Applied Rheology | DOI: 10.3933/APPLRHEOL-28-64175 | WWW.APPLIEDRHEOLOGY.ORG

A Study of the Flow Behavior of Prevulcanised Natural Rubber Latex/singlewalled Carbon Nanotubes (SWCNT) Blends Using Rotational Viscometry and Power Law Model

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Received: 3.5.2018, Final version: 17.7.2018

Abstract:
This work describes the flow behavior of prevulcanised natural rubber latex (PvNRL) and PvNRL nanoblends containing 0.02, 0.04, 0.06, and 0.08 wt.% of aqueous dispersion of single-walled carbon nanotubes (SWCNT). The assay was performed under varying shear rates (between 0.1 – 100 1/s) at three separate isothermal temperatures (25, 30, and 35 °C) on a Modular Compact Rheometer (MCR) fitted with a concentric cylinder measuring system. A steady decrease in viscosity upon every single shear rate increment was observed for all the samples analysed. Thus, each measured viscosity was considered an apparent-viscosity; which confirms a typical non-Newtonian flow behavior. PvNRL blends containing highest wt.% SWCNT exhibited higher apparent viscosity at low shear rates, whereas the lowest wt.% SWCNT displayed a lower apparent viscosity, thus signifying a dilution effect. The power law model showed good fitting and successfully predicted the flow behavior within the modelled shear rate region.

Key words:
Prevulcanised natural rubber latex, single-walled carbon nanotubes, flow behavior, shear rate, apparent viscosity, non-Newtonian, shear-thinning

1 INTRODUCTION

The exceptional properties of nanomaterials and their vast application potential has raised great interests, especially in the preparation of natural rubber latex (NRL) nanocomposites [1, 2]. For instance, single-walled carbon nanotubes (SWCNT), have been found to perform as excellent reinforcing filler for NRL at very low loadings due to their high aspect ratio and excellent strength [1, 3]. However, the sp2 hybridized SWCNT are largely insoluble in water and hence require special functionalisation to achieve the desired solubility [1, 2, 4]. Covalent functionalisation involves the introduction of suitable functional groups on the surface of nanomaterials; however, this method comes at the expense of compromising the structure of pristine SWCNT [5]. Non-covalent functionalisation involves either establishing hydrophobic interaction between an amphiphilic surfactant and the nanomaterial or via enthalpy-driven interactions such as π-π, CH-π, NH-π in order to promote solvation [1, 6 – 8]. Some of the most commonly used molecules for non-covalent dispersion of SWCNT include: sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS) and sodium carboxymethyl cellulose (NaCMC). These surfactant systems are preferred because they are water soluble and possess relatively high content of Hydrophyle-Lyphophyle blance (HLB) [9]. It is generally understood that the hydrophobic portion of the amphiphilic surfactant molecule adsorbs onto the surface of SWCNT, and the hydrophilic

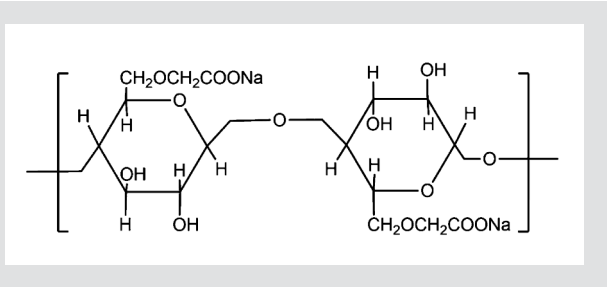

Figure 1: Chemical structure of sodium carboxymethyl cellulose showing 1 degree of substitution [12].

component interacts with water molecules to form a solution [1, 3, 7, 8]. The water-soluble anionic polymeric surfactant NaCMC is of interest to this study because it is a well-known viscosity modifier which is extensively used in latex compounding, pharmaceuticals and food industries. The solubility and viscosity η of NaCMC is influenced by factors such as concentration, degree of substituted hydroxyl group (otherwise referred to as degree of substitution as shown in Figure 1), degree of polymerization and the degree of neutralisation of carboxymethyl groups [1, 10 – 12].

Pre-vulcanised natural rubber latex (PvNRL) is prepared via the chemical modification of NRL using chemical additives such as crosslinking agent (mostly sulphur), accelerators (example includes zinc diethyl dithiocarbamate and sodium mercaptobenzthiazole), and stabilisers [13]. The pre-vulcanisation of NRL introduces sulphur crosslinks along the long hydrocarbon chains of NRL without causing any significant alteration of particle size or colloidal stability. Relative to unvulcanised NRL, PvNRL only requires low temperature curing to give rubber articles good properties [13, 14]. Different grades of PvNRL are commercially available and serve as convenient raw materials in the production of latex foam, dipped goods including gloves and condoms, as well as extruded goods [15].

The flow behavior of sulfur pre-vulcanised natural rubber latex (PvNRL) decides its storage-stability and processability. This is because flow behavior is a bulk material property which reveals the nature of inter/intra particle (and molecular) interactions. Dynamic manufacturing operations which involve pumping, agitation, dipping and casting, exposes PvNRL to different forms of shear stress that influences its flow behavior. PvNRL is considered to have two major phases, namely: an aqueous continuous phase (dispersion medium is mainly water) and a solid dispersed phase (mainly cross-linked cis-1,4-polyisoprene rubber particles) [14]. Studies have shown that significant electrostatic interactions occur between the components of both phases [10, 16]. Adsorbed layers of proteins and phospholipids introduce negative charges on rubber particles while the counter-charges are predominantly dissolved ammonium cations (NH_4^+) present in the dispersion medium [10, 17, 18]. Lim and Misni studied the flow behavior of NRL concentrates using the oscillation viscometry technique and reported that the electrostatic stabilisation emanating from the double layer repulsion formed around rubber particles influences the flow behavior of NRL [19]. Dynamic manufacturing operations which involve pumping, agitation, dipping and casting, exposes PvNRL to different forms of shear stress that influences its flow behavior [14].

