

Non-Newtonian behaviors of crumb rubber-modified bituminous binders

Wang, Haopeng; Liu, Xueyan; Apostolidis, Panos; Scarpas, Tom

DOI

[10.3390/app8101760](https://doi.org/10.3390/app8101760)

Publication date

2018

Document Version

Final published version

Published in

Applied Sciences (Switzerland)

Citation (APA)

Wang, H., Liu, X., Apostolidis, P., & Scarpas, T. (2018). Non-Newtonian behaviors of crumb rubber-modified bituminous binders. *Applied Sciences (Switzerland)*, 8(10), Article 1760. <https://doi.org/10.3390/app8101760>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

Article

Non-Newtonian Behaviors of Crumb Rubber-Modified Bituminous Binders

Haopeng Wang ^{1,*} , Xueyan Liu ¹, Panos Apostolidis ¹ and Tom Scarpas ^{1,2}

¹ Section of Pavement Engineering, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Stevinweg 1, 2628 CN Delft, The Netherlands; x.liu@tudelft.nl (X.L.); p.apostolidis@tudelft.nl (P.A.); a.scarpas@tudelft.nl (T.S.)

² Department of Civil Infrastructure and Environmental Engineering, Khalifa University of Science and Technology, Abu Dhabi 127788, UAE

* Correspondence: haopeng.wang@tudelft.nl; Tel.: +31-(0)625361801

Received: 27 August 2018; Accepted: 26 September 2018; Published: 29 September 2018



Featured Application: The evaluation procedure developed in this study can be generalized for characterizing the non-Newtonian behaviors of most modified bituminous binders.

Abstract: Crumb rubber-modified bitumen (CRMB) has been utilized in the asphalt paving industry for decades due to its various benefits. The complex interaction between bitumen and crumb rubber as well as the addition of warm-mix additives makes the typical laws of Newtonian fluids insufficient to describe the behaviors of highly modified bituminous binders. To systematically explore the non-Newtonian behaviors of CRMB, a dynamic shear rheometer was utilized to apply shear loading on the samples at various temperatures and shear rates. Results show that the viscosity of different binders are highly temperature- and shear rate-dependent, while highly modified binders exhibit more obvious shear-thinning behaviors at certain temperatures. With the help of zero shear viscosity and yield stress, the shear-thinning behaviors of non-Newtonian binders can be sufficiently characterized. The Arrhenius equation is invalid to describe viscosity-temperature characteristics of bitumen in the non-Newtonian region. A second-order polynomial function was proposed to characterize the viscosity-temperature dependence with a high correlation degree.

Keywords: non-Newtonian behavior; viscosity; bitumen; crumb rubber modifier (CRM); warm mix asphalt

1. Introduction

Bitumen is a complex mix of various hydrocarbons that is produced from the natural deposits or the residue of the crude oil distillation process [1,2]. The complex chemical composition of bitumen determines its various physical and mechanical properties. Bitumen is usually categorized as a viscoelastic material, which means its mechanical behavior is time of loading and temperature dependent. The primary application of bituminous binders is in road construction and other uses include roofing products, sealing and insulating materials. Viscosity, defined as a measure of resistance to deformation or flow, is one of the most important properties of bituminous binders used as paving materials. Profound knowledge of the viscosity of these binders at manufacturing and construction temperatures (generally above 135 °C) provides vital information about their pumpability, mixability and workability [3,4]. Workability can be defined as a property that describes the ease with which hot mix asphalt can be placed, worked by hand, and compacted. The viscosity of bitumen should be controlled within a certain range to facilitate its application in production and construction as well as to guarantee the bitumen grade [5].

