Polymer Bulletin 57, 385–393 (2006)
DOI 10.1007/s00289-006-0555-x

Polymer Bulletin

Preparation and mechanical properties of PP/PP-g-MA/Org-MMT nanocomposites with different MA content

M. L. López-Quintanilla (✉), S. Sánchez-Valdés (✉), L. F. Ramos de Valle and R. Guedea Miranda

Centro de Investigación en Química Aplicada (CIQA), P.O. Box 379, Saltillo, Coahuila, 25100, México
e-mail: mllq@ciqa.mx, saul@ciqa.mx; fax: 52 (844) 4389839

Received: 26 January 2006 / Revised version: 7 March 2006 / Accepted: 20 March 2006

Summary

Polypropylene-clay nanocomposites were prepared by melt intercalation in a twin screw extruder using two mixing methods: two-step mixing and one-step mixing. The effect of using two different kinds of PP-g-MA (polypropylene-grafted maleic anhydride), with graft efficiencies of 0.1 and 1.0 wt% of MA and with different molecular weight, on clay dispersion and mechanical properties of nanocomposites was investigated. Three different clays, natural montmorillonite (Cloisite Na+) and chemically modified clays Cloisite 20A and Cloisite 30B were used. The relative influence of each factor was observed from structural analysis by WAXD, TEM, and mechanical properties. X ray diffractometry (XRD) was used to investigate the intercalation effect in the nanocomposites. The results indicted that the intercalation effect and mechanical properties, specially modulus, tensile strength and impact strength, were enhanced by increasing the content of MA, using maleated PP with higher graft efficiency, and using the two step mixing conditions. Better dispersion and exfoliation were obtained when using clay 20A than 30B and natural Na+ montmorillonite. The results showed that clay dispersion and interfacial adhesion are greatly affected by the kind of maleated PP. The increase in content of polar groups gives as a result better interfacial adhesion and subsequent mechanical performance.

Introduction

The hybrid organic-inorganic nanoscale composites have received special attention, both in industry and in academia, because of their improved properties at very low loading levels compared with conventional filler composites. They often exhibit improved properties such as mechanical, dimensional, barrier to different gases, thermal stability and flame retardant enhancements with respect to the bulk polymer [1-4]. One of the most promising composites is the hybrid based on organic polymers and inorganic clays consisting of layered silicates. The hydrophilic clay needs to be modified prior to its introduction in most organophilic polymer matrices, in order to achieve good interfacial adhesion and therefore a better mechanical performance. Polypropylene (PP) exhibits an attractive combination of low cost, low weight and density, a heat distortion temperature above 100°C, and extraordinary versatility in terms of properties, applications, and recycling [5]. In order to improve the mechanical performance of PP for engineering plastics application, it is an important objective to increase its dimensional stability, heat distortion temperature, stiffness, strength and impact resistance without sacrificing its easy processabilty. Due to the low polarity of this resin, it is difficult to get the exfoliated and homogenous dispersion of the clay layer at the nanometer level in the polymer matrix. This is mainly due to the fact that the silicate clays layers have polar hydroxyl groups and are compatible only with polymer containing polar functional groups. Consequently the matrix modification with polar moieties is necessary prior to modified clay introduction in order to achieve nanometric dispersion of the clay [6].

It is widely reported [7-14] that it is possible to prepare PP-clay hybrids by simple melt mixing of three components: PP, maleic anhydride-grafted-polypropylene oligomers (PP-g-MAH) and clay. Polymer-clay nanocomposites are usually divided into three general types: conventional composites, in which the clay acts as a normal filler; intercalated nanocomposites, in which a small amount of polymer moves into the gallery spacing between the clay pallets; and exfoliated nanocomposites, in which the clay pallets are fully dispersed in a continuous polymer matrix [15-17]. When preparing nanocomposites by melt compounding, the exfoliation and dispersion of nanoclays in polypropylene depend on the organic modifier of the nanoclay, the initial interlayer spacing, the concentration of functional groups in the compatibilizer and its overall concentration in the composite, the viscosity of the plastic resin, and the operational conditions, such as screw configurations of extruders, rpm, temperature, residence time, etc. The effects of extrusion compounding conditions upon the properties of nanocomposites have been studied and had concluded that sufficient long residence time is necessary to intercalate or exfoliate the nanoclays in the polymer matrix [18-21]. Even though shear is an important factor to achieve a good clay dispersion in the polymer, shear alone is not enough to provide nanometric dispersion of the clay. Interfacial adhesion needs to be higher in order to improve clay dispersion and therefore a better performance of the nanocomposite.

