
THERMAL CONDUCTIVITY AND TENSILE PROPERTIES OF HOLLOW GLASS MICROSPHERE / POLYPROPYLENE COMPOSITES

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ABSTRACT

In this study, hollow glass microspheres (HGM) filled polypropylene (PP) composites were prepared by melt extrusion method. In order to understand the effect of structure and physical properties on the performance of composites, the morphologies, tensile properties and thermal conductivities of composites were investigated. The surface of HGMs were modified with 3-(Trimethoxysilyl) propyl methacrylate (TMSM) silane coupling agent to improve the compatibility between PP matrix and HGMs. The physical properties of silane modified and unmodified HGMs were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscope (SEM). The effect of HGM content and surface modification of HGM on morphological, mechanical and thermal conductivity properties of composites were evaluated. The results indicated that the surface modification of HGM enhance the interfacial region between HGM and polymer matrix. When 20 wt% modified HGM was added to neat PP, the modulus of the composite obtained was 1057 MPa, increasing by 15.1% compared with that of the PP/unmodified HGM composite. However, any positive or consistent effect of surface modification and HGM addition on thermal conductivity of samples can not be observed.

Keywords: Polypropylene, Hollow glass microspheres, Composite, Thermal conductivity, Tensile properties

1. INTRODUCTION

Polypropylene (PP) is extensively used in industrial and structural applications because of its easy processing in conventional equipment and good mechanical properties. However, its use has some disadvantages such as high shrinkage range and poor impact resistance. The performance of PP can be improved by adding rigid, inorganic fillers such as CaCO₃ and glass microspheres [1]. PP and its composites reinforced with glass fiber and glass microsphere have many applications in the automobile, aerospace, appliances, and subsea pipeline insulation [2].

Hollow glass microspheres are finely dispersed, free flowing powders and exhibit low thermal conductivity and low density, which make HGM a good candidate in insulation applications [3,4]. In addition, these micro-particles do not generate stress concentration at the interface between the fillers and the matrix owing to their smooth spherical surface [5]. They are preferred as fillers especially when composite properties such as isotropy or low melt viscosity are important. Moreover, the orientation effects associated with molding are minimal. Therefore, their application has gained interest in the polymeric and coating industry. Generally, polymer/HGM composites have good thermal and sound insulation, low density and good mechanical and rheological properties [6]. Foamed plastics are used as thermal insulation materials, however their application are limited considerably due to their poor mechanical properties. Therefore, there is a considerable interest on the fabrication of reinforced polymeric systems that have better mechanical strength and good thermal insulation properties [5]. HGMs hereby can offer the benefits in the enhancement of polymer properties [6]. These type of composites can be applied to building materials, space flight and aviation industry.

Silanes are efficient coupling agents extensively used in composites and adhesive formulations and they have been successfully applied in inorganic filler reinforced polymer composites such as glass fiber

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reinforced polymer composites and mineral filled polymer composites. Silane coupling agents have a generic chemical structure $R_{(4-n)}\text{-Si}(\text{R}'\text{X})_n$ ($n=1,2$) where R is alkoxy, X represents an organofunctionality, and R' is an alkyl bridge (or alkyl spacer) connecting the silicon atom and the organofunctionality [7]. The nonreactive alkyl group of the silane enhances the compatibility with non-polar matrix due to their similar polarities, whereas the reactive organofunctional group may covalently bond to the polymer matrix.

The aim of this study is to improve thermal insulation and mechanical properties of neat PP by the addition of HGMs at varying concentrations. The surfaces of HGMs are silane treated to improve the compatibility between the filler and PP matrix. The mechanical properties, morphologies and thermal conductivities of the resulted composites are investigated.

2. EXPERIMENTAL

2.1. Materials

Polypropylene with trademark of PETOPL EN EH 241, supplied by Petkim Petrochemical Corporation (Turkey), was used as the polymer matrix. The melt flow index (230 °C, 2160 g) of PP was 20-28 g/10 min. HGM, glass bubbles iM16K, with a true density of $0.46\text{g}\cdot\text{cm}^{-3}$ and significant crush strength of 16,000 psi, have been supplied by 3M™. These hollow glass microspheres (mean diameter 20 μm) are made from water-resistant and chemically-stable soda-lime borosilicate glass. The thermal conductivity of iM16K is 0.153 W/mK (at 21 °C). Silane coupling agent, 3-(Trimethoxysilyl)propyl methacrylate (TMSM) (98%, Aldrich) was used as received.

