

Rheological Properties of Nanoclay-Polyethylene Composite Through Capillary Rheometry

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Abstract

The rheological properties such as viscosity and flow rate are essential ones in determining the nanofillers in processing the nanoclay-polyethylene (NC-PE) composites in injection moulding. The aim of this paper is to investigate the rheological behaviour of plastic feedstock comprising of NC-PE composites by means of a capillary rheometry. In order to produce a defect-free component, the feedstock composition plays a critical factor and rigorous caution has to be taken while inserting feedstock with high solid loading and then excellent flowability. The viscosity and shear rate of various feedstock's at NC ratio ranging from 0, 1, 2, 3 %wt. were measured at L/D=10 die and a load ranging from 40 to 80 kgf at temperatures of 140, 150, and 160 °C. The viscosity of these three samples was determined to show that the corresponding flow behaviour index changes from 0.4 to 0.7 expressing the non-Newtonian behavioural of the samples. The activation energy of the three samples at the mentioned temperatures was determined and found to be 36.5 to 69.88 kJ/mole depending on the load applied.

Keywords: Composites; Injection moulding; Rheology properties; Feedstock

1 Introduction

The polymer technology plays an important role in industry and technology. Polymers appear in a very wide range of forms and could be found anywhere between the extremes of a soft to rigid thermoplastics. The easy changing in chemical composition as well as the molecular weight due to various methods of polymerization are behind the presence of almost uncountable polymers materials. In the last four decades, polymer manufacturers were able to produce the polymer that fits a certain criteria and purposes [1]. Accordingly, numerous research papers are found in the literature of high quality. The focus of these articles was on the chemical compositions/structure and how the microsphere morphologies are affected. In addition, other studies have focused on the physical and chemical properties of the nanocomposites of several types and groups. As an immediate result of these articles was developing various morphological models for polymer [2]; yet differences are still present amongst authors' perspectives. The demand for matrix PE is due to its high performance as elastomer and tough thermoplastics [3]. PE is linearly segmented copolymers composed of hard and soft segments. The hard segment is held by hydrogen bonds (the physical crosslink) which are very sensitive to temperature and they can be easily broken due to slightly high temperatures. For this reason, the rheological tests should be carried out carefully about the applied temperature. In addition, the soft segments-covalent bond, are also susceptible to dissociation at elevated temperatures. Based on the criteria of dissociation of both segments, the degradation of PE in melting state is unavoidable at or around the PE's thermal stability which is closely related to the activation energy.

The physical and chemical properties of pure polymers can be modified or manipulated using different techniques; one

of these techniques is the nanocomposites. In nanocomposites, particle-filled polymers for which at least one dimension of the dispersed particles is in the nano range, provide a potential solution to these inherent drawbacks of filled polymers [4]. In recent years, a new type of composite materials (nanoclays of structure NC-P) was increasingly used owing to their high improved heat deflection temperature, dimensional stability, gas barrier performance, enhanced mechanical properties, and optical clarity compared with the pure polymer or composites having conventional fillers [5-7]. In addition to polyethylene (PE), polypropylene (PP) was used with nanoclay and investigated by rheology technique [8].

The production of polymers is one of the steps that lead to unlimited applications of these polymers in industry and technology. An intermediate step between polymer production and subsequent applications is the rheology. The focus in this paper is on the polyethylene (PE) as one of the most important polymers in technology and, as such, PE is treated by rheology which plays a vital role in monitoring the flow behavior under different conditions such as shear rate, temperature, pressure, or time. Investigations on the rheological properties in heating and cooling processes are important for polymer operations because PE is mostly processed under high temperature followed by slow cooling to shape the final product [9]. The importance of rheological and viscoelastic measurements on PE is stemmed from the concept of rheological techniques which can be used as a noninvasive experimental tool for the investigation of the rich phase transition/relaxation behavior of this class of composites, and secondly due to the usefulness of rheology in investigating the effect of phase transitions or relaxations. According to many research groups, the high temperatures viscoelastic of PE have employed a technique known as

