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RHEOLOGICAL PROPERTIES OF VACUUM GAS OIL – POLYPROPYLENE BLENDS SYSTEM

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ABSTRACT: -The present work is concerned with study of the flow behavior of poly propylene (PP) and Vacuum Gas Oil (VGO) blends. Viscosimetry measurements of the blends with different polymer weight fractions between 0 and 10 wt%., temperatures between 391 K and 491 K at shear rates up to 1000 S-1 were performed. These blends were shown to have peculiar flow behavior exhibiting Newtonian fluid flow property at higher temperatures and lower polymer concentrations, while at lower temperatures and at higher polymer concentrations, showing non-Newtonian shear thinning or pseudo-plastic behavior. These properties have been shown to be more pronounced at lower shear rates than at higher shear rates. The application of Ostwald-De Waele power law model for the prediction of the viscosity under different operating conditions of shear rates, temperature and base components weight fractions has been given a good fit for the experimental viscosimetry data.

Keywords: Rheological properties, Vacuum gas oil, Polypropylene, Power law.

1- INTRODUCTION

In the plastic industries, polymer blends processing is an important issue since the deformation and thermal histories of a specific process on a great scale impacts on the mechanical properties of the obtained product. Furthermore, research on the processing of oil – plastic waste blends as a new plastic recycling alternative are increasingly been carried out with promising results [1]. In the oil and gas industry, viscosity has been extensively used for the calculation of pipeline fluid transportation. The transportation of a mixture of fuel and polymer such as poly propylene is of no doubt challenging due to the resulting very high viscosity as a result of the polymer addition. The viscosity of such blends coupled with the dependency on temperature and components concentration is of great research interest since this property greatly affects crucial processes such as fluid atomization in a Fluid Catalytic Cracking (FCC) unit as an example, and flow through heated pipelines or tubes [2], on the other hand, the reactors performance and operations are often influenced by the viscous flow properties of the reacting fluids or medium [3].

There are numerous studies related to these topics. Arandes, J.M. study the transformation of several plastic wastes into fuels by catalytic cracking [1].Garcia-Morales, M., investigated the effect of waste polymer addition on the theology of modified bitumen, they have notice the viscosity of such blends is strongly dependent on temperature and components concentration [2]. Krishna et al. investigated the effect of conversion –dependent viscosity on the nonlinear behavior of a polymerization reactor and observed that multiple steady states can occur in reactor systems where viscosity significantly increases with conversion in the reactor [4]. Ng, S. H., study the conversion of polyethylene blended with VGO to transportation fuels by catalytic cracking, they have notice the viscosity increases with polyethylene conversion in the reactor [5].

The influence of temperature and mass fraction of Pluonic F127 on the rheological properties of polyvinyl butyric (PVB)/Pluronic F127/polyethylene glycol (PEG) 200 blend systems was investigated and Shear thinning behavior is observed for all the blend systems at different temperatures and is enhanced by increasing Pluronic F127 content [6].

The scope of this present work is thus limited to study the flow properties of vacuum gas oil – poly propylene blends under varying shear rates, concentration and temperature, and also Ostwald-De Waele (Power Law) model have been used to fit the experimental data of the apparent viscosity of vacuum gas oil – poly propylene blends.

2- EXPERIMENTAL WORK:

2.1 Materials:

Commercial grade poly propylene density of (0.98 g/cm^3), melt flow index of (11 g/10 min) and melting temperature of (180 C^o) supplied by Sabic Saudi Arabic Company (SABIC) were used in this work. The vacuum gas oil (VGO) boiling point range (300-400 C^o) and density (0.87 gm /cm^3) is an available in Al-Dora refinery was also used.

2.2 Samples preparation:

Samples of the vacuum gas oil – poly propylene blends were prepared by continuously stirring used mechanical stirrer at (60 rpm) and at temperature (185 C^o) for (45 min) after the polymer melting took place mixtures of the base components with different weight fractions (0, 2.5, 5, 7.5 and 10 wt%) of the polymer, the obtained blends were left to chill to room temperature before proceeding to the viscosity measurement. Viscosity measurements were performed using Rotational viscometer model (VDJ-4), were carried out at 391, 416, 441, 466 and 491 K at shear rates up to 1000 S^{-1}.

