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Research Article

Thermal and Rheological Formulation and Evaluation of Synthetic Bitumen from Reprocessed Polypropylene and Oil

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Bitumen from the catalytic cracking of petroleum is widely used in the construction industry as a binder for mineral aggregates paving asphalt cement (PAC). However, this material has serious limitations for use at different temperatures. Modifications with polymers have been widely studied to improve the properties of this material and increase its useful life. As a result of the increased environmental risk, the volume of solid waste (MSW) can be used as an alternative to the best use of this material. One of these is the formulation of synthetic bitumen (binders) from mixtures of lubricant oil/polymer that can show better when compared to traditional and modified bitumen. In this work, a mixture of lubricating oil and recycled polypropylene (PP) was made for the formulation of synthetic bitumens. The rheological analyses carried out on the material indicate that at low temperatures the formulated material shows high loading modulus values, indicating high mechanical strength, and the material also presented high resistance to permanent deformation; the viscosity profile indicates that the material is highly pseudoplastic presenting high viscosity at zero shear rate and low visibility at high shear rates, highlighting the samples containing 10 and 20% of polymer material in the formation as the best for use as one of the components of the pavement cement.

1. Introduction

Bitumen is a construction material used as binder in flexible pavements. The increase in road transport flow, environmental and external factors, and the failures incurred during the construction phase can reduce the useful life of the pavements to the greater occurrence of permanent faults in the asphalt pavement. Thus, solutions such as the modification of bitumen with polymeric materials have been used to improve the bitumen properties of the petrochemical cracking, with respect to the adhesiveness, elasticity, and thermomechanical resistance, thus the behavior of pavements [1–6].

Bitumens originating from petroleum may be actively or passively modified. Passive modifiers are those that are added to the base material but do not react with it, such as polypropylene (PP), polyethylene (high-density HDPE and low-density LDPE), ethylene-vinyl acetate (EVA), styrene butadiene rubber (SBR) and styrene butadiene styrene (SBS), acrylonitrile-butadiene-styrene (ABS), and crumb rubber. Active modifiers are known to react chemically with the base polymers; however, the main concern with respect to bitumen/polymer blends is the lack of stability during prolonged storage at elevated temperatures. The physicochemical properties of polymer-modified bitumen (PMB) are strongly dominated by the chemical characteristic of the base bitumen [7–12].

An excellent bitumen should behave as an elastic solid at low temperatures or during rapid loading and as a viscous liquid at high temperatures or slow loading. In other words,

Table 1: PP reprocessing conditions in double screw extruder.

Sample	Temperature (°C) Zone							Speed (rpm)	
	1	2	3	4	5	6	7	Extruder	Granulator
PP extrusion	80	150	170	180	190	200	80	100	40

at low temperatures, around 0°C, the bitumen needs to be able to withstand repeated loads and discharges without failure or fatigue leading to cracks, at moderate temperatures, around 50°C, bitumens must withstand loading to avoid permanent deformations, storing the deformation in the form of energy, and at high temperatures (around 135°C), the material must be easy workability, easy transportation, compactness, applicability, and storage. Another behavior that should be avoided is the loss of adhesion between the bitumen and the mineral aggregates that make up the paving cement [13–17].

An alternative in the substitution of petroleum bitumen has been discussed, being denominated synthetic bitumen. They are thermorheologically complex materials since the mixture between the oil and the polymer can form complex three-dimensional structures. This material is sensitive to temperature changes that modify the viscosity. Techniques such as rheometry can be used to study properties and characteristics with respect to dynamic viscosity, viscoelasticity, complexity modulus, and activation energy to synthetic mixtures [18, 19].

The present work is aimed at formulating synthetic bitumens from reprocessed and reused materials that can be used as one of the components of asphalt paving cement and performing the rheological characterization to determine its potential as one of the asphalt components.

2. Materials and Methods

The oil used to prepare the synthetic bitumen compositions was the postconsumed AC Delco-5w30 API SL (group III mineral type), removed from a vehicle after it was changed. The polymer used to carry out the work was PP H301 from Braskem company. The characteristics of PP can be observed in Table 1.

The polymer was reprocessed in the Extrusa Brasil-DRC 22 double screw type extruder; the aim of which was to simulate the formulation of synthetic bitumen using post-consumed polymeric material. The material was extruded 5 times under the same conditions, presented in 1, and the flow rate used was 5 kg/h.

