World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:9, No:12, 2015

Effect of Modified Layered Silicate Nanoclay on the Dynamic Viscoelastic Properties of Thermoplastic Polymers Nanocomposites

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Open Science Index, Chemical and Molecular Engineering Vol:9, No:12, 2015 publications.waset.org/10003276/pdf

***Abstract*—**This work aims to investigate the structure–property relationship in ternary nanocomposites consisting of polypropylene as the matrix, polyamide 66 as the minor phase and treated nanoclay DELLITE 67G as the reinforcement. All PP/PA66/Nanoclay systems with polypropylene grafted maleic anhydride PP-g-MAH as a compatibilizer were prepared via melt compounding and characterized in terms of nanoclay content. Morphological structure was investigated by scanning electron microscopy. The rheological behavior of the nanocomposites was determined by various methods, viz melt flow index (MFI) and parallel plate rheological measurements.

The PP/PP-g-MAH/PA66 nanocomposites showed a homogeneous morphology supporting the compatibility improvement between PP, PA66, and nanoclay. SEM results revealed the formation of nanocomposites as the nanoclay was intercalated and exfoliated. In the ternary nanocomposites, the rheological behavior showed that, the complex viscosity is increased with increasing the nanoclay.

The results showed that the use of nanoclay affects the variations of storage modulus (G′), loss modulus (G″) and the melt elasticity.

***Keywords*—**Nanocomposites, polypropylene, polyamide66, modified nanoclay, rheology.

I. Introduction

A new class of polymer nanocomposites based on organically modified montmorillonite (OMMT) has received a great deal of attention from both academic researchers and industrial personnel from the very inception of its discovery because it exhibits a significant improvement of macroscopic material properties at very low filler contents [1]. The enhancement of material properties of polymer-layered silicates hybrid composites is attributed to their nanometer dimension features i.e. the extraordinarily high surface area of the dispersed nanofiller and the unique intercalation and/or exfoliation microstructure characteristics that make them excellent candidates as reinforcing materials for polymers in multifunctional nanocomposites [2].

Two types of morphology are generally developed when polymer and clay are blended to prepare layered silicate nanocomposites; these are intercalation and exfoliation. Intercalated structures are formed when a single or sometimes more extended polymer chain is intercalated between the silicate layers. The result is a well-ordered multilayer structure of alternating polymeric and inorganic layers, with a characteristic repeating distance between them, whereas the exfoliated or delaminated structures are obtained when the clay layers are well separated from one another and individually dispersed in the continuous polymer matrix. In the latter case, the polymer separates the clay platelets more than in the first one. The exfoliation or delamination configuration is of particular interest because it maximizes the polymer–clay interaction making the entire surface of layers available for the polymer. This could lead to the most significant changes in mechanical and physical properties [3]. For most technologically important polymers, a direct melt intercalation method is the most versatile and environmentally benign among all the methods of preparation of polymer–clay nanocomposites.

The layered silicates (clays if they are of natural origin) may be exfoliated and/or intercalated in the related nanocomposites. Only a few standard tools can be used to characterize the formation of nanocomposites. The most suitable techniques to detect the dispersion of layered silicates are transmission electron microscopy (TEM), X-ray diffraction (XRD) and rheological measurements [4]–[10].

In [11], [12] it is shown that the nanoclay dispersion in polyamide 66/polypropylene (PA66/PP) blends.

The major results of this work revealed that the exfoliated/intercalated clay layers are exclusively located in the more polar PA6 phase in unmodified blends, and that adding nanoclay results in a finer dispersion state of the nanoclay (octadecylamine intercalated montmorillonite). Furthermore, it was established that the clay layers are preferentially embedded in a PA6-grafted polyolefin phase, formed via chemical reactions between the amine groups of the PA66 and the anhydride groups of the maleated PP (PP-g-MAH). It was suggested that the melt viscosity of the treatment also affects the dispersion state of the nanoclay. It would be quite difficult to get proper information on the dispersion of the organoclay in PA6/PP blends solely using rheometers as “confirmations tools”. The scenario is different, however, if the clay dispersion is known from SEM and XRD results. Therefore, this paper was aimed studying the rheological behavior of PA6/PP/organoclay nanocomposites at both high and low shear rates and to interpret the rheological characteristics as a function of the morphology of the nanocomposites.

