COMPARING THE EFFECT OF NANO-CaCO$_3$ AND NANO-ZnO ON RHEOLOGICAL PROPERTIES OF POLYPROPYLENE USING SEVERAL MODELS

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Introduction

Polymer nanocomposites have attracted increasing attention in recent years because of their significant improvement of physical and/or chemical properties over the matrix polymers [1-2]. Melt rheometry is vitally important for processing of polymer-based nanocomposites. Also, it is a powerful tool for inspecting the internal microstructure of polymer nanocomposites [3-5]. In order to understand how the nanofillers enhance the properties of the polymers, many studies have been performed using dynamic mechanical thermal analysis (DMTA) and scanning electron microscopy (SEM), to find a link between the structure and the properties of the nanocomposites [4]. There are no comprehensive studies reported on the effect of nano-structured CaCO$_3$ and ZnO on the rheological properties of PP using literature models. In the current study, we will report on these effects.

Experimental

Materials

Polypropylene (homopolymer) was provided by Jam Petrochemical Company (Iran) under the trade name X30S; the density was 0.9 g/cm^3 and the melt flow index was 9 g/10min. ZnO and CaCO$_3$ nanoparticles were supplied by Rahpooyan Nano Shahreza Co. (Iran) and had a density of 2.7 and 5.6 g/cm^3 respectively. Both nanoparticles had a diameter mean of d=30-40nm. Stearic acid supplied by Kymia Fanavari Aria Co. (Iran).

Apparatus and Procedures

The CaCO$_3$ and ZnO nanoparticles were dried in an oven at 60°C for 12 hours before melt extrusion. The PP pellets and nanoparticles were melt-compounded in a co-rotating twin screw extruder (Dr. Collin Company, ZK 25 Model, Ebensburg, Germany) at a temperature in the range of 155 to 190°C and a screw rotation rate of 60 rpm. The ZnO nanoparticle contents were 5, 10 or 15 wt% with the addition of 1 wt% stearic acid in order to prevent coalescence of nanoparticles. The extrudates were pelletized at the die exit, dried and then compression molded into 1cm thickness sheets (30cm×30cm×1mm) at 180°C.

SEM was performed to investigate the morphology of the nanocomposites by a SEM Instrument (Stereoscan-260, Cambridge, UK). The specimens (pieces of compression molded nanocomposite) were fractured in liquid nitrogen and coated with gold using a sputter coater, mounted and observed.

All rheological measurements were performed on a controlled strain rheometer (MCR 300 Rheometer, Anton Paar Physica, Otriš) with a torque transducer range of 1-15000 µNm using 25 mm diameter parallel plates at 180°C.

Results and Discussion

The morphology of nanocomposites was evaluated by SEM to observe the distribution of nanoparticles within the extruded materials. Fig. 1 shows micrographs of a cryofractured surface of the nanocomposites containing 5% nanoparticles. Moderate nanoparticle dispersion is seen in this micrograph. However, partial coalescence was unavoidable especially in PP/nano- ZnO composite.
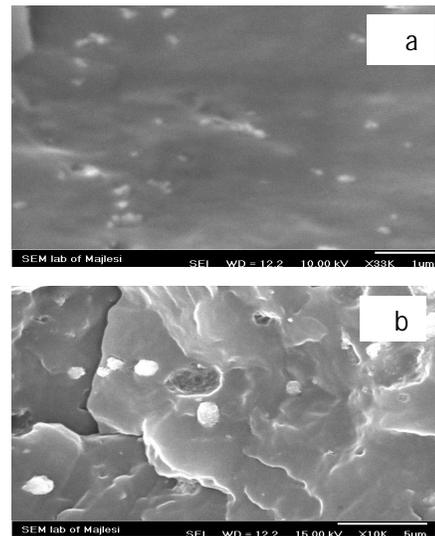

Fig. 1 Scanning electron micrographs of a cryofractured surface of a) PP/nano-CaCO$_3$ b) PP/nano-ZnO nanocomposites containing 5% nanoparticles.

The storage modulus and tanδ against frequency are presented in Fig. 2. As can be directly seen, the moduli of nanocomposites increased with increase in
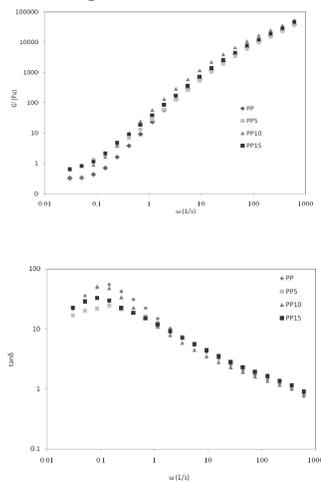

Fig. 2 Dynamic modulus, G' and tanδ of PP/nano-ZnO composites vs. frequency at 180°C and 5% strain.

nanofiller concentration; however this increase was greater in the high frequency region. Moreover the nanofiller had a more significant effect on the elastic behavior than the viscous behavior. As seen, there is a significant decrease in tanδ with increase in nanoparticle content. Finally the experimental and predicted viscosity of pure PP and its nanocomposites is plotted in Figure 3. In order to use several models for prediction of viscosity [5], the nanocomposites melts were considered as a suspension at this temperature. As shown all of these models underestimated the viscosity of both nanocomposites. The data was obtained from different models was close, but there was a significant negative deviation from the experimental values. It is due to the nano size of particles. It seems that these models hadn't the potential for a good prediction in nano-structured particles. The best model that is close to experimental values for PP/nano-CaCO$_3$ composites is Roscope [eq. (11)]. While in the case of PP/nano-ZnO composites Einstein (equation 9) is the best. Solving the Einstein model [eq. (10)] with K_E=1 showed more deviation from the experimental values comparing to that of K_E=2.5. Therefore it was concluded that according to Einstein model there is no slippage at the interface.

Conclusion

The rheological properties of nanocomposites were investigated. The nano particles were observed to be dispersed uniformly but with a different level of coalescence.
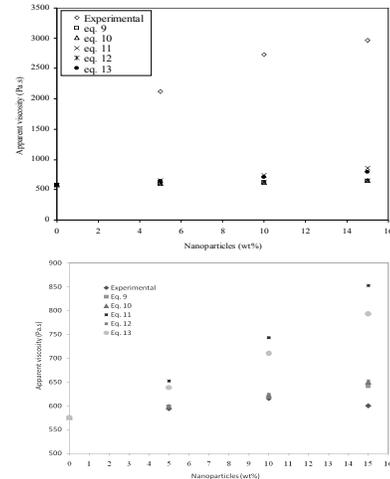

Fig. 3 Comparing the models used for rheology of suspensions, apparent viscosity vs. nanoparticles wt%, of PP/nano-CaCO$_3$ composites (up) and PP/nano- ZnO (down) at 180°C and constant shear rate of 100 s^{-1}.

Rheometry showed that both of the nanofillers had a more significant effect on the elastic behavior than the viscose behavior. The rheological behavior of nanocomposites is more sensitive to nanoparticles concentration at low frequencies. The investigated models hadn't the potential for a good prediction in nano-structured particles. The best model that to some extent is close to experimental values in PP/nano-CaCO$_3$ and PP/nano-ZnO is Roscope (equation 11) and Einstein (equation 9) respectively.

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