

## 실리카/폴리프로필렌 복합재료의 기계적 및 열적 물성에 미치는 실란 커플링제의 영향

이민철 · 김영선 · 류현준 · 백성현 · 심상은<sup>†</sup>

인하대학교 화학 & 화학공학융합학과

(2016년 12월 18일 접수, 2017년 2월 10일 수정, 2017년 3월 6일 채택)

### Effects of Silane Coupling Agent on the Mechanical and Thermal Properties of Silica/Polypropylene Composites

Minchul Lee, Yeongseon Kim, Hyunjun Ryu, Sung-Hyun Baek, and Sang Eun Shim<sup>†</sup>

Department of Chemistry & Chemical Engineering, Inha University, Incheon 22212, Korea

(Received December 18, 2016; Revised February 10, 2017; Accepted March 6, 2017)

**초록:** 실란 커플링제 도입에 따라 silica가 충전된 폴리프로필렌의 기계적, 열적 물성에 미치는 영향을 살펴보았다. Epoxy, amino와 methacryloxy 작용기를 가지고 있는 실란 커플링제를 사용하였다. 종류, 농도와 실란 커플링제의 처리방법에 따라 silica/PP 복합체의 인장강도, 굴곡강도, 충격강도 및 열적안정성을 분석하였다. 용융혼합 및 압축성형에 의해 제조된 복합재료 샘플의 기계적 특성을 조사하기 위해 만능재료시험기와 충격시험기를 사용하였고, 열적 특성을 조사하기 위해, TGA와 DSC를 사용하였다. 건식방법으로 amino 작용기를 가지고 있는 실란 커플링제를 5 wt% 혼합한 silica/PP 복합체가 기계적 물성과 열적 물성이 가장 우수한 것으로 확인되었다.

**Abstract:** The effect of silane coupling agent on the mechanical and thermal properties of silica/polypropylene composite was studied. Epoxy, amino, and methacryloxy silanes were introduced as coupling agents. Silica/PP composites were investigated in terms of flexural, tensile, impact strength, and thermal stability in accordance with type, concentration, and processing methods of silane coupling agent. Mechanical properties of the composites prepared by melt-mixing and compression molding were tested by UTM and impact tester, and thermal properties were analyzed by TGA and DSC. As a result, it was confirmed that the silica/PP composite mixed with 5 wt% amino-functionalized silane prepared by dry method showed the highest mechanical and thermal properties.

**Keywords:** polypropylene, silica, silane coupling agent, composite.

## Introduction

A composite material is formed by the combination of two or more materials in which the individual components retain their physical and chemical properties; yet, the resulting composite exhibits superior properties as compared to those of the individual constituent materials. Polymer composites are formed using relatively flexible polymers that are surrounded by particles of a filler material exhibiting higher mechanical strength.<sup>1</sup>

Polypropylene (PP), which exhibits a low specific gravity, superior plasticity, chemical stability, and outstanding mass

producibility, is being used in many applications.<sup>2</sup> For a long time, researchers have been exploring methods suitable for enhancing various properties of the PP matrix by adding different types of inorganic fillers.<sup>2,3</sup> However, when good PP matrix-filler interface interaction cannot be achieved, most of the filler materials serve as “extenders” that take up the space and do not substantially contribute toward improving the mechanical properties of the combined materials.<sup>2</sup> Usually, inorganic filler materials of different types and compositions are employed with PP, e.g., silica, talc, mica, CaCO<sub>3</sub>, and glass fiber.<sup>4,6</sup> The properties of PP reinforced with fillers are determined by measuring the extend of physical and chemical bonding between the PP and the filler materials. The mixing of silica containing considerable amounts of silanol groups on its outer surface with the hydrophobic PP is difficult due to poor dispersion.<sup>7,8</sup> This challenge has inspired many researchers to

<sup>†</sup>To whom correspondence should be addressed.

E-mail: seshim@inha.ac.kr

©2017 The Polymer Society of Korea. All rights reserved.

study the physical and mechanical properties achieved by using surface treated silica for improving the properties of PP.<sup>9,10</sup> One of the methods is surface treatment using coupling agents in order to increase the interfacial bonding and increase the number of interfacial bonds. A coupling agent has two functional groups, one of which is connected with the organic polymer and the other with the inorganic material, thereby bridging molecules of the two constituent materials. Coupling agents are roughly divided into two groups: reactive and non-reactive. Reactive agents, including silane, titanate, and maleic acid, cause chemical reactions to occur between the polymer and the inorganic material to form a chemical bond.<sup>11,12</sup> Non-reactive agents induce physical attraction rather than chemical attraction between the polymer and the filler material, thereby improving the interfacial bonding. Non-reactive agents include amphoteric surface agents containing polar groups on each side of the long aliphatic fatty chain. Typically, three types of surface treatment methods, namely wet, dry, and spray methods, are used for modifying silica using a silane coupling agent. The wet method involves the dispersion of a silane coupling agent into the solvent, followed by immersing silica in the solvent for forming bonds with silica. In the spray method, a silane coupling agent is dispersed in the solvent, followed by mist-spraying the dispersion onto silica in order to improve its surface treatment. In the dry method, the filler material is deposited along with the silane agent into the matrix for combining.

In this study, silane coupling agents containing epoxy, methacryloxy, and amino functional groups are used; the agent is

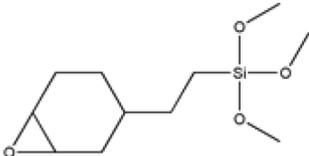
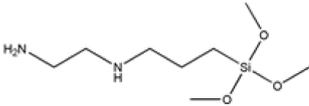
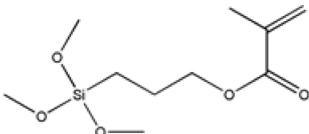
subjected to wet and dry surface treatment methods in order to improve the reforming of the silica surface. The changes in the mechanical and thermal properties occurring when changing the functional groups and concentration levels are investigated by measuring the tensile, flexural, and impact strength of the specimens using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

## Experimental

**Materials.** PP, purchased from the Chinese manufacturer Shinopex, used in this study was PHH-T03, which exhibits a melt flow index (MFI) of 3 g/10 min and a density of 0.9 g/cm<sup>3</sup>. Silica (filler material), obtained from the Korean supplier Solvey, exhibited an average particle size of ~2.3 μm (Rhodoline HP 34 M). The silane coupling agents, 2-(3,4 epoxy-cyclohexyl) ethyltrimethoxysilane (EHTMS), *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (APS), and 3-methacryloxypropyl trimethoxysilane (MPS), used in this study were manufactured by Shin-Etsu Korea without performing any refinement. Table 1 summarizes the properties of the silane coupling agents. Methanol, acetic acid anhydrides, and primary distilled water were used as the solvent in the silica surface treatment process.

