Assessment of reinforcement in polymer nanocomposites using cumulative rheological parameters

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Abstract
Multiphase polymer systems, like polymer nanocomposites, exhibit complex rheological behaviour due to physical and also possibly chemical interactions between individual phases. Up to now, rheology of dispersed polymer systems has been usually described by evaluation of viscosity curve (shear thinning phenomenon), storage modulus curve (formation of secondary plateau) or plotting information about damping behaviour (e.g. Van Gurp-Palmen-plot, comparison of loss factor tan δ). On the contrary to evaluation of damping behaviour, values of cot δ were calculated and called as “storage factor”, analogically to loss factor. Then values of storage factor were integrated over specific frequency range and called as “cumulative storage factor”. In this contribution, LDPE-ZnO-clay nanocomposites with different dispersion grades (physical networks) have been prepared and characterized by both conventional as well as novel analysis approach. Next to cumulative storage factor, further cumulative rheological parameters like cumulative complex viscosity, cumulative complex modulus or cumulative storage modulus have been introduced.

Keywords: shear flow, oscillatory shear, polymer, clay, nanocomposites

1. Introduction
Polymer nanocomposites using organically modified clays have been intensively investigated due to enhancement of processing as well as utility properties. Using nanoparticles is an interesting way for preparation of polymer tailored materials. The enhancement of material properties because of nanoparticles addition has usually been analysed using a combination of morphological (X-ray diffraction (XRD), transmission electron microscopy (TEM)), mechanical (tensile testing) and possibly rheological (rotational rheometry) measurements [1-17]. Using 2-5% of clay, significant improvement of material properties can be reached: high elastic modulus, tensile strength, thermal resistivity, low gas and liquid permeability, reduced flammability [18] and improved rheological properties compared to the unfilled polymer matrix [1-17]. High reinforcement due to addition of the layered silicates results from their large surface area (specific surface of montmorillonite is about 700-800 m²/g) [19, 20]. In the case of highly dispersed systems, a three dimensional physical network is achieved, formed due to interactions between silicate platelets and the polymer chains. This phenomenon can be investigated by analysis of the melt elasticity using rotational rheometry [1-40]. These studies are mainly based on evaluation of viscosity curve shape (shear thinning phenomenon), storage modulus curve at low frequencies (formation of secondary plateau), phase homogeneity (Cole-Cole plot) or plotting information about damping behaviour (e.g. Van Gurp-Palmen-plot, comparison of loss factor tan δ). In order to enable simple comparison of nanocomposites reinforcement in the shear flow, new way to analyze data of the shear flow has been tested [31, 32]. The storage modulus G’ describes the elastic part while the loss modulus provides us with information about the viscous part of the shear flow. The relation G’/G’’ is defined as tan δ and reflects damping behaviour in the polymer system. According available literature, the G’/G’’ ratio (cot δ) has not been used for rheological evaluation of nanocomposites up to now. Compared to tan δ (loss factor), cot δ (called as storage factor, SF) reflects melt rigidity, which can be associated with reinforcement effect in polymer (combination of chain elasticity with silicate layers rigidity in the polymer melt). In order to reduce the magnitudes of storage factor to one representative value for one sample, G’ as well as G’’ curves have been integrated over the measured frequency range as following:

\[
CSF = \frac{\int_{0.1\text{rad/s}}^{628\text{rad/s}} G'}{\int_{0.1\text{rad/s}}^{628\text{rad/s}} G''}
\]

(1)

In this way, cumulative storage factor (CSF) and some further cumulative rheological parameters (e.g. cumulative complex viscosity CCV, cumulative complex modulus CCM, cumulative storage modulus CSM) were introduced [31]. It was proven that values of CSF can be correlated with values of melt strength, i.e. the reinforcement in polymer nanocomposites can be assessed and compared in both, shear as well in elongational flow [32]. In this paper, LDPE-ZnO-clay nanocomposites with different dispersion grades (physical networks) are reported. It is shown that nano-scaled ZnO can be used not only as UV stabilizer but also as reinforcement and dispersion agent, respectively. The obtained data is analysed in this paper using typical rheological approaches as well as cumulative rheological parameters like CSF or CCV.
2. Materials and Method

CA9150 low-density polyethylene for extrusion coating has been used for the preparation of nanocomposites (supplied by Borealis Inc., Linz, Austria). The used nanoclayCloisite 20 (Cl20) as well as LDPE masterbatch with 30% nano-scaled ZnO (Nanobyk) were supplied by BYK-Chemie Ltd, Wesel, Germany / POLYchem Ltd, Markt Allhau, Austria, respectively. Mixtures have been prepared using laboratory compounding MiniLab II Haake Rheomex CTW5 (Thermo Fisher Scientific, Germany). Performance of four different compositions (pure PE matrix, 5wt.% of Cl20, 5wt.% of ZnO, 2.5/2.5 wt.% of Cl20/ZnO) have been compared. Rheological properties in the shear flow were studied using a Physica MCR 502 rheometer (Anton Paar Ltd., Graz, Austria) with the cone-plate geometry of 25 mm diameter and measuring gap of 43 μm.