3- MATHEMATICAL MODEL

The Ostwald-De Waele (Power Law) model has been employed to fit the experimental data of the viscosity of the VGO–PP blends at varying shear rates. The model proposed by Ostwald-De Waele is given by Equation (1).

$$\eta = K\,\gamma^{n-1} \tag{1}$$

Where (η) is viscosity of blend, (K) is a constant, (γ) is the shear rate, and (n) is a dimensionless constant (which defines the flow behavior of the mixture at a given temperature). The constant (n) can be used to preliminarily predict the flow behavior of the VGO-polymer system. Generally, the flow index (n) has values between 0 and 1 and above, in which case, blends with the index value closer to (1) exhibit Newtonian flow behavior, characterized by a constant shear viscosity value under varying shear rate. The higher the deviation from this value towards (0) the higher the shear-thinning or non-Newtonian behavior is exhibited by the blend.

The Andrade equation was used for the correlation of liquid viscosity and temperature, as shown in the following equation [7].

$$\ln \eta = A + \frac{B}{T} \tag{2}$$

Where (A) and (B) are the parameters of a given liquid, and (T) is the absolute temperature. In order to accurately predict the temperature dependency of the viscosity of the VGO-Polymer blend under varying shear rates, equation (2) was integrated into the Ostwald-De Waele model (Equation (1)), taking into consideration the variation of the model parameters with temperature. It was expected that an increase in the blend temperature will lead to an increase in the consistency index (K). As such, the increase in the parameter (K) was assumed to have a similar relation given by Equation (2), as shown in (Equation (3)).

$$\ln K = A_{T,K} + \frac{B_{T,K}}{T} \tag{3}$$

Díaz et.al [8] obtained linear relationship between the Andrade parameters and compositions concentration for a number of oil blends as shown in (Equations (4) and (5)).

$$A_{T,K} = px + q \tag{4}$$

$$B_{T,K} = yx + z \tag{5}$$

Where (x) is the mass fraction of the polymer component and p, q, y and z are constants. The substitution of these equations (4 and 5) in the consistency index (K) equation (3) as given in its logarithmic form results in the following (Equation (6)).

$$\ln K = x\left(\frac{p}{T} - y\right) - z + \frac{q}{T} \tag{6}$$

A simple rearrangement of Equation (6).

$$\ln K = -z - yx + \frac{q}{T} + \frac{px}{T} \tag{7}$$

The above derived equation is in agreement with the equation obtained by Krisnangkura et. al. [9], which is based on the relation between fluids Gibbs free energy of activation, the number of carbon atoms in a homologous series and the increment in free energy per carbon atom, for the determination of free fatty acid viscosity at different temperatures and concentration, as given by Equation (8).

$$\ln \eta = -\alpha - bx + \frac{c}{T} + \frac{x\,d}{T} \tag{8}$$

Where α, b, c and d are constants and x is the number of carbon atom of the homologous series. Nguyen et. al. [10], obtained a similar relation by fitting viscosity experimental data into Andrade's semi-empirical equation and exponential law to predict the viscosity of a number of solutions.

Better results were obtained with the assumption of a simple linear relation between flow behavior index (n) and the blends temperature and concentration as given below in Equation (9).

$$n = A_n + B_n T - C_n\,x \tag{9}$$

Where A_n,B_n and C_n are constants. The last equation show that the increase in the polymer concentration inserts a decrease on the flow behavior index, tending the blend towards a more shear-thinning or pseudo-plastic behavior, while an increase in temperature will tend to increase this value to 1, towards the Newtonian region.

A unified master Equation (10) derived from the substitution of Equations (7) and (9) into Equation (1) was used to fit the experimental data obtained from the shear viscosity measurements of VGO-PP blends at varying shear rates, concentrations of the polymer (0, 2.5, 5, 10 wt%) and at temperatures between 391 and 491 K.

$$\eta = \exp^{\left(-z-yx+\frac{q}{T}+\frac{px}{T}\right)} \times \gamma^{(A_n+B_nT-C_nx)-1} \tag{10}$$

The parameters of the proposed unified master Equation (10) obtained by using statistica software from the fitting of the experimental data are given in Table (1)

4-RESULTS AND DISCUSSION:

The viscosity of fluids is greatly affected by a number of factors which includes the physical and chemical properties of the components such as density, compositions concentration, molecular weight, and melting point. However, the temperature is a great scale effect on the viscosity of fluids.

