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The Effect of the Kaolinitic Clay and Asphaltenes on the Rheological Properties of Trinidad Lake Asphalt and Trinidad Petroleum Bitumen-Clay Composites

Rean Maharaj[1,*]

[1]*Process Engineering Programme, University of Trinidad and Tobago, Point Lisas Campus, 540517 Trinidad and Tobago, Trinidad*

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*Correspondence
Email: rean.maharaj@utt.edu.tt
(Rean Maharaj)

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Abstract

Trinidad Lake Asphalt (TLA) is a source of superior quality asphalt and is often specified as a mandatory ingredient for paving in high-demand applications. The TLA resource is limited and expensive and the ability to synthetically convert refinery petroleum bitumen such as Trinidad Petroleum Bitumen (TPB) into a TLA-like material would be a very profitable and more sustainable approach. The objective of this paper is to determine whether kaolinitic clay and asphaltenes when blended with TPB can improve its rheological properties and produce a TLA-like material. Studies were conducted using dynamic (oscillatory) shear rheology (DSR) to measure changes on the rheological properties of complex modulus, G (degree of stiffness) and phase angle, δ (degree of elasticity) of blends. Although the addition of kaolinite to TPB resulted in changes to the rheological properties (G* and δ) of the blends to values closer in magnitude to TLA, the properties of TLA were not achieved. Removal of the inorganic kaolinitic component from TLA resulted in a significant decrease in the complex modulus and an increase in the phase angle to values close to TPB (δ = 89.6 for TLA and δ = 89.1), demonstrating the key role played by the kaolinitic clay in the rheological properties of TLA. The addition of Valencia clay and asphaltenes to TPB clearly showed that in tandem, they play a significant rheological role in the TPB blends as it was possible to produce blends with similar or even better rheological properties compared to pure TLA. The TPB blend containing 30% Valencia clay and 30% asphaltenes exhibited a G* higher than that of TLA and a δ that was marginally less than that of TLA. This study also demonstrated the ability to create customized TPB blends to suit special applications by manipulating the kaolinitic clay and asphaltenes content.*

Keywords

Trinidad Lake asphalt; Trinidad petroleum bitumen; Rheological properties; Complex modulus; Phase angle; Asphaltenes; Kaolinitic clays

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1 Introduction

Although Trinidad Lake Asphalt (TLA) has been internationally well established as a commercial product and a source of superior quality asphalt (due to its consistent properties, resistance to cracking, stability and durability), and is often specified as a mandatory ingredient for paving in high demand situations such as those encountered in airport runways[1], the resource is limited, and the product is expensive. The ability to synthetically convert refinery petroleum bitumen such as Trinidad Petroleum Bitumen (TPB) into TLA-like material is a very profitable and more sustainable approach since this base material is a plentiful by-product formed during the refining of most crude oils. TLA contains about 35% by weight of an inorganic material that was identified as being mostly kaolinitic clay and almost three times more asphaltenes than TPB (30.7% for TLA and 11.7% for TPB), and it is suggested by researchers that these compositional differences play a crucial role in its superior performance qualities[2-4].

There exists a relationship between the changes in the colloidal properties of clay-modified asphalt and the resultant changes in the rheological properties of the modified asphalt. The influence of clays on the colloidal and rheological properties of emulsions such as heavy oil systems and bitumen was studied by Gelot et al.[5] and Yan and Masliyah[6], who found that the presence of fine clays influenced its colloidal properties as it resulted in emulsion stability, and they demonstrated that the degree to which the presence of the clays influences the emulsion stability depends on the amount of asphalt coated on the clay. Subsequent work conducted by Gu et al.[7] on the role of fine kaolinite clay in toluene-diluted bitumen or water emulsions found that the addition of kaolinite clay (1 g L^{-1}) resulted in the conversion of the gel-like water-in-oil emulsion to an oil-in-water emulsion. This study also investigated the influence of the kaolinite clay on the rheological properties of the emulsions and showed that the viscosities of emulsions are dependent on the shear rate. Incremental increases in clay concentration up to a maximum of 1 g L^{-1} in the water-in-oil emulsion resulted in significant decreases in viscosity as well as an inversion of the emulsion to an oil-in-water type. Further additions of clay resulted in an increase in the viscosity of the emulsion. The incorporation of kaolinitic clay in heavy oils and bitumen emulsions can be used to tune the type of emulsion and control the rheology of the emulsion system.

