Wollastonite and talc reinforced polypropylene hybrid composites: Mechanical, morphological and thermal properties

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Abstract
This study focused on evaluating the mechanical, thermal, and morphological properties of polypropylene (PP) hybrid composites containing two different inorganic mineral fillers, namely wollastonite (WO) and talc. The composites were prepared by melt mixing process using a twin screw extruder and an injection molding machine. All composites contained a constant filler loading at 20 wt% with varying WO/talc weight ratios (20/0, 15/5, 10/10, 5/15, and 0/20). Melt flow index (MFI), mechanical properties (impact strength and tensile properties), heat distortion temperature (HDT) fractured surface morphology, and thermal behaviors of the resulting composites were investigated. The results revealed an enhancement in the MFI, HDT, impact strength, Young’s modulus, crystallization temperature, melting temperature, and degree of crystallinity with a decline in the elongation at break and a small increase in the tensile strength of the composites compared to those of the pure PP. These were according to the lubricating effect (increased flowability), reinforcing effects (increased mechanical properties), barrier properties (increased HDT and melting temperature), and nucleating effect (increased crystallization temperature and crystallinity) of the fillers.

1. Introduction

Polypropylene (PP) is one of the most versatile and important commodity plastics [1-3]. In addition to the conventional applications, PP can also be widely employed as fibers and engineering plastics due to its excellent balance of mechanical, thermal, chemical, and electrical properties. The major users of PP are related to the packaging industries, household appliances, electrical devices, automotive industries, ropes, upholsteries, constructions, etc., because PP has several beneficial and desirable properties, such as light weight, good stiffness, high tensile and flexural strength, good chemical, fatigue, thermal and electrical resistances, easy processability, and recyclability [1-7]. Nevertheless, PP has been found to suffer from some shortcomings, including poor toughness and notched impact resistance especially at low temperature, which may be due to its relatively high glass transition temperature ($T_g \sim -10^\circ C$ to $0^\circ C$) and crystallized ability that generally forms large spherulites, leading to the presence of voids at the spherulite boundaries and the reduction in its toughness and impact resistance [5,8-10]. However, the consumption of PP over the years has been very high and continuously increased, mainly owing to a large variety of available added fillers, and the steady improvement of its property profiles in all fields (academia and industry) [11]. Use of inorganic mineral fillers for preparing polymer composites is a straightforward and convenient method for reducing the cost of plastic products and also improving some properties of polymers, especially mechanical and thermal properties, such as tensile strength, stiffness, tear strength, abrasion resistance, heat distortion temperature (HDT), flame retardancy, and thermal stability [2,6,7,11-16].

A hybrid composite can be referred to a multi-phase polymeric material, consisting of two or more different types of reinforcing material in a polymer matrix or a single reinforcement in a polymer blend matrix [17]. It has been proved to receive a lot of interest as it combines the desirable properties of different materials. For example, short-fiber of eucalyptus kraft pulp/talc [17], wollastonite (WO)/glass fiber [18], calcium carbonate (CaCO₃)/mica [19], CaCO₃/ talc [19-21], and wood flour/talc [22] were added and integrated into either PLA or PP matrix. Their property profiles were found to be much different from those of the original polymers and the composites of individual reinforcing component. Hybrid composite can offer a better balance in mechanical and thermal properties than the non-hybrid one. In addition, it is beneficial to reduce the production cost by replacing the more expensive filler with a cheaper one. The final properties of the hybrid composites depend not only by the types and geometries of the reinforcements but also by the interaction between the polymer matrix and the fillers and by the morphology formed during processing [11]. This work demonstrated a comprehensive study on the PP-based hybrid composites with two different types of inorganic mineral fillers, namely WO and talc in an effort to improve some mechanical and thermal properties of PP, which would be useful for specific applications.
WO (CaSiO₃), a naturally occurring mineral that exists as aggregates of acicular (needle-shaped) crystals with high aspect ratio (L/D = 10-20) [23] (Figure 1(a)). It is a low cost industrial filler, containing about 48.3% CaO and 51.7% SiO₂ with a trace amount of Al, Mn, Mg, Fe, K, and Na [21]. Recently, WO has been used as a nonhazardous anisotropic reinforcement for replacing asbestos and glass fiber [23-26], and also other high-price fillers. WO utilized in polymer industries has high chemical purity, low health hazard, good chemical stability, high level of whiteness and hardness (Moh’s hardness 4.8), and low coefficient of thermal expansion [6,17,24-27].

