



Mechanical properties and flame retardancy of surface modified magnesium oxysulfate ($5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$) whisker for polypropylene composites

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ARTICLE INFO

Article history:

Received 15 January 2018

Received in revised form

2 February 2018

Accepted 6 February 2018

Available online 9 February 2018

Keywords:

Magnesium oxysulfate

Surface modification

Mechanical properties

Flame retardant

ABSTRACT

Magnesium oxysulfate (MOS) whisker is considered as a promising inorganic material recently attracting a great attention for being used as a reinforcing filler for polymer composites due to high aspect ratio and extremely-low bulk density. In this study, the MOS was treated with 3-methacryloyloxypropyl-trimethoxy silane (MPS) via sol-gel condensation reactions, which successfully allowed melt mixing with polypropylene (PP) up to 30 wt% of MOS. The tensile strength at yield and modulus of the MOS/PP composites were substantially increased by 50.8% and 362%, respectively, when compared with the pristine PP. As a novel finding, the flame retardancy of MOS was proved by identifying water evolution at elevated temperatures giving out 9 wt% of water in 250–320 °C and 14 wt% in 350–420 °C in two steps. This work demonstrated that the MOS could be an excellent filler for PP not only increasing the mechanical properties in a great extent but also imposing flame retarding capability.

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1. Introduction

Magnesium oxysulfate ($5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$, MOS) whisker is inorganic fibrous crystals that is recently paid attention for as an alternative reinforcement filler to glass fibers in the development of polymer composites particularly in automobile industry [1,2]. The MOS whisker has a one-dimensional structure with an average length of 20–50 μm and diameter of 0.2–1.0 μm giving large aspect ratio (50–250) [2]. Compared with glass fibers, its unique geometry is considered to provide an excellent reinforcing capability particularly ensuring large-volume and rapid-production of composite

parts desirably in such processes as extrusion and injection molding. In addition, the bulk density of MOS is extremely low at 0.25 g/cm³ indicating that it hardly agglomerates in powder form seemingly stemming from its one-dimensional shape and strong electrostatic repulsive charge, which may well be greatly advantageous in storage, handling, and fabrication. However, MOS is hydrophilic in nature containing crystalline water and hydroxide groups and, thus, its utilization has been limited in those water-based composite materials like cement [3]. Using MOS with organic polymers like PP or other engineering plastics as a filler has not been intensively investigated yet, which requires the fundamental knowledge and database of processing-property-structure relationship of MOS-based polymeric composite materials.

Crystalline water and hydroxyl groups included in MOS make it almost impossible to be compatible with most organic polymer matrices. When the compatibility is poor with polymers, it is practically difficult to increase the filler loading content over 20 wt % in melt processing and the resulting composites usually contain

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Peer review under responsibility of The Chinese Ceramic Society.

tremendous amount of air pockets and interface defects in the final products [4–6]. In this sense, the surface modification converting hydrophilic nature of the MOS surface to hydrophobic nature is the key issue for the development of MOS-based composite materials [7]. When the filler surface becomes compatible with polymer matrices mechanical properties and long-term durability of composites can be greatly improved [8].

Various compatibilizers have been used for PP since it is intrinsically nonpolar and lacks compatibility with most fillers including whiskers, fibers, minerals and nanoplatelets [9–11]. Silane coupling agents have been commonly used in PP composites for the modification of inorganic fillers including glass fibers, silica, and aluminum nitride in order to improve the interfacial adhesion with the polymer matrix so that desired performance can be obtained [12–14]. The silane coupling agents that have been used for PP composites are the ones having organic functional group of methacrylate, amino, epoxy, etc. for different filler systems [15–17]. In the case of MOS in PP composites, the appropriate coupling agent has not been reported yet.

Flame retardancy of PP is usually required for various applications in automobile parts, stadium chairs, interiors, appliances, etc [18]. The flame resistance of PP can be improved by adding flame retardants most commonly magnesium hydroxide and aluminum hydroxide [19–21]. The hydroxide groups included in those inorganic flame retardants evolve water vapor at high temperatures through decomposition reactions [20,21]. The water vapor generated through the thermal dehydration of magnesium hydroxide or aluminum hydroxide serves to extinguish fires by preventing ignition [22]. However, it should be mentioned that the incorporation of such inorganic flame retardants usually degrades the mechanical performance of their composite materials. On the other hand, we believe that the MOS whisker used in this study could be an excellent flame retarding-material as well as a reinforcing filler in PP composites. One mole of MOS ($5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$) contains not only 3 mol of crystalline water but also 5 mol of water that can be generated from the hydroxides collectively resulting in 30.9 wt% of water in theoretical calculation. It is well comparable with commonly-used flame retardants. Therefore, MOS could be an ideal filler material that can not only increase the mechanical properties but also impose the flame resistance to the PP composites.

