Water Assisted Exfoliation of PA6/Clay Nanocomposites Using a Twin Screw Extruder: Effect of Water Contact Time

Vadoud Molajavadi, Hamid Garmabi

Department of Polymer Engineering, Amirkabir University of Technology, Tehran, Iran

ABSTRACT: Polyamide 6/Na$^+$ montmorillonite (Na$^+$ MMT) nanocomposites (NCs) were produced in a corotating twin screw extruder. Water was injected into the extruder as an intercalating/exfoliating agent. The wide angle X-ray diffraction and linear dynamic measurements were used to investigate the structure of the prepared samples. The results showed that the contact time between water and melt PA6/Na$^+$MMT in the extruder is an important factor to achieve a high level of exfoliation. The ratio of water-injection rate to clay feeding rate did not reveal a major effect on the exfoliation of pristine MMT. The results also demonstrated that the order of injection of water during the mixing process did not have a distinguishable effect on the level of exfoliation. This processing method was found to be controlled by a diffusion mechanism caused by the presence of water molecules during the process. Improvement of tensile properties is in a great agreement with the rheological and morphological findings. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 736–743, 2011

Key words: extrusion; nanotechnology; composites; X-ray; mechanical properties

INTRODUCTION

Polymer layered silicate nanocomposites(NCs) have attracted considerable scientific and commercial interest since 1993 when the synthesis of nylon6/clay nanocomposite was reported by Toyota Central Research Laboratories.[1] Engineering properties of layered silicate NCs exhibit substantial improvement in mechanical/physical properties of the obtained nanocomposites.[2,3] These novel materials also show high gas barrier properties[3–5] and improved flame retardancy.[6]

The enhancement of properties is obtained through exfoliation and dispersion/distribution of clay laminates (having a large surface area and a high aspect ratio) inside the polymeric matrix. Among the different preparation methods,[7] the melt mixing method utilizes the conventional polymer processing techniques, such as extrusion, thus making it easier for the polymer processing industry to adopt and integrate it within the production line. The first requirement of this process involves modification of clay surface to increase the d-spacing of clay galleries. Such initial intercalated structure is believed to be necessary to allow polymeric chains to penetrate within the clay galleries. There is a very strong cohesion between unmodified clay platelets.[8] Therefore, in spite of high interaction between clay platelets and a polar matrix such as PA6,[9] polymer chains can not diffuse into the basal spacing and hence, even at high shear rates, it is not possible to prepare an intercalated or exfoliated NC.

However, organic modification has some disadvantages, as well. It has been found that the binding energy between nylon6 and the clay platelet decreases almost linearly with the volume of the adsorbed modifier.[10] Consequently, pristine clay yields the highest binding strength to the nylon.[10] Also, the presence of organic modifier accelerates the thermo-oxidative mechanism and results into matrix degradation.[11] In addition, the organic modifier, which has a low molecular weight, can act as a plasticizer and decreases the level of mechanical improvement.

Water assisted melt blending is a new method to prepare nanocomposites using the benefits of both solution and conventional melt mixing methods. This method does not require the pretreatment of clay mineral with an organo-cation. Due to the lack of modifier, water assisted extrusion has some advantages to that of conventional extrusion approach from the financial and commercial viewpoints. This procedure was described for the first time by Korbee and Geenen,[12] in which the pristine clay particles were introduced with the PA6 pellets

into the extruder. Water was then injected directly into the extruder downstream. After interactions with the melt compound, the water was evacuated further downstream via a vacuum pump. This idea has been developed more recently by Yu et al.,[13] Kato et al.,[14] and Fedullo et al.[15]

Hasegawa et al.[16] used aqueous slurry of Na$^+$ MMT that was melt blended with PA6. The WAXS patterns and TEM micrographs clearly indicated the exfoliation of Na$^+$ MMT layers. The major drawback of Hasegawa's method is that it requires a large amount of water to be pumped into the extruder to reduce the slurry viscosity.

The presence of water plays two different roles. As a solvent, it reduces the interaction between the clay platelets with increasing the gallery spacing. On the other side, water can reduce the matrix (PA6) viscosity and thus increase the chain mobility. Both of these effects facilitate the chain penetration between the clay platelets. It has been found that nylons can be brought into the same structural state at lower temperatures in the presence of solvents like water than dry conditions, and this temperature difference (70–100°C for water) can be used to quantify the effects of solvent.[17] Wevers et al.[18] showed by DSC measurements that PA6 is soluble in water under high vapor pressure in the whole concentration range and that water acts as a crystallization point and melting point suppressor. According to their findings, the maximum temperature depression is ∼ 60°C and this value is independent of concentration over a large range (10–70 wt % PA6 in water). Based on the above discussion, arises a question in the mind; "Which of these two cited roles is dominant?" Both PA6 and Na$^+$ MMT are hydrophilic materials. Thus; there would be a competition between them on water absorption.

