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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1016/j.compscitech.2005.09.012>

Composites Science and Technology, 66, 10, pp. 1274-1279, 2006-08-01

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Effect of clay types on the processing and properties of polypropylene nanocomposites

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Received 9 February 2004; received in revised form 22 August 2005; accepted 15 September 2005

Available online 13 December 2005

Abstract

The effect of clay chemistries and sources on the processing and properties of the nanocomposites made therefrom has been studied. A number of nanocomposites were prepared using different types of clay by melt processing using a Brabender plasticorder. Various analysis techniques were used to characterize the dispersion and the properties of the nanocomposites, using scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and dynamical mechanical analysis (DMA).

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Keywords: Polypropylene; Intercalant; Nanoclay; Intercalation; Exfoliation; Coupling agent

1. Introduction

Polymer nanocomposites is a new class of composite materials derived from nanoparticles with at least one dimension in the nanometer range. These nanoparticles are dispersed in the polymer matrix at a relatively low loading (often under 6% by weight). Because the nanoparticles (such as nanoclays, nanofibers, carbon nanotubes, etc.) are so small and their aspect ratios (largest dimension/smallest dimension) are very high, even at such low loadings certain polymer properties can be greatly improved without the detrimental impact on density, transparency, and processability associated with conventional reinforcements like talc or glass. In general, nanoparticles can significantly improve the stiffness, heat deflection temperature (HDT), dimensional stability, gas barrier properties, electrical conductivity, and flame retardancy of the polymer matrix [1,2].

Among polymer nanocomposites, those based on polypropylene (PP) and nanoclay have attracted considerable interest [3–13] because PP is one of the most widely used and fastest growing class of thermoplastics, while nanoclay is one of the most widely accepted and effective nanoreinforcements. However, scientists and engineers are faced with several challenges. Nanoclay is naturally hydrophilic whereas PP has no polar groups in its backbone and is one of the most hydrophobic polymers. The result is usually a low level of dispersion of the clay platelets in the PP matrix and a poor interfacial bonding between the clay surface and the PP matrix. This limits the advantages of incorporation of the nanoclay into the polymer matrix. Attempts to resolve these problems involve modification of the nanoclay surface and the matrix. Several types of commercial organo-clay are currently available [14,15]. In general, the main difference among them concerns the organic modifiers (intercalants), whose organic cations can replace the cations (Na^+) on the clay surface and are tailored to the polymer in which the clay would be incorporated. Some examples of these organic cations are alkyl ammonium ion, alkyl amine, etc. Therefore, the intercalants

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are widely used to improve the compatibility of nanoclay with the matrix.

The objective of the work described here is to study the effect of intercalants chemistry and concentration on processing, morphology, and properties of PP nanocomposites. The preparation method used in this work is melt compounding and compression molding, rather than twin-screw extrusion followed by injection molding as normally done. This is to obtain knowledge on the behavior of the nanocomposites when they are prepared using this technique. This paper reports preliminary results on the effect of different types of clay, which contain different intercalants, on processing and mechanical properties of PP nanocomposites.

2. Experimental

2.1. Materials

The polypropylene (PP) used in this study was PP6100SM, a general-purpose injection grade from Montell.

Six different types of commercial clay tabulated in Table 1 were used. Na denotes the non-modified montmorillonite clay. Cloisite 15A, 20A and 30B, provided by Southern Clay Products Inc., are clays modified by alkyl ammonium. Nanomer I30E and I31PS, supplied by Nanocor Inc., are clays modified by alkyl amine. Table 1 provides the technical details of nanoclays used in this study [14,15].

2.2. Nanocomposite preparation

The mixtures were prepared by mixing in a C.W. Brabender PL2000 Plasticorder. The mixing temperature was kept at 180 °C in order to ensure proper viscosity for the mixing while at the same time minimizing degradation. The rotation speed was set at 60 rpm. After all ingredients were introduced into the Brabender, melt mixing was continued for an additional period of 5 min. The total weight of material per batch was 40 g, which gives a suitable volume for the Brabender mixer. In all the nanocomposite samples, the concentration of nanoclay was kept at 3 wt.%.

Specimens for testing were prepared in a Model M Carver Laboratory Press under a pressure of 40,000 psi, with a temperature of 180 °C for both upper and lower platens.

