

An Analysis of the Energy Requirement for the Improved Mechanical Properties of a Polymer-Clay Nanocomposite

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Abstract

Because of their perceived primary benefits over those of traditional composites, polymer-clay nanocomposites (PCN) have generated much interest in the field of science, technology, and engineering. These benefits include efficient reinforcement, thermal endurance, flame resistance, improved barrier properties, improved abrasion resistance, reduced shrinkage and residual stress, and altered electrical, electronic, and optical properties.

Polymerization of monomers in the presence of clay particles and incorporation of the clay particles into a molten polymer matrix (melt compounding/blending) are two preferred methods for preparing PCN. Melt blending presents a thermodynamic mixing problem if the polymer matrix is hydrophobic, such as polypropylene, and the clay particles are hygroscopic. To solve this problem, a compatibilizer is employed to improve the interaction between the polymer molecules and the clay particles. Another important problem with the melt blending process is that the clay particles exist naturally as layers of platelets. To achieve optimal PCN properties, it is important for the platelets to be separated from each other (a process also known as exfoliation) and uniformly dispersed in the polymer matrix. Dolgovskij et al. [1] have shown that exfoliation of clay particles depends on a combination of shear rate and residence time in the mixer. Moreover, other studies have shown that the relationship between shear intensity and the degree of exfoliation is not linear. Our study seeks to correlate the degree of exfoliation to the energy requirements associated with the improvement in PCN properties such as tensile strength and modulus. The ultimate goal of this work is to determine if the gain in PCN properties justifies any increase in energy usage. A twin-screw extruder will be used as a mixer in compounding the PCN.

Introduction

Stewart's featured article in the April 2006 edition of the *Plastics Engineering Journal* was titled, "Nanomaterials: Still Climbing the Steep Curve of Material Development." Justifying the title, the author explains, "While most people can appreciate the increased strength, lighter weight, improved barrier properties, and other benefits offered by nanomaterials in plastics applications, nanocomposites are still perceived by many as too

expensive and too difficult to process successfully with conventional equipment” [2]. Since this statement was made in 2006, there appears to be no significant development in the preparation of PCN to change the status quo. However, this is not attributed to a lack of research efforts in PCN, for many researchers have been diligently working on the commercialization of PCN. Some researchers, such as Okada and Usuki [3], have approached the subject through the polymerization of PCN, while others chose the melt blending method [4, 5, 6]. The melt blending method is preferred to the polymerization method because it does not use the expensive solvents required in polymerization, nor is it limited to specific polymeric materials. Thus, it appears that the melt blending method is more versatile than the polymerization method. In spite of their differences, both methods utilize clay particles as reinforcing agents. But since the clay particles exist as layers of platelets, as shown in Figure 1, their separation from each other (exfoliation) and uniform dispersion in a polymer matrix is necessary to realize optimal benefits in the properties of PCN. To achieve this goal, the experimenter uses process equipment, such as twin-screw extruders, to affect the breakup of the layered platelets of the clay particles, while simultaneously incorporating the individual platelets into the polymer matrix to form a polymer-clay nanocomposite.

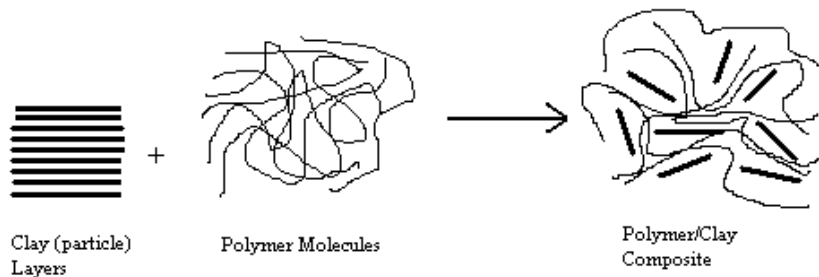


Figure 1. Schematic diagram of the melt blending process

Many studies have examined different aspects of the melt blending method of PCN, but there appears to be no study that has evaluated the additional energy required to break up and incorporate the clay platelets into the polymeric matrix to improve the mechanical properties of PCN. In this study, the authors examine the incremental energy requirement associated with the improved tensile strength and modulus of a PCN to determine if any increased energy usage justifies the gain in the named properties.