**Silica Surface Treatment and Specimen Preparation.** For performing the surface treatment of silica samples, both the wet and dry methods were employed. In the former method, each of the three silane coupling agents (EHTMS, APS, MPS) was diluted in the co-solvent of methanol and dis-

**Table 1. Characteristics of the Silane Coupling Agent**

Silane coupling agent name	Chemical structure	Molecular weight (g/mol)	Boiling point (°C)
2-(3,4 epoxy-cyclohexyl) ethyltrimethoxysilane (EHTMS)		246.4	310
<i>N</i> -(2-Aminoethyl)-3-aminopropyltrimethoxysilane (APS)		222.4	259
3-Methacryloxypropyl trimethoxysilane (MPS)		248.4	255

**Table 2. Compositions of the Prepared Silane/Silica/PP (wt%)**

PP	Silica	Silane coupling agent (conc. of silane: 5 wt% compared silica)		
		EHTMS	APS	MPS
80	20	-	-	-
		5	-	-
		-	5	-
		-	0.5	-
		-	1	-
		-	10	-
		-	-	5

tilled water (weight ratio of 95:5), followed by adjusting the pH to 4 using acetic acid and carrying out hydrolysis using a magnetic stirrer for 2 h. Silica, which was dried for 24 h in a reflux dryer at 120 °C, was then immersed in the hydrolytic solution for 24 h, followed by filtering and drying the sample without further cleaning the reflux dryer at 120 °C for 24 h in order to obtain the surface treated silica samples using the silane coupling agents. The surface-treated silica and PP were melt-mixed for 12 min at 220 °C and 100 rpm using a high viscosity kneader tester (internal mixer, TO-350, test one) in the form of a co-rotating twin screw. This step was followed by press molding using a hot press (12 ton) that was pre-heated to 220 °C in order to fabricate the specimen. In the dry method, the silane coupling agents were mixed into the melt-mix of PP and silica, keeping the remaining procedures the same as that in the wet method. Table 2 lists the ratio of PP, silica, and coupling agents used for the study. For examining the changes obtained with different agents, the concentration of silane against silica was fixed at 5 wt%. In order to examine the changes occurring on changing the APS concentration levels, the silane concentration was varied as 0.5, 1, 5, and 10 wt% against silica.

## Characterizations

**Properties of Silica with Improved Surface Treatment.** Using X-ray photoelectron spectroscopy (XPS; Thermo scientific K-Alpha), the changes in the surface composition of silica were examined. Al K<sub>α</sub> (1485.6 eV) was used as X-ray light source. For quantitatively determining the amount of silane coupling agents on the silica surface, TGA (TA Q50) was employed. The changes in the weight (behavior) of the silane-treated silica samples were measured under nitrogen atmo-

sphere with a heating rate of 10 °C/min in the temperature range of 40-800 °C.

**Morphology.** Using field emission scanning electron microscopy (FE-SEM; Hitachi S-4300), the dispersion quality of silica inside the PP matrix was investigated. The specimen was sufficiently cooled in liquid nitrogen, followed by inducing fracture. The cross section of the fractured specimen was then coated with platinum by employing vacuum evaporation for performing the FE-SEM measurements.

**Mechanical Properties.** To study the mechanical properties of the specimen, the tensile strength of the samples was measured as per ASTM D 638 using a universal testing machine (UTM; INSTRON 5569) at room temperature at a crosshead rate of 5 mm/min with a 50 kN load cell. The flexural strength of the specimen was measured according to ASTM D 790 using the UTM (INSTRON 5569) at room temperature with a 5 mm/min crosshead rate and a 1 kN load cell. For measuring the impact resistance, the Izod impact test was conducted as per ASTM D 256 using an impact tester (Ceast Resilimpactor) at room temperature. The dimension of the specimen (without notches) used was 12.7 mm (width) × 7.5 mm (height) × 63.6 mm (length).

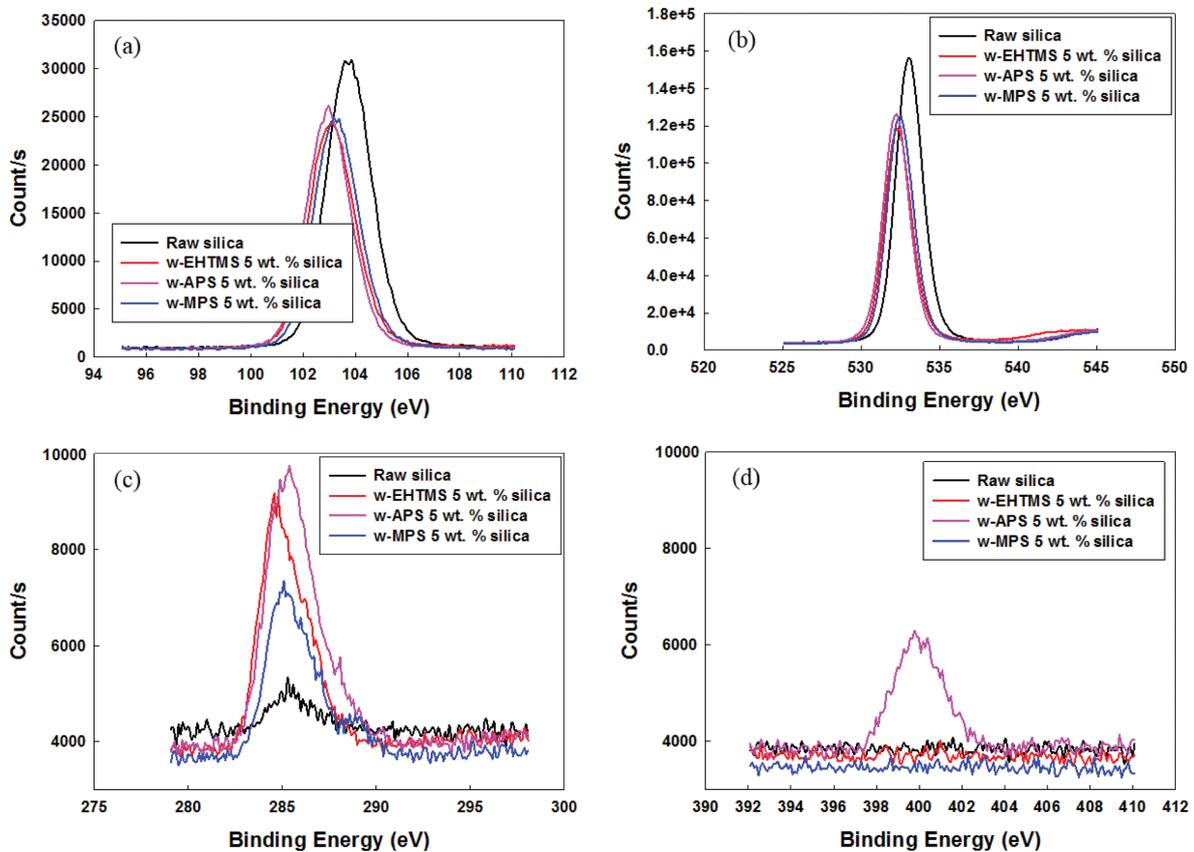
**Thermal Properties.** Using a TGA instrument (TA Q50), the weight-change behaviors of the composite specimen were examined under nitrogen atmosphere at a heating rate of 10 °C/min between 40 and 800 °C. For performing DSC measurements (Perkin Elmer Jade DSC lab system), the specimen was subjected to nitrogen atmosphere with a heating rate of 10 °C/min for two cycles, and the data obtained from the second cycle were used for the analysis. The degree of crystallinity ( $X_c$ ) of each specimen was obtained from eq. (1):