The influence of clays on the rheological characteristics of modified asphalts was investigated by Zare-Shahabadi et al.[8] using bentonite clay and organically modified bentonite. The addition of the clay increased the softening point and viscosity and decreased the ductility of the modified asphalts. Dynamic shear rheological testing showed improved dynamic rheological properties due to the incorporation of the clays to the base asphalt as the modified asphalt had higher complex modulus and lower phase angles (higher rutting performance). Investigations conducted by Jahromi et al.[9], demonstrated that the modification of asphalt with nanoclay resulted in improvements in stability, resilient modulus, tensile strength and dynamic creep. Other studies offered supporting evidence that clay can improve the performance and rheological characteristics of bituminous materials[10-13].

Due to the fact that asphaltic binders exhibit viscoelastic properties, the technique of dynamic (oscillatory) shear rheology (DSR) has proven to be applicable for measuring the rheological properties of asphaltic materials and their modified blends. This is achieved by measuring changes on the rheological properties of complex modulus, G^* (degree of stiffness) and phase angle, δ (degree of elasticity)[14-25].

The objectives of this study are to determine whether additives such as the kaolinitic clays and the organic asphaltenes when blended with TPB can improve its rheological properties and transform the rheological properties of the modified TPB blends to match or surpass that of TLA.

These objectives were accomplished by observing the effect of the additives on the rheological properties $G^*(\omega)$ and the phase angle (δ).

2 Experimental

2.1 Raw Materials

The TLA and TPB used in this study were obtained from the Lake Asphalt Company of Trinidad and Tobago and The Petroleum Company of Trinidad and Tobago respectively. Table 1 shows the source and specifications of the TLA and TPB used in this study[4,23].

The clays used in this study for blending with the TPB were mined from the Longdenville and Valencia deposits in Central and north-eastern Trinidad, respectively. They were obtained through the Department of Physics, University of the West Indies, St. Augustine, Trinidad.

Table 1. Source and specifications of the TLA and TPB used in this study[4,23].

	TLA	TPB
Source	Natural product mined from the Pitch Lake. It is obtained from the Lake Asphalt of Trinidad and Tobago Limited.	By-product of the Petroleum Fractionation Process. It is obtained from the Petroleum Company of Trinidad and Tobago Limited.
Packaging	Drum	Drum
Penetration at 25°C (ASTM D5)	0-5	60-70
Specific Gravity (ASTM D70)	1.3-1.5 g cm^{-3}	1.00-1.06 g cm^{-3}
Softening Point (ASTM D36)	225 °C	89-99 °C min
Flash Point (ASTM D92)	255-260 °C	49-56 °C

To compensate for the variability in clay quality with depth and lateral location as mining progresses, an appropriate sampling technique similar to that used by Knight[26], was employed. The samples were crushed, grounded and sieved through a 100 *µ*m sieve size mesh. The chemical compositions of the naturally occurring clays were previously reported[4]. Kaolinite was commercially obtained (*CAS* 1318-74-7).

2.2 Experimental Procedures

The modified asphalt materials used for the rheological studies were prepared using the following process utilized by previous researchers[14-25]. Approximately 250 g of the TPB was placed in aluminium cans and heated to 180°C using a Thermo Scientific Precision (Model 6555) Mechanical Convection Oven. Appropriate amounts of the natural clays and kaolinite were added incrementally (5 g min^{-1}) to the mixture while continuously stirring it. The kaolinitic materials were added up to 30% by weight of the TPB. The material was mixed using a digital IKA (Model RW20D) Overhead Stirrer, at 3,000 rpm. At the end of the mixing period (30 minutes), the material was cooled to room temperature and stored in a refrigerator at −10°*C* for subsequent testing.