Experimental

Polypropylene (PP) homopolymer resin (Pro-fax® 6524 from LyondellBasell Industries) was melt blended with organoclay nanoparticles (Closite 20A from Southern Clay Products) and a compatibilizer, maleic anhydride grafted polypropylene (MA), specifically Polybond® 3200 from Chemtura Corporation. The organoclay (density of 1.77 g/cm^3), a powder with a mean particle size of 9 micrometer (μm), the MA, and the PP resins were premixed in gallon paint cans with a paint shaker for approximately 20–30 minutes. This resulted in individual PP resin being coated by the clay particles. PP/MA/Clay mixtures of 96/2/2, 94/3/3, and 90/5/5 wt% were premixed. These mixtures

were subsequently melt-blended with a 42-mm Brabender counter-rotating twin-screw extruder at 204 °C. A screw speed of 40 rpm was used. Neat PP, used as the control material, was similarly processed with the twin-screw extruder. Extrudates from the extruder were air-dried and pelletized with a Killion pelletizer at 30 rpm. During the melt blending processes, the A/C current usage by the extruder was recorded. The neat PP and PCN pellets obtained from the Killion pelletizer were dried and subsequently injection-molded into tensile test specimens with a 60-ton Sandretto injection molding machine. The following temperature profile was used in the injection molding process: mold temperature = 38 °C, injection machine rear barrel = 182 °C, middle barrel = 193 °C, front barrel = 199 °C, and nozzle = 204 °C. Tensile test specimens were tested with the Instron test instrument at room temperature, according to ASTM D 638.

Results and Discussion

Since the mean size of the Cloisite 20A clay particles was 9- μm , and given that each platelet was 1 nanometer (nm) thick, a clay particle would have approximately 3,000 layered platelets. In this study, the authors used the modified Halpin-Tsai equation, proposed by Brune and Bicerano [7]. Zhang et al. [8] used the same equation to determine the extent of exfoliation of the clay particles in the three PP-Clay nanocomposites studied. It should be noted that an alternate definition of exfoliation is given by Dennis et al. [6]. They describe exfoliation as a process where polymer molecules move into the spacing between platelets, causing the spacing to increase to 8 nm or greater. Both definitions of exfoliation will be considered with the modified Halpin-Tsai equation expressed below.

$$\frac{E_{\text{composite}}}{E_{\text{matrix}}} \left(\frac{E_c}{E_m} \right) = \frac{1 + 2A'_f \eta' \phi'}{1 - \eta' \phi'} \quad [\text{eqn. 1}]$$

where

$$\eta' = \frac{E'_r - 1}{E'_r + 2A'_f}, \quad A'_f = \frac{A_f}{\widehat{N}} \left[\frac{1}{1 + \left(1 - \frac{1}{\widehat{N}}\right) \left(\frac{s}{t}\right)} \right]$$

$$E'_r = E_r \left[\frac{1}{1 + \left(1 - \frac{1}{\widehat{N}}\right) \left(\frac{s}{t}\right)} \right] + \left[\frac{\left(1 - \frac{1}{\widehat{N}}\right) \left(\frac{s}{t}\right)}{1 + \left(1 - \frac{1}{\widehat{N}}\right) \left(\frac{s}{t}\right)} \right]$$

$$\phi' = \phi \left[1 + \left(1 - \frac{1}{\widehat{N}}\right) \left(\frac{s}{t}\right) \right], \quad \widehat{N} = N + (1 - N) \left(\frac{s}{t}\right) \left(\frac{\phi}{1 - \phi}\right)$$

E_r = ratio of the platelet modulus (1.7 GPa) to the matrix modulus (1.1MPa)

A_f = aspect ratio of the platelet

ϕ = volume fraction of platelets in the composite

N = number of platelets per stack. $N = 1$ for completely exfoliated platelets

s/t = ratio of platelet spacing to platelet thickness

Using equation 1, an average platelet aspect ratio of 100 was assumed given that the platelets aspect ratio ranged from 70–150 [9]. Figure 2 shows that at a spacing of 2 nm between platelets, the number of platelets per particle was reduced from 3,000 platelets per clay particle (stack) to between 15–50 platelets per particle, suggesting that some exfoliation of the clay particles took place during the melt blending process. Figure 3 shows that at 30 platelets per stack, most platelets had spacing of 2 nm (s/t) = 2, rather than spacing of 8 nm or greater. These results suggest that most exfoliation of the clay particles occurred by the breakup of the layered platelets as opposed to the movement of the polymer molecules into the particles spacing, thereby increasing the separation between platelets, as suggested by Dennis et al. [6]. Figure 2 shows that the degree of exfoliation was greater for the PCN with 2 and 3 wt% clay particles than for the PCN with 5 wt% of clay particles. This trend was also observed by Zhang et al. [8] in their work.

