

Oscillatory Shear Rheology of PE/PP/MWCNT Nanocomposites [†]

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Abstract

The present paper focuses on the effect of carbon nanotubes (CNTs) on the rheological behavior of polyethylene/polypropylene (PE/PP) blends to improve PE/PP mixtures for industrial applications. In our research, 40 wt% HDPE-60 wt% PP blends were produced by extrusion, and 0.59%, 1.18%, and 2.35% multiwalled carbon nanotubes (MWCNTs) were added. Oscillation rheometry was used to study the HDPE-PP-MWCNT nanocomposites and the unfilled polymers at temperatures of 210, 220, 230, 240, and 250 °C in the angular frequency range of 0.05–628.32 rad/s, with 5% deformation. It was demonstrated that in the presence of CNTs, both the complex viscosity and modulus values increase above the percolation threshold. Additionally, it was observed that the crossover modulus (G_x) for all mixtures decreases with increasing temperature. In addition, at 1.18% CNT content, a second crossover appears at all temperatures, and its value increases with temperature.

Keywords: polyolefin blend; rheology; nanocomposite; carbon nanotube; polymer

1. Introduction

Polyolefin composites have huge potential in the automotive, aviation, electronic, and packaging industries [1], especially the so-called nanocomposites, when at least one dimension of the reinforcing material is in the nano range [2]. The most widespread nano-reinforcing materials are montmorillonite (MMT) [3], graphene [4], or carbon nanotubes (CNTs) [5]. The nanoparticles have some advantages over the microparticles: they have a higher specific surface area, so depending on the size and dispersion of the nanoparticles, advanced properties can be achieved. Two thermodynamically incompatible, hydrophobic polymers, such as polypropylene (PP) and polyethylene (PE), can also be compatibilized by adding nanoparticles. Applying blends of polyethylene and polypropylene is beneficial not only through motivating waste management but also through developing blends with specific properties. The PE phase has a good impact and cold resistance, while it does not change the structure of the PP excessively; however, in some cases, the size of spherulites in the PP phase will be smaller because of the presence of PE spherulites [6]. The similarity in the structure of PP and PE enhances the properties. PP has a linear structure, which is different from LDPE (low-density polyethylene), but LLDPE (linear low-density polyethylene) has little synergism with it. The best results can be obtained in the case of isotactic PP (iPP)/high-density polyethylene (HDPE) blends, because strong interfacial bonding is created between the phases, but only at certain compositions [7]. According to studies, the reason why the tensile strength and modulus of an 80/20 wt% iPP/HDPE blend can be higher than in the case of PP is that HDPE melt flows amongst the



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PP spherulites, which induces a nucleation effect in PP [1]. The compatibility of immiscible blends can be assisted by carbon nanotubes, because CNTs diffuse selectively into either one phase or are located at the interface, which increases the interfacial adhesion between the phases [8]. Based on previous papers, there is a huge developmental potential in the selective localization of CNTs. There are several studies in which composites with some kind of polyethylene (HDPE, LDPE, or UHMWPE) or iPP matrix modified with single-walled (SWCNT) or multiwalled carbon nanotube (MWCNT) reinforcing materials were tested. However, just a few studies investigated PE/PP blends with nano-reinforcing.

Studies found that the affinity of the reinforcing materials (CNT, carbon black, carbon fibers, or graphene nanoplatelet (GNP)) is higher for the PE phase, so they are always localized in that phase [4,9–11], even if the nanocomposite is made from PP/MWCNT masterbatch prepared by melt-mixing [12]. When the CNT concentration is high (20 wt%) and the HDPE content is low (maximum 10 wt%), the PE phase will be saturated, so the CNTs also diffuse to the PP phase [13]. Regarding the rheological properties of polyolefin/CNT composites, CNTs generally increase complex viscosity [14], but not in every case [15]. A low amount of CNTs can function as a lubricant for HDPE so that its complex viscosity can decrease [16]. Viscosity can also decrease if the matrix material is bimodal or if it has a high molecular weight distribution (MWD). In this case, CNTs are selectively localized at the surface of the high MWD fraction molecules, so the branching density and relaxation time of the freestanding matrix fraction are even lower [17]. At low CNT content, a Newtonian plateau can be generally observed, which disappears above a certain critical CNT content [15]. At this so-called percolation threshold, the CNT particles form an interconnected network in which CNT-CNT interactions dominate [18]. From the rheological approach, the gelation process takes place at the rheological percolation threshold, whose value increases with the aspect ratio of CNTs [19]. Several studies have found that above the percolation threshold, the storage modulus is not frequency-dependent (at low frequency), which indicates solid-like behavior due to the CNT network [14]. Generally, the values of storage and loss moduli increase with CNT content, but the loss factor $\tan\delta$ decreases [14,15,19]. At low frequency, the $\tan\delta$ curve also has a plateau, and even a small-scale increase in the values indicates elastic behavior [19]. The Cox–Merz rule is valid yet at low CNT content (maximum 10 wt%), but at higher amounts, the solid-like behavior of the materials results in a higher shear rate—viscosity ratio [15]. Based on previous investigations, it can be concluded that the viscosity of the nanocomposites depends on the polymer-CNT and the CNT-CNT interactions; moreover, the structure and type of materials influence the CNT content needed to reach the percolation threshold. In this research, HDPE/PP/MWCNT nanocomposites were prepared by melt-mixing, and their rheological behavior was investigated.