Talc is a clay mineral, having a chemical formula of Mg₃Si₄O₁₀(OH)₂ with lamellae or platelets structure (Figure 1(b)) [14,16,17,19-21,28]. Naturally, Si can be substituted by a small amount of Al or Ti, and Mg by a small amount of Fe, Mn, Al and Ca [16,28]. Talc in a fine powdered form can be used as an important ingredient in the production of ceramics, rubbers, plastics, paints, cosmetics, textile, and paper [28]. Talc has been found to enhance the mechanical properties of plastics by increasing tensile and impact strength, stiffness, and hardness [28]. Talc can be used as a nucleating agent and dimensional stabilizer for PP or as a filler to reduce the production cost [1,3]. Due to its hydrophobicity, talc is easily incorporated into PP without the use of a chemical surface treatment, which allows a strengthening effect to the obtained composites [1,3]. However, either compatibilizer or surface treatment of talc may be necessary for dispersion of the very fine particles at high loading level to hinder its agglomeration and to ensure stronger adhesion at the matrix/filler interfaces [1,3]. Talc is often combined with other minerals such as mica [19], CaCO₃ [19-21], WO [29,30], kaolin clay [31,32], and zeolite [33] to improve the mechanical and thermal properties of various thermoplastics.

In this study, the hybrid composites were assigned to consist of a constant loading level of fillers at 20 wt% with varied WO/talc blend ratios. The mechanical, morphological, and thermal properties of the resulting products were comparatively investigated.

2. Experimental

2.1 Materials

PP (POLIMAXX 1100 NK), a homopolymer for injection molding process, having a melt flow index (MFI) of 11 g·10 min⁻¹ (230°C/2.16 kg) and a density of 0.9 g·cm⁻³ was supplied as pellets by IRPC Public Company Limited. The WO (HJ-2000) with a density of 2.85 g·cm⁻³, a particle size of 5 μm to 10 μm, and an aspect ratio of 10 to 20 was obtained from H&J Mineral Fiber Technology Co. Talc (No. 2, 325 mesh) manufactured by Haichen Minchem Co., Ltd, containing about 54% to 55% SiO₂ and 33% to 34% MgO with a trace amount of CaO, Fe₂O₃ and Al₂O₃ (as mentioned in data sheet of the company) was kindly donated by Rungroj Fiberglass Part., Ltd. All ingredients were used as received.

2.2 Composite preparation

Before processing, WO and talc were separately oven-dried at 100°C for 8 h to remove the absorbed moisture. In each composite, a total mineral loading in the PP matrix was held constant at 20 wt%. Five different WO/talc weight ratios (20/0, 15/5, 10/10, 5/15 and 0/20) were melt mixed with PP on a co-rotating twin-screw extruder (DTE-D16L512, Charoen TUT Co., Ltd., Thailand), having a 15.75 mm screw diameter and 32 L/D ratio, operated under a temperature profile of 145, 170, 180, and 180°C from the feed zone, compression zone, metering zone, and die zone, respectively, using a screw speed of 60 rpm. After that, the extrudates were pelletized, dried at 80°C for 8 h, and then injection molded into the standard impact and tensile test specimens at a melt temperature of 190°C to 200°C using an Arburg Allrounder 470C (Germany).

2.3 Characterization of the samples

2.3.1 Melt flow index

MFI measurement of the pure PP and its composites with WO and/or talc was conducted on an Instron melt flow tester (Ceast MF20, Italy) at 230°C under a 2.16 kg weight according to ASTM D1238.

2.3.2 Notched izod impact strength

The notched Izod impact test was carried out on a specimen with dimension of 12.7 x 63.5 x 3 mm³ according to ASTM D256 using an impact tester (Ceast 9709, Italy) with a hammer energy of 2 J.

2.3.3 Tensile test

The tensile test was performed on a standard dumbbell-shaped specimen according to ASTM D638 (Type I) using a universal testing
machine (Hounsfield H 50 KS, UK) with a 10 kN load cell and a crosshead speed of 50 mm·s⁻¹. The value of each property was obtained from an average of at least five specimens for each composition.

### 2.3.4 Morphology

The morphology of the impact fractured surface was observed by a scanning electron microscopy (SEM, JEOL JSM-5410LV, Japan) at an accelerated voltage of 15 and 20 kV, respectively. Prior to observation, platinum was sputter coated on the specimen for electron conductivity.