In this study, we used 3-methacryloyloxypropyltrimethoxy silane (MPS) to treat MOS in an aqueous solution. Afterwards, the PP composites were prepared by melt mixing with 10, 20, 30 wt% of silane-treated MOS whiskers using extrusion and injection molding processes. The developed MOS/PP composites were thoroughly investigated in terms of processing characteristics, mechanical properties and flame retardancy identifying the role of surface treatment of the silane coupling agent.

2. Experimental

2.1. Materials

The polymer matrix used in this study was PP (M1500, ethylene-propylene block copolymer, manufactured by LG Chemical, Korea). Magnesium oxysulfate (Fig. 1, $5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$, MOS) whisker was purchased from Ube Materials Industries, Japan. The MOS had an average length of 10–20 μm and an average diameter of 0.5 μm giving large aspect ratio (20–40). 3-methacryloyloxypropyltrimethoxy silane (MPS, 98%) was provided by Sigma Aldrich. Acetic acid (99.5%) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$, 95%) were purchased from Samchun, Korea.

2.2. Surface modification of MOS

Firstly, the silane aqueous solution was prepared by hydrolysis of silane coupling agent (MPS) in DI water. DI water was adjusted to pH 4 using acetic acid, and 0.5 wt% of the silane coupling agent (MPS) was added and hydrolyzed for 1 h at room temperature. The MOS powder was mixed with silane aqueous solution for 2 h at room temperature for the salinization of MOS. The ratio of MPS to MOS was controlled to 5 wt%. The MOS was washed with plenty of water, filtered, and dried at 110 $^{\circ}\text{C}$ in a vacuum oven for 3 h.

2.3. Preparation of MOS/PP composites

The pristine MOS and chemically-modified MOS were mixed with PP at 10, 20 and 30 wt%, respectively. Extrusion mixing was carried out at 200–210 $^{\circ}\text{C}$ using a twin-screw extruder (BA-19, Bautech, Korea, 40 L/D ratio), and injection molding was performed at 230 $^{\circ}\text{C}$ to prepare dumbbell specimens (Type I of ASTM D638) using an injection molding machine (Promat 40/SG25A, Sumitomo, Japan).

2.4. Characterization

The silicon content of the modified MOS was determined via X-ray fluorescence (XRF, S4, Bruker, Germany). ASTM D638 was applied to measure the tensile properties at a cross-head speed of 50 mm/min using a universal testing machine (WL2100, Withlab, Korea) with a load cell of 3000 N at room temperature. Five specimens were tested for each composite system, and the average was taken after eliminating the maximum and minimum values. The morphology of the MOS and MOS/PP composites was observed via scanning electron microscopy (SEM, Hitachi S-2140, Japan). The tensile specimens were immersed in liquid nitrogen and were fractured through abrupt bending to investigate the morphology and adhesion between matrix and fillers.

Differential scanning calorimetry (DSC) was performed in a nitrogen environment using a DSC 6100 system (Seiko instruments, Japan). The samples were heated to 220 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ and were kept for 10 min to remove the thermal history. The samples were then cooled to 30 $^{\circ}\text{C}$ at a controlled cooling rate of 10 $^{\circ}\text{C}/\text{min}$. After that, they were reheated from 30 $^{\circ}\text{C}$ to 220 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The endothermic and exothermic peaks were ascribed to the recrystallization temperature (T_c) in the cooling step and the crystalline melting temperature (T_m) in the second heating step, respectively. The heat of the recrystallization (ΔH_c) and the heat of the crystalline melting (ΔH_m) were also determined by integrating the area of crystallization and the crystalline melting peaks, respectively. The thermogravimetric analyses (TGA) were performed in a nitrogen environment using a TG/DTA7300 system (Seiko instruments, Japan), where the specimens were heated up to 1,000 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$.

Limited oxygen index (LOI) measurements were carried out using limited & temperature oxygen index tester (FT-LOI-404) according to the principle of ASTM D2863 standard. LOI was defined as the lowest oxygen concentration in the carrier gas flow at which full flaming combustion of the samples observed.

3. Results and discussion

3.1. Composition analysis of the untreated and MPS-treated MOS

Table 1 shows the levels of magnesium, sulfur, and silicon elements obtained via XRF measurements for the pristine MOS and MPS-MOS. The theoretical weight ratio of magnesium to sulfur (R_A) of MOS is 4.55, which can be validated by the XRF results to be 4.4