2. Materials and Methods

MOL TIPPLEN H 145 F polypropylene (PP), TIPELIN FA 381-10 high-density polyethylene (HDPE), and Nanocyl PlasticylTM PP2001 type PP/MWCNT masterbatch were chosen to produce nanocomposites. According to the literature, CNT is effective even under 5 wt%. From this aspect, 40 wt% HDPE-60 wt% PP- MWCNT blends were made based on the masterbatch data sheet, then CNT content was clarified by Thermogravimetry (TGA Q50) for 0.59, 1.18, and 2.35 wt%, as can be seen in Table 1.

Table 1. Investigated material compositions.

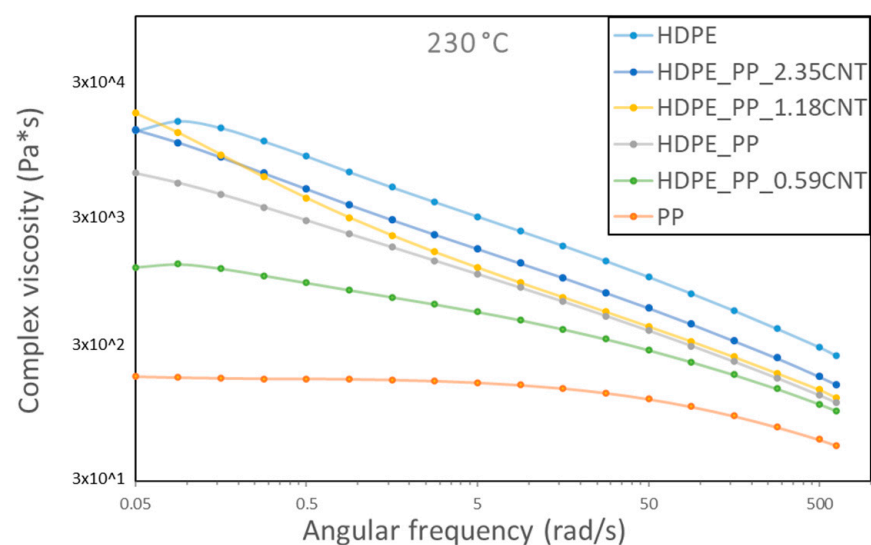
Identification	HDPE Ratio	PP Ratio	MWCNT Ratio
HDPE	100%	-	-
PP	-	100%	-
HDPE_PP	40%	60%	-
HDPE_PP_1.18CNT	40%	58.82%	1.18%
HDPE_PP_2.35CNT	40%	57.65%	2.35%
HDPE_PP_0.59CNT	40%	59.41%	0.59%

The production line consisted of a Brabender extruder, whose tool was connected to an IDMX[®] mixer (Independently driven Dynamic Melt Mixer), a cooling tub full of water, and a Collin Teach-Line CSG171T grinder. The applied zone temperatures in the Brabender Plastograph extruder were 210, 210, 200, and 190 °C. The screw speed was 80 1/min. The IDMX mixer consists of stationary and rotating elements, which provide dynamic mixing. The applied temperature was 210 °C, and the screw speed was 40 1/min. Each blend was mixed two times through the production line for the purpose of increasing the dispersion of the MWCNT.