Previous studies,[12,13,15] have shown that the water-injection rate higher than 10% of the feeding rate did not reveal a major effect on the exfoliation of the pristine MMT in PA6 matrix. In this study, we investigated the effect of (a) the contact time between water and melt PA6/Na$^+$ MMT, and also (b) the ratio of water injected to the clay content of the feeding compound on the dispersion level of MMT and the tensile properties of obtained NCs. Trying to answer the proposed question, the sample preparation method was designed in order to highlight one of the mentioned roles for water presence in a ternary blend of water/PA6/Na$^+$ MMT.

EXPERIMENTAL

Materials

Polyamide 6 (Akulon F223 D) produced by DSM was used as the polymeric matrix. Pristine MMT
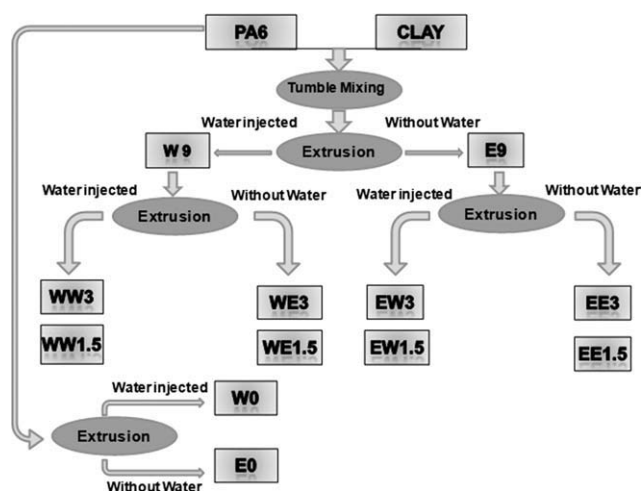

Figure 1 Schematic representation of the mechanism used to prepare the samples and their nomenclature.

was prepared by Southern Clay Products under the trade name of Cloisite Na$^+$.

Sample preparation

Corotating intermeshing twin screw extruder, DSE20, from Brabender (L/D = 40, D = 20 mm) was used to prepare the NCs. The samples were prepared at a barrel temperature of 220°C and a screw speed of 275 rpm. The feeding rate was 2.2 kg/h and the water was injected into the extruder at a rate of 300 g/h using a liquid pressure pump. The water was removed from the vent by a vacuum pump, downstream. As shown Figure 1, two types of master batches were used to prepare the NCs. One of them was extruded in the presence of water (W9) and the other one was extruded without water injection (E9). Then, each of them was diluted in the second step of the extrusion, which was performed with and without water injection, to the desired clay content, as well. As mentioned at the end of the sample codes (Fig. 1), the nominal clay contents of samples were 1.5 and 3 wt %. The nominal clay content of a sample is the ratio of nanoclay (weighted by a balance) inside the feeding compound to the total weight of the feeding compound (nanoclay and PA6).

Characterization

X-ray diffraction (XRD) over a range of 2–10° in the steps of 0.04° and with a counting time of 1s per angular position, was performed using a Philips Analytical Xpert X-ray diffractometer with Cu Ka radiation (=1.54 Å) generated at 30 mA and 40 kV.

Melt state rheological measurements were carried out using small amplitude oscillatory frequency sweep mode by RMS-900 (Paar Physica). In the
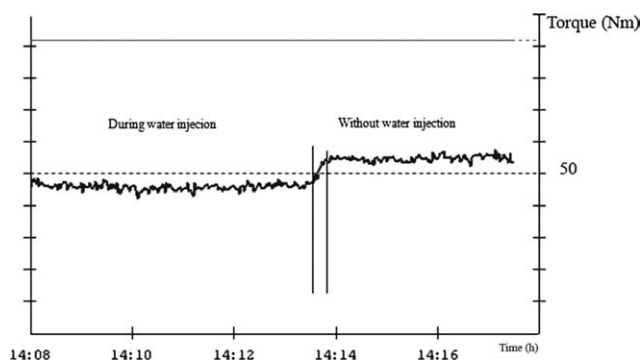
Figure 2 The torque value required during the second step of extruding E9 master batch to prepare EW3 (left side of the curve) and EE3 (Right side of the curve).

oscillatory shear measurements, a fixed strain of 1% was used to ensure that the measurements were taken well within the linear viscoelastic range of the materials investigated. All rheometrical measurements were performed at 235°C. To prevent moisture effects, all the samples were predried in an oven at 80°C for 24 h.

