

Mechanical and Gas Permeation Properties of Compatibilized Polypropylene–Layered Silicate Nanocomposites

Vikas Mittal

Department of Chemistry and Applied Biosciences, Institute of Chemical and Bioengineering, ETH Zurich, 8093 Zurich, Switzerland

Received 5 March 2007; accepted 3 June 2007

DOI 10.1002/app.26952

Published online 10 October 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Nanocomposites of polypropylene with montmorillonite modified with dimethyldioctadecylammonium ions were prepared and the effect of compatibilizers on the mechanical and permeation properties was investigated. Compatibilizers were selected on the basis of their chemical nature, molecular weight, amount of grafting and location of the polar groups. Addition of small amount of compatibilizers led to improvements in the basal spacings of clay platelets indicating enhanced exfoliation. The modulus of the composites increased as compared with the values without compatibilizer. The oxygen permeation through the composite films either increased or remained unaffected due to possible interfacial free volume enhancement owing to the incompatibility of the surface modification and the compatibilizer. Increasing the amount of com-

patibilizer also increased correspondingly the extent of exfoliation. The modulus reached a plateau value after which the increasing compatibilizer led to its decrease. The gas permeation through the composite films remained unchanged with increase in the amount of compatibilizer owing to a possible balance between the decrease in permeation due to path tortuosity and exfoliation and increase in permeation due to interfacial incompatibility. The improving exfoliation improved the yield and break stress indicating that the absence of tactoids can hinder the premature failure owing to better stress transfer. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1350–1361, 2008

Key words: poly(propylene) (PP); layered silicates; surface modification; compatibilization; nanocomposites

INTRODUCTION

Polymer nanocomposites have been extensively studied in the recent years owing to the tremendous improvements in the properties of the polymers at much lower filler volume fractions.¹ These properties included thermal stability, heat deflection temperature, flame retardancy, barrier and mechanical response, etc. The organically-modified montmorillonite has been most commonly used as filler reinforcement. The montmorillonite tactoids consisting of a large number of platy layers held together by electrostatic forces are required to be exfoliated into the primary nanometer thin layers to achieve the optimum improvement in properties. The surface modification of the montmorillonite particles by exchange of the surface inorganic cations with long alkyl

ammonium chains, therefore, is carried out.^{2,3} The surface modification helps to achieve the compatibility between the organic polymer chains by lowering the interfacial tension thus helping in driving the individual clay layers apart by the incorporation of polymer chains in the intergallery space. The high aspect ratio platelets are responsible for the property enhancement. The approach has been successfully applied to a large number of polar polymers viz. polyurethanes, epoxies, polydimethylsiloxanes, etc. owing to the easy penetration of the polar clay interlayers by the polar polymer or prepolymer chains.^{1,4–10} However, the clay interlayer, which is still partially polar even after the surface modification, could not be intercalated when nonpolar polymers like polyethylene and polypropylene were used. At best, only a partial exfoliation has been reported and thus, the increase in the properties could not be considered optimum. Polymers like polypropylene are one of the most extensively used polymers with a wide spectrum of applications. Its beneficial properties include high thermal and dimensional stability, low density, better processability, high water permeation resistance, and resistance to corrosion. Development of the exfoliated nano-

Correspondence to: V. Mittal, SunChemical, St. Mary Cray Technical Centre, St. Mary Cray, Kent BR5 3PP, England (vikas.mittal@eu.sunchem.com).

Contract grant sponsors: Swiss National Science Foundation (SNF), TOP NANO 21.

composites, therefore, can further enhance the range of applications to upgrade it from a commodity plastic to an engineering plastic.

The interplay of enthalpic and entropic forces governs the nanocomposites synthesis. The absence of strong enthalpic interactions between the OMMT and polypropylene chains, therefore, is expected to bring about a limited development. Many approaches have thus been employed to achieve better distribution and dispersion of the clay layers in polypropylene. Polypropylene-*graft*-maleic anhydride (PP-*g*-MA) has been commonly used as amphiphilic compatibilizer or nonionic surfactant to compatibilize both the organic polymer and inorganic filler phases.^{11–19} The compatibilizer is directly added while melt compounding the polymer with treated clay. Effect of molecular weight of PP-*g*-MA, amount of PP-*g*-MA and extent of grafting of MA on filler exfoliation and composite properties has been extensively studied. Much better dispersions of OMMT in the composites have been reported when amount of PP-*g*-MA with respect to OMMT was increased, but an optimum amount of grafting was required to achieve better mixing as higher grafting can also create immiscibility with the polymer matrix.^{11–13} Although mechanical properties also enhanced with the amount of PP-*g*-MA but after a certain weight percent of PP-*g*-MA, a decrease in the properties was also observed.^{20,21} Also the mechanical properties were observed to be better for the PP-*g*-MA of higher molecular weights, though the lower molecular weight counterparts had better dispersion.¹⁷ Another important point to note here is that although increasing the amount of PP-*g*-MA in the matrix led to an increase in the *d*-spacing, but the gains in *d*-spacing have not been generally reciprocated with the diffusion of pure PP chains inside the clay interlayer. Ammonium terminated polypropylene has also been used to modify the montmorillonite surfaces and exfoliated composites were obtained, although no properties for such composites were reported.²² Although exfoliated composites incorporating only PP-*g*-MA as matrix have been reported also, but they do not fulfill the goal of achieving exfoliated polypropylene nanocomposites.^{23–24} Theoretical studies have also indicated the importance of Flory Huggins parameters or the solubility parameters for miscibility between the two phases and the stability of the dispersion. Polypropylene composites with OMMT were predicted to be only intercalated at best. Benefit of amphiphilic compatibilizer to shift the morphology of the resulting composites from unintercalated or weakly intercalated to almost exfoliated was also suggested.^{25–29} Tendency of OMMT to exfoliate in the polymer matrix has also been predicted to be dependant on the length of the surfactant chains ionically attached to the clay surface for surface modification. Su

et al.³⁰ reported the improvement in mechanical properties when composites were prepared using polymerically-modified clays containing polystyrene oligomers in the modification. But these approaches were only partially successful with polypropylene owing to decreased miscibility at the interface. Apart from that, *in situ* polymerization of propylene by using Ziegler Natta catalysts immobilized on the surface was also reported. Although clay exfoliation levels were improved, but only low molecular weight polymers could be formed thus badly affecting their mechanical properties.^{31,32} The dispersion attained by *in situ* polymerization is also thermodynamically unstable. Apart from that, melt compounding approach with direct addition of compatibilizer is also preferable from process ease point of view. By employing the melt compounding approach using PP-*g*-MA as compatibilizers, the nanocomposites have been observed to attain higher stiffness than the pure polymer, but no general trends were observed for the other mechanical properties. Elongation and impact strength generally decreased on increasing the weight fraction of the compatibilizer, whereas the yield strength was much more dependant on the process and subsequent morphology.