temperature sweep mode [10]. Rheology is not about viscosity but also about elasticity as most polymers exhibit the elasticity behavior. In injection, many processes are taking place such as stirring, dispersing, and pumping the product where all these properties have a certain dependency on the viscosity. PE is described as a pseudoplastic fluid chemical which becomes thinner when the shear rate increases until it stabilizes at a plateau called viscosity limit. The effect of viscosity on polymer injection has to be considered individually due to behavioral differences of polymers regarding their molecular weight and other relevant properties. For carbon nanofiber-thermoplastic polyurethane (CN-TPU), as the clay content increases, the viscosity of the CN-TPU composite increases [11]. Ariff et al. (2012) reported that an increase in the storage modulus values was observed because of adding tethered and nontethered clays. However, lower storage modulus value with the unmodified clay was ascribed to the presence of aggregates of clay in micron size scale and owing to poor clay-polymer interaction. The highest value of storage modulus was found in a case of the nanocomposite containing tethered clay [12]. This has also been argued to be due to the greater interaction between the polymer and clay because of tethering. The knowledge about rheology could help in determine the optimal design of processing equipment such as extrusion dies design, the shape of the screw, or the properties of the cavity. Briefly, rheology is the key to efficient design, selection of materials, and others [13].

In rheology, determining the strain hardening and strain softening are the real problems that face the rheological properties of the plastics prior to its injection [14]. One problem came from the fact that plastics, generally, show Newtonian and non-Newtonian behaviour because, at a high shear rate, plastics molecules disentangle from each other and aligned with the direction of the flow expressing non-Newtonian behaviour. Prior to injection, it was very important to find the Newtonian conditions and set the injection speed accordingly [15]. As the polymer or the composites injected into the mould, high shear forces could be applied to them. The shear rate has a severe influence on the viscosity and, as such, the results from the injection moulding vary significantly, which makes the results in many cases inconsistent. In addition to injection speed, the injection and mould temperatures have to be re-evaluated. The challenge of determining these parameters depends on empirical formulas where experimental work is the source of the variations of these parameters. All these parameters were formulated according to the optimized parameters in the mould injection are considered a vital step that shapes the quality of the product [16]. The reinforcement of polymers by adding nanofillers such as clay minerals or carbon nanotubes has attracted much attention in polymer engineering since many decades [15, 17]. This study investigates and determines the rheological properties of NC-PE composites.

2 The Importance of Rheology in Injection Moulding

In injection moulding, the process becomes very complicated due to the many factors that affect injection. The final step in fabricating polymers is carried out in injection where polymers turned into the product for marketing. Fabrication involves knowledge of flow rate of the polymers and deformation which is considered the bases of rheology. The extrusion, moulding, and shaping depend on the available data of the polymer. It was found that many real fluids have to be stressed to a certain level, known as a critical stress, to initiate flow. The fluid below this stress behaves as a solid while above this threshold, the material yields to flow at a stress known as yield stress. After the yield, most materials do not exhibit Newtonian flow but their viscosity decreases

until stability attained as in most plastics. If the material does not have a yield stress, it may behave nonlinearly as in the case of pseudoplastic. PE matrix is highly considered in engineering for its versatility and importance in connection with properties. The basic characteristics of PE include high tensile, high abrasion resistance, high wear, and tear resistance, and resistance to oil and many solvents. The chemical structure of PE is susceptible to phase and structural changes when blending with other polymers [18]. The drawback of the temperature sweep mode is that the measurement has to be stopped when the sample begins to flow. The rheological viscosity of a fluid increases with time under shear rate. For this type of fluids, the viscosity-shear rate curve forms a hysteresis loop whose characteristics are seen as a guide to determine the type of fluid. Polymers are normally dissolved in solvents and, sometimes, are treated with surfactants. Rheological tests can be used to evaluate the behavior of these materials. The basic challenge for these tests is the polymer degradation under shear stress which indicates the effectiveness of the test. In the capillary rheometer, the aspect ratio (L/D) die, the temperature, and the applied pressure was provided at certain values of 10, 130–220 °C, and 5-100 kgf. The feedstock is injected into the barrel and lightly pressed for 10 to 15 min to reach thermal equilibrium. The flow rate is calculated by the provided software [18] through the following empirical equation 1.

