Structure and Properties of Phenolic Resin/Nanoclay Composites Synthesized by *In Situ* Polymerization

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ABSTRACT: An *in situ* semibatch polymerization process for making phenolic resin/montmorillonite clay nanocomposites is developed. It is found that auxiliary mixing in phenol allows intercalation of the monomer and polymer between montmorillonite clay layers. At 2.7% clay by mass the montmorillonite is predominantly exfoliated (fully dispersed). At higher clay loading, a substantial amount of the clay remains in aggregate or intercalated form. When the montmorillonite is exfoliated, the material is mechanically superior. The composite has a tensile modulus that is 21% higher than the neat resin and has 87% improved fracture strength, 100% larger fracture energy, and strain to failure 13% above the pure resin. Thermogravimetric analysis shows the montmorillonite system maintains its thermal stability up to 200°C. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1169–1174, 2005

Key words: phenolic; montmorillonite; mechanical properties; nanoclay

INTRODUCTION

Toyota researchers caused a stir in 1987 with investigations leading to the development of a commercial montmorillonite/nylon nanocomposite.[1] They were able to show significant increases in tensile modulus and tensile strength while improving toughness. Montmorillonite clay is in the smectite clay family. It consists of nanometer thick polysilicate sheets that have a characteristic length between 100 and 1000 nm. The clay has a specific area of 760 m^2/g.

In order to take advantage of montmorillonite's high aspect ratio and nanometer-scale thickness, it is necessary that the polymer (or monomer) penetrate the interlayer gallery of the nanoclay (intercalation). There are three methods for doing this: *in situ* polymerization, melt intercalation, and synthetic clay (mica) fabrication. In *in situ* methods, the monomer diffuses to the interior clay surface and polymerizes within the platelet galleries. Melt intercalation is a method in which the polymer diffuses into the galleries after it is fully formed via mixing at a temperature high enough to melt the polymer. To obtain the benefit of exfoliated clay without worrying about clay processing treatments, synthetic nanoclays such as mica can be fabricated and dispersed in a polymerization reactor.[2,3] This has the advantage of limiting tactoid (aggregate) formation, but it requires fabrication of the mica sheets.

Several polymer/montmorillonite composites have been developed. Results show an increase in stiffness, regardless of the base polymer. Reported values of the elastic modulus are improved by as much as 65% (polyethylene). Toughness and elongation measurements are mixed. Most polymers have higher fracture toughness (or breaking energy). An exception is the polycarbonate/epoxy system examined by Wan et al.[4] Few composites demonstrate any increase in strain to failure over the pure polymer matrices. The plastic/nanoclay systems that do increase in ductility tend to be those of brittle polymer resins, and the increases are slight.[5–9]

Smectite clay has a crystallographic structure. Conventional composite theory predicts that adding montmorillonite will embrittle a polymer; this is the case when the clay is in aggregate form.[8] To avoid embrittlement, montmorillonite must be in an intercalated or exfoliated form. By dispersing montmorillonite at the nanometer level, several nanocomposites (polymer/nanoclay materials among them) have been shown to avoid this embrittlement problem or even increase the ductility of the polymer.[2,9–12]

Thermal properties have been improved in phenolic resin, poly(methyl methacrylate) (PMMA), nylon 66, epoxy resin, poly(ethylene terephthalate), and other polymers.[3,7,13–15] It is argued as well that nanoclay sheets induce charring and make polymer nanocomposites effective flame retardants.[15]

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Two groups have created phenolic resin/montmorillonite composites. Wu et al.[16] synthesized both Novolak and resole nanoclay resins by a suspension condensation (*in situ*) reaction. They compared clay compounds that used untreated montmorillonite with those that were pretreated (ion exchange) to increase basal spacing. They investigated the structure of the oligomer and resin, finding that the clay is intercalated and partially dispersed, but did not test the mechanical properties of the material. Choi and Chung[7] used melt intercalation of commercial grade oligomer to synthesize Novolak nanoclay resin. Tensile tests show increases in tensile strength, tensile modulus, fracture strain, and toughness from the neat resin. These values hit a maximum at around 3% clay loading.

In this work, it is argued that intercalation and exfoliation can be achieved by premixing untreated montmorillonite clay and dodecyl amine in a solution of monomer at reduced pH. This requires no further change to the reaction scheme. Previous clay treatment used extensive mixing in water to swell the clay. This swelling allows dodecylamide and polymer better access into the platelet galleries; the problem is that it is necessary to remove the water at some point, typically by drying. When phenol is used as both a swelling agent and a reactant, the drying step is avoided. This is advantageous in that it readily lends itself to scale-up application. This method is simpler than previous work and affords competitive enhancements in material properties. It is worth noting that montmorillonite clay particles are so small that they do not wear machinery as much as hard fillers like crushed glass.

