# Polypropylene-Organoclay Nanocomposite: Preparation, Microstructure, and Mechanical Properties

**H. Shariatpanahi,[1] F. Sarabi,[2] M. Mirali,[2] M. Hemmati,[2] F. Mahdavi[1]**

[1]*Coating Research Center, Research Institute of Petroleum Industry (RIPI), Tehran, Iran*
[2]*Department of Polymer Science and Technology, Research Institute of Petroleum Industry (RIPI), Tehran, Iran*

**ABSTRACT:** A series of polypropylene (PP) nanocomposites containing 2, 4, and 6 wt % of an organophilic montmorillonite clay was prepared via direct melt mixing in the presence of maleic anhydride grafted polypropylene (PP-*g*-MAH) as compatibilizing agent. Microstructure characterization was performed by X-ray diffraction analysis. Nanocomposites exhibited a 15 and 22% enhancement in tensile modulus and impact strength, respectively. The heat deflection temperature of PP nanocomposites was 36°C greater than for pure PP. Thermal and mechanical properties of nanocomposites were compared to properties of traditional PP-talc and PP-glass fiber composites. The results showed that the properties of nanocomposites improved compared to ordinary polypropylene composites. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 922–926, 2009

**Key words:** polypropylene (PP); nanocomposites; organoclay; compatibilization; mechanical properties

## INTRODUCTION

Polypropylene (PP)-clay nanocomposites are organic/inorganic hybrid materials that exhibit significantly improved mechanical and flammability properties. The outstanding properties of polymer clay nanocomposites come from the structural nature of clay, including large surface area, high aspect ratio, and good interfacial interaction with the polymer matrix, which can be observed especially in exfoliated nanocomposites.[1]

Compatibility and optimum interaction between polymer matrix, organic surfactant, and silicate layer are crucial to fabricate exfoliated nanocomposites. However, there are many cases where polymer and organic clay are not compatible enough to form nanocomposites.[2] PP-based nanocomposites are one of these mentioned cases. PP does not include any polar groups in its backbone and is not even compatible with organic montmorillonite modified by nonpolar long alkyl surfactant. To make the nanoscale dispersion of clay in PP matrix, a third component can be employed as compatibilizer to assist intercalation of polymer chains.[3]

Some researchers succeeded in preparing polypropylene/montmorillonite (PP-MMT) nanocomposites in the presence of maleic anhydride modified PP compatibilizer. In this research, some mechanical properties of PP/clay nanocomposites were investigated.[4–11] In our work we prepared PP/MMT nanocomposites in different amounts of MMT and PP, by using maleic anhydride grafted homopolymer polypropylene as compatibilizer. The effect of nanoclay and maleic anhydride concentration on the state of intercalation of nanoclay was investigated. Impact and tensile strength, tensile elongation, and heat deflection temperature (HDT) properties as a function of clay and maleic anhydride (MAH) concentration were studied. The objective of this work is to show the advantages of using nanoclays as a suitable alternative for conventional fillers, which are used for enhancing mechanical and thermal properties of polymers. We present for the first time a complete comparison between mechanical and thermal properties of nanocomposites and conventional composites. The mechanical properties of nanocomposites were compared to the properties of neat PP, PP/talc, and PP/glass fiber composites.

## MATERIALS AND METHODS

### Materials

The materials used for the preparation of PP nanocomposite are the commercialized PP with the trade name of Moplen HP 500 J from Iran Petrochemical, Arak Products (melt flow index (MFI) = 2.5 g/10 min, melting point = 161°C), maleic anhydride grafted PP (PP-*g*-MAH) with the trade name of Fusabond® P-MZ109D (MFI = 120 g/10 min,

melting point = 162°C, and graft efficiency = 0.1–3%) from DuPont Products (USA), and organophil montmorillonite with the trade name of Cloisite® 20A from Southern Clay Product (Gonzales, TX), which is a natural montmorillonite modified with a quaternary ammonium salt, dimethyl, dehydrogenated tallow ammonium chloride. The d-spacing of Cloisite 20A® is 24.2 Å.

