

# Effect of the Silane Modification of Clay on the Tensile Properties of Nylon 6/Clay Nanocomposites

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Received 24 October 2008; accepted 4 July 2009

DOI 10.1002/app.31077

Published online 26 March 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A commercially available organomodified clay, Cloisite 25A, was modified with 3-aminopropyltriethoxysilane, 3-(glycidoxypropyl)trimethoxysilane, and 3-isocyanate propyltriethoxysilane to enhance its interaction with the nylon 6 matrix. Composites made of nylon 6 and clays modified with the different silane compounds were prepared by melt mixing with a twin-screw extruder. The dispersion and degree of exfoliation of the organomodified clays were evaluated from

X-ray diffraction patterns and transmission electron microscopy images of the corresponding composites. The tensile properties of the composites were measured, and their enhancement was attributed to the work of adhesion and interfacial tension of the composites. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 809–816, 2010

**Key words:** clay; composites; nylon

## INTRODUCTION

Polymer/clay nanocomposites present outstanding mechanical properties such as stiffness and strength with only a small amount of nanofillers.<sup>1–4</sup> This is due to the large surface-area-to-volume ratio of the nanofillers compared to conventional macrosized fillers.<sup>4–8</sup> Other important advantages of polymer/clay nanocomposites include barrier resistance,<sup>9–13</sup> flame retardancy,<sup>14–18</sup> and desirable electrical properties.<sup>19,20</sup>

Nylon 6/clay nanocomposites were initially developed by Usuki and coworkers<sup>21,22</sup> and were the first commercially produced polymer nanocomposites. They were prepared by the monomer intercalation method, wherein an organomodified clay is swollen in a monomer ( $\epsilon$ -caprolactam) followed by the polymerization of the monomers that intercalate the clay layers.<sup>23,24</sup> Another *in situ* polymerization method known as *one-pot polymerization* was proposed by Kojima et al.<sup>25</sup> With simultaneous mixing of montmorillonite,  $\epsilon$ -caprolactam, and phosphoric acid in a glass-receptacle and the initiation of the polymerization, a nylon 6/clay nanocomposite was produced quite readily.

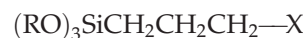
In addition to the *in situ* polymerization method, the direct melt mixing of nylon 6 with an organomodified clay is another effective method for the production of polymer/clay nanocomposites.<sup>26,27</sup> Shah and Paul<sup>28</sup> prepared nylon 6/clay nanocomposites

via the master batch method. Hasegawa et al.<sup>29</sup> used a pristine clay slurry to manufacture nylon 6/clay nanocomposites more economically. However, the heat distortion temperature of the resulting nanocomposites was somewhat lower than that of nanocomposites prepared by the conventional melt-mixing method.

The organomodification of clay is an important step in the preparation of polymer/clay nanocomposites. The superior mechanical properties of the polymer/clay nanocomposites are achieved not only through the molecular-level dispersion of the aluminosilicate layers but also through the strong interactions between the polymer matrix and the clay layers. To enhance the interaction between the polymer matrix and the clay layers, the clays can be modified by various cationic organosurfactants.<sup>30</sup> However, even after modification, numerous silanol groups remain on the clay layers.

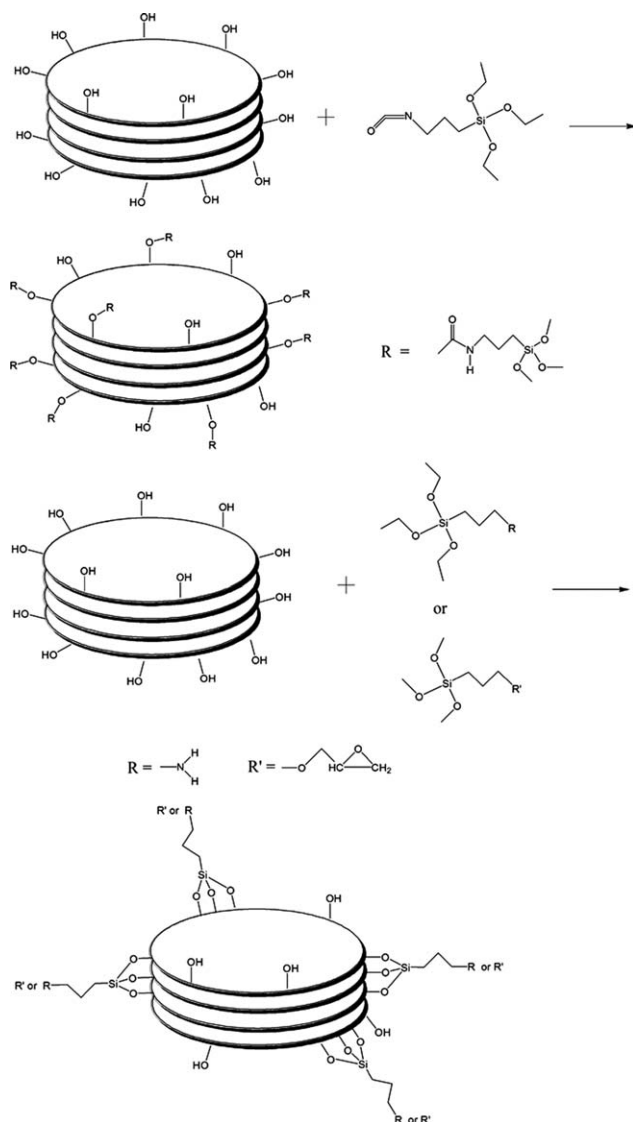
In this study, further modification of clay previously treated with cationic organosurfactants was attempted to increase the compatibility between the polymer matrix and the clay layers.<sup>1,31–33</sup> Silane coupling agents were chosen for the modification of Cloisite 25A (C25A), a sodium montmorillonite modified by an ammonium salt bearing long alkyl chains.