EXPERIMENTAL

Synthesis

The reaction occurred in a 450-mL three-necked flask. Twenty grams of untreated montmorillonite clay was fed into the reactor with 206 g of 91% phenol (9% water). Two grams of dodecyl amine were added along with 1 g of anhydrous oxalic acid. The vessel was maintained at room temperature. To investigate the exfoliation kinetics, the batch was stirred for 48, 24, or 2 h or not at all. The reactor was then heated to reflux; 2 g of oxalic acid and 142 g of formalin were charged into the reactor. After 30 min, 1 g of oxalic acid was added as make-up. The reaction was quenched 90 min after being heated.

Quenching was done by adding 200 mL of water to the flask. After settling, the aqueous layer was siphoned off. Vacuum distillation (up to 185°C) stripped the remaining volatiles off the Novolak. The reactor was allowed to cool until it reached 115°C.

To cure, 20 g of hexamethylenetetramine was added and the contents stirred vigorously. The curing was considered complete when the viscosity was too high for mechanical mixing to be effective, the polymer flow became laminar, and the resin took on a bright yellow hue (or caramel, depending on the additives).

Compression molding was conducted on a Carver press at 120–180°C. The powder was first preformed in a cast, and then it was compression molded into tensile bars (2 in. long, 0.5 × 0.125 in. at the neck). Because of the conditions of molding, it is reasonable to assume that some crosslinking continued while the resin was in the molding press.

An analogous reaction procedure was used to synthesize neat phenolic Novolak as well as composites filled with magnesium oxide (particle diameter < 1 mm) and crushed glass (particle diameter < 2 mm). Because no clay was added for these three comparative materials, the reaction began with charging all reactants and filler into the vessel at 110°C. The procedure following this was identical to that for the nanoclay composite.

Characterization

The morphology of the polymer was examined by X-ray diffraction. Analysis was done with a Scintag Inc. XDS-2000 X-ray diffractometer. The diffractometer uses a copper X-ray source that has an emission wavelength of 1.54 Å. X-ray tests were done on all types of samples.

Testing

Mechanical testing was done on an Instron 4202 tensiometer. The tensile bars were placed in the machine and loaded at a strain rate of 0.1 in./min at room temperature. Results were compiled and analyzed for statistical accuracy. At least a dozen tests were performed for each variable that was considered. Density was measured by weighing the samples and measuring the displaced water volume in a graduated cylinder.

The thermal properties were investigated via thermogravimetric analysis (TGA). The device used was a Perkin Elmer TGA 7 thermogravimetric analyzer.

Materials

Montmorillonite clay was provided by the Materials Science Department at Rensselaer Polytechnic Institute as well as the American Colloid Company via Rennecker Ltd. Chemical reactants were purchased from Fischer Chemical.

RESULTS

Effect of stirring time on exfoliation

In analyzing the structure of the clay, we first varied the prestirring time while holding the clay amount

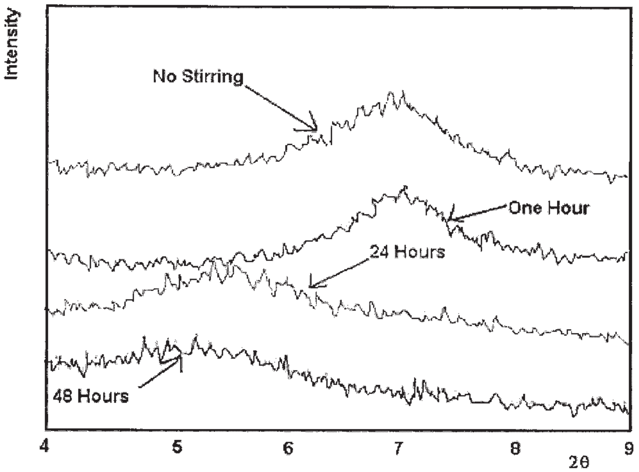

Figure 1 The effect of the stirring time on the clay morphology in phenolic resin (5.4% by mass).

constant. It was found that both the mean platelet spacing and the level of dispersion vary with the ancillary stirring time. Figure 1 compares exfoliation and intercalation for the phenolic resin with 5.4% by mass montmorillonite that was stirred prior to reaction for 1 h, overnight, 2 days, or not stirred at all. X-ray diffraction analysis shows that the mean basal spacing for untreated montmorillonite is 1.1 nm. In the polymer matrix, the platlet spacing increased to 1.2 nm for the minimally stirred samples, 1.6 nm when the clay was mixed in phenol for 24 h, and 1.7 nm when the stirring was done for 48 h.

