

Effect of the Silane Modification of an Organoclay on the Properties of Polypropylene/Clay Composites

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ABSTRACT: A commercial clay, Cloisite[®]20A (C20A) was modified with three different silane compounds, propyltrimethoxy silane, octyltrimethoxy silane, and octadecyltrimethoxy silane, to control the hydrophobicity of C20A. The amount of the silane compounds grafted to C20A was quantified from the weight loss by using TGA, and the hydrophobicity was evaluated by the amount of water absorption. The variation of the interlayer distance was traced by XRD and TEM observation. SEM/EDS was employed to visualize the morphology of the fractured surface and the degree of dispersion of the clay layers in the PP/clay composites. Measurements of the tensile prop-

erties of the PP/clay composites indicated that the composite made from PP and the C20A modified with octadecyltrimethoxy silane exhibited the most excellent tensile properties. This was ascribed to the fact that the C20A modified with octadecyltrimethoxy silane possessed the most favorable interfacial interaction with PP and thus the degree of dispersion of the clay layers was the best in the PP matrix. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3645–3650, 2008

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INTRODUCTION

Polypropylene (PP) has low density and chemical stability together with excellent processability and price competitiveness. PP has been compounded with various inorganic fillers such as CaCO₃, talc, mica, and glass fiber to improve mechanical properties of PP.^{1–4}

During the past few years, clays composed of inorganic layers of a few nanometer thickness has attracted considerable attention as an effective reinforcing filler for many polymers because of its platelet structure with high aspect ratio, which may enhance mechanical and thermal properties of the polymers considerably even with much smaller amount of the nano-sized filler when compared with the micro-sized composite counterparts.⁵ Smectite clays such as montmorillonite are most frequently employed for this purpose. Since the silicate layers of the clay are hydrophilic in nature, they are seldom compatible with organic polymers. And thereby the smectite clays are usually treated to make them more compatible with the organic polymers by ionic exchange of the interlayer metal cations with onium cations bearing long alkyl chains.⁶ Yoon and coworkers^{7–9} introduced func-

tional groups to the clay, once modified with ammonium alkyl compounds, by having silane compounds reacted with the Si-OH groups on the clay layers. The chemical reaction between the functional groups of the modified clay and the matrix polymer promoted interactions between the composite constituents.

Nanocomposites based on PP prepared by melt blending using the conventional plastic compounding tools constitute a major challenge, especially for the automotive industry. However, most of the PP-based nanocomposites have shown a morphology with a relatively limited intercalation and coupling agents such as maleic acid grafted PP have been used to improve the clay intercalation.¹⁰ However, the addition of the coupling agents usually affects the morphology of the PP-based nanocomposites. Moreover, the maleic acid grafted PP is very high in cost and the improvement of mechanical properties has mostly been unsatisfactory.^{11–13}

In this study, we attempted to prepare PP/clay nanocomposites with a good dispersion of the clay layers through melt mixing without the aid of the coupling agents. Silane molecules bearing alkyl chains with different chain length were introduced to the clay to raise the compatibility with the matrix polymer. The hydrophobicity of the clay before and after the modification with the silane compounds was evaluated by measuring the water uptake. Morphology and mechanical properties of the resulting PP/clay composites were explored.

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EXPERIMENTAL

Materials

A commercial grade of homo PP produced by Korea Petrochemical (Korea) was used. Its melt index and density were 8.5 g/10 min and 0.9 g/cm³, respectively. Cloisite[®]20A from Southern Clay (USA) was used as a nanofiller. It is a commercially available natural montmorillonite exchanged with dimethyl dehydrogenated tallow quaternary ammonium chloride. Propyltrimethoxy silane, octyltrimethoxy silane and octadecyltrimethoxy silane were purchased from Aldrich (USA).

Methods

Preparation of silane-modified C20A

After the silane compound was hydrolyzed at pH 4.0 for 4 h in a solution of acetic acid in ethanol (90%)/deionized water (10%) mixture, C20A was added and the mixture was then heated with reflux at 70°C for 24 h. The product was diluted several times with ethanol and hot water to remove the unreacted silane compound. The resulting product was then dried in vacuum oven at 60°C for at least 48 h and was ground to 53 μm size in a ball mill. The C20As modified with propyltrimethoxy silane (SIII), octyltrimethoxy silane (SVIII), and octadecyltrimethoxy silane (SXVIII) were abbreviated as C20AIII, C25AVIII, and C25AXVIII, respectively.