TA ARES G2 (TA Instruments, Inc., New Castle, DE, USA) type oscillation rheometer was used with a 25 mm diameter cone–plate geometry, with a 0.1 rad cone angle. The measuring gap was 0.04 mm. The HDPE-PP-MWCNT nanocomposites and the unfilled materials were tested at temperatures of 210, 220, 230, 240, and 250 °C in the angular frequency range of 0.05–628.32 rad/s, with 5% deformation. In function of angular frequency, complex viscosity, storage, and loss moduli values were noted. In further calculations, cross modulus (G_x) and activation energy were determined.

3. Results and Discussion

As presented in Figure 1, the complex viscosity of the 40–60 wt% HDPE_PP blend is between the values of HDPE and PP at each temperature. At 628.32 rad/s, the complex viscosity of PP is 55.73 Pas, while that of HDPE_PP is more than doubled, with 116.93 Pas, which is almost half of HDPE (265.15 Pas). At 0.09 rad/s, the value of HDPE_PP (5440.0 Pas) is 30 times higher than that of PP (181.7 Pas) and almost three times lower than that of HDPE (15,994.8 Pas).

**Figure 1.** Complex viscosity as a function of angular frequency at 230 °C.

The values of the composite with 0.59% CNT content are lower, and those with 1.18 and 2.35% CNT content are higher than those of the 40–60% blend (Figure 1). These results are in agreement with the findings of Gill et al., who attributed this fact to the lubricating effect of the CNT at a low concentration regime [16]. The difference between the curves of the matrix and the nanocomposites is minimal above 50 rad/s (maximum 45 Pas between HDPE_PP and the nanocomposites), but it is significant at lower frequencies (maximum 10,555 Pas). Zhang et al. also determined similar results above 0.5% CNT content [18].

The viscosity curves of the blends and of HDPE are steeper with increasing temperature, while in the case of PP, they flatten out; thus, the deviation between the curves increases. Depicting the curves of any blend or HDPE at each temperature, there is generally an angular frequency value where the curves cross. This means that viscosity is not temperature-dependent at that certain frequency (Figure 2). There is no such crossing of the viscosity values of PP. For all the blends and HDPE, the intersection point is at about 0.16 rad/s, apart from the blend of 2.35% CNT, where the intersection point is at about 0.5 rad/s. These intersection points are not perfect; thus, there are always curves that are crossing elsewhere. The frequency at the intersection point can correlate with the liquid-solid transition [14]. With more reinforcement, the Newtonian behavior of the melt can be expanded to higher frequencies.

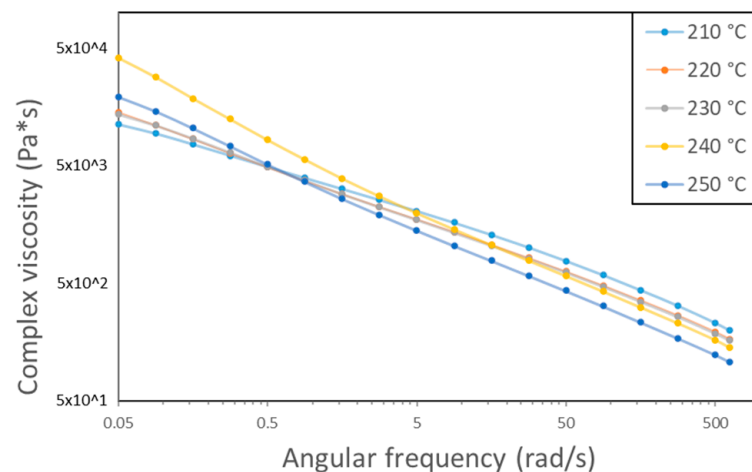


Figure 2. Complex viscosity as a function of angular frequency of HDPE_PP_2.35CNT blend at 210–250 °C temperature range.

Storage (G_1) and loss modulus (G_2) values of the blends are between the values of the unfilled materials at each temperature (Figure 3). The values of the composite with 0.59% CNT are lower, and with 1.18 and 2.35% CNT are higher than those of the 40–60% blend. Storage modulus values of blends with 1.18 and 2.35% CNT content are very similar to HDPE at low angular frequency, but at higher frequencies, the difference is significant. At low angular frequency, a Newtonian plateau appears due to the CNT particles, which becomes more considerable with increasing CNT content [19]. At higher temperatures, the slope of the curves is lower; therefore, the differences are minimal in the first section. Pötschke et al. determined the value of the percolation threshold from the storage and loss modulus values in the low-frequency range [20]. Based on the results, the rheological percolation threshold is between 0.59 and 1.18% CNT content at each temperature. However, there is almost no difference between the curves of the matrix and those of the 0.59% CNT blend, which suggests that the percolation threshold can vary with temperature.