Numerical analysis shows that the sample stirred overnight has a significant level of exfoliation. Completely dispersed clay platelets have no defined interlayer spacing, and thus no X-ray signal.[17] The area under the overnight stirred sample is 24% less than the other two curves. Stirring for an additional 24 h lowers the area again by 25%. Similar results were seen for polymer composites of 8.1% montmorillonite. There is a 10% reduction in area between the clay that was not stirred at all and the clay that was stirred for 2 h. This indicates that the level of exfoliation and intercalation can be controlled by the stirring time.

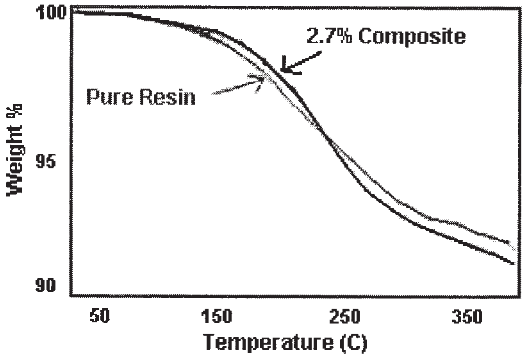

Figure 3 A thermal degradation comparison by TGA.

Effect of clay content on exfoliation

The average montmorillonite platelet spacing does not seem to depend on the clay mass fraction. This indicates that intergallery diffusion and polymerization are independent of the long-range material structure. As seen in Figure 2, the peak location of the 8.1% loaded composite is the same as that of the 5.4% loaded composite.

Although peak location is not a direct function of the clay content, the peak area is strongly dependent on the gross mass fraction of clay in the matrix. For 8.1% clay, there is a large peak suggesting that, although intercalation has occurred, the extent of exfoliation (complete platelet dispersion) is less. For 5.4%

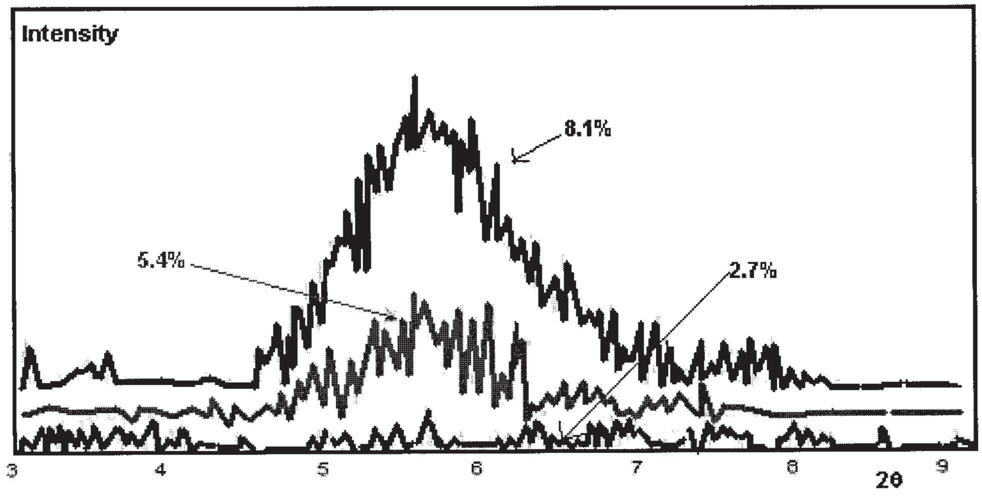

Figure 2 A comparison of exfoliation related to the amount of clay, given 24 h of auxiliary stirring.