2.2. Composite Preparation

The surface of glass microspheres were coated with silane coupling agent, 3-(Trimethoxysilyl)propyl methacrylate. 0.5 g silane was added to 20 ml acetone and HGMs were added to this mixture. The suspension was mixed for 1 hour using a magnetic stirrer and were vacuum dried at 55 °C for 35 minutes. After drying, the suspension particles were washed with acetone 3 times. Last, the particles were vacuum dried at 55 °C for 24 hours.

PP/HGM composites were prepared by melt mixing process using a twin-screw micro compounder (DSM Xplore 15 ml Microcompounder – The Netherlands). PP was dried in vacuum oven prior to dry-mixing with microspheres at varying concentrations of 5, 10, 15 and 20 wt% and then the mixtures were compounded at process temperature of 170 °C and screw speed of 100 rpm for 3 minutes. Specimens for thermal and mechanical analyses were molded by using an injection molding device (DSM Xplore 12 ml Injection Molding Machine – The Netherlands) at a nozzle temperature of 180°C. Injection pressure was 8 bar and the mold temperature was kept at 30 °C.

2.3. Characterization

The morphological study was carried out by using a ZEISS SUPRATM 50 VP Scanning Electron Microscope (SEM) to investigate the fractured surfaces of composites. Before observing the surfaces they were sputtered with palladium-gold to provide conductive surfaces. The distribution of the glass beads in PP matrix and interfacial adhesion between the microspheres and polymer matrix were observed.

The Fourier transform infrared spectrum of PP and PP/HGM composite samples was investigated by using a Bruker TENSOR 27 FTIR spectrometer. Samples were added in KBr (1:100, w/w) and pelletized. The spectra were recorded between 4000 and 400 cm^{-1} and 16 scans were taken at a resolution of 4 cm^{-1} with the transmission mode.

Thermal effusivity measurements were carried out by a Perkin Elmer Pyris TC Probe device at room temperature on samples with dimensions of $50 \times 20 \times 1 \text{ mm}^3$. An average of at least three measurements was taken. In order to determine heat capacity (C_p) values, DSC analysis was performed using a Perkin Elmer Diamond DSC equipment under nitrogen atmosphere.

The thermal conductivity, k (W/mK), of the composites was calculated from *eqn. 1*,

$$e = \sqrt{k\rho C_p} \quad (1)$$

where e is thermal effusivity ($\text{W}\sqrt{\text{s/m}^2\text{K}}$), ρ is density (g/m^3), and C_p is heat capacity (Ws/gK).

In order to determine the densities of polymer and composites, masses of specimens $10 \times 4 \times 2 \text{ mm}$ in size were measured with an electronic balance. The density values were calculated from the mass/volume ratio. Three measurements were done for three different samples with the same composition, and the average value was reported.

The effect of HGM content on the tensile properties of the composites were determined using an Instron-Mechanical Testing Machine 5581 equipped with 2 kN load cell according to the ASTM D638 standard. Strain rate was set to 10 mm/min. The arithmetic mean of five samples and their standard deviations were reported. The elastic modulus, tensile strength and elongation at break values with the varying content of HGM were obtained.

3. RESULTS AND DISCUSSION

The appearance and the size distribution of HGM's obtained by SEM analysis is shown in Figure 1a. A wide variation is appeared in the size of HGMs. Comparing this with Figure 1b, where silane was used to modify the surface of the HGMs, the results are more or less the same as the ones for the original HGMs. This suggests a low level of physical bonding also confirmed by the FTIR analysis.