Fig. 1 and 2 show the experimental viscosity of the VGO-PP blends as a function of shear rate with different poly propylene weight fractions between 0 and 10 wt% and at temperature 391and 416K correspondingly, Within the shear rate range and polymer concentrations employed in this work, from the presented Fig. 1 and 2, it was observed that the base VGO showed Newtonian flow behavior [viscosity was independent on the applied shear stress], while all curves showed varying degree of pseudo-plastic non-Newtonian flow behavior, characterized by the decrease in viscosity with increase in shear rate, this decrease, and hence the deviation from Newtonian behavior was more pronounced as the concentration of the polymer in the blends was increased. Furthermore, this decrease was higher at lower shear rates.

The experimental viscosity of the (VGO-PP) blends at temperatures 441, 466, and 491K are generally similar to that shown in Fig. 3, characterized by practically parallel horizontal straight lines representing constant viscosity as the shear rate is increased, the viscosity curves obtained have leveled off. In other words, at higher temperatures and shear rates, the viscosity of the blends was independent on the shear rates.

As expected, the viscosity of the mixtures generally increases with increasing polymer concentration at each temperature. The obtained experimental shear viscosity was inferior to that of the base polymer at the same conditions of temperature and shear rate. Furthermore, a general decrease in the blends viscosity was also observed as the temperature was increased. This observed trend may be associated with the incorporation of the oil molecules into the polymer matrix exerting, as a result, a plasticizing effect on the polymer, with the consequent decrease in the viscous flow activation energy of the polymer [11, 13].

Fig. 4, 5 and 6 shows the viscosity flow curves obtained from experimental data as well as the curves obtained from fitting these data to the proposed unified master model Equation (10). For clarity reasons, the temperature interval (441-491) K, only the fitted flow curves at (441 K) was presented here. Fig. 6 since at this temperature interval, similar flow patterns was obtained. From the obtained curves, some general trends can be observed a gradual transformation from a non-Newtonian flow behavior at lower temperatures and higher concentrations, to Newtonian at higher temperatures, a decrease in the blend viscosity as the temperature is increased, and an increase in viscosity as the concentration was increased as expected, under the shear rates range employed. A good fit can be observed from the figures using the proposed model, considering the high number of experimental data and model parameters fitted.

5- CONCLUSION:

The present work was carried out to study and predict the concentration, temperature and shear rate dependency of the viscosity of VGO-PP blends. It was found that the blends generally show Newtonian flow behavior at higher temperatures and lower polymer concentrations, and shear thinning pseudo-plastic non-Newtonian behavior at higher polymer concentrations and lower temperatures. These behaviors are more pronounced at lower shear rates than at higher shear rates. Very good fits to the experimental viscosity data were obtained using the Ostwald-De Waele (Power Law) model.

6- NOMENCLATURE

n	flow index (-)
T	absolute temperature(K)
x	mass fraction of the polymer component **(-)**
Greek Letters	
η	Viscosity of blend (Pa.s)
γ	Shear rate (S^{-1})

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Table (1): Parameters obtained from the fitting of the experimental data to the proposed unified master equation (Equation 10).

Parameters	Values
z	1.733
y	5.943
q	- 534.125
P	2646.496
A_n	0.997
B_n	- 0.001
C_n	- 0.105

