RHEOLOGY AS A POWERFULL TOOL FOR SCIENTIFIC AS WELL INDUSTRIAL CHARACTERISATION OF NEW MATERIALS BASED ON POLYMER-CLAY NANOCOMPOSITES

Milan Kracalik

Johannes Kepler University Linz, Institute of Polymer Science, Altenberger Str. 69, 4040 Linz, Austria

Milan.Kracalik@jku.at

Abstract

Polymer-clay nanocomposites are interesting class of materials due to possibility of fine tuning of processing as well as utility properties. On the one hand, enough studies have been performed until now concerning principles of clay dispersion in different polymer matrices and effect of clay structure on the final material performance. On the other hand, there are still not many products on the market based on polymers reinforced with nano-scaled layered silicates. One of the main difficulties during development of new materials using clay particles consists in long development times, which reflect the complexity of relevant processing processes (compounding, extrusion, injection moulding). Comparing to conventional composites systems, different physical as well as chemical reactions can occur during the mixing of polymer with organically modified clay and, consequently, long development time to find a proper processing routes (temperature profile, screw geometry, screw speed etc.) is necessary. In this contribution, shear as well as elongational rheometry has been applied for the estimation of physical and chemical interactions during the processing. It is shown that combination of shear and extensional rheology can be used for both research structural characterisation as well for fast industrial quality control of nanoclay-based materials.

Keywords: rheology, polymer nanocomposites, clay, shear flow, elongational flow

1. INTRODUCTION (10 pt, bold, gaps 18 and 0)

Polymer-clay nanocomposites have been intensively investigated in the last years because of the significant improvements of processing as well as utility properties [1-3]. Consequently, new tailored materials based on virgin as well on recycled polymers can be prepared [4-5]. The improvement in material properties due to clay addition has usually been evaluated using a combination of morphological (X-ray diffraction, transmission electron microscopy), mechanical (tensile testing) and sometimes also rheological (rotational and capillary rheometry) analyses. However, these conventional methods require expensive scientific instruments as well as additional processing step (sample preparation) and long characterization times. Generally, appropriately dispersed polymer nanocomposites reveal significant enhancements in their properties: higher elastic modulus, tensile strength, thermal resistivity, lower gas and liquid permeability, reduced flammability and improved rheological properties (e.g. higher melt strength and melt elasticity, respectively) compared to the unfilled polymer matrices [6-10]. It was already published that reinforcement in polymer-clay nanocomposites can be estimated very fast using extensional rheometer in combination with a capillary rheometer. Furthermore, it has been proven that the magnitude of melt strength can be correlated with that of tensile strength, i.e. 3D physical network made of layered silicate and polymer matrix, which is responsible for material reinforcement, can be monitored directly using data of extensional rheometry [6]. Therefore, additional time for samples preparation by press or injection moulding as well for long measurements by tensile testing is not required any more if only assessment of the material reinforcement has to be analyzed. In this contribution, selected results of extensional rheometry measured directly during compounding process as well as results of rotational shear rheometry are presented and suitability for industrial and scientific characterization, respectively, is discussed.

2. EXPERIMENTAL

2.1 Materials

For the compounding process, a co-rotating twin screw extruder Theysohn TSK30/40D (Theysohn Extrusionstechnik Ltd., Korneuburg, Austria) using 10 barrel segments and a string die has been employed. The feed rate was set at 10 kg/h with the screw speed variation between 75 - 300 rpm. High as well as low shear screw geometries (indicated as G1 and G2, respectively) have been applied.

2.2 Extensional rheometry

For the fast industrial characterisation, Rheotens 71.97 equipment (Göttfert Ltd., Buchen, Germany) in on-line assemblage with the extruder through a by-pass die has been used. The Rheotens equipment has been set applying wheel acceleration of 60 mm/s^2 and gap between wheels of 0.6 mm. In order to compare the melt strength level of different nanocomposites, the tensile force at a draw rate of 300 mm/s has been chosen as a comparative value. The data have been evaluated from at least 3 measurements for each sample and then average data have been plotted.

