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PREDICTING THE FLOW PROPERTIES OF POLYAMIDE NANOCOMPOSITES BY USING VINOGRADOV-MALKIN MODEL

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ABSTRACT

This article reports the prediction of the theoretical flow curves of polyamide composites by using Vinogradov-Malkin model. Determination of the melt flow index of polymeric materials is the first step to study viscosity-shear rate relationship. The viscosity of the composites at different temperatures were calculated by using the Williams, Landel'a and Ferry (WLF) equation. Other important rheological characteristics were calculated by using appropriate equations. One point method is employed to correlate the changes in viscosity with temperatures. As expected, it is found that incorporation of nanoclay to polyamide 6 (PA6) significantly decreases the Melt Flow Rate of the composites and hence, increases density. Addition of stabilizer further increases density of the PA6/nanoclay composites. The simulations of viscosity curves for PA6 composites were carried out at measurement temperature, 240°C and in the range of 180°C - 350°C with shear rate of 10^{-1} – 10^{3} 1/s. It is found that addition of nanoclay and stabilizer to PA6 decreases viscosity of the composites in the order of PA6/OMMT > PA6 > PA6/I1098 > PA6/OMMT/I1098 > PA6/MMT/I1098 > PA6/MMT. At higher shear rates, viscosity decreases in the same sequence as low shear rates. At further higher shear rates (> 1000 1/s), filler particles are arranged in the flow direction thus exerting no significant effect on viscosity of composites both with and without the stabilizer. During injection moulding in the shear rate ranging from 10^{1} – 10^{4} 1/s at 240°C temperature, it is evident that viscosity decreases drastically with increase in shear rate.

Indexing terms/Keywords

polyamide composites, rheology, processing technologies, modelling and simulation, vinogradov-malkin model

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INTRODUCTION

The determination off low curves or curves of viscosity over a wide range of shear rates and at different temperatures is expensive and time consuming. Alternatively, Melt Flow Index (MFI) can be determined to study the rheological properties of polymeric materials. In order to study the rheological properties, Melt Flow Index may be determined. This method can be used to determine both the density and the volumetric flow rate of the polymeric materials flowing out of the capillary under standard test conditions. The melt flow rate is defined as the reciprocal of viscosity and represents a single point on the viscosity curve at a specified measuring temperature [1-6]. The point that represents the melt flow rate of the viscosity curve can be determined using the following equation:

$$\eta_p = \frac{\tau_w}{\dot{\gamma}_p} \; [Pas] \tag{1}$$

where: η_p – apparent viscosity; τ_w – tangential stress on the wall of the capillary; $\dot{\gamma}_p$ – shear rate at the wall of the capillary.

The tangential stress and shear rate at the wall of the capillary tube are determined by the following equations:

$$\tau_w = \frac{\dfrac{F}{\pi R_c^2}}{2L_k} R_k \; [Pa] \tag{2}$$

where: R_k – radius of the capillary; L_k – the length of the capillary; F – the force acting on the piston; R_c – radius of the cylinder.

$$Q = \frac{m/t}{\rho} \; [cm^3/s] \tag{3}$$

where: m – mass of the sample; t – time of measurement: ρ – density of the material.

$$\dot{\gamma}_p = \frac{4Q}{mR_k^3} \; [1/s] \tag{4}$$

where: Q – volumetric flow rate of the polymeric material; R_k – radius of the capillary.

Determination of apparent viscosity and their corresponding shear rate is the basis for the designation of approximate viscosity curves based solely on the rheological measuring point. For this purpose, a universal Vinogradov-Malkin model can be used equation (5) [7-11].

$$\eta(\dot{\gamma}, T) = \frac{\eta_0(T)}{1 + A_1[\dot{\gamma}\,\eta_0(T)]^a + A_2[\dot{\gamma}\,\eta_0(T)]^{2a}} \tag{5}$$

where: $\eta(\dot{\gamma}, T)$ - a viscosity corresponding to the shear rate at a temperature of T; $\eta_0(T)$ – a viscosity corresponding to zero shear rate $(\dot{\gamma} \to 0)$ at a temperature of T; $A_1 = 1.386 \cdot 10^{-2}$; $A_2 = 1.462 \cdot 10^{-3}$; $a = 0.355$.