Preparation of PP/silane-modified clay nanocomposites

PP/clay composites were prepared by melt compounding of PP with the various clays at 200°C by using a twin screw extruder ($L/D = 40$; Bau Technology, Korea). The clay content was fixed at 2 wt %. The product was dried in a vacuum oven at 60°C for at least 24 h.

Characterization

Measurement of water uptake of the clays

Hydrophobicity of the clays was evaluated by measuring the water uptake. The clays were firstly dried in a highly vacuum state oven at 80°C for 12 h and then their weight was measured. The dried clays were kept in an oven saturated with water at 80°C for 12 h and the weight gain was examined.

Wide angle X-ray diffraction

The interlayer distance between the silicate layers was measured by wide angle X-ray scattering (Rigaku DMAX 2500). Cu K α ($\lambda = 0.154$ nm) radia-

tion source was operated at 40 kV and 40 mA. Patterns were recorded by monitoring those diffractions appeared in the 2θ range from 2° to 10° with a scanning rate of 1°/min.

Scanning electron microscope

Morphology of the composites was examined by using a scanning electron microscopy (SEM) (S-4200; Hitachi, Japan) coupled with energy disperse X-ray spectrometer (EDS).

Transmission electron microscope

Transmission electron microscopy (TEM) images were obtained by using TEM 2000 EX-II instrument (Jeol, Japan) operated at an accelerating voltage of 100 kV to observe the nanoscale structures of the nanocomposites. All of the ultrathin sections (less than 100 nm) were microtomed using a Super NOVA 655001 (Leica, Swiss) with a diamond knife at a liquid nitrogen temperature and were then subjected to TEM observation without staining.

Tensile properties

The specimens for the tensile tests were prepared from hot-pressed sheets of PP and its composites. The specimens were subjected to uniaxial elongation at room temperature. All the measurements were carried out by using UTM (Hounsfield, UK) at a cross head speed of 50 mm/min.

RESULTS AND DISCUSSION

C20A was reacted with propyltrimethoxy silane(SIII), octyltrimethoxy silane(SVIII), and octadecyltrimethoxy silane(SXVIII) to have the silane compounds reacted with the silanol groups on the silicate layers of C20A to prepare C20AIII, C20AVIII, and C20AXVIII, respectively.

Figure 1 shows the thermogravimetric analysis results of C20A, C20AIII, C20AVIII, and C20AXVIII. The weight losses of C20AVIII and C20AXVIII were more significant than that of C20A because of the additional weight decrease coming from the degradation of the grafted silane molecules. However, contrary to the expectation, C20AIII lost less weight than C20A did. This was attributed to the fact that some of the surfactant molecules were leached out during the clay modification by using the silane compounds. Hydrophobicity of the silane modified C20A was assessed by measuring the amount of water uptake as shown in Figure 2. The longer the alkyl chain length of the silane compound, the smaller the water uptake. And thereby the water

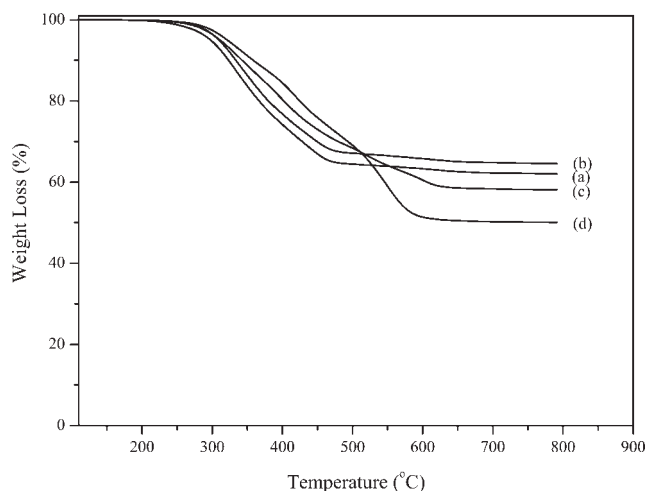


Figure 1 Weight loss of the clays measured by TGA: (a) C20A, (b) C20AIII, (c) C20AVIII, (d) C20AXVIII.

uptake decreased significantly in the order of C20A > C20AIII > C20AVIII. However, the water uptake of C20AXVIII was only slightly smaller than that of C20AVIII in spite of the fact that the weight loss of C20AXVIII during the thermogravimetric analysis was far larger than that of C20AVIII (Fig. 1) and that SXVIII was much more hydrophobic than SVIII. Therefore, it can be said that the water uptake can not be a linear index as a function of the hydrophobicity of the modified clays.