The preparation of PvNRL-nanoblends through latex stage mixing require careful dispersion and stabilization of the nanomaterial in a suitable solvent, preferably water before blending [6]. Subsequently, the overall flow behavior of the resulting nano-blend is also expected to match the intended manufacturing conditions whilst maintaining PvNRL's colloidal stability. This is important because the viscosity of PvNRL under varying processing conditions goes a long way in determining the storage-stability, ease of production and quality of the end products [10, 14]. In this study, PvNRL and PvNRL/SWCNT compounds were prepared via the latex stage mixing method to match the intended manufacturing conditions whilst maintaining PvNRL colloidal stability. To ensure their good dispersion in the matrix, nanomaterials are often first stabilized in a suitable solvent, preferably water before blending [6]. In this study, commercially available SWCNT suspension composed of SWCNT non-covalently dispersed in water using NaCMC as a surfactant/dispersant was used. Flow behavior of compounds was studied by varying shear rates (0.1 – 100 1/s) on a rotational viscometer fitted with concentric cylinder measuring system. The analyses were performed at 3 isothermal temperatures: 25, 30, and 35 °C to study the effect of temperature on the flow behavior. The selection of temperature and shear rate range was based on the probable conditions reached during storage, handling and processing. In addition, the Power law model was fitted to experimentally obtained results and used to estimate and further elucidate the observed flow behavior.

2 MATERIALS AND METHOD

2.1 MATERIALS AND SAMPLE PREPARATION

Medium modulus pre-vulcanised natural rubber latex (PvNRL) GIVUL MR with total solid content (TSC) of 60.42 % and 58.85 % dry rubber content (DRC) (GETAHINDUS (M) SDN. BHD, Tangkak, Malaysia) was supplied by Carst &Walker (South Africa). Surfactant stabilised SWCNT suspension with trademark TUBALL™ LATEX H2O was supplied by OCSiAl (Grand-Duche de Luxembourg) and was used as received. The composition of the suspension as specified by the supplier include; water = 99.7 wt.%, SWCNT = 0.1 wt.%, and NaCMC = 0.2 wt.%.

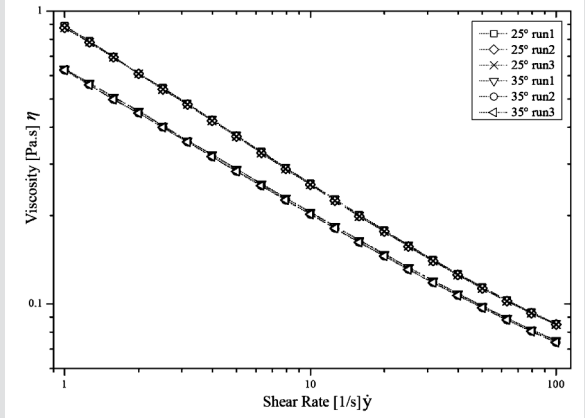

Figure 2: Viscosity versus shear rate of PvNRL at 25 and 35 °C showing the overlay of run1, run 2, and run 3.

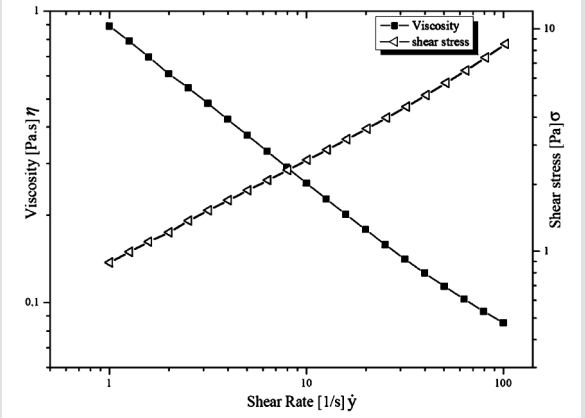

Figure 3: Plot showing the relationship between shear stress and apparent viscosity of PvNRL under varying shear rates.

2.2 PREPARATION OF BLENDS

The blends were prepared by directly mixing precise volumes of SWCNT suspension into PvNRL. The PvNRL and SWCNT suspensions were thoroughly mixed using a Heidolph RZR1 (Heidolph, Germany) overhead stirrer fitted with a gate-geometry impeller. The prepared blends were assigned the following alphanumeric codes: Pv-NB/1, Pv-NB/2, Pv-NB/3, and Pv-NB/4. The numerical aspect of the codes signifies the increasing loading of SWCNT suspension as follows; 0.02, 0.04, 0.06, and 0.08 wt.% (solid SWCNT per 100 g rubber). A more detailed description of the formulation employed is as represented in Table 1. The pH of PvNRL blends was monitored using a probe pH metre (OHAUS Europe GMBH, Switzerland), and maintained at 10.7 using 0.5 M potassium hydroxide solution. The pH measurements were performed at 20 ± 2 °C.

