RHEOLOGY AS A TOOL FOR EVALUATIONOF Hybrid STRUCTURE IN THERMO PLASTIC POLYMER NANOCOMPOSITES WITH GRAPHENE AND CARBON NANOTUBES

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Abstract: Experimental and theoretical rheology was used as a tool for characterizationof hybrid structure of thermoplastic polymer nanocomposites filled with graphene and carbon nanotubes. Different rheological approaches were applied to evaluatethe degree of nanofiller dispersion, the effect of nanofiller shape on viscosity, as well as the particle-particle and polymer-particle interactions.Rheological percolation threshold was proposed as important characteristic related to the reinforcement effects of nanofillersin polymer.

Keywords: Graphene, Multiwall Carbon Nanotubes, Thermoplastic Polymers, Rheology, Percolation Threshold, Dispersity.

I. INTRODUCTION

One- and bi-dimensional (1D and 2D) nano-materials likemultiwall carbon nanotubes (MWCNTs) and graphene nanoplates (GNPs) became a great scientific and technological interest, due to their unique physical and mechanical properties, that make them extremely importantnanofillersfor polymer nanocomposites. Depending on the degree of dispersion and the polymer-nanofiller interactions, the nanocomposites have been found to possess promising properties such as mechanical, barrier, thermal, and electrical. These properties are advantageous for applications in the field of food packaging, automotive, airplane, sport products, textile, electronic devices, membranes, and coatings/inks. Among the different methodologies to incorporate 1D and 2D nanofillers in a polymer matrix, melt blending is usually the most appropriate economical and industrial approach when compared with others. However, the effective reinforcement of polymers is still a challenge due to the poor dispersion and the lack of interfacial interactions between the nanofiller and the polymeric matrix.

Carbon nanaotubesand graphene have a tendency to form agglomerates during synthesis as dry powders because of van der Waals attraction between nanofillers. During polymer processing to composites, these agglomerations are difficult to disperse, so they decrease the surface area and disturb the formation of network structure of single nanotubes which is essential for the improvement of mechanical and physical properties. Therefore, uniform dispersion of carbon nanotubes and graphene is required to realize the potentiality of the nanotubes as reinforcing fillers [1,2].

It is still a challenge to control the structure and properties of polymer nanocomposites at the stage of their preparation [3].To find a way for the processability control of polymer nanocomposites filled with graphene and carbon nanotubes is a goal of our study. In this work we propose an easy and simple tool for evaluation of the hybrid structure of polymer nanocomposites based onrheological methodology. Using the experimental and theoretical rheologywe characterize the degree of nanofillerdispersion, effect of nanofiller shape on viscosity, as well as evaluate particle-particle and polymer-particle interactions and other structural peculiarities of nanocomposite melts. Using rheological methods, we also investigate how the compatibilizer maleic anhydride (MA) improves the dispersity of carbon nanofillers in polypropylene.

II. DETAILS EXPERIMENTAL

2.1. Materials and Procedures

The poly(lactic) acid (PLA) polymer used in this study was Ingeo™ Biopolymer PLA-3D850 (Nature Works) with glass transition temperature 55-60 °C.Industrial Graphene Nanoplates (GNPs) with number of layers >20 and aspect ratio ~240, as well as Multiwall Carbon Nanotubes (MWCNTs) with diameter ~30 nm and average aspect ratio ~1000 was supplied from Times Nano, China. Nanocomposites of GNP/PLA and MWCNT/PLA were prepared by melt extrusion as varying the filler contents from 0 to 12 wt%. Additionally, Isotactic Polypropylene (PP)Buplen 6231 with MFI (230/2.16) of 12.2 g/10 min was supplied by Lukoil Neftochim Co, Bulgaria. Masterbatch of 20 wt% MWCNTs in polypropylene was obtained in pellet form from Hyperion Catalysis International, USA. Typical outside diameter range of the MWCNTs in masterbatchwas 10 - 15 nm and the aspect ratio is ≥1000. The chemical compatibilizer used for PP was maleic-anhydride-grafted polypropylene (MA-g-PP), Licomont AR504, produced by Clariant International Limited.

The rheological measurements were performed with AR-G2 Rheometer (TA Instruments), at steady-state shear flow and oscillatory flowregimes using parallel-plate geometry at gap size between plates of 500 μm. Measurements were performed at temperature 200°C

for the polymer melts. The shear rate range was 0.05 – 600 s^{-1}, and the oscillatory flow was performed in angular frequency range of 0.05 – 100 rad/s.