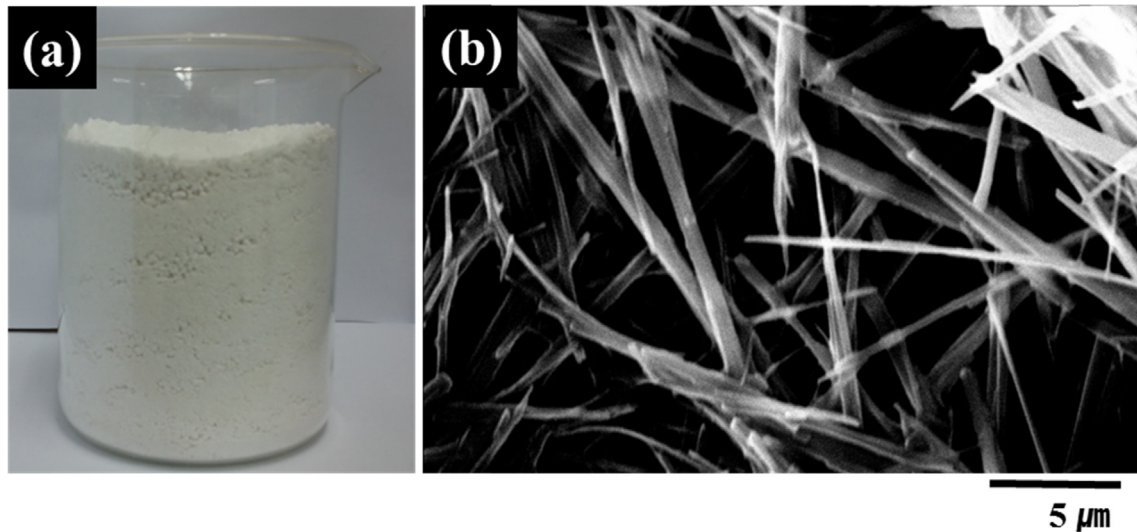


Fig. 1. Images of MOS: (a) MOS powder, and (b) SEM morphology of MOS.

Table 1

Atomic composition of Mg, S and Si of MOS and MPS-MOS by using XRF experiment.

Samples	Atomic weight % in MOS			Atomic weight ratio		W_{MPS} (g) ^a	W_{MPS} (%) ^b
	Mg	S	Si	R_A (W_{Mg}/W_S)	R_B (W_{Mg}/W_{Si})		
Untreated MOS	6.78	1.54	N/A	4.4 ^c	N/A	—	—
MPS-MOS	15	3.15	0.267	4.76 ^c	56.2	23	4.9

^a Weight of MPS in 1 mol of MOS.

^b Weight (%) of MPS.

^c Theoretical molecular weight ratio is 4.55.

and 4.76 for the untreated MOS and MPS-MOS, respectively. The amount of MPS (W_{MPS} %) in the MPS-MOS specimen can be calculated using the measured weight of Mg and Si (or the ratio of Mg to Si, R_B) because each represents the relative weight of MOS and MPS, viz:

$$W_{MPS}\% = \left(\frac{M_{W, MPS} \times W_{Mg}}{M_{W, MOS} \times A_{W, Si}} \right) \times R_B \times 100 \quad (1)$$

where the molecular weight of MPS ($M_{W, MPS}$) is 248 g/mol, the molecular weight of MOS ($M_{W, MOS}$) is 465.8 g/mol, the weight of magnesium (W_{Mg}) in 1 mol of MOS is 145.8 g, and the atomic weight of silicon ($A_{W, Si}$) is 28 g. Using Eq. (1) and the measured weight ratio of MPS-MOS specimen ($R_B = 56.2$) in Table 1, the amount of silane (MPS) incorporated in our MPS-MOS specimen can be calculated as 4.9% which agrees well with the silane concentration prepared for the MOS treatment condition at 5 wt%.

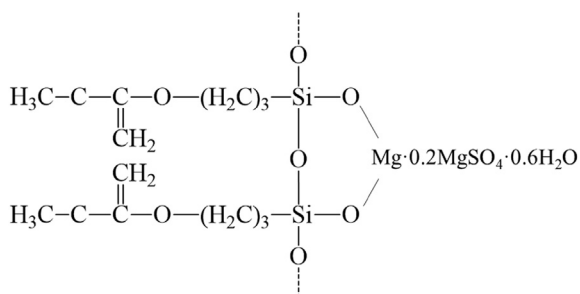


Fig. 2. Schematic of chemical bonds of the MPS-MOS grafted via sol-gel condensation.

Fig. 2 shows a schematic of the reaction between MPS and MOS to form Si-O-Mg bonds on MOS surfaces through the sol-gel condensation reactions of silanol and hydroxyl groups under heating [23].