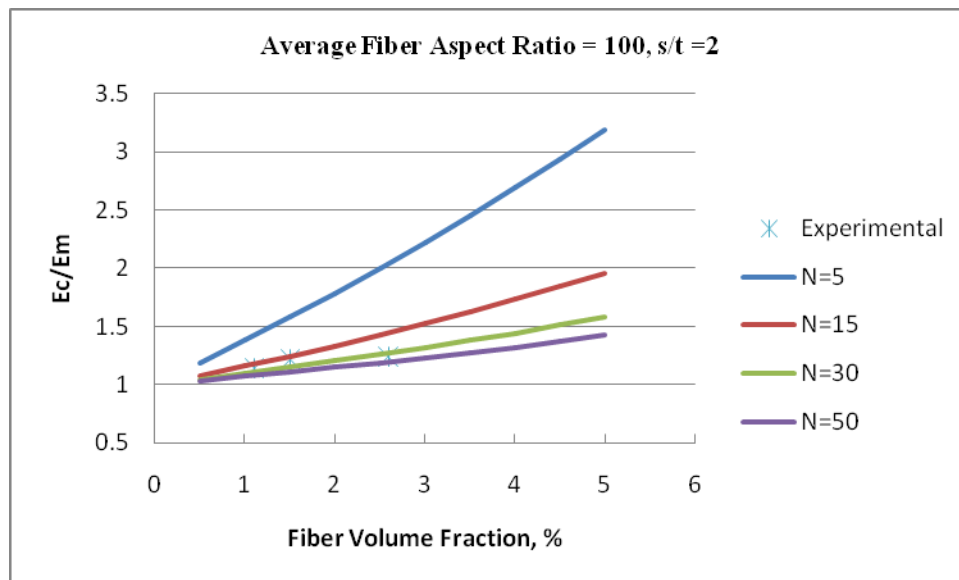


Figure 2. Exfoliation of platelets

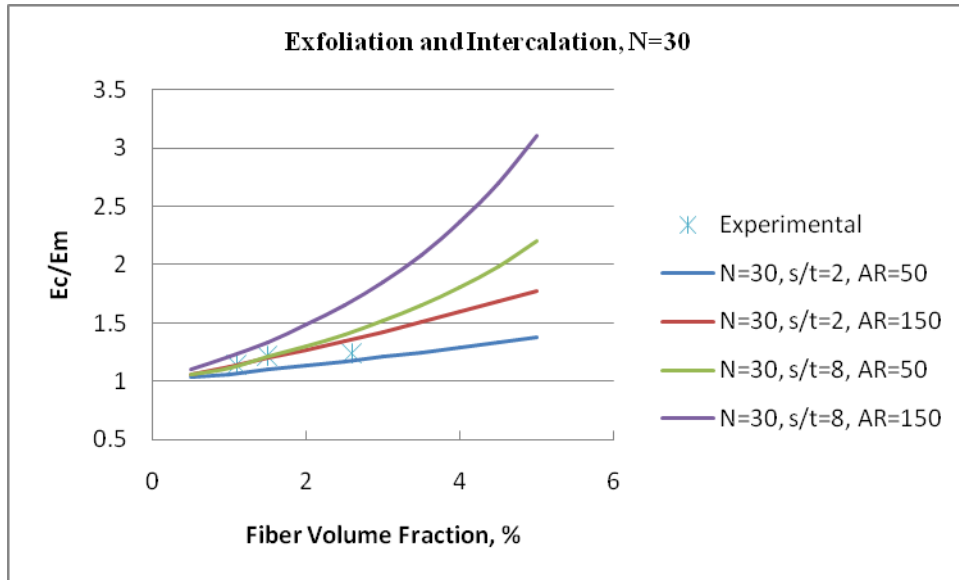


Figure 3. Exfoliation of platelets by break up of layered platelets

Table 1. Tensile properties of PP and PCN

Material	Tensile Strength at Yield (psi)		Tensile Modulus (psi)		AC Current Usage (amp)	
	Measured	% Change	Measured	% Change	Measured	% Change
Neat PP	4688±49	--	101578±4414	--	4	--
PP/MA/Clay 96/2/2 wt%	4918±37	4.9%	114922±6009	13.1%	4.3	7.5%
PP/MA/Clay 94/3/3 wt%	4980±23	6.2%	122529±5928	20.6%	4.6	15%
PP/MA/Clay 90/5/5 wt%	4975±20	6.1%	124864±5101	22.9%	4.5	12.5%

Table I shows the tensile strength at yield, tensile modulus, and the associated current usage for preparing the PCN. The extruder had current supplied at 208 volts. Shown also are the percent increases of these properties over that of the neat PP, which was used as the control material. Figure 4 shows the ratio of percent increase in tensile strength at yield to percent increase in energy usage, while Figure 5 shows the ratio of percent increase in tensile modulus to percent increase in energy usage. The results in Figure 4 suggest that on a one-to-one basis, the marginal increase in tensile strength at yield is not justified by the increase in energy usage, assuming that tensile strength at yield is the sole property of interest in the PCN. However, Figure 5 shows that with the tensile modulus, the results appear favorable because the ratios are greater than one.