2.3. Characterization

The characterization of the materials was done using the following instruments. Data concerning the rheological behavior during mixing was collected directly from the Brabender mixer.

A JEOL JSM-840A SEM was employed to observe the microstructures of the materials. This can be used to evaluate the dispersion of the clay inside the polymeric materials.

TA Instruments – DSC 2010 was used to obtain the crystallization and melting curves. The samples were heated to 200 °C under nitrogen atmosphere and kept at this temperature for 5 min before cooling down in order to assure that the materials melted uniformly and to eliminate the thermal history. The sample was then cooled down to room temperature at a cooling rate of 10 °C/min. From the crystallization curves that were recorded by computer, crystallization temperature (T_c) and crystallinity degree (X_c) can be obtained. Melting temperature (T_m) was detected under the same conditions at heating rate 10 °C/min.

A Du Pont 983 DMA instrument was used to characterize the mechanical behavior of the material at different temperatures. Specimens with dimensions $L/T > 10$ (where L is the length and T is the thickness) were prepared by compression molding. The dynamic properties were studied in fixed frequency mode at a frequency of 1 Hz, and the strain amplitude was 0.2 mm. The samples were heated in the temperature range from –40 to +160 °C at a heating rate of 5 °C/min.

3. Results and discussion

3.1. Rheological behavior

In general, it is difficult to compare the torque values for different composites because the torque is strongly deter-

Table 1
Characteristics of the nanoclay

Sample	Intercalant	Modifier concentration (meq/100 g)	Gallery distance (X-ray results) (Å)	Supplier
Na	–	–	–	Southern Clay Products Inc.
15A	2M2HT ^a	125	28.5	Southern Clay Products Inc.
20A	2M2HT	95	24.2	Southern Clay Products Inc.
30B	MT2EtOH ^b	90	18.5	Southern Clay Products Inc.
I30E	Octadecylamine	–	–	Nanocor Inc.
I31PS	Octadecylamine + silane	–	–	Nanocor Inc.

Note: meq/100 g is a measure of the cation exchange capacity (CEC). This is the milliequivalents of charge exchanged per 100 g mass of the clay. It represents a charge per unit mass, and in SI units, is expressed in “coulombs per unit mass”. A CEC of 1 meq/g is 96.5 coulombs/g. Cation exchange capacity measurements are performed at a neutral pH of 7. The CEC of montmorillonite varies from 80 to 150 meq/100 g.

^a 2M2HT = dimethyl di(hydrogenated tallow) quaternary ammonium.

^b MT2EtOH = methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium.

mined by the total volume of material in the mixing chamber. Since it is difficult to control the volume of the system, the amount of sample introduced into the chamber was controlled by weight. Because each ingredient has a different density, the total volume differed for different composites even though the total weight was the same. It is therefore more meaningful to compare the trend of the torque curve during mixing. During the first five minutes of mixing the system was not stable because it took some time to introduce the ingredients one by one into the chamber and also to heat and melt them. Thus it is more reasonable to look at the change of the torque in the later stage after all ingredients have been added, melted, and well mixed. Therefore, only the torque curves after 300 s since the beginning of the process are presented.

Different types and concentration of intercalants that are used to modify the clay surface may have effects on the rheological behavior of mixtures. Fig. 1 shows the torque curves for the PP and its composites with different clays. Some obvious differences in the trend of the curves can be observed. The temperature of the chamber was very stable during all experiments (180 °C); therefore, these changes are likely due to the change in the materials themselves. The torque curve of PP became relatively stable after 5 min of mixing and showed only a slight downward trend with time, indicating little change in the viscosity of the sample. However, the presence of nanoclays in the mixtures has definite impact on the torque as shown in Fig. 1. The torque curves of the mixtures with Na clay, 15A clay, 20A clay and 30B clay, are nearly parallel with the PP curve. These stable curves imply almost constant viscosity of systems during mixing. However, I30E- and I31PS-mixtures curves have significantly downward trend compared with the PP curve. In other words, the viscosity of these composites was reduced greatly during mixing, which can be caused by reduction in molecular weight due to oxidation or/and degradation of the matrix. Moreover, during the Brabender mixing, the color of composites based on I30E and I31PS turned brown and their odor turned odious as the residence time increased. This can be another indication that degradation or/and oxidation had happened. The degradation/oxidation should be related to the differences in organic surface modification.