2.3 FLOW BEHAVIOR MEASUREMENTS

The flow behavior of PvNRL, Pv-NB/1, Pv-NB/2, Pv-NB/3, and Pv-NB/4 was evaluated 72 hours after preparation using an Anton Paar Modular Compact Rheometer (MCR 502) fitted with a coaxial cylinder (bob and cup) geometry measuring system and a Peltier temperature control system. Samples were stirred for a few minutes before transferring precise volumes (20 ± 0.01 mL) into the sample container and placed in the test-chamber to equilibrate to the programmed isothermal test temperature (25, 30, and 35 °C). The analysis sequence was pre-programmed using the RheoCompass™ software to measure the viscosity η and shear stress σ response of the samples to the applied shear rate $\dot{\gamma}$ range. Shear rate $\dot{\gamma}$ was logarithmically ramped from 0.1 – 100 1/s. A total of 30 data points with 10 seconds interval between each data point was recorded. The choice of $\dot{\gamma}$ and °C was based on the probable conditions experienced during pumping, mixing, and dipping.

To assess the repeatability of the results obtained, the analysis sequence was repeated thrice (runs 1, 2, and 3) on PvNRL sample with a 2 minutes interval. As represented in Figure 2, the overlap of the three curves from the repeated sequences at 25 and 35 °C (minimum and maximum test-temperatures) confirms reproducibility of results. There is also a clear decrease in η upon raising temperature by 10 °C. It can be seen in Figure 3 that an inverse relationship exists between η and σ at any specific $\dot{\gamma}$. This highlights "$\dot{\gamma}$ dependent" η of PvNRL, more accurately referred to as an "apparent η" which is the η of a non-Newtonian fluid at a specific $\dot{\gamma}$. Newtonian fluids on the other hand maintain a constant η value irrespective of changes to $\dot{\gamma}$ [20].

Sample description	PvNRL[a]		SWCNT[b] suspension		Final DRC[c] (%)	Increase in continuous phase (%)
	Wet weight (g)	DRC[c] (g)	SWCNT (wt.% DRC)	Volume used (~ mL)		
PvNRL	169.9	100	0	0	58.85	41.14
Pv-NB/1	169.9	100	0.02	20.0	52.67	47.33
Pv-NB/2	169.9	100	0.04	40.0	47.66	52.34
Pv-NB/3	169.9	100	0.06	60.0	43.52	56.48
Pv-NB/4	169.9	100	0.08	80.0	40.05	59.95

Table 1: The formulations used in the preparation of SWCNT/PvNRL blends (a = pre-vulcanised natural rubber latex, b = single walled carbon nanotube, c = dry rubber content ~58.85 %, Pv-NB = PvNRL containing varying amounts of SWCNT).

2.4 POWER LAW MODEL

The Ostwald de Waele or Power Law model is an empirical mathematical expression that is often used to elucidate the rheological data of non-Newtonian liquid behavior [21 – 23]. The power law mathematical equation takes on two forms as represented in Equations 1 and 2. In this work, the power law model was used to describe the linear shear-thinning region of the double logarithmic plots viscosity η versus shear rate $\dot{\gamma}$. This linear region represents the shear thinning range where the decrease in the apparent η with increasing $\dot{\gamma}$ is in agreement with the power law model relationship [20 – 24].

$$\sigma = k\dot{\gamma}^n \quad (1)$$

or

$$\eta = k\dot{\gamma}^{n-1} \quad (2)$$

where k is the consistency index and n the power law index. Shear-thinning hydrocolloid liquids such as PvNRL often reveal a three-staged viscous response when subjected to a wide shear rate $\dot{\gamma}$ range as represented in Figure 4. Firstly, they exhibit an initial zero-shear viscosity η_0 at very low shear rates followed by a shear thinning range and lastly infinite shear viscosity η_∞. The power law index n for a shear thinning fluid is always $0 < n < 1$. Several polymeric solutions and polymer melts are known to show an n value between the range 0.3 and 0.7, whereas Newtonian fluids have n value of 1 [20, 21]. The value of n is the slope of the linear region (dash lines in Figure 4) from the log-log plot of viscosity η or shear stress σ and shear rate $\dot{\gamma}$. The numerical value of the consistency index k is the viscosity measured at 1 1/s and describes the consistency of the fluid at that shear rate. Subsequently, the apparent viscosity of a fluid at any shear rate $\dot{\gamma}$ within the shear thinning region can be estimated if the values of n and k are known. However, the power law model is unable to predict neither the upper nor the lower Newtonian plateaus where the viscosity approaches zero ($\eta \rightarrow 0$) or infinity ($\eta \rightarrow \infty$). This limitation can easily be explained by employing the well-known Cross-WLF viscosity model [20, 21, 23].

3 RESULTS AND DISCUSSION

3.1 EFFECT OF SHEAR RATE AND TEMPERATURE ON THE VISCOSITY OF PVNRL

The effect of shear rate $\dot{\gamma}$ on the viscosity η of prevulcanised natural rubber latex (PvNRL) studied at 25, 30 and 35 °C is shown in Figure 5. The measured η is an "apparent η" since it is seen to decrease with increasing $\dot{\gamma}$, which indicates pseudoplasticity or shear-thinning. The pseudoplastic behavior arises from the varying contributions of the highly dissolved aqueous phase (mainly water) and the dispersed phase (mainly rubber particles) with respect to applied $\dot{\gamma}$. Several studies on rubber lattices have reported similar flow behavior [10, 14, 19, 24, 25]. Two considerations are often used to explain pseudoplastic behavior of PvNRL, namely:

- The network of asymmetric rubber particles at rest are extremely entangled and randomly orientated. However, the gradual application of $\dot{\gamma}$ begins to align particles to the direction of flow, reducing the degree of entanglement and consequently reduction in apparent η. The effects of Brownian motion could also oppose orientation of particles. Nevertheless, complete orientation may be achieved at very high $\dot{\gamma}$ thus, favoring stronger particle-particle interactions, which ultimately results in irreversible coagulation.
- Dispersed rubber particles are highly solvated at rest and the resulting effect of this interaction is a positive contribution to apparent η. However, increasing $\dot{\gamma}$ could end-up shearing away the solvated layers leading to decreasing interaction and a subsequent reduction in apparent η.