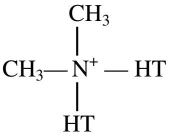
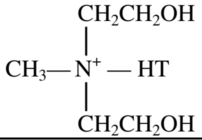
In this article, PP-clay nanocomposites were prepared by melt mixing with three different commercial montmorillonite clays, in a twin-screw extruder using two mixing methods: one-step mixing and two-step mixing. Two different PP-g-MAH compatibilizing agents, with different molecular weights and different contents of MAH were used. The effect of these factors was observed from structural analysis by WAXD, TEM, and mechanical properties.

Experimental

Materials

Commercial homopolymer, PP HP423, used for this study was produced from Indelpro with an MFR of 3.2 g/10min. Two commercial maleated polypropylenes (PP-g-MA), with graft efficiencies of 0.1 wt%, named PPgMAL (Polybond 3001) and 1.0 wt%, named PPgMAH (Polybond 3200) were obtained from Crompton. Three different commercial clays were used as received: an unexchanged natural montmorillonite, (Cloisite Na+), and two modified with a quaternary ammonium salt (Cloisite 20A and Cloisite 30B) from Southern Clay Products Co. The main characteristics of the materials used is listed in Table 1.

Table 1. Main characteristics of the materials used

Material	**PP**	**PP-g-MAH1** **(PPgMAL)**	**PP-g-MAH2** **(PPgMAH)**
Grade	Valtec HP423	Polybond 3001	Poybond 3200
Supplier	Indelpro	Crompton	Crompton
MFR (190°C/2.16 kg) (g/10min)	3.2*	5.1*	110.1*
Mw (g/mol)	307 137*	270 899*	95 804*
Density at 23°C (g/ml)	0.9	0.91	0.91
Melting Point (°C)	162*	164	157*
Grafting level (wt %)	N/A	0.12*	1.05*
Nanoclays			
Material	Nanoclay CNa+	Nanoclay C20A	Nanoclay C30B
Supplier	Southern Clay Products	Southern Clay Products	Southern Clay Products
Organic modifier	Unexchanged Natural MMT	Dimethyl, dehydrogenated tallow, quaternary ammonium chloride, where HT is hydrogenated tallow (65%C18, 30%C16, 5%C14); Anion: Chloride	Methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride, where HT is hydrogenated tallow (65%C18, 30%C16, 5%C14); Anion: Chloride
Structure of organic modifier	N/A	 $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle HT}{N^+}}-HT$	 $CH_3-\overset{\displaystyle CH_2CH_2OH}{\underset{\displaystyle CH_2CH_2OH}{N^+}}-HT$
X ray d_{001}(nm)	1.17	2.42	1.85

(*) Data obtained in the Lab

Preparation of polypropylene-clay nanocomposites

Nanocomposites were obtained by previous preparation of a master batch of maleated PP and clay (60/40) by mixing in a Werner and Pfleiderer twin screw extruder with an L/D = 29:1 and D= 30 mm operating at 190-200°C and 50 rpm in corrotating mode. The clay was added through a side feeder. Subsequently, the desired amount of pure PP, master batch and grafted PP were mixed in the twin screw extruder at 190-210°C and 100 rpm for the one step mixing. Then the samples were pelletized and mixed again passing through the twin-screw extruder in a two-step mixing at 190-210°C and 200rpm. The composition of nanocomposites is detailed in Table 2.