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II. Experimental Part

A. Nanocomposite Preparation

The PP (MOPLEN) was supplied by Himont Company. The MFI of PP is 28 g/10 min (at 230 °C and 2.16 kg load).PA66 (Technyl®A216) used in this study was a commercial product from Rhone Poulenc Company (France). Nanoclay (DELLITE 67G) was a commercial product from Laviosa Company (Italy). The mean dry particle size of nanoclay was between 7 and 9 µm. PP-g-MA compatibilizer was synthesized by [13].

The formulations were extrusion compounded and injection molded as described in [11], [12]. The designation and composition of the materials is given in Table I.

B. Morphological Characterization Scanning Electron Microscopy Analysis

Notched fractured surfaces of the different formulations were examined under a scanning electron microscopy operating at 10-15KV. Before scanning, a conductive coating layer was spread on the surface of the sample.

C. Rheological Measurements

The melt flow index of various nanocomposites was measured by using Melt Flow Indexer (at 230°C, load 2.16 kg). Rheological measurements were made in dynamic mode on a rheometer Rheo Stress 600 (Thermo Hakee) equipped with parallel plate geometry (plate diameter 20 mm). Dynamic frequency scan tests were conducted for all samples at a strain sweep of 1% at 240 °C. The strain amplitude (1%) was within the linear viscoelastic region as deduced from dynamic strain scan tests performed for all PP/PA66//nanoclay nanocomposites.

III. Results and Discussion

A. Morphological Characterization Scanning Electron Microscope Analysis

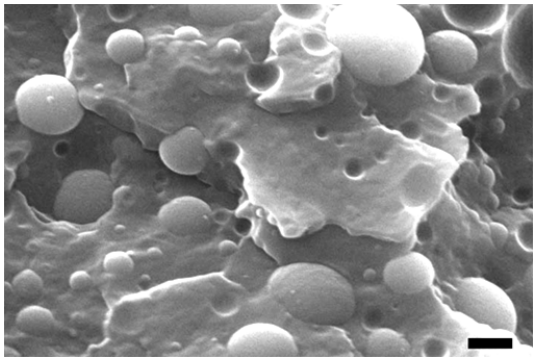
Fig. 1 represents the morphology of the impact fractured surfaces of unmodified nanocomposites (S0) and modified ones containing 4, 5 and 6 wt% nanoclay (S4,S5,S6). Micrograph (a) shows a classical alloy where the particles of dispersed phase (PA66) are well anchored the matrix (PP) and a good interaction between PP and PA66. Similar observations have been reported elsewhere [14].

Figs. 1 (b)-(d) represent the effect of the nanoclay content. A drastic change in morphology is clearly observed. Flow induced morphology has been introduced for the nanoclay. Well aligned molecular chains are observed. This stacking behaviour is due to the lamellar shape of the clay, the enhanced clay treatment surface and the intercalation phenomena [15], [16].

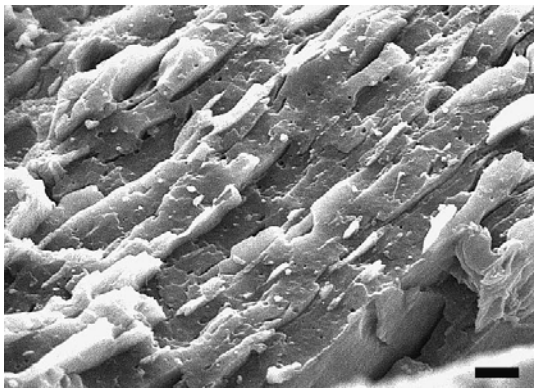
The realised morphology shows exfoliated silicate layers distributed in the PP phase. However, there are also some layered silicate agglomerates which coexist with the exfoliated and intercalated ones in the PP phase. It also indicates the interaction between the amine groups of octadecylamine intercalate of the exfoliated nanoclay and amide groups of the PA66 and PP-g-PA66 [17], [16].