$$X_c = \frac{\Delta H_f}{\Delta H_f^0 w} \times 100 \quad (1)$$

Here,  $\Delta H_f$  refers to the heat of fusion of the silica/PP composite,  $\Delta H_f^0$  is the heat of fusion of the pure PP with a crystallinity of 100 % (137.9 J/g), and  $w$  is the mass fraction of the PP in the silica/PP composite.

## Result and Discussion

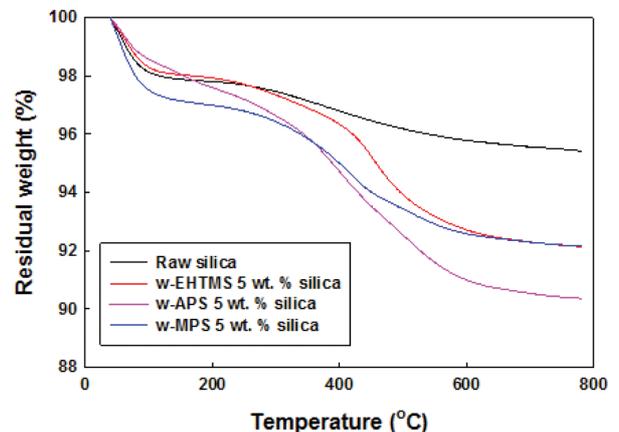
**Properties of Silica Obtained Before and After Improving the Surface Treatment.** Figure 1 illustrates the XPS results of the samples obtained with the wet method, revealing the composition of the surface structure of the silane coupling agent-improved silica. The bond energy values of Si-



**Figure 1.** XPS analysis of silica coupled by wet method with various silane at 5 wt%: (a) Si 2p; (b) O 1s; (c) C 1s; (d) N 1s.

O-Si and Si-O bonds on the surface of the silica were found to be 103.43 and 102.4 eV, respectively (Figure 1(a)).<sup>13,14</sup> Figure 1(b) confirms the presence of the bond between Si-O-Si and Si-O, from the observed bond energy values of 533.2 and 532.2 eV.<sup>15</sup> From the values listed in Figure 1(c), the improvement in the surface treatment of the silane-treated silica can be confirmed as a bond energy value of 286.7 eV (CH<sub>2</sub> bond) was obtained.<sup>16</sup> In the case of APS, a bond energy value 286.4 eV (C-N bond) was obtained.<sup>17</sup> Figure 1(d) indicates bond energy values of 399.8 and 300.5 eV, revealing the existence of a bond between NH<sub>2</sub> and C-N in APS.<sup>18,19</sup>

The amount of the silane agents bonded on the surface of the silica was examined using TGA. Figure 2 shows a TGA curve of the silane-improved silica. The loss of weight observed was two different temperatures: at 40 °C for the 200 °C zone and at 300 °C for the 600 °C zone. Furthermore, a weight loss of 2.5% was observed in the temperature range of 40-200 °C. This decrease could be attributed to the moisture already present on the surface of silica.<sup>20,21</sup> For the raw silica sample, a weight decrease of 1% was obtained in the 200-600 °C range, which could be attributed to the impurities formed during the



**Figure 2.** Thermogravimetric analysis of raw and various silane-modified silica.

silica manufacturing process. The w-EHTMS silica sample exhibited a weight loss of 5%, while the w-APS silica and w-MPS silica samples exhibited a weight loss of 6% and a 4%, respectively. This could be attributed to the elimination of the water molecules in the Si-OH condensation reaction occurring on the surface of the silica and the thermal decomposition of

the silica surface-bonded silane coupling agents.<sup>21</sup>

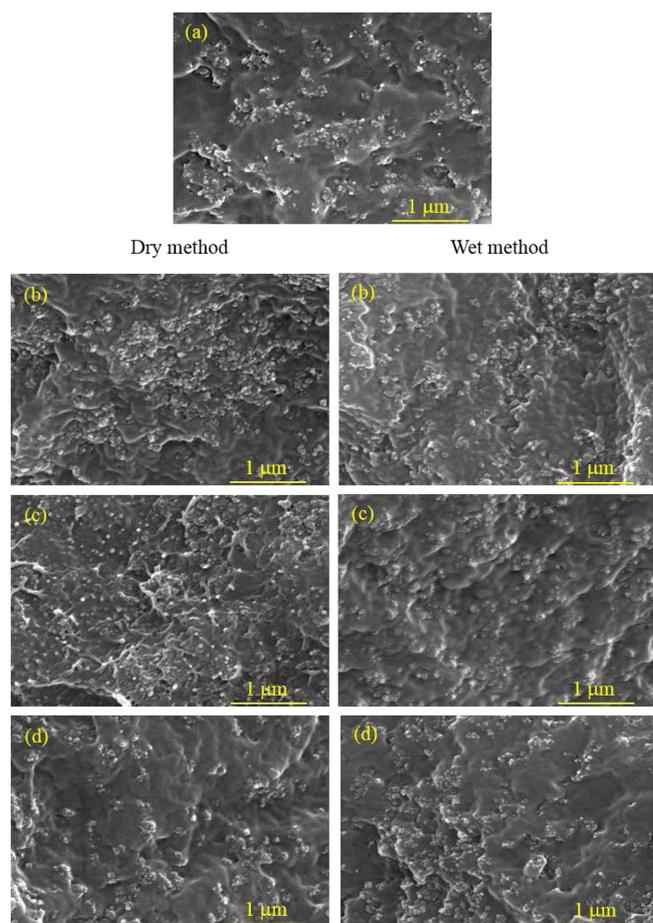
**Morphology.** Wetting and wrapping of the silica particulates by the melted PP would be difficult as silica has a large surface area and a rough surface. This leads to the formation of air-filled voids on the silica/PP interfaces, causing degradations in the mechanical and thermal properties. Figure 3 shows the SEM images of the silane agent-treated samples and the surface configuration of the fractured silica/PP composite samples. When no coupling agents were added, silica lumps were observed in many places in the PP matrix (Figure 3(a)). Furthermore, the above-mentioned air-filled voids can be seen. This could be attributed to the poor affinity between the hydrophobic PP and the hydrophilic silica. Additionally, the silica/PP composites shown in Figures 3(b) and (d), which were treated with the wet and dry methods using EHTMS and MPS, exhibited near identical dispersion profiles as compared with those obtained with the silica/PP composite without adding