Tensile properties were obtained using SUN2500 tensiometer (GALDABINI) according to the ASTM D 638 test method at a cross head speed of 50 mm/min at room temperature. The injection molded samples were immediately put in a desiccator, containing silica gel, to avoid any moisture absorbsion.

Thermo-gravimetric analysis (TGA) was performed on a Shimodzo TGA60 instrument with aluminum pans. The heating rate was 10°C/min and the atmosphere was nitrogen with the flowing rate 30 cm^3/min.

RESULTS AND DISCUSSION

The reported value for the equilibrium water vapor pressure at 225°C is equal to 26 bar.[19] Therefore, the pressure pump should be able to inject the water into the mixing zone at a pressure higher than 26 bar. Figure 2 shows the value of the torque required to turn the screw at 275 rpm during the second step of the processing in order to prepare the samples; EW3 and EE3. When water was injected into the extruder (to prepare EW3), the required and stable torque value was 8 Nm lower than its value when no water was injected into the extruder (to prepare WE3). This shows that the water molecules were successfully soluble with the melt compound in the zone between the water-injection point and the venting point, resulting into the reduction of melt viscosity in that zone. TGA measurements were also carried out on these two samples. Both samples showed a weight loss lower than 1% up to 200°C. This indicates that the vacuum pump could success-

fully collect the water, injected into the extruder during the process.

The exact amount of the MMT in each NC was determined by placing the predried pellets in a furnace at 900°C for 45 min and calculating the MMT wt % according to the method used by Fornes et al.[10] The exact value of the MMT content was 1.35 and 2.7 wt % for the samples with the nominal clay content of 1.5 and 3 wt %, respectively. The difference between the nominal and exact values of the MMT for a sample is due to (a) the existence of water molecules between the clay platelets before processing and (b) the possible nonuniformity of the feeding due to simultaneous feeding of granule and clay powders.

X-ray patterns

Figure 3 shows the XRD pattern of pristine MMT. It has an intense diffraction peak at $2\Theta = 7.6°$ and also a very small peak at $2\Theta = 9.2°$ corresponding to the basal spacings of 1.18 nm and 0.96 nm, respectively. This indicates that the majority of the clay platelets were hydrated by one layer of water molecules between the clay platelets and a very small number of the clay platelets were dehydrated. Clay platelets begin to swell in a stepwise manner,[20] and the gallery spacing increases from 0.96 nm in the dehydrated state to 1.2 nm in one layer hydrate.

Figure 4 shows the WXRD patterns of pure PA6 and NCs with the clay content of 2.7 wt %. EE3, which was extruded without any water injection, showed a very broad peak at $2\Theta = 4.6°$ corresponding to the basal spacing of 1.92 nm. Therefore, the polymer chains penetrated into the gallery spacing even when the unmodified clay platelets were used. This intercalation may be related to the presence of water in the gallery spacing. It can be claimed that the water molecules evaporated with the increasing of temperature during the extrusion process and this
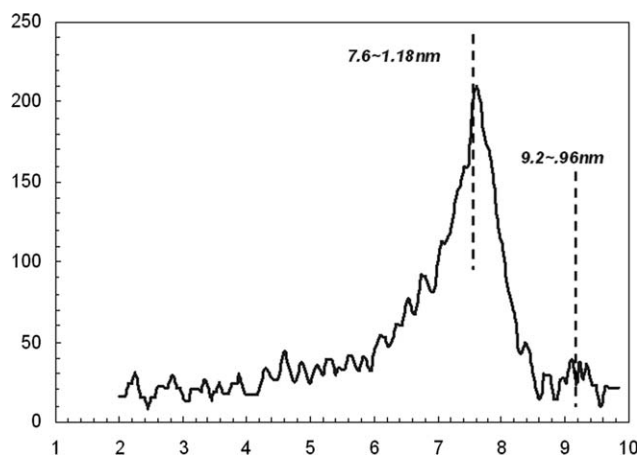

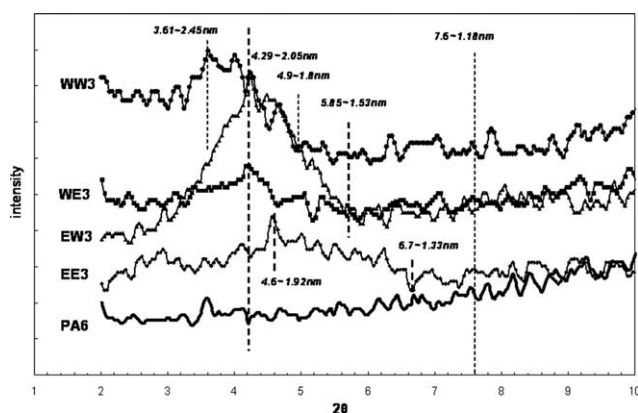**Figure 3** XRD pattern of untreated nanoclay.

