Rheological Characterization of Melt Compounded Polypropylene/clay Nanocomposites.

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ABSTRACT

Polypropylene/clay nanocomposites were prepared by using a two step melt compounding process on twin screw extruders. The PP-clay nanocomposites were rheologically investigated. The melt rheological measurements were performed using an ARES-rheometer in the dynamic mode at 220°C over frequency varying from 100 to 0.017 rad/s and in the parallel plate geometry with 25 mm diameter.

The results showed that the storage modulus and viscosity are found to be increased with the incorporation of clay into PP. The values of storage modulus and viscosity are significantly increased by the incorporation of modified clay and their rheological behavior changed completely.

The results of samples with modified clay showed an evidence of the exfoliation which could be detected rheologically.

Key words: PP/Clay Nanocomposities, Intercalation, Exfoliation, Rheology

1 INTRODUCTION

Polymer nanocomposites are nowadays the subject of intense research efforts owing to their various unique properties [1-2]. In recent years, polymer/clay nanocomposites have attracted great attention both in industry and academia in achieving various excellent properties of nanocomposites compared to conventional ones. These nanocomposites based on nanoscale-layered silicates exhibit remarkable improvement compared to the conventional micro-composites in various properties as reported by many authors [3-15]. Nanoscale-layered silicates does not use as only reinforcement material for polymers but also can change morphology of immiscible polymer blends. Nanocomposites based on clay and polypropylene have given currently considerable attention because of their potential in improvements the mechanical properties, heat resistance, gas permeability, and flammability barrier properties and the thermostability [16-27]. Clay-based nanocomposites have been studied for different polymers such as polypropylene, polystyrene, polyethylene, polyethylene oxide , poly (ε-caprolactone), and polyamide, etc. [28-36]. Polymer/clay nanocomposites have been widely studied using different preparation methods such as in-situ polymerization, solution blending and melt mixing to get the intercalated or exfoliated structures in homopolymers [37-43]

Melt rheology has been reported as a tool to characterize the polymer–clay nanocomposites [44]. It is known that melt rheology is very sensitive in characterization of the formation of percolated structures of anisotrop fillers in polymeric matrices. This was shown for different kind of fillers, like micrometer sized fibres, montmorillonite nanocomposites as for carbon nanotubes composites [45]. Therefore, it was the task of this study to characterize rheologically the polypropylene/clay nanocomposites with different weight ratios, detect the exfoliation with hope to determine the degree of the exfoliation using the rheology tool.

2 EXPERIMENTAL

Materials: In this work, Polypropylene/clay nanocomposites with an inorganic content of 5 wt% were prepared by melt compounding using a two step melt compounding process on a co-rotating twin screw extruder ZE 25 (Berstorff, Hannover). In the first step a masterbatch of an organically modified montmorillonite (Nanofil® 15 from Süd-Chemie, Moosburg) and a maleic anhydride-modified polypropylene (PP-g-MAH grade TPPP 2112 FA from Kometra, Merseburg) was compounded. In the second step this concentrate was diluted in the PP matrix to the nanocomposite with the focused clay content. This procedure results in optimum polypropylene nanocomposites performance concluded from comprehensive investigations of the compounding process [46]. Additionally, the influence of the process regime in the batch stage by combination of a reactive modification of PP-g-MA in situ with poly(alkyleneoxide)diamines with the compounding of the organoclay was investigated. Improved adhesion of this compatibilizer and the clay platelets in comparison to PP-g-MA, as no debonding could be observed in TEM images, and supported exfoliation of the clay using rheological methods was obtained [47].

Rheology: The PP/clay nanocomposites were rheologically investigated. The melt rheological measurements were performed using an ARES-rheometer (Rheometrics Scientific, USA) in the dynamic mode at 220°C over frequency varying from 100 to 0.017 rad/s and in the parallel plate geometry with 25 mm diameter. The strain amplitude was kept in the linear viscoelastic range.diameter and gap about 1mm.

3 RESULTS AND DISCUSSIONS

The rheological characterization of PP/clay nanocomposites in terms of the storage modulus, G', loss tangent and complex viscosity as function of frequency will be presented in this section.