The materials used for the preparation of traditional PP-talc and PP-glass fiber composites are as follows: with the trade name of Z-Talc 1090 from Sigma International (particles < 3 μm ≈ 40%, density = 2.8 g/cm³) and glass fiber with the trade name of E-glass fiber from Owens–Corning (USA) (chopped length = 4 mm, diameter = 10 μm, and density = 2.44 g/cm³).

## Preparation of PP/clay nanocomposite

To obtain a good dispersion of nanoclay in PP matrix, PP-g-MAH, clay, and PP were first melt mixed to make master batches in different ratios of PP-g-MAH to clay, using a Brabender internal mixer plasticorder PL 2000 at 180°C and 45 rpm for 15 min. The compositions and abbreviations of the master batch samples are listed in Table I.

To prepare nanocomposites, each sample of these master batches was mixed with different amounts of PP by using a Brabender internal mixer at 190°C and 60 rpm for 15 min. Compositions and abbreviations of prepared nanocomposite samples with different clay loading ratios (2, 4, and 6 wt %) are listed in Table II.

The resulting nanocomposites were compression molded at 190°C for 4 min into plates with a thickness of 3 mm.

## Preparation of PP-talc and PP-glass fiber composites

For preparation of PP-talc (20 wt %) and PP-glass fiber (10 wt %), the desired amount of talc and fiber glass were dry blended with PP. Compounding was carried out by using a Brabender internal mixer PL 2000 at 190°C and 60 rpm for 15 min. The resulting composites were compression molded at 190°C for 4 min into plates with a thickness of 3 mm.

**TABLE I**
**Compositions and Abbreviations of PP Master Batch Samples**

|  | PP-g-MAH (wt %) | PP (wt %) | Clay (wt %) |
|---|---|---|---|
| R1 | 25 | 50 | 25 |
| R2 | 33 | 50 | 17 |
| R3 | 37.5 | 50 | 12.5 |

**TABLE II**
**Compositions and Abbreviations of Nanocomposite Samples**

|  | Clay (wt %) | PP-g-MAH (wt %) | PP (wt %) |
|---|---|---|---|
| NC2R1 | 2 | 2 | 96 |
| NC4R1 | 4 | 4 | 92 |
| NC6R1 | 6 | 6 | 84 |
| NC2R2 | 2 | 4 | 94 |
| NC4R2 | 4 | 8 | 88 |
| NC6R2 | 6 | 12 | 82 |
| NC2R3 | 2 | 6 | 92 |
| NC4R3 | 4 | 12 | 88 |
| NC6R3 | 6 | 18 | 76 |

## Measurements

Microstructure characterization of nanocomposites was evaluated by an X-ray diffractometer using a Philips PW1840 (tube Cu Kα, λ = 1.54 Å) at room temperature. The X-ray diffraction patterns were scanned in the 2θ range from 0° to 10°. The interlayer distance of nanoclay in nanocomposites was calculated from the (001) peak by using Bragg's equation (λ = 2d sin θ). To examine heat resistance of nanocomposites, the HDT test (ASTM D 648) was performed by using an HDT tester, CEAST model 6510/517.

Mechanical tests were performed according to tensile (ASTM D 638) and impact (ASTM D 256) standards. An INSTRON (1123) tensile tester was used to measure the tensile properties, while an impact tester (Karl Frank GMBH, Type 565M) was used for measuring notched impact strength.

## RESULTS AND DISCUSSION

### X-ray diffraction analysis

The X-ray diffraction patterns of PP, organoclay (Cloisite 20A), and PP/PP-g-MAH/organoclay nanocomposites are shown in Figures 1–3.