After being dried at 80°C for 16 h, pellets of the nanocomposites were injection molded into test pieces for mechanical tests by using a Battenfeld injection molder. The temperature of the cylinder was 185-215°C and that of the mold was 40°C.

Evaluation of nanocomposites

X ray diffraction of the clays and nanocomposites, in order to evaluate the evolution of the clay d_{001} reflection, was performed in a Siemens D5000 using CuKα X ray radiation. The X ray samples were obtained form compression moulding in order to avoid the preferred orientation of the clay when samples are prepared from injection moulding. The XRD patterns were scanned in the 2Θ range 1.5-12 ° at a rate of 2°/min. Melt flow rate was evaluated on the samples after one and two passes through the extruder according to ASTM D 1238. The mechanical properties of the resulting nanocomposites, modulus, and tensile strength, were measured according to ASTM D 638 with an Instron Model 4301. Notched Izod Impact resistance was evaluated according ASTM D256. Ultrathin section for TEM analysis, approximately 70-100 nm in thickness, were cut from Izod bars, with a diamond knife using a Leica microtome. The TEM observations were performed for the thin sections of thin films with a Jeol-2000EX microscope with a field emission gun at a accelerating voltage of 200 kV.

Table 2. Sample designation

Sample	PP,%	PPg, wt%	Type clay	Clay, wt %
PP	100	--	--	--
PP/PPgMAL	84	PPgMA(0.1), 16	--	--
PP/PPgMAH	84	PPgMA(1.0), 16	--	--
PP/PPgMAL 4, Na+	84	PPgMA(0.1),12	Na+	4
PP/PPgMAL 2, 20A	92	PPgMA(0.1), 6	20A	2
PP/PPgMAL 4, 20A	84	PPgMA(0.1),12	20A	4
PP/PPgMAL 6, 20A	76	PPgMA(0.1),18	20A	6
PP/PPgMAL 4, 30B	84	PPgMA(0.1),12	30B	4
PP/PPgMAH 4, Na+	84	PPgMA(1.0),12	Na+	4
PP/PPgMAH 2, 20A	92	PPgMA(1.0),6	20A	2
PP/PPgMAH 4, 20A	84	PPgMA(1.0),12	20A	4
PP/PPgMAH 6, 20A	76	PPgMA(1.0),18	20A	6
PP/PPgMAH 4, 30B	84	PPgMA(1.0),12	30B	4

Results and discussion

Effect of MA content and mixing method on melt flow behavior

Table 3 shows the melt flow rate results of the samples after one and two step mixing in the twin-screw extruder. It can be seen that after the second passing the MFR increases for all the samples indicating a lower viscosity related to the thermal degradation of the PP because of the increased residence time in the extruder. A more drastic increase in MFR for the virgin polypropylene, around 66%, and its blends with maleated PP, around 50% is observed. This increase in MFR is attributed to a more drastic chain scission process during the longer residence time in the extruder. It can be observed that all the nanocomposite samples shows lower percent of change in MFR, this is because the presence of clay increases the viscosity of the composites. It can be observed that the percent of change in MFR from step 1 to 2 is significantly reduced, of around 20%, for the nanocomposites with C20A and PP with maleated PP with higher MA content (PPgMAH) as compatibilizer. On the other hand it can be seen that the samples with C20A and maleated PP with lower MA content (PPgMAL) as compatibilizer, shows a higher percent of change in MFR from step 1 to 2, of around 30-40%. This could be related with the more polar interactions between the clay and the MA groups in the PP with higher content of MA (PPgMAH) that could be changing the viscosity of the composite.

It also can be observed that the samples with C20A have in general lower MFR than C30B and CNa+ for both mixing steps, and with both maleated PP, this could be indicating that C20A is more capable of interact with the MA groups.