Silane coupling agents are silicon-based chemicals that afford two types of reactivity (inorganic and organic) in the same molecule. A typical structure is



where RO is a hydrolyzable group, such as methoxy, ethoxy, or acetoxy, and X is an organofunctional

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Contract grant sponsors: Inha University.



**Scheme 1** Modification process of C25A.

group, such as epoxy, amine, or isocyanate. Silane compounds improve the wettability at the interface between inorganic substrates and organic materials through the bonding or coupling of two dissimilar materials. The induction of chemical reactions between the functional groups of the silane-modified clay and the polymer matrix further enhance the interaction between the components of the polymer/clay composites.<sup>31</sup> Three kinds of silane compounds were used for the modification of the clays to enhance the interaction of the silicate layers with the nylon 6 matrix. Evidence of the grafting of the silane compounds to C25A was provided by corresponding Fourier transform infrared (FTIR) spectra.<sup>31–33</sup> The morphology and mechanical properties of the resulting nylon 6/clay composites were investigated in accordance with the functional groups introduced onto the surface of the silicate layers.

## EXPERIMENTAL

### Materials

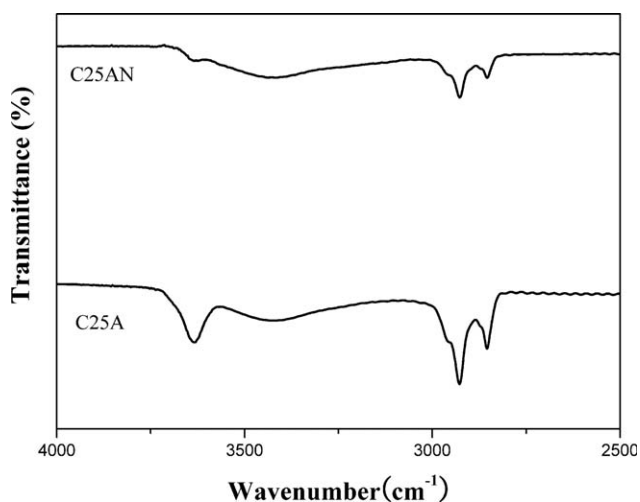
The clay used in this study was C25A purchased from Southern Clay (Gonzales, TX). 3-(Glycidyloxypropyl)trimethoxysilane (GPS) and 3-aminopropyltriethoxysilane (APS) were supplied by Aldrich (St. Louis, MO) and 3-isocyanate propyltriethoxysilane (IPS) was purchased from Shin-Etsu (Tokyo, Japan). All of the silane compounds were reagent grade and used without further purification. Nylon 6 was supplied by Rhodia (Saint-Fons Cedex, France) with a specific gravity of 1.14.

### Clay modification

After APS (3.5 g) was hydrolyzed at pH 4.0 for 4 h in a solution of acetic acid in an ethanol (80 wt %)/deionized water (20 wt %) mixture (200 ml), C25A (10 g) was added to the double-jacketed reactor, and the mixture was then heated with reflux at 80°C for 14 h. The product was diluted several times with alcohol to remove the soluble homocondensates. The resulting product [C25A modified with 3-aminopropyltriethoxysilane (C25AN)] was then filtered and repeatedly washed with ethanol at room temperature and dried in a vacuum oven at 50°C for at least 48 h. C25A modified with 3-(glycidyloxypropyl)trimethoxysilane (C25AE) and C25A modified with 3-isocyanate propyltriethoxysilane (C25AI) was made with the same procedure used for the preparation of C25AN.