In order to quantify the role that the naturally occurring inorganic constituents play in determining the rheological properties of TLA, the inorganic constituents were removed from it following the ASTM D2172-86 procedure[27]. The TLA sample (250 g) was extracted with 1500 mL of trichloroethylene by agitating in a flask for 1 hour to facilitate the breakup of large clumps, aggregates or flocs. After centrifugation, the solution was washed through glass microfibre filters with a pore size of 0.8 µm until the filtrate was of a light straw color. The filtrate was collected and allowed to dry in a fume hood for 2 days. The dry inorganic-free bitumen sample was then used for further rheological analysis.

The rheological properties of the asphaltic materials were determined using an ATS RheoSystems Dynamic Shear Rheometer (Visco analyzer DSR). Consistent with previous work by Maharaj[4], the analyses were performed under the strain-control mode and the applied strain was kept low enough to ensure that all the analyses were performed within the linear viscoelastic range. The test geometry used was the plate-plate configuration (diameters 25 mm) with a 1 mm gap and the measurements were conducted at the temperatures of 293, 303, 313, 323 and 333 K for TPB and its blends; and 333, 353, 363 and 373 K for TLA with a frequency range of 0-16 Hz that corresponds to a shear stress varying between 0 and 580 Pa. The lower temperature range was used for TPB due to its lower softening point. The data obtained at different oscillating shear frequencies and temperatures were stored in the computer and the results obtained were analyzed using the Visco analyzer software. The value of the rheological parameters associated with the complex modulus and phase angle were calculated at the different oscillating frequencies and temperatures using the instrument's software.

3 Results and Discussions

The variations of the rheological properties of complex modulus *(G*)* and the phase angle *(δ)* of TPB and TLA with frequency *(ω)* over the temperature range of 293-333 K (for TPB) and 333-373 K (for TLA) are depicted in the master rheological curves in Figures 1 and 2.

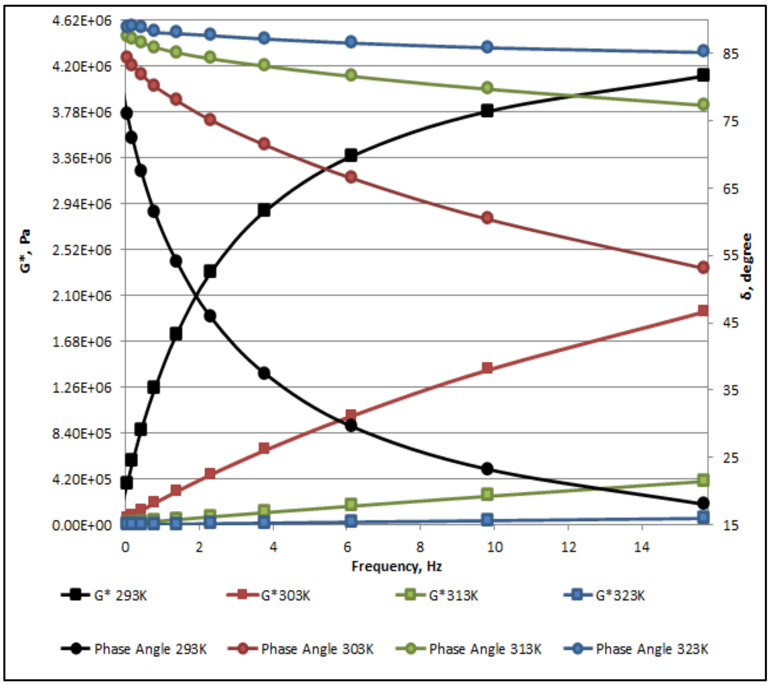

Figure 1. The effect of temperature and frequency on the rheological properties of TPB.

The results in Figure 1 indicate that for TPB, the highest value of *G** (4.1×10^6 Pa) and the lowest value of δ (18 degrees) occured at the minimum measured temperature of 293 K and at the maximum oscillating frequency of 16 Hz. At this oscillating frequency as can be seen in Figure 2, the TLA material exhibited a relatively stiff and elastic response. The lowest value of *G** obtained was 28.9 Pa at the maximum measured temperature of 323 K and at the minimum oscillating frequency of 0.0025 Hz whereby the TPB exhibited a more liquid-like, viscous behaviour. In fact, TPB exhibited a viscous behaviour at temperatures greater than 313 K whereby the highest values of *δ* (>85 degrees) were observed. It is for this reason that rheology measurements above a temperature of 333 K were not possible as the sample flowed out of the parallel plates.