### 2.3.5 Differential scanning calorimetry analysis

Thermal measurement was determined using a DSC analyzer (Netzsch DSC 200 F3, Germany) under a nitrogen atmosphere with a gas flow rate of 60 mL·min⁻¹ throughout the experiment. About 10 mg of sample was heated from 0 to 250°C (first heating) and held isothermally for 2 min to erase any previous thermal history of the material and then cooled down to 0°C (cooling). The sample was then reheated to 250°C (second heating) and cooled down to 0°C. All measurements were conducted at the same heating/cooling rate of 10°C·min⁻¹. The obtained DSC thermograms exhibited crystallization temperature (T_c), melting temperature (T_m), enthalpy of crystallization (ΔH_c), and melting enthalpy (ΔH_m), while the degree of crystallinity (χ_c) for samples was determined according to the following equations:

\[
χ_c(\%) = \frac{ΔH_c/ΔH_m w}{100}
\]

\[
χ_o(\%) = \frac{ΔH_o/ΔH_m w}{100}
\]

where ΔH_m is the heat of fusion for 100% crystalline of PP (207 J·g⁻¹) [2,3,6,7], and w is the weight fraction of each component in the sample.

### 2.3.6 Heat distortion temperature

For the HDT test, a constant bending load of 1.82 MPa was applied at the center of a rectangular bar sample (13 × 127 × 3 mm³) which was placed in a silicone oil bath of the heat deflection tester (Ceast, Italy), according to ASTM D648 (Method A). The temperature was increased at a rate of 2±0.2°C·min⁻¹ until the specimen deflected 0.25 mm.

### 3. Results and discussions

#### 3.1 Melt flow index (MFI)

The MFI values of the pure PP and its binary composites and ternary hybrid composites with WO and talc are presented in Table 1. The values were obtained at melt temperature of 230°C and piston load of 2.16 kg. The MFI is an important parameter that represents the rheological behavior and processability of the polymers and also correlates with the final product properties [34]. The addition of inorganic mineral fillers to thermoplastic polymers often increases the viscosity and decreases the MFI of the composites owing to the rigidity of mineral particles that restricts flowability of polymer melt [35]. However, all the prepared PP-composites showed an unexpected increase in the MFI over the pure PP. This indicated a better molecular movement of the PP chains according to the poor interfacial interaction between the fillers and PP and the surface lubricity of these two fillers that partially ignored their rigidity [36]. The low coefficient of friction of the fillers relates to the long needle shape of the WO crystal and the weak Van der Waals force between the talc layers [1]. Besides, the MFI of the composites was found to decrease gradually along with higher talc loadings from 0 wt% to 20 wt% in the formulations, indicating the higher mobility restriction of the PP chains by the talc platelets. However, the MFI of the prepared PP-composites in the range of 10 g·10 min⁻¹ to 12.3 g·10 min⁻¹ is still in an appropriate range for the general injection molding of PP [37]. This suggested that the addition of WO, talc and their combination in the evaluated range (20 wt%) had no influence on the processability of the resulting composites.

#### 3.2 Mechanical properties

The notched Izod impact strength and tensile properties (Young's modulus, elongation at break, and tensile strength) of the investigated samples are presented in Figure 2 and Table 2. It is seen that the impact strength of pure PP (94.5 J·m⁻¹) was lower than that of all the prepared composites (102.6 J·m⁻¹ to 113.4 J·m⁻¹), suggesting that the addition of WO, talc and their combination at 20 wt% to PP improved the toughness over the whole composition range. In addition, the composite with solely WO exhibited the highest impact strength, while that with only talc exhibited the lowest. This may be due to the fine acicular WO particles provided much larger specific surface area and also greater interaction and wettability with the PP matrix than the plate-like talc particles, and hence allowing a better dispersion and stress transfer across the phases of the materials, and thus the energy required for breaking the impact test specimen was subsequently enhanced. Therefore, higher content of talc in hybrid composites led to a gradual decrease in the impact strength and so the 80/15/5 (w/w/w) PP/WO/talc hybrid composite exhibited the highest impact strength. In the case of Young’s modulus, the incorporation of rigid mineral fillers into polymers generally increases the modulus of composites. This is mainly because of the higher stiffness of fillers over the polymers [21]. Thus, the modulus of all resulting composites (2166-2668 MPa) was noticeably higher than that of the pure PP (1148 MPa). However, the Young’s modulus of all composites was slightly different. It was also found that as the stiffness of the composites increased, the elongation at break continuously decreased along with increasing talc loadings. This is because of the larger barrier properties of the talc platelets over the WO acicular particles [31]. Moreover, the tensile strength of all composites (34.5 MPa to 38.3 MPa) was found to be slightly higher than that of the pure PP.

