

# Investigating the use of fibrillar clays for reinforcement of polymer composites

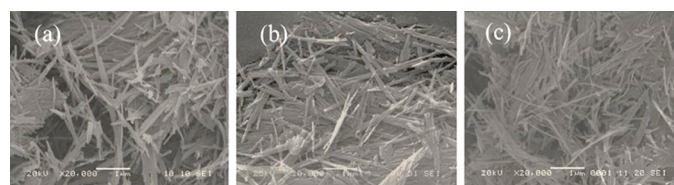
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*Surface modifications to palygorskite promote its dispersion within nylon 6, which in turn improves the thermal and mechanical properties of the resultant nanocomposites.*

Clay nanoparticles—because of their large specific surface area, stiffness, good thermal stability, and high aspect ratio—are commonly used as polymer reinforcements. Indeed, several polymer/clay nanocomposites based on laminar clays (e.g., montmorillonite) have previously been reported.<sup>1–5</sup> However, bending and curling of laminar clays during melt processing has also been observed. Such distortions to the clay platelets can diminish their reinforcing properties within nanocomposites. An alternative reinforcing material for polymer composites is therefore required, and fibrillar clays present several advantages over laminar clays (e.g., they are easier to disperse and they have greater stiffness at the nanoscale). Despite these desirable characteristics, fibrillar clays have so far been used in the production of polymer nanocomposites far less often than their laminar counterparts.

Palygorskite (pal) is a specific fibrillar clay that exhibits a high elastic modulus and aspect ratio, as well as good chemical and thermal stability. The desirable characteristics of this clay mean that it has already been used to prepare and improve the properties of several nanocomposite systems, i.e., that are based on various polymers, including nylon 6,<sup>6–9</sup> polypropylene,<sup>10–12</sup> polystyrene,<sup>13</sup> epoxy resin,<sup>14</sup> polyaniline,<sup>15</sup> poly(butylene succinate),<sup>16</sup> and natural rubber.<sup>17</sup> Nonetheless, in these earlier studies, surface modification of pal—with the use of silane coupling agents—was frequently required to promote polymer–pal miscibility. To date, however, there has been little focus on the use of other common surface modification agents (e.g., cationic surfactants). A comprehensive understanding of how pal surface modifications affect pal dispersion (and thus improve nanocomposite properties) is therefore still lacking.

In this work,<sup>18</sup> we therefore explored the use of pal as a nanoreinforcer for thermoplastic polymers. In particular, we investigated the

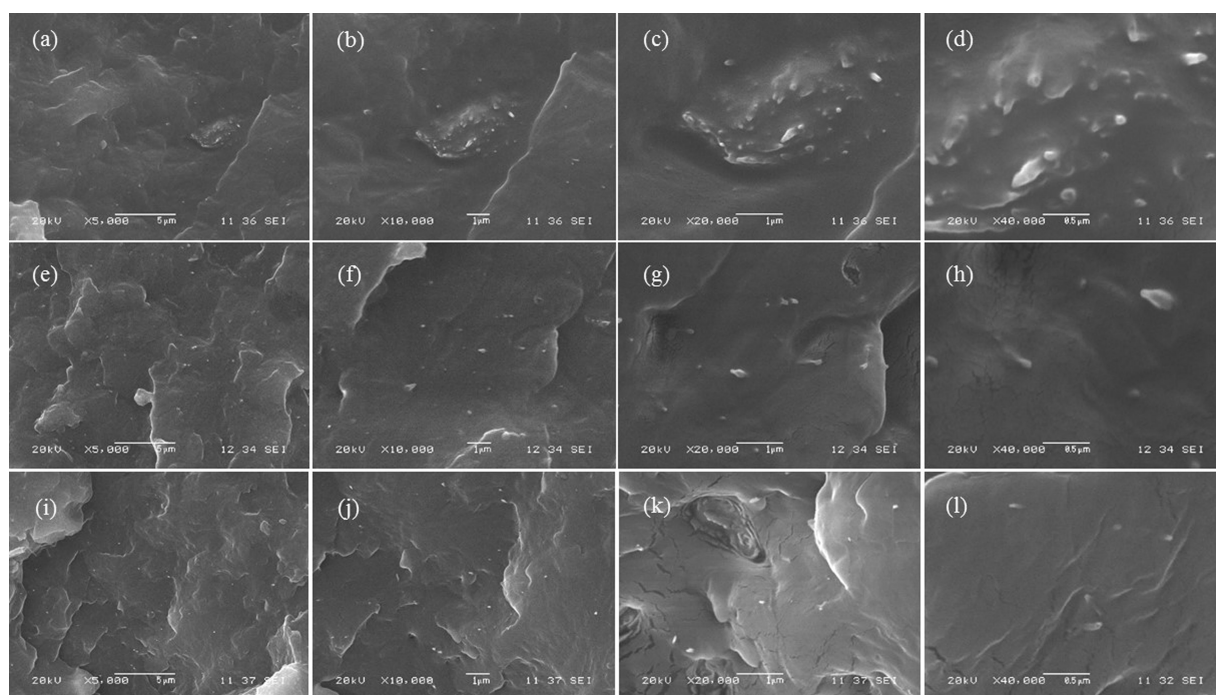


**Figure 1.** Scanning electron microscope (SEM) images of (a) purified palygorskite (pal), (b) pal modified with 3-aminopropyltrimethoxysilane (APTMS-pal), and (c) pal modified with hexadecyl tributyl phosphonium bromide (HDTBP-pal), from which the fibrillar morphology of the samples can be seen. Scale bars indicate 1  $\mu\text{m}$ .

