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Note

Recycled clay/PET nanocomposites evaluated by novel rheological analysis approach

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ABSTRACT

Clay-polymer nanocomposites exhibit complex rheological behavior due to physical and also possibly chemical interactions between individual phases. Up to now, rheology of clay-polymer nanocomposites has been usually described by evaluation of complex viscosity curve (shear thinning phenomenon), storage modulus curve (G´ secondary plateau) or plotting parameters characterizing damping behavior (e.g. Van Gurp-Palmen-plot, Cole-Cole plot). On the contrary to evaluation of damping behavior, new approach – based on evaluation of rigidity behavior – was tested, where the values of cot δ were calculated and called as „storage factor", analogically to broadly used loss factor. Afterwards, values of storage factor were integrated over measured frequency range and called as "cumulative storage factor". In this contribution, clay-PET nanocomposites with different organoclays have been prepared and characterized by both conventional as well as novel analysis approach. Rheological results have been supported by AFM micrographs.

1. Introduction

Nanotechnology was already introduced as a new method of improvement of polymer properties in 1995. The technology involves not only incorporation of nanosized particles into the polymer but, more importantly, investigation of interactions between the polymer matrix and the enormously large nanofiller surface. Especially for clay/polymer nanocomposites (CPNs), the surface effects are responsible for improvement of barrier, mechanical and rheological properties, dimensional stability, heat, flame and oxidative resistance. In comparison with traditional fillers (20–40 wt% loading), 2–5 wt% filling of clay minerals is sufficient to achieve analogous material improvement. Generally, the primary particle shape of different nanofillers can be sphere, needle or a plate. High aspect ratio (particle length/thickness) of filler facilitates high reinforcement of polymer. Therefore, layered and needle-formed fillers have been widely used for enhancement of polymer property profile. Montmorillonite belongs to the group of phyllosilicates and theoretically it is possible to reach aspect ratio of 1000 by proper dispersion of this mineral in polymer matrix. Montmorillonite is a three-sheet-silicate where the primary layer consists of one octahedral sheet surrounded by two tetrahedral sheets. Na^+ or Ca^{2+} ions in the interlayer space have been usually replaced by long alkylammonium ions in order to increase interlayer space and, consequently, to facilitate dispersion in polymer melt during melt-compounding process. Nanocomposites using different polymer matrices and clay minerals have been intensively investigated because of the improvements in their processing and use properties. Consequently, it is possible to prepare new, tailored, materials or to use nanofillers in polymer recycling (Ghanbari et al., 2013; Cassagnau, 2008; Laske et al., 2012; Paul and Robeson, 2008; Ray et al., 2002; Százdi et al., 2006). Especially using nanoparticles for enhancement of recycled PET (Banda-Cruz et al., 2017; Gao, 2012; Liang et al., 2015; Majdzadeh-Ardakani et al., 2017; Mallakpour and Javadpour, 2016; Rosnan and Arsad, 2013; Kracalik et al., 2005) is of great interest due to broad potential applications.

The enhancement of material properties because of nanoparticles addition has usually been analyzed using a combination of morphological (X-ray diffraction (XRD), transmission electron microscopy (TEM)), mechanical (tensile testing) and rheological (rotational rheometry) measurements. In the case of highly dispersed systems, a three dimensional physical network is achieved, formed due to interactions between clay mineral layers and the polymer chains. This phenomenon can be investigated by analysis of the melt elasticity using rotational rheometry. Such 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 behavior (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

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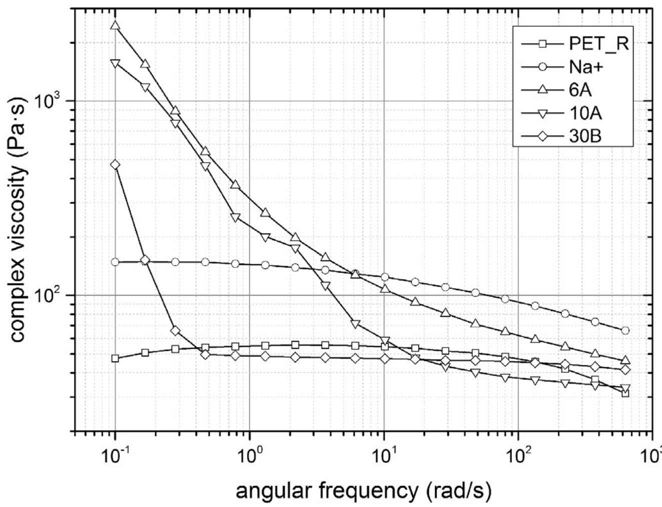

Fig. 1. Complex viscosity of nanocomposites.

