

Network Formation in PP/Layered Silicate Nanocomposites: Modeling and Analysis of Rheological Properties

János Kovács,^{1,2} Zita Dominkovics,^{*1,2} György Vörös,^{1,3} Béla Pukánszky^{1,2}

Summary: PP/organophilic montmorillonite composites were prepared from PP homopolymer, maleinated polypropylene and a clay organophilized with octadecyl amine. Various approaches were used to analyze the rheological properties of the composites. Cole-Cole plots proved to be useful, since they detect the network very sensitively. The frequency dependence of the real part of complex viscosity was described with a series of Maxwell bodies coupled parallel to each other. The relaxation time of the melt changed in the range of 0.0005 and 200 sec. Under certain conditions long relaxation times appear in the spectrum, which indicate the formation of new structural units, probably a silicate network. A certain number of silicate layers are needed to create a house-of-cards structure. A threshold concentration of MAPP exists for network formation, which depends on silicate content.

Keywords: layered silicates; PP; rheology; silicate network; structure

Introduction

Recently, many attempts are in progress to modify PP with layered silicates to prepare nanocomposites. However, such nanocomposites cannot be produced from an organophilized silicate, mainly montmorillonite (OMMT) and the polymer, since the exfoliation of the clay does not take place spontaneously during processing; a functionalized polymer, usually maleinated PP (MAPP), must be added to the composite.^[1] The introduction of MAPP leads to intercalated and/or partially exfoliated structures with improved properties. Modulus, strength and some other characteristics often have a maximum as a

function of silicate content, which indicates changes in the structure with composition. Layered silicates easily exfoliate in water to individual silicate layers. At large clay content the layers interact with each other in the slurry. Face-to-face interactions lead to aggregation, while edge-to-face interactions result in the formation of a network, often referred to as house-of-cards structure. Both interactions are claimed to occur also in PP/layered silicate composites. Aggregation obviously deteriorates properties. Relatively little is known about the formation of the network structure and its effect. The exact conditions for network formation are not known either, they must depend on the properties of the components, composition, processing conditions, which all influence the extent of exfoliation and the number of platelets dispersed in the matrix. Usually the network is detected either by transmission electron microscopy (TEM) or rheology, or both. The TEM micrographs presented in papers on house-of-cards structures are not very convincing and do not differ much from other pictures taken from PP/layered silicate nanocomposites

¹ Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, P.O. Box 91, Hungary Fax: 0036-1-463-3474; E-mail: zdominko@mail.bme.hu

² Institute of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary

³ Department of General Physics, Eötvös University Budapest, H-1518 Budapest, P.O. Box 32, Hungary

not having such a morphology. Rheology is less subjective than TEM, but the small changes usually detected in the shape of viscoelastic functions might render detection difficult.^[2,3] The goal of our study was to find approaches which detect network formation more sensitively than usually applied techniques and make possible the determination of the conditions of its formation.

Experimental Part

The Tipplon H 649 grade PP homopolymer (MFR=6.0 g/10 min at 230 °C, 21.6 N) produced by TVK, Hungary, was used as matrix, while Nanofil 848 (Süd-Chemie GmbH) was employed as clay. The silicate (CEC = 120 meq/100 g) was compatibilized with 25 wt% octadecyl amine corresponding to about 103% surface coverage. A small molar mass maleinated PP, Licomont AR 504 (MA content 3.5 wt%, viscosity 0.8 Pas at 170 °C, Clariant GmbH), was used to promote exfoliation. The organo-clay content of the composites changed from 0 to 3.0 vol%, while the amount of MAPP varied between 0 and 50 vol%. The components were homogenized in a Brabender W 50 EH internal mixer at 190 °C, 50 rpm for 10 min and then compression molded to 1.0 mm thick plates. Disks of

25 mm diameter were cut from the plates for rheological testing. The measurements were carried out using a Paar-Physica UDS 200 apparatus at 200 °C in oscillatory mode in the frequency range between 0.1 and 600 sec⁻¹. The amplitude of deformation was 5%, which was in the linear elastic region as confirmed by an amplitude-sweep with controlled shear deformation. Other techniques were also used for the characterization of the structure and properties of the composites, but only the results of rheological measurements are reported here.