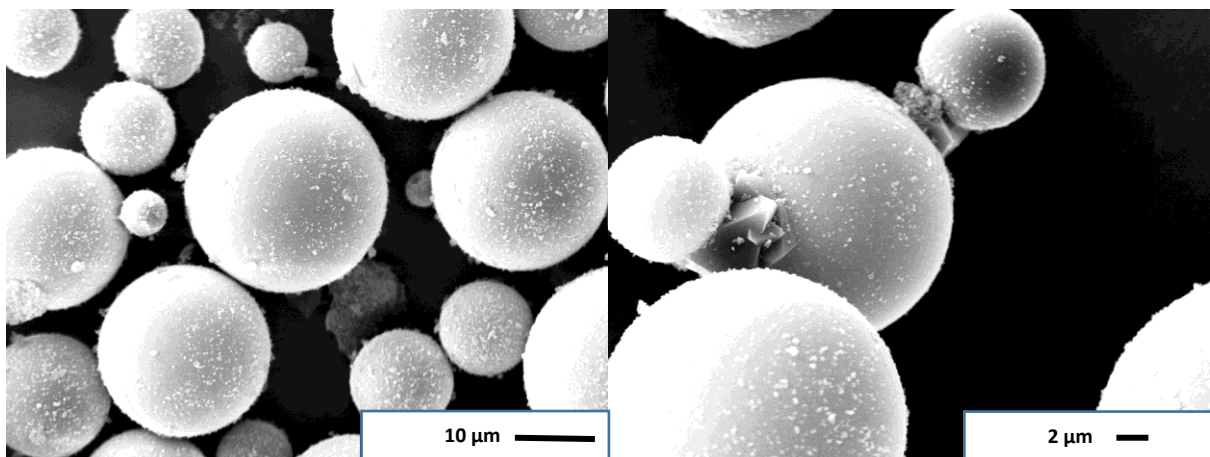


Figure 1. SEM micrograph of a) as-received HGM, b) HGM modified with silane treatment

Figure 2 is the micrograph of the fracture surfaces of neat PP and PP/HGM composites. SEM micrograph of neat PP (Figure 2a) shows a relatively smooth surface without any phase separation. Composites containing 20wt% HGM exhibit a homogeneous and dense structure. In the absence of silane, HGM surface is very clean and the interface between the HGM and PP matrix is discrete with no sign of any bonding (Figure 2b, c, d) [8].

In the presence of silane, fracture surface of PP/HGM composites reveal that HGMs are damaged and cavities are left by removal of HGM during the fracture process (Figure 3). Probably addition of small quantity of silane enhances the compatibility between PP and HGM surface. The observation that most of the microspheres are embedded rather than pulled out from the PP matrix shows a strong interfacial adhesion between the fillers and matrix. The contact between HGM and PP is more tight in the composites filled with modified-HGM, suggesting the enhancement of interaction between them.