TABLE I
Designation, Composition, MFI, and Density Values of Samples

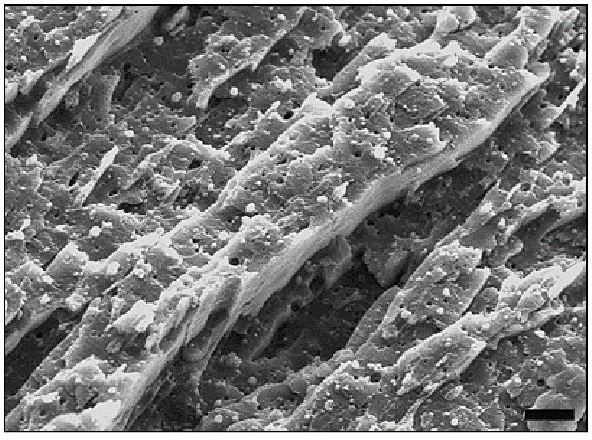
Sample designation	Composition (Phr)	MFI (g/10min)	Density (g/cm^3)
S0	PP/PA66/PP-g-MAH/DELLITE67G (70/30/5/0)	76.76	0.933
S2	PP/PA66/PP-g-MAH/DELLITE 67G (70/30/5/2)	32.41	0.955
S4	PP/PA66/PP-g-MAH/DELLITE 67G (70/30/5/4)	8.81	0.926
S5	PP/PA66/PP-g-MAH/DELLITE 67G (70/30/5/5)	4.67	0.930
S6	PP/PA66/PP-g-MAH/DELLITE 67G (70/30/5/6)	3.72	0.931
S8	PP/PA66/PP-g-MAH/DELLITE 67G (70/30/5/8)	3.69	0.950



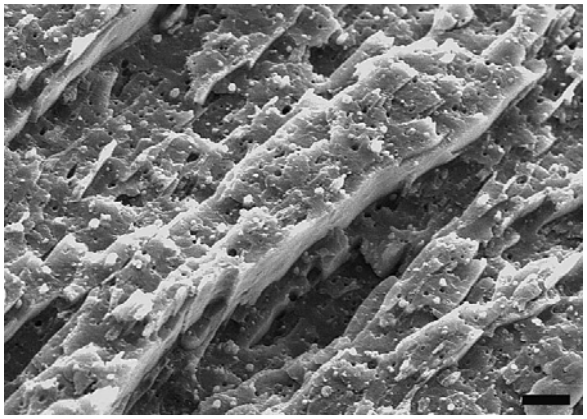
(a) Gr.x4000 (5µm)



(b) Gr.x1000 (20 µm)



(c) Gr.x2000 (10µm)



(d) Gr.x2000(10μm)

Fig. 1 SEM micrographs of impact fractured surfaces of samples: (a) unmodified nanocomposite S0, (b) modified nanocomposite with 4%wt nanoclay S4,(c) modified nanocomposite with 5%wt nanoclay S5, (d) modified nanocomposite with 6%wt nanoclay S6.

B. Rheological

Table I shows the MFI values of the nanocomposites. Note that the MFI decreases with increasing nanoclay content. The decrease in the MFI may be traced to two possible factors: (a) flow hindrance by the nanoclay particles, and (b) interaction between the nanoclay (mainly primary amine groups) and the PA66. Amine (nanoclay)-amide (PA66) interaction via hydrogen bonding may be at work. Furthermore, filling of the polymers along with the related filler-filler interaction reduced the melt flow of the polymer matrix. This may be attributed to the formation of a graft copolymer, viz PA66-g-PP, due to the chemical reactions between the amine (primary, secondary) and anhydride groups. All of the listed interactions raise the melt viscosity and thus reduce the MFI. These results are in harmony to the MFI data (Table I). A deeper insight into the morphology-dependent flow behavior was expected from the rheological measurements performed in the viscoelastic range.