$$Q = \frac{0.4}{t} \text{ (cm}^3\text{/s)} \dots\dots (1)$$

where *t* is the time for the piston to travel from 3 to 7 mm point in the barrel. The shear rate γ of the flow through the die capillary diameter *D* (in mm) is calculated by Equation 2:

$$\gamma = 32/\pi D^3 * 10^3 \text{ (s}^{-1}\text{)} \dots\dots (2)$$

The Arrhenius's equation (Equation 3) is then applied to determine the activation energy:

$$\eta = \eta_0 \exp \left(\frac{E}{RT} \right) \dots\dots (3)$$

where η_0 is the viscosity at the reference temperature, *R* is the gas constant, *T* is the absolute temperature, and *E* is the activation energy? By taking the natural log for both sides, the result is shown in the following Equation 4:

$$\ln \eta = \ln \eta_0 + E/RT, \ln \frac{\eta}{\eta_0} = \frac{E}{RT} \dots\dots (4)$$

The last equation is a straight line equation between $\ln(\eta/\eta_0)$ and $1/T$ whose slope is *E/R* which can be used to calculate the activation energy *E*, Fig. 1 shows the Arrhenius's Equation 4 which is used to calculate the activation energy [3].

The viscosity calculation was not a straightforward process; it requires two-step applications. In the first application, the shear rate for non-Newtonian liquids should be determined according to Equation 5. The second application is to determine the shear stress at the wall, τ_R , using Ostwald-de-Waele equation [19, 20]:

$$\tau_R = K\gamma^n \dots\dots (5)$$

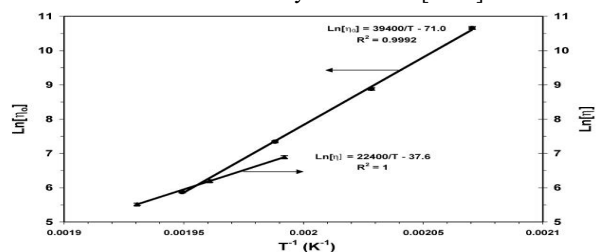
Where $\gamma = du/dy$ is the velocity gradient which strictly measures the rate of deformation (s^{-1}) and *n* and *n* the flow behavior index [21] which follows the following criteria:

- $n < 1$, pseudoplastic behavior
- $n = 1$, Newtonian fluids
- $n > 1$, dilatant behavior

The rheological characterizations of PE can be evaluated by [22]. This follows determining the viscosity η which is a function of velocity gradient (γ) according to equation (6).

$$\eta(\gamma) = K\gamma^{n-1} \dots\dots (6)$$

Where *K* is fluid consistency coefficient [Pa.sⁿ].



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Figure 1. The graph of \ln apparent shear rate vs. \ln shear stress for PE [3]

3 Materials and Methods

3.1 Material

Polyethylene (PE) of shore hardness of nearly 85 imported from Global Innovations-Polycarbonates Bayer Material Science AG, D-51368 Leverkusen, was used in this research while NC was imported from Sigma Aldrich, 3050 Spruce Street, Saint Louis, MO 63103, USA. The hollow tubular a two-layered aluminosilicate structure NC is known for its submicron range and similarity to kaolin 1,2. The length of the natural NC ranges from 1 to 20 microns while its inner diameter ranges from 10 to 150 nm depending on its origin.

Table 1. some properties of components

Type	Density (g/cm ³)	Melting Temperature (°C)	Decompose Temperature (°C)
PE	0.96	210 – 230	210

3.3 Rheology Characterization

CFT-500D Shimadzu capillary Rheometer manufactured by Toyoseiki in Capnograph-1B, as shown in Fig. 2 was used to measure the viscosity of the flowing fluid. The procedure includes measuring the viscosity of the melted materials as they pass through the die orifice whose aspect ratio is $L/D=10$

The type of NC under study has particle size 20 nm, tubular average diameter of 60 nm, lumen inner diameter of 20 nm, specific surface area of 59 m²/g, pore volume of ~1.22 mL/g, refractive index 1.58, and specific gravity 2.4 g/cm³.

3.2 Feedstock Preparation

Table 1 contains some physical properties of the components. In this study, the ratio of NC was set at 0 (neat), 1, 2, and 3 wt.%. The compound mixture was blended using Brabender mixer (40 rpm, 210 °C, and for 40 minutes). The dough was converted into feedstock of granular shape. Three samples were prepared using 1 wt.% NC-PE, 2 wt.% NC-PE, and 3 wt.% NC-PE composites.

and attached to the bottom of the barrel. The temperature range starts at 130 °C to 220 °C incrementally increased by 10 °C intervals. The shear rate range between 100 and 10,000 s⁻¹ is expected as the load applied to the tester varies from 5 to 100 kgf (1 kgf = 9.81 N).