Figure 4 XRD patterns of PA6 and samples with the clay content of 2.7 wt %.

phenomenon assisted the diffusion of melted polymer chains between clay platelets. Accordingly, it can be concluded that the evaporation of water molecules in the gallery space occurred when the matrix was in the melt state. Otherwise, if the water molecules were released before the polymer chains could be able to move, the gallery spacing would be decreased to 0.96 nm.

WW3, which was extruded two times in the presence of water, had a basal spacing of 2.45 nm. EW3 and WE3, which had the same contact time between water and melt PA6/MMT in the extruder, showed similar basal spacing of 2.05 nm. The difference between the morphology of WE3 and WW3 can be attributed to the effect of water on the polymer chain mobility. These two samples were prepared by dilution of W9, which was extruded in the presence of water. WE3 was extruded without water injection in the second step of the extrusion, while WW3 was processed in the presence of water. As shown in Figure 4, the features of WAXS patterns of these samples are similar with a difference in the place of the peak and the higher rate of intensity increment at lower angles for WW3 (difference in the left shoulder of the peaks). Lower viscosity of the matrix due to the presence of water enhanced the mobility of polymeric chains and accelerated their diffusion into the gallery spacing. Increase in the water content of the NCs decreases the viscosity and plays two contradictory roles in the mechanism of delamination. It decreases the amount of stress inserted to the clay tactoids from the matrix. Otherwise, it increases the diffusion rate of the water molecules and polymer chains into the gallery spaceing. Fornes et al.,[21] who used organoclay NCs based on treated clay and three different molecular weights of polyamide 6, concluded that the degree of exfoliation increases with increasing of the molecular weight of the polyamide matrix and therefore, with the increase of the shear stress that plays a dominant

role. Opposite results were reported by Woo Kim et al.[22] on a quite similar system. In fact, they found that a high degree of platelet delamination was obtained with a rather low viscosity of the matrix (low shear stress). They explained their results by a diffusion controlled process that requires low viscosity of the matrix. It seems that the competition between the shear induced and the diffusion controlled exfoliation determines the final results. The difference between the level of exfoliation between WW3 and WE3 shows that, similar to the results of Woo Kim et al., this system is diffusion control in the second step of extrusion which is expected due to the presence of water molecules in the system. Also the difference between the WAXS patterns of EE3 and WE3 and between E9 and W9 identify that the process is diffusion control in the first step of the extrusion, as well. The WAXS patterns of EE1.5 and WE1.5 were similar to those of EE3 and EW3, respectively. For EW1.5 and WW1.5, the patterns were slightly shifted to the lower angles in comparison to those of EW3 and WW3.

Linear dynamic viscoelasticity

The change in the linear viscoelastic behavior from liquid-like for the unfilled polymer to solid-like for the NCs was observed. Figure 5(a) shows the frequency dependence of storage modulus (G') for the pure PA6 and NCs. All the NCs demonstrated higher storage modulus at both low and high frequencies and exhibited more solid-like behavior than the neat nylon6. As can be seen in Table I, the slope of G' at the low frequencies changed from 1.65 for the pure PA6 to 1.2 and 0.6 for EE3 and WW3, respectively. This shows the effectiveness of water injection on the delamination of platelets, making a higher network connection between the clay tactoids resulting into a more solid-like behavior.[23–25] This value for WE3 and EW3 was 0.9, and 0.8, respectively. Figure 5(b) shows the loss modulus (G'') of PA6 and NCs versus frequency. For both WW3 and EW3, the whole curves were shifted upward. As Table I shows, the slope of G'' curve at the low frequencies decreases slightly from PA6 to the NCs.