The binary mixtures between the automotive paraffinic oil and the PP were performed on the IKA C-MAG HS7 agitator plate with the IKA ETS-D7 heating controller. The temperature used in the process was maintained at 165°C. A mechanical stirrer with a propeller-type stirring rod (four blades) with a rotation of 450 rpm was used. The mixtures were stirred for 2 hours. The mixing proportions were 5, 10, 15, and 20% (w/v) of PP in paraffinic oil.

2.1. Rheological Tests. Rheological tests including dynamic oscillatory, creep-recovery, and steady shear tests were performed on a HAAKE MARS II, Thermo Electron Corporation rheometer, using a parallel-plate geometry set of 35 mm and gap adjusted to 2 mm.

Dynamic frequency sweep tests were conducted in the frequency range of 0.01 to 100 rad·s^{-1} with a constant applied stress of 1 Pa, which is within the linear viscoelastic region. The analyses were carried out in the range of 25, 50, 75, 100, 125, and 150°C.

In creep-recovery experiments, the constant shear stress was set to 1 Pa. The creep time and recovery time were set at as 400 s each. The analysis temperatures were 15 and 50°C.

The recovery measurements were started immediately after the end of the creep phase.

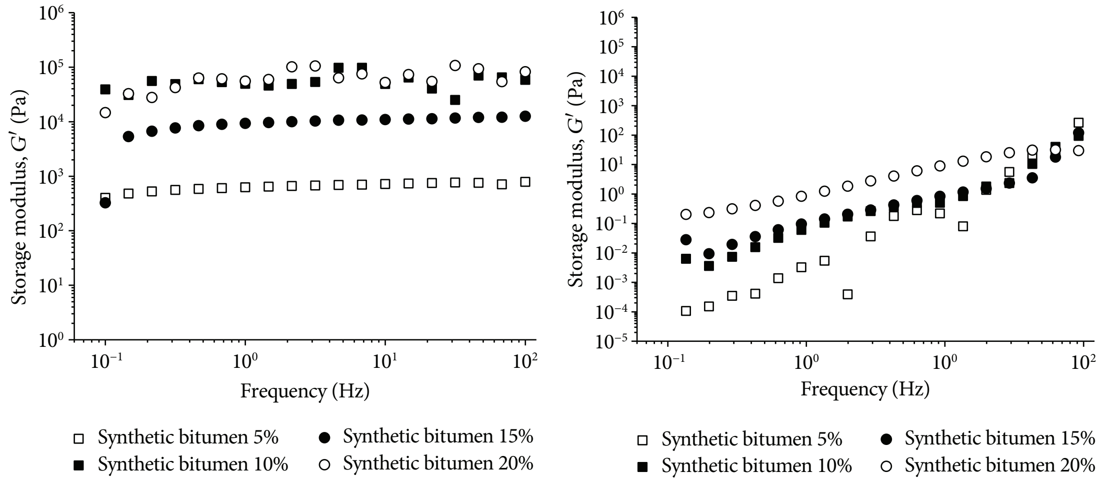
The steady shear measurements of synthetic bitumen samples were evaluated by a controlled shear rate method. The shear stress and shear viscosity values were determined at 160°C over the shear rate range of 0.1 to 300 s^{-1}.

The dynamic melt rheological properties of the synthetic bitumens were measured in order to gain a fundamental understanding of elastic and viscous material behavior at different temperatures and thus to determine the better composition to be used as an asphaltic binder. In oscillatory analysis, $G'(\omega)$ and $G''(\omega)$ values represent the elastic and viscous behavior of samples, respectively. $G'(\omega)$ is called the "dynamic storage modulus," and $G''(\omega)$ is called the "dynamic loss modulus." The relationships between these properties with complex viscosity are showed below:

$$\eta^* = \frac{\sigma^*}{\dot{\gamma}^*} = \frac{\eta_0}{1 + i\lambda\omega} = \frac{\eta_0}{1 + \lambda^2\omega^2} - i\frac{\eta_0\lambda\omega}{1 + \lambda^2\omega^2}. \quad (1)$$

The two components of η^*, η' (dynamic viscosity) and η'' (imaginary viscosity), can be expressed by the following equations:

$$\begin{aligned} \eta'(\omega) &= \frac{\eta_0}{1 + \lambda^2\omega^2}, \\ \eta''(\omega) &= \frac{\eta_0\lambda\omega}{1 + \lambda^2\omega^2}, \\ G'(\omega) &= \frac{\eta_0\lambda\omega}{1 + \lambda^2\omega^2}, \\ G''(\omega) &= \frac{\eta_0}{1 + \lambda^2\omega^2}, \end{aligned} \quad (2)$$



(a) (b)

Figure 1: Storage modulus, $G'(\omega)$, (a) for synthetic bitumen compositions at 25°C and (b) for synthetic bitumen compositions at 150°C.

where $G'(\omega)$ and $G''(\omega)$ are the real and imaginary components, respectively, of a "complex modulus" defined as follows:

$$G^*(\omega) \equiv G'(\omega) + iG''(\omega). \tag{3}$$

3. Results and Discussion

3.1. Dynamic Oscillatory Tests. The results of dynamic frequency sweep tests are shown in Figure 1, which presents the storage modulus, $G'(\omega)$, for synthetic bitumen compositions at 25 and 150°C.