Although PP-*g*-MA with different specifications have been commonly used to achieve the nanocomposites, the use of block copolymers for such purposes have been rarely reported for polypropylene composites. Block copolymers have been found to show better performance than the graft polymers because of better defined polar and nonpolar halves.³³ Therefore, it would also be of interest to study the behavior of block copolymers with polypropylene as one half. Chou and coworkers^{34,35} reported a simple approach for the synthesis of such copolymers. Apart from that, the polypropylene composites generated so far only for mechanical application point of view, but other properties which could also be of importance have been neglected. Polypropylene finds an extensive use in the packaging industry, therefore, its gas permeation behavior apart from the mechanical strength is of prime importance. Although the mechanical properties are always morphology dependant, but the same cannot be true for the permeation properties.

The goal of the present investigation was to study the effect of compatibilizers with different architecture and amount on the filler exfoliation, mechanical and gas permeation properties of the OMMT-polypropylene nanocomposites. PP-*g*-MA of two different molecular weight and grafting were used along with a PP-*b*-PPG. The surface modification of the filler was always kept the same to be dioctadecyldimethylammonium ions. Properties of the composite were correlated with the surfactant concentration and the basal plane spacing of OMMT in the composites.

EXPERIMENTAL

Materials

Sodium montmorillonite with a trade name of Cloisite Na was purchased from Southern Clay (Gonzales, TX). The cation exchange capacity (CEC)³⁶ of the sodium montmorillonite was determined by exchanging its sodium ions with Cu(trien)²⁺. Two different kinds of compatibilizers were used: PP-g-MA1 with a trade name of Admer QF551E was supplied by Alcan Packaging (Neuhausen, Switzerland), whereas PP-g-MA2 was procured from Aldrich (Buchs, Switzerland). Dimethyldioctadecylammonium bromide was supplied by Acros Organics (New Jersey, USA). Polypropylene glycol monobutyl ether was supplied by Aldrich (Buchs, Switzerland). Polypropylene used was the homopolymer grade H733-07 from Dow (Dow Plastics, Horgen, Switzerland). It has a melt flow index of 7.5 g 10 min⁻¹ (230°C at 2.16 kg load) and a density of 0.9 g cm⁻³.

Synthesis of PP-*b*-PPG

To a 100-mL three-neck-round-bottom flask, equipped with condenser, nitrogen inlet-outlet lines and thermometer, finely powdered PP-g-MA2 (3.4 g) and toluene (20 mL) were placed. The mixture was then transferred to an oil bath heated at 100°C and stirred overnight to totally dissolve PP-g-MA chains in toluene to give a yellowish colored homogenous mixture.^{34,35} Polypropylene glycol monobutyl ether (5 g, in excess) with a molecular weight (M_n) of 1000 was added in one portion. The temperature was increased to 110°C and the reaction was maintained at this temperature for 5 h. The mixture was then cooled and filtered. The product was extracted repeatedly with acetone to remove the excess ether. Figure 1 details the outline of the process.

Filler surface treatment

To render the aluminosilicate surface organophilic, the exchange of the inorganic cations with organic

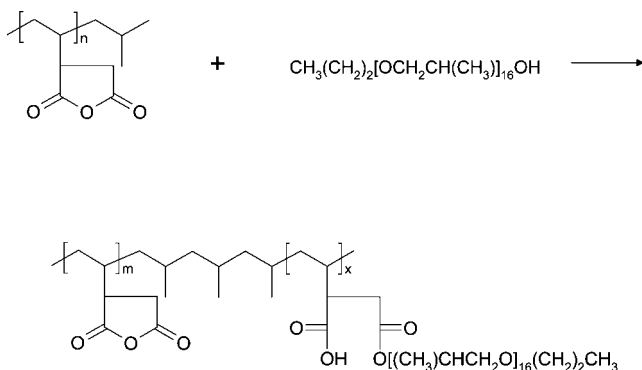


Figure 1 Reaction strategy to modify PP-g-MA molecules with polypropylene glycol monobutyl ether.

ammonium ions was carried out as earlier reported.³⁷ To remove any unattached modifier molecules, the product was again suspended in the hot ethyl acetate-ethanol (9 : 1) mixture for few hours at 70°C, sonicated, filtered, washed, and dried under vacuum at 70°C. Both degree of exchange and the purity of the product were monitored by Hi-Res TGA. All measurements were carried out in air in the temperature range 50–900°C. If the TGA thermogram indicated the presence of unattached modifier molecules, the washing step was repeated until the purity of the product was satisfactory. Thus it was always ensured that the OMMT is free from any excess modifier molecules which if present can adversely affect the properties of composites owing to their low temperature stability.^{38,39} Finally the modified clay was suspended in 400 mL of dioxane, sonicated and freeze dried. The freeze dried clay was sieved (60 μm mesh) to obtain the fine OMMT powder.

Composite preparation and characterization

The required amounts of OMMT and polymer were calculated on the basis of desired inorganic volume fraction as reported earlier using the equation³⁷:

$$M_{\text{OMMT}} = M_M + (M_M \times \text{CEC} \times M_{\text{OC}})$$

$$M_P = (M_M \times V_P \times \rho_P / V_M \times \rho_M) - (M_M \times \text{CEC} \times M_{\text{OC}})$$

where M_{OMMT} is the mass of the OMMT, M_M is the mass of the inorganic aluminosilicate, M_{OC} is the molar mass of the organic ammonium cation used to modify the montmorillonite surface, M_P is the mass of polypropylene, V_M is the inorganic volume fraction, ρ_M is the density of sodium montmorillonite (2.6 g cm⁻³), V_P is the polypropylene volume fraction, and ρ_P is its density. Twin blade compounder (Plasticorder W 50 EH, Brabender, Duisburg, Germany) equipped with a cavity of 60 cm³ was used to prepare polypropylene-OMMT composites with rotors operated in counter rotation mode. All the details regarding the procedure of compounding and compression molding to generate thick composite plates and thin films is reported before.³⁷

Wide angle X-ray diffraction (WAXRD) and transmission electron microscopy (TEM) was performed on the composite films and oxygen permeation (23°C, 0%RH) through the composite films was measured as reported earlier.³⁷

Tensile testing

Dumbbell-shaped samples (type 5B) were stamped out of the compression molded plates using a stamping press (H. W. Wallace, Croydon, Surrey, England)

TABLE I
Details of the Compatibilizers/Grafted Oligomers used in the Study
(Supplier Information)

Property	PP-g-MA1	PP-g-MA2	PPG monobutyl ether
M_n (g/mol)/MFI	5.6 g (10 min, 230°C, 2.16 kg)	3900	1000
Density (g/cm ³)	0.89	0.934	0.989
Viscosity	2.3 P at 190°C	4 P at 190°C	140 cSt at 20°C
MA content (wt %)	0.1	4	–

with a die conforming to the standard ISO 527-2. Tensile tests on the stamped samples were carried out (ISO 527-1) at room temperature using a Zwick Z020 universal testing machine with testXpert 9.01 software (Zwick, Ulm, Germany) coupled with a Video-Extensometer V4.19.02 (Messphysik, Furstentfeld, Austria) for accurate measurement. The drawing speed of 0.1 mm min⁻¹ was used for the measurement of elastic modulus and modulus was determined in the range of 0.05%–0.25% strain. A speed of 6 mm min⁻¹ was used for the measurement of other tensile properties and an average of five measurements was taken.