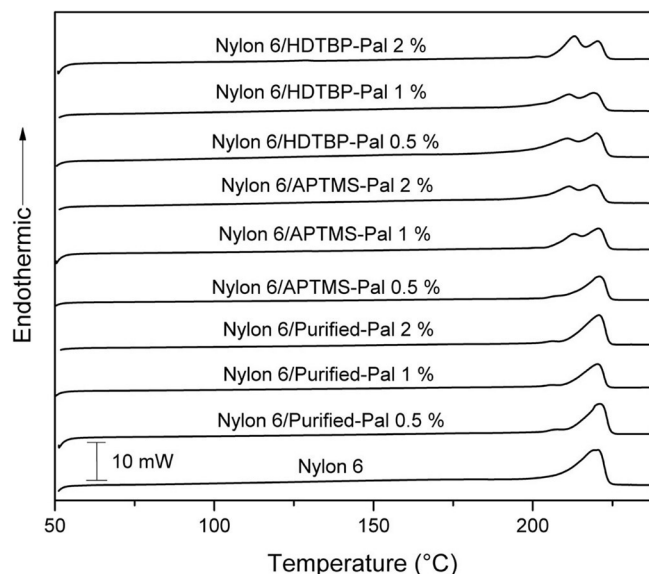
effect of two different pal surface modifications on the surface energy and dispersion of the clay particles within nylon 6/pal nanocomposites, as well as on the thermal and mechanical properties of the samples. To prepare our nanocomposites, we first purified and characterized the pal (sourced from Yucatan, Mexico). Next, we used common procedures<sup>19,20</sup> to modify the pal with either a cationic surfactant (hexadecyl tributyl phosphonium bromide, HDTBP) or a silane coupling agent (3-aminopropyltrimethoxysilane, APTMS) to produce new thermally stable ‘organopals’ with different surface energies. In the last stage, we performed melt compounding to blend the surface-modified pals (at concentrations between 0 and 2wt%) with nylon 6, and to thus produce the final samples.

To assess the different effects of the pal surface modifications, we followed the Owens-Wendt approximation method<sup>21</sup> to evaluate the surface energy of the different surface-modified pals. We thus obtained values of  $70.11 \pm 1.90$ ,  $65.91 \pm 0.73$ , and  $63.84 \pm 0.37 \text{ mJ/m}^2$  for the purified, APTMS-modified, and HDTBP-modified pal samples, respectively. We also used scanning electron microscopy (SEM) to examine the fibrillar morphology of the three pal types (see Figure 1). These images show that the surface treatments caused no substantial changes

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**Figure 2.** SEM images (at a variety of magnifications) of the cryogenically fractured surfaces of the nylon 6/pal 2wt% nanocomposites. Images are shown for (a–d) the purified pal, (e–h) APTMS-pal, and (i–l) HDTBP-pal samples.



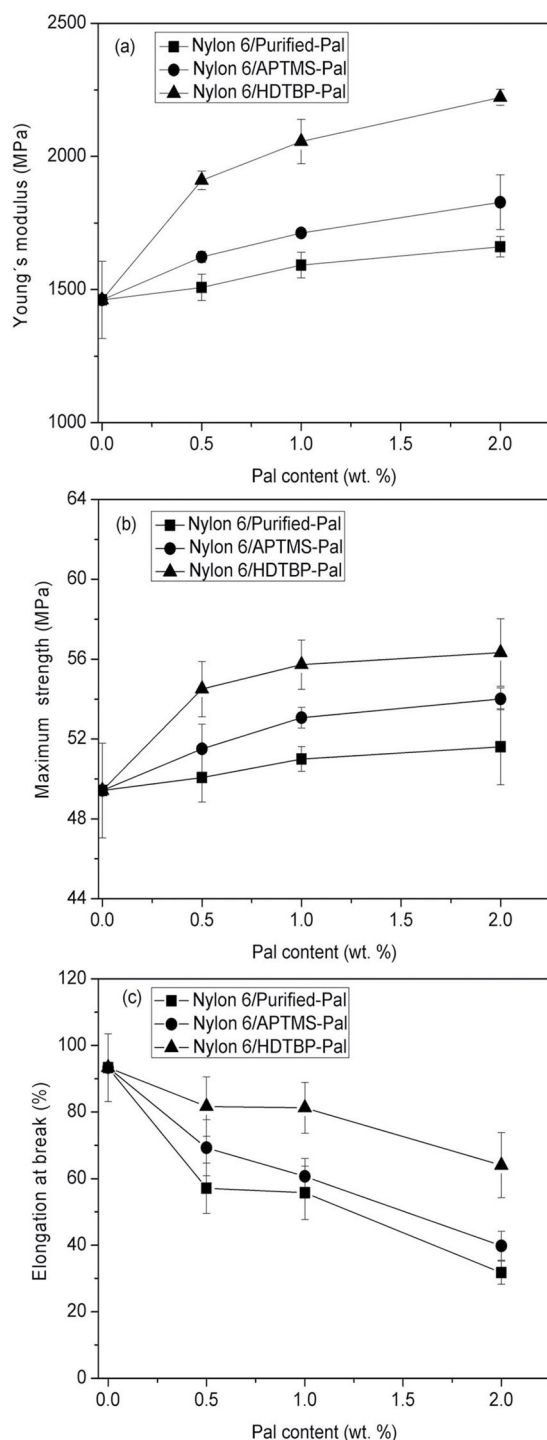
**Figure 3.** Differential scanning calorimetry thermograms for the neat nylon 6 and nylon 6/pal nanocomposites (containing purified pal, APTMS-pal, or HDTBP-pal at concentrations of 0.5, 1, or 2wt%).