Table I summarizes the interlayer spacings, which were determined from the WAXD diagrams of the clays as displayed in Figure 3. It can be seen that the d_{001} spacings of C20A, C20AIII, C20AVIII, and C20AXVIII were almost identical with each other, indicating that the reaction between the silane compound and C20A took place mainly on the outside of the clay layers. This assumption carries validity since the silanol groups locate mostly on the edges of the clay layers rather than on their plane sur-

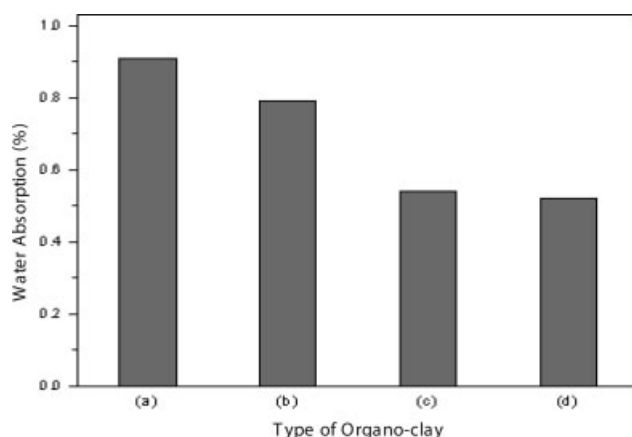


Figure 2 Variation of water uptake of the clays (a) C20A, (b) C20AIII, (c) C20AVIII, (d) C20AXVIII.

TABLE I
Interlayer Distance of the Clays Measured by WAXD

Samples	2θ ($^{\circ}$)	d_{001} (nm)
C20A	3.7	2.4
C20AIII	3.7	2.4
C20AVIII	3.6	2.5
C20AXVIII	3.3	2.7
PP C20A	2.7	3.3
PPC20AIII	2.9	3.0
PPC20AVIII	2.9	3.0
PPC20AXVIII	2.9	3.0

face.^{9,14–17} Herrera et al. also observed similar phenomena.¹⁸

PP was compounded with C20A, C20AIII, C20AVIII, and C20AVIII to prepare PPC20A, PPC20AIII, PPC20AVIII, and PPC20AXVIII, respectively. The XRD diagrams and TEM images of the composites are exhibited in Figures 4 and 5, respectively. Comparison of the XRD results in Figure 4 with those in Figure 3 reveals that the d_{001} spacing of the clay layers was enlarged discernibly as a result of the compounding with PP. However, once compounded, the d_{001} spacing was nearly constant

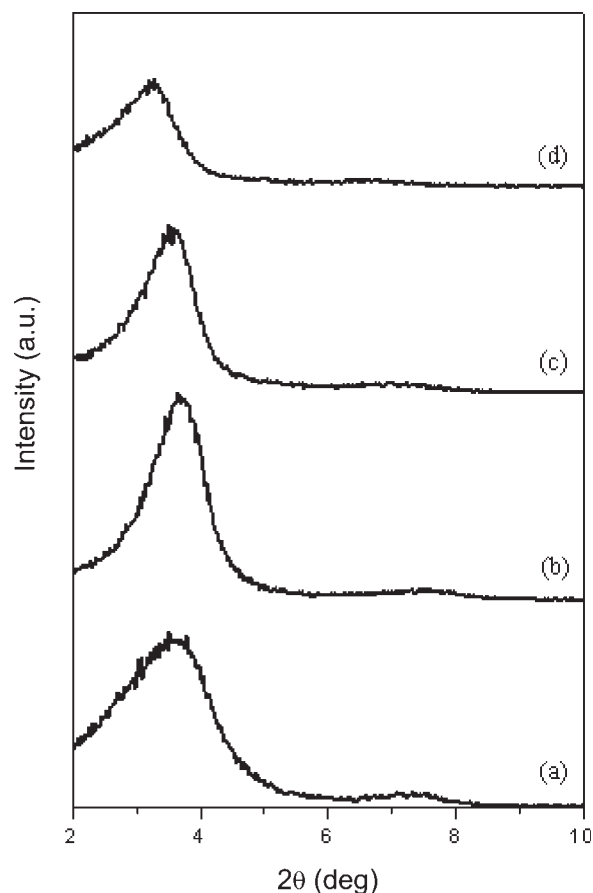


Figure 3 X-ray diffraction patterns of the clays (a) C20A, (b) C20AIII, (c) C20AVIII, (d) C20AXVIII.