Thermal analysis

Differential scanning calorimetric measurements were carried out on a DSC 7 (Perkin–Elmer, Norwalk, CT) under nitrogen at a heating rate of 10°C min⁻¹, adopting the procedure for measuring heat capacities.^{37,40} High-resolution (Hi-Res) thermogravimetric analysis (TGA) of OMMT, in which the heating rate is coupled to mass loss, that is, the sample temperature is not raised until the mass loss at a particular temperature is completed, was performed on a Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE). All measurements were carried out in air in the temperature range 50–900°C at a heating rate of 20°C min⁻¹. Both degree of exchange and the purity of the OMMT were monitored by Hi-Res TGA. TGA of the composites was also performed at the same specifications to study the thermal behavior of the composites as a function of the increasing amount of OMMT.

RESULTS AND DISCUSSION

To study the effect of nonionic compatibilizers on the permeation and mechanical performance of the OMMT-polypropylene nanocomposites, different compatibilizers have been selected on the basis of chemical composition and the location of the polar groups in the polymer chain. PP-g-MA has been extensively studied compatibilizer in the literature for reducing the interfacial tensions between the OMMT and the polymer. Two different kinds of PP-g-MA have been employed in the present study as is

shown in Table I. PP-g-MA1 has a high molecular weight as indicated by its low MFI and the MA content is low, whereas PP-g-MA2 has a M_n of only 3900 (MW 9100) and has 4 wt % of MA content corresponding to 3.7 MA units per polymer chain, thus, making it a high MA compatibilizer. Acid number of PP-g-MA2 is 47 mgKOH g⁻¹ of PP-g-MA. The densities of both compatibilizers are very near to that of polypropylene. The limited availability of any block copolymers of polypropylene with other polar polymers has hindered their use for such applications. To analyze the effect of block copolymers on the performance of nanocomposites, PP-*b*-PPG (polypropylene glycol) was synthesized following the approach reported in literature.^{34,35} Although the resulting copolymer is not strictly diblock copolymer, but can be represented as a polypropylene chains containing polar blocks as side chains instead of small MA molecules. The properties of PPG chains attached to the PP-g-MA2 have been shown in Table I. The synthesis of the PP-*b*-PPG was confirmed by IR as shown in Figure 2. The FTIR analysis of PP-g-MA2 showed the characteristic absorption at 1852 and 1780 cm⁻¹ for anhydride carbonyls and an additional carbonyl absorption at 1710 cm⁻¹, revealing the existence of free carboxylic acid [Fig. 2(a)]. The presence of ester adsorption peak of 1734 cm⁻¹ and C–O–C polyoxyalkylene absorption at 1107 cm⁻¹ in the FTIR of the product [Fig. 2(b)] confirmed the required reaction. The amount of the compatibilizer in the composites was also kept to be low in order not to affect the crystallization behavior of the composites. A compatibilizer/OMMT weight ratio of 0.16 was used in the composites. Cloisite was used as the inorganic montmorillonite owing to its relatively high cation exchange capacity of 880 μ equiv g⁻¹ which leads to a dense packing on the clay surface when the inorganic cations present on the surface are ion exchanged with long chain alkyl ammonium ions. Dimethyldioctadecylammonium ions were exchanged on the surface because of their similar chemical nature of polypropylene chains. As mentioned earlier, the clay was carefully exchanged to have full exchange on the surface and to avoid the presence of any excess surfactant molecules because of the detrimental effect of these excess molecules on the properties of the composites owing to their low

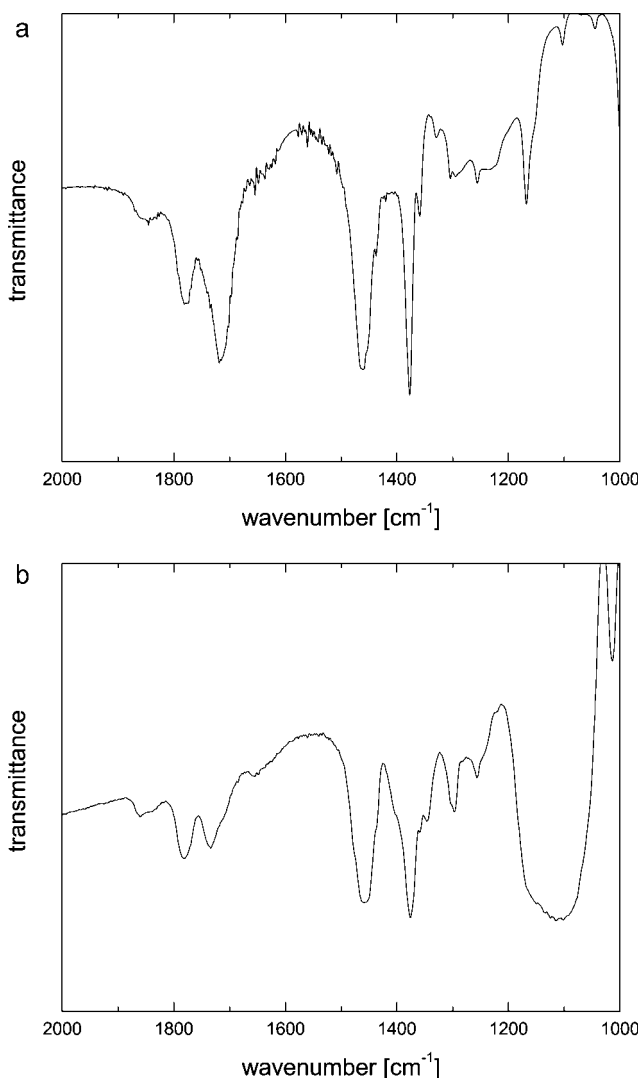


Figure 2 FTIR spectrum of (a) PP-g-MA2 and (b) the product obtained after the reaction of PP-g-MA2 with polypropylene glycol monobutyl ether.

temperature stability. Apart from that, the compounding temperatures were also kept not high so as to degrade the ammonium ions, but high enough for efficient mixing.

The 001 basal plane spacing values of the composites with different compatibilizers have been reported along with the composite without any compatibilizer in Table II. Figure 3 contains the WAXRD diffractograms of composites with and without compatibilizer for comparison. The basal plane values were augmented marginally on the addition of compatibilizers. The increase in the d -spacing was however observed to be proportional with the polarity of the compatibilizer molecules. One thing to be noted here is that the presence of diffraction peaks in every composite indicates that the clay was never fully exfoliated in any composite. The clay without any compatibilizer was in fact also marginally intercalated as is evident from an increase in the basal

TABLE II
 d -Spacing and Oxygen Permeability of 3 vol % 2C18 OMMT-Polypropylene Nanocomposites using Different Compatibilizers

Compatibilizer (2 wt %)	d -spacing (nm)	Permeability coefficient ^a ($\text{cm}^3 \mu\text{m}/\text{m}^2 \text{ day mmHg}$)
Pure PP	–	89
No compatibilizer	2.82	59
PP-g-MA1	2.68	84
PP-g-MA2	2.89	63
PP- <i>b</i> -PPG	3.09	79

^a In the range of 5% error.

plane spacing from 2.56 to 2.82. Because of its high molecular weight and very low grafting percent of MA, PP-g-MA1 can be expected to be least helpful in improving the d -spacing. PP-g-MA2 also showed almost the same d -spacing as the composite without the compatibilizer. The basal plane spacing of OMMT in composite with PP-*b*-PPG as compatibilizer was highest owing to its substantially polar nature. Since the intensity of the reflections in the diffractogram is dependant on the orientation of the tactoids, thus, it cannot be used to compare with each other to get a quantitative idea of exfoliated tactoids.