### Preparation of the nylon 6/organoclay nanocomposites

All of the nylon 6/clay composites were prepared by melt compounding with a twin-screw extruder



**Figure 1** FTIR spectra of C25A and C25AN.

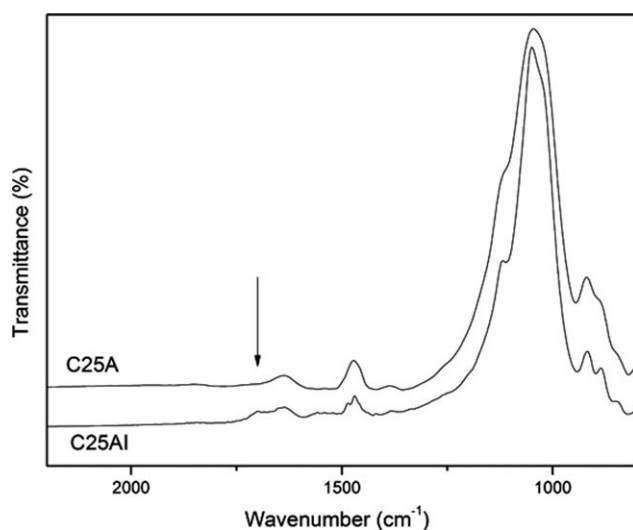


Figure 2 FTIR spectra of C25A and C25AI.

(length/diameter = 40, Bau Technology, Korea) at 240°C and 200 rpm. The clay content was fixed at 3 wt %. The product was dried in a vacuum oven at 60°C for more than 24 h.

### Characterization

The grafting behavior of the silane compounds was monitored by FTIR spectrophotometry. The FTIR spectra were recorded on a PerkinElmer Spectrum 2000 spectrometer (Fremont, CA) over a wave-number range of 4000–400  $\text{cm}^{-1}$ . The quantitative analysis for the atomic content of the modified clays were identified through elemental analysis (CE Instruments Thermo EA111,2, Wigan, England) The variation of the interlayer distance of the clay layers in the composites was analyzed by means of wide-angle X-ray scattering (XRD; Rigaku DMAX 2500, Tokyo, Japan). The  $\text{Cu K}\alpha$  radiation source was operated at 40 kV and 40 mA. The patterns were recorded by the monitoring of those diffractions appearing in the  $2\theta$  range from 2 to 10° with a scanning rate of 1°/min.

The morphological aspects of the composites were examined with transmission electron microscopy (TEM) to determine the internal micromorphology. A Philips CM200 (Amsterdam, Netherlands) with an acceleration voltage of 100 kV was used.

The tensile properties of the composites were measured with a universal testing machine (UTM; Hounsfield H 10KS-0061, Horsham, United Kingdom). The specimens were prepared according to ASTM D 638. The crosshead speed was 50 mm/min. The results of five measurements were averaged.

The contact angles were measured in a sessile drop mold with a KRUSS DSA100 (Hamburg, Ger-

many). The nylon 6 sample for contact angle measurements was compression-molded between clean Teflon films at 240°C for 3 min and then cooled to 25°C under pressure for 1 min. The clay powders were compression-molded with a special mold at room temperature under a specific pressure. The contact angles were measured on 3 ml of wetting solvent at 20°C, and the results reported are the mean values of 10 replicates.

## RESULTS AND DISCUSSION

### Silane modification

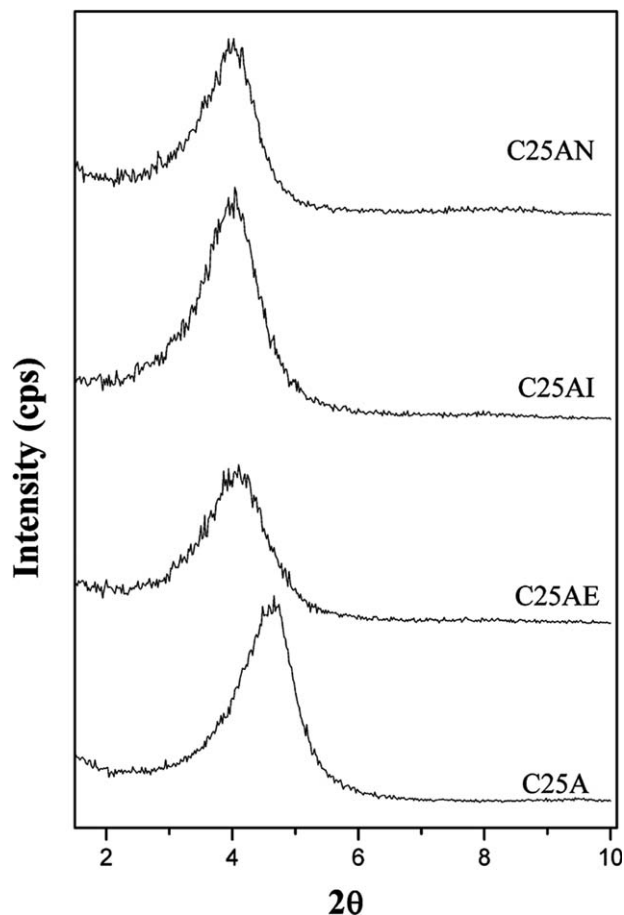
The commercial clay C25A is sodium montmorillonite modified with a quaternary alkyl ammonium compound bearing long alkyl chains. However, lots of silanol groups remain on the edges of the C25A platelets even after the modification step. Epoxy and amine functional groups were introduced onto the surface of the C25A layers to prepare C25AE and C25AN, respectively, by way of the reaction of the silanol groups of C25A with GPS and APS, respectively. C25AI was prepared by the treatment of C25A with IPS.