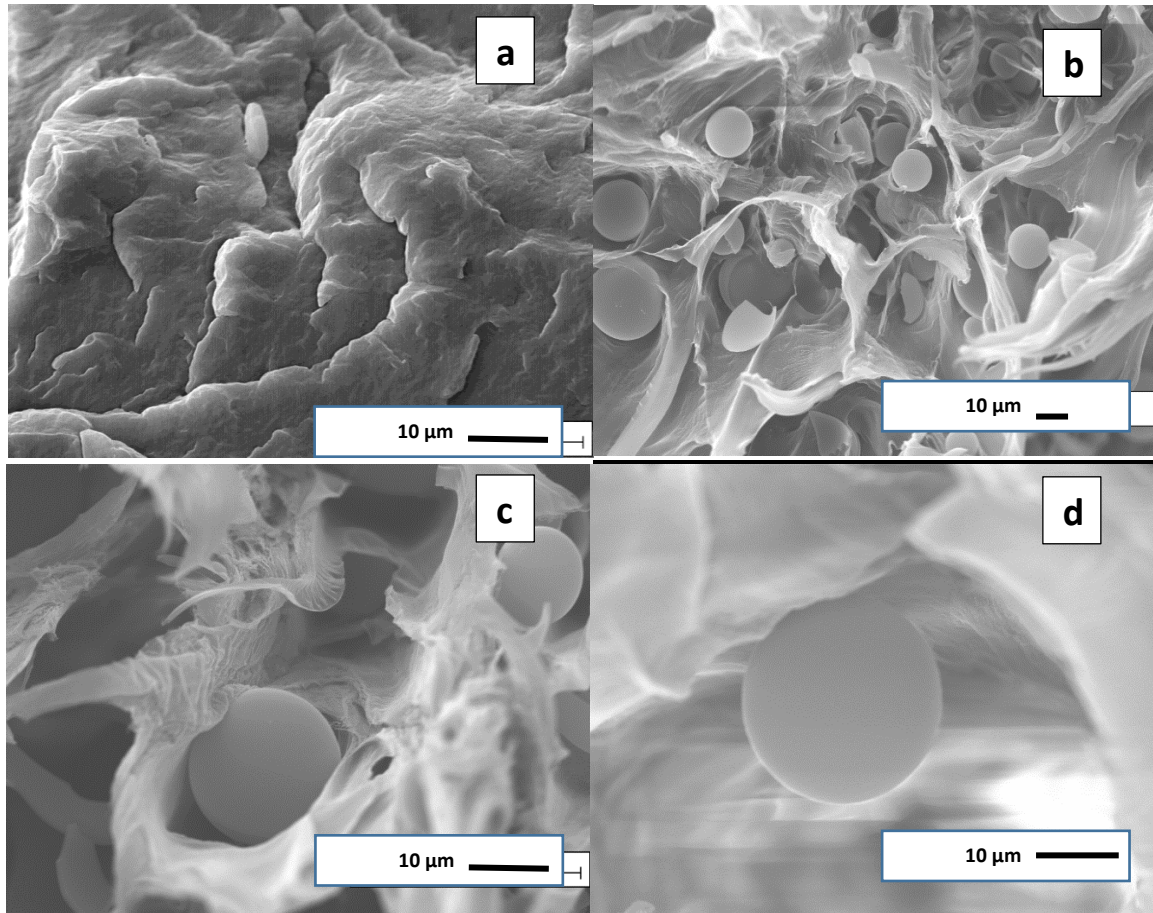


Figure 2. SEM micrograph of a) neat PP, b-c-d) PP/20% HGM (unmodified HGM) composite