The gas permeation of the composite without the addition of compatibilizers was reduced by around 35% indicating that a partial exfoliation still could take place even without the addition of the compatibilizer. The addition of the compatibilizers was expected to bring about a decrease in the permeation through the composites films, but opposite behaviors were observed. Permeation through the composite films was observed to increase in PP-g-MA1 and PP-

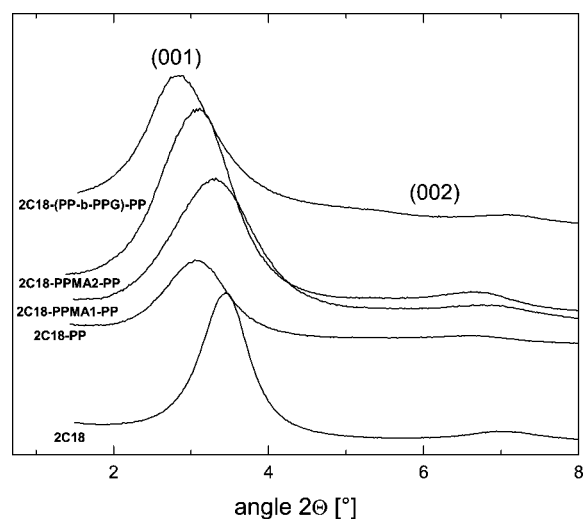


Figure 3 X-ray diffractograms of 2C18 OMMT and its 3 vol % nanocomposites with and without the addition of 2 wt % compatibilizer.

TABLE III
Calorimetric Behavior of 3 vol % 2C18 OMMT-Polypropylene Nanocomposites using Different Compatibilizers

Compatibilizer (2 wt %)	$T_{m,onset}^a$ (°C)	T_m^b (°C)	ΔH_m polymer (J/g)	Crystallinity ^c (X_c)	$T_{c,onset}^d$ (°C)	T_c^e (°C)
Pure PP	152	162	96	0.58	114	112
No compatibilizer	152	163	94	0.57	115	112
PP-g-MA1	153	162	96	0.58	120	114
PP-g-MA2	152	163	94	0.57	115	110
PP- <i>b</i> -PPG	151	163	95	0.57	115	109

^a Onset melting temperature.

^b Melt peak temperature.

^c Degree of crystallinity calculated using ΔH of 100% crystalline PP = 165 J/g (Refs. ^{42, 43}).

^d Onset crystallization temperature.

^e Peak crystallization temperature.

b-PPG, whereas it was almost unchanged in PP-g-MA2. Although a little better exfoliation of the platelets can definitely be expected from PP-g-MA2 and PP-*b*-PPG as indicated by the improvements in *d*-spacing, the permeation results do not seem to correlate with these gains in *d*-spacing. Although it is commonly suggested, that the properties of the polymer composites are dependant on morphology and, therefore, more exfoliation should bring further enhancements in all the properties. But this observation is more reliable and relatable to the bulk mechanical properties rather than the gas permeation behavior because of the sensitivity of these micro properties to many other factors also. One prime reason is the compatibility of the treated clay with the compatibilizer molecules. Although these molecules can adsorb on the surface and increase the clay interlayers by intercalation, but their compatibility with the surface modification can play a very decisive role on the permeation properties. Microvoids or increase in free volume generated at the interface because of the incompatibility of these two phases can lead to an increase in the permeation, though the clay is more exfoliated thus counterbalancing the effect of exfoliation leading to no decrease or increase in the permeation. Similar behavior have also been observed earlier in polyurethane and epoxy composites in which OMMT modified with dioctadecyldimethylammonium ions led to an increase in oxygen permeation owing to the incompatibility of polar polymer with the 2C18 chains, whereas this behavior was absent when 2C18 was replaced by polar surface modifications.^{6,41} Thus, permeation apart from morphology is also dependant on the interaction of the functionalized polymer (i.e., compatibilizer) and the surface modification. The increase in the permeation through the composite containing PP-*b*-PPG as compatibilizer can, therefore, be explained as due to the incompatibility between the compatibilizer and surface modification. Too high polarity of PP-*b*-PPG can also be held responsible for its incompatibility with the polymer matrix. PP-g-

MA1 although least polar has maximum increase in the oxygen permeation. Owing to its very high molecular weight and the presence of very few MA molecules present per chain, the entanglement of these long chains can be visualized to increase the free volume at the interface with clay surface, leading to much higher increase in permeation. PP-g-MA2 on the other hand, owing to its low molecular weight can well mix with the polymer and can adsorb on the surface and enter the clay interlayers easily, thus improving their exfoliation. Thus, in this case, a balance of two factors i.e., increase in permeation because of increase in voids at the surface and decrease in permeant mobility and increase in tortuous path owing to exfoliation seem to occur. Very different results were observed in polyethylene composites using PE-g-MA as compatibilizer indicating the sensitivity of the permeation behaviors to the system changes.³³

It was established in the earlier study that the presence of the OMMT did not lead to any substantial changes in the crystallization behavior of polypropylene.³⁷ Thus the change in the properties was solely related to the effect of tortuosity generated by the platelet exfoliation and interfacial interactions. Although the amount of the nonionic surfactant was kept low in the present study in order not to affect the crystallinity of the polymer, however, calorimetric studies were necessary to monitor the effect of compatibilizer addition. As is evident from Table III, no changes in melting and crystallization behavior of polymer could be observed when the different surfactants were added. Percent crystallinity values calculated from the enthalpy of melting of the polymer in the composites and the enthalpy of melting of purely crystalline polypropylene sample were also observed to be unchanged. It confirms that the surfactants did not induce any changes in the calorimetric behavior of the polymer. To supplement the X-ray findings, the microstructure of the composites was also studied by transmission electron microscopy. Figure 4 shows the TEM micrographs of 2C18