Rheology, Representation

In order to study the results of rotational viscometry carried out in the oscillatory mode, the various viscoelastic characteristics of the material are usually plotted as a function of frequency. Such a graph is presented in Figure 1a for the composite containing 2.0 vol% organophilic silicate and 40 vol% MAPP. Very little information can be derived from the figure showing the frequency dependence of the storage and loss moduli, as well as that of the complex viscosity of the composite. One can see that moduli increase, while complex viscosity decreases with increasing frequency as expected. Occasionally characteristic values are derived from such graphs, like the cross-over frequency or the corresponding modulus. These quantities are claimed to be

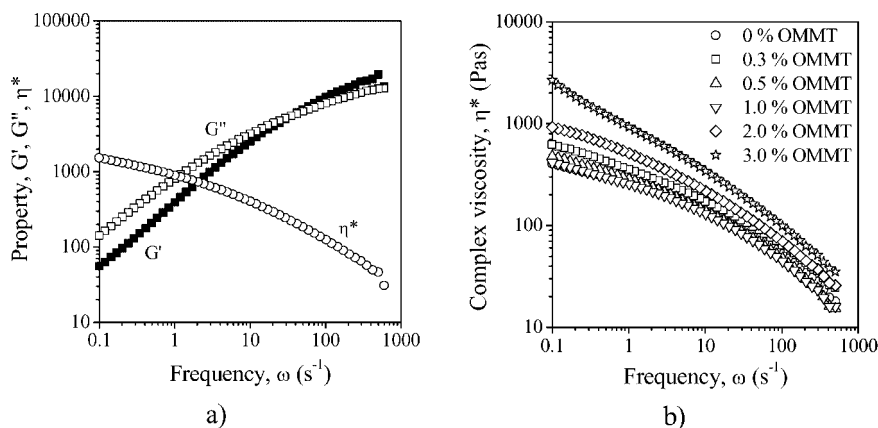


Figure 1.

Frequency dependence of the viscoelastic characteristics of PP/OMMT/MAPP melts. a) 2.0 vol% silica, 40 vol% MAPP, b) effect of silicate content on the complex viscosity of the composites at 50 vol% MAPP content.

related to molecular structure in neat polymers, but their physical meaning is less clear in heterogeneous polymer systems. We also plotted various dynamic characteristics of our materials (G' , G'' , η' , η'' , η^*) determined at various frequencies (0.1 and 100 s⁻¹) as a function of composition (not shown), but could not derive any important information related to the structure of the melt from them.

A closer scrutiny of the correlations presented in Figure 1a and its comparison to the similar plots of other materials show slight differences as a function of composition in the low frequency range. A small upward turn can be detected both in storage modulus and complex viscosity at large silicate and MAPP contents. The phenomenon is demonstrated in Figure 1b, in which the complex viscosity of the composites is plotted against frequency at 50 vol% MAPP and various silicate contents. The tendency mentioned above is clearly seen in the figure; changes can be detected first at 2.0 vol% silicate content, but significant effect is observed only at the largest OMMT content studied.

In an earlier study^[3] we observed that differences in the viscoelastic behavior are indicated much more sensitively by another representation of the experimental data, by

the so called Cole-Cole plots.^[4] The real and imaginary components of viscoelastic properties are plotted against each other in such representation and a regular semi arc is obtained if the deformation behavior of the material can be described with a single relaxation time,^[4] which is usually not the case. In real materials, processes with more than one relaxation time take place leading to the distortion of the arc or to the appearance of a second arc. The effect of silicate content on the viscoelastic behavior of the melt is shown in the Cole-Cole representation in Figure 2 at two different MAPP contents. At 10 vol% MAPP content distorted semi arcs are obtained indicating that the rheological characteristics of the matrix polymer dominate the behavior of the composite. The correlations are completely different when the amount of functionalized polymer is larger (50 vol%). The change in the shape of the plot indicates the appearance of a process with long relaxation times; earlier we related this behavior to the formation of a silicate network.^[3]

Modeling

Although Cole-Cole plots indicate the formation of the silicate network very sensitively, they offer only qualitative

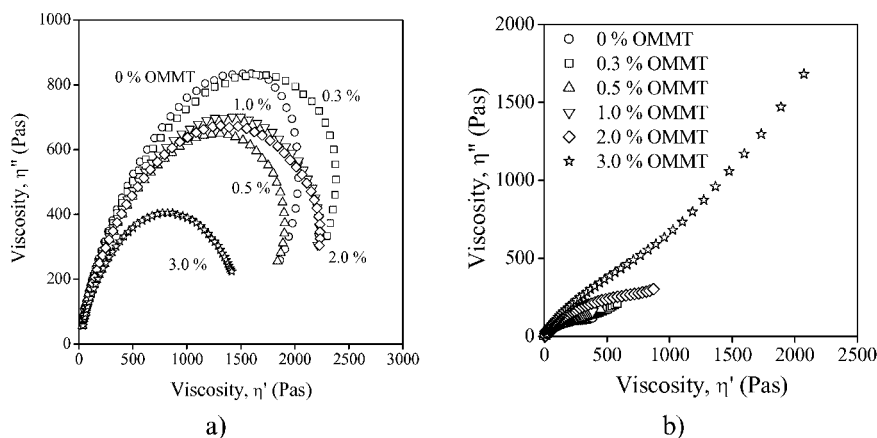


Figure 2.