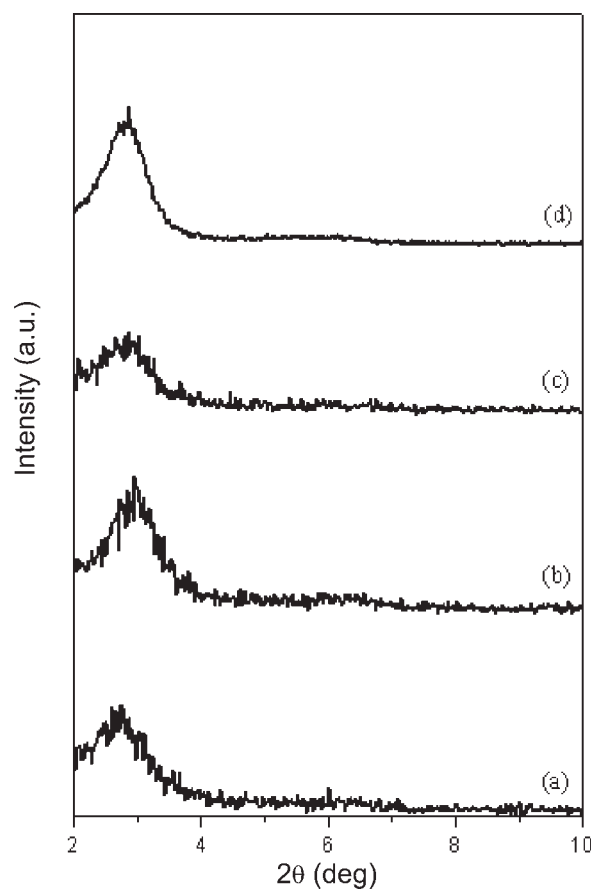


Figure 4 X-ray diffraction patterns of PP/clay composites: (a) PPC20A, (b) PPC20AIII, (c) PPC20AVIII, (d) PPC20AXVIII.

irrespective of the clay types. The morphology observed by TEM in Figure 5 demonstrates that not only PPC20A but also PPC20AXVIII possesses nanometer-range intercalated tactoids and that their d_{001} spacings are almost identical with each other in spite of the huge difference in the hydrophobicity of the clays in line with the observations in Figure 4.

Figure 6 shows the SEM micrographs and EDS Si mapping results of the fractured surfaces of PPC20A, PPC20AIII, PPC20AVIII, and PPC20AXVIII. The bright dots in the EDS Si mappings correspond to Si atoms. According to Figure 6, the bright dots are the most numerous in PPC20A and the number of the bright dots decreases in the order of PPC20AIII > PPC20AVIII > PPC20AXVIII. Therefore it can be said that the silicate layers protruded out most abundantly in PPC20A followed by PPC20AIII, PPC20AVIII, and PPC20AXVIII in decreasing order. Since the cracks propagate mainly through weak points, the results in Figure 6 reveal that the degree of aggregation of the clay layers was lowered in the order of PPC20A > PPC20AIII > PPC20AVIII > PPC20AXVIII. Especially, few bright dots are observed in the EDS Si mapping of PPC20AXVIII indicative of the best dispersion of C20AXVIII in the PP matrix among the used clays. Hence it can be concluded that the modification of C20A with a long alkyl-chain silane compounds improved considerably the compatibility between the clay and PP.¹⁹

Tensile properties of PP, PPC20A, PPC20AIII, PPC20AVIII, and PPC20AXVIII were measured by using UTM at room temperature and the results are