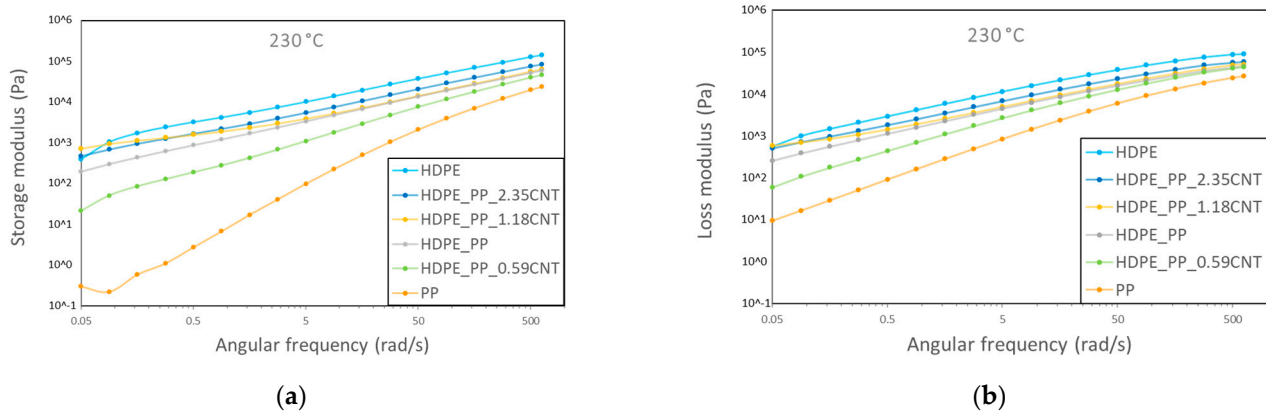


Figure 3. (a) Storage (G1) and (b) loss modulus (G2) as a function of angular frequency at 230 °C.

The cross modulus (G_x) is determined by the crossing of the storage and loss modulus curves, and it is proportional to the polydispersity index (PDI) (Figure 4). The nanocomposites differ from the unfilled materials because they show more intersection points. The value of G_x decreases with increasing temperature for each blend. However, at 1.18% CNT content, the value of the second intersection point increases. At 0.59% CNT content, there is one intersection point at 210 °C, but there are two extra points at 250 °C, which can indicate the formation of a percolation threshold. In fact, each material has one PDI, as demonstrated in the study of Agrawal et al. [21]. The measured extra intersection points do not have physical meaning but indicate a shear sensitivity of the polymer melt.

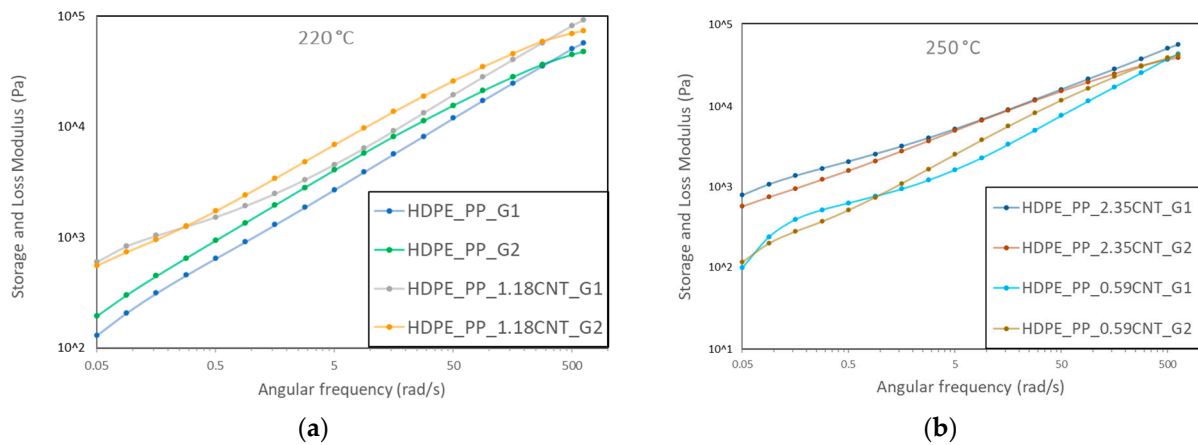


Figure 4. Storage (G1) and loss moduli (G2) as a function of angular frequency (a) at 220 °C and (b) at 250 °C.