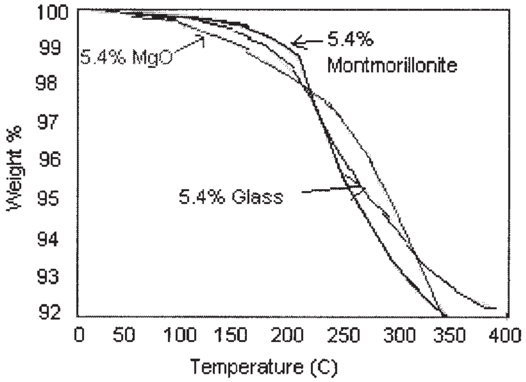

Figure 4 Thermal degradation versus additive degradation.

clay, the area of the peak is 36% of the area in the 8.1% peak. Yet, the ratio of clay is 2:3; this suggests that exfoliation is more substantial. For 2.7% clay, there is no particular peak that shows that the montmorillonite is almost completely dispersed. It is not known if this is purely a kinetic phenomenon. As seen in Figures 1 and 2, more stirring increases the exfoliation for higher clay loadings.

Whether further stirring can cause complete exfoliation is questionable. It is posited that there is an effective solubility limit for montmorillonite in a phenol oligomer solution; thus, higher clay loading will inevitably lead to a certain amount of the montmorillonite being in an aggregate (tactoid) phase. This position is supported by the work of Choi and Chung[7] with melt intercalated phenolic nanoclay composites: stirring caused much of the treated clay to exfoliate, but a constant fraction (evidenced by X-ray diffraction peak location and area) remained in intercalated form regardless of excessive stirring. There is no evidence of performance enhancement with excessive stirring either. Chang et al.[2] found the same phenomenon occurred in a poly(lactic acid) system mixed with natural montmorillonite or synthetic mica. It was not possible to perfectly exfoliate the organic clay and, although the mica dispersed better, it still aggregated to some extent regardless of treatment methods.

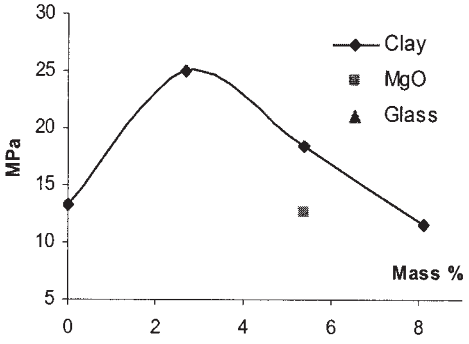

Figure 5 The fracture strength.

TGA comparisons

Figure 3 compares the thermal degradation curves for the nanocomposite and neat resin. It is seen that up to 225°C the nanocomposite retains its mass better than the unmodified resin.

Figure 4 shows the comparison of the thermal degradation depending on which filler is added. The composite of phenol with montmorillonite outperforms the glass and magnesium oxide reinforced materials. Improved thermal behavior was also observed when montmorillonite was added to other polymers (nylon 66, PMMA, epoxy resin, etc.).[7,10,14,15] This is because the clay stabilizes the polymer in the interface region. Smectite binds the polymer more effectively than the traditional composites, and this lower energy interface must be overcome by additional heating in order to melt the material.[10]

Mechanical strength

Table I is a summary of the tensile testing results. Figures 5–8 show comparisons of the mechanical properties for varying levels of montmorillonite (pre-

TABLE I
Tensile Properties

Composite (% mass)	Loading	Prestirring (h)	Strain to Failure (% elong.)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Fracture Energy (mJ)	Density (g/cm^3)
Pure	0.00	0	3.1	13.3	1.20	252	1.29
Clay	2.70	24	3.6	24.9	1.53	503	1.31
Clay	5.40	2	3.5	14.3	1.11	332	1.31
		24	3.4	18.4	1.69	281	1.30
		48	4.1	18.9	1.65	330	1.30
Clay	8.10	24	3.4	11.5	1.07	242	1.33
		48	4.5	15.9	1.03	408	1.32
MgO	5.4	0	3.5	12.7	1.16	262	1.31
Glass	5.4	0	3.5	7.2	0.66	193	1.32

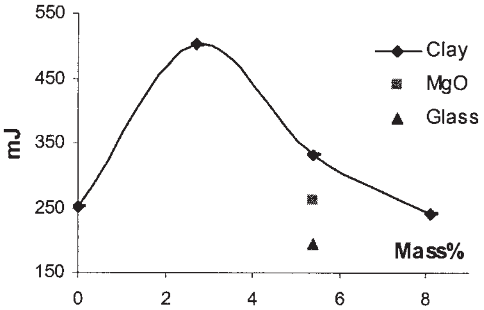

Figure 6 The fracture energy.