III. RESULTS AND DISCUSSION

3.1. Effect of nanofiller shape on viscosity

In Fig. 1(a,b),we compare the shear flow viscosity of two types nanocmposite melts of Poly(lactic) acid polymer (PLA) filled with multiwall carbon nanotubes (MWCNTs/PLA) and graphene nanoplates (GNP/PLA), at 200°C and the filler contents varying in 1.5- 12 wt%.
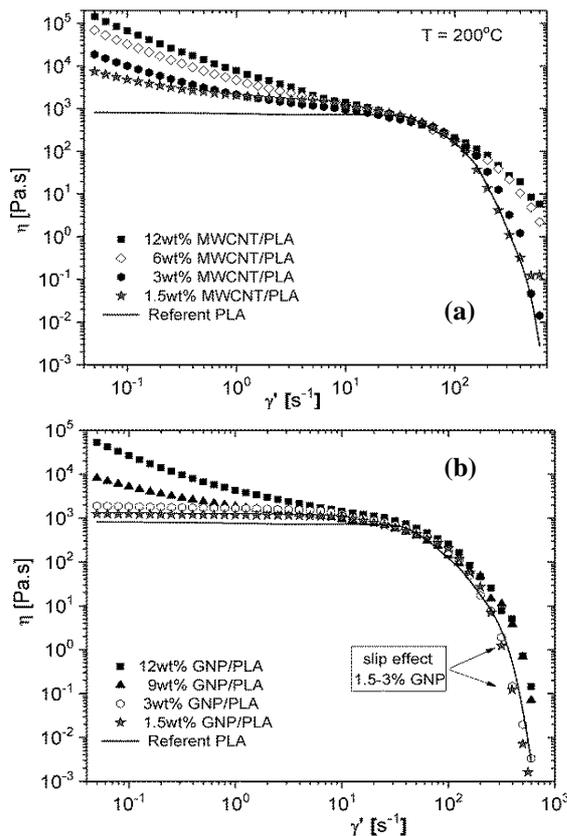
Fig, 1(a&b). Steady-state shear viscosity vs. shear rate for MWCNT/PLA and GNP/PLA melts at constant filler contents of 1.5- 12 wt.%. Arrows point the slip effect in GNP/PLA.

It could be seen that small amounts of 1.5% MWCNTs increase strongly the viscosity at low shear rates (<1 s^{-1}) and the flow in this range becomes non-Newtonian. In contrast, the effect of GNP is insufficient in this flow range, and the viscosity become non-Newtonian onlyat 9% GNP content. This difference may be attributed to the (1D) shape and high aspect ratio (~1000) of MWCNTs in comparison with the platelet shape (2D) and low aspect ratio (~250) for graphene, GNP. The transition from Newtonian to non-Newtonian flow behavior is usually related to the percolation threshold, due to interconnections of nanofiller particles in the matrix polymer. Thus, the rheological percolation threshold was determined at $\varphi_p \geq$ 6 wt% for GNP/PLA and $\varphi_p \leq$ 1.5 wt% for MWCNT/PLA composites.

Particularly, at high shear rates >100 s^{-1}, we found that the viscosity values of GNP/PLA melts at low filler contents (1.5-3 wt%) become lower than that of the neat PLA (Fig. 1b). This effect can be associated with an alignment and slip effects of graphene nano-sheets in the flow field.

3.2. Percolation threshold due to particle-particle interconnections.

The steady-state viscosity of nanocomposites with anisotropic fillers, such as graphene and carbon nanotubes is strongly dependent on the nanofiller content and aspect ratio. Only few theoretical predictions are proposed in order to describe the viscosity function vs. concentration of high aspect ratio fillers [2]. For the viscosity at low filler concentrations we apply an Einstein type equation, proposed by Utraski[4], for nanoparticles withnanofilleraspect ratio,p ~ 300,