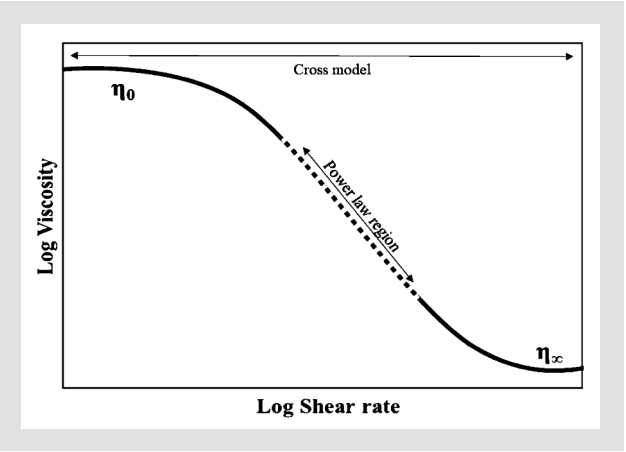

Figure 4: An idealised flow curve showing the power law region, zero shear and infinite shear viscosity regions [21].

An increase in temperature from 25 to 35 °C resulted in a decrease in viscosity, especially at low shear rate ranges (between 1–10 1/s) as shown in Figure 5. This could partly be due to an increase in free volume of the dispersion medium (aqueous phase) with increase in temperature and/or due to the removal of water molecules adsorbed to rubber particles via van der Waals forces upon raising $\dot{\gamma}$ [10]. The apparent volume V of colloidal latex at any temperature is the sum the volume of the individual rubber molecules V_o and the free volume V_f. Therefore, raising the temperature is more likely to increase the free volume which leads to the flow unit's experiencing fewer restriction, increased energy and becoming less organized [10]. This agrees with observations reported by Sridee [25]. The decline in apparent η or shear thinning behavior suggests a changing colloidal structure with increasing $\dot{\gamma}$ (Figure 5). However, it is evident that the colloidal structure is quickly restored upon withdrawal of $\dot{\gamma}$, suggesting that PvNRL has no "shear-memory", hence considered to also be pseudoplastic.

3.2 EFFECT OF SWCNTS SUSPENSION ON THE VISCOSITY OF PVNRL

The effect of SWCNTs suspension loadings on the apparent viscosity η of PvNRL is shown in Figure 6. The blend with the least loading of the SWCNT suspension exhibited the smallest apparent η, as seen for Pv-NB/1 blend at all shear rate $\dot{\gamma}$ ranges. Although the viscosity

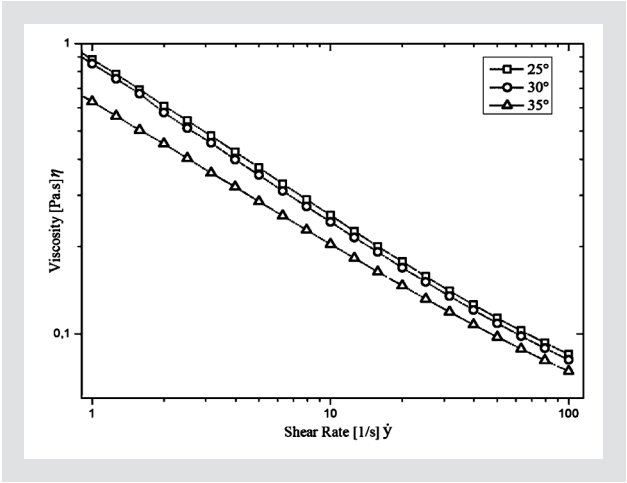

Figure 5: Viscosity versus shear rate of PvNRL at 25, 30, and 35 °C showing shear thinning behaviour.

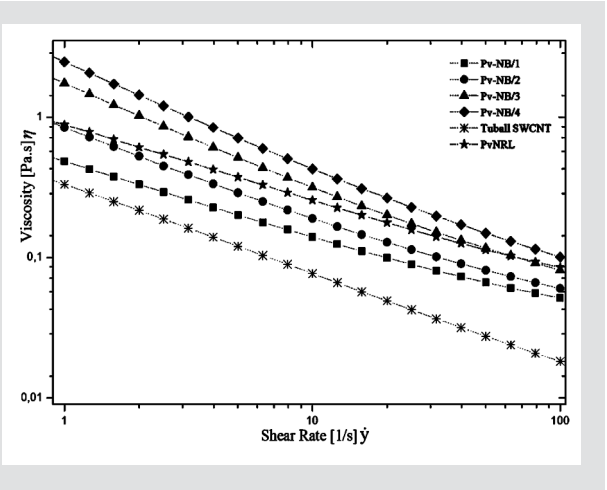

Figure 6: Plot of viscosity versus shear rate at 25 °C of PvNRL, SWCNT suspension, and the four PvNRL/SWCNT blends.