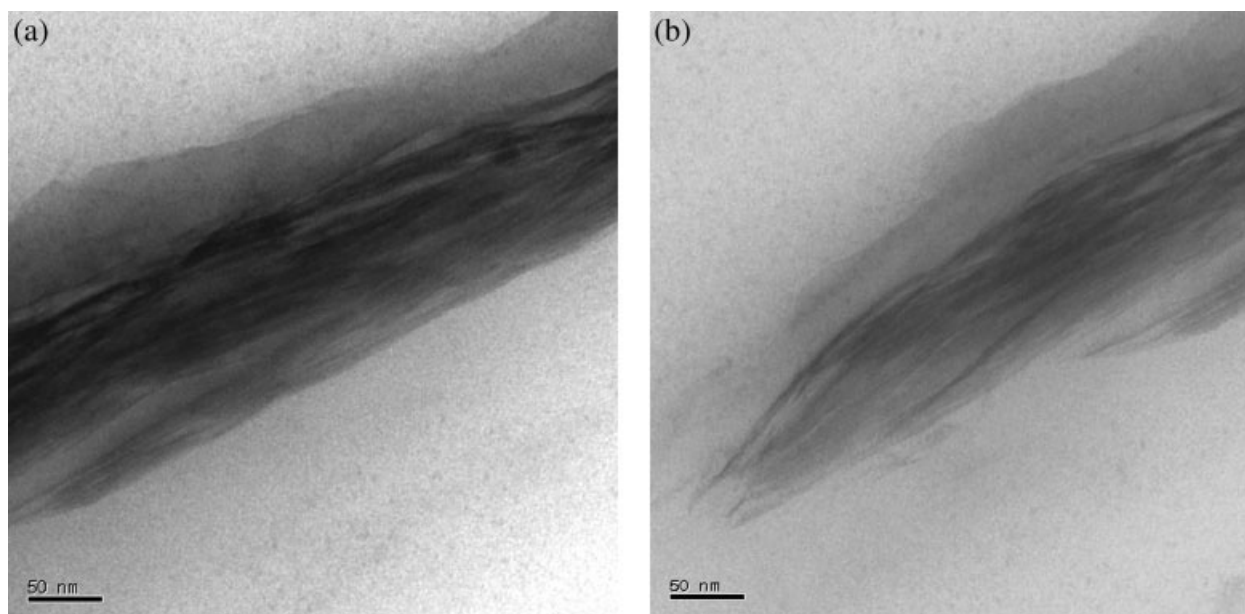


Figure 5 TEM images of PP/clay composites: (a) PPC20A, (b) PPC20AXVIII.

