanical Proprieties of PP/20%PTW/10%CPE/10%Talc and PP/20%PTW/10%CPE/0%Talc

	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
PP+20%PTW+10%CPE+10%Talc	33 ± 3%	650 ± 2%	47 ± 2%	2003 ± 4%	59 ± 5%
PP+20%PTW+10%CPE+0%Talc	33 ± 3%	598 ± 3%	45 ± 2%	1666 ± 3%	64 ± 5%

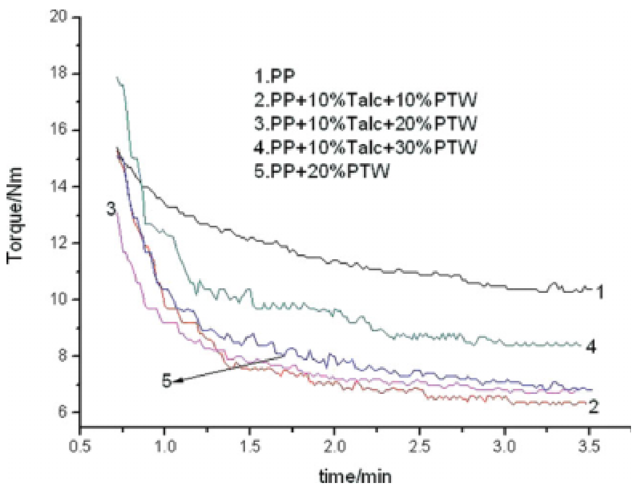

Figure 4 Torque value against mixing time for PP/PTW/Talc/CPE composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

addition, causing the initial crack in the neighborhood of whisker in PP matrix. The low content of whisker can be distributed uniformly in PP matrix, and shows certain toughness for PP composites. While up to high content, they will easily agglomerate due to its nanoscale in the diameter size. Therefore when PP composites suffer from impact, the crack will soon begin in the place of agglomerate whisker leading to PP composites break.

It also can be seen from Table II that the composite containing 10 w/w% talc is conductive to improve the PP composite's mechanical properties except for impact strength. This is because too many inorganic filler can break the continuity of PP matrix and also some whisker agglomeration can be responsible for this decrease in impact strength. It is well-known that only uniformly distributed filler in the continual matrix can produce well toughness. The nonuniform distribution of inorganic filler like 20 w/w% whisker and the extra addition of 10 w/w% talc will dramatically affect the continuity of PP matrix compared to the ingredient of single 20 w/w% whisker without talc, which cause the more decrease in the field of impact strength.

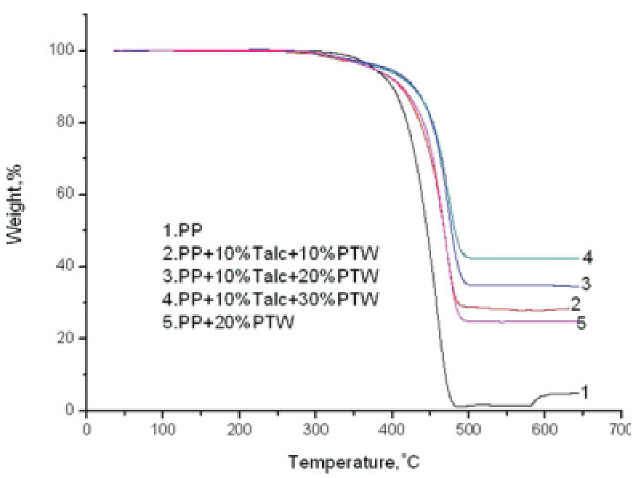

Figure 5 TG curves for PP/PTW/Talc/CPE composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Thermogravimetric Properties of PP Composites

Sample (°C)	1	2	3	4	5
T (−5%)	376.9	375.6	394.7	388.4	375.2
T (−10%)	399.8	410.5	428.0	426.3	412.3

Torque measurements

The torque value is usually recognized as the viscosity and a good parameter for evaluating the processing condition of the composites. Figure 4 shows the plots of torque value against mixing time for