Scheme 1 exhibits the clay modification process. The alkoxy groups of the silanes were converted into hydroxyl groups because of the hydrolysis. The hydroxyl groups of the silanes may have reacted with the hydroxyl groups on the edge of the clay. Because isocyanate groups are more reactive with the silanol group of C25A than the other functional groups of IPS, C25AI should have had silanol groups after the modification.<sup>34</sup>

The FTIR spectrum of C25AN in Figure 1 reveals that the peak at 3638  $\text{cm}^{-1}$  of C25AN, corresponding to the stretching band of the terminal Si—OH on the silicate surface, was much less intense than that of pristine C25A; this confirmed the occurrence of a chemical reaction between the hydrolyzed silane monomers or oligomers with the silanol groups of C25A. Wei et al.<sup>35</sup> and Chen and coworkers<sup>31–33</sup> observed similar results when they treated C25A with GPS. Figure 2 discloses the FTIR spectrum of C25AI. The new peak appearing in the range 1740–1680  $\text{cm}^{-1}$  corresponded to the carbonyl group of the urethane linkage; this indicated that IPS was

TABLE I  
Atomic Contents of the Clays

Clay	Atomic content (wt %)			
	Nitrogen	Carbon	Hydrogen	Nitrogen/carbon
C25A	0.94	21.87	4.22	0.043
C25AN	1.19	18.52	3.63	0.064
C25AI	0.99	14.53	3.27	0.068



**Figure 3** XRD patterns of C25A, C25AE, C25AI, and C25AN.

chemically bound to C25A through urethane formation.

To identify the silane reaction with the clay more clearly, elemental analyses were performed for the modified clays. According to Table I, the N/C ratio of C25A was 0.043, whereas those of C25AI and C25AN were 0.068 and 0.064, respectively. The nitrogen atoms came from the attached silane compounds on clay and from the surfactant originally present in C25A. Therefore, the higher N/C ratio of C25AI and C25AN in comparison to that of C25A confirmed the successful grafting of the silane compounds to the clay layers. Figure 3 presents XRD patterns of C25AE, C25AI, and C25AN, respectively. The modification with the silane compounds shifted the XRD peak of pristine C25A to a slightly lower angle, which indicated that the interlayer spacing of C25A was somewhat enlarged, that is, from  $d_{001} = 1.89$  nm for pristine C25A to  $d_{001} = 2.15$  nm for C25AE,  $d_{001} = 2.17$  nm for C25AI, and  $d_{001} = 2.17$  nm for C25AN. In contrast, Chen and coworkers<sup>31–33</sup> observed that  $d_{001}$  of C25A was almost equivalent to that of C25AE. The different experimental results seem to originate from the fact that Chen and coworkers<sup>31–33</sup> modified C25A with GPS at room tem-