Figure 2. Shimadzu Capillary Rheometer

4 Results and Discussions

4.1 Initial Preparation for the NC-PE Composites

The three composite samples were tested at selection temperatures of 140, 150, and 160 °C. The selection is very critical because, at a lower temperature (140 °C), the sample starts flowing at the minimum load prescribed by the study. However, at higher temperatures, the feedstock started flowing normally indicating that the onset of fluid behaviour. The tests for the rheological properties of the samples of 1, 2, and 3 wt.% NC-PE composites are shown in Fig. 3 (a, b, and c), respectively. The results suggest clearly that the apparent viscosity is not linearly dependent on shear stress which

characterized the non-Newtonian behaviour of these samples. For all chosen runs, the viscosity decreases non-linearly with increasing temperatures as expected for non-Newtonian materials. Based on these preliminary results, the samples have shown that as more sheared is applied, the less viscous the sample becomes. This behaviour suggests that the feedstock samples of 1, 2, and 3 wt.% NC-PE composites are classified as pseudoplastic. The preliminary rheological tests are in a good agreement with the results presented for the mixture of NC and polyester [23] and NC-PE and ethylene [18]. Based on this support, the injection moulding process was tested.

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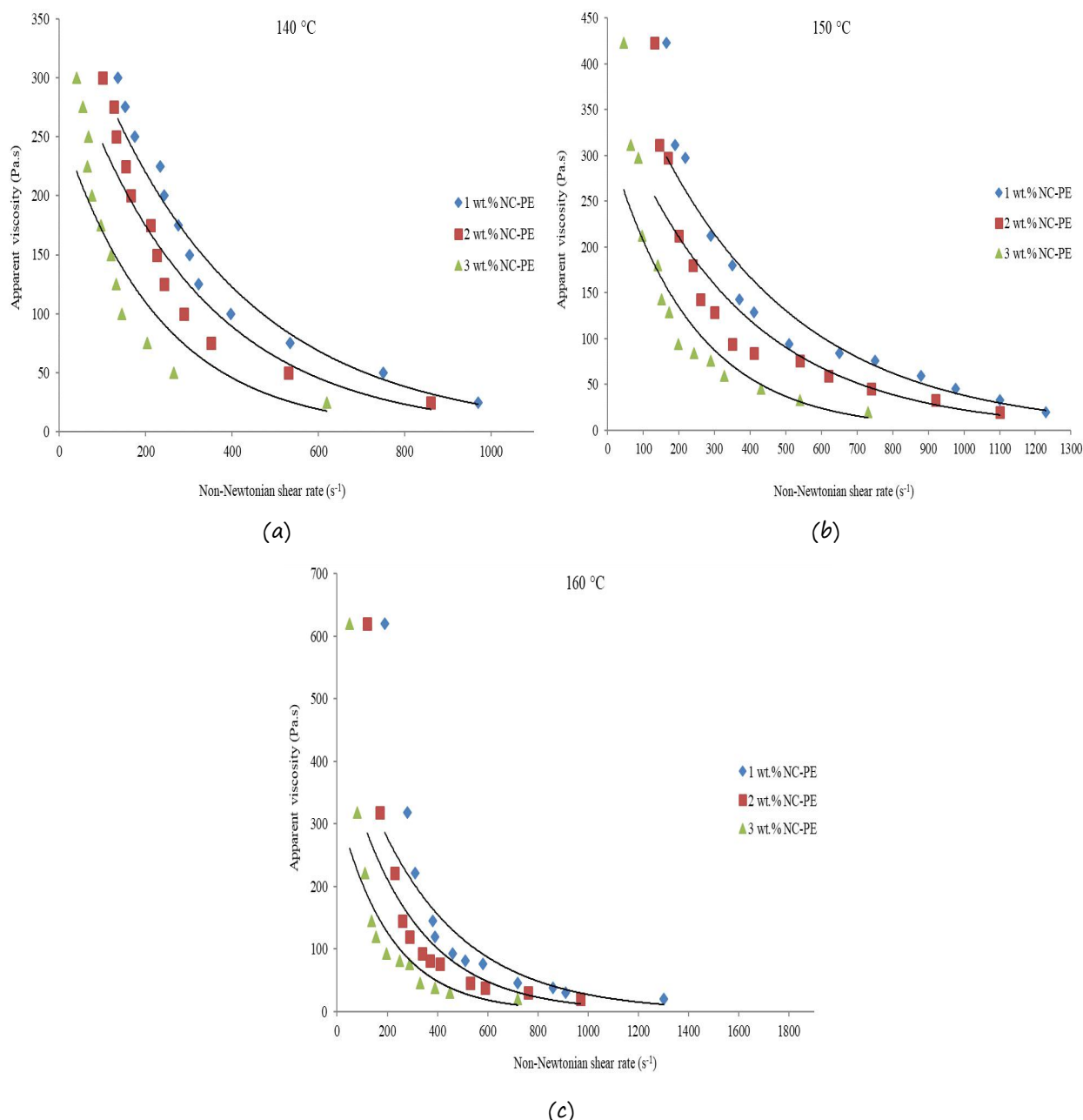