Table 3. MFR results (g/10min)

Sample	1st step	2nd step	% Increase Step1 to Step2
PP	4.5	7.5	66
PP/PPgMAL	5.1	7.4	47
PP/PPgMAH	6.5	9.9	51
PP/PPgMAL 4, Na+	4.9	6.8	40
PP/PPgMAL 2, 20A	3.8	4.9	29
PP/PPgMAL 4, 20A	3.5	4.6	31
PP/PPgMAL 6, 20A	3.2	4.5	40
PP/PPgMAL 4, 30B	4.5	6.4	42
PP/PPgMAH 4, Na+	6.1	7.5	24
PP/PPgMAH 2, 20A	3.6	4.3	20
PP/PPgMAH 4, 20A	3.7	4.6	23
PP/PPgMAH 6, 20A	3.6	4.5	25
PP/PPgMAH 4, 30B	5.3	6.5	23

Mechanical properties of the nanocomposites

Table 4 shows mechanical properties of the composites obtained for the 2nd step mixing, specifically Young´s modulus, tensile strength, and notched Izod impact resistance. It can be seen that the modulus is almost the same for the samples of PP and its blends with maleated PP. Higher values in modulus can be seen in the samples with clays specially with C20A. The increase in modulus is observed when the clay content increases from 2 to 6% being the most noticeable change at low contents (2 and 4%), with less drastic improvement with further addition of the clay content. It can be seen that the highest values in modulus are for the samples with C20A when using PPgMAH as compatibilizer, an increase of around 35% of the value for simple PP, compared with the samples with PPgMAL, with only a 12% of increase compared with simple PP. It also can be seen the influence of the type of clay on this property, since all the samples containing clays CNa+ and C30B have lower values in modulus compared with the samples with C20A.

The effects of the amount of MA on tensile strength and impact strength of the nanocmposites are shown in this table (table 4) . As the content of C20A clay is increased the tensile strength is increased specially when using PPgMAH as compatibilizer. The maximum increase is observed when the clay content is increased from 2 to 4 %. The maximum values in this property were achieved when using C20A and PPgMAH. The impact strength increased when the clay content increases. The more notorious increase is seen when the clay content is increased from 2 to 4%. The maximum values of impact strength were for the samples with C20A and PPgMAH as compatibilizer. This could be attributed to higher interactions that can be achieved between the polar groups in the maleated PP with higher MA content and the clay

C20A. It can also be found the influence of the kind of clay on impact strength and tensile strength, as all samples with C20A have higher values of these properties than the samples containing CNa+ and C30B.

The difference in mechanical performance shows the importance of the content of polar groups in the polyolefin and the clay treatment process. Even though both maleated polypropylenes were used, as comaptibilizers, at the same final composition in the nanocomposite, that polymer with higher MA groups content shows a better compatibilizing effect, because the polar interactions with the polar clay are more favorable compared with that with lower MA groups content.

Table 4. Mechanical Properties after 2nd step mixing

Sample	Modulus (MPa)	Tensile Strength (MPa)	Izod Impact Strength (J/m)
PP	1180±25	32±0.7	12.2±0.4
PP/PPgMAL	1190±15	32±0.4	12.8±0.7
PP/PPgMAH	1178±21	31±0.7	13.1±0.5
PP/PPgMAL 4, Na+	1195±31	30±0.5	12.1±0.9
PP/PPgMAL 2, 20A	1210±30	32±0.7	13.6±0.2
PP/PPgMAL 4, 20A	1380±26	33±0.5	14.7±0.4
PP/PPgMAL 6, 20A	1390±18	32±0.4	15.0±0.3
PP/PPgMAL 4, 30B	1242±14	31±0.6	12.9±0.6
PP/PPgMAH 4, Na+	1255±40	32±0.4	11.5±0.4
PP/PPgMAH 2, 20A	1525±12	35±0.3	18.5±0.2
PP/PPgMAH 4, 20A	1635±25	38±0.4	18.4±0.8
PP/PPgMAH 6, 20A	1655±35	39±0.5	17.7±0.9
PP/PPgMAH 4, 30B	1398±25	34±0.5	12.5±0.3

