

PERFORMANCE OF PP/CLAY NANOCOMPOSITES WITH EDGE FUNCTIONALIZED CLAY

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Abstract

The effects of specific functionalization of montmorillonite clay on the mechanical properties of melt-processed PP/clay nanocomposites have been investigated with three different clays. Organically modified montmorillonite was subjected to appropriate silane treatment in order to functionalize the edges. Each of the organoclays was compounded with a maleated polypropylene (PP-g-MA) and a PP in the proportion 5:10:85 by wt. The clay siled in this work was confirmed by XRD to be edge functionalized. This clay led to the composite with the greatest level of exfoliation as determined by both XRD and dynamic viscosity measurements. The same composite also had the highest tensile modulus. However, the flexural modulus was found to be insensitive to additional treatment of the clay. Hence the increase in tensile properties reflects the greater extent of dispersion as well as a higher degree of orientation achieved during molding.

Background

Polymer-layered silicate nanocomposites have been a focus of great interest over the last decade after the pioneering work done by researchers at Toyota for nylon-6 based materials. Layered smectite clays exist naturally in a tactoid structure comprised of several tens of stacked layers with a typical lateral dimension of 100-200 nm, a layer thickness of 1 nm, and an interlayer spacing of about 1 nm. The high aspect ratio of delaminated or exfoliated platelets has the potential for producing striking improvements in a variety of polymer properties with the incorporation of small amounts of these clays¹⁻³.

Montmorillonite is a 2:1 smectite: each nanolayer is comprised of an aluminum-oxygen-hydroxyl octahedral sheet sandwiched between two silicon-oxygen tetrahedral sheets⁴. The interlayer galleries contain exchangeable cations (usually sodium) due to the charge imbalance in the system. These clays with plate like morphology (as opposed to fibrous clays like sepiolite) have hydroxyl groups at the slightly positive edges of the platelets. In order to enhance the interaction between the mineral and the organic polymer, the hydrophilic face of the clay platelets is modified by pre-intercalating long chain alkyl ammonium ions as surfactants. The length of the surfactant chain is an important variable that influences the level of exfoliation and the effectiveness of a C18-onium ion has

been established⁵. Such organophilic clays have been incorporated into a variety of polymer matrices by melt mixing, with additional help from compatibilizer polymer chains in some cases.

The coupling between the clay and the matrix can be further enhanced by silane treatment of the clays⁶⁻⁷. But some silanes may move into the interlayer galleries and react with the surfactant and or the clay faces, leading to stronger intercalated structures. Other silanes have been shown to react with the edges mainly⁸. The objective of this work is to investigate the effectiveness of the later class of silanes in producing exfoliated polypropylene nanocomposites and the associated mechanical performance. For comparison, composites were made with two other commercially available organoclays -- one of them containing a mixture of silane-coupling agents. All composites were characterized structurally and the performance of the nanocomposite evaluated to understand the effect of edge treatment.

Experimental Framework

The basic organoclay used here is I.30P montmorillonite, modified by the exchange of 95-98% of the sodium cations in the clay gallery with octadecyl-ammonium ions. This material from Nanocor has a specific gravity of 1.9 and a gallery spacing of 2.3 nm. The polypropylene (PP) matrix is Basell Polyolefin's PP 6323, which has a weight average molecular weight of 280,000 and a melt flow index of 12. The silane employed for the work is phenyl-trimethoxy silane available from Dow Corning. A different commercially available siled clay I.31PS was received from Nanocor and compared with the I.30P clay as well as with the I.30P siled in this work.

The compounding was carried out at 180°C in a lab scale Banbury Mixer by running it at 150 rpm for 10 min. The compounded material was then granulated, which was then compression-molded at 200°C and 20 tons of pressure for 10 min, into disks that were 50 mm in diameter and 1.0-1.2 mm in thickness. The characterization of the structure by XRD is performed on these disks with a Rigaku Rotaflex Ru-200BH X-ray diffractometer, which is equipped with a Ni-filtered Cu K α radiation source and operated at 45 kV and 100 mA. The sample is scanned over a 2 θ range of 0.5° to 15° at a rate of 0.5°/min and measurements are recorded at equal increments of 0.01°.