any coupling agents. On the contrary, the silica/PP (Figure 3(c)) composite material treated with APS using the wet and dry methods exhibited a better dispersion quality than that obtained with the coupling agent-free silica/PP composite. This composite also exhibited fewer voids due to the enhanced wetting and wrapping interactions. This is presumably attributed to the ability of APS in increasing the interfacial bond between the PP matrix and silica.

**Mechanical Properties of the Silica/PP Composite.** Figure 4 illustrates the tensile properties of the silica/PP composite specimens with respect to the agent treatment method, type, and concentration levels. On comparing the type-specific tensile properties, EHTMS-treated and MPS-treated specimens (except with APS) exhibited lower tensile strength values than that of the non-treated specimens. However, the APS-treated specimens exhibited an increased tensile strength value. This could be attributed to the improvement in the silica/PP interfacial bond achieved with APS, causing an increase in the wetting and wrapping of the silica particles in the PP melt. Additionally, the enhanced mechanical properties could be attributed to the enhancement in the interfacial bond between the silica and PP due to the coupling interactions occurring between the amino group (APS functional group) and the peroxide and carbonyl groups (PP)<sup>9</sup>: The carbonyl and peroxide groups of PP are resulted from thermoxidation during compounding process, and their formation mechanism<sup>22,23</sup> and interactions are displayed in Scheme 1 and 2, respectively.

The most bond- and affinity-efficacious silane coupling agent APS was employed in the wet- and dry-surface treatment method with 0.5, 1, 5, and 10 wt% in order to compare the tensile properties. Except for the sample obtained with 0.5 wt%, the samples obtained with 1, 5, and 10 wt% exhibited increased tensile strength values. The sample obtained with 10 wt% APS exhibited a tensile strength of 36 MPa, which is equivalent to that obtained with 5 wt%; however, an elongation ratio of 9% was achieved, which was three times higher than that of the non-treated composite specimens. This could be because the excess APS remains at the silica/PP interface and PP matrix, acting as a plasticizer.<sup>24</sup> On the contrary, silica/PP composite specimens treated with the wet method exhibited a decreased tensile strength value with APS concentrations of 0.5 and 1 wt%, whereas with 5 and 10 wt%, APS failed to act as an effective coupling agent between silica and PP on the interface, acting only as a plasticizer for the PP matrix.

The dry method was found to be more effective in enhancing the tensile properties as compared to the wet method. In the



**Figure 3.** Cryo-fractured SEM images of silane/silica/PP composites (conc. of silane: 5 wt% to silica): (a) untreated silica; (b) EHTMS; (c) APS; (d) MPS-treated silica.