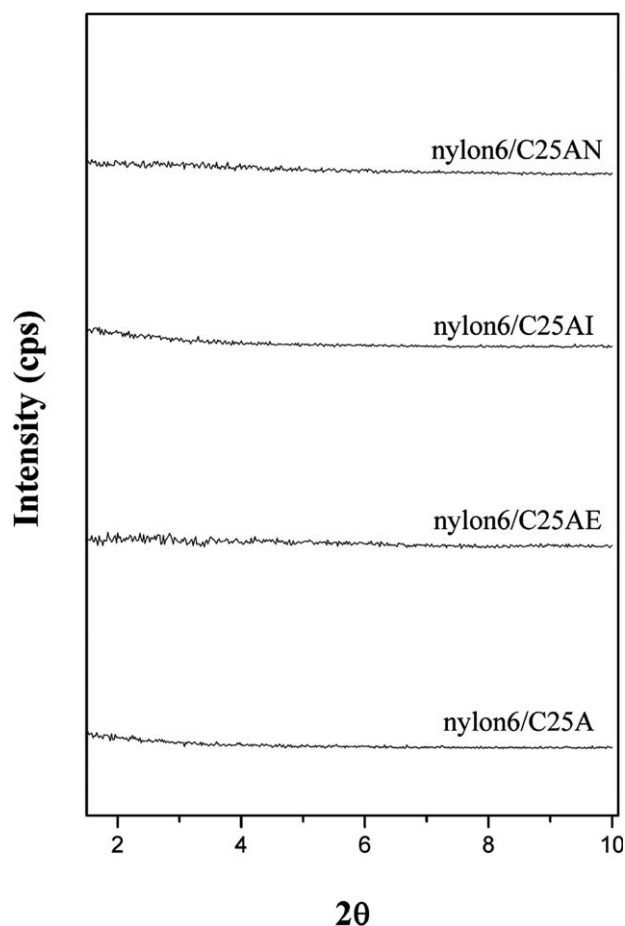
perature, whereas the temperature used for the same purpose was 80°C in this study.

### Morphology of the nylon 6/clay nanocomposites

XRD measurements were performed to characterize the nanostructures of the nylon 6/clay composites, as XRD analysis is a very sensitive and convenient tool for the detection of the crystalline structure of clay layers in polymer/clay composites containing even a small amount of clay.<sup>1</sup>

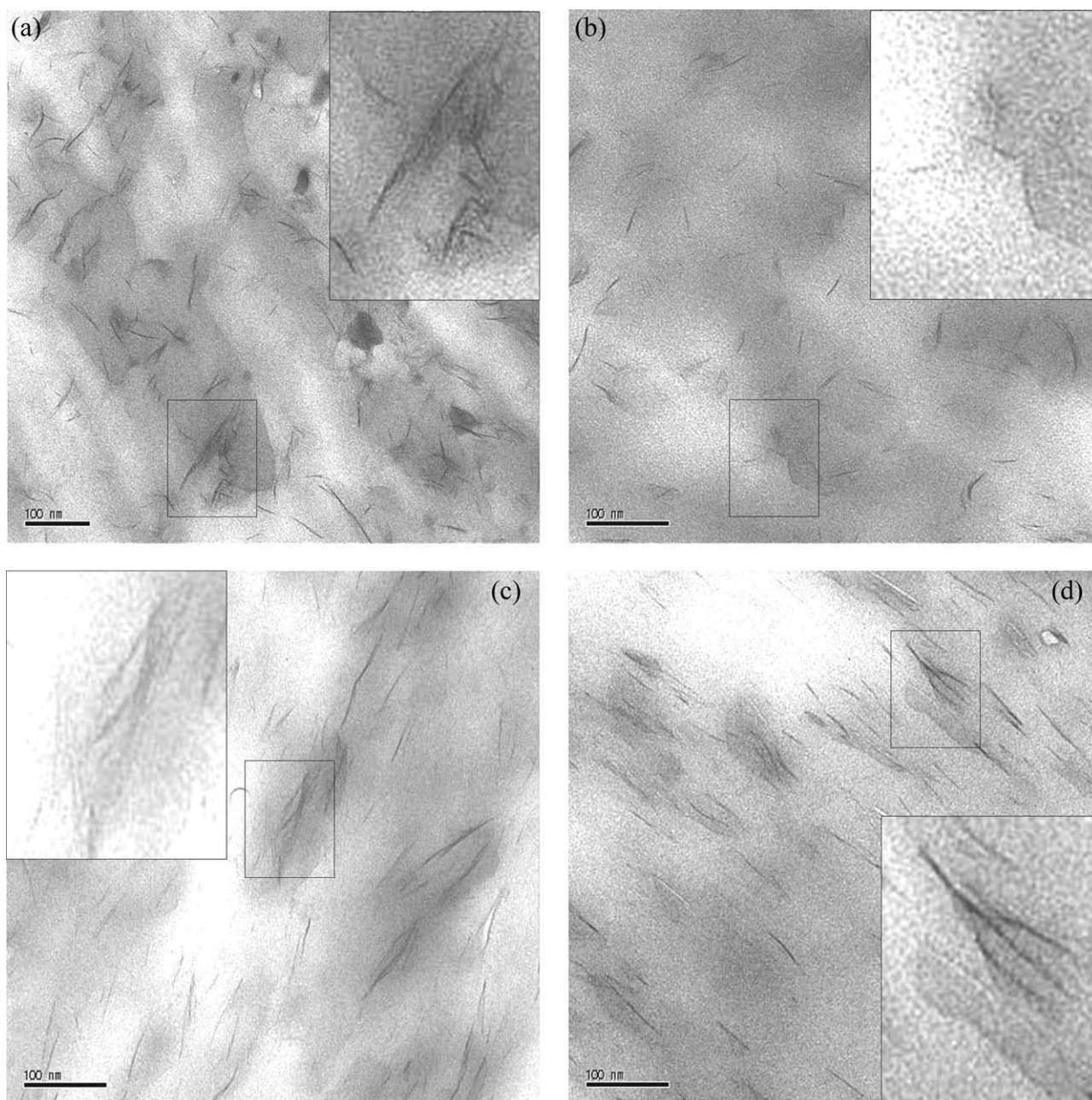
Figure 4 exhibits the XRD patterns of the nylon 6/C25A, nylon 6/C25AE, nylon 6/C25AI, and nylon 6/C25AN composites. For all of the composites, the respective XRD diffraction peaks disappeared almost completely, which indicated that the stacked structure of the silicate layers was destroyed, which led to full exfoliation and random distribution within the nylon 6 matrix.