3.2. Mechanical properties

Fig. 3 shows the tensile stress–strain curves of MOS/PP composites plotted for different MOS and MPS-MOS contents. With the

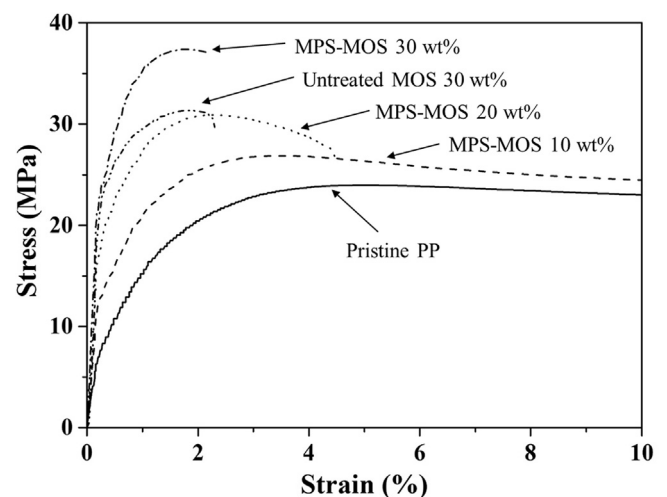


Fig. 3. Stress–strain curve of MOS/PP composites and pristine PP at a cross-head speed of 50 mm/min.

addition of MOS and MPS-MOS, the slope of the PP composites increases sharply relative to that of pristine PP, corresponding to an increase in stiffness of PP matrix. While the pristine PP used in this study shows a ductile behavior giving the ultimate strain at 241%, which is not seen in Fig. 3, the MOS-loaded PP composites; untreated MOS 30 wt%, MPS-MOS 20 wt%, and MPS-MOS 30 wt% represent a relatively-brittle behavior giving ultimate strains at 2–4%. The ultimate strain of The MPS-MOS 10 wt% composite is about 33% and it can be considered as a relatively-ductile behavior. Since the formation of rigid interface between MOS filler and PP matrix hinder the mobility and flexibility of PP chains, the increase in filler loading leads to decreased ductility of the composites. Furthermore, comparing untreated MOS and MPS-treated MOS, the MPS-MOS/PP composite (30 wt% of MPS-MOS) has higher mechanical stress than that of the untreated MOS. The presence of MPS on the surface of MOS reduces significantly the hydrophilicity. This might be due to the formation of intermolecular bonding between filler and PP matrix, which facilitates the stress transfer between the matrix and filler, leading to an increase in the mechanical stress of the composite.

Fig. 4 plots the tensile strength at yield, elongation at break and tensile modulus of the MOS/PP composites as a function of the MOS content. With the addition of MOS and MPS-MOS, tensile strength at yield increases gradually relative to that of pristine PP while the elongation at break decreases (Fig. 4a). The tensile strength at yield of the pristine PP is 24.8 MPa, and it increases up to 37.4 MPa for 30 wt% of MPS-MOS, corresponding to an increase of 50.8% (Fig. 4a). The tensile strength at yield of the PP composite containing 30 wt% of untreated MOS is 32.1 MPa, corresponding to an increase of

29.4% when compared to pristine PP (Fig. 4a). Thus, the tensile strength at yield of the PP composites containing 30 wt% of MPS-MOS is 16.5% higher than that of untreated MOS. The elongation at break decreases from 241% for pristine PP to 1.9% for 30 wt% of untreated MOS (Fig. 4a). With the addition of MOS and MPS-MOS, tensile modulus increases sharply from the pristine PP (Fig. 4b) as already seen in Fig. 3. The tensile modulus of the pristine PP is 1330 MPa, and it increases up to 4820 MPa for 30 wt% of MPS-MOS corresponding to 362% of increment (Fig. 4b). The tensile modulus of PP composite containing 30 wt% of untreated MOS is 4110 MPa, corresponding to an increase of 309% when compared to pristine PP. As an effect of MPS treatment, the tensile modulus of the MPS treated MOS composite is 17.3% higher than the untreated one for 30 wt%. It demonstrates that the silane coupling agent used in this study acts as an effective surface modifier, enhancing compatibility between the polymer matrix and MOS. As reported in several investigations [24–26], the interfacial adhesion of PP matrix and hydrophilic MOS fillers is likely to increase by the MPS silane coupling agent that could convert the inorganic surface from hydrophilic to hydrophobic nature. Overall, the MPS-treated PP composite provides a great improvement of mechanical properties in both modulus and strength over 362 and 50.8%, respectively.

3.3. Morphologies

Fig. 5 shows the fractured surfaces of the transverse-to-flow sectional areas of the MOS/PP composite specimens. The white fibrous particles in the composite specimens are MOS, and the holes show that the fillers are pulled out of the fracture surfaces. According to the filler content, the composites containing 30 wt% of untreated MOS and MPS-MOS has more holes than that containing 10 wt%. The fractured surfaces of the composites containing 10 and 30 wt% of untreated MOS (Fig. 5a and b) show many holes pulled out of the fracture surface. The MPS-MOS/PP composites (Fig. 5c and d) show that the holes pulled out of the fracture surface are substantially decreased exhibiting much less holes than untreated MOS composites. The pulled-out holes are likely to represent poor adhesion between the polymer matrix and the filler [27–29], suggesting that the MPS treatment of the MOS improves the interfacial adhesion in composites, all of which is supported by the results of the mechanical properties shown in Fig. 4.