The flow activation energy of polymer melts indicates the temperature sensitivity of the viscosity. The higher its value, the higher the dependence on temperature. The activation energy values were calculated at each temperature from the gradient of the complex viscosity–reciprocal temperature curves, according to the general form of the Arrhenius Equation (1) (Figure 5a) [22]:

$$\eta(T) = A \exp\left(\frac{E_a}{R}\right) \quad (1)$$

where η is the apparent shear viscosity, A is a viscosity-dependent constant (can be calculated from the axial section, when $1/T \rightarrow 0$), E_a is the flow activation energy of the polymer melt, and R is the gas constant ($R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$).

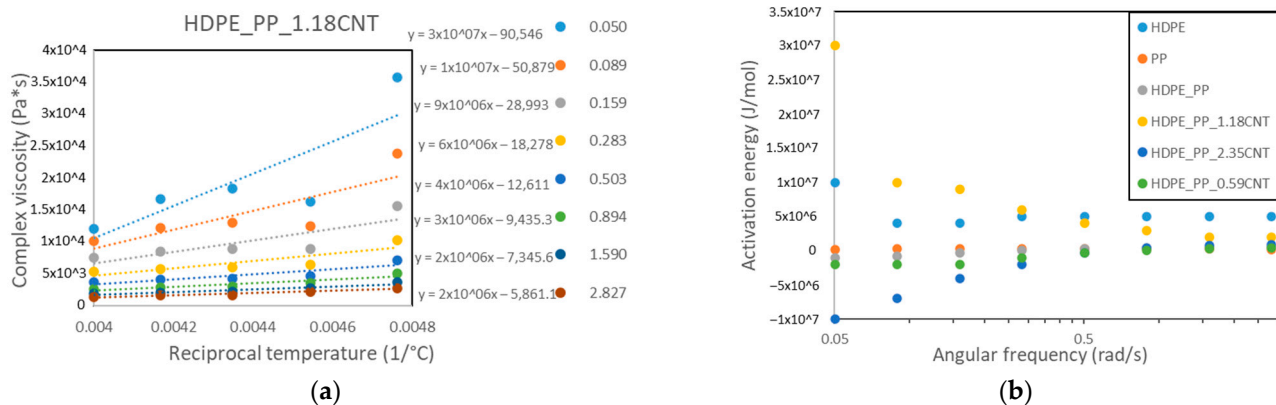


Figure 5. (a) Determination of the activation energy; (b) activation energy of PE/PP/MWCNT nanocomposites between 0.05 and 5 rad/s angular frequency range.

We experienced that at lower frequencies than 0.5 rad/s, the activation energy of the nanocomposites differs from that of the unfilled materials (Figure 5b). Further calculations proved that the absolute value of deviation is high under 3 rad/s, likely because of the percolation threshold. The high similarity between the matrix and the 0.59% CNT content nanocomposite can be a reason for this behavior. The formation of the percolation threshold causes inhibited relaxation of the macromolecules.

The activation energy of the unfilled materials and the 40–60 wt% HDPE_PP blend is mostly constant at all frequencies. The values of the 40–60 wt% blend are similar to the values determined in the case of PP. At highly modified nanocomposites, the values approached the results of PP. Above 0.5 rad/s, all the activation energy values can be considered permanent.

4. Conclusions

In our study, PE/PP/MWCNT nanocomposites were made by melt-mixing, and their oscillation rheological properties were determined in a low angular frequency range. It was found that the values of complex viscosity and storage and loss modulus for the 40–60% PE/PP mixture fall between those of the individual components. It was demonstrated that due to the CNTs above the percolation threshold, both the complex viscosity and modulus values increase. Additionally, it was observed that the crossover modulus (G_x) for all mixtures decreases with increasing temperature. However, at 1.18% CNT content, a second intersection point appears at all temperatures, and its value increases with temperature. At 0.59% CNT content, two additional intersection points are observed at 250 °C, which may indicate the formation of the percolation threshold. The results indicate that the CNT-CNT interactions are fulfilled, and further investigations, such as DSC, SEM, and mechanical measurements, will take place in the future. For a PE/PP mixture with better properties, several potential applications could arise from the automotive to the packaging industry.

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