2.3 Rotational rheometry

Rheological properties in the shear flow (scientific characterization) were studied using a Physica MCR 501 rheometer (Anton Paar Ltd., Graz, Austria) with the cone-plate geometry of 25 mm diameter and automatically controlled gap of 50 µm. The samples thickness was 0.7 mm. Experiments were performed under nitrogen to prevent degradation of samples. The following types of rheological measurements were carried out: (1) dynamic strain sweep test (at angular frequency of 6.28 rad/s) to confirm the linearity of viscoelastic region, (2) dynamic frequency sweep test over a frequency range of 0.1 - 500 rad/s, at the strain 0.01 %. The data have been evaluated from at least 3 measurements for each sample and then average data have been plotted.

3. RESULTS AND DISCUSSION

3.1 Extensional rheometry

In Fig. 1, the melt strength level of different nanocomposites in dependency on screw speed and screw geometry is plotted. It is obvious that for specific screw geometry a critical screw speed with optimal shear rate as well as residence time occurs. For geometry 2 this critical screw speed is shifted from 100 rpm (G1) up to 150 rpm, because no kneading blocks in G2 geometry have been assembled and the shear rate acts proportionally to the screw speed. That means, with higher screw speed higher shear energy is applied to the melt and a lower amount of kneading blocks is required. As a consequence of increased screw speed, the residence time is shortened. This explains generally reduction in melt strength when applying screw speed higher than 100 rpm (G1) and 150 rpm (G2), respectively, because silicate dispersion in polymer melt is a diffusion process as well and appropriate residence time is required. Comparing the shear energy applied during compounding, nanocomposites prepared using low shear screw geometry revealed higher level of the melt strength than those prepared with high shear screw geometry.

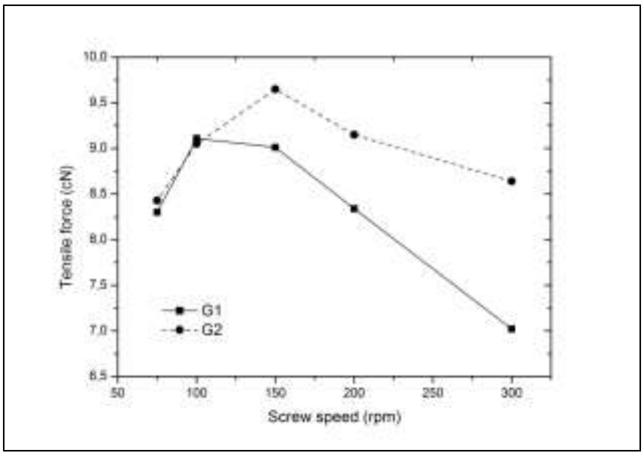

Fig. 1: Melt strength level of nanocomposites

3.2 Rotational rheometry

In Fig. 2-5, magnitudes of complex viscosity as well as storage modulus in dependency on angular frequency are plotted. According to Fig.2, the systems prepared with high shear screw geometry revealed pronounced shear-thinning behaviour except of nanocomposite prepared using screw speed of 300 rpm. This nanocomposite revealed the lowest level of melt strength (Fig. 1) as well. However, the G1-100 system exhibiting the highest melt strength level in the G1 sample group did not show the highest values of complex viscosity. The remaining samples in G1 group show no correlation between elongational and shear data as well.

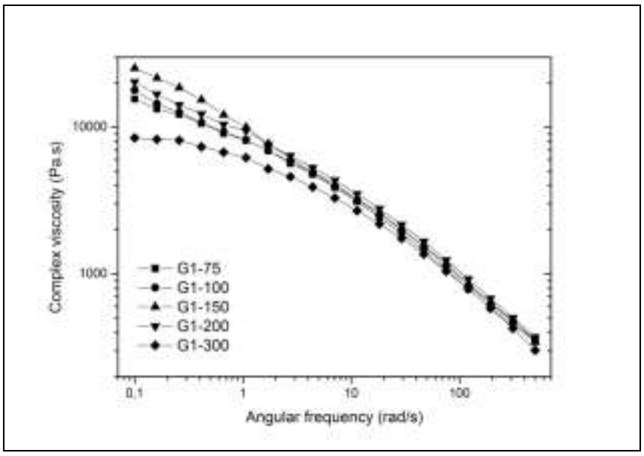

Fig. 2: Viscosity curves of nanocomposites (G1)