Figure 3. Relation between apparent viscosity and non-Newtonian shear rate for NC-PE composites at (a) 140 °C, (b) 150 °C and (c) 160 °C

4.2 Determination of Activation Energy

The activation energy (E), expressed in J/mole or kJ/mole, is defined as the minimum energy required to start a chemical reaction. The type of the material of being a pure substance or in compound form, the viscosity, the temperature, and, to a certain extent, the pressure are the main parameters that determine the activation energy [24]. A series of three multiple-graph of $\ln(\eta)$ versus $1/T$ of NC-PE composites at 1, 2, and 3 wt.% NC loading were plotted for three shear rates

of 200, 400, and 600 s^{-1} as shown in Fig. 4 (a, b, and c), respectively. The selecting of these three shear rates is based on selecting any three values that should appear in the viscosity tests presented in Fig. 3. All curves were linearly fitted and the correlation (R^2) is shown along with the equation of the straight lines. The linear relationship between $\ln \eta$ versus $1/T$ was previously reported for PE-steatite powder [16] and PE [3] which reflects the same behaviour of NC-PE composites.

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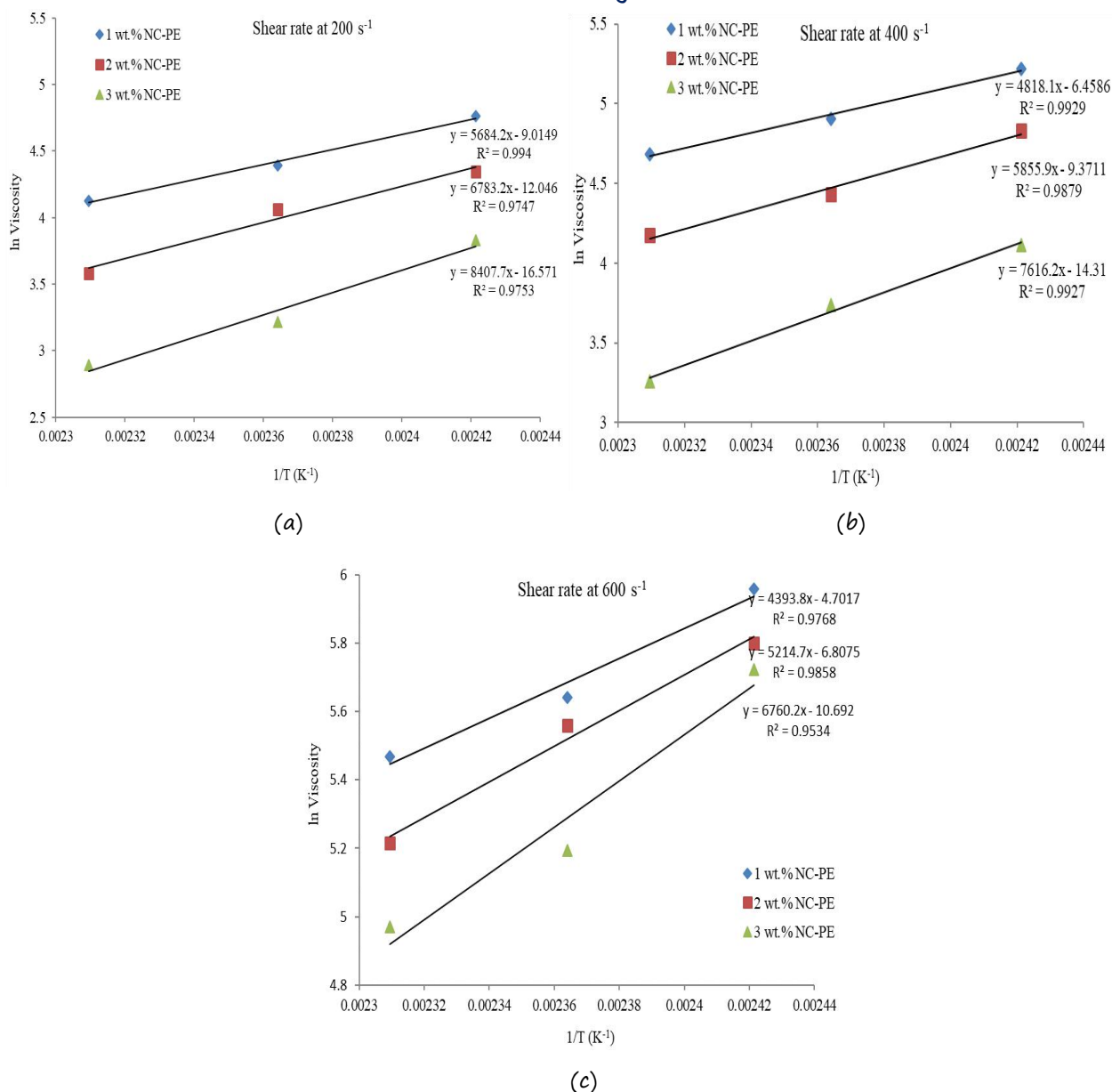