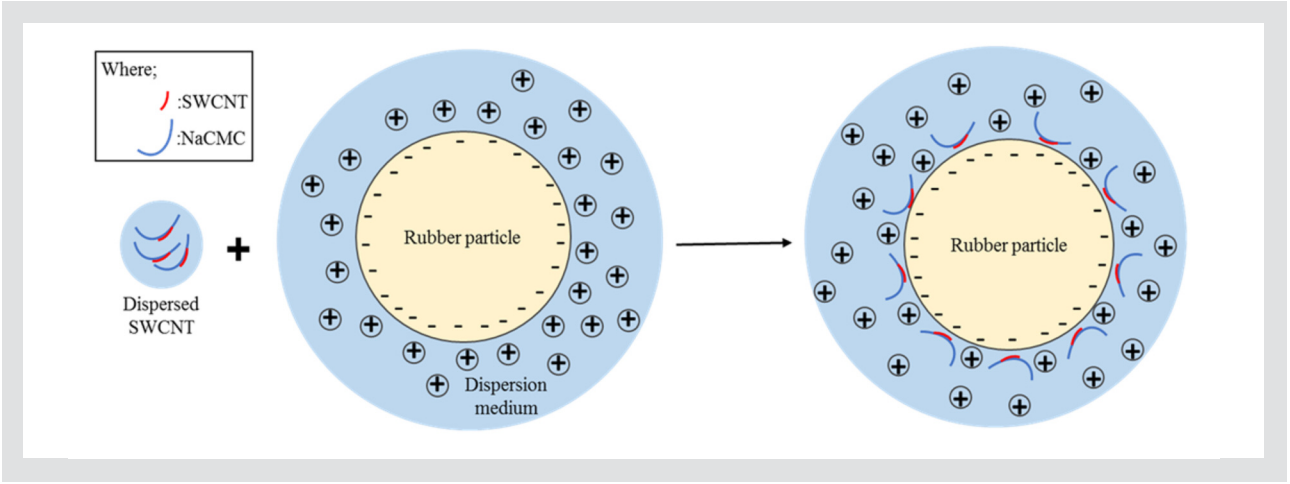

Figure 7: A schematic showing proposed interaction between surfactant (NaCMC) stabilized SWCNT and a solvated rubber particle (note that sizes are exaggerated for clarity).

of Pv-NB/2 matched that of PvNRL at $\dot{\gamma}$ of 11/s it quickly diminishes as the $\dot{\gamma}$ increases. The decrease in apparent η could be due to an increase in continuous phase of PvNRL upon the addition of the water based SWCNT suspension, from ~ 41.14 % in PvNRL to ~47.33 % in Pv-NB/1 (see Table 1). However, this is not the case for Pv-NB/3 and Pv-NB/4 blends which instead show higher apparent η compared to PvNRL. This is despite the increase in continuous phase to about ~ 56.48 – 59.95 %. Consequently, the observed modification of the bulk flow behavior is speculated to be likely because of the growing interaction between the PvNRL matrix and the surfactant stabilised SWCNT.

The nano-suspension is also seen to exhibit shear-thinning behavior (Figure 6). Solutions of NaCMC are known to readily show pseudoplastic behavior as detangled polymer chains NaCMC align to the direction of flow, although low degree of polymerization would result in thixotropic flow behavior [12]. Owing to the amphiphilic nature of NaCMC, the hydrophilic carboxymethyl cellulose units of NaCMC become solvated in water (dispersion medium), whilst the hydrophobic SWCNT bound to the anhydroglucose units of NaCMC adsorbs onto the surface of the rubber particles [10, 26, 27]. Therefore, the increasing associative structure could contribute towards the observed higher apparent η of Pv-NB/3 and Pv-NB/4 as seen in Figure 6. Nevertheless, this contribution is seen to quickly diminish with increasing $\dot{\gamma}$. The extent of shear thinning is increased with higher loadings of nano-suspension, most especially for Pv-NB/3 and Pv-NB/4 where their apparent η is seen to approach that of PvNRL at $\dot{\gamma}$ > 10 1/s (see slope of graph in Figure 6). A schematic showing a proposed interaction between the surfactant stabilised SWCNT present in the nano-suspension and a rubber particle is represented in Figure 7.

Another possible explanation to the observed increase in apparent η of Pv-NB/3 and Pv-NB/4 could arise from the increase in concentration and networks of adsorbed polyelectrolyte NaCMC onto rubber particles. This could increase the surface charge density of colloidal latex which could raise the extent of the electroviscous effect experienced during laminar shear flow, this is known to contribute to the increase in viscosity