Generally, bituminous binders can exhibit Newtonian or non-Newtonian behaviors under different conditions. The dominant characteristic of a Newtonian behavior in simple shear experiments conducted at constant temperature and pressure is the exerted shear stress that is constantly proportional to the applied shear rate. In contrast, any deviation from the Newtonian behavior (i.e., viscosity is dependent on applied shear rate and shear stress) is called non-Newtonian. Non-Newtonian fluids have two main categories: shear-thinning (pseudoplastic) fluids and shear-thickening (dilatant) fluids. Shear thinning is the behavior of fluids whose viscosity decreases with the rate of shear strain while the viscosity increases with the rate of shear strain for shear-thickening fluids. Apart from the applied shear rate, shearing time and temperature also have effects on the non-Newtonian behaviors [6]. Different mathematical equations were developed to describe the flow curves (viscosity measured over a range of shear rates or shear stresses under isothermal conditions) of various products, among them the Cross model, the Carreau model and the Sisko mode which are the modified versions of the Cross model [7]. The temperature dependence of viscosity can be characterized by the William–Landel–Ferry (WLF) function and the Arrhenius-type equation or some empirical equations [8]. However, these equations developed based on different theories have different applicable conditions. Misuse of these equations may result in biased predictions and explanations [9]. This issue will be addressed in the results section.

Practically, two measures of viscosity in asphalt paving industry have been used: absolute viscosity and apparent viscosity [10]. Performing absolute viscosity assumes the material as a Newtonian fluid whose properties are independent of applied shear rate or stress level. Unmodified bituminous binders usually exhibit Newtonian behavior at relatively elevated temperatures (generally above the softening point) or at very low shear rates. However, considering the large service temperature range of these binders or short loading times, their viscosity is not always an absolute value at intermediate and low temperatures. Rather, it varies with the applied shear rate and shear stress. That is why it is an apparent value which needs a well-defined temperature, shear rate and shear stress. For the majority of highly modified bituminous binders, they exhibit obvious non-Newtonian behaviors due to the interaction between the bitumen and the modifier [11]. Apart from the difference among the viscometers and rheometers, the non-Newtonian behavior of some binders (e.g., polymer modified bitumen) is a main reason for the observed measurement difficulties and this subsequently leads to issues in the interpretation and comparison of interlaboratory test results [12]. Therefore, it is necessary to investigate the non-Newtonian behaviors of highly modified bituminous binders and propose universal parameters (e.g., zero shear viscosity) [13] that are independent of applied shear loading instead of merely comparing the apparent viscosity values.

Crumb rubber modified bitumen (CRMB) has been utilized in the asphalt paving industry for decades due to its various benefits. It not only provides an environmental friendly disposal solution to scrap tires, but also improves the overall pavement performance, e.g., higher resistance to rutting, ageing, fatigue and thermal cracking [14]. The increasing use of crumb rubber modifiers (CRMs) in bituminous pavements requires a better understanding of their effects on the chemical, physical and rheological properties of CRM binders so that their processing at the plant can be optimized, their production at the site can be controlled, and their performance in the field can be more accurately predicted [15,16]. It was shown that the interactions of bitumen and rubber and their effects on the final properties of CRMB depend on the raw material parameters (e.g., bitumen composition, CRM type, morphology, particle size and dosage) and interaction conditions (e.g., mixing temperature, time and rate, energy type of the mechanical mixing exerted) [17,18]. Many studies have demonstrated that CRMs improve the rheological properties of base bitumen with evident non-Newtonian behaviors [19,20]. The addition of CRMs into base bitumen dramatically increases the viscosity of the binder, which on the one hand improves the rutting resistance, but on the other hand creates workability issues through pumping, mixing and compaction [21]. The technology of warm mix additives offers promising solutions to the above drawback which can significantly lower the viscosity of binders at mixing and construction temperatures [14,22]. As mentioned before, the neat

bitumen's viscosity can be measured at 60 °C or higher in the Newtonian region. This statement is of no validity for the CRMB binders. The addition of warm-mix additives further complicates the non-Newtonian behaviors of CRMB.

Based on the above considerations, this study aims to investigate the fundamental non-Newtonian behaviors of CRMB with/without warm-mix additives from the prime parameter in rheology-viscosity. The shear rate dependency of viscosity and temperature effects were investigated with different rheological models.