Figure 4. $\ln \eta$ versus $1/T$ for 1, 2, and 3 wt.% NC-PE composites for shear rate (a) 200 s⁻¹, (b) 400 s⁻¹, and (c) 600 s⁻¹

Table 2. Activation energy of NC-PE at different shear rates and NC loading ratios

Sample	Shear rate s ⁻¹	Activation energy (kJ/mole)
1 wt.% NC-PE composites	200	47.24
	400	40.04
	600	36.51
2 wt.% NC-PE composites	200	56.37
	400	48.67
	600	43.33
3 wt.% NC-PE composites	200	69.88
	400	63.24
	600	55.87

The calculation was carried out by equating the slope of each curve and E/R . The results are presented in Table 2. The results show the activation energy values. The results of the activation energy presented in Table 2 are plotted versus T and NC loadings of 1, 2, and 3 wt.% as shown in Fig. 5. All lines shown in Fig. 5 are a straight line. For the lines

representing the activation energy and NC loadings, the activation energy is linearly related to the proportion of NC added to PE to form a composite. As the NC proportion increases, the activation energy increases similar to other work conducted on [25]. Moreover, the activation energy was found to increase linearly with the temperature. This result is supported by other published work [26].

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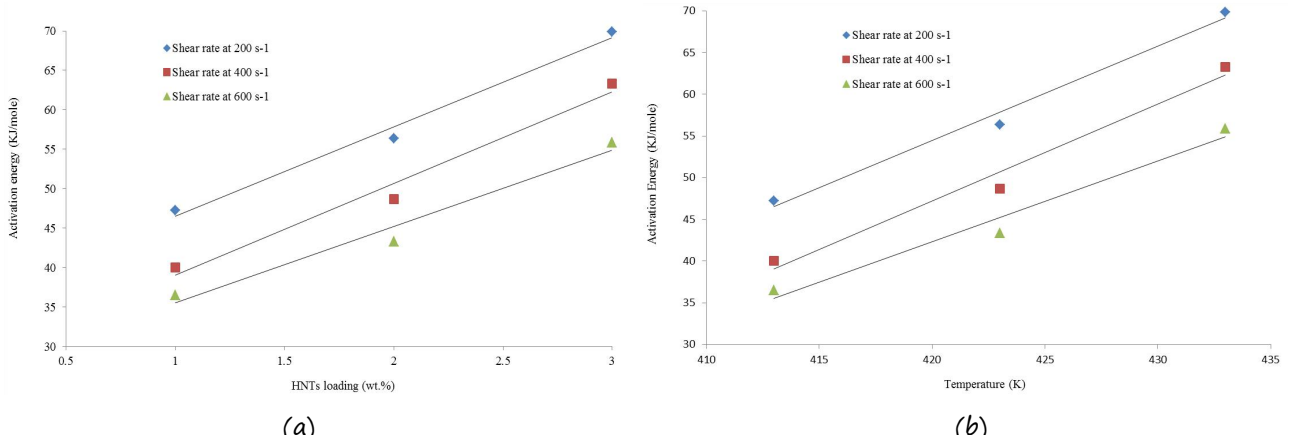


Figure 5. Activation energy versus (a) 1, 2, 3 wt.% NC loadings and (b) temperature 140 °C, 150 °C, and 160 °C

The activation energy is an important guide associated with the reaction which is carried out at a given temperature and pressure. The flow of PE was found to be highly dependent

on certain temperatures [3]. However, regarding NC-PE nanocomposites, the number of studies is found to be very limited.