Fig. 6 shows orientation and dispersion of the whiskers in injection-molded PP composite specimen (30 wt% of MPS-MOS). The transverse and longitudinal sections of the injection molded specimens are presented in Fig. 6a. In Fig. 6b and c, it can be seen that the MPS-MOS is aligned in the melt flow direction of the polymer during injection molding due to the large aspect ratio of MOS. Since MOS has a large aspect ratio of 20–40 (see Fig. 1), the flow-induced orientation is not seemingly avoidable for composite processing through injection molding. Furthermore, the whiskers are well dispersed in the PP matrix. The good dispersion of the fillers effectively increases the mechanical properties of the polymer matrix [30]. The fiber orientation in the melt flow direction usually results in a higher strength and modulus in the aligned direction for the polymers and composites [31,32]. It may suggest that the alignment of the MOS in the PP matrix could lead to an additional increment in the tensile strength at yield and modulus by processing conditions.

3.4. Thermal properties

Fig. 7 shows the DSC thermograms of the MPS-MOS/PP composite specimens (see also Table 2). Second heating and first cooling curves are presented in Fig. 7a and b, respectively. The crystalline melting temperature (T_m) of both the pristine PP and MPS-MOS/PP

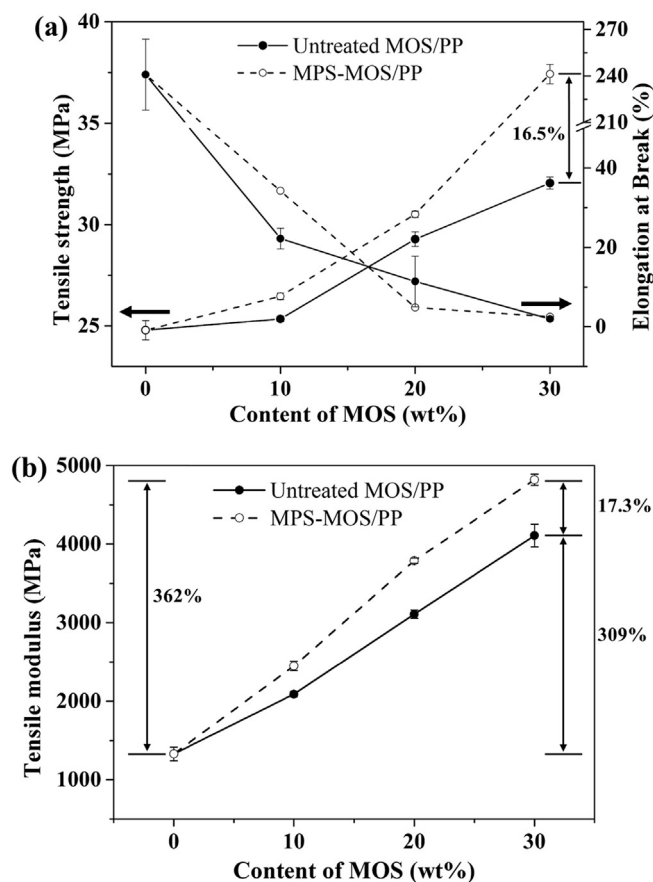


Fig. 4. Tensile properties of MOS/PP composites as a function of MOS content: (a) tensile strength at yield and elongation at break, and (b) tensile modulus.