3. Results & Discussion

The nanocomposites dispersion grade and effect of matrix molecular weight on final morphology can be evaluated using analysis of viscosity curve (shear-thinning effect) in combination with information obtained from the storage modulus curve \(G'(\omega)\) secondary plateau; [33]). In Figs. 1 and 2, magnitudes of complex viscosity as well as storage modulus in dependency on angular frequency were plotted. As can be seen from Fig. 1, the systems prepared with Cl20 and Cl20/ZnO revealed pronounced shear-thinning behavior, as result of disruption of network structures and, consequently, by orientation of filler particles in flow. On the other hand, CA9150 matrix as well as nanocomposite only with ZnO showed typical liquid viscoelastic behaviour. The lower viscosity values of nanocomposite only with ZnO comparing with pure CA9150 matrix can be explained by significantly lower viscosity of LDPE matrix used for preparation of ZnO masterbatch. Therefore, higher admixture of ZnO masterbatch to CA9150 matrix results to higher “dilution” of CA9150 matrix, i.e. the average molecular weight in such polymer blend will be lowered.

For systems with high dispersion grade, the dependence of \(G'(\omega)\) becomes almost invariable at low frequencies. Such “secondary” plateau indicates the formation of a network structure (“rubber-like” behavior) reflecting the exfoliation of silicate layers in nanocomposites [34, 47, 48]. As can be seen in Fig. 2, systems prepared with Cl20 and Cl20/ZnO showed “rubber-like” behaviour i.e. high dispersion grade, while pure CA9150 matrix as well as nanocomposite with ZnO exhibited typical viscoelastic behaviour. It means, in 2.5 Cl20/2.5 ZnO nanocomposite, two physical interactions are acting simultaneously: on one hand, melt elasticity is increased by formation of 3D-physical ntwework between polymer chains and silicate platelets, and, on the other hand melt elasticity is decreased due to decrease in polymer average molecular weight. As can be seen from Figs. 1 and 2, the decrease in polymer average molecular weight is dominating in 5% ZnO nanocomposite system comparing to pure CA9150 matrix.

The van Gurp-Palmen (vGP) plot as a dependency of loss angle \(\delta\) on complex modulus \(|G^*|\) can be used to analyze the spatial structures of polymers [41-45]. In Fig. 3, vGP plot is shown for prepared samples. For the polymer samples with rather linear chain structure, a continuous shaped curve has been published. On the contrary, long chain branched (LCB) polymers showed a developed bump between the \(|G^*|\) minimum and the 90° plateau [44]. As can be seen in Fig. 3, systems prepared with Cl20 and Cl20/ZnO show spatial structure similar to mentioned LCB polymers with even two bumps or peaks (Cl20), indicating complex 3D structure made of filler and polymer chains [49]. The CA9150 matrix and nanocomposite with ZnO exhibit behaviour connected with linear chain structure. In order to get additional information about viscoelastic damping behaviour of the prepared samples, phase shift \(\delta\) in dependency on angular frequency has been plotted (Fig. 4). The curves are similar to those of vGP and confirm formation of differently organized structures (combination of agglomerated, delaminated and exfoliated structure) depending on achieved 3D network.
Another approach for description of viscoelastic damping behaviour is so called “Cole-Cole” figure, in which imaginary part of complex viscosity over the real part is plotted. This figure has been widely used to assess miscibility/homogeneity of polymer blends and composites in the way that a smooth, semi-circular shape can be interpreted by better compatibility and homogeneity, respectively [23,46]. As shown in Fig. 5 the CA9150 matrix and nanocomposite with ZnO showed semi-circle shapes, reflecting high homogeneity of the system. However, for the analysis of polymer nanocomposites performance, not only homogeneity but also reinforcement should be addressed. Using Cole-Cole plot, it can be said, that systems prepared with Cl20 and Cl20/ZnO revealed deviation from semi-circle shape and, therefore, are rather not homogeneous. Nevertheless, no information about reinforcement level can be obtained from this figure and this problem is actually concomitant with each previously described rheological analysis based on damping behaviour.

Using previously introduced analysis based on “rigidity” behaviour [31, 32], there is possibility to analyze reinforce level as result of 3D physical network between polymer chains and filler particles and, consequently, to obtain some information hidden in analysis based on damping behaviour.

The CSF plotted over CCV in Fig. 6 shows clearly other trend as trends obtained from figures analyzed previously in this paper. For CA9150 matrix it can be seen that viscosity value is high, but reinforcement level represented by CSF (comparing to all nanocomposites) is low. Comparing to CA9150, the nanocomposite with 5% of ZnO revealed lower value of viscosity, but higher value of reinforcement, followed by nanocomposite with 2.5/2.5 wt.% of Cl20/ZnO and finally followed by nanocomposite with 5wt.% of Cl20 showing the highest reinforcement and approximately same level of viscosity. In this way, it was possible to divide contribution of “internal reinforcement” coming from internal friction (high molecular weight and viscosity values, respectively) – represented by viscosity values – and “external reinforcement” coming from 3D physical network between polymer chains and nanofiller particles – represented by CSF values. This division was not possible to analyze using evaluation methods based on damping behaviour.
Comparing to Fig. 6, coefficient of linear regression in Fig 7 is very high. It means, if only polymer nanocomposites are compared, there is high correlation between CSF and CCV values, giving possibility to compare previously described “external reinforcement” not only in cases of nanocomposites using one polymer matrix, but also in cases of nanocomposites based on polymer blends. This result will be proved in further work using not only polymer matrices with different molecular weight but also with different chemical compositions.

4. Conclusions

Complex polymer nanocomposites with different molecular weight polyethylenes and clay/ZnO nanoparticles were prepared and analyzed by conventional as well by new rheological analysis. Using novel approach based on melt rigidity analysis the reinforcement caused by 3D physical network between polymer chains and nanofiller particles could be divided from that coming from internal friction (polymer molecular weight). In this way, new inside into performance characterization of polymer nanocomposites has been introduced and will be tested on nanocomposites based on different polymer blends in future work.

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