Analogical, the values of storage moduli i.e. melt elasticity (Fig. 3) of the G1 samples revealed indication of G´ secondary plateau except of G1-300 sample. This can be assumed to delaminated (partially exfoliated) structure in G1-75 – G1-200 samples and rather low level of silicate delamination in G1-300 sample [7].

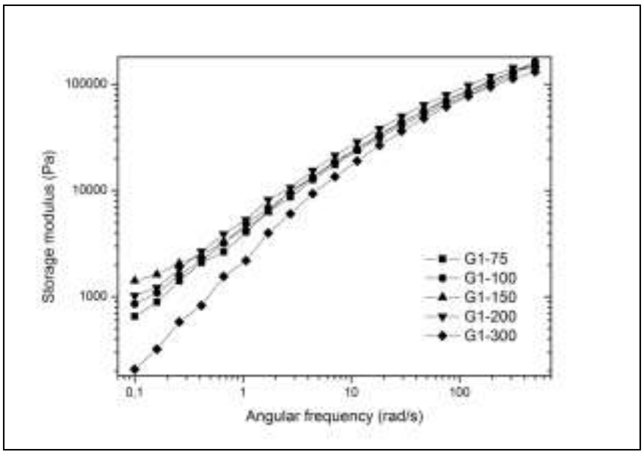

Fig. 3: Melt elasticity of nanocomposites (G1)

In the G2 sample group (Fig. 1, 4, 5), the highest values of melt strength level, complex viscosity and melt elasticity exhibited G2-150 system while the lowest values have been found in G2-300 sample. However, the differences in complex viscosity and storage modulus values within the G2 sample group are not pronounced enough to ensure reliable interpretation. Furthermore, it is not possible to correlate elongational data with shear data for the G2-75, G2-100 and G2-200 samples.

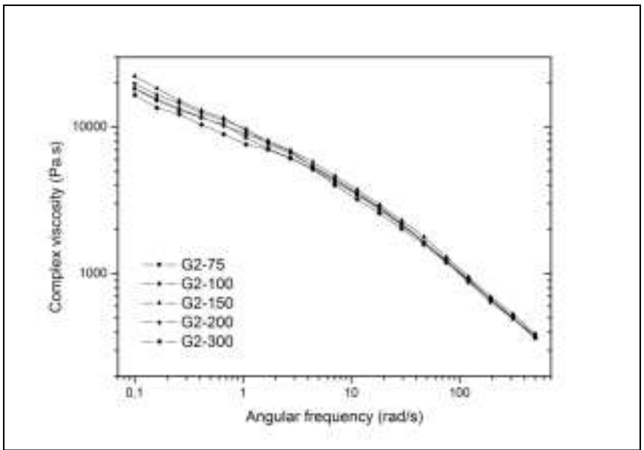

Fig. 4: Viscosity curves of nanocomposites (G2)

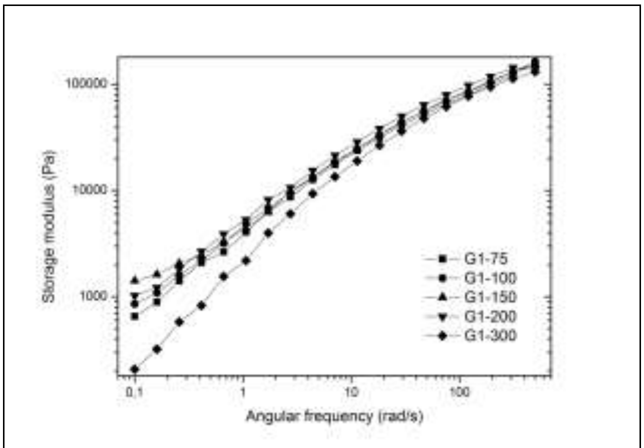

Fig. 5: Melt elasticity of nanocomposites (G2)