Figure 6 shows the complex viscosity behavior of the neat nylon6 and NCs with the clay content of 2.7 wt % at 235°C. At low frequencies, the neat nylon6 exhibited Newtonian behavior. EE3, which was prepared without water injection, showed a behavior similar to that of the PA6. Other samples exhibited viscosity upturn behavior with decreasing in the frequency. For polymer composite systems, the state of the dispersion, the size, shape and concentration of the filler can have a significant effect on the rheological properties in the melt state.[24] Generally, the complex viscosity of molten reinforced polymer/clay
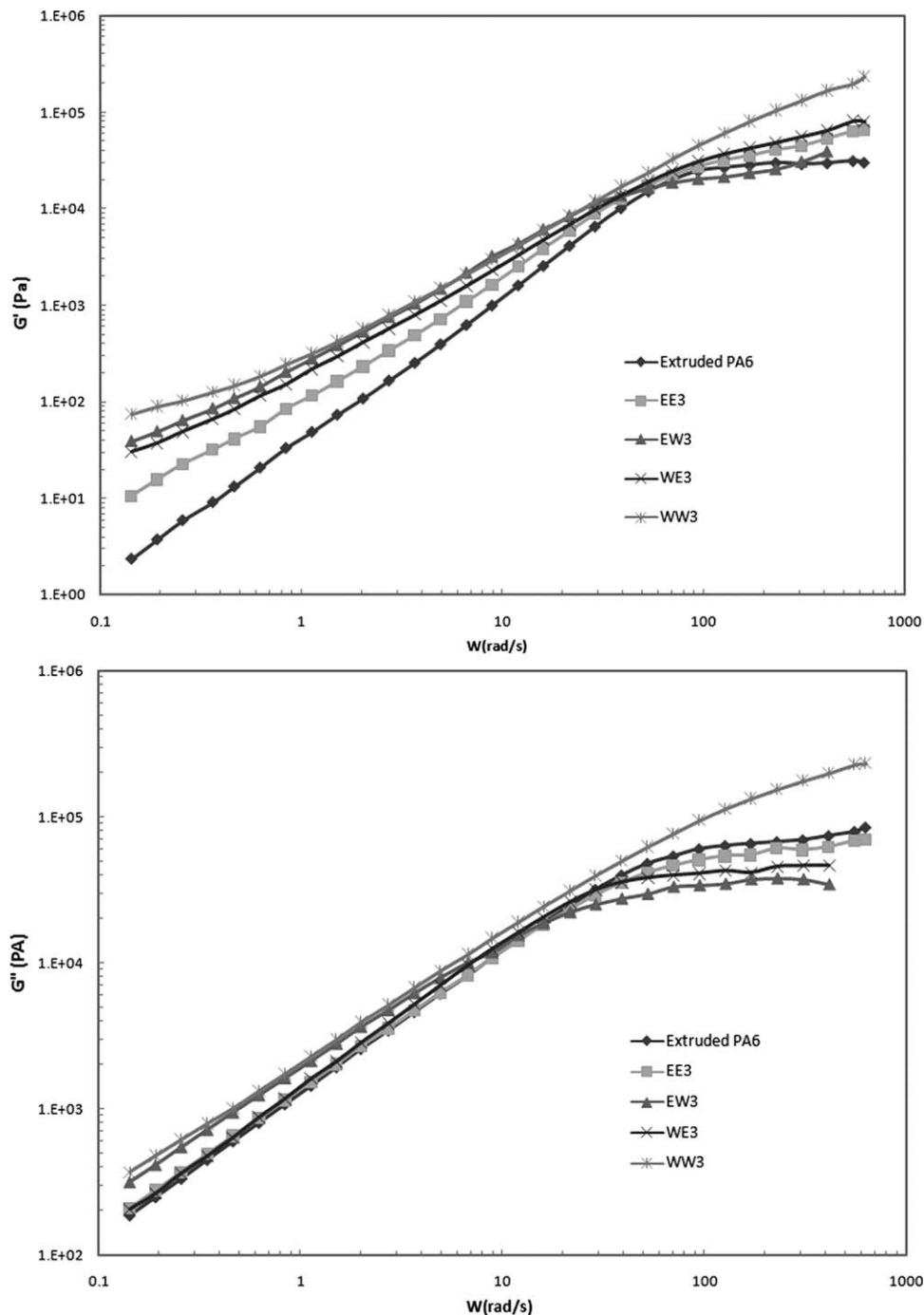
Figure 5 Storage modulus (a) and Loss modulus (b) versus Frequency for PA6 and the NCs with the clay content of 2.7 wt %.

NCs exhibits viscosity upturn at low frequencies with decreasing in the frequency.[23–26] The results indicated that the contact time between water and polymer melt in the extruder was an important factor that caused a more solid-like behavior in the NCs with the same nanoclay content. It shows that contact time has the same effect of silicate content[24] on the flow behavior; in other words, higher contact times cause a higher delamination of clay platelets,

promoting the tendency to form a three-dimensional structure between clay tactoids.