Figure 5 presents the TEM images of the nylon 6/C25A, nylon 6/C25AE, nylon 6/C25AI, and nylon 6/C25AN composites. The dark lines correspond to the silicate layers, whereas the gray region represents the nylon 6 phase. The TEM images clearly



**Figure 4** XRD patterns of the nylon 6/C25A, nylon 6/C25AE, nylon 6/C25AI, and nylon 6/C25AN composites.





**Figure 5** TEM images of the (a) nylon 6/C25A, (b) nylon 6/C25AE, (c) nylon 6/C25AI, and (d) nylon 6/C25AN composites.

show that the silicate layers in the nylon 6 matrix were fully exfoliated for all of the clays, in accordance with the XRD results.

**Tensile properties of the nylon 6/clay nanocomposites**

The tensile properties of the neat nylon 6 and nylon 6 compounded with 3 wt % of the different clays are summarized in Table II. The incorporation of C25A, C25AE, C25AI, and C25AN into nylon 6 raised the tensile strength and modulus regardless of the clay

types because of the reinforcing effect by the disordered silicate layers with a high aspect ratio.

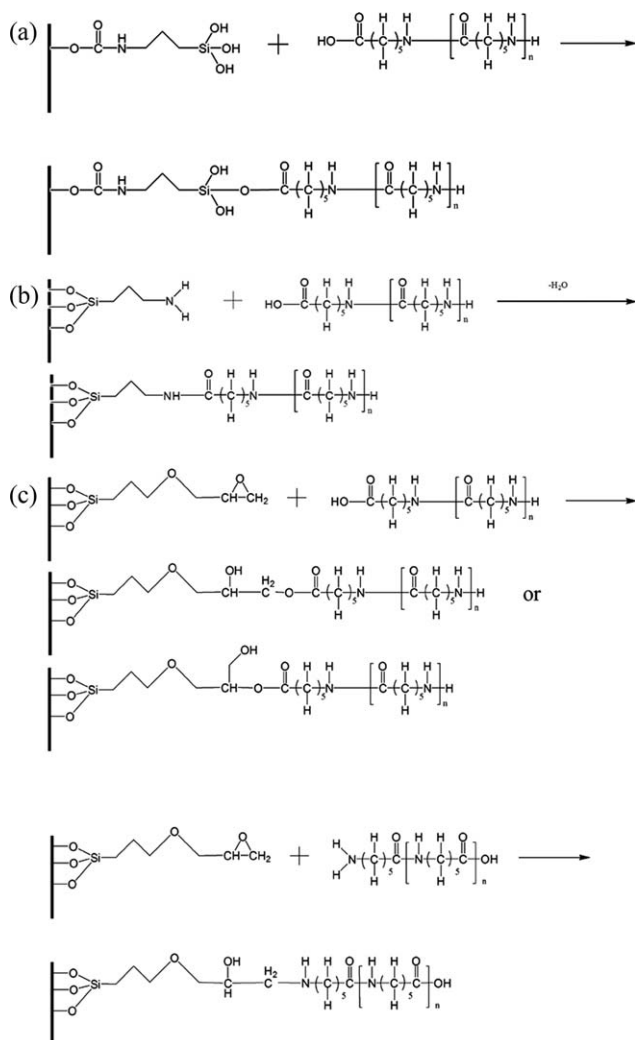
The enhancements in the tensile strength and tensile modulus were more pronounced when C25AE was incorporated instead of the other clays. Moreover, the extension at yield strength also increased as a result of C25AE incorporation, whereas decreased or at best marginally increased when the other clays were incorporated. The reinforcing effect of a filler should depend on the interaction between the solid filler and the matrix polymer as well as the interfacial area.<sup>30</sup> Scheme 2