Figure 1 shows an intense and sharp peak at 2θ = 3.7, which corresponds to an interlayer spacing of 23.3 Å for Cloisite 20A and at 2θ = 3.4° for NC6R1 sample (d = 26.8 Å). The increase of the basal spacing of clay platelets indicates that macromolecule chains had intercalated into the galleries. The presence of broad peak for NC4R1 and NC2R1 samples suggests a coexistence of an intercalated and exfoliated structure. Figure 2 shows that in the NCR2 systems, when the ratio of maleic anhydride to organoclay increased, a clear diffraction peak was not observed (basal spacing > 8.8 nm), so it seems good exfoliation had occurred.[12–14] This can be related to a strong attraction between polar PP-g-MAH molecules and the silicate layer. In NCR3 systems with the highest content of maleic anhydride (Fig. 3), the
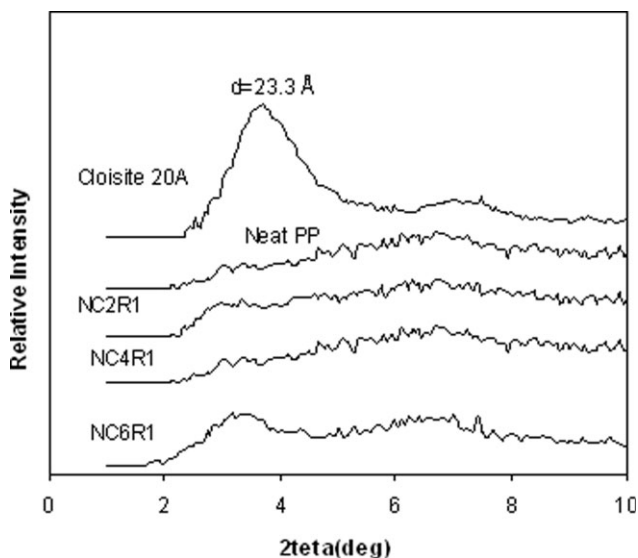
**Figure 1** X-ray patterns for clay, neat PP, and NCR1 nanocomposites.

overall degree of exfoliation decreased. Because of higher intensity, the NCR3 systems had less exfoliation compared to NCR2 systems. This indicates that the content of maleic anhydride in the NCR3 systems was undesirable. Although we can confirm the positive role of MAH, it is noteworthy that excess MAH will cause self-aggregation, which can deteriorate the dispersion of clay.[15] This can be related to high MFI of PP-g-MAH (maleic anhyride grafted polypropylene) (PP-MA), which can reduce the shear viscosity of the whole matrix that can decrease the stress transfer from matrix to organoclay. Therefore, making a suitable balance between the compatibilizer amount and the clay loading is required to achieve good exfoliation. In our work the best exfoli-
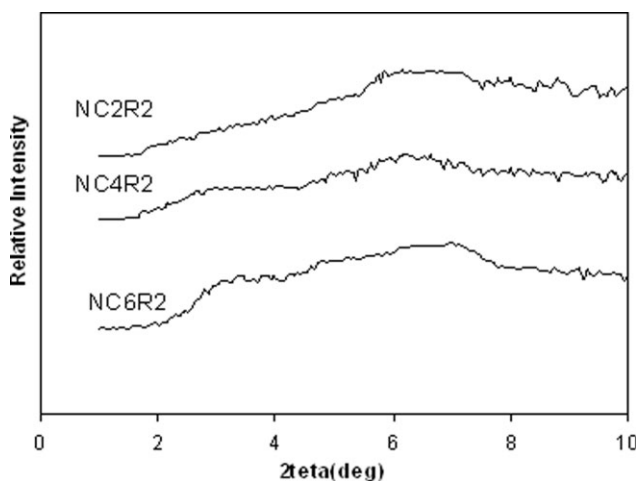


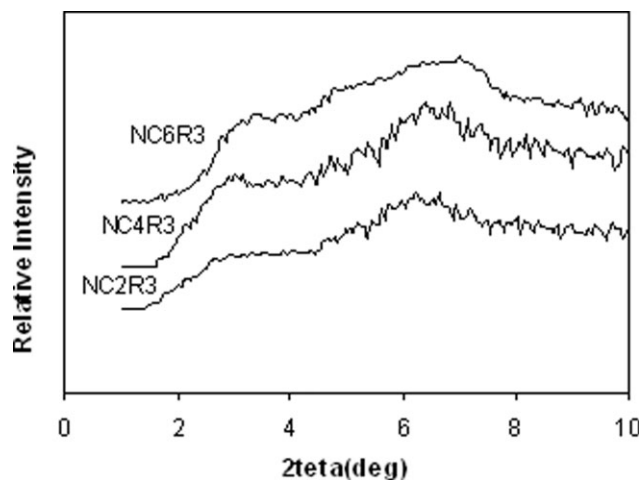**Figure 2** X-ray patterns for NCR2 nanocomposites.