Mechanical properties

Table II shows the effect of MMT content on the modulus of different samples. "P" shows the directly injected pristine nylon6 sample without any extrusion process and W0 indicates the extruded

TABLE I
Slope of Loss Modulus and Storage Modulus at Low
Frequencies for Different Samples

Slope of the curve at low frequencies		
Loss modulus	Storage modulus	Sample name
0.99	1.65	Extruded PA6, without water injection (E0)
0.99	1.65	Extruded PA6, water injected (W0)
0.96	1.1	EE3
0.94	0.8	EW3
0.94	0.9	WE3
0.83	0.6	WW3
0.94	1.0	WW1.5

TABLE II
Mechanical Properties of Different Samples

Sample	Elastic modulus (GPa)	Yield strength (MPa)	Yield strain (%)
p	3.5 ± 0.2	101 ± 3	5
W0	3.6 ± 0.1	103 ± 2	4.8
EE3	4.2 ± 0.1	113 ± 3	4.5 ± 0.2
WE3	4.4 ± 0.2	120 ± 1	4.5 ± 0.2
EW3	4.5 ± 0.2	120 ± 3	4.4 ± 0.2
WW3	4.8 ± 0.1	116 ± 3	4.4 ± 0.2
EE1.5	3.9 ± 0.1	110 ± 3	4.6 ± 0.2
EW1.5	4 ± 0.1	113 ± 3	4.6 ± 0.2
WW1.5	4.2 ± 0.1	110 ± 3	4.5 ± 0.2

nylon6 in the presence of water. The relative tensile modulus (RTM) of EE3, WE3, EW3, and WW3 samples was measured as 1.16, 1.22, 1.25, and 1.35, respectively (Fig. 7). The value for EE1.5, WE1.5, and WW1.5 was 1.09, 1.11, and 1.19, respectively. The addition of untreated MMT to the polymer matrix increased the modulus in all cases even for the samples produced without water injection (i.e., EE3 and EE1.5). The incorporation of MMT to PA6 has resulted into significant enhancement of the modulus of the matrix. In comparison, modulus ratio value of 1.9 has been reported for PA6/glass fiber composite[26] but only at addition levels higher than 18 wt %. In the same study,[26] 10 wt % of glass fiber gave the modulus ratio value of 1.3. Thus, the modulus ratio of 1.35, exhibited by the WW3 nanocomposite containing 2.7 wt % MMT, appears excellent in comparison to the modulus ratio of a glass fiber composite. For the NCs with the similar clay contents, the modulus showed higher improvement for the WW samples, which their contact time between water and melt PA6/Na$^+$MMT in the extruder was
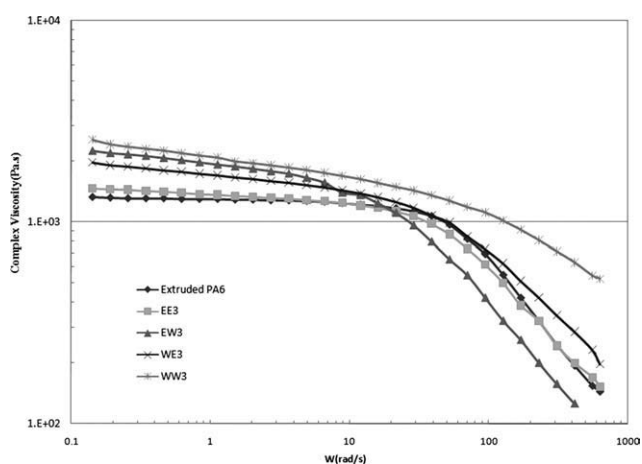
double as compared to the EW and WE samples. The RTM of EW3 was slightly higher than that of WE3. For the samples with similar processing method, the RTM depended linearly on the weight percent of clay, which is comparable to some of the previous studies on PA6/Organo-MMT NCs.[7,21,,27] Although, it is worth noting that linear relationship between volume fraction (or weight fraction at low filler loading) of nanoclay and reduced modulus ratio is true when the morphology is not affected by clay content. Indisputably, the morphology of the prepared NCs strongly affects their properties such as modulus and barrier property. In some studies,[26,28] increasing in the filler volume fraction of nanoclay caused a much ordered structure but decreased the exfoliation level.