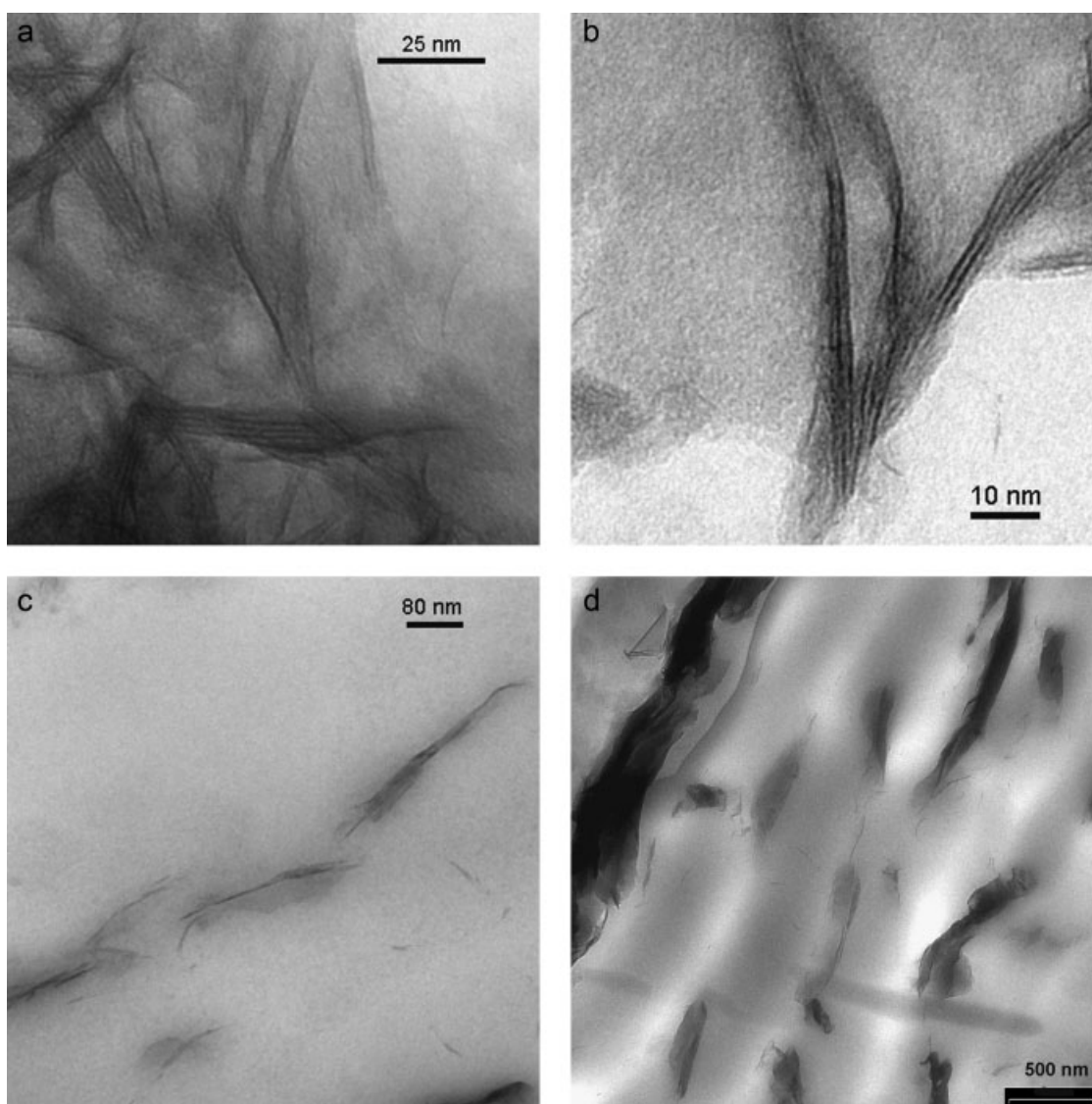


Figure 4 SEM micrographs of 3 vol % 2C18 OMMT-polypropylene nanocomposites containing 2 wt % of PP-g-MA2 compatibilizer.

OMMT-PP nanocomposites with 2 wt % of PP-g-MA2. A number of well exfoliated single layers are clearly visible indicating the higher extents of exfoli-

ation. But thin tactoids are also seen which further indicates the presence of mixed morphology containing thin tactoids and exfoliated layers. Another im-

TABLE IV
Tensile Properties of 3 vol % 2C18 OMMT-Polypropylene Nanocomposites using Different Compatibilizers

Compatibilizer (2 wt %)	Tensile modulus ^a (MPa)	Yield stress ^b (MPa)	Yield strain ^c (%)	Stress at break ^d (MPa)
pure PP	1510	36	9.4	29
No compatibilizer	2016	28	4.3	25
PP-g-MA1	2131	28	5.3	26
PP-g-MA2	2124	28	4.4	23
PP- <i>b</i> -PPG	2088	27	3.3	26

^a Relative probable error 5%.

^b Relative probable error 2%.

^c Relative probable error 5%.

^d Relative probable error 15%.

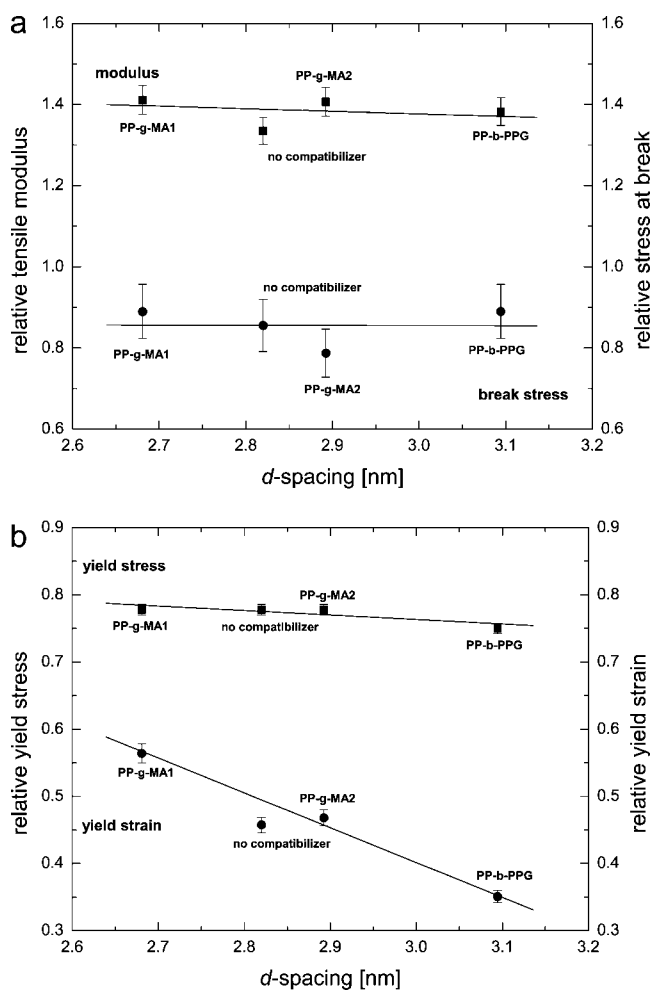


Figure 5 (a) Tensile and break stress and (b) yield stress and strain of 3 vol % OMMT-polypropylene nanocomposites with and without compatibilizer.

important observation was the misalignment, folding and bending of the clay platelets and tactoids. Lowering the magnification did seem to show a global orientation of the tactoids but at the higher magnifications, this orientation seem to be absent.

Table IV contains the tensile properties of the OMMT-polypropylene composites with and without the compatibilizers consisting of 3 vol % of inorganic filler fraction. The properties of these composites are compared with the pure polypropylene processed similarly as the composite materials. The composite without compatibilizer was observed to have an improvement in the modulus owing to the partial exfoliation of the OMMT. All other properties were observed to decrease indicating lack of attractive interactions at interface and the presence of brittleness. Tensile modulus was enhanced on the addition of compatibilizers indicating increased exfoliation of the OMMT resulting in better morphology and hence modulus. One thing to notice here is the deterioration of the permeation behavior happened par-

allel to improvement in mechanical performance. Mechanical properties owing to their macro nature seem to remain independent or less affected by micro voids generated owing to incompatibility of the surface modification and the compatibilizer and thus more and more load could still be transferred to the clay platelets. Figure 5(a) also shows the correlation between the relative modulus and the *d*-spacing of OMMT in these composites. The modulus was observed to be roughly unchanged with respect to *d*-spacing indicating only exfoliated layers are responsible for the improvement in modulus. Also the plasticization effects generally associated with the compatibilizers may also limit the further improvement of the modulus. Yield stress of the composites was observed to remain unchanged as compared with the composite without compatibilizer indicating the presence of little brittleness and nonoptimum interfacial interactions. Yield strain and the breaking stress of the compatibilized composites had occasional marginal increase as compared with the uncompatibilized composite indicating the weak plasticizing effect of the compatibilizers (Table III). Relative break stress was also observed to be independent of *d*-spacing, while the yield stress and strain were observed to decrease with increase in *d*-spacing [Fig. 5(a,b)]. The presence of tactoids which are not efficient enough for load transfer can be a reason for this decrease.