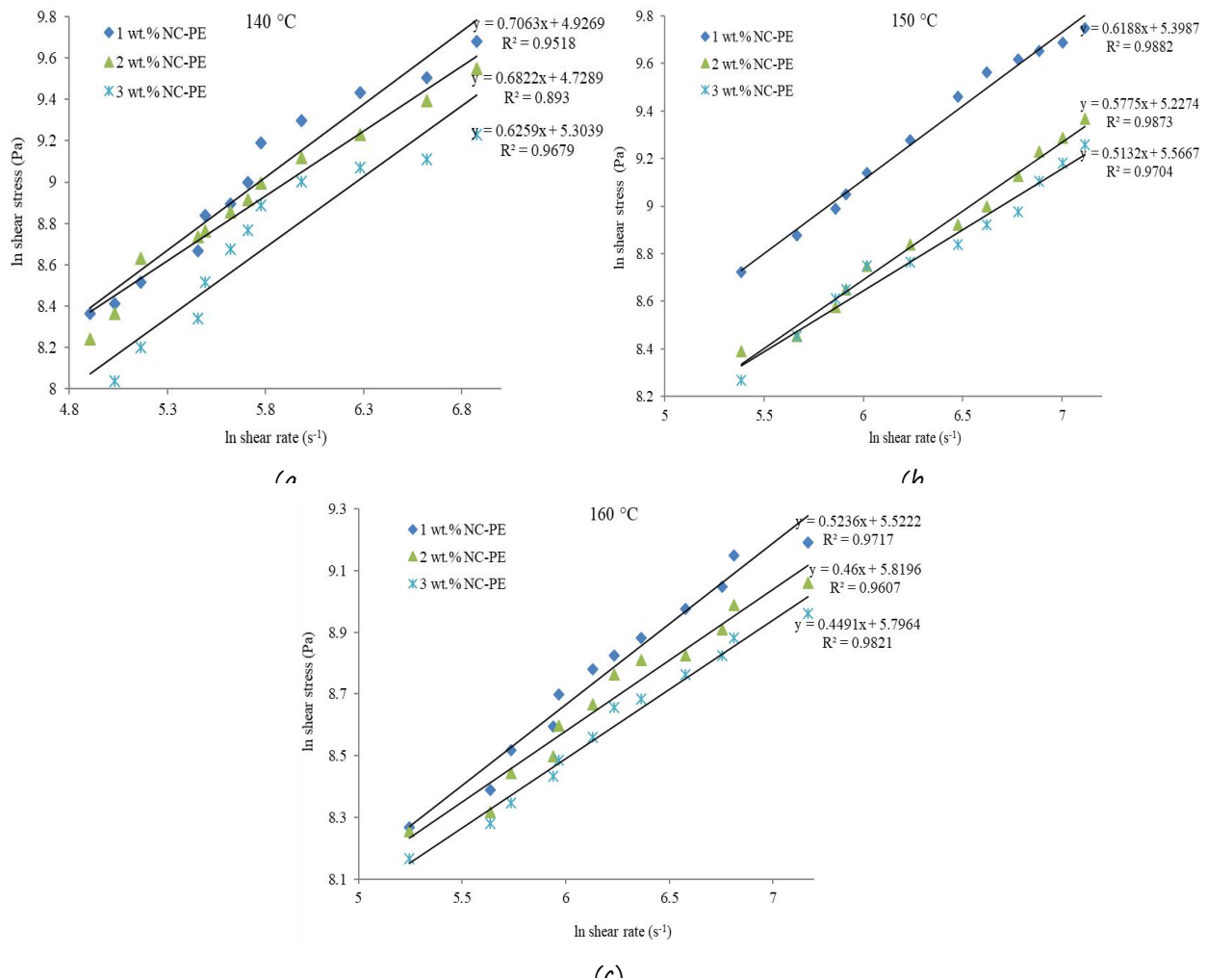


Figure 6. Shear stress versus shear rate at temperature 140 °C, 150 °C, and 160 °C