For the NCs with similar matrix (as PA6) and similar filler (as Na$^+$MMT), the modulus increment will mostly be dependant on the value of the filler content and the effects of the processing conditions on the level of the filler dispersion and distribution in the matrix. Assuming that the filler content does not change the processing performance on the dispersion and distribution level of the filler in the matrix, it can be estimated that there would be a linear relationship between the clay content and the modulus
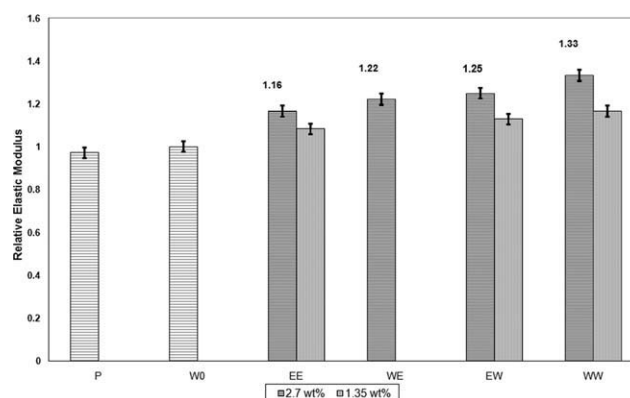

Figure 6   Complex viscosity versus frequency.

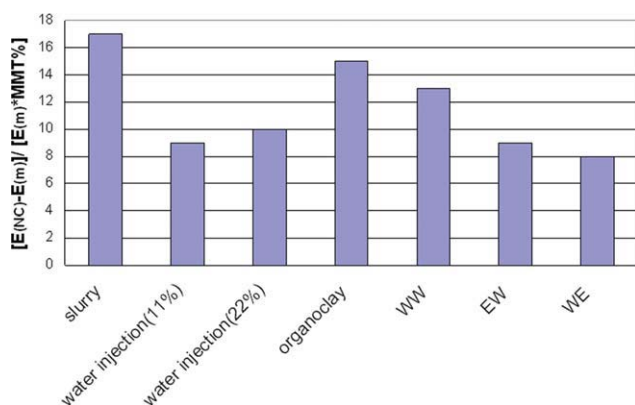Figure 7   Relative tensile modulus of PA6 and NCs.

Figure 8 Normalized reduced elastic modulus with respect to the clay weight percent for different prepared samples (WW, EW, and WE) as the results reported in Ref. 16 (slurry), Ref. 13 (water-injection), and Ref. 21(organoclay). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

improvement but only at the low filler contents (i.e. to neglect the filler–filler interactions). The Young's modulus predictions of the Halpin-Tsai model show such a linear behavior.[27] The results obtained in this research regarding the modulus improvement were compared with the results of similar works, that can be seen in Figure 8. In this figure, the vertical axis shows the percent of modulus increment owing to the addition of 1 wt % MMT. The highest value was reported by Hasegave et al.[14] They used the slury method to prepare PA6/ Na$^+$ MMT nanocomposite with the clay content of 1 wt % and received a fully exfoliated morphology. The residence time in the cylinder durig the extrusion was ~10 min. Yu et al.,[13] prepared PA6/Na$^+$MMT NCs containing 5 wt % of Na$^+$MMT with two different water-injection rates. Their results showed that this variation did not affect the improvement of the tensile modulus. Based on the above discussion, assuming that the rate of modulus increament is independent of the clay content, the value of modulus increment owing to 1 wt % MMT will be equal to 9 and 10% for the samples with 11 and 22% ratios of water-injection rate/feeding rate, respectively. Fornes et al.[21] prepared PA6/Organo-MMT NCs with different clay contents. They also varied the molecular weight of PA6. They showed that there is nearly a linear relationship between the clay contents of the prepared NCs and their Young's modulus increment which is similar to our experimental findings. The normalized relative modulus increment with respect to the clay weight percent, as reported by Fornes et al.,[21] for the high molecuar weight PA6/Organo-MMT was 15%. This value for the WW, EW and WE samples was 13%, 9%, and 8%, respectively.

Based on the above discussion, similar to the those of X-ray patterns and linear viscoelastic propertis,

the level of modulus improvement shows the importance of contact time between water and melt PA6/Na$^+$ MMTto reach a high level of exfoliation. The presence of water in both steps of extrusion resulted into higher basal spacing, more solid-like behavior and higher tensile modulus improvement.

Table II also shows the development in tensile strength for different sample preparation procedures and for the addition levels of MMT. In contrast to the RTM, the relative yield strength did not increase simultaneously with increasing the contact time between water and PA6 melt inside the extruder. The relative yield strength for both EW3 and WE3 samples was 1.16, which was higher than the value of 1.10 obtained for EE3 and 1.13 for WW3.