As PP-g-MA2 had superior improvement in the mechanical performance and the permeation through its composites was better than other surfactant containing composites, it was of interest to analyze these behaviors with respect to increasing concentration of PP-g-MA2. Figure 6 shows the WAXRD diffracto-

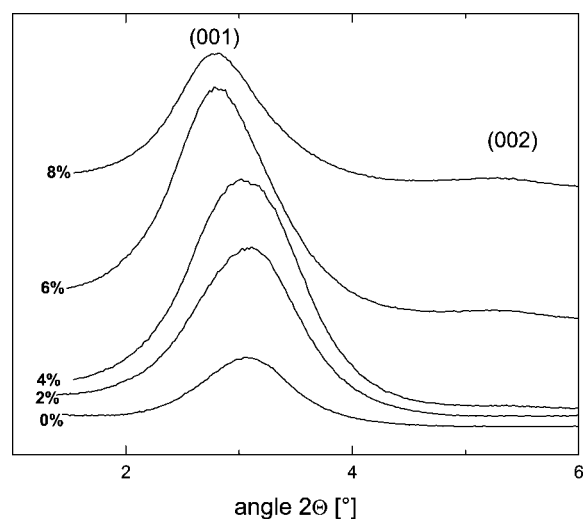


Figure 6 X-ray diffractograms of 3 vol % OMMT-polypropylene nanocomposites with varying amounts of PP-g-MA2 compatibilizer.

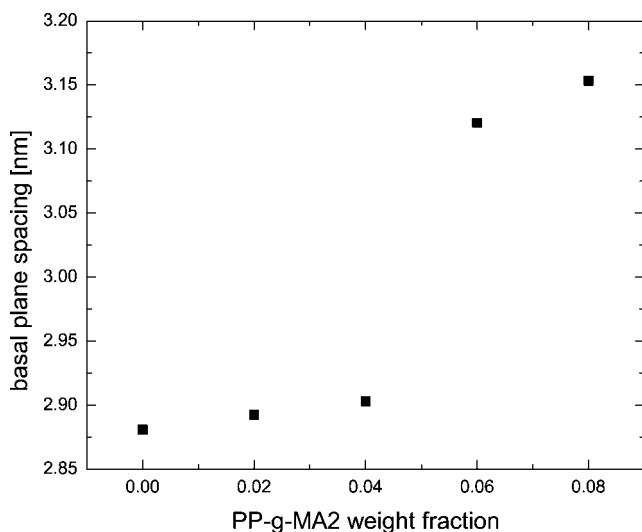


Figure 7 Enhancement of the basal plane spacing with increasing PP-g-MA2 weight fraction in the composites.

grams of the composites with 2, 4, 6, and 8 wt % of PP-g-MA2 compatibilizer. As can be seen, that the d -spacing was enhanced on increasing the content of compatibilizer and the peak width also seemed to increase indicating qualitatively more and more separation and loss of order among the tactoids. However, the presence of 001 peak even at 8 wt % PP-g-MA2 content also indicates that not all of the clay platelets have been exfoliated. The basal plane spacing values have been plotted against the PP-g-MA2 content in Figure 7. The d -spacing did not increase linearly with the compatibilizer content. It seems that there was present a threshold value of d -spacing, after which the weakly held platelets were intercalated significantly even on the addition of same amount of compatibilizer. The oxygen permeation coefficients of the composites with different concentrations of compatibilizers have been reported in Table V. The oxygen permeation coefficients of composite without compatibilizer, pure PP and a blend

TABLE V
Effect of PP-g-MA2 Weight Fraction on d -spacing and Oxygen Permeability of 3 vol % 2C18 OMMT-Polypropylene Nanocomposites

PP-g-MA2 (wt %)	d -spacing (nm)	Permeability coefficient ^a (cm ³ μm/m ² day mmHg)
Pure PP	–	89
2.0, no filler	–	83
0.0	2.82	59
2.0	2.89	63
4.0	2.90	62
6.0	3.12	62
8.0	3.15	61

^a In the range of 5% error.

of PP and PP-g-MA2 (2 wt %) have also been compared. The oxygen permeation through the blend of PP and PP-g-MA2 remained almost unchanged as the pure PP indicating that at this concentration of compatibilizer, it was compatible with PP and did not affect its crystallization characteristics. On the other hand, as already reported that the oxygen permeation decreased by roughly 35% when no compatibilizer was added indicating that the interactions between the OMMT and the compatibilizer are the responsible forces for the permeation deterioration observed on the addition of compatibilizer. This also supports the suspicion of generation of voids at the interface on the addition of compatibilizer. The permeation coefficient of the composites with different amounts of compatibilizer remained unchanged as the composite without compatibilizer (Fig. 8). It can only be possible if the compatibilizer did not intercalate inside the interlayer and remained outside in the matrix and thus did not affect the microstructure. But the increase in the basal plane spacing and the improvement in the mechanical performance earlier observed indicate that the microstructure was definitely altered from less exfoliated to more and more exfoliated state with increasing the amount of compatibilizer. This can only be justified by the earlier explained balance of improved permeation performance due to tortuosity generated and exfoliation of the platelets versus the deteriorated permeation behavior due to increase in the number of voids due to more and more exfoliation. Calorimetric studies were also performed on the composites containing different amounts of compatibilizer as shown in Table VI to see the effect of compatibilizer. The melting and the crystallinity behavior were observed to

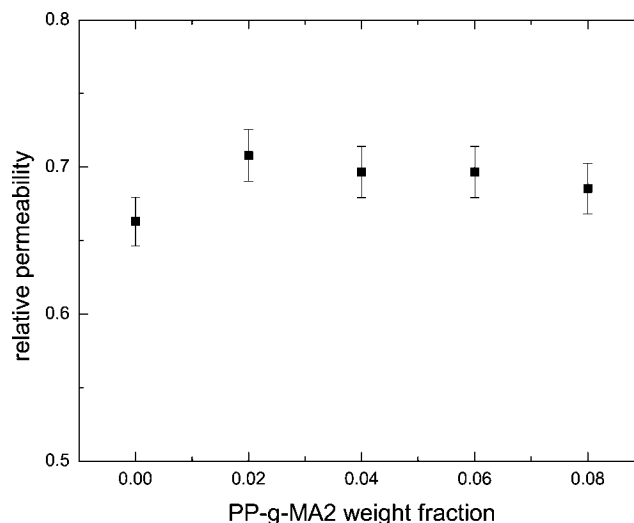


Figure 8 Relative oxygen permeability through the composite films containing 3 vol % of 2C18 OMMT and varying weight fractions of PP-g-MA2.