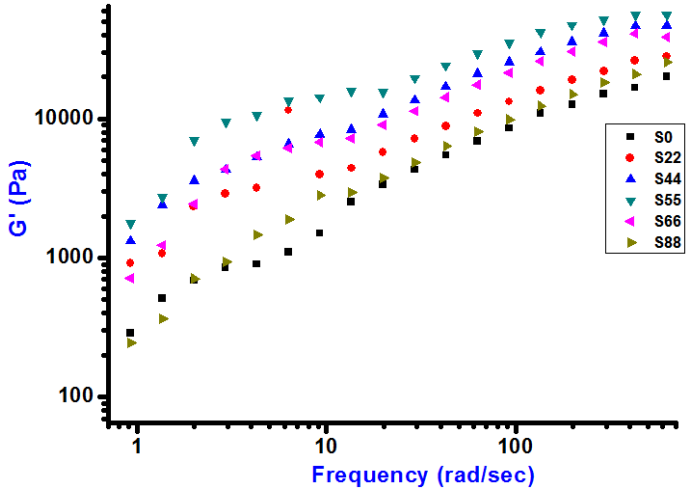


Fig. 2 Storage modulus vs frequency

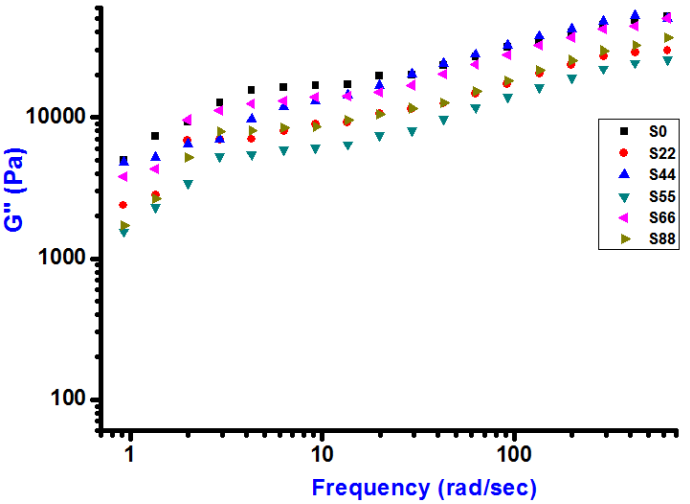


Fig. 3 Loss modulus vs frequency

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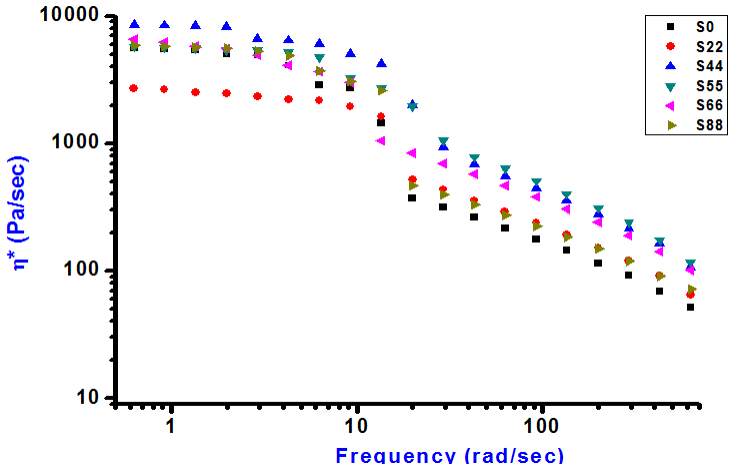


Fig. 4 Complex viscosity vs frequency

The storage (G') and loss (G") moduli resulting from dynamic frequency scans are depicted in Figs. 2 and 3, respectively. Both G' and G" increased monotonically in the covered frequency range when nanoclay was introduced to the PA66/PP blends. This reflects the strong effect of the intercalated/ exfoliated clay layers on the viscosity of the PP, which forms the continuous phase (matrix) in the blends. Recall that the clay is exclusively located in the PA66 phase. G' and G" at the same frequency strongly increase with nanoclay content.