15A, 20A and 30B were modified by alkyl ammonium, whereas I30E and I31PS were modified by alkyl amine. The residual amine in I30E and I31PS can greatly affect the oxidation and the degradation, resulting in poor thermal stability of mixtures. From the curves, the order of the effect of the different clays on the oxidation or/and degradation appears to be: I30E > I31PS > 15A ≈ 20A ≈ 30B ≈ Na ≈ None (PP). However this requires to be confirmed through further testing using TGA.

Although torque curves of Na, 15A, 20A and 30B are stable, there are some differences between them. Torque values for Na, 20A and 30B curves are higher than that for PP. Torque value for Na is the highest, and torque value for 15A is lower than that for PP. These differences indicate the viscosity of various mixtures was different. Introduction of pure clay can cause an increase in viscosity because clays are rigid particles. However, the low molecular weight intercalant used to modify the clay surface can result in the decrease in viscosity of the mixture. The reduction of viscosity becomes more significant with increase of the intercalant concentration. 15A, 20A were modified with the same type of intercalant (Table 1), but the intercalant amount decreases from 15A to 20A (from 125 meq/100 g to 95 meq/mg). As a result, the torque of the 20A was higher than that of 15A. 20A and 30B have similar intercalant and concentration, their torque curves are nearly same. The general order of the composites viscosity among different clays is thus: Na > 20A ≈ 30B > PP > 15A > I31PS > I30E.

3.2. Dispersion behavior

SEM observation showed that the clays were dispersed into the PP matrix in the form of large and small aggregates. It is very difficult to estimate the size of the aggregates because the aggregates are non-isometric and

Fig. 1. Torque-time curves of the mixtures with different nanoclays.

Fig. 2. SEM observation of the Na composite.

Fig. 3. SEM observation of the 15A composite.

randomly dispersed in the matrix. The size of the observed aggregates is, therefore, strongly dependent on the orientation of the particles. However, the fracture mode of samples and the dispersion quality of clays, such as aggregates concentration, can be observed. Figs. 2 and 3 are the SEM micrographs of the mixtures containing Na and 15A clay, respectively. In Fig. 2, relatively large aggregates and poor interfacial bonding between the matrix and the aggregates are observed. However in Fig. 3 (for 15A clay) the size of nanoclay aggregates is reduced significantly. This means that the dispersion of nanoclay is improved significantly by intercalants. Therefore, surface treatment for nanoclay is very important to improve the affinity between the nanoclay and the matrix and to break down the large aggregates. This can be attributed to the ability of surface treatment in reducing particle-particle attraction and promoting the expansion of the gallery distance between clay sheets [15]. An intercalant can open up the gallery distance of clay from 1 nm (for Na-montmorillonite) to 2.8 nm (for 15A). At the same time, the intercalant makes the clay become more hydrophobic and increases the compatibility with matrix.

3.3. Thermal properties

Crystallization of polymers with nanoclay has been studied extensively. Many studies have shown a nucleating effect of nanoclay for different polymers [16–18]. This effect can be used to enhance the mechanical and thermal properties of the polymer. Fig. 4 and Table 2 show the crystallization behavior of samples obtained from DSC test. Crystallization temperature T_c of pure PP was found to be 107.6 °C. The presence of the nanoclays in the mixtures increased the T_c significantly, from 107 °C (PP) to about 115 °C. These increases indicate the nucleating effect of the nanoclays in the crystallization of PP. The extent of increase of T_c varied slightly with the types of clay. The order of magnitude of T_c for the different clays is:

Fig. 4. Crystallization (cooling) curves of the mixtures with different clays.

Table 2

Crystallization and melting behavior of the composites with different clays

Sample	T_c (°C)	T_m (°C)	X_c (%)
PP	107.6 ± 0.3	165.9 ± 0.2	43.9 ± 0.8
PP + 15A	116 ± 0.2	165.6 ± 0.2	46.1 ± 0.7
PP + 20A	115.9 ± 0.2	164 ± 0.4	43.0 ± 1.2
PP + 30B	113.9 ± 0.6	163.5 ± 0.3	41.5 ± 0.6
PP + I30E	114.2 ± 0.3	162.5 ± 0.3	42.3 ± 1.5
PP + I31PS	114.5 ± 0.4	162.5 ± 0.5	40.5 ± 0.7

15A ≈ 20A > I31PS ≈ I30E ≈ 30B > PP. The degree of crystallinity (X_c) also varied with the type of clay as shown in Table 2. PP/15A mixtures had higher X_c than pure PP, while PP with other clays had lower X_c than pure PP. The magnitude of X_c of these PP/clays is: 15A > PP > 20A ≈ I30E > 30B > I31PS.