2. Materials and Methods

2.1. Materials

Base bitumen of 70/100 penetration grade commonly used in the Netherlands was provided by Nynas (Stockholm, Sweden). The specification of the base bitumen is shown in Table 1 according to EN 12591. The SARA (saturated hydrocarbons, aromatic hydrocarbons, resins, asphaltenes) analysis of base bitumen was done by Iatroscan TLC-FID (Bechenheim, Germany). The four-component proportions are 7% for saturates, 51% for aromatics, 22% for resins, and 20% for asphaltenes, respectively. The ambient grinding CRM from waste truck tires has particle sizes ranging from 0 to 0.5 mm. The gradation of CRM particles is shown in Table 2. The basic properties and composition of CRM are shown in Table 3. The morphology of CRM and base bitumen was obtained through environment scanning electron microscopy (ESEM) in Figure 1. The ESEM images confirmed that rubber particles from ambient grinding have an irregular shape and porous appearance. The surface of bitumen is very smooth and homogenous except for some impurities. This study included two types of non-foaming warm mix additives, the wax-based product W and the chemical-based product C. Additive W is a synthetic microcrystalline wax that is free of sulfur and other impurities. Additive C is a liquid blend of chemicals, such as surfactants and polymers.

Table 1. Specifications of Nynas 70/100.

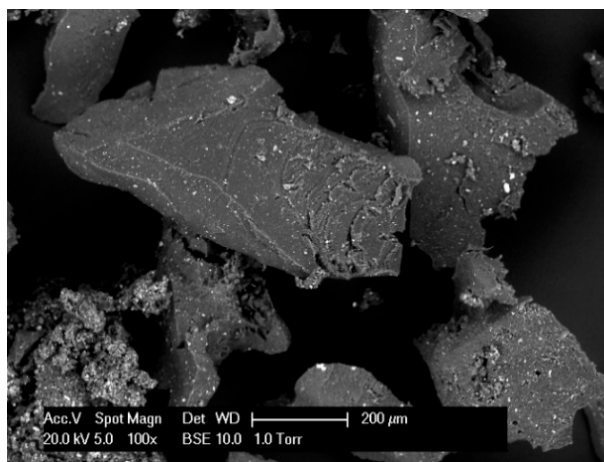
	Test Description	Unit	Value
Consistency at intermediate service temperature	Penetration at 25 °C	mm/10	80
Consistency at elevated service temperature	Softening Point	°C	46
Resistance to hardening at 163°C	Change in mass	%	0.72
	Retained penetration	%	52
	Softening point after hardening	°C	51
Technical characteristic	Density at 25 °C	g/cm ³	1.027
	Kinematic viscosity at 135 °C	mm ² /s	265
	Solubility	%	>99.0

Table 2. Particle size distribution of crumb rubber modifier (CRM).

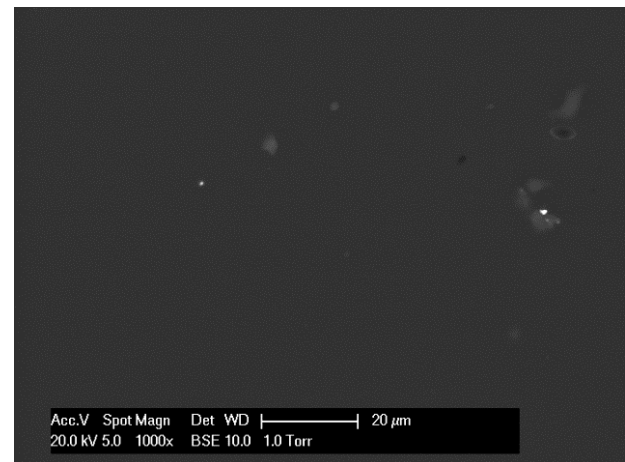
Sieves (mm)	Passing (%)
0.710	100
0.500	93
0.355	63
0.180	21
0.125	9
0.063	2

Table 3. Basic properties of CRM.

Properties	Description or Value
Source	Scrap truck tyres
Colour	Black
Morphology	Porous
Specific gravity (kg/L)	1.15
Decomposition temperature (°C)	~200
Total rubber (natural and synthetic)	55
Carbon Black (%)	30
Zinc oxide (%)	1.5
Sulphur (%)	1
Benzene extraction (%)	5.5
Ash content (%)	7



(a)



(b)

Figure 1. Environment scanning electron microscopy (ESEM) images of (a) CRM and (b) base bitumen.