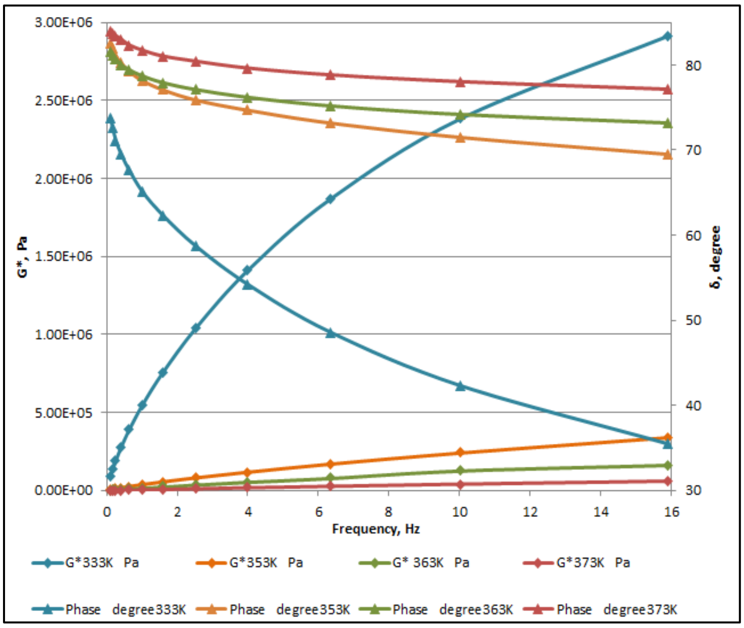

Figure 2. The effect of temperature and frequency on the rheological properties of TLA.

The variations of the rheological properties of complex modulus *(G*)* and the phase angle *(δ)* of TLA with frequency *(ω)* over the temperature range of 333-373 K are depicted in the master rheological curves in Figure 2. Rheological analysis of TLA below 333 K was not possible as the material existed as a rigid solid, unlike TPB which existed as a viscous liquid above this temperature, highlighting the significant difference in the physical properties of the two materials. The highest value of *G** (2.91 x 10^6 Pa) and the lowest value of *δ* (35.5 degrees) occured at the minimum measured temperature of 233 K and at the maximum oscillating frequency of 1.6 Hz. The lowest value of *G** obtained was 6.7 × 10^2 Pa at the maximum measured temperature of 373 K and at the minimum oscillating frequency of 0.0025 Hz.

The trends in Figures 1 and 2 also indicate that for both TLA and TPB, the phase angles *(δ)* increased with increasing temperature and the values of the complex modulus *(G*)* decreased with increasing temperature. For example, at a shear frequency of 15.9 Hz, the phase angle *(δ)* for TPB increased from 18 to 86.4 and the complex modulus *G** decreased by as much as 36 times as the temperature moved from 293 to 323 K. Similarly, the phase angle *(δ)* for TLA increased from 35.5 to 79.4 and the complex modulus *G** decreased 50 times as the temperature increased from 233 to 373 K. The temperature increased the changes to the physical properties for both TLA and TPB as a consequence of the changes in the rheological properties (increase in the phase angles *(δ)* and decrease in the complex modulus (*G**)). This is reflective of a decrease in the rigidity and elasticity of the materials, rendering them more susceptible to stress relaxation under load[28].