At low temperature, the analyzed synthetic bitumen compositions displayed a Newtonian behavior. It can be also observed that both 10% and 20% samples showed high storage modulus, $G'(\omega)$, at low temperature. At high temperature, 150°C, and lower frequency range, the sample with 10% presented the lower $G'(\omega)$ values, indicating its higher viscous behavior in relation to 15% and 20% samples. This characteristic is desirable because at high temperature, the material must not withstand to applied deformation. The sample with 5% showed lower $G'(\omega)$ values, both at low and high temperatures, indicating that this composition did not present a synergistic effect on the viscoelastic property. The results obtained at temperatures of 50, 75, and 100°C showed no significant change compared to 25°C.

Figure 2 represents G^* versus temperature (at $10\,\text{rad·s}^{-1}$) for synthetic bitumens; G^* can reveal aspects of the material structure indicating strength of the material [20].

The figure shows that samples with 10% and 20% present the highest G^* values, indicating that these compositions have a positive synergistic effect of improving viscoelastic properties. Xia et al. [21] carried out a frequency sweep test in pure bitumen at a temperature of 60°C; the material exhibits a value of G^* around 10^3 Pa at a frequency of $10\,\text{rad·s}^{-1}$, 2 decades smaller than synthetic earnings with 10 and 20% of PP presented in this work.

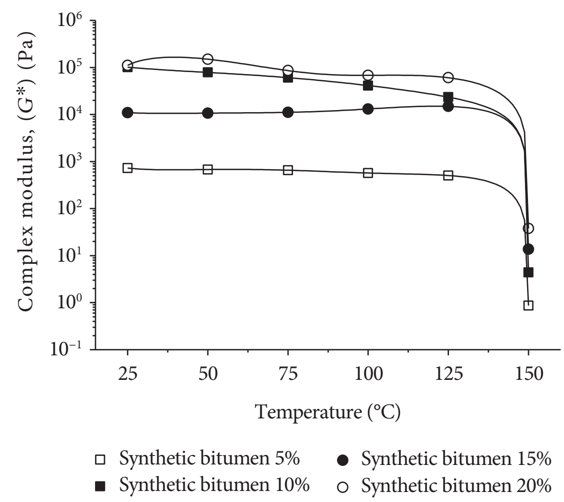


Figure 2: G^* versus temperature for synthetic bitumens.

Figure 3 shows the results of $\eta^*(1/\text{T})$ obtained from temperature ramp tests for synthetic bitumens. It can be observed that only for 10% and 20% samples η^* increases. According to Parvez et al., high G^* values are expected at low temperature. As $G^* = \eta^* \cdot \omega$, high values of η^* indicate high rutting resistance at high temperature. The relationship between viscosity and temperature for synthetic bitumens is expressed by the Arrhenius equation as follows:

$$\frac{G^*}{\omega} = \eta^* = \text{A}e^{E_a/RT}, \tag{4}$$

where E_a is the flow activation energy, A is the preexponential parameter, and R is the universal gas constant. It is known that E_a is an important factor that strongly influences the viscosity.

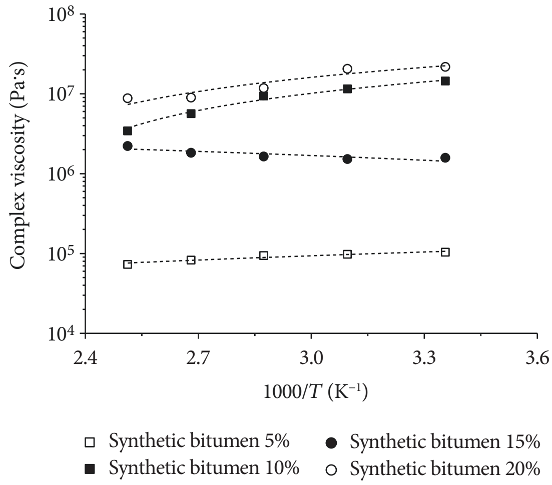


FIGURE 3: Complex viscosity, $\eta^*(1/T)$, for sample compositions.