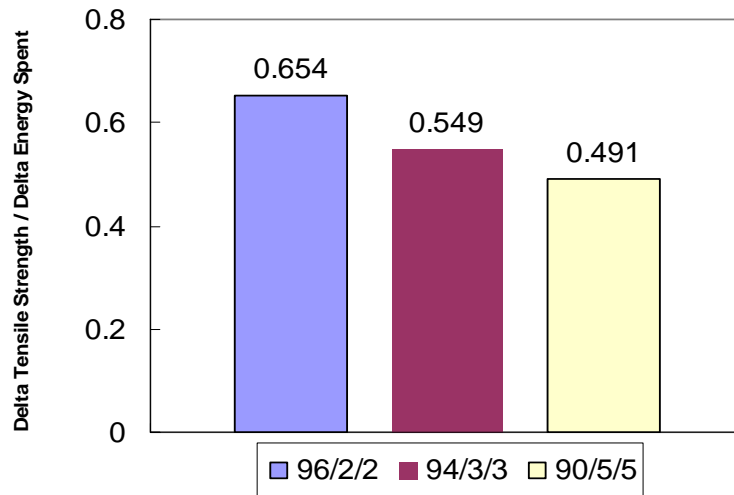


Figure 4. Change in tensile strength per unit change in energy usage

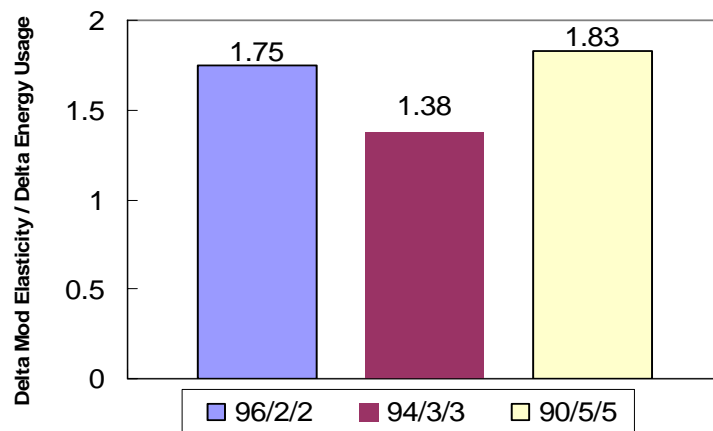


Figure 5. Change in tensile modulus per unit change in energy usage

This implies that if tensile modulus is the primary PCN property for which improvement is desired then the gain in the tensile strength is justified in terms of the incremental energy usage.

A question that this study seeks to address is, “How does the degree of exfoliation affect the mechanical properties of the PCN?” As results in Figure 2 and Table 1 indicate, this may not be an easy question to answer. This is because, as Figure 2 shows, the PCN with 2 wt% (volume fraction = 1.1%) and 3 wt (volume fraction = 1.5%) clay particles tend to show a higher degree of exfoliation than the PCN with 5 wt% (volume fraction = 2.6%). However, Table I shows that the PCN with 5 wt% of clay particles had the highest percent increase in tensile modulus of the three PCN. This suggests, as was remarked by Zhang et al. [8], that the degree of exfoliation of the clay particles may not be the only factor responsible for the improved mechanical properties of PCN; orientation of the exfoliated particles may be an important contributing factor. It is generally known that

the orientation of fibers in materials, such as wood, is responsible for their anisotropic properties.

Conclusion

In this study, the authors found that exfoliation of clay particles happens mainly through the breakup of the layered platelets structure of the particles. Little evidence was found that exfoliation occurred by increasing the platelets spacing from 2 nm to 8 nm and greater. The PCN with 2 and 3 wt% of clay particles exhibited higher degrees of exfoliation than the PCN with 5 wt%. However, the difference in the degree of exfoliation was not reflected in the tensile modulus of PCN because the PCN with the 5 wt% of clay had the highest tensile modulus. Based on the observation, it is proposed that exfoliation may not be the only factor responsible for the improved mechanical properties of PCN; orientation of exfoliated particles may be a contributing factor as well. It was observed that of the two mechanical properties examined, the gain in tensile modulus was proportionally greater than the energy employed to achieve the improvement. This was not so for the tensile strength at yield; its gain or improvement was proportionally less than the amount of energy used for the improvement.

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Biography

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