$$\eta = \eta_o (1 + [\eta] \phi), \qquad (1)$$

at $[\eta] = 2.5 + a(p^b - 1)$

where a = 0.025 ± 0.05 and b = 1.47 ± 0.05. We calculate the characteristic viscosity [η]by Equation (1), for aspect ratio, p = 240 for GNP and p = 1000 for MWCNT, using values of a = 0.02 and b = 1.42, and obtain values for [η] of 50 and 366, respectively. Figure 2 compares the experimental data and model predictions by Eq, (1) for the concentration dependence of viscosity for both GNP/PLA and MWCNT/PLA composites at 200°C.
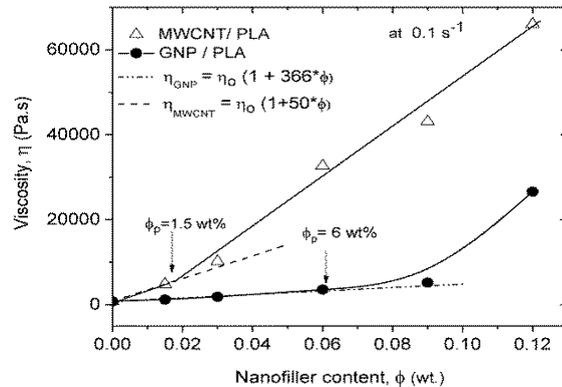
Fig.2. Viscosity vs. filler contents at low shear rates (0.1 s^{-1}), comparing the graphene and MWCNT-based PLA composites. Arrows point the rheological percolation threshold.

The percolation threshold was determined as the critical concentration for the deviation of experimental viscosity results from the model curve (initial straight line at low filler contents). Thus, the percolation threshold was identified of $\phi_p \leq$ 1.5wt% for MWCNT/PLA and $\phi_p >$ 6wt% for GNP/PLA composites by using this rheological criteria. The larger the aspect ratio of nanofiller, the lower is the rheological percolation threshold [1,2,4].

3.3. Determine the degree ofnanofillerdispersion.

The dynamic storage modulusG' at 200°C is compared for PP/MWCNT composite melts with and without MA compatibilizer. In Figure 3(a,b), the storage modulus, G' (ω) is plot as a function of the angular frequency, as varying the MWCNT content from 0.05 to 1 wt% for non-modified and MA modified composites.
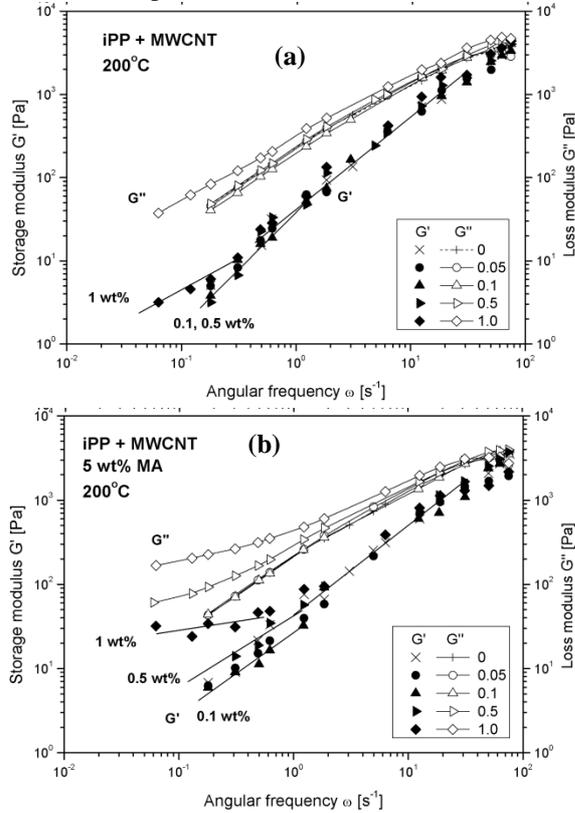
Fig.3. Dependence of storage and loss moduli G' and G'' on angular frequency ω at T = 200 °C, as varying the nanotube content from 0 to 1 wt%: a) non-modified PP/MWCNT; b) 5% MA modified PP/MWCNT

As seen, the frequency dependence of G' for PP melt shows typical homopolymer-like terminal behavior and this indicates that polymer chains are fully relaxed at low frequencies (Eq.2). The typical slope value is (m=2) for the storage modulus of the neat polymer.

$$G' \sim \omega^m \qquad (2)$$

It is apparent that for composites the values of the storage modulus increase and the terminal slope decrease with increasing the MWCNT content. Moreover, a tendency to plateau ($m \rightarrow 0$) of the G' modulusat low frequencies is observed for 0.5-1wt% MWCNTs for the samples, modified with MA compatibilizer. Such plateau was not observed in the G'(ω) of the non-modified PP/MWCNT composites. We attribute this effect to a better dispersion of nanotubes by the presence of MA compatibiliser, this resulting in solid-like structure of MWCNTs in the matrix PP [5,6]. The solid-like behavior can be related with the increased content of the single nanotubes and small aggregates of MWCNTs dispersed in the polymer matrix, thus the nanotube–

nanotube interactions begin to dominate, thus leading to percolation [7-14].