4. CONCLUSION

Different polymer-clay nanocomposites have been prepared by advanced compounding using a melt pump and special screw geometries. Employing on-line extensional rheometry and off-line rotational rheometry, effect of processing conditions (screw speed and geometry in the twin-screw extruder) on elongational and viscoelastic properties has been investigated. It has been found that the level of melt strength measured by extensional rheometry correlates with dynamic rheological data (evaluation of melt viscosity and elasticity, respectively) measured by rotational rheometry. It was hereby confirmed that the network structure made of silicate platelets in polymer melt is reflected in both elongational as well in shear flow in the same way. Therefore, extensional rheometry for the fast industrial characterisation as well as rotational rheometry for accurate scientific characterisation can be applied in the field of complex multiphase systems like polymer-clay nanocomposites.

ACKNOWLEDGEMENTS

This research was supported by the NanoComp – 0901 PlaComp1 Project, which was part of the NanoComp research project cluster founded by Austrian Nanoinitiative.

LITERATURE

[1] M. Kracalik, S. Laske, M. Gschweitl, W. Friesenbichler, G. R. Langecker: Advanced compounding: extrusion of polypropylene nanocomposites using the melt pump, J. Appl. Polym. Sci., 2009, 113 (3), 1422 – 1428.

[2] A. Witschnigg, S. Laske, M. Kracalik, M. Feuchter, G. Pinter, G. Maier, W. Märzinger, M. Haberkorn, G. R. Langecker, C. Holzer: In-line characterization of polypropylene nanocomposites using FT-NIR, J. Appl. Polym. Sci., 2010, 117 (5), 3047 – 3053.

[3] S. Laske, M. Kracalik, M. Feuchter, G. Pinter, G. Maier, W. Märzinger, M. Haberkorn, G. R. Langecker: FT-NIR as a determination method for reinforcement of polymer nanocomposites, J. Appl. Polym. Sci., 2009, 114 (4), 2488 – 2496.

[4] M. Kráčalík, L. Pospíšil, M. Šlouf, J. Mikešová, A. Sikora, J. Šimoník, I. Fortelný: Recycled Poly(ethylene terephthalate) Reinforced with Basalt Fibres: rheology, structure and utility properties, Polym. Compos., 2008, 29 (4), 437 – 442.

[5] M. Kráčalík, L. Pospíšil, M. Šlouf, J. Mikešová, A. Sikora, J. Šimoník, I. Fortelný: Effect of Glass Fibres on Rheology, Thermal and Mechanical Properties of Recycled PET, Polym. Compos., 2008, 29 (8), 915 – 921.

[6] S. Laske, M. Kracalik, M. Gschweitl, M. Feuchter, G. Maier, G. Pinter, R. Thomann, W. Friesenbichler, G. R. Langecker: Estimation of reinforcement in compatibilized polypropylene nanocomposites by extensional rheology, J. Appl. Polym. Sci., 2009, 111 (5), 2253 – 2259.

[7] M. Kracalik, S. Laske, A. Witschnigg, C. Holzer: Elongational and shear flow in polymer-clay nanocomposites measured by on-line extensional and off-line shear rheometry, Rheologica Acta, 2011, 50 (11-12), 937-944.

[8] S. Laske, A. Witschnigg, H. Mattausch, M. Kracalik, G. Pinter, M. Feuchter, G. Maier, C. Holzer: Determining the ageing of polypropylene nanocomposites using rheological measurements, Applied Rheology, 2012, 22, 24590-24614.

[9] M. Kracalik, S. Laske, A. Witschnigg, C. Holzer: Effect of the mixture composition on shear and extensional rheology of recycled PET and ABS nanocomposites, Macromolecular Symposia, 2012, 311, 33-40.

[10] M. Kracalik, S. Laske, C. Holzer: Extensional Rheology as Effective Tool for Characterization of Polymer Nanocomposites, AIP Conference Proceedings, 2011, 1375, 208-218.