TABLE VI
Effect of PP-g-MA2 Weight Fraction on the Calorimetric Behavior of 3 vol % 2C18 OMMT-Polypropylene Nanocomposites

PP-g-MA2 (wt %)	$T_{m,onset}^a$ (°C)	T_m^b (°C)	ΔH_m polymer (J/g)	Crystallinity ^c (X_c)	$T_{c,onset}^d$ (°C)	T_c^e (°C)
Pure PP	152	162	96	0.58	114	112
2.0, no filler	152	165	94	0.57	112	106
0.0	152	163	94	0.57	115	112
2.0	152	163	94	0.57	115	110
4.0	152	163	93	0.56	115	110
6.0	152	163	93	0.56	115	110
8.0	152	160	93	0.56	114	109

^a Onset melting temperature.

^b Melt peak temperature.

^c Degree of crystallinity calculated using ΔH of 100% crystalline PP = 165 J/g (Refs. 42, 43).

^d Onset crystallization temperature.

^e Peak crystallization temperature.

be unchanged and the degree of crystallinity was also found to be slightly decreasing with increasing the amount of the compatibilizer. This indicates that the thermal behavior of the polymer remained overall unchanged even at 8% addition of PP-g-MA2.

The tensile properties of the composites with varying amounts of compatibilizer were measured and are shown in Table VII along with pure PP, blend of PP and PP-g-MA2 and OMMT-PP composite without compatibilizer. The modulus of the PP and PP-g-MA2 blend was marginally decreased as compared with that of pure PP indicating the plasticization effect of the compatibilizer. As a result, the yield strain was also observed to increase. It should also be noted that no such effect was observed when same amount of compatibilizer was added in the presence of the OMMT. The relative values have also been plotted with respect to the compatibilizer weight fraction in Figure 9. The tensile modulus initially increased but then decreased with augmenting the amount of compatibilizer. As reported earlier,³³ the improvement in the mechanical properties are jointly affected by the plasticization and exfoliation. At low weight fraction of the compatibilizer, the

exfoliation effect is more significant, but become less pronounced when the amount of compatibilizer is increased. Thus the presence of low molecular weight chains in large amount hinder the process of stress transfer thus reducing the modulus. Stress at break was observed to increase whereas yield stress remained unchanged for the composites with increasing the amount of compatibilizer due to similar plasticization effect. The yield strain decrease slightly indicating further brittleness. It is also important to note that the break stress and the yield stress are generally observed to decrease on increasing the filler volume fraction in the absence of compatibilizer. This clearly indicates that the presence of tactoids in the system can lead to early failure, whereas the system situation improves as the amount of this tactoids is reduced.

Thermogravimetric studies were also carried out on the composites to analyze the effect of the increasing amount of compatibilizer on the thermal stability of the composites. Figure 10 shows the TGA thermograms of the composites (represented as b containing 0, 2, 4, 6, 8 wt % compatibilizer). Also shown are the TGA curves for pure polypropylene

TABLE VII
Effect of PP-g-MA2 Weight Fraction on the Tensile Properties of 3 vol % 2C18 OMMT-Polypropylene Nanocomposites

PP-g-MA2 (wt %)	Tensile modulus ^a (MPa)	Yield stress ^b (MPa)	Yield strain ^c (%)	Stress at break ^d (MPa)
Pure PP	1510	36	9.4	29
2.0, no filler	1463	33	10.5	36
0.0	2016	28	4.3	25
2.0	2124	28	4.4	23
4.0	2075	28	3.9	27
6.0	1984	27	3.3	27
8.0	1913	28	3.3	27

^a Relative probable error 5%.

^b Relative probable error 2%.

^c Relative probable error 5%.

^d Relative probable error 15%.

and the blend of PP and PP-g-MA2 (2 wt %) represented as a in the figure. It is clear from the thermograms that the presence of compatibilizer in the composites did not lead to any unwanted premature thermal degradation of the composites irrespective of the low molecular weight of the compatibilizers. Thus, the presence of OMMT is much more significant in improving the thermal behavior and is not affected by the presence of low molecular weight compatibilizer.

CONCLUSIONS

Addition of compatibilizers help to exfoliate the clay platelets by bringing down the interfacial surface energy. The more the polar compatibilizer is, the more improvement in the basal plane spacing can be observed. The exfoliation achieved help to improve the mechanical performance of the composites. However, the gas barrier properties are not similarly enhanced owing to suspected negative effect from the incompatibility of the surface modification with

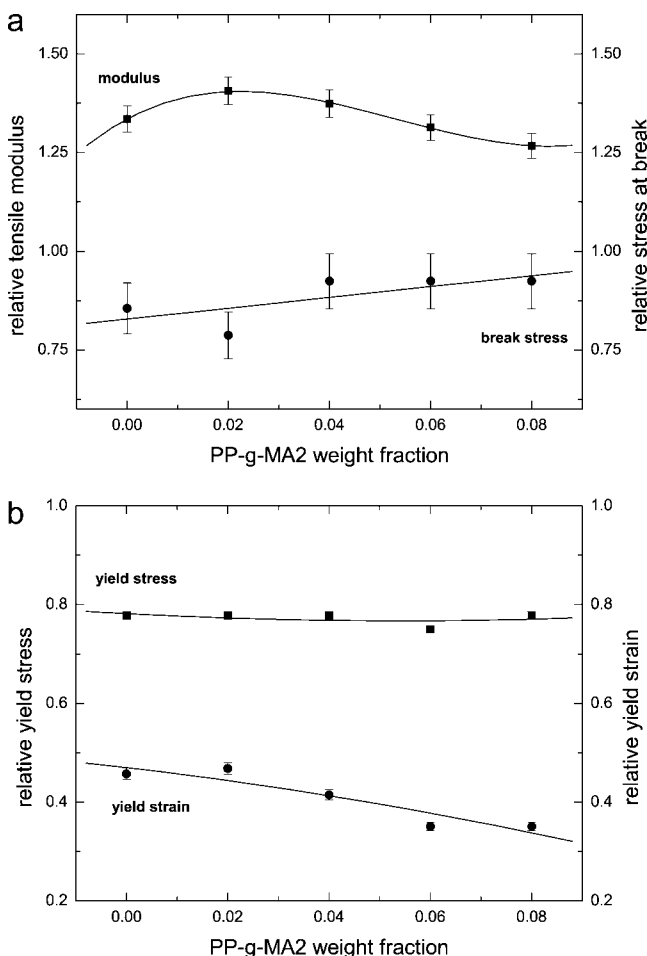


Figure 9 (a) Tensile and break stress and (b) Yield stress and strain of 3 vol % 2C18 OMMT-polypropylene composites as a function of PP-g-MA2 weight fraction.