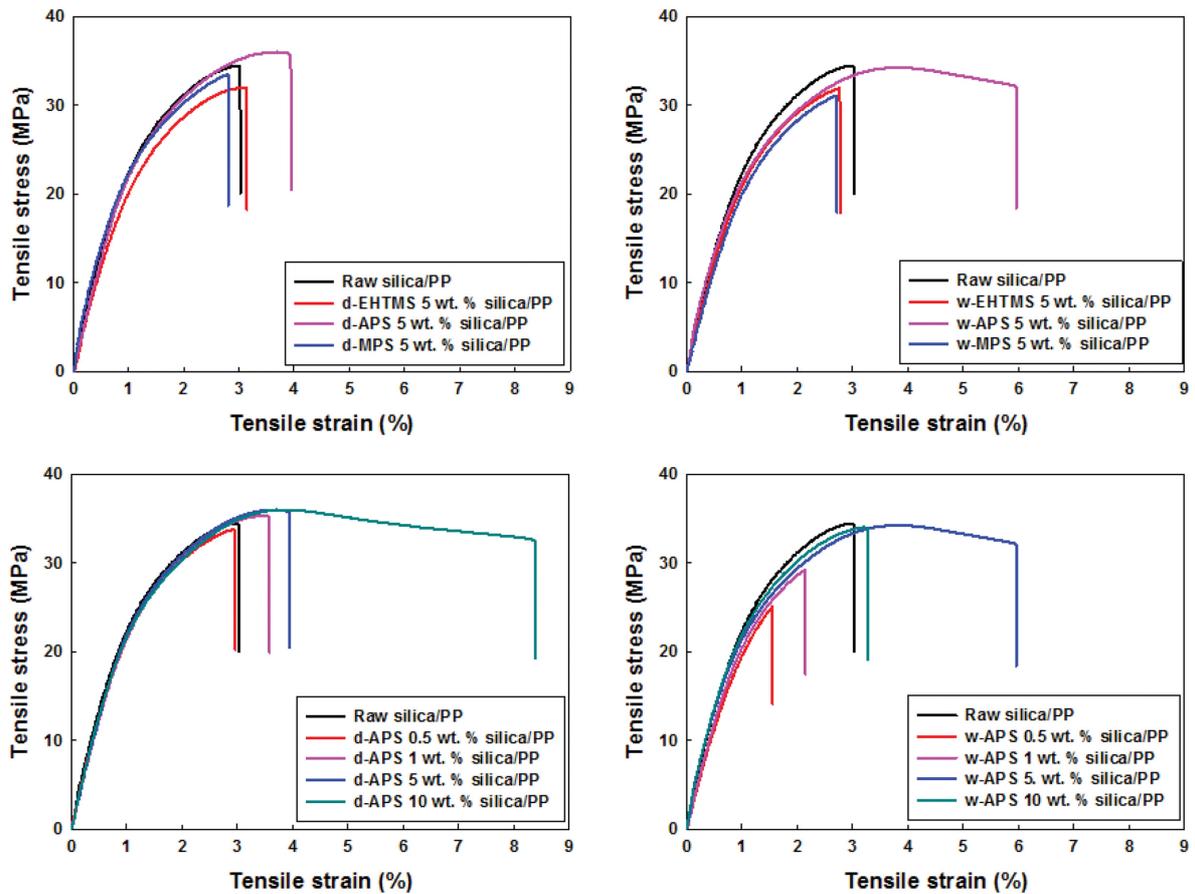
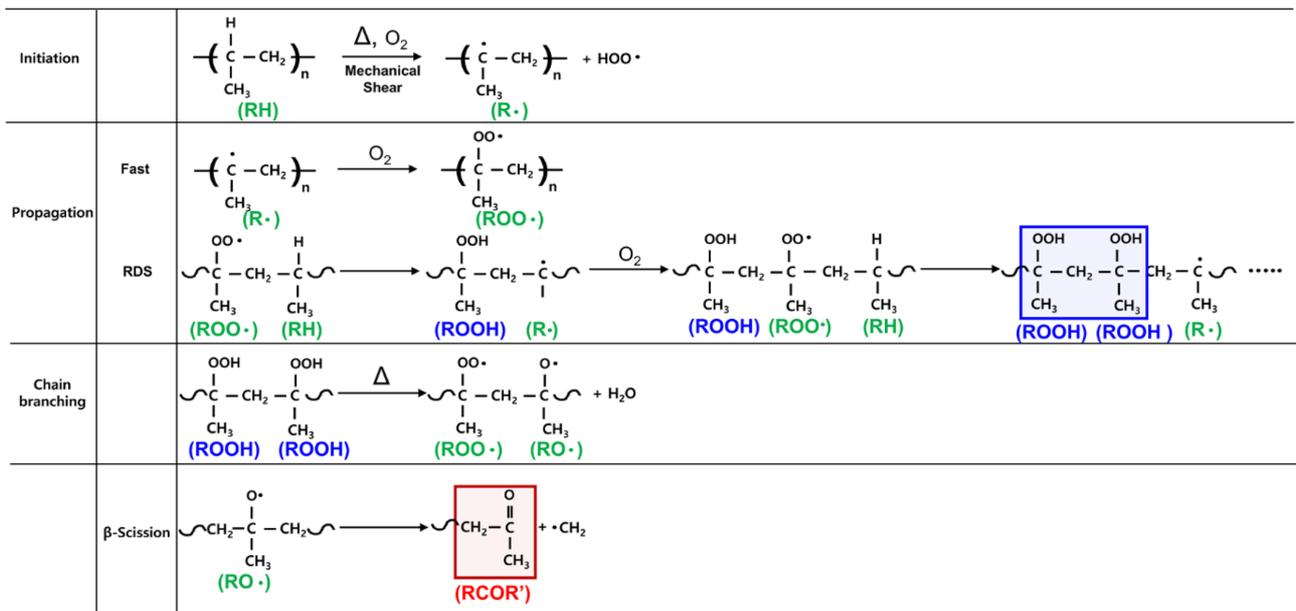
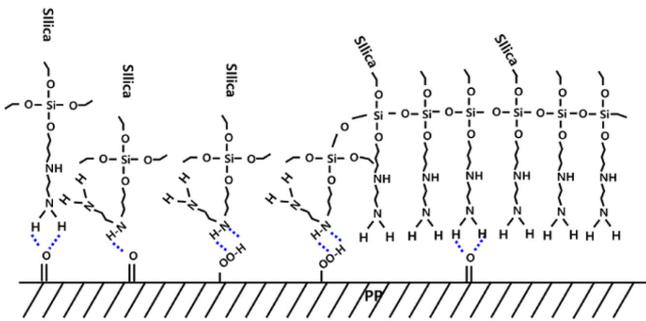


Figure 4. Tensile properties of raw and various silane-modified silica/PP composites.



Scheme 1. Thermoxidation mechanism of PP during melt processing.



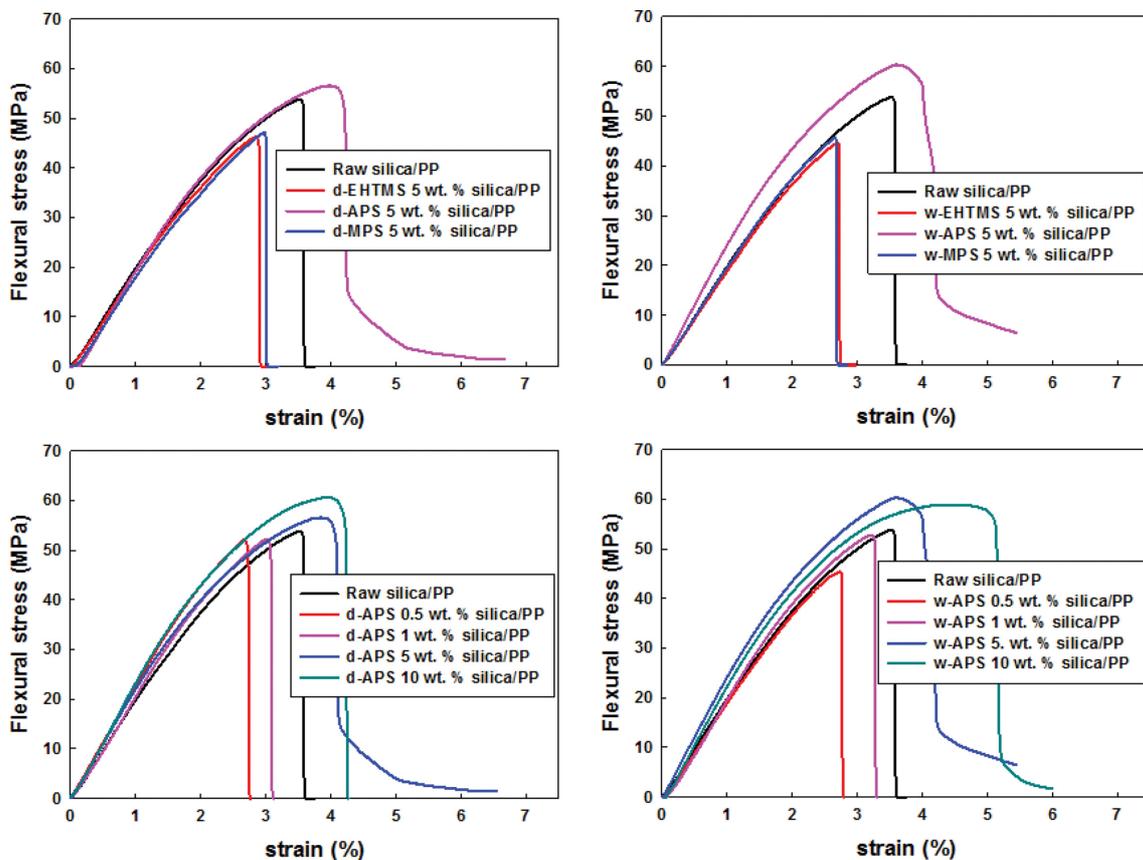
**Scheme 2.** Interaction between the coupling agent treated-silica and thermally oxidized-PP.

wet method, the amount of coupling agent mobilized on silica was presumably not fully utilized for improving the surface treatment, whereas the amount used in the dry method was completely used for improving the surface treatment. Additionally, the boiling point of the silane coupling agents is lower than the process temperature of 220 °C; hence, the coupling agent did not evaporate during the process and was presumably adsorbed fully onto the surface of silica, thereby improv-

ing its surface treatment.