Knowledge of zero viscosity allows to calculate the viscosity at different values of shear rate at the measurement temperature (240°C). If viscosity value at the reference temperature is known, the viscosity of the material at different temperatures can be determined by applying Williams, Landel'a and Ferry (WLF) equation [12-14].

$$\eta(T) = \eta(T_R)\exp\left[\frac{8.86(T_R - T_g - 50)}{101.6 + (T_R - T_g - 50)} - \frac{8.86(T - T_g - 50)}{101.6 + (T - T_g - 50)}\right] \tag{6}$$

where: $\eta(T)$ – viscosity of the material at a different temperature [Pas]; $\eta(T_R)$ – viscosity of the material at a known temperature (reference) [Pas]; T_R – reference temperature [°C]; Tg – glass transition temperature of polymeric material [°C].

In this paper, Vinogradov-Malkin theoretical model is used to determine flow curves of polymeric composites. Existing technology does not allow to measure many rheological parameters corresponding to the processing conditions. These calculations made according to model equations let us to carry out a simulation in wide range of shear rate and temperatures. In order to overcome the limitations, a simulation based on Vinogradov-Malkin model can be carried out to determine the flow curves of PA6 composites at wide range of shear rate and temperatures. From technological point of view this is very important as it enables to foresee polymeric composites behaviour during high-temperature processing.

EXPERIMENT

Materials and sample preparation

The particulate composites used were produced from a PA6 melt-compounded with either an unmodified sodium montmorillonite (MMT) or an organo-modified montmorillonite (OMMT). BASF Chemical Company supplied the injectable grade PA6 (Ultramid® PA6), which offer an easy-flowing extrusion. The Na^+-MMT (Cloisite-Na^+), supplied by Altana BYK-Chemie GmbH, was nanoclay based on a natural mineral for aqueous polymers having optimized surface properties and cations composition for exfoliation in aqueous systems. The OMMT (Cloisite 11), supplied by Altana BYK-Chemie GmbH, was a nanofiller organofilized using benzyl(hydrogenated tallow alkyl)dimethyl salt, developed for extrusion compounding with engineering polymer matrices. N,N'-hexane-1,6-diylbis(3-(3,5-di-tert.-butyl-4-hydroxyphenylpropionamide)) (Irganox 1098) was supplied by BASF Chemical Company, as a phenolic primary antioxidant for processing and long-term thermal stabilization. To observe the effect of either adding stabilizer with nanoclay or reacting the stabilizer with nanoclay, Irganox 1098 was added into system by physical addition during melt blending.

Table 1. Content of nanofiller and stabilizer in composite system

Name of sample	Content of MMT [wt%]	Content of stabilizer [wt%]
PA6	0	0
PA6/I1098		2.5
PA6/MMT	5	0
PA6/MMT/I1098		2.5
PA6/OMMT	5	0
PA6/OMMT/I1098		2.5

Before the preparation of nanocomposites, materials were dried in a laboratory vacuum oven at 80°C for 3 hours. Dried components were mechanically premixed then compounded using a twin co-rotating screw extruder Brabender KETSE 20D with a screw speed of 250 rpm, a temperature profile of 220°C (feed throat) to 240°C (die). The compounds were extruded as single lace of 4 mm diameter, which were hauled into a quenching water trough prior to being pelletized. After processing, all composite samples were dried at the same condition as previous.

Melt Flow Index

The measurement of the melt flow index was performed by using Zwick Melt Flow 4106 coupled with an analytical balance Kern ABS80-4 (d = 0.1mg, the maximum load capacity of 83 g) in accordance with ISO1133, ASTMD 1238. Tests were performed at 240°C using a piston thrust load equals 2.16 kg. Sample was pumped through the nozzle of the capillary at the appropriate time for determining mass, density and then viscosity of the material at the test temperature. The viscosity of the materials at melt temperature allows to determine full rheological characteristics based on universal Vinogradov-Malkin model. The viscosity of the material at different temperatures can be determined by using the Williams, Landel'a and Ferry (WLF) equation.

RESULTS AND DISCUSSION

Calculation of rheological properties from Melt Flow Index

Melt Flow Index can be used to determine the density of the polymeric materials. Table 2 shows the rheological properties of PA6 and its composites. The rheological properties were calculated from the average values of melt flow rate (MFR) and melt volume-flow rate (MVR) by a single point method.

The Melt Flow Rate (MFR) of PA6 is found 6.6 g/10min. On addition of stabilizer (Irganox1098) to PA6, Melt Flow Index is increased to 7.07 g/10min. It should be noted that increase in Melt Flow Rate indicates decrease in the density of the materials and vice-versa.

As expected, incorporation of nanoclay to PA6 significantly decreases the Melt Flow Rate of the composition. Addition of stabilizer further decreases Melt Flow Rate and thereby, increases density of the PA6/nanoclay composition. The interesting finding is that PA6/OMMT composition shows lower Melt Flow Rate than PA6/MMT composition. However on the addition of stabilizer, both composition shows similar Melt Flow Rate and hence, density.