In Fig. 4 the complex viscosity is plot versus filler content. As seen, above critical filler content,the complex viscositysharply increases for the MA modified composites, while this effect is lower for the non-modified composites. This is associatedwith the rheological percolation threshold (ϕ_p) as in Fig.2. Arrows in Fig. 4 show thatfor the MA modified composites the percolation threshold appears at lower filler contents,$\phi_p \sim 0.3$ wt.%, while $\phi_p \sim 0.5$ wt.% was determined for the non-modified composites. The result confirms the positive effects of MA-g-PP compatibilizer for a better dispersion of carbon nanotubes in polypropylene. Fig.4 compare the rheological behavior with the microstructure of composites visualized by scanning electron microscope. Small aggregates of MWCNTs are visible in the MA modified composites (upper picture), whilelarge aggregates of carbon nanotubes are visible in the non-modified PP/MWCNT composites.
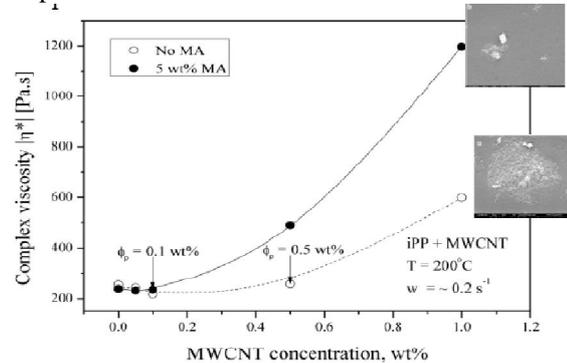
Fig.4. Viscosity vs. filler contents of non-modified and MA modified PP/MWCNT composites. Pictures show the dispersion of MWCNTs to smaller aggregates (upper picture) for the MA modified PP/MWCNT composites, and large aggregates in non-modified composites (down picture).

3.4. Determine the interfacial nanofiller-to-polymer interactions

Rheological experiments can be used to determine the dynamics of polymer molecules in the polymer nanocomposites by calculation of the linear relaxation time spectrum H(τ)[2,9]. The relaxation processes are usually suppressed by the presence of strong interfacial polymer-filler interactions. As nanofilleris added, the mobility of the polymer chains is altered. Thus, the relaxation spectra can eithershift to higher weight (if the interface causes global changes in the polymer relaxation times) or broaden (if the interface creates only local changes in polymer relaxation behavior). [9,11]. Figure 5 represents the relaxation time spectraof MWCNT/PLA composite melts for three fillercontents of1.5; 3 and 12wt% MWCNTs. The relaxation spectra become broaden e.g. shifted to higher relaxation timesby increasing the nanofiller contents. However, the weight of the spectra for those composites is similar to that of the neat PLA at low relaxation times (< 0.01 s). This assume, that the

MWCNTs cause local changes in polymer relaxation behavior, due to their presence in the polymer and the formation of a continuous network. However the polymer-nanofiller interactions are not very strong, thus they have a weak effect on the global polymer relaxation.
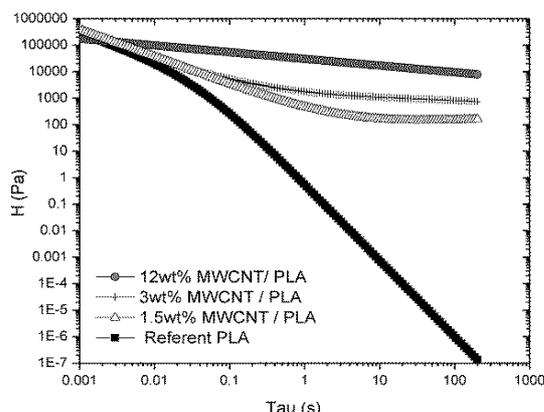
Fig. 5.Relaxation time spectra of MWCNT/PLA composite melts at 200°C for different filler contents.

CONCLUSIONS

Rheology is a powerful tool for evaluation of the hybrid structure in polymer nanocomposites with 1D and 2D fillers. Therheological percolation threshold is an important characteristic that is usually related to the reinforcement effects ofnanofillers on the matrix polymer due to particle-particle and polymer-particle interactions.The rheological evaluation confirmed the positive effect of MA compatibiliser for good dispersion of MWCNTs in PP, this resulting in a lower value of rheological percolation thresholds compared to the composites without MA compatibilizer.

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