Figure 1 shows an increase in the storage modulus, by the incorporation of clay into neat PP matrix. This enhancement in the dynamic modulus is significant, in particular, at low frequencies regime. As shown in Figure 1, the loading of 5wt% clay results in rising G' by factor around 4 at frequency 0.056 rad/s. This increase origins from the formation of physical network-like structure by the polymer chains and nano-filler. Additionally, the incorporation of high modulus material (clay) into PP leads to increase the dynamic modulus. However, the rheological behaviour does not change by the addition of 5 wt% unmodified clay. Since at low frequencies zone the PP/clay(5% non-modified) composite has liquid-like behavior as well as neat PP. The same weight of organomodified clay (5w%) changes the rheological behavior from liquid like to solid-like material . As shown in Figure 1 at low frequencies G' becomes nearly independent on the frequency at which second plateau appears in the low frequencies regime starting from ω 0.1 rad/s. This is an evidence of the exfoliation or rather partial exfoliation. This mechanism can be explained as; the diffusion of polymer molecules is favoured by making the galleries chemically compatible with the polymer. The comptability occurs by exchanging interlayers inorganic clay cations with organic cations (such as the alkylammonium cations) . Therefore, layer distance, gallery distance, of modified clay increases due to the modifier. Particles are distributed into single platelets . Clay platelets are distributed and dispersed into polymer matrix. The Compatibilizer (PP-g-MA) decreases the surface tension between silicate and polymer matrix. That enhances the dispersion, thus, the exfoliation.Meanwhile, the contribution of intercalation can not be ignored in such system. The values of storage modulus for PP/clay composite with modified clay increase by many order of magnitude. At ω 0.056 rad/s G' of PP/clay nanocomposite with 5wt% modified clay is greater by factor about 150 times than neat PP, meanwhile, its value higher by factor around 40 times than this composite with the same loading of non-modified nano-clay (5wt%). That reflects the development of the physical interaction between polymer chains and the layers of nano-clay.

The effect of reactive addition on the exfoliation was insignificant as shown in Figure 1, thus, G' shows nearly no improvement.

The same scenario was found in the melt viscosity. As shown in Figure 2, the viscosity increases by the incorporation of clay into neat PP, particularly, at low frequencies regime. At which the Newtonian behavior is clearly seen for both of neat PP and PP/clay composite with 5wt% non-modified clay. Modified 5wt% clay changes the behavior and values of viscosities drastically. As shown in Figure 2, at low frequencies, the viscosity changes from Newtonian to shear thinning behavior. The increase of the viscosities values prove the physical network-like structure. Pronounced shear thinning has been reflected the nanodispersion. This is another evidence of the exfoliation which could be detected rheologically. 5wt% of organophilic montmorillonite in presence of PP-*g*-MAH which promotes clay exfoliation and sufficient interfacial adhesion between filler and PP. The well-distributed, very thin silicate packages within he PP matrix results in high degree of exfoliation. Shear thinning behavior with higher slope for better clay dispersion was previously observed for other nanocomposites in the literature [48].

Again the effect of reactive is invisible. This is, may be, related in somehow to the full exfoliation of nano-clay ,therefore, the influence of reactive addition is insignificant.

non-modified claysince h results in increasing G' In this article we are going to focus on The results showed that the dynamic mechanical moduli and viscosity increase with the incorporation of clay into PP and their values are found to increase with increasing the clay loadings particularly is significant at low frequencies. This increase origins from the formation of network-like structure, in addition to, the incorporation of high modulus material (clay) into PP.

Figure 3 shows the influence of clay feeding position on the viscosity of PP/clay composites with non-reactive modifier. As shown in this Figure there is , nearly, no difference between the viscosities of sample with side feeding clay and hoper feeding clay.

Here we can conclude that the prepared samples with reactive modifier, clay side feeder at 220°C show enhancing “slightly” the degree of exfoliation or rather it does not influence the values of the absolute viscosity.

The loss factor, tan δ, is plotted versus ω in Figure 4. tan δ relates the loss modulus to the storage modulus. It , somehow, indicates the viscoelasticity of the material. The addition of clay changes the viscoelasticity of PP. As shown in Figure 4, tan δ decreases by incorporation of clay into PP. That is noticeable in particular at low frequencies lower than 3 rad/s. This indicates the increase of the elasticity of the material. 5wt% loading of modified clay results in drop of tan δ at low frequencies which it becomes , nearly, independent on frequency along the measured frequencies. This is because of the development of the elastic component due to the high density of the physical interactions (Formation of elastic network-like structure). It is an indicator of exfoliation.

The effect of thermal treatment is clearly seen in Figure5. In this figure the viscosity increases by increasing the annealing time. As shown in this Figure the shear thinning exponent increases as well as the absolute values of the viscosity with increasing the annealing time up 6 hours at 220 C . followed by stability. This is, may be, because of enhancing of exfoliation. The degree of exfoliation was increased with increasing the annealing time at 220°C up to 6 hours followed by independent on the time. Here, the increasing in the degree of exfoliation is attributed to the enhanced dispersion of clays. The dispersion of clay layers in the molten polymer depends on thermal diffusion of polymer molecules in the interlayer space galleries. The swelling effect of the clay layers up to a certain limit can be the reason.

4 CONCLUSION

In this work, polypropylene/clay nanocomposites were prepared by using a two step melt compounding process on twin screw extruders.

The materials were rheologically characterized. The rheological measurements are performed using an ARES-rheometer in the dynamic mode at 220°C over frequency varying from 100 to 0.017 rad/s .

The results showed that the the storage modulus and the viscosities are increased with the incorporation of clay into PP.

The exfoliation was detected rheologically and the results was given an evidence of the exfoliation for the samples with modified clay. However, the unmodified clay showed no sign of the exfoliation.