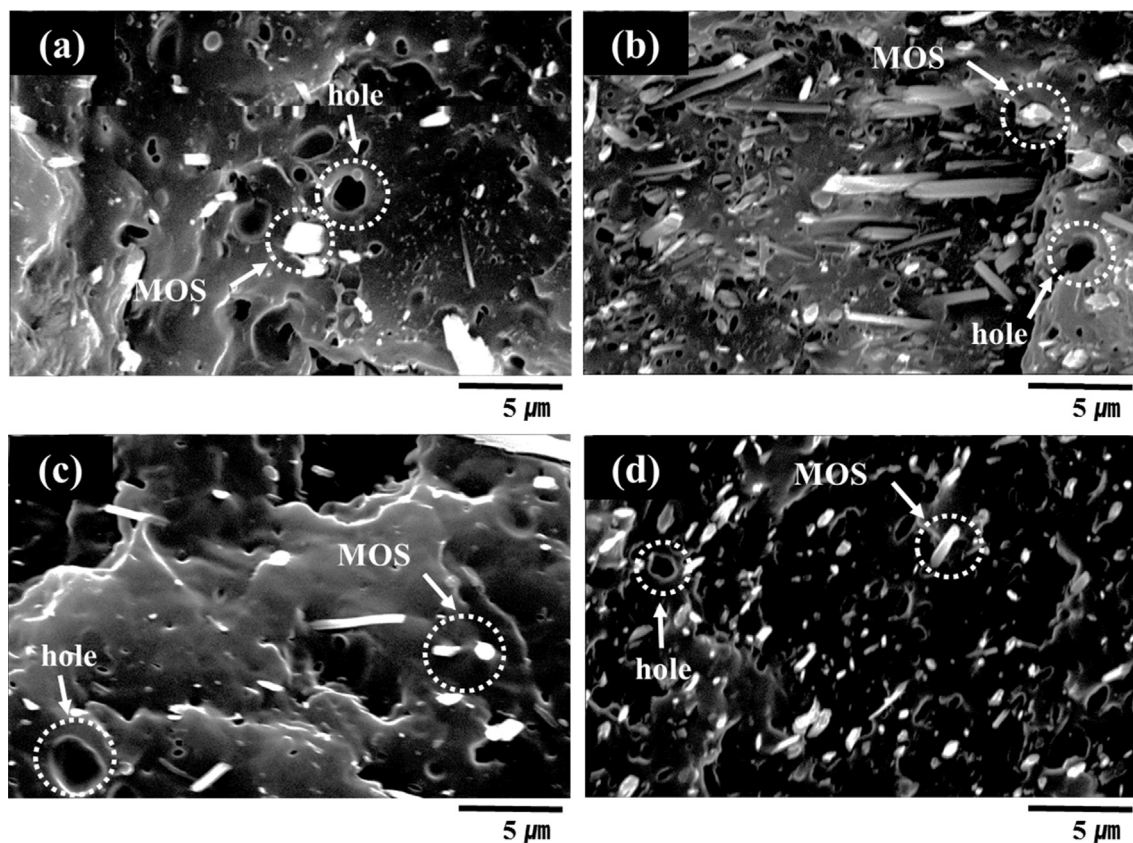
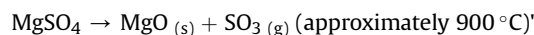
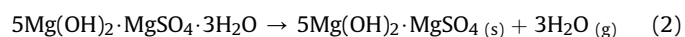


Fig. 5. SEM morphologies of the fractured surfaces of MOS/PP composite specimens: (a) Untreated MOS 10 wt%, (b) Untreated MOS 30 wt%, (c) MPS-MOS 10 wt%, and (d) MPS-MOS 30 wt%.

composites is about 167.4 ± 0.6 °C by the standard deviation, which indicates that the MOS does not affect the crystalline melting temperatures (Fig. 7a). However, the recrystallization temperature (T_c) changes with the addition of MOS giving 113.8 °C for pristine PP and 117.6 °C for 30 wt% MPS-MOS/PP (Fig. 7b). In addition, the heat produced during crystalline melting (ΔH_m) and during recrystallization (ΔH_c) of the specimens increase compared with those of pristine PP (Table 2). The recrystallization temperature is measured during cooling, and thus the increased T_c would represent the accelerated recrystallization. It appears that the MOS facilitates the crystallization of PP seemingly by acting as nucleating sites. The nucleation activity of MOS has been associated with the unique shapes and surface activity of MOS. With the thin MOS filler it has been demonstrated that nucleation occurs at the whiskers edges, which agrees with previous finding observed with fillers acting as nucleating sites [33,34].

Fig. 8a compares the TGA thermograms of the MOS to those of magnesium hydroxide ($Mg(OH)_2$), a flame retardant that is commonly-used. MOS has three crystalline water molecules and magnesium hydroxide ($5Mg(OH)_2$), which can produce five water molecules upon decomposition at elevated temperatures. The decomposition reaction mechanism of MOS is as follows:



In comparison, the decomposition reaction mechanism of

$Mg(OH)_2$ is as follows:



As can be seen in Fig. 8a, the first weight loss stage, 9 wt%, of the MOS appears in 250–320 °C, which corresponds to the release of the three crystal water molecules in Eq. (2). The second weight loss, 14 wt%, of the MOS appearing in 350–420 °C corresponds to the thermal dehydration of $5Mg(OH)_2$ to produce five water molecules. Magnesium hydroxide ($Mg(OH)_2$), on the other hand, produces water molecules in a single decomposition stage between 320 and 420 °C complying with Eq. (3). As shown in Fig. 8a, the MOS and magnesium hydroxide release 23 and 28 wt% of water molecules, respectively, demonstrating similar fire extinguishing capability to magnesium hydroxide. It should be addressed that the MOS has two stages of water release, giving out water vapor earlier than magnesium hydroxide, and subsequently the flash over point of fire may be delayed in an efficient way.

Limited oxygen index (LOI) measures the ignition of fire, which is mostly influenced by the free radicals generated by the matrix materials or chemical retardants. Although there is no chemical retardants included in the MPS-MOS/PP composites, the LOI linearly increases with MOS contents in Fig. 8b. The flame retardancy of the developed MOS composites systems should be further investigated in terms of burning velocity, gas generation, char formation, etc. in the future.