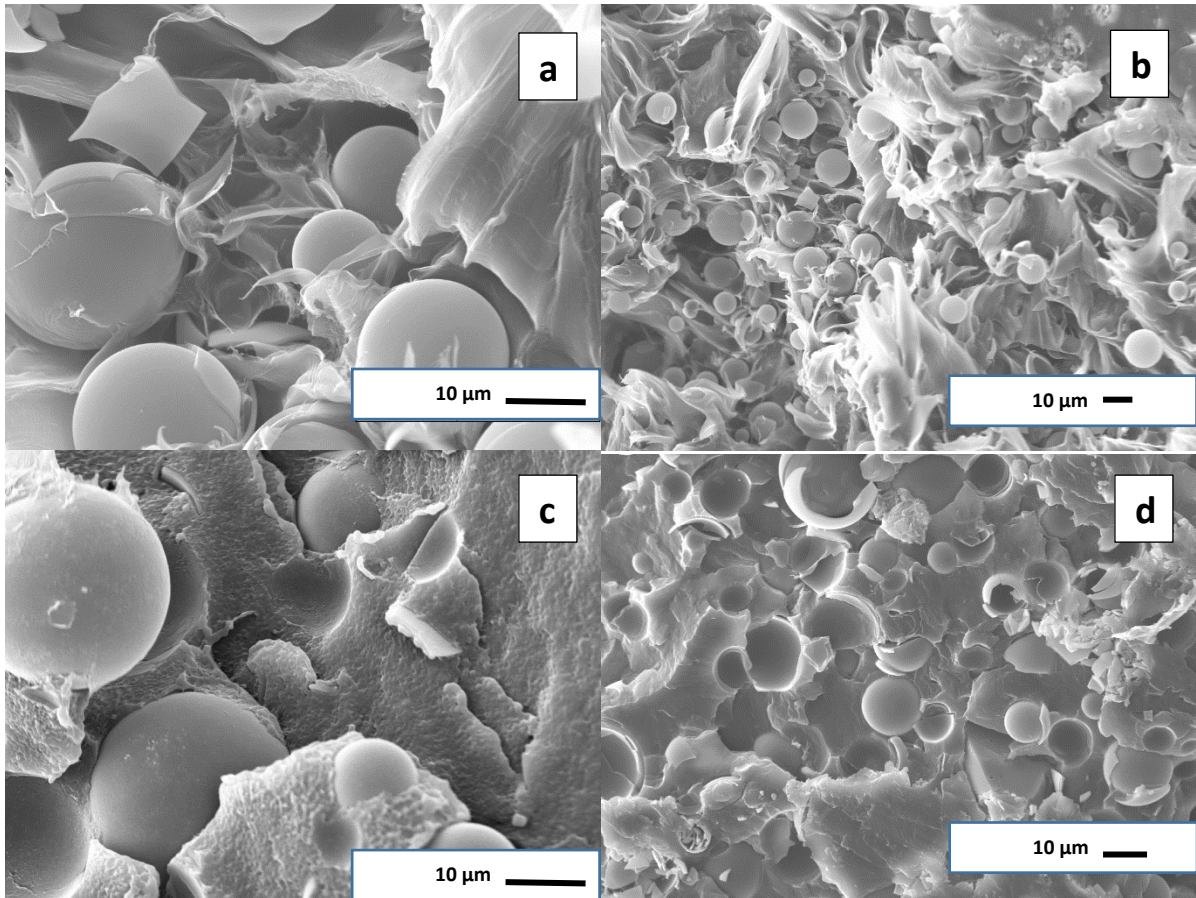


Figure 3. SEM micrograph of PP/20%SHGM (silane-modified HGM) composite

Figure 4 shows the FTIR spectra of unmodified-HGM and modified-HGM. Surface modification is carried out at weight ratio of silane to HGM of 3 and 5 wt%. Silanization has been determined to first proceed by hydroxyl group of silanol to form Si-O-Si bridges [9]. The three methoxy groups of TMSM could readily hydrolyse to form hydroxyl groups, which are susceptible to condensation with each other as well as the surface hydroxyl groups. It is expected that TMSM is hydrolyzed to form the silanol. Then, the silanol reacts with the hydroxyl groups on the surface of HGM to form a thin film on the surface of HGM [10]. At the same time, alkyl group of silane has compatibility with the polymer matrix, which may form an interlayer with HGM by silane modification. The peaks at 1086 , 799 and 467 cm^{-1} are observed in the spectra of unmodified- and modified-HGM samples, and these peaks correspond to Si-O-Si stretching vibration. The spectra of unmodified- and modified-HGM samples are similar, although the C-H stretch peak (1454 cm^{-1}) is more pronounced in SHGM sample [11,12]. The peak at 1454 cm^{-1} corresponds to the stretching vibration of methylene C-H of TMSM that indicates the presence of silane on HGM.

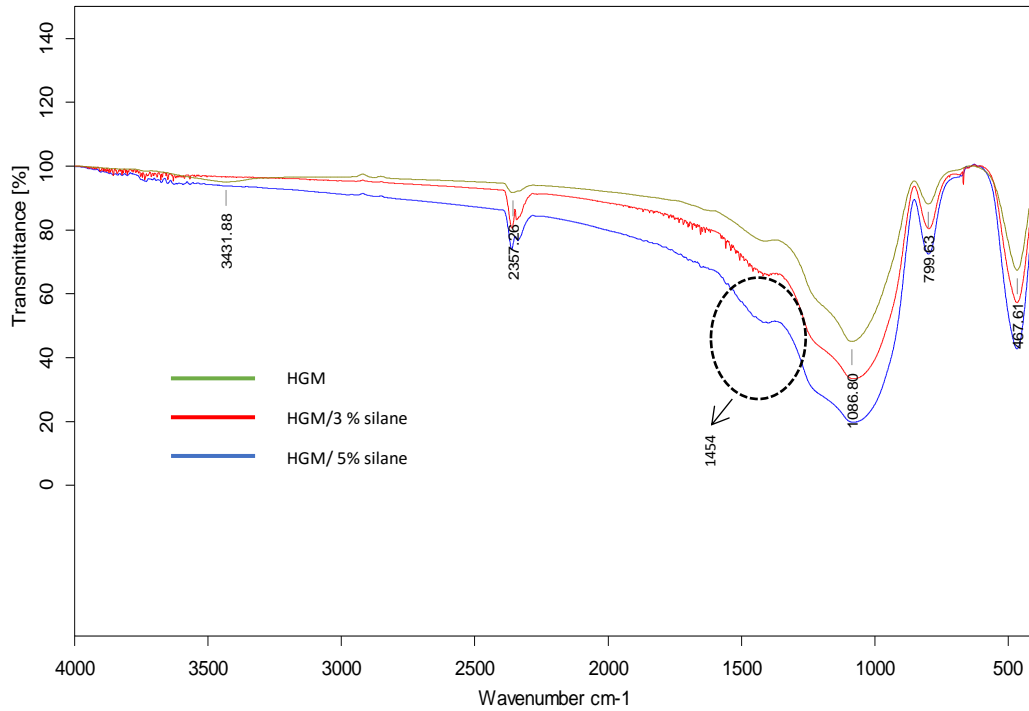


Figure 4. FT-IR spectra of unmodified-HGM and modified-HGMs

HGM has a unique structure with glass shell and gas core and the gas has very low thermal conductivity, which results in low thermal conductivity of SHGM filler [10,13]. However, the thermal conductivity for samples with varying content of SHGM given in Figure 5 indicate that the thermal conductivity of the composites are nearly same with neat PP. The thermal conductivity of neat polypropylene is 0.176 W/mK. When the SHGM content increases to 20 wt%, the thermal conductivity of the composite increases to 0.205 W/mK. An increase of 14 % is seen compared to neat PP. Despite the aim of the study, any positive or consistent effect of surface modification and HGM addition onto thermal conductivity of samples can not be observed.