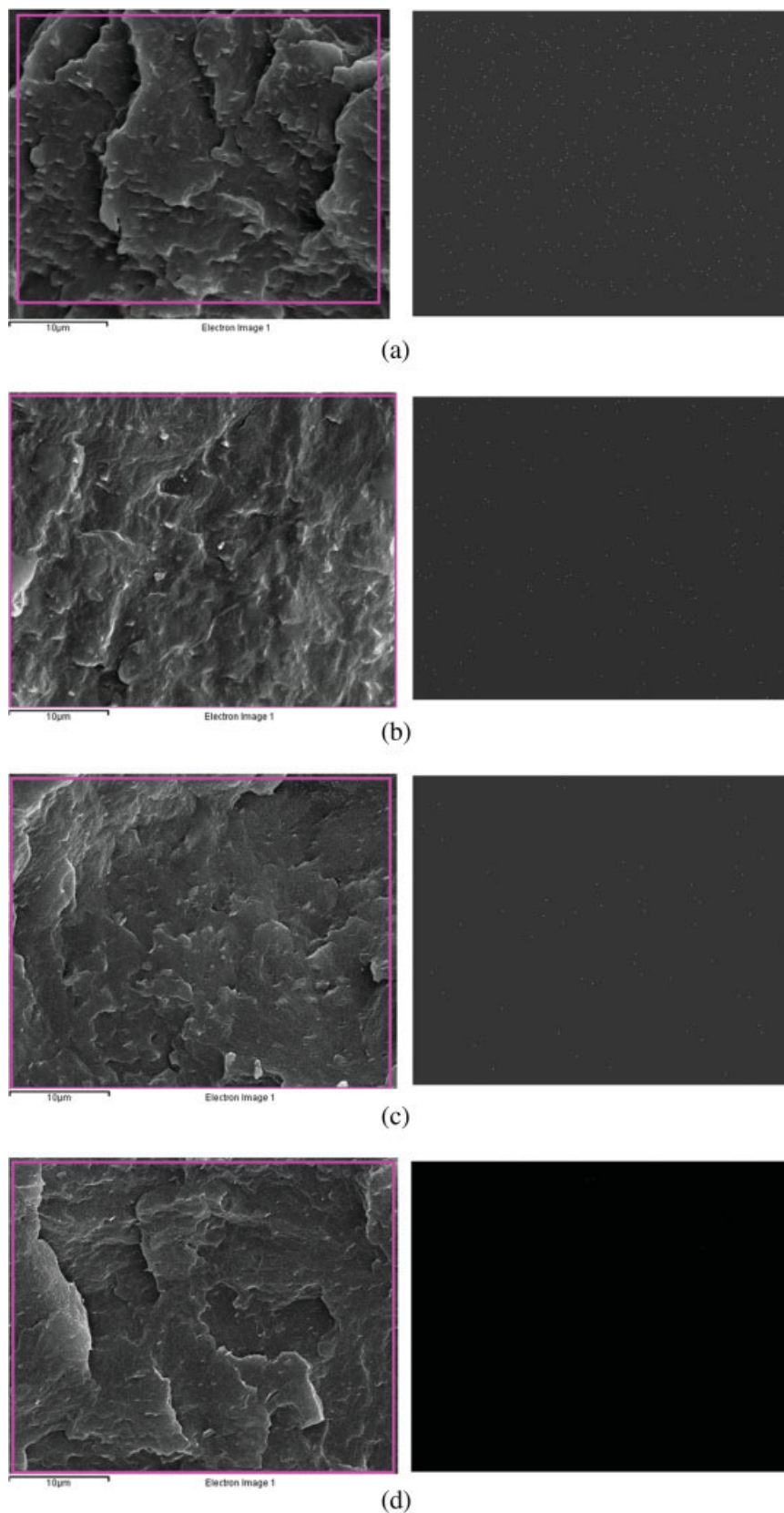


Figure 6 SEM micrographs and EDS Si mapping of PP/clay composites: (a) PPC20A, (b) PPC20AIII, (c) PPC20AVIII, (d) PPC20AXVIII. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
The Tensile Properties of PP and Its Composites
With Various Clays

	Young's modulus (MPa)	Extension at break (%)	Yield stress (MPa)
Neat PP	1480	148	36
PPC20A	1610	10	35
PPC20AIII	1830	10	36
PPC20AVIII	2010	10	37
PPC20AXVIII	2340	85	36

collected in Table II. The content of the clays was fixed at 2.0 wt %.

Tensile modulus was raised owing to the incorporation of all the types of the clays because of the reinforcing effects of the platelet fillers. Tensile modulus went up in the order of PP < PPC20A < PPC20AIII < PPC20AVIII < PPC20AXVIII and thereby the tensile modulus of PPC20AXVIII was 1.6 times higher than that of neat PP. However, elongation at break decreased precipitously from 148% to as low as 10% because of the incorporation of 2.0 wt % of C20A. Addition of C20AIII and C20AVIII instead of C20A to PP did not ameliorate the elongation at break either. In sharp contrast, the decrease of the elongation at break was much less significant when C20AXVIII was compounded with PP and the elongation at break of PPC20AXVIII was as high as 85%. Among the composites, the increasing order of the tensile properties was in line with the increasing order of hydrophobicity of the silane compounds used for the modification and with the increasing order of hydrophobicity of the clays. Since PP is extremely hydrophobic, the clay modified with the most hydrophobic silane compound was believed to be more compatible with PP to lead to the most enhanced tensile properties of PPC20AXVIII in comparison with the other composites.

CONCLUSION

PP/clay nanocomposites were prepared without resort to the compatibilizing substances such as maleic anhydride-grafted-PP. To enhance the compatibility between Cloisite20A (C20A) and PP, C20A was treated with propyltrimethoxy silane, octyltrimethoxy silane and octadecyltrimethoxy silane to

prepare C20AIII, C20AVIII, and C20AXVIII, respectively. PPC20A, PPC20AIII, PPC20AVIII, and PPC20AXVIII were fabricated by compounding PP with C20A, C20AIII, C20AVIII, and C20AXVIII, respectively. Exfoliation of the clay layers was not observed and only intercalated morphology was seen by XRD and TEM in all the composites. Tensile modulus increased in the order of PP < PPC20A < PPC20AIII < PPC20AVIII < PPC20AXVIII. Fewer Si elements were detected on the fractured surface of PPC20AXVIII than those of the other composites as observed by SEM/EDS indicating the highest compatibility between C20AXVIII and PP among the four different clays to lead to the best tensile properties of PPC20AXVIII.

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