**TABLE II**  
Tensile Properties of the Neat Nylon 6 and the Nylon 6/C25A, Nylon 6/C25AE, Nylon 6/C25AI, and Nylon 6/C25AN Composites

	Yield strength (MPa)	Modulus (MPa)	Extension at yield strength (%)
Nylon 6	46.1 ± 1.5	512 ± 10.3	21.0 ± 3.2
Nylon 6/C25A	65.4 ± 5.3	621 ± 25.2	16.8 ± 4.7
Nylon 6/C25AE	78.9 ± 7.2	938 ± 17.6	28.7 ± 5.3
Nylon 6/C25AI	66.4 ± 5.3	751 ± 15.2	23.6 ± 4.7
Nylon 6/C25AN	66.1 ± 3.7	788 ± 22.6	21.8 ± 5.3

demonstrates the likely reactions between the functional groups of the modified clays and the end groups of nylon 6.

Given that the clay layers were fully exfoliated regardless of the clay types and, therefore, the total



**Scheme 2** Likely reactions between the functional groups of the modified clays and the end groups of nylon 6: (a) nylon 6/C25AI, (b) nylon 6/C25AN, and (c) nylon 6/C25AE.

**TABLE IV**  
Interfacial Tension ( $\gamma_{AB}$ ) and  $W_{AB}$  of the Nylon 6/Clay Composites

	$\gamma_{AB}$ (mN/m)	$W_{AB}$ (mN/m)
Nylon 6/C25A	0.06	54.13
Nylon 6/C25AE	0.21	57.42
Nylon 6/C25AI	0.17	55.02
Nylon 6/C25AN	0.15	54.65

interfacial areas of the solid fillers were almost identical, the superior improvement of the tensile properties of the nylon 6/C25AE were attributed to the nylon 6 matrix and C25AE having the strongest interaction among the clays tested. Epoxy groups on the C25AE may have reacted with the hydroxyl and carboxyl groups of the polymer chain end.<sup>31</sup> The amino group of APS may have also formed chemical bonds with the end group of nylon 6.

The previous results pertaining to the tensile properties indicate that the incorporation of epoxy groups was more effective in terms of enhancing the interaction than the inclusion of amino groups.

#### Work of adhesion ( $W_{AB}$ )

The surface energy of a solid at a given temperature determines its adsorption wettability, catalysis, permeation, dyeability, painting, and adhesion.<sup>36–39</sup>  $W_{AB}$  per unit area is the work done on the system when two condensed phases, A and B, forming an interface of unit area, are separated reversibly to infinite distance. According to Wu,<sup>39</sup>  $W_{AB}$  can be calculated from the interfacial tension.

The contact angles with respect to water and ethylene glycol are listed in Table III. With these data, the surface tension ( $\gamma$ ) and the dispersion and polar components of the surface tension ( $\gamma^d$  and  $\gamma^p$ , respectively) of the materials were estimated with eqs. (1) and (2):<sup>40</sup>

$$(1 + \cos\theta_{\text{H}_2\text{O}})\gamma_{\text{H}_2\text{O}} = 4 \left( \frac{\gamma_{\text{H}_2\text{O}}^d \gamma^d}{\gamma_{\text{H}_2\text{O}}^d + \gamma^d} + \frac{\gamma_{\text{H}_2\text{O}}^p \gamma^p}{\gamma_{\text{H}_2\text{O}}^p + \gamma^p} \right) \quad (1)$$

**TABLE III**  
Contact Angles and  $\gamma$  Values of the Nylon 6, Commercial Clay, and Silane-Modified Clays

	Contact angle		$\gamma$ (mJ/m <sup>2</sup> )		
	Water	EG	$\gamma$	$\gamma^d$	$\gamma^p$
Nylon 6	98.6	72.3	26.37	26.2	0.17
C25A	98.5	66.1	28.62	28.38	0.23
C25AE	93.8	63.7	31.26	31.09	0.17
C25AI	107.9	47.5	28.82	28.21	0.61
C25AN	108.2	48.6	28.43	27.82	0.62

$$(1 + \cos \theta_{\text{HOCH}_2\text{CH}_2\text{OH}}) \gamma_{\text{HOCH}_2\text{CH}_2\text{OH}} = 4 \left( \frac{\gamma_{\text{HOCH}_2\text{CH}_2\text{OH}}^d \gamma^d}{\gamma_{\text{HOCH}_2\text{CH}_2\text{OH}}^d + \gamma^d} + \frac{\gamma_{\text{HOCH}_2\text{CH}_2\text{OH}}^p \gamma^p}{\gamma_{\text{HOCH}_2\text{CH}_2\text{OH}}^p + \gamma^p} \right) \quad (2)$$