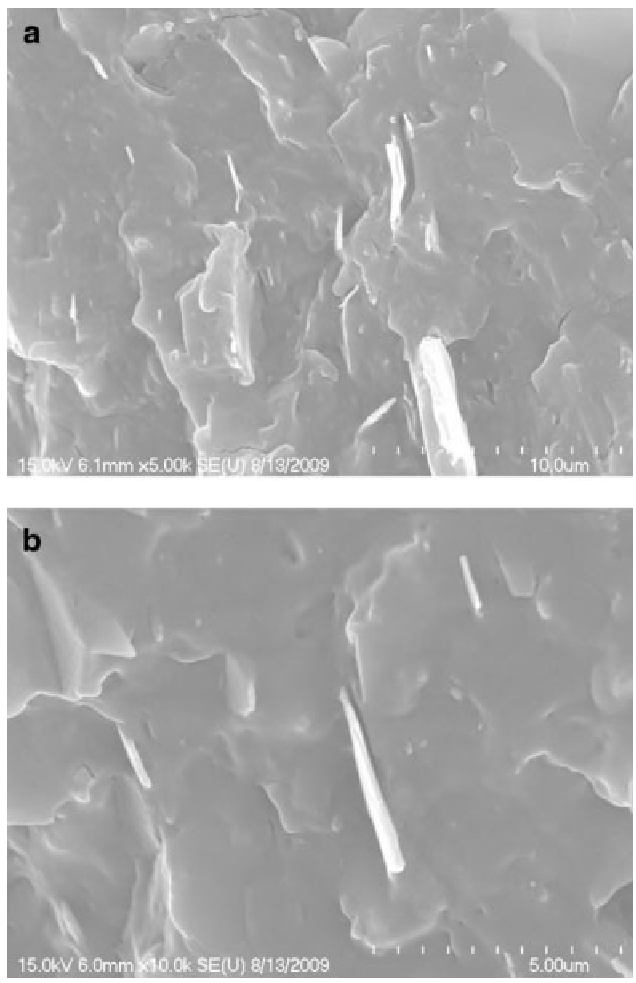

Figure 6 (a) SEM micrographs of PP/20%PTW/10%CPE/10%Talc composites (×5000), (b) SEM micrographs of PP/20%PTW/10%CPE/10%Talc composites (×10000).

different content of whisker reinforced PP. It is well-known that the incorporation of discontinuous fibers or whisker into matrix lead to a dramatic increase in melting viscosity. Talc is a kind of cheap inorganic filler used to reduce melt viscosity due to its unique characteristic. However, the cures of viscosity of the PP composite containing PTW are all below the curve of pure PP. The curve of PP/20%PTW/10% talc is slight lower than PP/20%PTW/0%talc on Figure 4, curve 3 and curve 5, respectively. And curve 1 with a relative lowest torque value can be explained by the composite system viscosity reached its lowest critical melt viscosity. PTW has good lubrication due to the perfection in crystalline structure is beneficial to reduce the PP composite's viscosity. Furthermore, a few content of low molecule substances like TiO_2 and K_2O (These two raw materials are made for PTW) are also helpful to reduce melt viscosity.

Thermal properties

Figure 5 shows the TG curves for different content whisker composite. The 5 and 10% loss temperature (T-5%, T-10%) for the composite are listed in Table III. This table reveals that containing 20 w/w% PTW and 10 w/w% talc leading to an increase in T-5% from 376.9 to 394.7°C. There is no dramatic increase because of the decomposition of CPE. T-10% of composite is improved obviously when containing 20 w/w% PTW and 10w/w% talc. The PP/20%PTW/10%Talc composite's T-5% is 394.7°C, while the PP/20%PTW/0%Talc composite's T-5% is 375.2°C. Talc also plays a synergist role in improving thermo oxidative stability.

Morphology

Figure 6 shows the morphology of PP/20%PTW/10%CPE/10%Talc composite viewed parallel to the flow direction. It can be clearly seen that almost all the whisker are embedded in the matrix with a certain orientation. This may be due to a good interfacial interaction between the modified whisker and PP matrix.[13]

CONCLUSIONS

The incorporation of whisker and talc into PP lead to increase in modulus, flexural strength, impact strength, and heat-resistance property. The tensile strength of PP composite is slight lower than PP. However, the Young's modulus curve of these composite is below the Tsai-Halpin equation. Moreover, notched impact strength initially increase with whisker content up to 10 wt %, thereafter begin to decrease when the whisker content reaches 30 wt %. The torque value reveals PP composite has a lower viscosity due to the lubrication of whisker and talc. SEM morphology shows a good interfacial interaction between the modified whisker and PP matrix. Talc plays a synergistic role in proving mechanical properties, heat-resistance, and reducing cost.

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