**Figure 3** X-ray patterns for NCR3 nanocomposites.

ation of nanoclay in PP-clay nanocomposites was obtained for NCR2 systems in which the ratio of maleic anhydride to organoclay was 2. In NCR2 series good exfoliation was obtained for 2 and 4 wt % clay concentrations.

## Mechanical properties

In our work the mechanical properties of nanocomposites were determined as a function of clay content (2, 4, 6 wt %) and ratio of maleic anhydride to organoclay (1, 2, 3). Mechanical properties were compared to the same properties of neat PP, PP-talc (20 wt %), and PP-glass fiber (10 wt %) composites.

Tensile strength for all nanocomposite systems (NCR1, NCR2, and NCR3) is plotted against filler content in Figure 4.

As shown in Figure 4, for R1 and R2 there is a sharp improvement in tensile strength up to 4 wt % clay. Further addition of clay leads to a decrease of the tensile strength in these two systems. Because the mechanical properties are determined to closely depend on the interfacial interaction between clay
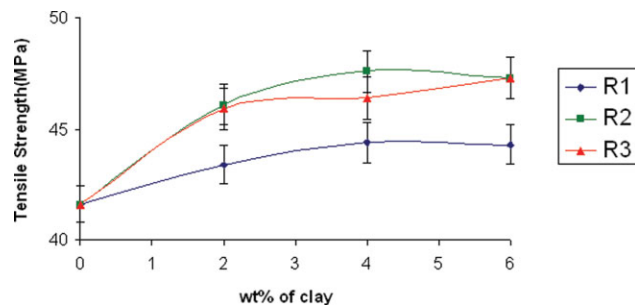


**Figure 4** Tensile strength of nanocomposites versus clay content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
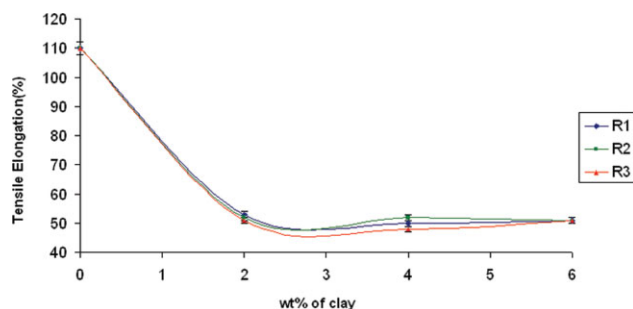
**Figure 5** Variation of tensile elongation of nanocomposites against clay concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and polymer, the best tensile strength as expected was found in nanocomposites of R2 systems, which had the best exfoliation of clay in PP. Decreasing tensile strength in R3 systems relative to R2 nanocomposites may be attributed to less exfoliation of organoclay, which can lower the extent of the organoclay reinforcement effect. As shown in Figure 2 the best tensile strength was obtained in the NC4R2 nanocomposite.

The tensile elongation of nanocomposites compared to neat PP decreased with clay loading. Figure 5 shows the tensile elongation of nanocomposites versus clay concentration.

There is a sharp decrease in tensile elongation up to 2 wt % clay, which is in accordance with the result of other inorganic fillers. Further addition of clay lowers the tensile elongation only slightly. Although elongation values for all samples are nearly the same, the best tensile elongation is found in the NC4R2 nanocomposite. The decrease in tensile elongation of nanocomposites compared to PP-talc (20 wt %) and PP-glass fiber (10 wt %) is lower (Table III). This phenomenon can be related to the small loading (4 wt %) and also to the high aspect ratio of

organoclay relative to glass fiber (10 wt %) and talc (20 wt %) and thus good interfacial interaction of nanoclay and polymer, which does not exist in PP-talc and PP-glass fiber composites.

The variation of impact strength of nanocomposites with clay concentration is shown in Figure 6. The nanocomposites of the R2 systems showed the best impact strength among other systems. Figure 6 shows that in R2 systems, when clay concentration increases, the impact strength increases. The enhancement of impact strength was due to the fact that exfoliated or intercalated clay layers in compatibilized nanocomposites play a role in hindering the crack patch caused by impact. In R1 and R3 systems with increasing clay concentration the impact strength decreases. The best impact strength was obtained in the NC6R2 nanocomposite. High MAH content generally enhances the melt intercalation of PP oligomers into clay layers; however, in our work and some research,[16,17] it led to immiscibility with the PP matrix and harmed the impact and tensile strength of the nanocomposites.