A comparison of the information represented in Figures 1 and 2 shows that TLA exhibited lower δ and higher G* values than those of TPB. Since the rheological measurements of TPB above 333 K and TLA below 333 K was not possible, a direct comparison of the rheological properties of the phase angle (*δ*) and the complex modulus *(G*)* for TPB and TLA can only be done at 333 K. At a temperature of 333 K and at a frequency of 4.0 Hz, TPB exhibited a phase angle of 88.4 degrees (viscous liquid) whereas the phase angle for TLA was 54.2 degrees (a moderate degree of elasticity). Under similar conditions, the complex modulus, *G*,* of TLA was approximately 2,000 times larger than that of TPB, demonstrating TLA's higher degree of stiffness. The viscoelastic properties of asphalt and, in particular, the magnitude of the dynamic modulus *(G*)* and phase angle *(δ)* observed can be directly related to pavement performance and the occurrence of various failure mechanisms such as rutting, fatigue damage and thermal cracking described previously[28]. The higher *G** values and lower *δ* values exhibited by TLA compared to those of TPB provide rheological evidence supporting previous reports of the superior physical and mechanical properties of TLA[1,18-19]. Based on these findings, the following sections will focus on exploring the feasibility of upgrading the rheological properties of TPB by incorporating various additives such as clays and (or) asphaltenes and determining the impact they have on the rheological properties of TPB blends.

The differences in the rheological properties between TPB and TLA have been attributed to the differences in the chemical composition between the two materials, particularly due to the presence of the inorganic component in TLA[18-19]. These previous studies found that TLA contained about 35% inorganic material that was identified as virtually kaolinitic clay, a compound that does not exist in TPB. The results suggest that the incorporation of kaolinitic materials into TPB affects the colloidal properties of TPB by increasing the extent of aggregation within the asphaltic blends, thereby resulting in observed decreases of the value of the Korcak particle size distribution parameter, D, of the blends. One of the primary objectives of this research is to confirm this suggestion by observing the effect of added kaolinitic clays on the rheological properties of TPB blends and thus to provide evidence for the dependence of the rheological properties of the asphaltic blends on their colloidal structure as described by the Korcak size distribution, *D*.

The impact of the source from which the naturally occurring clays were obtained on the rheology of TPB is shown in Figure 3.

The methodology followed previous work done by Maharaj[4] and demonstrated that while the shape of the curves and the general trends were similar, the addition of the naturally occurring clays and kaolinite to the TPB resulted in a decrease in the phase angle *(δ)* values and an increase in the complex modulus *G** values of the blends. The changes in these rheological parameters caused by the addition of the kaolinitic materials to TPB are reflective of a higher degree of elasticity and rigidity as described by Bahia[28] and the blends display rheological properties closer to that of TLA. The additional observation that the changes in the rheological properties were similar for all modified TPB blends suggests that it is the kaolinite itself, which is the common constituent in all three additives that play a key role in the rheology of the bitumen blends.

Further rheological evidence to support this suggestion was obtained by observing the effect of the % of clay content on the rheological properties of complex modulus (G*) and the phase angle (*δ*) of the blends. The results obtained at 333 K at shear stress 24 Pa are depicted in Figure 4. In Figure 4, 0% clay represents TPB and 35% clay represents the naturally occurring TLA. The blends containing 10%, 20% and 30% clay content were obtained by blending appropriate amounts of Valencia clay into TPB. Attempts to prepare blends containing more than 30% added clays proved futile as the resultant material was not homogeneous in nature.

The results obtained demonstrate that an increase in the % clay content resulted in a decrease in the phase angle (*δ*) values as well as an increase in the values of the complex modulus *(G*).* The results also showed that the trends in the changes in the rheological parameters of δ and *G** due to the influence of incremental increases in % clay content were towards that of TLA. Although the complex rigidity modulus of the naturally occurring TLA is much higher than any of the blends obtained using TPB and Valencia clays (*G** ≈ 60,000 Pa), this value was severely reduced in TLA in which the kaolinitic inorganic component was removed. De-mineralization of TLA also results in a material with a phase angle very close to that of TPB (*δ* = 89.6 for TLA and *δ* = 89.1 for TPB at a shear stress of 24 Pa). These observations provide further evidence of the key role played by the kaolinitic clay in the rheological properties of asphalts.