Table 2. Rheological properties of PA6 and its composites

Sample	Mass [g]	MFR [g/10 min]	MVR [cm^3/10 min]	Density [g/cm^3]	Flow rate [cm^3/s]	γ [1/s]	η [Pas]
PA6	0.344	6.60	6.69	0.99	0.011634	12.89	1502.76
PA6/I1098	0.355	7.07	7.37	0.96	0.012353	13.68	1418.51
PA6/MMT	0.364	5.62	7.59	0.74	0.016396	18.16	1067.61

PA6/MMT/I1098	0.329	4.93	7.30	0.68	0.016238	17.99	1077.75
PA6/OMMT	0.291	5.44	6.00	0.91	0.010683	11.83	1639.37
PA6/OMMT/ I1098	0.209	4.98	4.04	0.89	0.014236	15.82	1228.78

Using the above equations, values of melt volume-flow rate, the shear rate and viscosity of the materials tested under the conditions of the measurement, were carried out. The resulting viscosity values correspond to different values of shear rate. It can be concluded that different shear rate at the capillary wall surface is the cause of such different melt flow rates. Higher viscosity (low MFR values) indicates a significant effect of organic fraction in the organo-complex or stronger interaction between filler and polymer matrix.

Simulation of rheological curves using Vinogradov-Malkin model

The theoretical viscosity curves of PA6 and its composites were determined by using Vinogradov-Malkin model. The simulations were carried out at measurement temperature, 240°C and in the range of 180°C-350°C with shear rate of 10^{-1} – 10^{3} 1/s. Figure 1 shows the flow curves of PA6 and PA6/I1098. Figure 2 and 3 show the flow curves for the composites containing the sodium clay and organo-clay, respectively. Viscosity curves at 240°C temperature possess a typically text book character. In case of low shear rates, the addition the sodium clay and stabilizer did not increase viscosity either for PA6 or PA6/I1098. In this range, the viscosity decreases in the following order: PA6/OMMT > PA6 > PA6/I1098 > PA6/OMMT/I1098 > PA6/MMT/I1098 > PA6/MMT.

At higher shear rates, viscosity decreases in the same sequence as low shear rates. At further higher shear rates (> 1000 1/s), filler particles are arranged in the flow direction thus exerting no significant effect on viscosity of composites both with and without the stabilizer.

The one-point method can be used to predict the change in viscosity of the polymer material during high temperature processing. Shear rates are not only important in the cylinder of the extruder but also the entire process of flow through extruder or injection moulding machine. Volume elements of the molten polymer composite at any point of screws are also subjected to various types of flow with shear rates ranging from 0.01 to 1000 1/s [15-16]. In such conditions it is difficult to define viscosity for a given volume element of material and predict whether the selected processing conditions are suitable or not. Similarly, in the process of injection mould filling, a wide range of changes in the shear rate can be found. The changes in the shear rates can be comprised of more than four orders of magnitude. Table 3 summarizes the calculated viscosity of PA6 and its composites in the range of 10^{1} – 10^{4} 1/s. It should be noted that shear rates ranging from 10^{1} – 10^{4} 1/s is conventionally considered during injection moulding.