<table>
<thead>
<tr>
<th>Sample PP/WO/talc</th>
<th>MFI (g·10 min⁻¹)</th>
<th>HDT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0/0</td>
<td>9.5 ± 0.4</td>
<td>63.5 ± 1.4</td>
</tr>
<tr>
<td>80/20/0</td>
<td>12.3 ± 0.7</td>
<td>73.2 ± 1.2</td>
</tr>
<tr>
<td>80/15/5</td>
<td>11.8 ± 0.4</td>
<td>76.0 ± 1.5</td>
</tr>
<tr>
<td>80/10/10</td>
<td>10.7 ± 0.3</td>
<td>76.5 ± 2.5</td>
</tr>
<tr>
<td>80/5/15</td>
<td>10.4 ± 0.5</td>
<td>78.2 ± 2.5</td>
</tr>
<tr>
<td>80/0/20</td>
<td>10.0 ± 0.6</td>
<td>78.7 ± 2.5</td>
</tr>
</tbody>
</table>
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Figure 2. Mechanical properties of the pure PP and composites in terms of (a) impact strength, (b) Young’s modulus, (c) elongation at break, and (d) tensile strength.

Table 2. Mechanical properties of the samples.

<table>
<thead>
<tr>
<th>Sample PP/WO/talc (w/w/w)</th>
<th>Impact strength (J·m⁻¹)</th>
<th>Young’s modulus (MPa)</th>
<th>Elongation at break (%)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0/0</td>
<td>94.5 ± 2.6</td>
<td>1148 ± 61</td>
<td>41.3 ± 1.0</td>
<td>33.3 ± 0.6</td>
</tr>
<tr>
<td>80/20/0</td>
<td>113.4 ± 3.4</td>
<td>2166 ± 63</td>
<td>32.4 ± 1.3</td>
<td>35.5 ± 0.5</td>
</tr>
<tr>
<td>80/15/5</td>
<td>107.0 ± 6.8</td>
<td>2269 ± 167</td>
<td>32.0 ± 1.0</td>
<td>38.3 ± 1.3</td>
</tr>
<tr>
<td>80/10/10</td>
<td>105.7 ± 5.0</td>
<td>2416 ± 125</td>
<td>28.4 ± 1.6</td>
<td>34.5 ± 1.2</td>
</tr>
<tr>
<td>80/5/15</td>
<td>104.5 ± 5.5</td>
<td>2517 ± 146</td>
<td>26.7 ± 1.8</td>
<td>35.3 ± 1.3</td>
</tr>
<tr>
<td>80/0/20</td>
<td>102.6 ± 2.6</td>
<td>2668 ± 175</td>
<td>24.4 ± 1.3</td>
<td>34.5 ± 1.6</td>
</tr>
</tbody>
</table>

(33.3 MPa). This could be mainly because the high aspect ratio filler particles were aligned along the injection flow direction, and were also dispersed parallel to the tensile force. However, the surface lubricity of the fillers and the weak interfacial adhesion between the PP and fillers led to a small increase in the tensile strength of the composites. Among the five composites, that with 15 wt% WO and 5 wt% talc also imparted an optimum tensile strength (38.3 MPa).

3.3 Morphology

Figure 3 shows the SEM images (1,000× magnification) of the impact fractured surface of the pure PP and its composites. The pure PP exhibited a smooth surface with a few low ridges (Figure 3(a)) according to its relatively low toughness. The dispersion of WO and talc in the PP matrix was also evaluated visually by SEM images, as can be seen in Figures 3(b-f). The 80/20 (w/w) PP/WO composite showed the embedded WO particles within the PP matrix and there was no pullout of the filler particles on the fractured surface (Figure 3(b)). The ends or tips of the acicular WO particles were observed as white dots, distributing well throughout the PP surface, suggesting the particles alignment along the injection flow direction, which was thus responsible to the increased impact strength, as previously mentioned. On the contrary, the 80/20 (w/w) PP/talc composite revealed large talc platelets detached from the PP matrix during impact testing, and so leaving some big cavities on the fractured surfaces (Figure 3(f)). This may be due to the weak or insufficient adhesion between filler and polymer matrix, which was then limited the increase in the impact strength of the composites.

Moreover, the SEM images of the hybrid composites with three different WO/talc weight ratios (Figures 3(c-e)) revealed the combination morphology of WO and talc particles on the specimen fractured surfaces in a dose-dependent manner. Thus, the mechanical properties of composites greatly depended not only on the size and shape of the fillers but also on the filler dispersion and sample morphologies.
3.4 Heat deflection temperature

To measure thermal resistance, HDT was determined and the values of the evaluated samples are also listed in Table 1. As can be seen, the HDT of the composites was amended by 9.7°C to 15.2°C with the addition of 20 wt% inorganic fillers (WO, talc and their blends) to the PP. The HDT values were gradually increased with increasing talc loadings from 0 to 20 wt% compared to that of the pure PP. This finding was due to the plate-like structure of talc that provided a greater tortuous path length within the matrix than the needle-shaped WO fibers, leading to the higher thermal barrier effect. Therefore, the partial replacement of WO by talc in the hybrid composites caused an increment in the HDT in a talc-dose-dependent manner. Moreover, the increased HDT may also be related to the high modulus of the resulting composites that obstructed the deflection at high temperature [36].