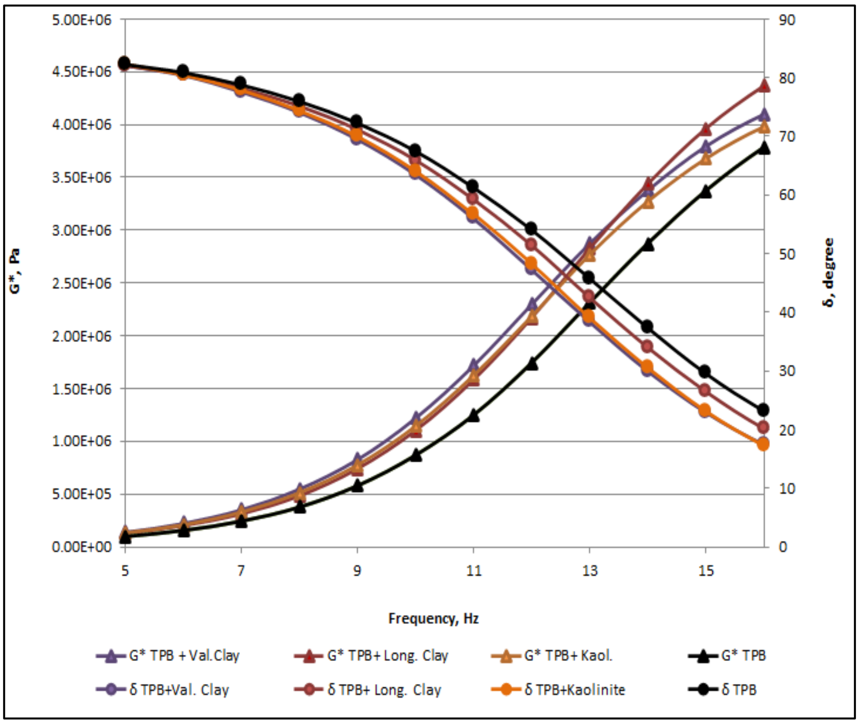

Figure 3. The effect of clay source on the rheological properties of TPB blends (20% clay additions) at 323 K.

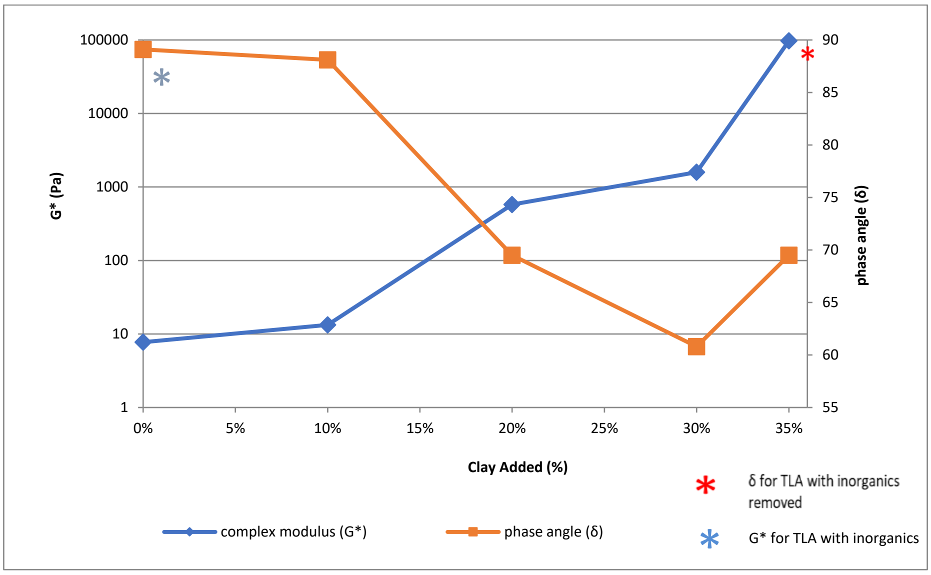

Figure 4. The effect of the % clay content on the rheological properties of complex modulus (G*) and the phase angle (δ) at 333 K at a shear stress of 24 Pa.

The findings of several investigators[5,7] support the conclusion that the addition of kaolinitic clays influences the colloidal and rheological properties of asphaltic materials. Yan and Masliyah[5] demonstrated that the addition of kaolinites in various heavy oil and bitumen emulsion systems changed the colloidal structure and rheological properties of the emulsions. Further evidence for the relationship between the colloidal structure of asphalt and its rheological properties was recently reported by Zare-Shahabadi et al.[8] and Jahromi et al.[9]. They demonstrated that the addition of clays to asphalt resulted in improving its rheological properties such as stability, resilient modulus, tensile strength, rutting and dynamic creep due to changes in the colloidal nature of the blends.