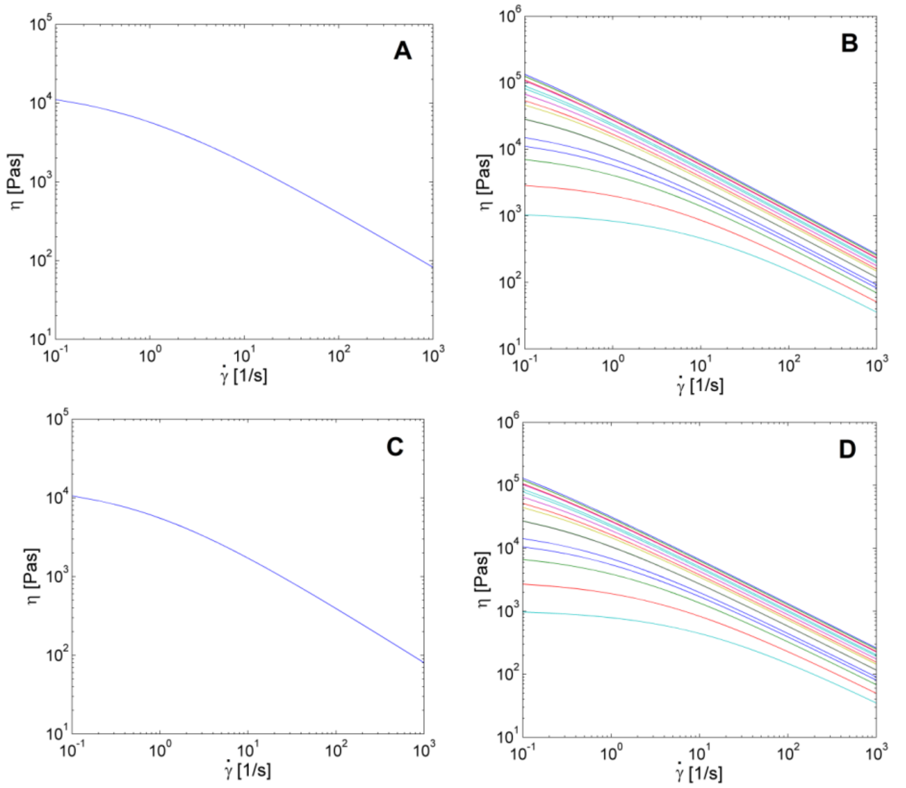

Fig 1: Flow curves for: (A) PA6 at 240°C; (B) PA6 at the range of 180°C-350°C; (C) PA6/I1098 at 240°C; (D) PA6/I1098 at the range of 180°C-350°C

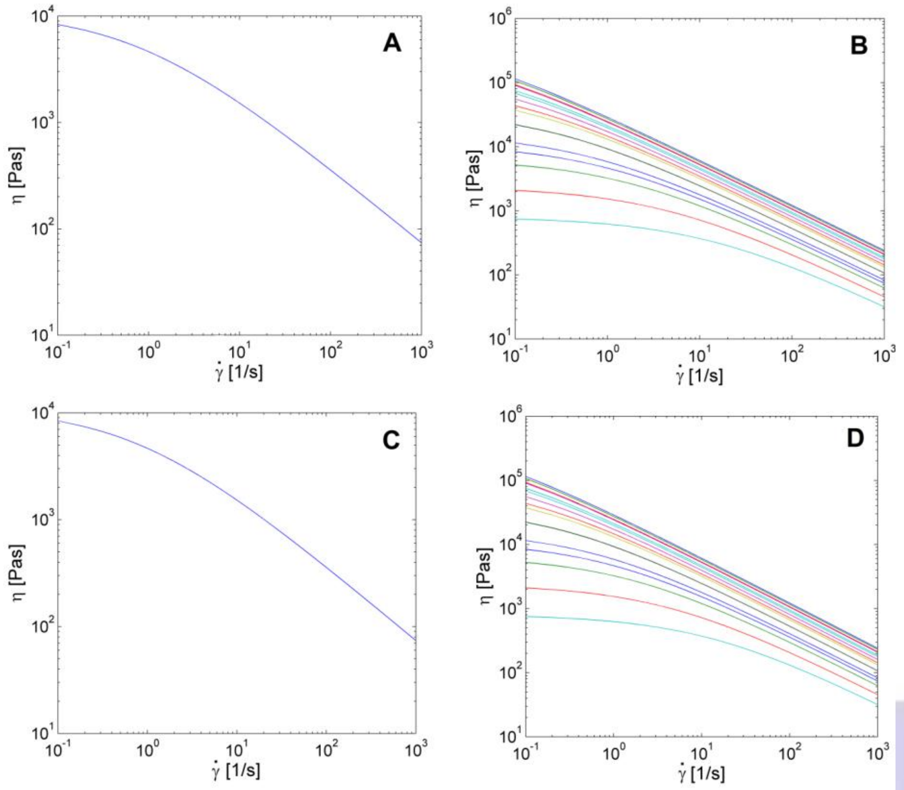

Fig 2: Flow curves for: (A) PA6/MMT at 240°C; (B) PA6/MMT at the range of 180°C-350°C; (C) PA6/MMT/I1098 at 240°C; (D) PA6/MMT/I1098 at the range of 180°C-350°C