CONCLUSIONS

PA6/Na$^+$MMT nanocomposites were prepared by direct injection of water into the extruder. Based on the obtained results, it is concluded that in this processing method, the contact time between water and melt PA6/Na$^+$ MMT is an important parameter to obtain a high level of exfoliation. Therefore, a diffusion mechanism caused by the presence of water molecules is dominant mechanism for intercalation/exfoliation of MMT. Increasing of water-injection rate (to levels higher than 10 wt % of feeding rate) and also decreasing of the clay content of the feed showed no distinguishable effect on the efficiency of the production method. It was also shown that the tensile modulus improvement correlated with the rheological data and seemingly it can be used to predict the level of exfoliation.

References

1. Usoki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. J Mater Res 1993, 8, 1179.
2. Powel, C. E.; Beal, G. W. Curr Opin Solid State Mater Sci 2006, 10, 73.
3. Moghri, M.; Garmabi H. Int Polym Process 2008, 5, 430.
4. Takahashi, S.; Goldberg, H. A.; Feeney, C. A.; Karim, D. P.; Farrel, M.; O'Leary, K.; Paul, D. R. Polymer 2006, 47, 3083.
5. Moghri, M.; Garmabi, H.; Molajavadi, V. J Vinyl Addit. Technol 2010, 16, to appear.
6. Morgan, A. B. Polym Adv Technol 2006, 4, 206.
7. Ray, S. S.; Okamoto, M. Prog Polym Sci 2003, 28, 1539.
8. Bousmina, M. Macromolecules 2006, 39, 4259.
9. Fermeglia, M.; Ferrone, M.; Pricle, S. Fluid Phase Equilib 2003, 215, 315.
10. Fornes, T. D.; Hunter, D. L.; Paul, D. R. Macromolecules 2004, 37, 1793.
11. Fornes, T. D.; Yoon, P. J.; Paul, D. R. Polymer 2003, 44, 7545.
12. Korbee, R. A.Geenen, A. A. V. U. S. Pat. 6,350,805, B1 (2002).
13. Yu, Z. Z.; Hu, G. H.; Varlet, J.; Dasari, A.; Mai, Y. W. J Polym Sci B 2005, 43, 1100.
14. Kato, M.; Matsushima, M.; Fukumori, K. Poym Eng Sci 2004, 44, 1205.
15. Fedullo, N.; Sclavons, M.; Bailly, C.; Lefebvre, J. M.; Devaux, J. Macromol Symp 2006, 233, 235.

16. Hasegawa, N.; Okamoto, H.; Kato, M.; Usuki, A.; Sato, N. Polymer 2003, 44, 2933.
17. Murthy, N. S. J Appl Polym Sci 2006, 44, 1763.
18. Wevers, M. G. M.; Pijpers, T. F. J.; Mathot, B. F. Thermo Mechanica Acta 2007, 453, 67.
19. Weast, R. C.; Selby, S. M.; Hodgman, C. D. Handbook of Chemistry and Physics, 46th ed.; The Chemical Rubber Co, Cleveland, OH, 1965, p D-95.
20. Hensen, E. J. M.; Smit B. J. Phys Chem 2002, 106, 12664.
21. Fornes, T. D.; Yoon, P. J.; Keskkula, H.; Paul, D. R. Polymer 2001, 42, 9929.
22. Woo Kim, S.; Ho Jo, W.; Sung Lee, M.; Bae Ko Young Jho, J. Polym J 2002, 34, 103.
23. Hyun, Y. H.; Lim, S. T.; Choi, H. J.; Jhon, M. S. Macromolecules 2001, 34, 8084.
24. Lim, S. T.; Hyun, Y. H.; Choi, H. J.; Jhon, M. S. Chem Mater 2002, 14, 1839.
25. Krishnamoorti, R.; Yrekli, K. Curr Opin Colloid Interface Sci 2001, 6, 464.
26. Wilkinson, A. N.; Man, Z.; Stanford, J. L.; Matikainen, P.; Clemens, M. L.; Lees, G. C.; Liauw, C. M. Comp Sci Technol 2007, 67, 3360.
27. Sheng, N.; Boyce, M. C.; Parks, M. D.; Rutledge, G. C.; Abes, J. I.; Cohen, R. E. Polymer 2004, 25, 487.
28. Borse, N. K.; Kamal, M. R. Polym Eng Sci 2006, 46, 1094.