Previous work conducted by Chatergoon et al.[2] and Lin et al.[3] also suggest that the inorganic kaolinitic content of TLA plays a crucial role in its superior performance qualities. Their work investigated the role played by the kaolinitic material in determining the properties of TLA by observing the effect of clay compositions on the Korcak particle size distribution of clay or asphalt blends. Previous work conducted by Chatergoon et al.[2] showed that the Korcak size distribution value, D, for TPB is larger than that for TLA (1.60 compared to 1.13), suggesting that the range of particle sizes in TPB has a wider spread than that for TLA, probably due to the greater aggregation tendencies encountered in TLA. TLA was a gel-type material and the TPB material corresponded to a sol-type material. Incorporation of naturally occurring kaolinitic clays (Valencia clay and Longdenville clay) as well as commercial kaolinite to the TPB, altered the colloidal properties of the blends which resulted in an increase in the extent of aggregation within the asphaltic blends (decrease in the values of D). The results of research conducted by Menon et al.[29] and Schramm et al.[30] offered evidence to support the suggestion that the kaolinite affects the particle size distribution of asphaltic materials, as they showed that interactions between organic molecules and clay minerals does indeed occur and results in changes in interfacial tension and increased aggregation within the system. Since the Korcak particle size distribution D value of TLA (1.13) was not achieved by the addition of the kaolinite-containing material alone, it suggests that this parameter is dependent on the interaction between the inorganic kaolinitic and organic (asphaltenes) components of asphalt.

Although the addition of the kaolinitic materials to TPB resulted in changes to the rheological properties (G^* and δ) of the blends to values closer in magnitudes to those of TLA, the beneficial rheological properties of TLA were not achieved by the addition of the kaolinite-containing materials alone. Previous studies[2,18-19] found that TLA has a significantly higher asphaltene content compared to TPB and other asphaltic materials and they suggested that the relatively higher asphaltene content of TLA contributes to the material's superior performance qualities. It was therefore decided to explore whether the asphaltene content of the bitumen also affects the rheological properties of asphaltic blends and if so whether a combination of the additives, kaolinitic clays and asphaltenes, when blended with TPB can improve its rheological properties and transform the rheological properties of the modified TPB blends to match or surpass that of TLA.

A comparison of the rheological performance of the Valencia and Longdonville clays as shown in Figure 3 clearly demonstrated that the Valencia clay was rheologically superior as it exhibited relatively lower phase angle *(δ)* values and generally higher values of complex modulus *(G*)* over the frequency range. The Valencia clay was thus selected for further work to be used along with the asphaltenes as TPB additives. Figure 5 shows the effect of adding flow modifiers (Valencia clay and asphaltenes) on the complex modulus *(G*)* and phase angle *(δ)* for various TPB blends, TLA and TLA without its naturally occurring inorganic content. When compared to the results presented in Figure 2, the values of G* for TLA presented in Figure 5 is lower. The lower values are the results of a decrease in stiffness of the TLA material due to the additional mechanical stirring that the TLA and other mixtures were subjected to during the blending process. The TLA sample analyzed in the earlier experiment was not subjected to any mechanical stirring which resulted in the generally higher values seen in Figure 2. The master curves obtained in this case clearly demonstrate that both the asphaltenes and clay in tandem play a significant role in the rheological properties of the TPB blends as they show that incremental increases in the percentages of clays and asphaltenes in the TPB blends resulted in increases in both the complex modulus *(G*)* and phase angle *(δ)* values towards those of TLA. Of great interest was the TPB blend containing 30% Valencia clay and 30% asphaltenes which exhibited a complex modulus *(G*)* higher than TLA over the measured frequency range.