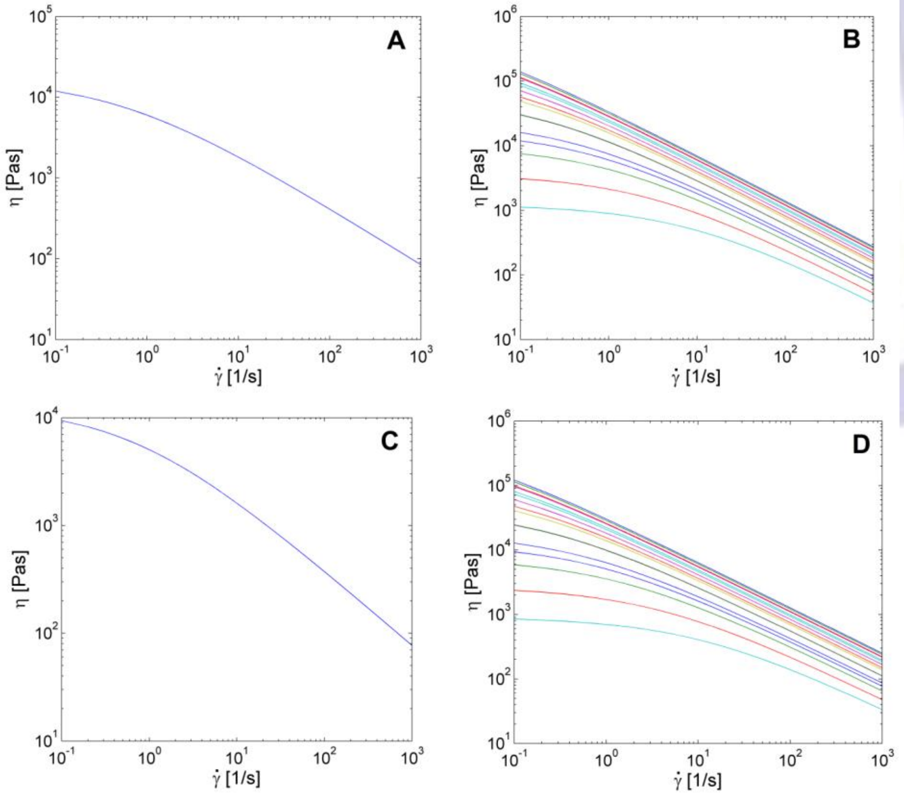

Fig 3: Flow curves for: (A) PA6/OMMT at 240°C; (B) PA6/OMMT at the range of 180°C-350°C; (C) PA6/OMMT/I1098 at 240°C; (D) PA6/OMMT/I1098 at the range of 180°C-350°C

Table 3. Viscosity of PA6 and its composites during injection moulding in the shear rate ranging from $10^1 - 10^4$ 1/s at 240°C temperature

Sample	η in terms of injection moulding [Pas]	η at the temperature of 240°C and at $\dot{\gamma} \to 0$ [Pas]	η at the temperature of 240°C and at $\dot{\gamma} = 10^1$ [Pas]	η at the temperature of 240°C and at $\dot{\gamma} = 10^3$ [Pas]
PA6	1751 – 16.28	16320	1751	81.96
PA6/I1098	1708 – 15.99	15270	1708	80.46
PA6/MMT	1519 – 14.71	11510	1519	73.83
PA6/MMT/I1098	1526 – 14.75	11630	1526	74.07
PA6/OMMT	1811 – 16.69	17650	1811	84.08
PA6/OMMT/I1098	1611 – 15.33	13250	1611	77.07

It can be seen from Table 3 that viscosity varies by 100 times in the shear rate ranging from $10^1 - 10^4$ 1/s. This variation in viscosity must be considered for the design of technological process. In stable temperature, profile indicates that there will not be accumulated flow instabilities leading to turbulent behaviour. This behaviour in composite materials is found in particular for systems containing particles of non-spherical shape, which at sufficiently high levels of shear stress begins to spin thus making it difficult to flow. During injection moulding in the shear rate ranging from $10^1 - 10^4$ 1/s at 240°C temperature, it is evident from the Figures 1, 2, 3 and Table 3 that viscosity decreases drastically with increase in shear rate.

CONCLUSIONS

Shear rate, flow rate and approximate temperature profile can be predicted with the help of simulation at different temperatures. It is also possible to determine the viscosity of the nanocomposite at room temperature which is equally important for designing the injection moulding process. The resulting viscosity of the polyamide composites are in the range of 10^{27} Pas, which helps in realizing the changes of order of magnitudes of viscosity of the composite during a few seconds of mould cooling process. Stress relaxations is then occurred at shear striving for zero where the elastic deformations are stopped during solidification of the melt. The range of changes in viscosity occurred during injection mould processing of the polymer is out of the measuring equipment and apparatus [17-21]. Therefore, the one-point method is often used in plastics processing and allows to simulate the technological process in technical and semi-technical conditions. In order to overcome the limitations, the proposed simulation method can be a promising tool to transfer technology from laboratory to industrial scale in order to manufacture polymer nanocomposites.

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