According to [18] changes of G' and G" in the viscoelastic range sensitively reflect the effect ofclay dispersion.

The higher the variation, the less stable the clay dispersion is. At lower frequency (at 1 rad/s) the polymer chains are fully relaxed and thus alterations in G' and G" including their slopes are likely to be linked to the effect of the clay dispersion. The variation in the low frequency viscoelastic range decreases with nanoclay loading. This holds for all nanocomposites at 1 and 100 rad/s frequencies. This change indicates that the nanocomposites attained a pseudo solid-like behaviour due to the nano-reinforcing effect of the intercalated/exfoliated clay. Similar results were reported by [19]. The higher the G' moduli and the smaller the value variation (at lower frequency), the more pronounced the interaction between the silicate platelets and their tendency to form a three-dimensional superstructure [19]. In the latter case, clay tactoids are easily discernable. One can thus underline that rheological characteristics (G'), in the low frequency viscoelastic range, may reflect even small changes in the clay dispersion accordingly.

Fig. 4 depicts the course of the complex viscosity as a function of frequency for the viscoelastic range assessed by a plate-plate rheometer. The viscosity increased with increasing nanoclay content. Note that the viscosity ofPA6/PP blends modified by nanoclay is higher than that of the unmodified PA6/PP blends. The higher viscosity value is probably attributed to the chemical reaction between the MAH group of the compatibilizer (PP-g-MAH) and the amino end-group of PA66 during the melt mixing process. According to [20] the increase in viscosity of PP/PA66/PP-g-MAH blends is due to the stronger interaction provoked by the presence of the maleic groups and/or by the formation of new covalent bonds between MAH groups and the terminal amine groups of the PA66. A similar observation was also reported by [21].Another possible reason is that the silicate layers of the nanoclay have been well exfoliated/intercalated in the presence of the compatibilizer. Thus, during low deformation (e.g. at low shear rate or frequency), the "original" dispersion of the nanoclay (being exfoliated/intercalated) could be observed through its effect on the rheological behavior. According to [22] at low shear rates, the silicate platelets of high aspect ratio are well separated and this strongly increases the viscosity of the melt. On the other hand, at higher shear rates the platelets are oriented in the flow direction, which consequently leads to a reduction in the viscosity.

It is worth noting that the viscosity changes observed (Fig. 4) are in harmony with the MFI results. One would expect that the higher the viscosity, the better the clay exfoliation. This prediction is due to the fact that an intimate clay/polymer interaction is accompanied with a strong viscosity increase. However, if the clay layers are well separated from each other (exfoliated stage) then shear thinning is more probable than in the case of intercalated tactoids. Recall that shear thinning presumes an alignment of the clay layer in the flow direction, which occurs easily in exfoliated stage. Interestingly, the cited argument holds also when viscosity data at 100 rad/s are considered.

IV. Conclusion

Based on the results of the present study, the important conclusions can be drawn: The rheological behavior showed that, the complex viscosity is increased with increasing the nanoclay content; however, at low frequencies this increase is governed by the content of nanofiller while at high frequencies it is mainly determined by nanoclay content. A similar trend was also observed for the variations of storage modulus (G′) and loss modulus (G″) with frequency. The results showed that the use of nanoclay considerably affects the melt elasticity. SEM analysis showed the development of a lamellar

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morphology by the clay treatment of nanoclays especially by incorporation of 5 wt.% of nanoclay.

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