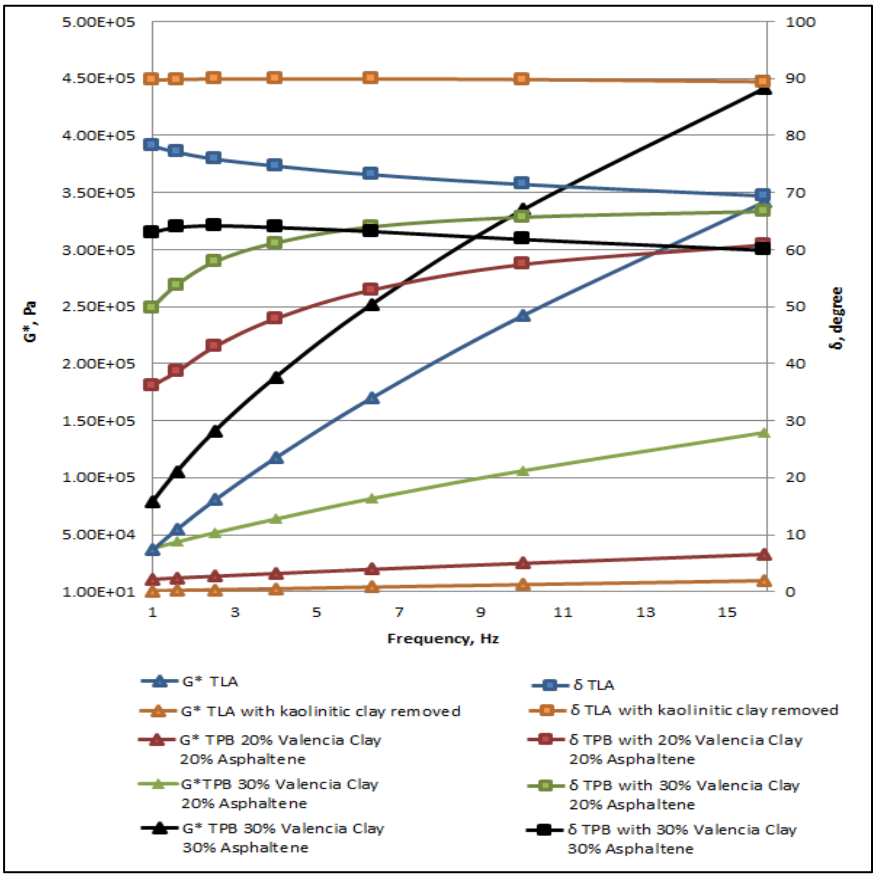

Figure 5. The effect of adding Valencia Clay and asphaltenes on the rheological properties of TPB at 333 K.

However, the phase angles obtained for these blends were found to be somewhat lower than those for TLA, particularly at low shear stress values (<15% over the frequency range). These results demonstrate the ability to manipulate the rheological characteristics of TPB blends, by adding specific quantities of kaolinitic clays and asphaltenes to produce materials of higher qualities. The preparation of blends containing added clay content and asphaltenes up to 40% for rheological analysis was attempted. The incremental additions of the clays beyond 30% resulted in a deterioration of the stability of the blends resulting in inhomogeneous mixtures unsuitable for analysis. Blends containing added asphaltenes beyond 30% were so sticky that the fusing of the parallel plates of the rheometer occurred. This also occurred with blends of TPB containing as low as 10% added asphaltenes. Although these blends did not produce any rheological results, it emphasized the intimate nature of the association between the clays and the asphaltenes and its effect on the rheological properties of the material.

4 Conclusions

Rheological studies of TPB blends formulated with different proportions of the naturally occurring Valencia clays and asphaltenes demonstrated that it is possible to produce asphaltic materials with rheological qualities that match or even surpass that of TLA. It also demonstrated the capability to create customized TPB blends to suit special applications by adding specific quantities of naturally occurring kaolinitic clays and asphaltenes. The TPB blend containing 30*%* Valencia clay and 30*%* asphaltene exhibited a complex modulus *(G*)* actually higher than TLA (stiffer) and phase angles *(δ)* that are slightly smaller (more elastic) than those for TLA over the measured frequency range.

Conflict of Interest

The author declares that there is no conflict of interest.

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Author Contribution

Conceptualization: Maharaj, R.
Data curation: Maharaj, R.
Methodology: Maharaj, R.
Formal analysis: Maharaj, R.
Visualisation: Not applicable
Software: Maharaj, R.
Writing (original draft): Maharaj, R.
Writing (review and editing): Maharaj, R.
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