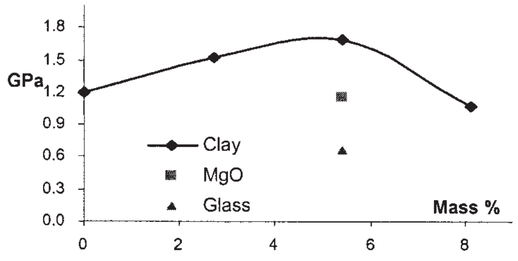

Figure 8 The tensile modulus.

stirred for 24 h) and 5.4% magnesium oxide and crushed glass. The overall mechanical properties were found to be improved with a moderate loading of montmorillonite clay.

From Figures 5–8 it can be seen that phenolic resin has significantly improved the mechanical properties when montmorillonite is used as a filler. The performance of the material is optimized at low concentration (3–5% by mass); a further increase in the mass fraction of clay is detrimental. This is explained by noting that, for a given amount of prestirring, a larger fraction of the montmorillonite is fully dispersed when the clay is at lower concentration.

The reason for the increased mechanical strength is exfoliation of clay in the polymer. The clay in intercalated form has improved properties, but intercalated clay retains some of its aggregate-like properties. Good bonding between the polymer matrix and the silicate platelets is due to the large surface area of the inorganic phase and the corresponding limited mobility of the polymer in the interfacial region. The formation of a constrained region in the vicinity of the clay sheets (particularly in intercalated form) acts to raise the observed elastic modulus.

There is an approximate 100% increase in the fracture energy. The mechanisms that govern the fracture properties are likely to operate at micro- and nanoscales, but they are not clearly established. Although the clay cannot absorb strain well, it can increase the material's toughness by roughening. Examination of the fracture surfaces reveals a substantial increase in the area of fracture via roughening. The implication is that the high strength of the smectite platelets prevents their fracture when the polymer fails. The bonding between the montmorillonite and the polymer is substantial enough to transmit stress through the interfacial area and spread the effective area of deformation. Cracks must propagate around the montmorillonite in a tortuous path that requires more energy.[8,18] Because the bonding is better in a nanocomposite, the crack must overcome a more significant barrier to move along the interface when compared to traditional composites.

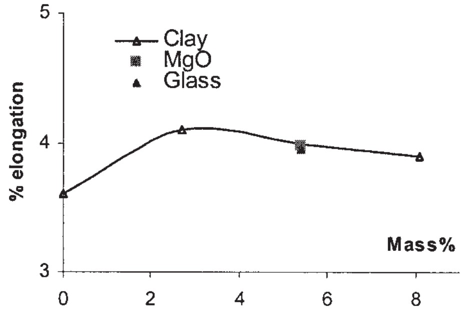

Figure 7 The elongation at fracture.

CONCLUSION

To make a nanoclay composite, polymer must penetrate and exfoliate the tactoid aggregates in montmorillonite clay. Proper exfoliation of clay in phenol was accomplished by treating it with dodecyl amine at low pH and stirring for 24 hours in phenol. X-ray diffraction showed good exfoliation and intercalation of clay in the polymer as a result of this stirring. Phenol was

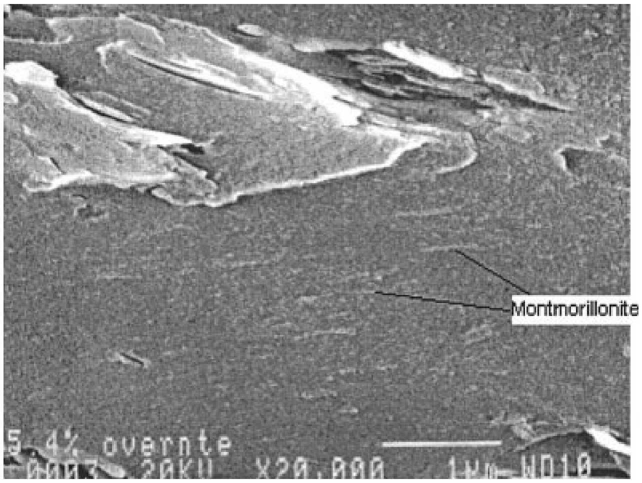

Figure 9 SEM image of 5.4% composite fracture surface.

oligomerized by suspension condensation and cured with hexamethylenetetramine.

Tensile bars of the polymers were prepared using compression molding. The results showed that clay loading of 2.7% by mass of clay produces improvement in the tensile property that is superior to that of traditional composites as well as pure resin. The thermal stability was also superior for montmorillonite reinforced resin.

From the above results, a very small mass fraction of clay was required to improve properties like the thermal degradation, stiffness, and strength. Using the primary reactant as a swelling agent provided a simple method of effective dispersion of the clay.

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