2.2. Binder Preparation

The CRMB was produced in the laboratory by blending 18% CRMs by the weight of the total blend based on the previous studies [23] and trial mixing. Adding more than 18% CRMs will cause mixing problems and undesired binder properties (e.g., extremely high viscosity). Manual stirring for 5 min was applied to pre-distribute CRMs into the base bitumen, then the blend was mixed using a Silverson high shear mixer with a square hole screen (Figure 2) at 180 °C with the shearing speed of 6000 rpm for 30 min. This mixing condition was optimized based on the criteria to obtain better mechanical properties of CRMB. During the bitumen–rubber interaction, there are generally two processes happens: rubber swelling and chemical degradation [24]. Mixing at relatively low temperatures causes inefficient swelling of rubber, while mixing at relatively high temperatures results in severe degradation of rubber particles. Both scenarios are detrimental to the property development of CRMB. During the laboratory mixing process, the mixing head was immersed into the hot bitumen to avoid vortex which may involve the potential oxygen. Each warm mix additive was incorporated into both base bitumen and CRMB with the same dosage at 140 °C. The percentages of additives W and C were 2.0% and 0.6% based on manufacturers' recommended dosage and preliminary tests. Therefore, a total of six types bituminous binders were prepared in this study, namely 70/100, 70/100-W, 70/100-C, CRMB, CRMB-W, and CRMB-C. To solely investigate the influence of warm mix additives on the rheological properties of binders, all binder samples were tested in fresh states without artificial ageing.

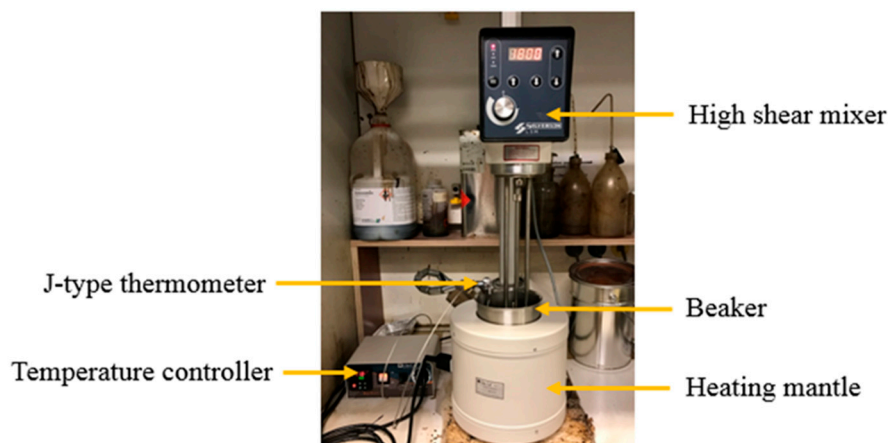


Figure 2. Laboratory equipment used to prepare crumb rubber-modified bitumen (CRMB).

2.3. Testing Methods

A dynamic shear rheometer (Anton Paar) was utilized to obtain the rheological parameters (complex shear modulus, phase angle and complex viscosity) of different binders following the standard test method. Frequency sweep tests were carried out from 0.01 to 100 rad/s over a temperature range of 10 °C–50 °C with an increment of 10 °C. Before the frequency sweep tests, strain amplitude sweep tests were conducted to identify the linear viscoelastic (LVE) range of different binders and thus to ensure the frequency sweep tests were undertaken within the binder's LVE region of response. The LVE limit was defined as the point where complex modulus has decreased to 95% of its initial value [25]. Based on the LVE limits, all the measurements were carried out at a strain level of 0.1% under strain-controlled mode. Complex viscosity is defined as complex modulus divided by angular frequency under dynamic conditions. It can be plotted as a function of angular frequency which can be further correlated to shear viscosity as a function of shear rate under steady-state conditions based on the Cox–Merz rule [26].