Effect of MA content and mixing method on intercalation behavior

The XRD patterns of the nanocomposites with C20A and PP with PPgMAH as comaptibilizer, for both mixing steps, are shown in figure 1. As can be seen from this figure, the composites with all the clay contents show an increase in intergallery spacing, as the d_{001} peak shifts to lower angles, showing that the intergallery distance was enlarged from 2.4 nm to around 3 nm. This clearly indicates that macromolecular links had intercalated into the interlayers of the modified clay. It can be observed that after the second step of mixing the intergallery distance is slightly increased, specially for the clay contents of 2 and 4%, meanwhile for the 6% is slightly reduced. This could be related with the obtained mechanical properties in which the best mechanical behaviour was obtained when using around 4% instead of 6% of C20A clay.

Figure 2 shows the XRD patterns of 4wt% of C20A with PP and the two maleated PP comaptibilizers, after the first and second step of mixing. It can be seen that the sample with PPgMAH shows higher intergallery spacing form around 2.4 to 3.3 nm than the sample with PPgMAL that showed only an inetragllery spacing from 2.4 to 2.9 nm after the first step of mixing. It can be observed that after the second step of mixing the sample of PPgMAL does not shift to lower angles and higher intergallery spacing, compared with the PPgMAH that increased this distance from 3.3 to 3.6 nm. This indicate that the PPgMAL compatibilizer segments can hardly intercalate into the interlayers of the modified clay and that a sufficient quantity of MA groups into the compatibilizer is the key to preparing a nanocomposite with higher polar interactions and thus better performance. Another possible explanation for this phenomenon is that when using PPgMAL as compatibilizer it has higher molecular weight, of around Mw = 270,899 g/mol, that could difficult the compatibilizer movement through the interface and thus limiting the interfacial interactions. On the other hand the PPgMAH has a lower molecular weight, of around Mw = 95,804g/mol, that is more favourable for the diffusion of the molecular chains to the interface and be intercalated into the interlayers of the organo-modified clay.

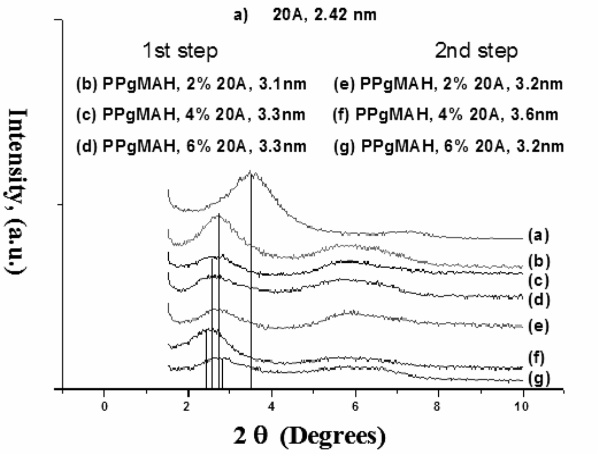


Figure 1. X ray diffraction patterns of nanocomposites PP/PPgMAH and C20A with different content of clay, after 1st and 2nd step of mixing.

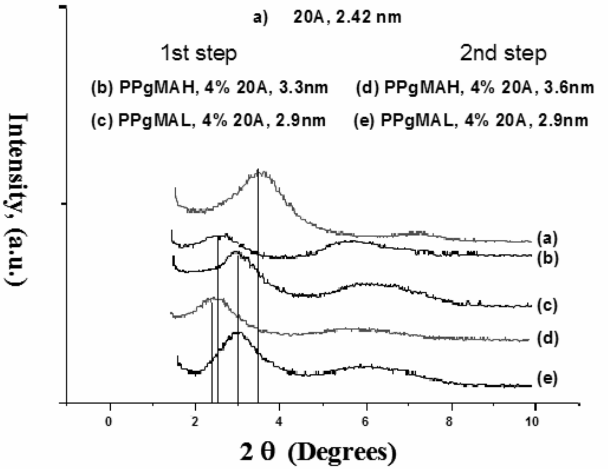


Figure 2. X ray diffraction patterns of nanocomposites of PP with different maleated PP, as compatibilizer and 4% of C20A after 1st and 2nd step of mixing.