The rheological characterization was done with a Rheometrics RMS 800; the sample was held between two parallel plates (50 mm) at 180°C and subjected to oscillatory shear over a frequency range of 0.05-100 rad/s at a strain amplitude of 2%, which was confirmed to be within the linear viscoelastic regime. The granulated pellets were melted in a DSM 15 cm³ Micro-Extruder at 5 rpm with a minimum input of additional shear and then injection molded at 100 psi in a DSM Injection Molding Machine to make flexural and tensile bars for mechanical testing.

Compound Formulations

The 3 different types of clay (I.30P, I.30P-Silated in this work and I.31PS) were compounded in the ratio 5-85% by weight with the homopolymer PP with the rest being maleated polypropylene PP-g-MA (acid number =23 and Mw=22000). The effectiveness of this compatibilizer has been established by earlier work done in our group⁹. The different formulations were as follows:

- **PP:** Homopolymer PP
- **NC1:** 85% Homopolymer PP + 10% PP-g-MA, and 5% I.30P Clay
- **NC2:** 85% Homopolymer PP + 10% PP-g-MA, and 5% I.30P-Silated in this work
- **NC3:** 85% Homopolymer PP + 10% PP-g-MA, and 5% I.31PS Clay

Results and Discussion

Fig 1 shows the XRD pattern of the I.30P, I.31PS and the I.30P-Silated in this work. The two clays I.30P and the I.30P-Silated in this work have approximately the same basal spacing of 2.3 nm as calculated by Bragg's Law. So, following the literature⁸ we can infer that only the edge hydroxyls are involved in the silane reactions. On the other hand the clay I.31PS has a basal spacing of about 2.8 nm. This increase in the basal spacing suggests that the silane involved in I.31PS is interacting with the surfactant in the clay galleries. This can impair the extent of exfoliation obtained with the clay and does as seen in the XRD of the corresponding composite NC3. Figure 2 shows the XRD's for the three composite formulations NC1, NC2 and NC3. The composite NC3 compounded using I.31PS (containing the silane coupling agent) shows a strong intercalation peak, which occurs at a 2θ value of approx 2.19, which translates to a basal spacing of 4 nm. The other composites NC1 and NC2 show significant levels of exfoliation with the latter having the most exfoliated morphology. The extent of exfoliation in these two composites can be compared quantitatively⁹ by evaluating the dynamic melt viscosity of the composites relative to the silicate free melt as shown in Fig 3. The viscosity measurements were made at low strain amplitudes because higher strains can result in possible platelet alignment¹⁰⁻¹¹. The relative viscosity at low frequencies, which has been shown to be an index for

exfoliation⁹, is tabulated in Table 1. The relative viscosity index for the nanocomposite NC2 was about 3 times the relative viscosity index for the nanocomposite NC1 containing the unsilated organoclay, with NC3 showing the lowest value. The silane treatment in our case has clearly enhanced the level of exfoliation.

The tensile modulus of the three nanocomposite specimens has been compared in Fig 4. The NC2 composite with the clay silated in our work shows the maximum increase in tensile modulus over the matrix. Hence the difference in level of exfoliation is reflected in the tensile modulus. The NC3 nanocomposite having significant intercalated structure shows the least improvement in tensile modulus. Fig 5 presents the increase in flexural modulus of these composites over the matrix. The improvement obtained here is roughly the same (about 35%) for all composites. The tensile modulus is more sensitive to the silane treatment probably because orientation differences would affect it more. The interactions of the silanol groups with the hydroxyl groups present at the edges of the nanolayers are being investigated further with the help of FTIR.

Conclusions

Our findings indicate that the use of appropriate silanes, which do not interact with the surfactant at the face of the nanolayers and also have an affinity to the matrix polymer, can enhance the level of exfoliation significantly. The increase in the tensile modulus also reflects these trends in exfoliation.