to the silicate fiber morphology. Furthermore, we used Fourier-transform IR and x-ray photoelectron spectroscopy, as well as thermogravimetric analysis to characterize the surface modifications and to determine the organic content and thermal stability of the samples.

We also obtained SEM images of cryogenic fractures within our nylon 6/pal nanocomposites so that we could assess the level of pal dispersion within the 2wt% pal samples (see Figure 2). We found—see Figure 2(a–d)—that the purified-pal was poorly dispersed within the samples. The APTMS-pal nanocomposites—see Figure 2(e–h)—however, exhibited better distributions of the clay particles. The best distribution

and dispersion of pal particles that we observed—see Figure 2(i–l)—were for the HDTBP-pal nanocomposites, in which we found no pal aggregates on the fractured surfaces. From these results it is clear that our surface treatments improved the dispersion of pal within the samples. That is, the interactions between individual pal crystals were weakened by the surface modifications and this allowed the fibers to separate from pal bundles during the melt-compounding process.<sup>8</sup> Our results also indicate that the distribution and dispersion of pal is dependent on the surface energy (i.e., the modified-pal types have lower surface energies).

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**Figure 4.** Experimentally measured (a) Young's modulus, (b) maximum strength, and (c) elongation at break results for the nylon 6/pal nanocomposites, as a function of pal content.

Dispersed clay nanoparticles can act as nucleation agents in polymer composites and may thus modify the thermal properties of the samples. In another part of our study, we therefore evaluated how different pal dispersions affected the thermal and mechanical properties of our nylon 6/pal nanocomposites. The differential scanning calorimetry we obtained for the neat nylon 6 and various nylon 6/pal nanocomposites (i.e., with different types of pal modification and pal concentrations) are shown in Figure 3. From these results we found that the neat nylon 6 resin and the nylon 6/purified-pal samples have a single melting peak at about 219.47°C. This nylon 6 melting peak splits into two separate spikes, however, for the 1 and 2wt% APTMS-pal composites, as well as for the HDTBP composites (regardless of pal concentration). The high-temperature part of the melting peak is associated with the thermodynamically stable so-called  $\alpha$ -crystalline form, whereas the lower temperature peak corresponds to the less-stable  $\gamma$ -crystalline form.<sup>8</sup>

We also found that the tensile modulus—see Figure 4(a)—of the samples increased monotonically with pal concentration, although the extent of reinforcement was dependent on the degree of pal dispersion. Similarly, as shown in Figure 4(b), the maximum strength of the composites increased linearly with pal content and was sensitive to the type of pal modification. In particular, we measured the lowest strength values for the samples containing poorly dispersed purified-pal, and the highest strength for the HDTBP-pal composites. Lastly, we observed a reduction in the elongation at break of the samples—see Figure 4(c)—with increasing pal content. The precise trend, however, was related to the type of pal surface modification. We attribute these mechanical testing results to the fact that filler agglomerates can act as stress concentration points and can thus cause deterioration of mechanical properties.<sup>22</sup>

In summary, we have investigated the use of palygorskite—because of its considerable thermal stability and low surface energy—as a suitable nanoreinforcement material in polymer composites. From our experiments, we found that the dispersion of pal within nylon 6 can be improved by lowering the surface energy of pal (i.e., through surface modifications). Indeed, the modified pal increased the crystallinity of nylon 6 and promoted the formation of  $\gamma$ -phase crystals. Furthermore, we found that the tensile modulus and maximum strength of our nylon 6/pal nanocomposites were improved when there was a good degree of pal dispersion and higher pal concentrations. In the next part of our research, we are using twin-screw extrusion to prepare a new set of polymer/pal nanocomposites. We plan to investigate the effect of various processing conditions (e.g., the configuration and speed of the screws) and the pal surface energy on the extent of pal dispersion within nylon 6 and polypropylene, and on the mechanical properties of the samples.

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