Figure 5 graphically represents the flexural properties of the silane/silica/PP composite specimens with respect to the surface treatment method-, type-, and concentrations. On comparing the silane type-specific flexural properties, the flexural properties were found to decrease with both the wet and dry methods regardless of the coupling agent used, except for the APS-treated silica/PP specimens. This is in agreement with the tensile strength results, indicating a poor interfacial affinity between EHTMS and MPS with PP. On the contrary, the APS-treated silica/PP composites exhibited improved flexural properties with different surface treatment methods. This, in agreement with the tensile property analysis, could be attributed to the formation of chemical bonds by APS with silica and PP on the interface, subsequently increasing the interfacial affinity and bond. Furthermore, the composite specimens obtained with 5 and 10 wt% APS with both the wet and dry methods, were found to exhibit a deformation of 4%, confirming the role of APS as a plasticizer for the PP matrix.

Based on the results obtained with different silane coupling

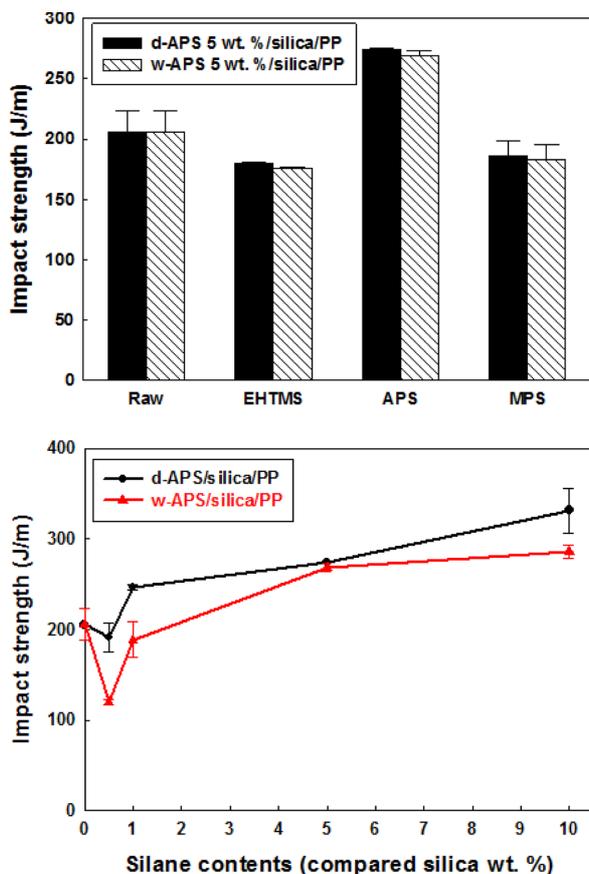


**Figure 5.** Flexural properties of raw and various silane-modified silica/PP composites.

agents, APS caused the highest level of improvement in the flexural properties when used in concentrations of 0.5, 1, 5, and 10 wt%. In both the wet and dry methods, the APS-treated specimens exhibited a decrease in the flexural performance at concentrations of 0.5 and 1 wt%, whereas their flexural strength increased with 5 and 10 wt%. This might be due to the greater affinity and bond between the silica and PP matrix achieved with APS.

On comparing the flexural properties obtained with the silane coupling agent treatment method, superior flexural properties were found to be obtained for specimens treated with the dry method and with 5 and 10 wt% APS. This trend, similar to that observed with the tensile properties of the specimens, could be attributed to the effectiveness of the dry method in fully grafting the coupling agent onto the surface of silica and subsequently improving the surface treatment.

Figure 6 presents the results of the unnotched Izod impact testing, indicating similar mechanical properties as those mentioned with the tensile and flexural property measurements.



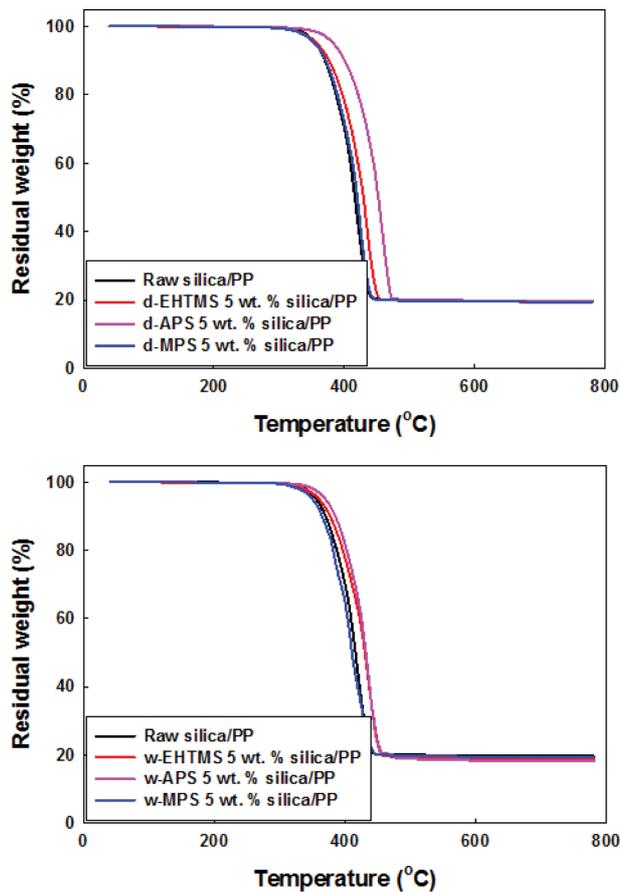
**Figure 6.** Impact properties of silane/silica/PP composites where silica was treated by wet and dry methods.