4.3 The Flow Behavior Index

The flow behaviour index (n) is another parameter indicates the sensitivity of the effect of the shear on the viscosity of the material which could be used to classify the type of the plastics. The relationship between shear rate and the viscosity is very well defined as in Fig. 6. The calculation of n is **Table 3**. The flow behaviour index as a function of temperature and NC loading

carried out through the relationship between the stress, τ_R , and shear rate, $\dot{\gamma}$, where K is a constant [21] as discussed. A logarithmic relation between the stress and the shear can be easily found and plotted as shown in Fig. 7. The results from Fig. 6 which show the values of the flow behaviour index n are tabulated in Table 3.

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Sample	Temperature (°C)	Flow behavior index (n)
1 wt.% NC-PE composites	140	0.71
	150	0.62
	160	0.52
2 wt.% NC-PE composites	140	0.68
	150	0.58
	160	0.46
3 wt.% NC-PE composites	140	0.63
	150	0.51
	160	0.45

The slope of the straight lines in Fig. 6 represents the value of the flow behavioural index (n). As shown in Table 3, the values of n are smaller than one which can be classified according to the criteria mentioned in Section 2. If n is smaller than one, the material is characterized by pseudoplastic fluids. The results of the flow behavioural

index suggest that n decreases as NC loading increases which could indicate that more shear stress is needed to deform the NC-PE composites. The results of n agree with the findings of the behaviour of lubricants with temperatures as pointed by [27,28,29,30]. The results in Table 3 are plotted in Fig. 7 to show how n is varying with NC Fig. 7 (a) loading and temperature Fig. 7 (b).

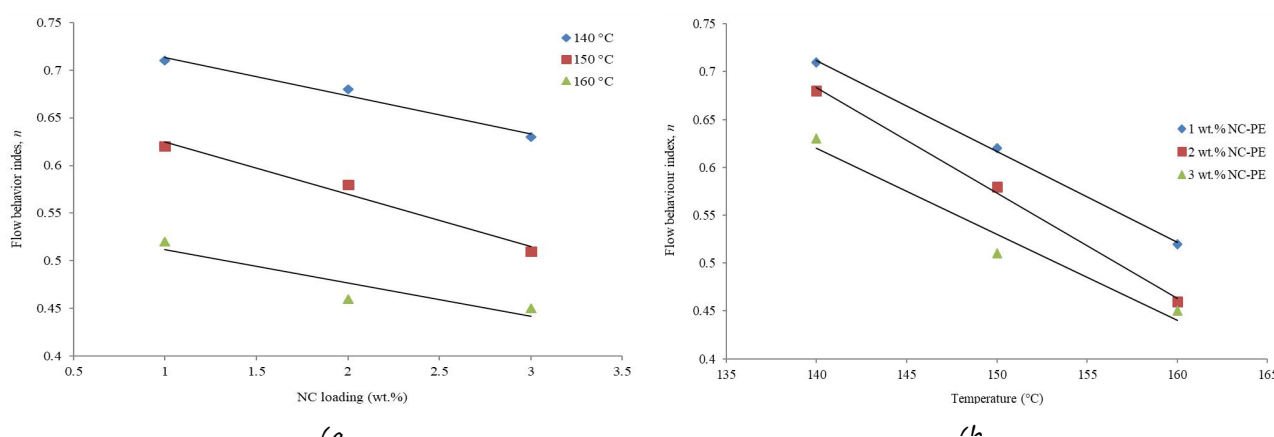


Figure 7. The flow behaviour index versus (a) NC loading and (b) temperature

5 Conclusion

The rheology results showed that as the additive amount of NC increases in the composites of NC-PE from 1 to 2 and then to 3 wt.%, the viscosity decreases due to decreasing temperature to keep the normal flow. The viscosity of the samples was determined by applying a load range from 40 to 80 kgf at temperatures of 140, 150, and 160 °C. A set of experimental results shows the change in the range of 0.4 to 0.7 which express the non-Newtonian behavioural of the samples. The values of the flow behavioural index support that the composites behaved as pseudoplastic fluids. The activation energy was also determined and found to be 36.5 to 69.88 kJ/mole depending on the load applied.

6 Conflict of Interests

The authors declare there is no conflict of interests.

7 Acknowledgments

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