Cole-Cole representation of the viscosity of PP/OMMT/MAPP melts; effect of silicate content. a) 10 vol% MAPP, b) 50 vol% MAPP.

information about changes in the viscoelastic properties of the melt. In order to describe the rheological behavior of our composites quantitatively, the real component of complex viscosity was modeled by a series of Maxwell models coupled parallel with each other.^[5] The dependence of viscosity on frequency was described as:

$$\eta'(\omega) = \eta_1 + \int_{\tau_a}^{\tau_f} \frac{m(\tau)}{1 + \omega^2 \tau^2} d\tau \quad (1)$$

where τ_a and τ_f indicates the lower and upper boundary of relaxation times, which are considered in the frequency range used in the study. η_1 takes into account the contribution of rapid processes having relaxation times shorter than τ_a . $m(\tau)$ indicates the relaxation time spectrum of the material. Relaxation times varied between 0.0005 and 200 s in our calculations. The first order Fredholm type integral equation presented above (Eq. 1) is very sensitive to the natural deviations of the experimental values. In order to decrease sensitivity, the function was supplemented with a smoothing term (λ). The minimum of the following function was determined in the procedure of least

squares calculations:

$$S = \sum_i^N \left[\eta(\omega_i) - \eta_1 - \int_{\tau_a}^{\tau_f} \frac{m(\tau)}{1 + \omega^2 \tau^2} d\tau \right]^2 + \lambda \int_{\tau_a}^{\tau_f} \left(\frac{\partial^2 m(\tau)}{\partial \tau^2} \right)^2 d\tau \quad (2)$$

where $\eta(\omega_i)$ is the viscosity measured at ω_i frequency. The value of η_1 and $m(\tau)$ was varied during the calculation and the relaxation spectrum was determined by using discrete values for the $m(\tau)$ function. The term with the λ smoothing parameter is proportional to the total curvature of the spectrum. If the measurements are accurate, its value is small, close to zero. Average relaxation times, $\langle \tau \rangle$, and zero shear viscosity, η_0 were calculated with the approach.

The composition dependence of the two quantities is plotted in Figure 3a and 3b. Average relaxation time starts to change above 20 vol% MAPP content. Interesting to note that average relaxation time increases also in the two-component PP/MAPP blend. We related this change to the phase separation of the two components. The small molecular weight functionalized

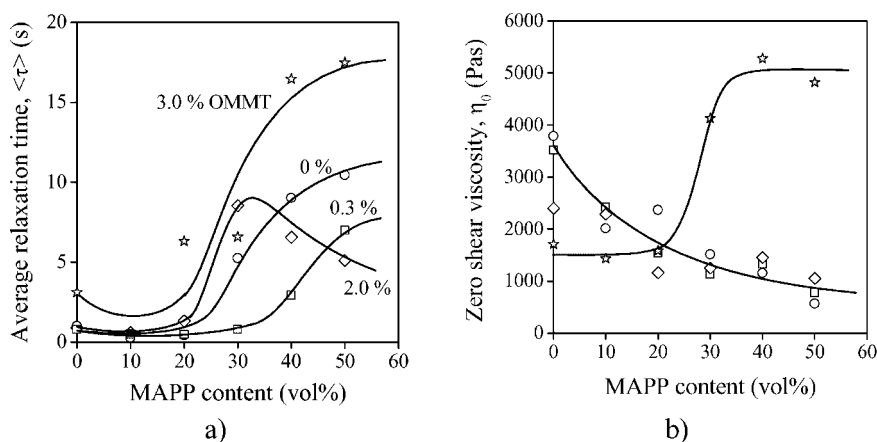


Figure 3.

Characteristic quantities derived from the results of rheological measurements by model calculation; a) average relaxation time, b) zero shear viscosity.

polymer with a relatively high amount of polar groups is not completely miscible with PP. A small amount of silicate decreases relaxation time which can be explained by the interaction of the silicate and the functionalized polymer, as described earlier.^[1] At large silicate content much longer relaxation times are observed, which can be assigned to the deformation of the silicate network. Network formation starts at around 2 vol% and develops fully at 3 vol% silicate content in the studied system. Sufficient number of silicate layers are dispersed already in the melt to form the network at these silicate contents, which is supported also by the disappearance of the silicate reflection from the XRD pattern.^[3] Zero shear viscosity reflects the same changes in a different way and slightly less sensitively. Similarly to earlier results,^[3] the analysis of the results revealed that a critical MAPP content exists for network formation, which depends on the amount of silicate. The critical value is about 40 vol% MAPP at 0.3 and 20 vol% MAPP at 3.0 vol% silicate content.

Conclusions

Under certain conditions a silicate network forms in layered silicate nanocomposites. Sufficient extent of exfoliation is needed for network formation. The silicate network initiates processes with long relaxation times, thus it can be detected very sensitively by rheology. Primary data are difficult to evaluate and interpret, but model calculation may supply data expressing changes quantitatively. Cole-Cole plots reflect changes in structure well.

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