The nano-dispersion of MMT in the PP-matrix also promotes a higher HDT of PP. Figure 7 shows the variation of HDT property of nanocomposites against clay concentration.

There is a sharp increase in HDT by adding only 2 wt % of organoclay to neat PP. This property increases slightly with an increasing amount of clay. The HDT of nanocomposites with 4–6 wt % organoclay has been improved about 80% relative to neat PP. The increase in HDT was attributed to better mechanical stability of nanocomposite and not to an increase in melting temperature, which remained invariant in the nanocomposite relative to the neat PP (Table III).[1]

In all systems the best mechanical properties of nanocomposites were found in 4 and 6 wt % clay concentrations. However, the values for 6 wt % are

**TABLE III**
**Comparison of Properties of Neat PP, Talc-PP, Fiberglass-PP, and PP-Clay Nanocomposites**

| Property | PP | PP-talc (20 wt %) | PP-glass fiber (10 wt %) | PP-clay (4 wt %) |
|---|---|---|---|---|
| Density (g/cm$^3$)[a] | 0.91 | 1.05 | 1.1 | 0.92 |
| Tensile strength (MPa)[b] | 41.6 | 42.3 | 46.8 | 47.6 |
| Tensile elongation (%)[b] | 110 | 5 | 2.7 | 51 |
| Impact strength (kJ/m)[c] | 3.54 | 2.45 | 1.07 | 4.3 |
| MFI (g/10 min)[d] | 2.5 | 1.2 | 0.9 | 2.4 |
| Processing temp. (°C) | 220 | 245 | 270 | 220 |
| Melting temp. (°C)[e] | 160 | 166.5 | 164.3 | 160.3 |

[a] ASTM D 792.
[b] ASTM D 632.
[c] ASTM D 256.
[d] ASTM D 1238 at 2.160 and 230°C.
[e] Resulted from DSC analysis.

nearly the same as for 4 wt % so using the 4 wt % clay is more economical.

Table III shows a comparison of some mechanical properties of nanocomposites with properties of neat PP, traditional PP-talc (20 wt %), and PP-glass fiber (10 wt %) composites.

As shown in Table III density of PP-clay (4 wt %) are nearly the same as neat PP but density of PP-talc (20 wt %) and PP-glass fiber (10 wt %) are 16 to 20% higher than neat PP. PP-talc and PP-glass fiber composites also show higher MFI and higher processing temperature compared to neat PP, while MFI and processing temperature of PP-nanoclay (4 wt %) are near to the PP matrix. Results show that there is a significant improvement in tensile properties of PP-nanocomposites compared to neat PP, which is higher than PP-talc and PP-glass fiber composite with higher loading of filler.

Table III shows that the impact strength of nano-composites has been improved relative to PP, while the PP composites show a decrease in this property. This result can be related to the high modulus and anisotropic shape of nanoclay inclusions and the large interfacial region at the clay surface.[18]

## CONCLUSION

PP-clay nanocomposites containing 2, 4, 6 wt % of organoclay and different ratios of PP-MAH to orga-noclay (1, 2, 3), as a compatibilizer, were prepared by melt compounding. X-ray diffraction results show nearly exfoliated structure for these nanocomposites. The highest extent of exfoliation was observed for 4–6 wt % of organoclay and for PP-MAH to an organo-clay ratio of 2. The best mechanical properties of nanocomposites are also observed in this region.

The nanocomposite containing 4 wt % organophil clay showed 15% enhancement in tensile strength and 22% enhancement in impact strength relative to pure PP. The HDT of the PP nanocomposite was 36°C greater than for pure PP. Comparison among PP-clay nanocomposites (4 wt %), PP-talc (20 wt %),
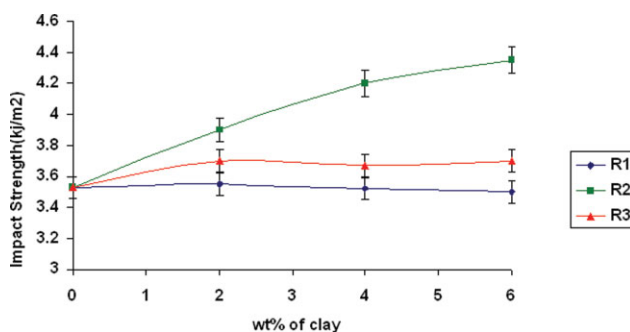