Table 2 presents the E_a values, calculated from (4). The data given in Figure 3 show good fit to the Arrhenius model for 10% and 20% binder compositions.

It is observed that the activation energy of 10% composition is lower than 20%. This suggests that the change in the viscosity with temperature is slow for 10% when compared with 20%. Hence, the high temperature resistance of 10% composition is better than 20%. Activation energy for pure asphalt is 112.53 kJ/mol [13].

3.2. Creep-Recovery Experiments. In a creep-recovery test, a constant stress (σ_0) is applied at initial time ($t = 0$) for t seconds such that steady state is not reached and then the recovery is monitored. During a creep test, slow development of deformations (ε_0) is observed. The shear strain ($\varepsilon(t)$) is then monitored as a function of time as follows:

$$\varepsilon(t) = \varepsilon_0(t, \sigma_0) + \Psi(t, \sigma_0) + \frac{t}{\eta(\sigma_0)}\sigma_0, \tag{5}$$

where ε_0 is an instantaneous deformation, $\Psi(t, \sigma_0)$ is a function describing delayed development of deformations, $\eta(\sigma_0)$ is viscosity, which can depend on stress, and t is the current time. The creep-recovery experiments were conducted in order to measure the viscoelastic properties of the synthetic bitumen, that is, the efficiency that binder composition has to withstand deformations induced by a constant applied stress. In case of occurring deformation, it also evaluated the material ability to recover from this deformation. Figure 4 shows the results of creep tests for all sample compositions analyzed at 25 and 50°C.

Figure 4(a) shows that the 5% synthetic bitumen composition presents the lower stress strength in relation to other compositions. This behavior is in accordance with dynamic oscillatory results. For this composition, when the stress is removed, it can be observed that part of deformation is recovered. For 20% synthetic bitumen composition, it was not possible to obtain deformation data, indicating that the stress value used in the experiment was not sufficient to provoke the material deformation. Figure 4(b) presents the

TABLE 2: Parameters for the Arrhenius model.

Samples	E_a (kJ/mol)	R^2
Synthetic bitumen 5%	—	—
Synthetic bitumen 10%	83	0.90
Synthetic bitumen 15%	—	—
Synthetic bitumen 20%	166	0.98

creep-recovery behavior for all sample compositions analyzed at 50°C. It is possible to highlight the deformation increase observed for 5% synthetic bitumen—around 0.5% to 1.1% at high temperature. To other compositions, the creep-recovery behavior remained constant. The addition of higher contents of polymeric material in the synthetic asphalt improves the deformation strength behavior, reduces the effect of asphalt flow at successive stresses, and increases the useful life of the asphalt.

3.3. Steady Shear Tests. The steady shear tests were done to measure the flow behavior of the synthetic bitumen compositions. The samples were analyzed at 160°C to ensure its complete melt. Figure 5 shows the curves of stress versus the shear rate for all compositions.

The results show that as PP content increases, the viscosity values increase. Figure 5 also shows that compositions present a pseudoplastic behavior, which is well described by an Ostwald-de-Waele model, which can be written as follows:

$$\sigma = K \cdot \dot{\gamma}^n, \tag{6}$$

where K and n are empirical parameters.

The Ostwald-de-Waele model parameters calculated from linear regression of the rheological data for different materials are presented in Table 3.

Analyzing the parameters determined from the Ostwald-de-Waele model, the data was applicable to all samples analyzed ($R^2 > 0.9$). The addition of PP increased the elastic behavior of the final composition, as seen earlier. The decrease in the n parameter indicated a more pronounced shear thinning behavior at lower shear rates. These results corroborate the data discussed previously in this paper. Figure 6 shows the viscosity versus shear rate curves for all samples analyzed.

The results from Figure 6 show that at lower shear rates, the synthetic asphalts tend to present higher viscosity values, except the 5% composition, which shows a Newtonian behavior, presenting very low viscosity values in the whole shear rate range evaluated. This behavior is not desirable because the viscosity values at lower frequency (η at $\dot{\gamma} \to 0 = \eta_0$) must be high, if not, the mineral aggregates of the asphalt would be easily sedimented due to the low flow resistance offered by the material. As polymeric material content increases, the viscosity values also increase at lower shear rate conditions, improving the flow resistance, which can keep the aggregates suspended. As shear rates increase, the viscosity values tend to decrease. This behavior suggests easy manipulation of the material during use