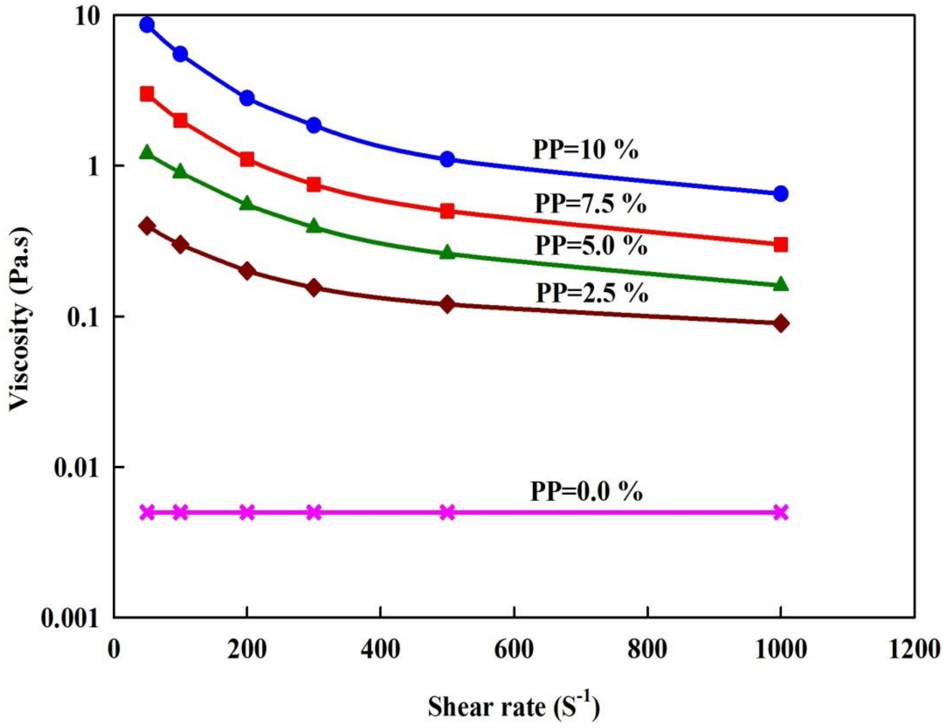

Fig. (1): Viscosity of VGO-PP blends as a function of shear rate at different weight percentage of poly propylene and at 391 K.

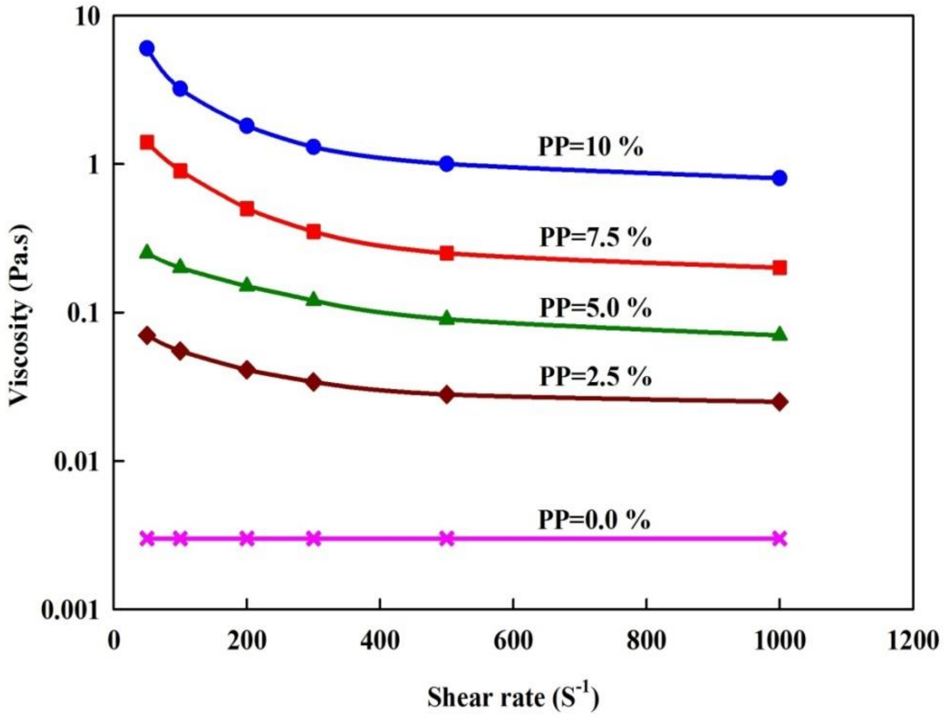

Fig. (2): Viscosity of VGO-PP blends as a function of shear rate at different weight percentage of poly propylene and at 416 K.