4. Conclusions

The surface modification of the MOS improved the mechanical

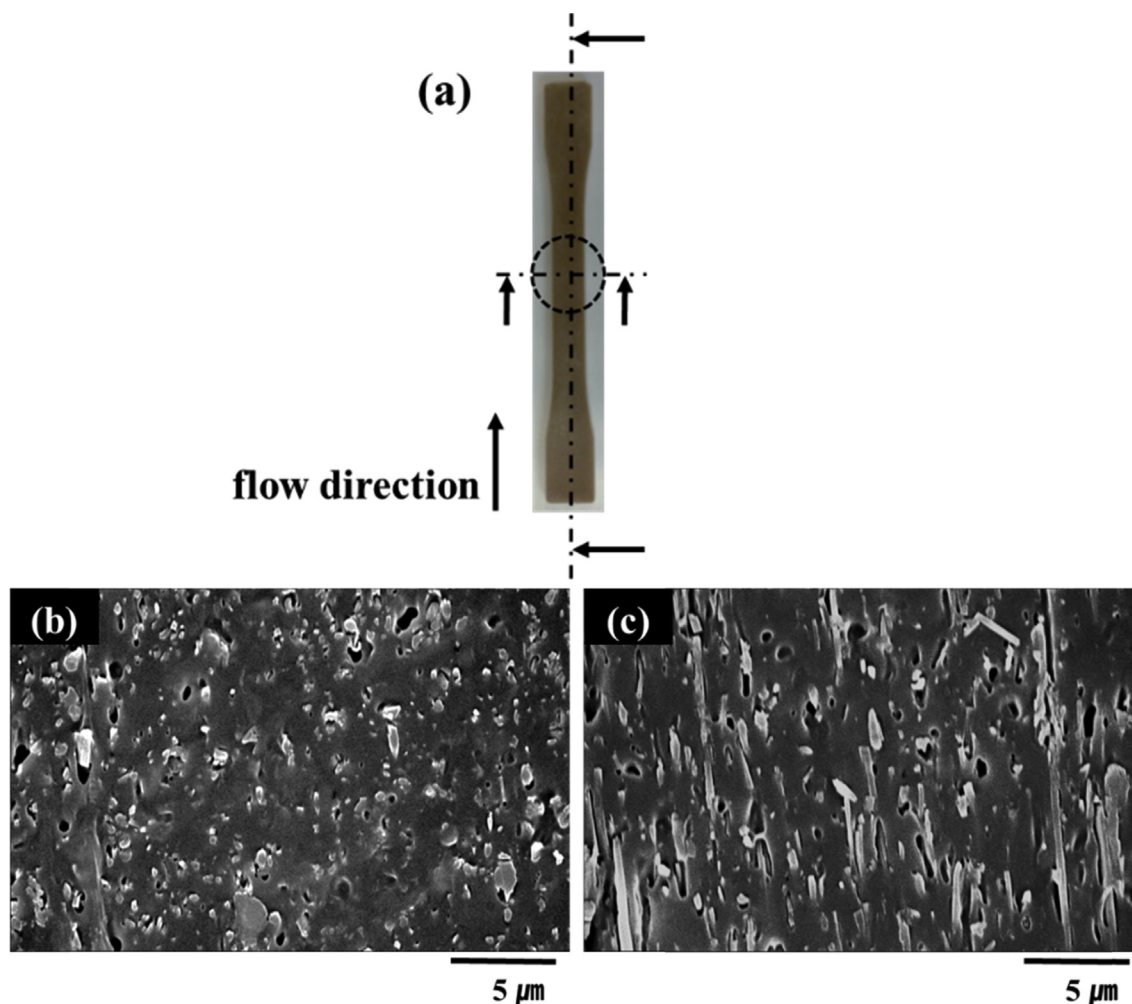


Fig. 6. Orientation and dispersion of the MPS-MOS whiskers at a high whisker content (30 wt%) in the MPS-MOS/PP composite specimen: (a) schematic of injection molded specimens in two directions, (b) transverse section and (c) longitudinal section.