References

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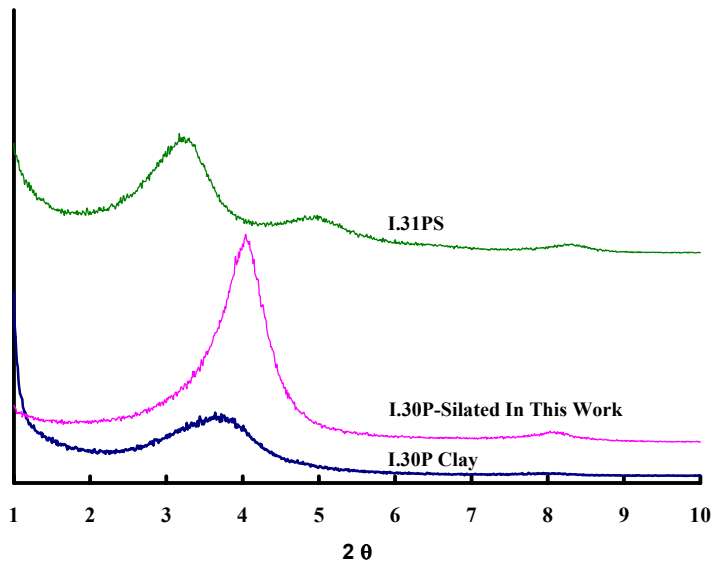


Figure 1. XRD for I.30P, I.30P-Silated in this work and I.31PS

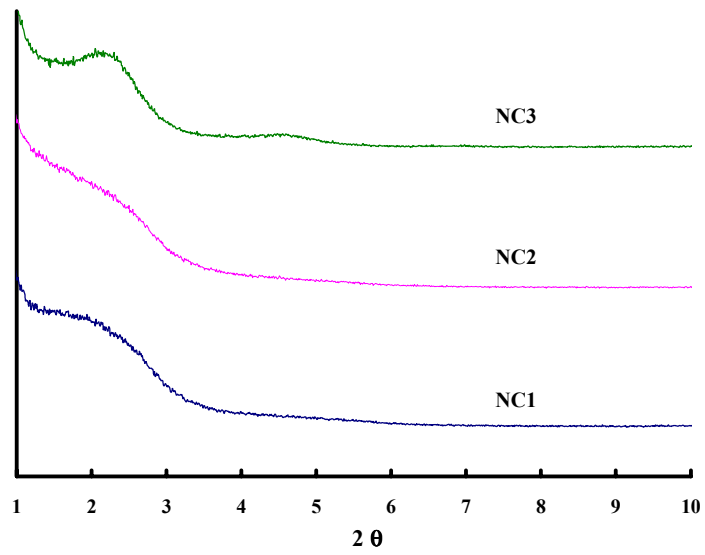


Figure 2. XRD for Nanocomposite Formulations
 NC1: 5% I.30P Clay; NC2: 5% I.30P-Silated in this work;
 NC3: 5% I.31PS Clay