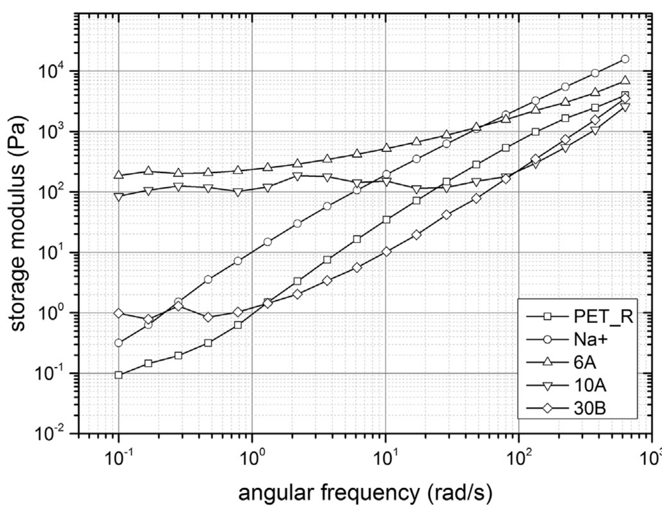

Fig. 2. Storage modulus of nanocomposites.

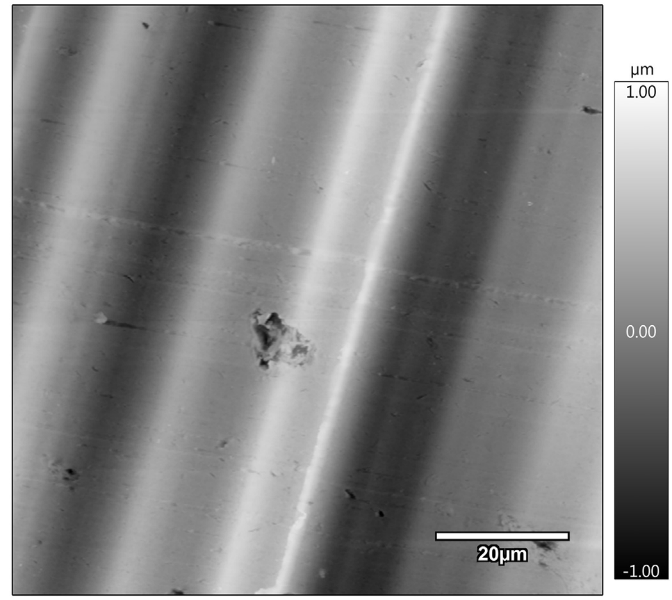

Fig. 4. AFM micrograph of PET/Cloisite 30B.

(Kracalik, 2015; Kracalik et al., 2011). The storage modulus G´ reflects the elastic part while the loss modulus gives information about the viscous part of the dynamic shear flow. The relation of G´´/G´ is defined as tan δ and describes damping behavior of the polymer system. On the contrary, 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 (named as storage factor, SF) reflects melt rigidity, which can be associated with reinforcement effect of nanostructured filler (combination of chain elasticity with clay layers rigidity in the polymer melt). In order to reduce the values of storage factor to one representative magnitude for one nanocomposite sample, G´ as well as G´´ curves have been integrated over the measured frequency range as following:

$$CSF = \int_{0.1rad/s}^{628rad/s} G' / \int_{0.1rad/s}^{628rad/s} G'' \tag{1}$$

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

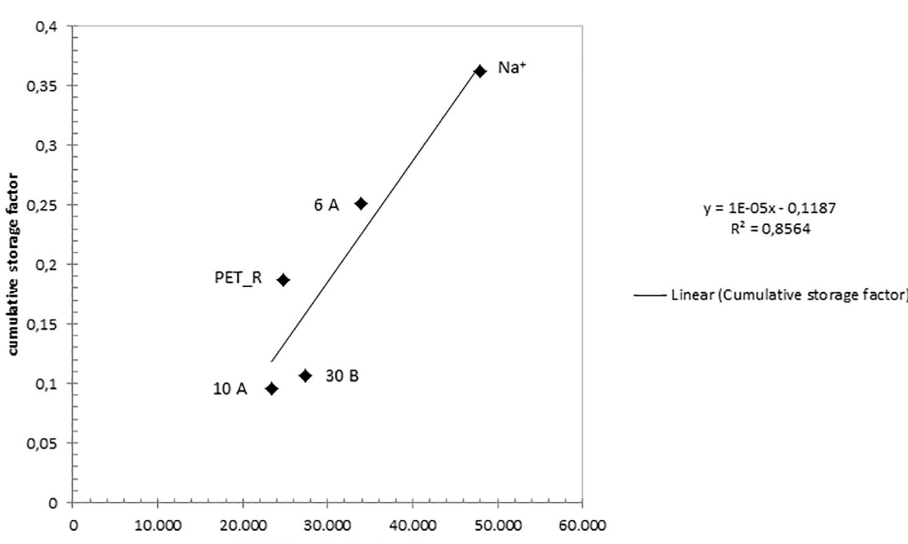

Fig. 3. Cumulative storage factor.