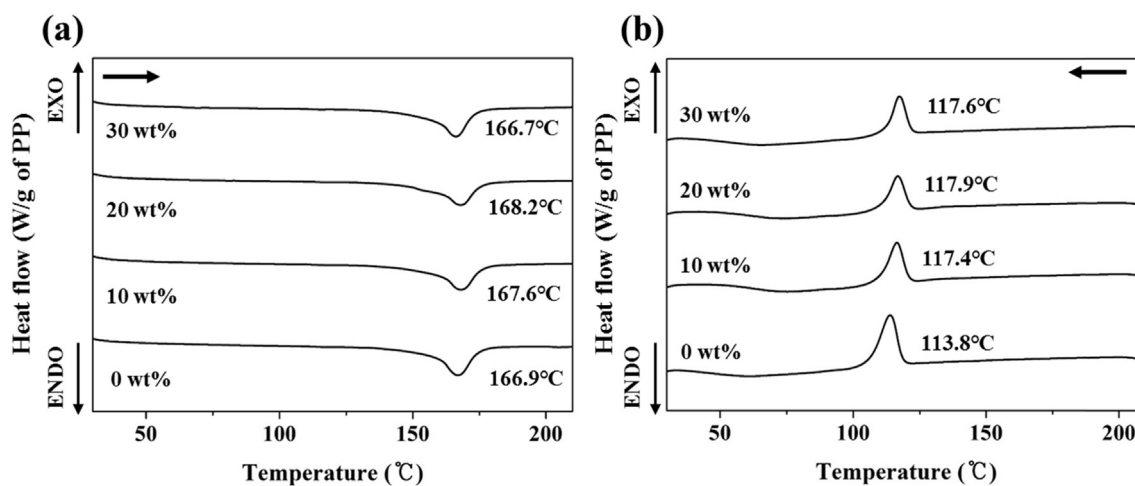


Fig. 7. DSC thermograms of MPS-MOS/PP composites according to different amounts of MPS-MOS measured at 10 °C/min: (a) second heating curves and (b) cooling curves.

properties of the PP matrix by improving the interfacial adhesion between the PP matrix and the MOS. It greatly improved the processing characteristics of MOS/PP composites allowing such a high loading of MOS up to 30 wt% and ensuring the injection molding

process. It also increased the tensile strength at yield and modulus of the MOS/PP composites accelerating the crystallization of PP by acting as nucleating sites. Furthermore, our work demonstrated that the MOS produces water molecules through a two-step weight

Table 2
Summary of thermal properties of MPS-MOS/PP composites.

MOS content (wt %)	Crystalline melting Temperature, T_m (°C)	Recrystallization temperature, T_c (°C)	Heat of crystalline melting, ΔH_m (J/g ^a)	Heat of recrystallization, ΔH_c (J/g ^a)
0	166.9	113.8	93.2	85.6
10	167.6	117.4	100	88.8
20	168.2	117.9	101	94.9
30	166.7	117.6	110	116

^a The basic of weight is the amount of PP at the subtraction of MPS-MOS from the composites specimens.

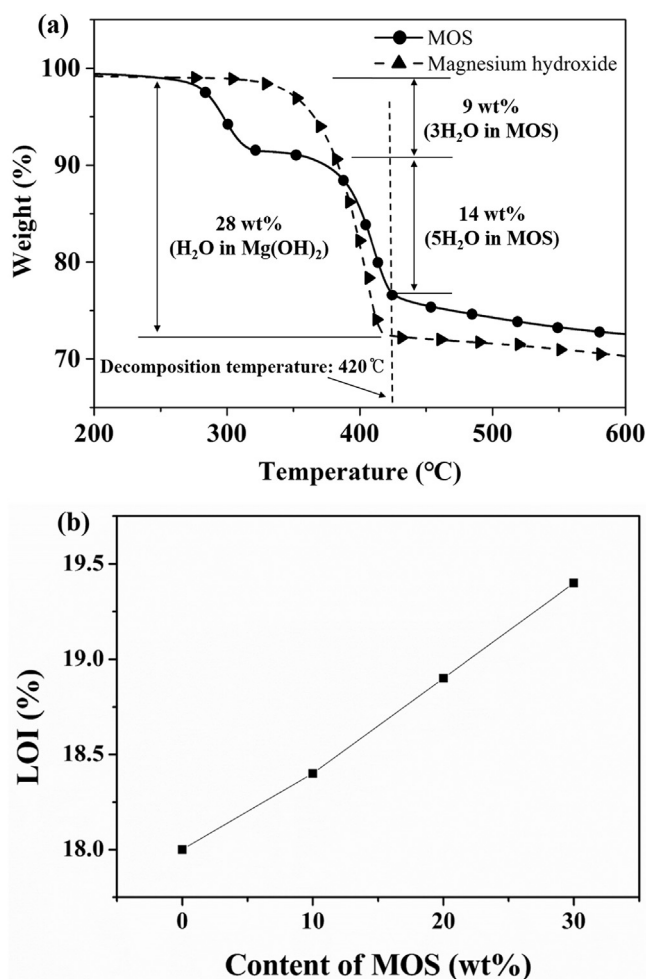


Fig. 8. (a) TGA thermograms of MOS and magnesium hydroxide and (b) limited oxygen index (LOI) of MPS-MOS/PP composites.

loss, which could extinguish fire upon elevated temperatures acting as a flame retardant.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (NRF-2014M3C1B2048175 and 2016R1A2B1007134), and Ministry of Trade, Industry and Energy (MOTIE) (10067690). We also appreciated the project and equipment support from Gyeonggi Province through the GRR program in Sungkyunkwan University. KJK would like to acknowledge this material is based upon work supported in part by the National Science Foundation under Grant No. IIA-1301726.

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