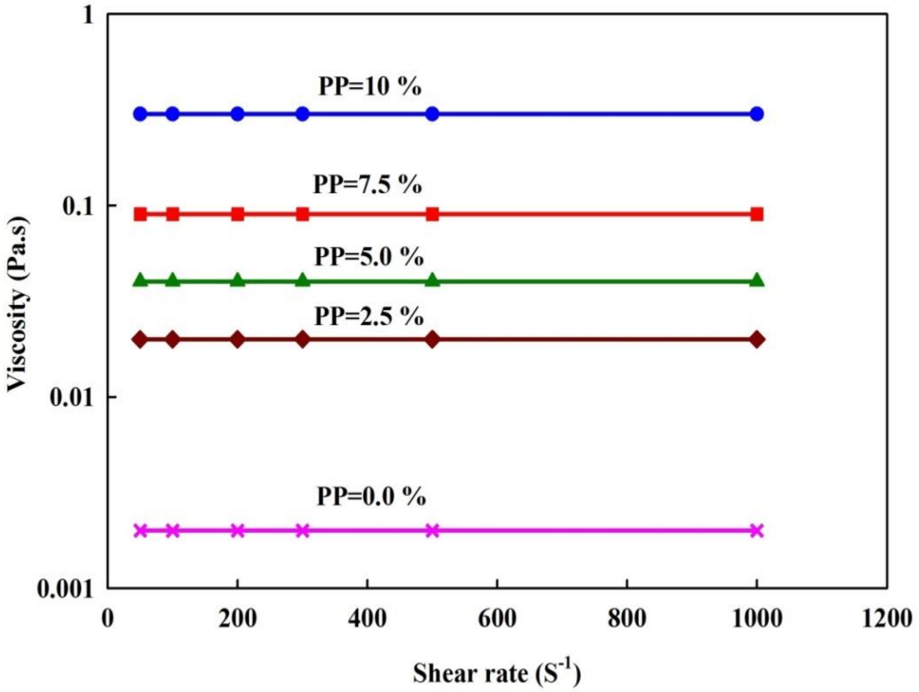

Fig. (3): Viscosity of VGO-PP blends as a function of shear rate at different weight percentage of poly propylene and at 441 K.

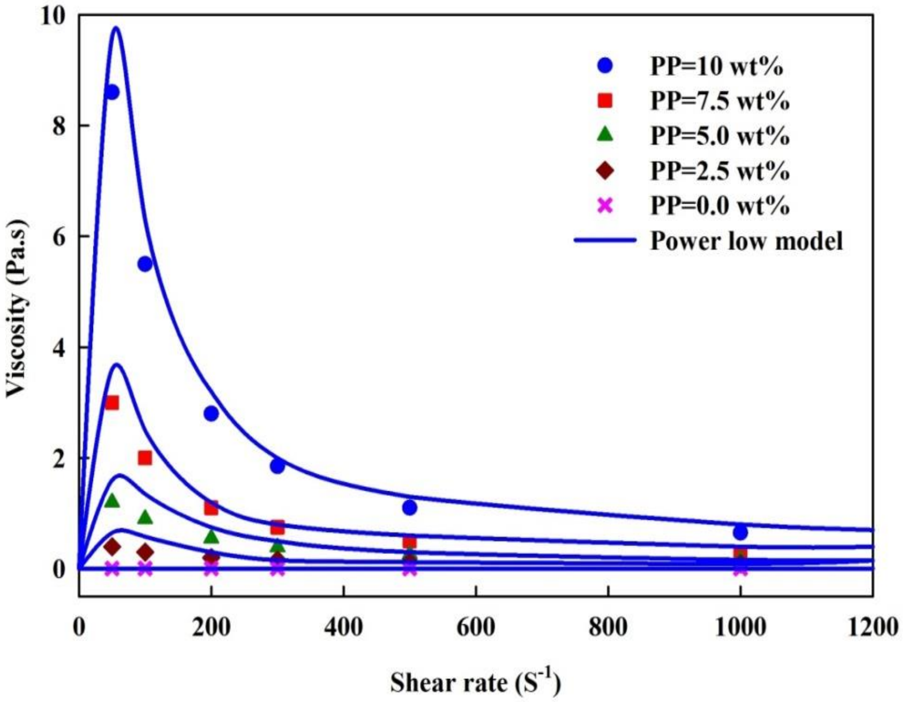

Fig. (4): Viscosity of VGO-PP blends as a function of shear rate at different weight percentage of poly propylene and at 391 K. (lines: Power low model, symbols: experimental data).