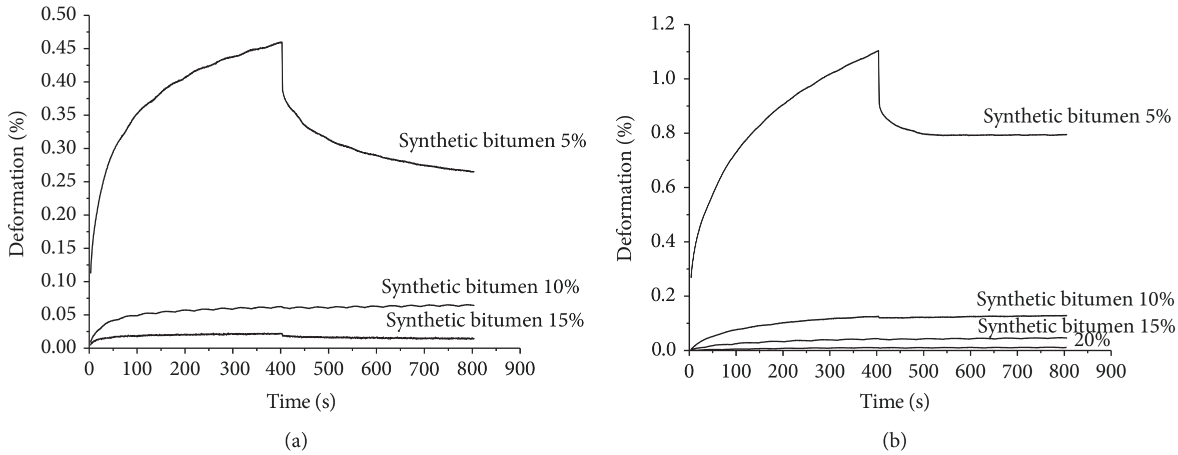


Figure 4: Creep-recovery tests for synthetic bitumen composition at (a) 25°C and (b) 50°C.

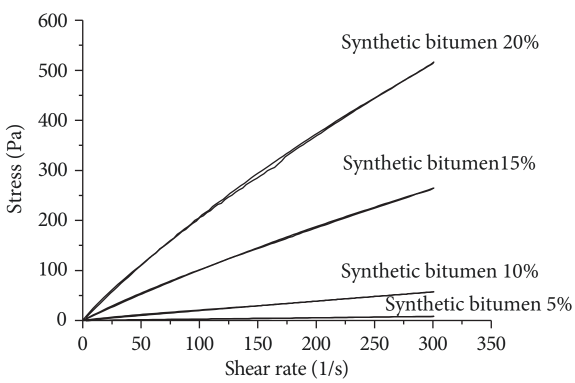


Figure 5: Stress versus shear rate for synthetic bitumens.

Table 3: Linear regression parameters for the Ostwald-de-Waele model.

Binder composition	K (Pa·s)	n	R^2
Synthetic bitumen 5%	0.03	0.97	0.99
Synthetic bitumen 10%	0.27	0.94	0.99
Synthetic bitumen 15%	1.76	0.88	0.99
Synthetic bitumen 20%	4.20	0.84	0.99

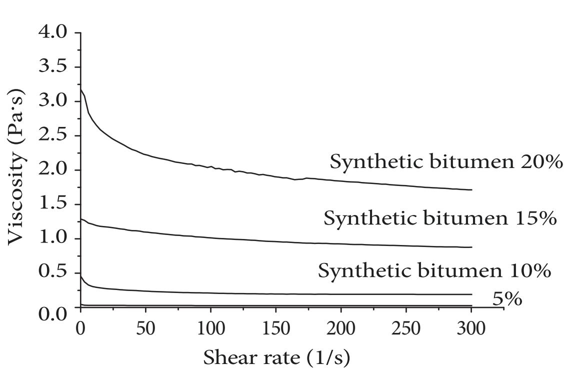


Figure 6: Viscosity versus shear rate for synthetic bitumens.

since it is submitted to high rates in its transport and during spreading.

4. Conclusions

The formulation of synthetic asphalt represents a great alternative for the improvement of pavement cement, as well as a man-made solid waste disposal. The analyses showed that the formulated materials presented high mechanical resistance, giving high values of $|G^*|$ at low temperature. These materials also have high resistance to deformations, with some samples reaching values of 0.02% of total deformation. At high temperatures (170°C), the material presents a distinct flow behavior, presenting low viscosities and ease of flow, an aspect that can contribute in a positive way, facilitating transportation and application.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors, Ricardo S. Souza, Leila L.Y. Visconte, Ana L.N. da Silva, and Valéria G. Costa, declare that there is no conflict of interest regarding the publication of this paper.

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