The XRD patterns for the nanocomposites with PP/PP-g-MA and CNa+ and C30B clays were obtained after second step of mixing were determined. It was expected that C30B would have better exfoliation and dispersion in PP because the organic modifier of this clay has two ethoxy groups (Table 1), which should have stronger interactions with the maleated PP. However the samples with clay 30B shows a d_{001} peak shift to higher angles, 6.1° and an intergallery spacing, 1.4 nm, smaller than the original clay, 5.9° and 1.8 nm, indicating a poor exfoliation of this clay and less effective reinforcement in mechanical properties as was observed in table 4 . This is in agreement with other studies[22,25] who found only a partial exfoliation of this clay in PP and was attributed to its poor thermal stability and its initial smaller interlayer spacing. In the samples with Na+ (7.3°, 1.17 nm) the shift is to higher angles, 8.9° and the spacing appears at lower values, 1.0 nm. This confirms that no exfoliation could be achieved by using the CNa+ clay and that this clay is less effective in the reinforcement of the nanocomposites as was observed in mechanical properties. This is in agreement with the results from other authors [23-25] and could be related with the dehydration of the clay during heating.

TEM micrographs of nanocomposites based on 4 wt% of C20A clay, PP and the two maleated polymers as compatibilizers, are shown in figure 3. It can be seen that in the sample with PPgMAL, figure 3-a, there are noticeable thickly clay tactoids, even larger than 200 nm, indicating a poor degree of clay exfoliation. On the other hand it can be seen in figure 3-b, sample with PPgMAH, that the clay layers show a more exfoliated morphology, and more homogeneous dispersion. This photograph shows that the thickly staked layers structures were separated into thinner ones when using PPgMAH through the processing of the composite. This results are in good agreement with the observed mechanical properties, and shows the intercalation effect of the content of polar groups in the polyolefin.

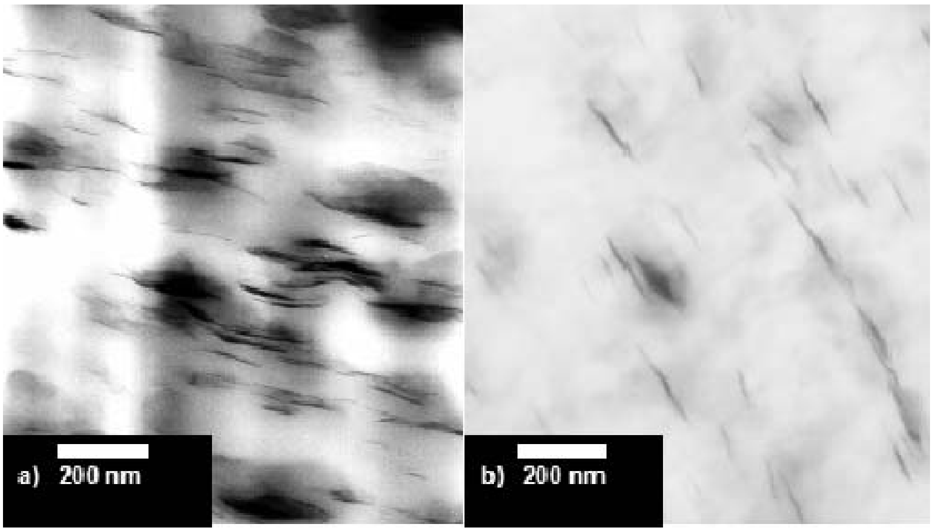


Figure 3. TEM images of nanocomposites with C20A at 4 wt% and (a) PP/PPgMAL and (b) PP/PPgMAH.