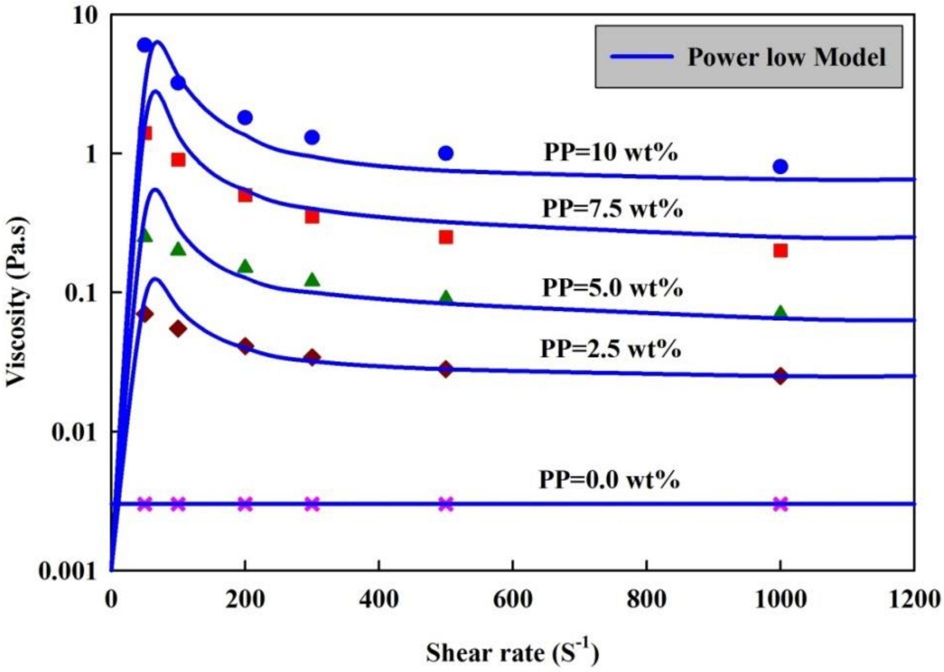

Fig. (5): Viscosity of VGO-PP blends as a function of shear rate at different weight percentage of poly propylene and at 416 K. (lines: Power low model, symbols: experimental data).

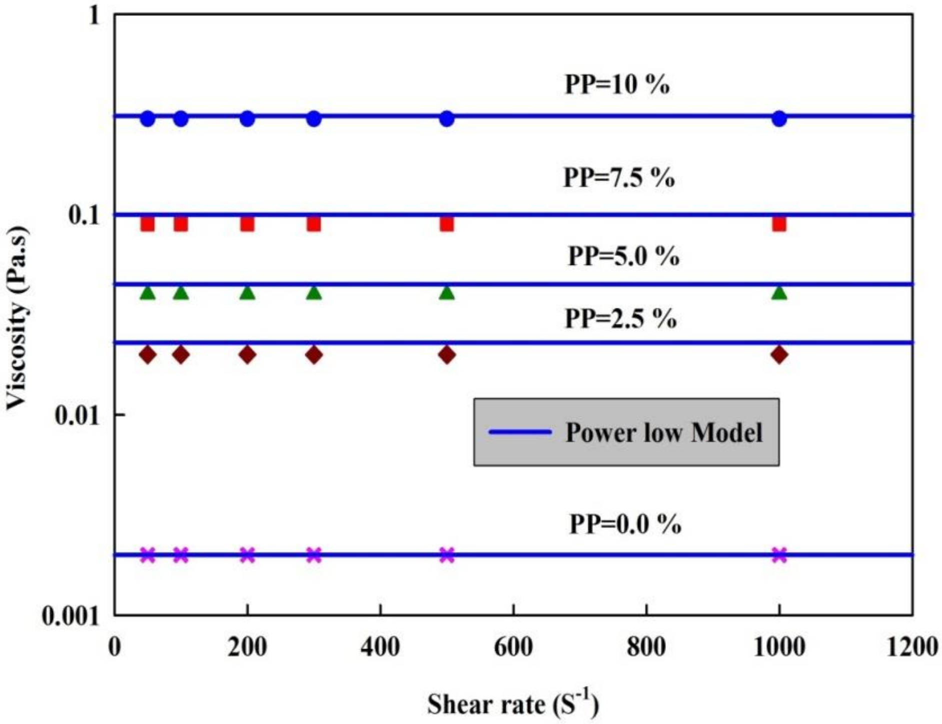

Fig. (6): Viscosity of VGO-PP blends as a function of shear rate at different weight percentage of poly propylene and at 441 K. (lines: Power low model, symbols: experimental data).

خصائص الجريان لمزيج زيت الغاز مع البولي بروبلين

الخلاصة:

في هذا البحث تم دراسة سلوك الجريان لمزيج من زيت الغاز والبولي بروبلين , حيث تم قياس اللزوجة للمزيج عند نسب مختلفة من البوليمر تتراوح بين (0−10)% ودرجات حرارة تتراوح بين 391 الى 491 كلفن وبمعدلات قص اعلى من 1000 ثانية$^{-1}$. اثبتت النتائج لهذا المزيج سلوك تدفق نيوتيني عند ارتفاع درجات الحرارة وتراكيز قليلة للبوليمر في حين , عند درجات الحرارة المنخفضة وبتراكز اعلى للبوليمر يكون السلوك غير نيوتيني, حيث تكون هذة الخصائص اكثر وضوحاً في انخفاض معدلات القص. تم تطبيق نموذج Ostwald–De Waele power law للتنبؤ بلزوجة المزيج في ضروف تشغيل مختلفة من معدلات قص ودرجة حرارة ونسبة البوليمر حيث اعطت النتائج تطابق جيد مع النتائج العملية.