Figure 6 Impact strength of nanocomposites versus clay content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
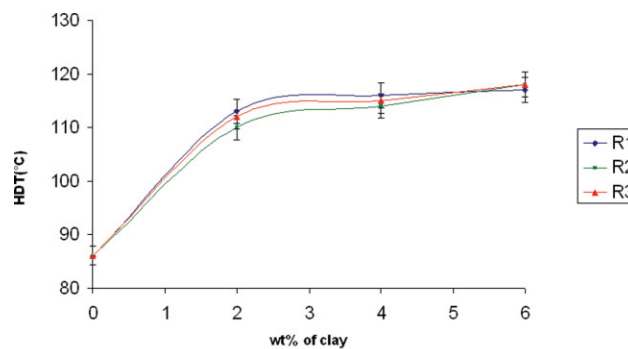
Fig.7 HDT of nanocomposites versus clay content

**Figure 7** The variation of HDT of nanocomposites against clay concentration. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

and PP-glass fiber (10 wt %) composites showed that only the addition of 4 wt % clay improved mechanical properties dramatically with nearly the same density, processing temperature, and MFI as for the neat PP, which make the nanocomposites suitable for applications that need lighter material with improved mechanical strength.

## References

1. Mirabella, F. M. Dekker Encyclopedia of Nanoscience and Nanotechnology; Marcel Dekker: New York, 2004; Vol. 4, p 3015.
2. Maier, C.; Calafut, T. Polypropylene: The Definitive User's Guide and Databook; Plastics Design Library: USA, 1998.
3. Maier, W.; Maier, G.; Zhai, H.; Tan, S.; Maier, G.; Pan, W. P. Eur Polym J 2003, 39, 1467.
4. Sovoboda, P.; Zeng, C.; Wang, H.; Lee, L. J.; Tomasko, D. L. J Appl Polym Sci 2002, 85, 1562.
5. Chen, L.; Wong, S. C.; Pisharath, S. J Appl Polym Sci 2003, 88, 3298.
6. Arunvisut, S.; Phummanee, S.; Somwangthanarjo, A. J Appl Polym Sci 2007, 106, 2210.
7. Pozsgay, A.; Frater, T.; Szazdi, L.; Muller, P.; Sajo, I.; Pukanszky, B. Eur Polym J 2004, 40, 27.
8. Maier, N.; Maier, H.; Maier, M.; Usuki, A. J Appl Polym Sci 2000, 78, 1918.
9. Reichert, P.; Nitz, H.; Klinke, S.; Maier, R.; Mulhaupt, R. Mac-romol Mater Eng 2000, 8, 275.
10. Yuan, Q.; Misra, R. D. K. Polymer 2006, 47, 4421.
11. Bureau, M. N.; Ton-That, M. T.; Perrin-Sarazin, F. Eng Fract Mech 2006, 73, 2360.
12. Kornmann, X.; Lindberg, H.; Berglund, L. A. Polymer 2001, 42, 1303.
13. Ratna, D.; Becker, O.; Krishnamurthy, R.; Simon, G. P.; Varley, R. J. Polymer 2003, 44, 7449.
14. Yasmin, A.; Abot, L. J.; Daniel, M. I. Scr Mater 2003, 49, 81.
15. Kim, K. N.; Maier, H.; Lee, J. W. Polym Eng Sci 2001, 41, 1963.
16. Kawasumi, M.; Hasagawa, N.; Kato, M.; Usuki, A.; Okada, A. Macromolecules 1997, 30, 6333.
17. Xu, W.; Maier, G.; Maier, W.; Tang, S.; Maier, P.; Pan, P. J Appl Polym Sci 2003, 88, 3225.
18. Solomon, M. J.; Somwangthanaroj, A. Dekker Encyclopedia of Nanoscience and Nanotechnology; Marcel Dekker: New York, 2004; Vol. 2, p 1483.