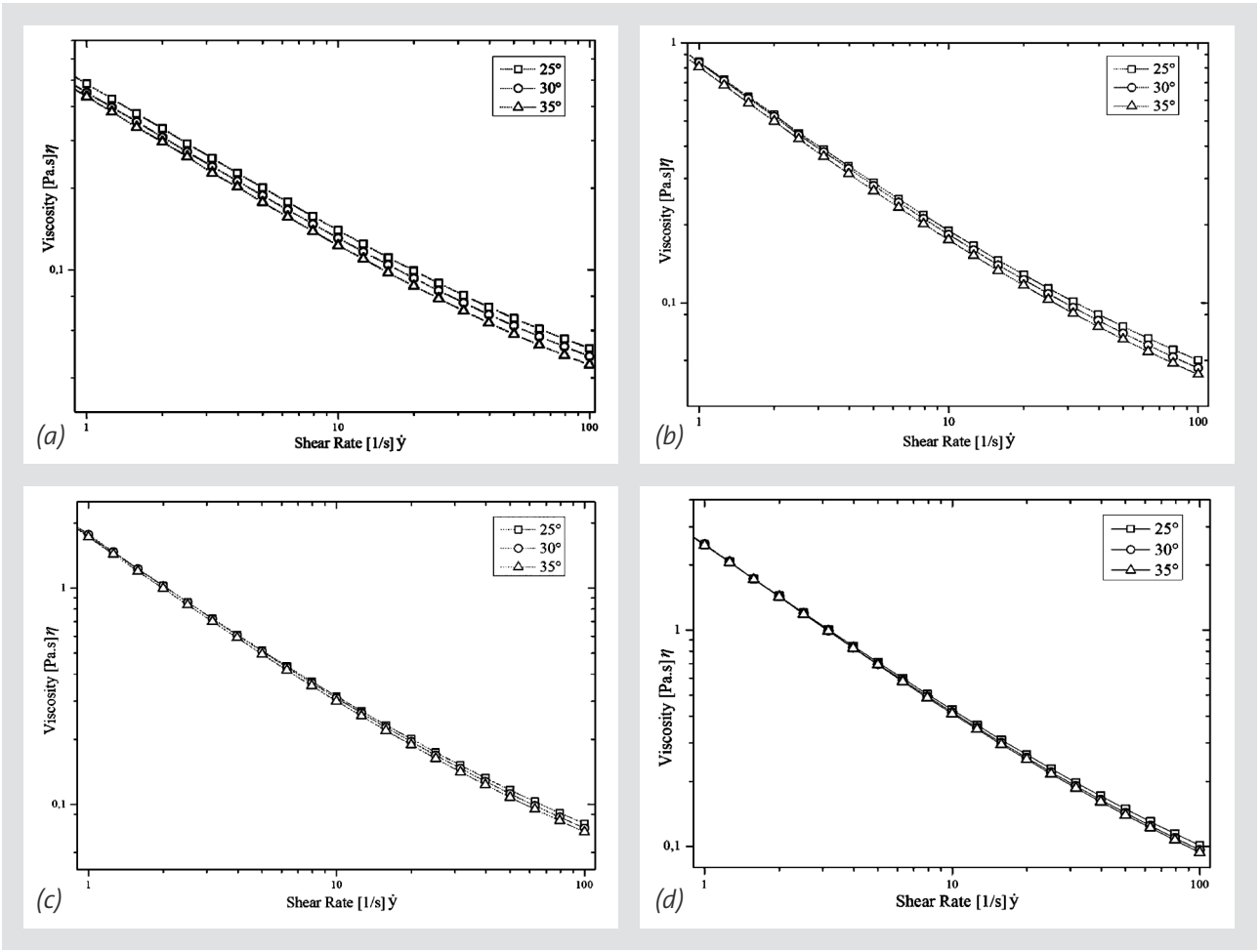

Figure 8: Viscosity versus shear rate at 25, 30, and 35 °C showing shear thinning behaviour: (a) Pv-NB/1, (b) Pv-NB/2, (c) Pv-NB/3 and (d) Pv-NB/4.

[28, 29]. The surface of colloidal rubber particles is negatively charged due to adsorbed proteins and phospholipids. The resulting van der Waals attraction between particles are counter balanced via coulumbic repulsive forces resulting from dissolved cations in the aqueous phase. Sunney and Thomas [10] investigated the flow behavior of low protein latex. The study revealed that higher protein content in natural rubber latex increased the contribution of electroviscous effect, which resulted in an increase in apparent η.

Electroviscous effects are electrokinetic phenomena linked to the additional stress required to deform the diffuse charged clouds of particles in a colloid [30]. The application of shear or electric fields to charged particle systems gives rise to this electrokinetic phenomena as a result of the disturbance of the equilibrium electrical double layer. Subsequently, Brownian and Electrostatic forces tries to re-establish equilibrium double layer via the relocation of ions relative to the fluid displacement, and by so doing dissipates energy [31]. Three main forms of the electroviscous effect can arise in a charged particle systems such as PvNRL, and is attributed to both inter- and intra-particle phenomena [32]. Firstly, when at rest, an electrical double layer (EDL) is formed around charged rubber particles by dissolved ions present in the dispersion medium. The distortion of the EDL upon shearing results to a primary electroviscous effect [10, 28–30]. According to Dickson and Stainsby, the shear induced distortion of the symmetric ionic cloud surrounding the particles leads to increasing viscosity, especially when compared to the viscosity of non-charged particles of comparable size [33]. Again, the case of increasing intrinsic viscosity at high dilutions could also arise due to the intensification of energy dissipation resulting from ionic interactions at high dilution [34].

Secondary electroviscous effect arises when the EDL of neighboring particles overlap as a result of shear flow [10, 28–30]. The subsequent change in the trajectories of charged particles on a collision course due to electrostatic repulsive forces would cause further energy dissipation and as such result to higher viscosity than for non-charged particles [35]. However, increasing shear or the addition of electrolytes into the colloidal suspension significantly reduces secondary electroviscous effect [32]. Finally, tertiary electroviscous effect describes the increase in viscosity associated with changes in shape or size of charged surface of the colloidal particles upon laminar shear [10, 28–30]. This change in dimensions is reported to be due to changes in pH, dielectric constant or valency [32]. Subsequently, the electrostatic repulsions experienced between like charges on

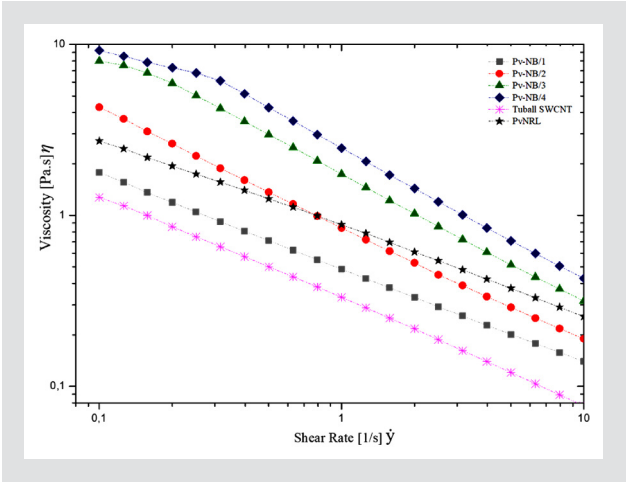

Figure 9: Viscosity versus shear rate 25 °C showing the flow behaviour of PvNRL, SWCNT suspension, and the PvNRL/SWCNT blends at low shear rates.

the same molecule results in the expansion of the polyelectrolyte chains at low ionic strength.