Conclusions

The polar groups content in the polyolefin is an important factor for preparing PP/PP-g-MA/Clay nanocomposites, and the intercalation effect of this nanocomposites can be enhanced by using maleated PP with higher MA graft efficiency as compatibilizer. The two step mixing conditions results in better dispersion and exfoliation for the nanofillers than one step mixing. Maximum values in mechanical properties such as modulus, tensile strength and impact strength, are achieved when using maleated PP with higher MA grafting content. Clay dispersion and interfacial adhesion are greatly affected by the polar groups content, clay modification and processing conditions. Modified clay C20A, showed a better performance than C30B and CNa+.

Acknowledgements. The authors gratefully acknowledge the financial support of CONACyT (SEP-2003-CO2-43983). And want to acknowledge the support of Ing. Adriana Espinoza and Flora Beltran, and the technical support of Blanca Huerta, Josefina Zamora, Concepcion Gonzalez, Rodrigo Cedillo, Sandra Peregrina, Teresa Rodriguez, Jesus A. Espinoza, Jesus Rodriguez and Francisco Zendejo.

References

1. Kato M, Usuki A, Okada A (1997) J Appl. Polym Sci , 66:1781
2. Zanetti M, Lomakin S, Camino G (2000) Macromol Mater Eng 279:1
3. Garcia LD, Picazo O, Merino J C, Pastor JM (2003) Eur Polym J 39:945
4. Alexandre M, Dubois P (2000) Mater Sci Eng 26:1
5. Moore E (1996) Polypropylene Handbook; Hanser: Munich
6. Manias E, Touny A, Wu L, Lu B, Strawhecker K, Guilman J, Chung T (2000) Polym Mater Sci Eng 82:282
7. Svoboda P,Zeng Ch,Wang H,Lee LJ, Tomasko DL (2002) J Appl Polym Sci 85:1562
8. Kim Y, White JL (2005) J Appl Polym Sci, 96:1888
9. Ton-That MT, Perrin-Sarazin F, Cole KC, Bureau MN, Denault J (2004) Polym Eng and Sci, 44:1212
10. Utraki LA, Simha R (2004) Macromolecules 37:10123
11. Wong S Ch, Chen L (2002) Proc SPE ANTEC
12. Vaxman A, Tsalic N, Benderly D, Shalom R, Narkis M(2004) ProcSPE ANTEC 1887
13. Weibing X, Guodong L, Wei W, Shupei T, Pingsheng H, Wei-Ping P (2003) J Appl Polym Sci 88:3225
14. Guodong L, Junting X, Suping B, Weibing X (2004) J Appl Polym Sci 91:3974
15. Lan T, Pinnavaia T (1994) Chem Mater 6:2216
16. Jeon HG, Jung HT, Lee SD (1998) Polym Bull 41:107
17. Zhu L, Xanthos M (2004) J Appl Polym Sci 93:1891
18. Anderesen P (2002) Proc SPE ANTEC 219.
19. Cho JW, Logsdon J, Omachiniski S, Qian G, Lan T, Wormer T W, Smith WS (2002) Proc SPE ANTEC, 214
20. Dennis H R, Hunter D L, Chang D, Kim S, White J L, Cho J W, Paul D R (2001) Polymer 42:9513
21. Kwak M, Lee M, Lee B (2002) Proc SPE ANTEC, 224
22. Lee J, Lim Y, Park O (2000) Polym Bull 45:191
23. Gopakumar T G, Lee J A, Kontopoulou M, Parent JS (2002) Polymer 43: 5483
24. Brindley GW, Brown G (1980) Crystal Structures of Clay Minerals and Their X ray Identification; Mineralogical Society: London
25. Lopez ML, Sanchez S, Ramos LF, Medellin FJ (2006) J Appl Polym Sci *in press*