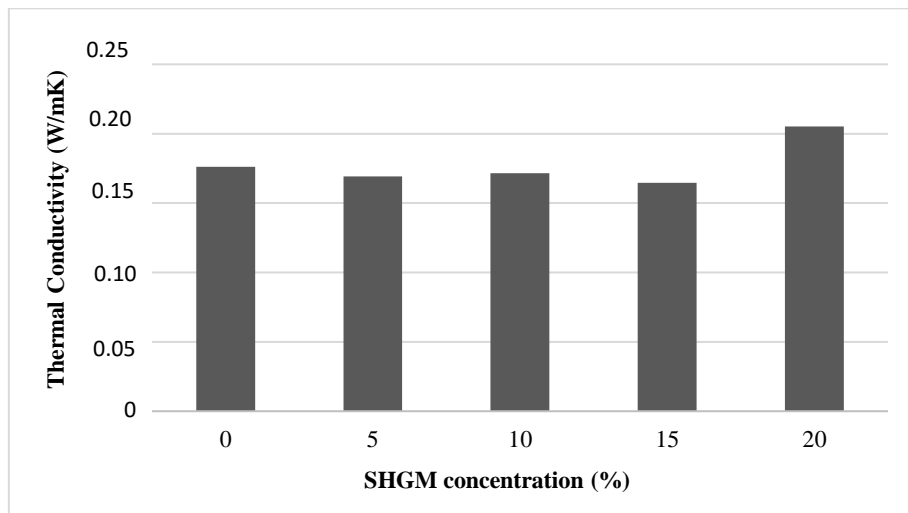


Figure 5. The thermal conductivity of composites as a function of SHGM content

Surface modification of HGM with silane decreases the gap between HGM particles and polymer matrix in the composites. Obviously, the decrease of gap between the filler and polymer matrix will effectively decrease the phonon scattering, and thus the thermal conductivity of the composites can be decreased [10]. However, in case HGM is not completely coated and the gap exists between HGM and PP, thermal conductivity of the composites may slightly increase.

As it is expected, tensile strength values of PP/HGM composites, decrease gradually by increasing the content of HGM loadings (Table 1). Neat PP shows the highest tensile strength value, whereas with the incorporation of HGM tensile strength value decreases to 21 MPa for 20 wt% HGM loading. This is reasonable due to poor interfacial adhesion between the matrix and the filler. On the other side, surface modification performed in order to increase the compatibility between the matrix and the filler has a positive effect. PP/HGM samples containing more than 5wt% modified HGM (SHGM) give higher tensile strength values compared with samples containing unmodified HGM. It is observed that HGM addition increases the elastic modulus of neat PP. As it is seen in SEM micrographs uniform distribution of particles provides an enhancement in mechanical properties. The surface modification of HGM results in significant enhancements of modulus. Great decrease is observed in elongation at break values of composites as compared to neat PP. Its value decreased from 251% to 4% for PP/20%HGM, which is even lower for SHGM loaded samples.

Table 1. Tensile test results of samples

Sample	Tensile Strength (MPa)	Elastic Modulus (MPa)	Elongation at Break (%)
Neat PP	38±2.3	723±40.4	251±9.3
PP/5%HGM	29±1.2	735±11.9	10±0.4
PP/10%HGM	26±1.1	869±15.0	5±0.2
PP/15%HGM	23±1.3	910±13.4	4±0.2
PP/20%HGM	21±2.4	918±61.0	4±0.9
PP/5%SHGM	29±1.0	868±16.9	8.61±0.3
PP/10%SHGM	28±0.2	917±28.4	7.09±0.3
PP/15%SHGM	26±0.2	999±15.7	5.15±0.1
PP/20%SHGM	23±0.8	1057±21.4	3.83±0.3

4. CONCLUSIONS

In this study the effects of HGM content and silane modification on the performance of PP composites were investigated. The results show that the mechanical properties of composites varied with HGM content. In the absence of silane modifier the interface between PP matrix and HGM is very discrete with no sign of interaction. The use of silane influences the mechanical properties of composites, however it has little or no effect on the thermal conductivity values. SEM analysis states that a more tight contact is formed between HGM and polymer matrix, which implies that a stronger interaction exists when compared with composites containing unmodified HGM. Thus also influences markedly the mechanical properties of the composite.

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