The change in the reactive modifier and clay feeding position did not influence the exfoliation.

The shear thinning exponent was increased with increasing the annealing time at 220°C up to 6 hours followed by independent on the time.

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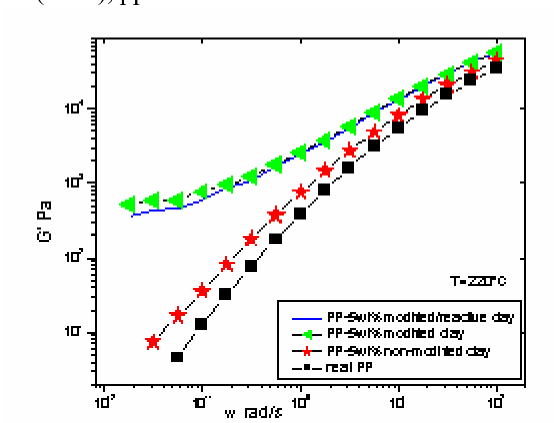

Figure 1. Frequency dependence of *G'* measured at 220 °C for the PP/clay nanocomposites.

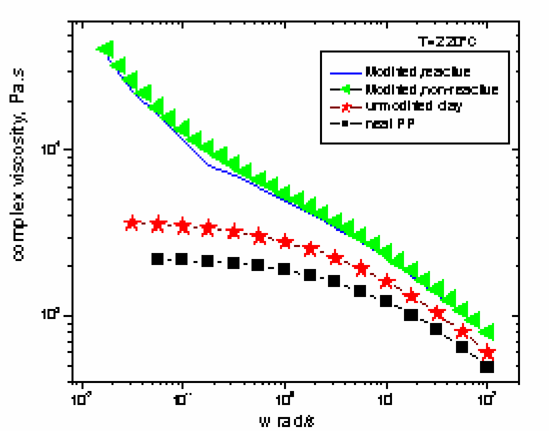

Figure 2. Frequency dependence of complex viscosity

$|\eta^*|$ measured at 220 °C for the PP/clay nanocomposites.

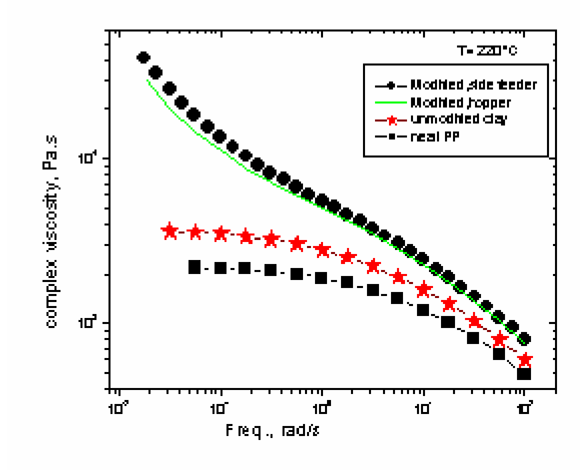

Figure 3. Frequency dependence of complex viscosity measured at 220 °C for the PP/clay nanocomposites.

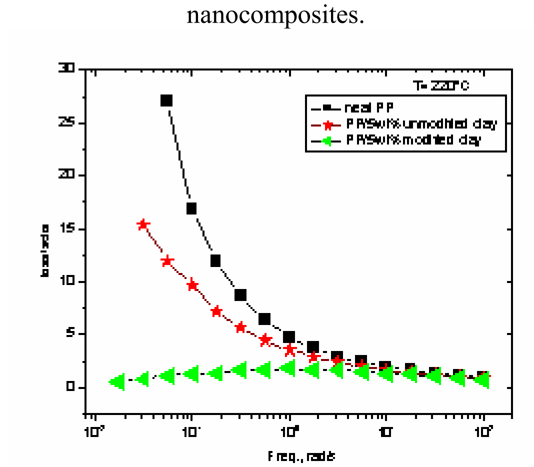

Figure 4. Frequency dependence of loss factor measured at 220 °C for the PP/clay nanocomposites.

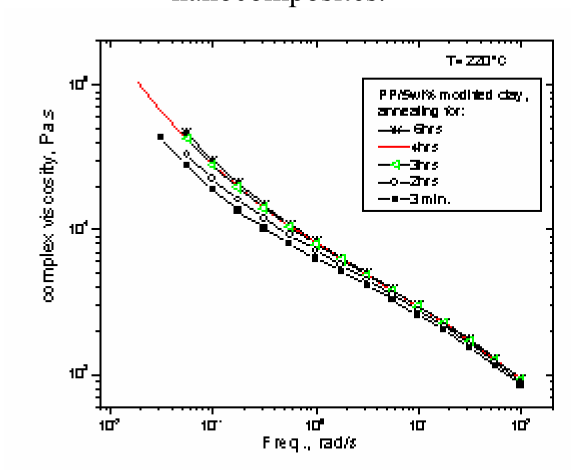

Figure 5: Effect of annealing time on the exfoliation process