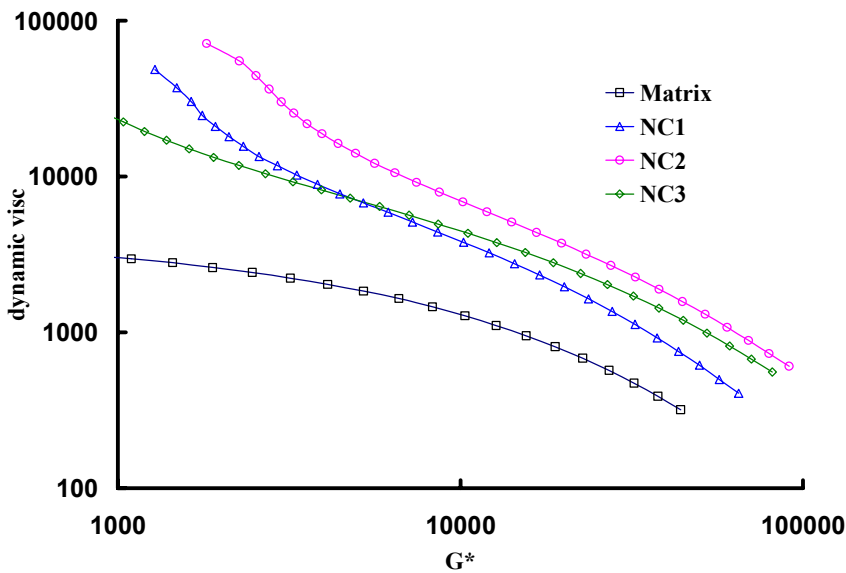


Figure 3. Dynamic Viscosity Measurements
 NC1: 5% I.30P Clay; NC2: 5% I.30P-Silated in this work;
 NC3: 5% I.31PS Clay

Table 1. Relative Viscosity Calculations
 NC1: 5% I.30P Clay; NC2: 5% I.30P-Silated in this work;
 NC3: 5% I.31PS Clay

Formulation	η_r
NC1	5.29
NC2	15.91
NC3	4.30

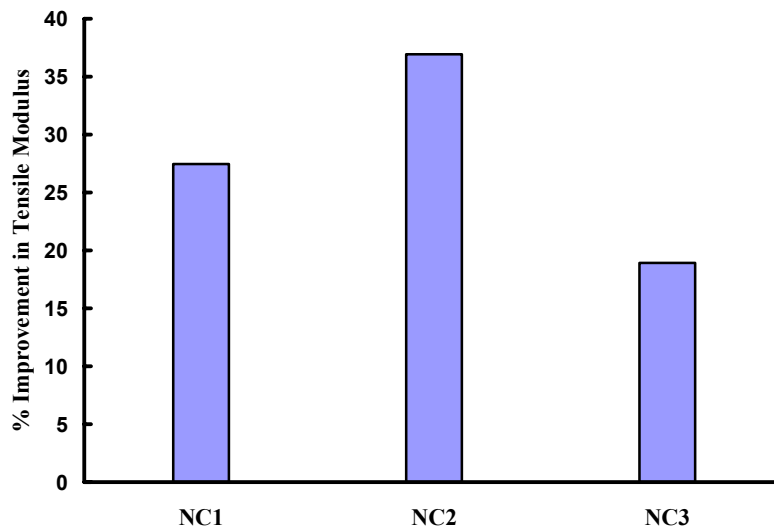


Figure 4. Improvements in Tensile Modulus
NC1: 5% I.30P Clay; NC2: 5% I.30P-Silated in this work;
NC3: 5% I.31PS Clay

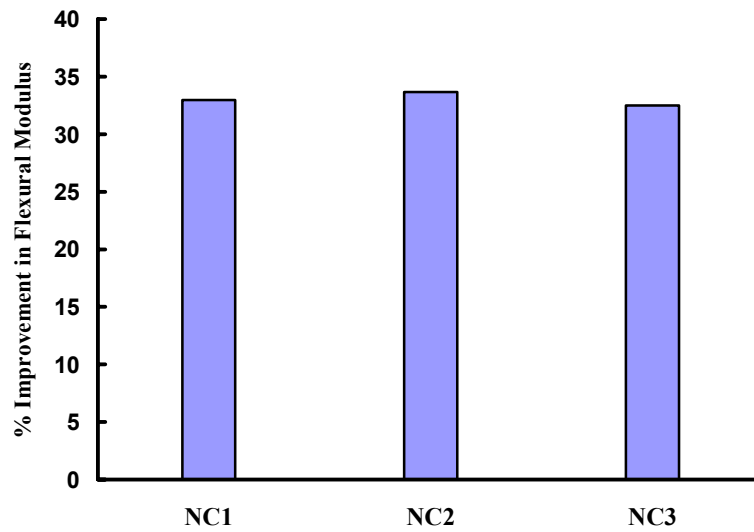


Figure 5. Improvements in Flexural Modulus
NC1: 5% I.30P Clay; NC2: 5% I.30P-Silated in this work;
NC3: 5% I.31PS Clay