Fig. 5 and Table 2 show the melting curves and values of T_m of the different mixtures, respectively. T_m of all mixtures decreased as compared to pure PP. This can be a result of the introduction of low molecular weight surface modifier. Among five types of clays, PP with 15A, 20A and 30B, which were modified by onium ion based intercalants, had higher T_m than PP with I30E and I31PS, which

Fig. 5. Melting behavior (heating curves) of the mixtures with different clays.

were modified by the amine based intercalants. The order of magnitude of T_m for these clay mixtures is $PP \approx 15A > 20A \approx 30B > I31PS = I30E$.

3.4. Dynamic mechanical properties

Fig. 6(a) shows the change in storage modulus E' at different temperatures for various mixtures of clay and pure PP. All the mixtures with nanoclay possessed higher storage modulus than pure PP all through the temperature range. The mixtures of 20A and 15A have higher storage modulus than ones of I30E and I31PS in the entire temperature range. Among them, the PP/15A sample had the highest E' , almost 20% higher than pure PP at room temperature.

Two apparent changes of E' with temperature can be observed for all the mixtures: a sharp drop in E' from -10°C to about 20°C and a reduction in the rate of drop in E' with temperature above 75°C . The first change between -10°C and 20°C may be associated with the relaxation of the amorphous phase (α relaxation). In this case, the glassy state of the amorphous phase goes through its glass transition and there is a sharp drop in E' . At about 15°C , E' continues to fall and slope is flatter than before. From 70°C to 80°C , the reduction in E' is less severe.

From Fig. 6b, the glass transition (T_g) and the softening point (T_s) of the mixtures were determined as the peak tem-

Table 3
Effect of clay on T_g and T_s

Samples	T_g ($^\circ\text{C}$)	T_s ($^\circ\text{C}$)
PP	6.2 ± 0.2	86.6 ± 0.6
15A	5.6 ± 0.2	85.3 ± 1.2
20A	6.0 ± 0.1	85.7 ± 1.6
I30E	4.7 ± 0.5	88.9 ± 2.1
I31PS	4.6 ± 0.3	94.0 ± 1.8

peratures of the E'' curves and are listed in Table 3. The first peak at lower temperature is thought to be T_g and the second peak at higher temperature is thought to be T_s . The mixtures have lower T_g than PP. However, the extent of decrease varied with the types of clay. The mixtures of 15A and 20A have a T_g similar to PP while ones of I30E and I31PS had much lower T_g . On the other hand, T_s of mixtures of I30E and I31PS were higher than that for pure PP by 2.3 and 7.4 $^\circ\text{C}$ respectively. The mixtures of 15A and 20A still had similar T_s with pure PP. The decrease of T_g in these four mixtures indicates that the amorphous molecules become mobile at lower temperature than ones in PP. This may be due to the existence of low molecular weight intercalants. The increase of T_s in the mixtures of I30E and I31PS implies that the mobility of rigid amorphous molecules in the crystal was limited to higher temperature. The difference of T_g and T_s between Cloisite (15A and 20A) and Nanocor (I30E and I31PS) can be attributed to the different types of modifier applied to the surface of nanoclay. 15A and 20A were modified by long alkyl chain with quaternary ammonium group while I30E and I31PS were modified by long alkyl chain with amine group. Further experiments must be conducted in order to have a better understanding of this effect.

4. Conclusions

From this preliminary study, several conclusions can be drawn. The surface treatment of clay can improve the clay dispersion in the PP matrix. Among the six types of nanoclay used in this study, alkyl onium ion intercalants treated clays have better thermal stability than ones treated by alkyl amine intercalants. All the types of clay have demonstrated the apparent nucleating effect because the crystallization took place at higher temperature upon cooling. The crystallization temperatures are also affected by the intercalant characteristics.

Acknowledgement

The financial support from the Natural Sciences and Engineering Research Council of Canada is appreciated.

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Fig. 6. DMA curves for the mixtures: (a) storage modulus and (b) loss modulus.

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