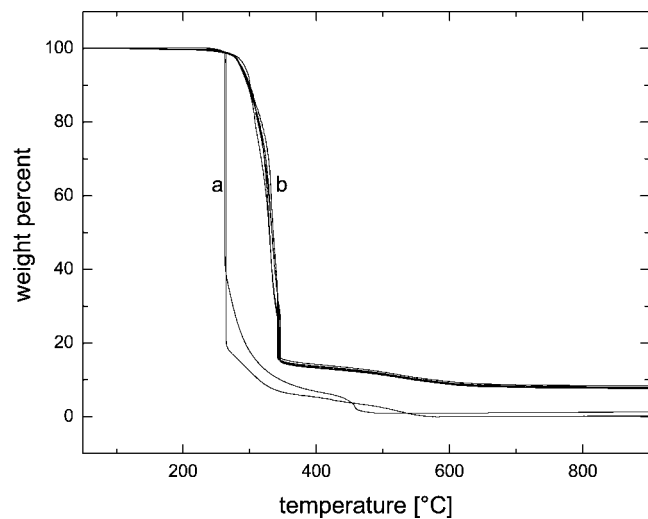


Figure 10 TGA thermograms of (a) pure PP and PP-g-MA2 and (b) 3 vol % OMMT-polypropylene with varying amounts of PP-g-MA2 compatibilizer.

the compatibilizers used leading to micro voids at the interface. The montmorillonite platelets are completely misaligned, bent and folded indicating a possible loss in the improvement in the properties due to misalignment. Increasing the amount of PP-g-MA2 further enhances the exfoliation, but the tensile modulus shows a decrease after reaching a maximum value owing to the low molecular weight of the compatibilizer. The permeation through the composite films is not affected with the concentration of the compatibilizer. The break stress increases while the yield stress is observed to be constant with respect to the compatibilizer concentration indicating the plasticization effect of the compatibilizer. The yield strain decreases with compatibilizer content indicating the brittleness of the system. The addition of even 8 wt % of the compatibilizer does not bring about any change in the crystallization behavior of polypropylene. Thermal behavior of the composites also remains unaffected.

The author thanks Prof. M. Morbidelli and Prof. U.W. Suter for allowing the use of their research facilities. Expert help of Dr. N. Matsko for TEM investigations is highly appreciated.

References

1. Giannelis, E. P. *Adv Mater* 1996, 8, 29.
2. Theng, B. K. G. *The Chemistry of Clay-Organic Reactions*; Adam Hilger: London, 1974.
3. Lagaly, G.; Beneke, K. *Colloid Polym Sci* 1991, 269, 1198.
4. Alexandre, M.; Dubois, P. *Mater Sci Eng* 2000, 28, 1.
5. LeBaron, P. C.; Wang, Z.; Pinnavaia, T. J. *Appl Clay Sci* 1999, 15, 11.
6. Osman, M. A.; Mittal, V.; Morbidelli, M.; Suter, U. W. *Macromolecules* 2003, 36, 9851.

7. Kornmann, X.; Thomann, R.; Mülhaupt, R.; Finter, J.; Berglund, L. A. *Polym Eng Sci* 2002, 42, 1815.
8. Fornes, T. D.; Yoon, P. J.; Keskkula, H.; Paul, D. R. *Polymer* 2001, 42, 9929.
9. Hu, X.; Lesser, A. J. *J Polym Sci Part B: Polym Phys* 2003, 41, 2275.
10. Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. P. *Macromolecules* 1995, 28, 8080.
11. Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. *Macromolecules* 1997, 30, 6333.
12. Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, A.; Okada, A. *J Appl Polym Sci* 1998, 67, 87.
13. Reichert, P.; Nitz, H.; Klinke, S.; Brandsch, R.; Thomann, R.; Mülhaupt, R. *Macromol Mater Eng* 2000, 275, 8.
14. Zhang, Q.; Fu, Q.; Jiang, L.; Lei, Y. *Polym Int* 2000, 49, 1561.
15. Svoboda, P.; Zeng, C.; Wang, H.; Lee, L. J.; Tomasko, D. L. *J Appl Polym Sci* 2002, 85, 1562.
16. Lopez, D. C.; Picazo, O.; Merino, J. C.; Pastor, J. M. *Eur Polym J* 2003, 39, 945.
17. Wang, Y.; Chen, F. B.; Li, Y. C.; Wu, K. C. *Compos Part B: Eng* 2004, 35, 111.
18. Chiu, F. C.; Lai, S. M.; Chen, J. W.; Chu, P. S. *J Polym Sci Part B: Polym Phys* 2004, 42, 4139.
19. Lertwimolnun, W.; Vergnes, B. *Polymer* 2005, 46, 3462.
20. Xu, W.; Liang, G.; Wang, W.; Tang, S.; He, P.; Pan, W. P. *J Appl Polym Sci* 2003, 88, 3225.
21. Narh, K. A.; Bhaskar, A.; Tortorela, N.; Beatty, C. L. *ANTEC* 61, 2003, 3717.
22. Wang, Z. M.; Nakajima, H.; Manias, E.; Chung, T. C. *Macromolecules* 2003, 36, 8919.
23. Hasegawa, N.; Okamoto, H.; Kawasumi, M.; Kato, M.; Tsukigase, A.; Usuki, A. *Macromol Mater Eng* 2000, 280/281, 76.
24. Kato, M.; Usuki, A.; Okada, A. *J Appl Polym Sci* 1997, 66, 1781.
25. Vaia, R. A.; Giannelis, E. P. *Macromolecules* 1997, 30, 7990.
26. Balazs, A. C.; Singh, C.; Zhulina, E.; Lyatskaya, Y. *Acc Chem Res* 1999, 32, 651.
27. Ginzburg, V. V.; Singh, C.; Balazs, A. C. *Macromolecules* 2000, 33, 1089.
28. Ho, D. L.; Glinka, C. J. *Chem Mater* 2003, 15, 1309.
29. Balazs, A. C.; Singh, C.; Zhulina, E. *Macromolecules* 1998, 31, 8370.
30. Su, S.; Jiang, D. D.; Wilkie, C. A. *Polym Degrad Stab* 2004, 83, 321.
31. Sun, T.; Garces, J. M. *Adv Mater* 2002, 14, 28.
32. Ma, J.; Qi, Z.; Hu, Y. *J Appl Polym Sci* 2001, 82, 3611.
33. Osman, M. A.; Rupp, J. E. P.; Suter, U. W. *Polymer* 2005, 46, 8202.
34. Lin, J. J.; Hsu, Y. C.; Chou, C. C. *Langmuir* 2003, 19, 5184.
35. Chou, C. C.; Lin, J. J. *Macromolecules* 2005, 38, 230.
36. Osman, M. A.; Suter, U. W. *J Colloid Interface Sci* 2000, 224, 112.
37. Osman, M. A.; Mittal, V.; Suter, U. W. *Macromol Chem Phys* 2007, 208, 68.
38. Osman, M. A.; Plötze, M.; Skrabal, P. *J Phys Chem B* 2004, 108, 2580.
39. Morgan, A. B.; Harris, J. D. *Polymer* 2003, 44, 2313.
40. Mathot, V. B. F. *Calorimetry and Thermal Analysis*; Hanser: Munich, 1993.
41. Osman, M. A.; Mittal, V.; Morbidelli, M.; Suter, U. W. *Macromolecules* 2004, 37, 7250.
42. Fatou, J. G. E. *Polym J* 1971, 7, 1057.
43. Wunderlich, B. *Macromolecular Physics*, Vol. 3; Academic Press: New York, 1980.