Since all the contributions of these electroviscous effects could influence the bulk rheology and effective particle interactions [32], it is therefore proposed to be the possible explanation for the observed increase in apparent-η of Pv-NB/3 and Pv-NB/4. Alternatively, it is also proposed that lower loadings of the SWCNT suspension diminished the contributions of electroviscous effect probably due to the decrease in thickness of the EDL; thus, resulting in lower apparent η of Pv-NB/1 and Pv-NB/2 as shown in Figure 6. This observation is supported by the assertion that the thickness of EDL is inversely proportional to the square root of the electrolytic concentration in the continuous medium [36]. Nonetheless, this peculiar behavior has been reported and attributed to the decline in the polyelectrolyte concentration and to decreasing ionic strength at high dilution, permitting polymer unfolding and yielding at lower concentrations [37, 38]. It is also evident that the earlier observed reduction in viscosity of PvNRL at 35 °C gradually diminishes upon raising the loadings of the SWCNT suspension (see Figure 8). This strongly suggests a reduction in temperature sensitivity upon increasing the loading of surfactant stabilised SWCNT suspension. This reduction in temperature sensitivity follows the order Pv-NB/4 > Pv-NB/3 > Pv-NB/2 > Pv-NB/1 > PvNRL.

3.3 EFFECT OF LOW SHEAR RATES ON THE FLOW BEHAVIOR OF PVNRL AND ITS NANOBLENDS

The flow behavior of PvNRL and Pv-NB nanoblends at low shear rates $\dot{\gamma}$ and 25 °C are represented in Figure 9. All samples exhibited shear-thinning behavior, however the onset of transition from non-Newtonian to Newtonian flow is seen for Pv-NB/3 and more pronounced for Pv-NB/4 at $\dot{\gamma}$ below << 1 1/s. The appearance of a slight Newtonian plateau suggests greater equilibrium colloidal particle-interactions. This further confirms earlier suggestions that the adsorption of surfactant stabilised SWCNT suspension at those loadings encouraged electroviscous effect and increased solvation of rubber particle, resulting in a slight increase in effective particle size.

This behavior however is not observed for PvNRL or the Pv-NB/1 and Pv-NB/2, which instead continued to shear-thin even at $\dot{\gamma}$ below 1 1/s suggesting that the colloidal flow units are more unevenly sheared in those respective blends. Pv-NB/2 is seen to show a higher apparent-η at shear rates below 1 1/s compared to Pv-NRL. However, it begins to show significant shear-thinning as $\dot{\gamma}$ is increased. An overlap of apparent η of Pv-NB/2 and PvNRL can be seen around $\dot{\gamma}$ =1 1/s before continuing with its downward shear-thinning trend. Pv-NB/1 remains the least viscous blend even at low $\dot{\gamma}$ ranges. The results indicate that at higher loadings of the surfactant-stabilised SWCNT suspension induces more pseudoplastic behavior to PvNRL, most likely due to the surfactant NaCMC. Claramma and Mathew [14] also reported a similar observation in a study that compared NaCMC to other viscosity modifiers. The instantaneous viscosity at very low shear rates is often referred to as the materials zero-shear viscosity [20]. Figure 9 also revealed that Pv-NB/3 and Pv-NB4 possessed the highest zero-shear viscosities compared to the other blends at 0.1 1/s. For a colloidal system like PvNRL, a high viscosity at rest improves colloidal stability due to low occurrence of particle-particle collision that would result in irreversible coagulation [39, 40]. Claramma and Mathew [14] also reported an increase in zero-shear viscosity of PvNRL upon addition of NaCMC compared to two other common viscosity modifiers.

3.4 FITTING THE POWER LAW MODEL FOR VISCOSITY MEASUREMENTS AT 25°C

The correlation between shear stress σ and shear rate $\dot{\gamma}$ is commonly used to demonstrate the flow behavior of fluids like PvNRL [24]. The results indicate that PvNRL and the Pv-NB blends behave in a non-Newtonian manner as they show a time-independent shear thinning or pseudoplastic behavior. The power law (Equation 1) was therefore used to model the shear-thinning region between $\dot{\gamma}$ of 1 – 10 1/s (see Figure 10). The power law index *n* and the consistency index *k* at 95 % confidence interval was calculated from the slope of the model fittings (Fitting parameters are summarised in Table 2). The correlation coefficient for all the fits at 95 % confidence interval are well above R^2 >> 0.9970. Also, the model prediction of *n* which is equivalent to the measured apparent η (at $\dot{\gamma}$ =1 1/s) shows good agreement, and thus confirms that the Power law model can adequately predict the flow behavior of shear-thinning colloidal fluids like PvNRL.

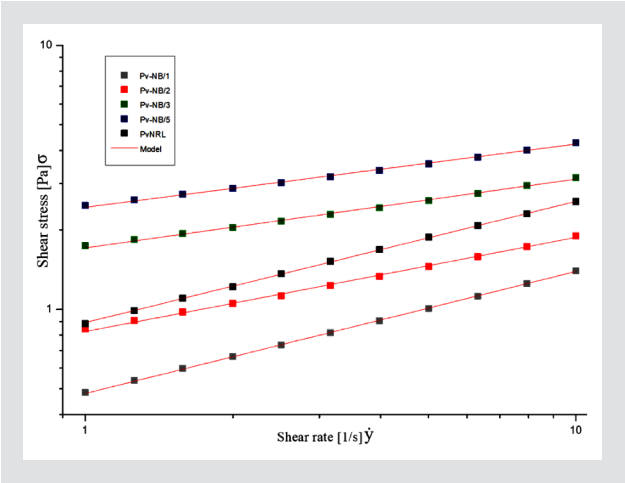

Figure 10: The log-log plot of shear stress versus shear rate of PvNRL and the four Pv-NB at 25 °C (the red-line shows the fitting of the power law model).