3.5 DSC analysis

To investigate the thermal and crystallization behaviors in terms of the $T_c$, $T_m$, $\Delta H_c$, $\Delta H_m$, and $\chi_c$, DSC analysis was performed by measuring the heat flow of samples as a function of temperature. The first heating scan was carried out to erase the previous thermal history of the samples. Representative DSC cooling and second heating curves are shown in Figure 4, and the corresponding parameters are all summarized in Table 3. The pure PP exhibited an intense exothermic

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Figure 3. Representative SEM images (×1,000) of (a) PP and composites of (b) 80/20 PP/WO, (c) 80/15/5 PP/WO/talc, (d) 80/10/10 PP/WO/talc, (e) 80/5/15 PP/WO/talc, and (f) 80/20 PPhalc.
crystallization peak \( (T_c) \) at 111.4°C in the cooling curve (Figure 4(a)), suggesting that PP is a typical semicrystalline polymer with a high tendency to crystallize due to its regulated isotactic structure. The \( T_c \) peaks of the composites with WO, talc and their blends were also clearly seen in the range of 120.7°C to 126.8°C. The increased \( T_c \) (9.3°C to 15.4°C) implied that the fillers acted as nucleating agent in the PP matrix. Besides, the \( T_c \) of PP in the composites was found to increase with increasing talc loading levels, indicating the stronger nucleating effect of the talc platelets, and so the PP spherulite size became smaller [38]. From Table 3, the \( \chi_c \) at the \( T_c \) peak of the samples was calculated from the \( \Delta H_m \) value using Equation 1. It is seen that the \( \chi_c \) of the pure PP (44%) was lower than that of the prepared composites (47.9% to 54.6%) due to the nucleating effect of the fillers, showing the highest \( \chi_c \) for the single PP/talc composite and the lowest for the single PP/WO composite. Moreover, the \( \chi_c \) of the hybrid composites increased with increasing talc content. This was due to the stronger nucleating effect of talc as mentioned above. From the second heating curve (Figure 4(b)), the endothermic melting peak \( (T_m) \) of the pure PP was visible at 162.8°C, while the characteristic melting peaks of all the composites were also clearly seen in the range of 164.7°C to 171°C. Moreover, the shift of the \( T_m \) to the higher temperature (2°C to 8.2°C), indicating that the addition of WO, talc and their combination to the PP had a positive effect on the \( T_m \) of the composites. The \( \chi_c \) can also be determined by dividing the \( \Delta H_m \) by \( \Delta H_{m1} \) as shown in Equation 2. The results showed a similar trend to the \( \chi_c \) derived from the \( T_c \) peak. The enhancement of \( \chi_c \) with increasing talc content was due to the same reason as mentioned above.

4. Conclusions

This work described how WO, talc and their combination were used as reinforcement in the PP single and hybrid composites. The influences of their weight fraction on the MFI, impact strength, tensile properties, morphology, HDT, and thermal and crystallization behaviors of the resulting composites were determined. The results of various properties were compared with those of pure PP and also with each other of single filler filled matrix. Increase in the MFI and HDT was attained for all the composites, indicating their higher flowability and thermal stability over the pure PP, respectively. Besides, the impact strength and Young's modulus of all the composites were obviously improved when using WO and talc as the reinforcements. Among the composites, the 80/20 (w/w) PP/WO single composite exhibited the highest impact strength (113 J·m⁻¹), while the 80/20 (w/w) PP/talc single composite exhibited the highest Young's modulus (2519 MPa). However, the hybrid composite of 80/15/5 (w/w/w) PP/WO/talc had a high toughness-stiffness balance with 111 J·m⁻¹ of impact strength and 2269 MPa of Young's modulus. Meanwhile, the incorporation of these fillers caused a small increase in the tensile strength, but at the expense of reducing the elongation at break. The DSC analysis revealed that all the evaluated samples exhibited \( T_c \) in the range of 111.4°C to 126.8°C during the cooling scan due to the crystallizability of PP and the nucleating effect of WO and talc for PP, as evident by the increased \( T_c \) and \( \chi_c \) of the composites compared to those of the pure PP. It was also found that the \( T_m \) of the composites was higher than that of the pure PP and also increased with increasing WO content, while the \( \chi_c \) increased with increasing talc loading levels.
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