where  $\gamma = \gamma^d + \gamma^p$ ,  $\gamma_{\text{H}_2\text{O}} = \gamma_{\text{H}_2\text{O}}^d + \gamma_{\text{H}_2\text{O}}^p$ , and  $\gamma_{\text{HOCH}_2\text{CH}_2\text{OH}} = \gamma_{\text{HOCH}_2\text{CH}_2\text{OH}}^d + \gamma_{\text{HOCH}_2\text{CH}_2\text{OH}}^p$ .  $\theta_{\text{H}_2\text{O}}$  and  $\theta_{\text{HOCH}_2\text{CH}_2\text{OH}}$  are the contact angles of the materials with respect to water and ethylene glycol, respectively. The numerical values used were  $\gamma_{\text{H}_2\text{O}}^d = 21.8$  dyne/cm,  $\gamma_{\text{H}_2\text{O}}^p = 51.0$  dyne/cm,  $\gamma_{\text{HOCH}_2\text{CH}_2\text{OH}}^d = 33.8$  dyne/cm, and  $\gamma_{\text{HOCH}_2\text{CH}_2\text{OH}}^p = 14.2$  dyne/cm.

The estimated values of the  $\gamma$ , dispersion, and polar components are also listed in Table III. The interfacial tension of each pair was determined from the  $\gamma$  values with the geometric mean equation proposed by Wu:<sup>39</sup>

$$\gamma_{AB} = \gamma_A + \gamma_B - 2(\gamma_A^d \gamma_B^d)^{1/2} - 2(\gamma_A^p \gamma_B^p)^{1/2} \quad (3)$$

where  $\gamma_{AB}$  is the interfacial tension and  $\gamma_A$  and  $\gamma_B$  are the surface tensions of the respective two materials in contact.

The thermodynamic  $W_{AB}$  was determined from the  $\gamma$  values with the following equation:<sup>41</sup>

$$W_{AB} = 2(\gamma_A^d \gamma_B^d)^{1/2} + 2(\gamma_A^p \gamma_B^p)^{1/2} \quad (4)$$

The interfacial tension and thermodynamic  $W_{AB}$  values of all of the nylon 6/clay composites are given in Table IV.

According to Table IV, the thermodynamic  $W_{AB}$  and the interfacial tension values of nylon 6/C25AE interface were higher than those of the other composites. The more improved tensile properties of the nylon 6/C25AE composites relative to those of the other clay-incorporated composites were attributed to the higher value of the thermodynamic  $W_{AB}$  of the former composites. The increased thermodynamic  $W_{AB}$  should come from the enhanced interaction between the constituents. The nylon 6 molecules chemically bound to C25AE should have contributed to the improved interaction. The higher thermodynamic  $W_{AB}$  of nylon 6/C25AE compared to the other composites may have been due to the higher amount of nylon 6 molecules chemically bound to C25AE than to the other clays because the reaction between the epoxy group and the amine end group of nylon 6 molecules was more reactive than that of the amine or silanol group with the end groups of nylon 6. We, thereby, concluded that the epoxy-terminated silane-modified clay was more effective for enhancing the interaction between the nylon 6 matrix and the clay surface, and the interface proved to be more durable during the tensile tests in comparison to the clays bearing amine or silanol groups.

## CONCLUSIONS

Reactive functional groups were introduced onto the surface of the silicate layers of C25A by the treatment of C25A with GPS, IPS, and APS, respectively. XRD patterns and TEM images of the respective composites revealed that the silicate layers were fully exfoliated in the nylon 6 matrix regardless of whether C25A was modified with the silane compounds. The incorporation of the clays increased the tensile strength and modulus because of a reinforcing effect of the exfoliated clay layers. The enhancement of the tensile strength and modulus was more pronounced when C25AE was compounded with nylon 6 instead of the other clays. The extension at yield point of the nylon 6/C25AE composites was also higher than that of neat nylon 6, whereas it decreased or, at best, marginally increased in the cases of the nylon 6/C25A, nylon 6/C25AN, and nylon 6/C25AI composites.

Because the clay layers were fully exfoliated regardless of the clay types, the total interfacial area of the clay layers should have been almost the same. Therefore, the more significantly enhanced mechanical properties of the nylon 6/C25AE composites relative to those of the other composites were attributed to a stronger interaction of nylon 6 with C25AE than with C25A, C25AN, and C25AI, respectively, as revealed by the variation in the values of the  $W_{AB}$  and interfacial tension of the respective composites.

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