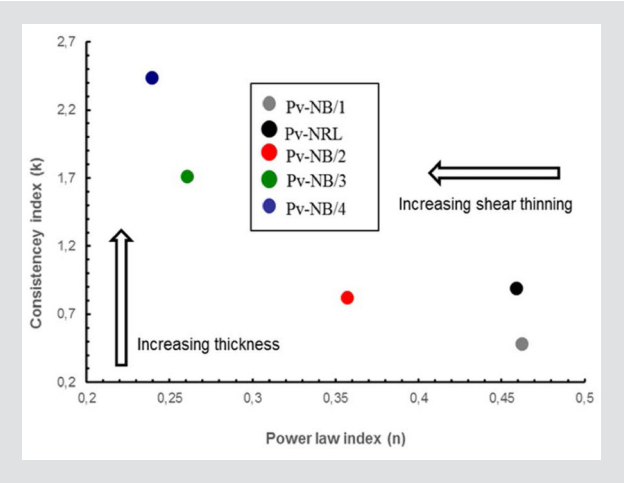

Figure 11: Interpretation of consistency k versus power law index n for all the samples studied (at 25 °C).

An ideal Newtonian fluid has a power law of $n = 1$, deviations from this unitary value indicates shear-thinning or pseudoplastic behavior when $n < 1$ and shear thickening or dilatant behavior for $n > 1$ [20]. The value of n decreased with higher loadings of the surfactant-stabilised SWCNT suspension (Table 2). This confirms that the higher loadings of the SWCNT suspension favors the increase in shear-thinning behavior (since $n < 1$). However, Pv-NB/1 is seen to be an exception because it is observed to exhibit shear-thinning behavior like that of PvNRL as reflected by their comparable power law indices (Table 2). The consistency index k, which is equivalent to the apparent η at $\dot{\gamma} = 1\,1/s$ reveals the consistency (or thickness) of the blends at that shear rate [20, 21]. Accordingly, the high apparent η recorded for Pv-NB/3 and Pv-NB/4 at low $\dot{\gamma}$ is affirmed by their large k values. This observation infers that those blends possess higher viscosity at rest.

Consequently, Figure 11 is used to show the relationship between the power law model terms k and n and the resulting significance on the flow behavior of Pv-NRL and its nanoblends. Taking a closer look at Figure 11, it is apparent that the blends with higher consistency k exhibited higher shear thinning behavior n. Again, Pv-NB/1 is an exception as it shows almost 50 % decrease in consistency k at $\dot{\gamma} = 1\,1/s$, when compared to PvNRL at the same $\dot{\gamma}$. This suggests that the concentration of surfactant stabilised SWCNT was not significant enough to cause an increase in viscosity. Instead, the low loading of the nano-suspension causes a decrease polyelectrolyte concentration of the charged rubber particles in PvNRL. This postulation is supported by the observed low apparent η and k of Pv-NB/1.

Sample description	Apparent-η ($\dot{\gamma} = s^{-1}$)	k	Standard Err (for k)	n	Standard Err (for n)	Adj. R^2	Reduced Chi-Sqr
PvNRL	0.8824	0.8915	0.0027	0.4591	0.0018	0.9999	3.9930E-5
Pv-NB/1	0.4845	0.4804	0.0017	0.4625	0.0021	0.9998	1.6008E-5
Pv-NB/2	0.8441	0.8238	0.0070	0.3571	0.0051	0.9981	2.2937E-4
Pv-NB/3	1.7438	1.7105	0.0122	0.2606	0.0045	0.9971	6.2609E-4
Pv-NB/4	2.4766	2.4368	0.0153	0.2396	0.0040	0.9973	9.4918E-4

Table 2: A summary of the fitting parameters of the power law model for Pv-NRL and the four Pv-NB (at 25 °C).

4 CONCLUSIONS

The Prevulcanised natural rubber latex (PvNRL) and its nanoblends exhibited non-Newtonian flow behavior. This is as expected since they are a complex colloidal fluid system. However, the decrease in apparent η for Pv-NB/1 blend implies a possible dilution of PvNRL and it is likely to be because of the increase in the free volume of PvNRL. The Pv-NB/2 clearly exhibited faster time-independent shear-thinning compared to PvNRL despite their similar apparent-viscosity low shear rate ranges. The increase in apparent-viscosity of Pv-NB/3 and Pv-NB/4 blends was observed, especially at shear rate ranges between 1–10 1/s. This is postulated to be due to (i) increased associative interactions between the surfactant stabilised SWCNT and the colloidal components of PvNRL, and/or (ii) the electroviscous effect arising from the adsorption of the polyelectrolyte surfactant (NaCMC) onto the rubber particles. Results from low shear rate (0.1–10 1/s) analysis exhibit an onset of transition from non-Newtonian to Newtonian flow behavior for PvNB/3 blend and even a more pronounced onset for the PvNB/4 blend. The power law model was successfully fitted between 1–10 1/s shear rate ranges. Interestingly, the results from the calculated values of consistency index k supported the notion that the apparent η of PvNRL increases with increasing loading of SWCNT. Also, looking at the values of the power law index n, it is obvious that the addition of SWCNT suspension results to increased shear-thinning behavior of PvNRL.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the Centre for Rubber Science and Technology and the Department of Civil Engineering (Nelson Mandela University) for their financial support and access to equipment.

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