Unlike the tensile strength that indicates the stress at the time of fracture of silica/PP, the impact resistance strength indicates the energy absorbed per unit-length of the specimens at the time of fracture or the total energy required. While the brittle fracture entails faster spread of cracks, ductile failure involves plastic deformation as the cracking progresses. Accordingly, the energy required for the plastic deformation is absorbed, thereby increasing the energy required for fracture, causing an increase in the impact resistance strength.<sup>25,26</sup> The non-silane treated composite specimens exhibited an impact resistance strength of 200 J/m, whereas that obtained with the EHTMS- or MPS-treated specimens is 175 J/m, indicating a downward trend in the impact resistance strength. The APS-treated specimens exhibited an increased value of 275 J/m. This finding confirms the ability of APS in increasing the interfacial bond between silica and PP matrix.<sup>27</sup>

According to the results obtained for the impact resistance for the APS-added specimens with 0.5, 1, 5, and 10 wt%, the impact resistance strength was found to increase with an increase in the APS concentrations. This could be attributed to the role of APS in increasing the silica-PP interfacial bond and acting as a plasticizer for the PP matrix, thereby inducing ductile fracture. As the cracking progresses, the ductile fracture leads to plastic deformation. As the plastic deformation is initiated, the energy gets absorbed, causing the energy required for fracture to increase and presumably increase the impact resistance strength as well.

The wet method-treated silica was found to be more impact-resistant for samples obtained with  $\geq 5$  wt%, while the specimens treated with the dry method exhibited increased impact performance for samples prepared with  $\geq 1$  wt%.

**Thermal Properties of the Silica/PP Composite Specimens.** TGA was employed to examine the thermal decomposition characteristics. Figure 7 illustrates the graphic representation of the results obtained with TGA for the silica/PP composite specimens treated with different silane coupling agents and surface-treatment methods; especially, the thermal degradation temperature at 5% and 10% mass loss of the composites are displayed at Table 3. The thermal decomposition of the non-silane-added specimens between the PP matrix and the silane coupling agent started to occur at 320 °C, causing a weight loss until 440 °C, with a residual silica of 20%. TGA results obtained for the sample treated with the wet method using the silane coupling agent indicated that the APS-surface treated specimens started to thermally decompose at 340 °C, at a temperature 20 °C higher as that of the raw silica/PP com-



**Figure 7.** Thermogravimetric analysis of silane/silica/PP composites where silica was treated by wet and dry methods.

posite specimens. This increase could be attributed to the ability of APS in increasing the silica-PP interfacial bond. With EHTMS and MPS, similar results were obtained in terms of the mechanical properties and the heat-resistant properties. With the addition of APS to the silica/PP composite material in the dry method, the temperature at which the composite started to thermally decompose was found to be 50 °C, indicating an

increase in the threshold. This could be attributed to the increase in the silica-PP interfacial bond strength caused by APS, causing subsequent delays in the rate at which the PP matrix undergoes thermal decomposition. These findings confirmed that APS affects the thermal stability of the silica/PP composite material.

Figure 8 and Table 3 summarize the surface treatment methods and the types of the coupling agents as well as the DSC results obtained for different composite specimens. The silane-treated specimens exhibited a downward trend in the crystalline melting point ( $T_m$ ) and crystallization temperature ( $T_c$ ) as compared with its non-treated counterparts, with each specimen exhibiting a decrease of 1.33 °C at 0.49 °C and a decrease of 5.98 °C at 2.15 °C. This could be caused by the role of the coupling agents as a plasticizer inside the PP matrix. The degree of crystallinity ( $X_c$ ) also decreased, indicating a reduction of 3.58% at 1.96%. This could be attributed to the presence of silane coupling agents, which caused an increase in the affinity as well as the bond between the silica and the PP interface on cooling the PP that starts to crystallize, thus impeding the crystallization process.<sup>28</sup>

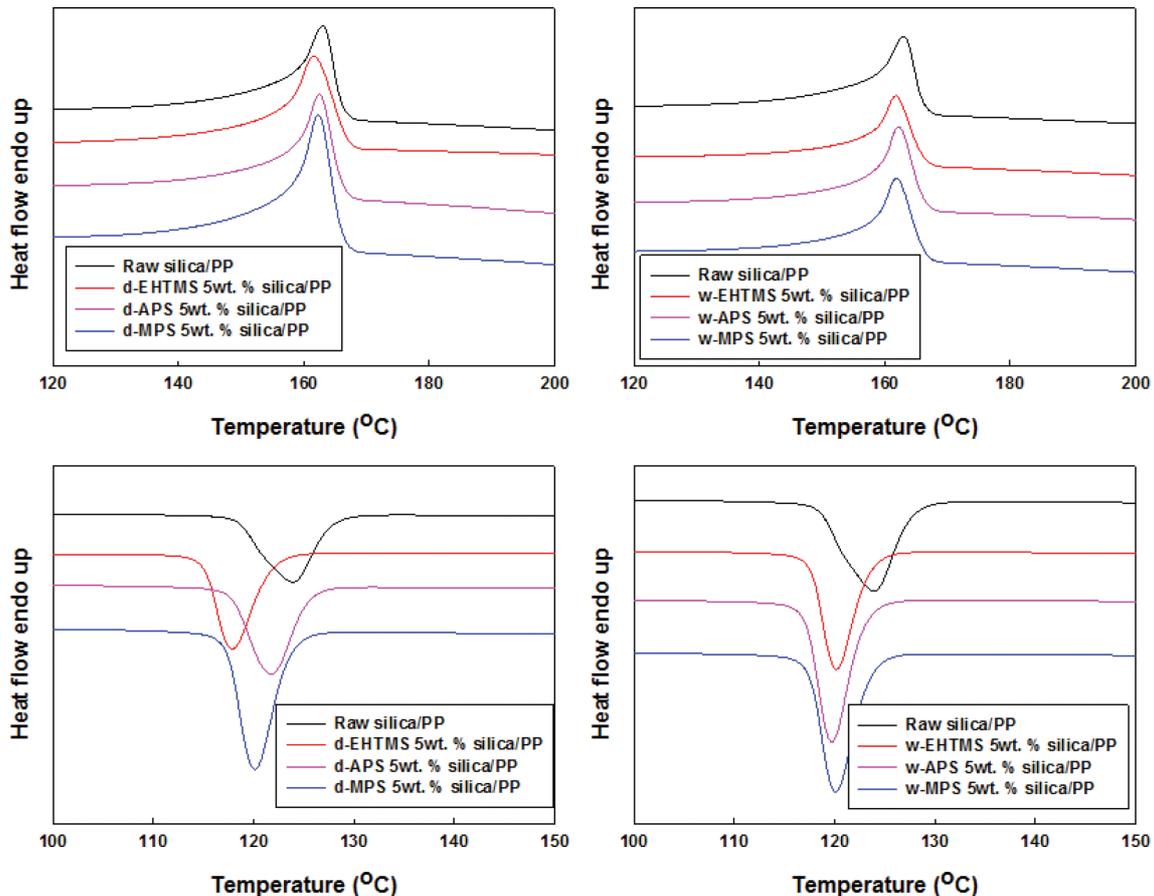
## Conclusions

In order to prepare a silica/PP composite material exhibiting superior mechanical strength and thermal properties, three types of silane coupling agents were added to the silica/PP composites using dry and wet surface-treatment methods. The specimens were subjected to tensile, flexural, and impact resistant strength measurements as well as SEM, TGA and DSC characterizations. The results obtained can be summarized as follows:

APS (a type of the silane coupling agents used for the study) that is capable of inducing a chemical reaction between the sil-

**Table 3.** Melting Temperature ( $T_m$ ), Crystallization Temperature ( $T_c$ ) and Crystallinity ( $X_c$ ) of Silane/Silica/PP Composites

	$T_m$ (°C)	$T_c$ (°C)	Crystallinity (%)	Thermal degradation temperature (°C)	
				@ 5% loss mass	@ 10% loss mass
Raw silica/PP	162.97	123.85	67.86	356.07	370.46
d-EHTMS 5 wt%/silica/PP	161.64	117.87	64.28	358.06	376.53
d-APS 5 wt%/silica/PP	162.48	121.70	65.26	383.45	400.64
d-MPS 5 wt%/silica/PP	162.29	120.08	65.90	354.98	371.64
w-EHTMS 5 wt%/silica/PP	161.82	120.19	64.58	360.26	374.57
w-APS 5 wt%/silica/PP	162.15	119.71	65.26	369.96	385.18
w-MPS 5 wt%/silica/PP	161.98	120.04	64.91	350.02	362.59



**Figure 8.** DSC thermograms for silane/silica/PP composites where silica was treated by wet and dry methods.

ica and PP was found to be the optimal coupling agent for improving the mechanical and thermal properties of the prepared silica/PP composite material. Furthermore, when APS was used with a concentration of 5 wt%, the obtained sample exhibited outstanding mechanical properties, while on using 10 wt% APS, it acted as a plasticizer.

Only minor differences were obtained with the mechanical and thermal properties of the composite samples obtained with the two surface-treatment methods (wet and dry). The different features of the two methods did not greatly affect the properties of the specimens. The complicated wet method caused an improvement in the surface treatment with a relatively greater consistency, and the dry method is simple and easy since the experiment can be performed at limited temperature ranges and concentrations.

TGA analysis of the specimens obtained with the wet method indicated variations in the amount of the coupling agent present on the surface of the silica, which depended on the type of the agent used. Thus, the dry method offers greater

advantages as compared to the wet method in controlling the concentrations of the agent on adding to silica in the preparation of the composite material.

**Acknowledgements:** This work was supported by a grant (no.; 10052976) by the Ministry of Trade, Industry and Energy (MOTIE), Republic of Korea.

## References

1. J. M. Kim, S. K. Jeoung, J. H. Shim, H. Y. Hwang, and K. Y. Lee, *Polym. Korea*, **34**, 346 (2010).
2. J. S. Kim, M. A. Choi, T. W. Park, and D. J. Kim, *Polym. Korea*, **24**, 700 (2000).
3. M. Bailly and M. Kontopoulou, *Polymer*, **50**, 2472 (2009).
4. J. Jancar and J. Kucera, *Polym. Eng. Sci.*, **30**, 714 (1990).
5. M. Fujiyama and T. Wakino, *J. Appl. Polym. Sci.*, **42**, 9 (1991).
6. W. Qui, K. Mai, and H. Zeng, *J. Appl. Polym. Sci.*, **71**, 1537 (1999).
7. M. Y. Lee, J. Y. Park, K. C. Song, and S. K. Kim, *Elastomer*, **51**,

- 106 (2016).
8. S. J. Park, K. S. Cho, and M. Zaborski, *Polym. Korea*, **26**, 445 (2002).
  9. O. H. Lin, H. M. Akil, and Z. M. Ishak, *Polym. Compos.*, **32**, 1568 (2011).
  10. C. Liang, C. Hu, Y. Zheng, K. Yan, and X. Zhu, *Polym. Compos.*, **37**, 1 (2016).
  11. X. Yuan, Y. Zhang, and X. Zhang, *J. Appl. Sci.*, **71**, 333 (1999).
  12. P. bajaj, N. K. Jha, and R. K. Jha, *Polym. Eng. Sci.*, **29**, 557 (1989).
  13. C. Y. Min, Y. D. Huang, and L. Liu, *J. Mater. Sci.*, **42**, 8695 (2007).
  14. X. Yang, N. Zhao, Q. Zhou, Z. Wang, C. Duan, C. Cai, X. Zhang, and J. Xu, *J. Mater. Chem.*, **22**, 18010 (2012).
  15. T. Cai, R. Wang, W. J. Yang, S. Lu, K. G. Neoh, and E. T. Kang, *Soft Matter*, **7**, 11133 (2011).
  16. G. Zhai, L. Ying, E. T. Kang, and K. G. Neoh, *J. Mater. Chem.*, **12**, 3508 (2002).
  17. O. M. Kwon, S. J. See, S. S. Kim, and H. Y. Hwang, *Appl. Surf. Sci.*, **321**, 378 (2014).
  18. P. Song, Y. Shen, B. Du, Z. Cuo, and Z. Fang, *Nanoscale Horiz.*, **1**, 118 (2009).
  19. A. Bartnik, W. Lisowski, J. Sobczak, P. Wachulak, B. Budner, B. Korczyk, and H. Fiedorowicz, *Appl. Phys. A*, **109**, 39 (2012).
  20. Y. Wang, L. Zhang, Y. Hu, and C. Li, *J. Mater. Sci. Technol.*, **31**, 901 (2015).
  21. J. B. Moon, *Elastomer*, **36**, 237 (2001).
  22. J. Karger-Kocsis, *Polypropylene: An A-Z reference*, Kluwer Publishers, Dordrecht, 1999.
  23. F. Gugumus, *Polym. Degrad. Stab.*, **62**, 235 (1998).
  24. M. Sonmez, M. Georgescu, M. Valsan, M. Radulescu, D. Ficai, G. Voicu, A. Ficai, and L. Alexandrescu, *J. Appl. Polym. Sci.*, **132**, 42163 (2015).
  25. O. S. Lee, J. W. Han, S. W. Hwang, and M. S. Han, *KSME*, **19**, 1630 (1995).
  26. H. Kim, D. S. Lee, J. S. Lim, and M. Y. Lyu, *Polym. Korea*, **36**, 59 (2012).
  27. Y. W. Seo and D. S. Kim, *Polym. Korea*, **38**, 327 (2014).
  28. D. N. Bikiaris, G. Z. Papageorgiou, E. Pavlidou, N. Vouroutzis, P. Palatzoglou, and G. P. Karayannidis, *J. Appl. Polym. Sci.*, **100**, 2648 (2006).