3. Results and Discussion

3.1. Influence of Temperature and Shear Rate on Complex Viscosity

Figure 3 plotted the complex viscosity of different bituminous binders as a function of shear rate (angular frequency) at 10 °C and 50 °C respectively. Viscosities at other temperatures showed similar trends between these two cases therefore omitted here. In Figure 3a, the behaviour of binders is non-Newtonian and dependent on frequency and temperature. Figure 3b shows that at 50 °C, base bitumen 70/100 and chemical additive modified bitumen 70/100-C both behave like Newtonian fluids, whose viscosities are almost independent of shear rates. In contrast, 70/100-W and all CRMB based binders exhibit non-Newtonian behaviors as the viscosities increase significantly with the shear rate decreases, which is categorized as the shear-thinning behavior. However, the above statements are of no validity when the testing temperature shifted to 10 °C while all binders exhibit obvious non-Newtonian behaviors as shown in Figure 3a. In addition, it is notable from Figure 3a that although the viscosity of CRMB is higher than that of base bitumen at lower shear rates, it becomes lower when the shear rate reaches 100 rad/s. This is due to the more evident shear-thinning behavior of CRMB, whose mechanism will be explored in the following subsections.

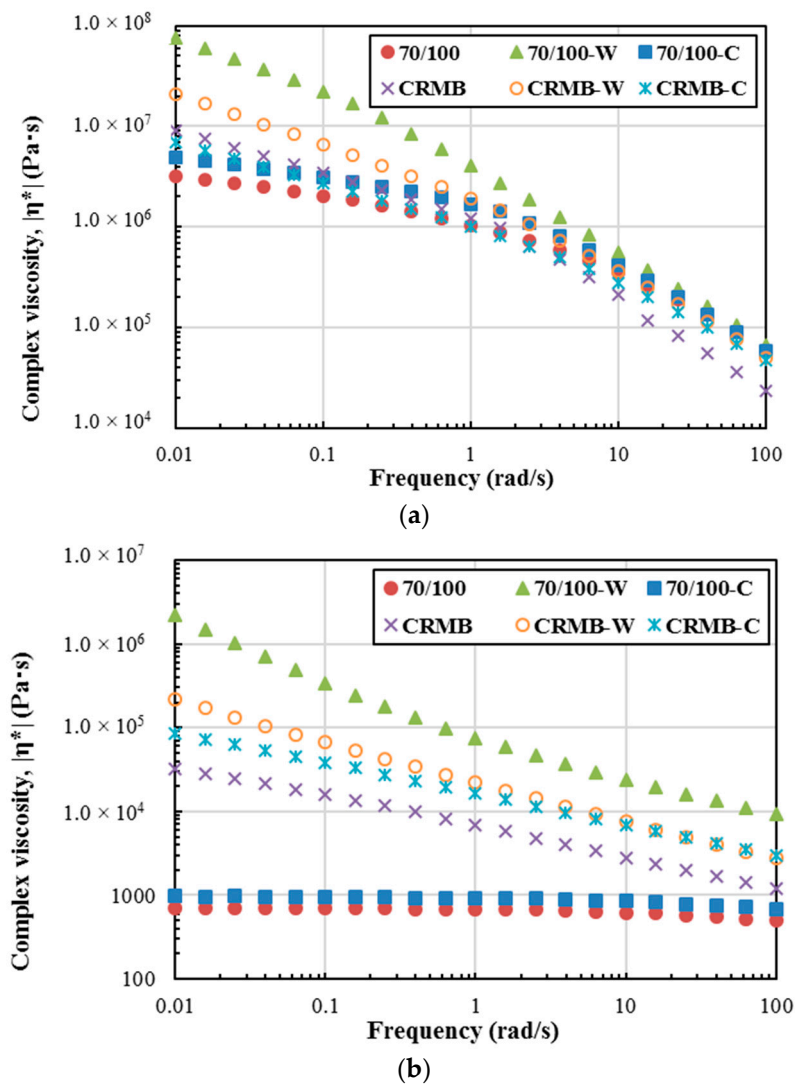


Figure 3. Complex viscosity as a function of shear rate (a) at 10 °C; (b) at 50 °C.

In terms of the warm additives, the addition of chemical additive slightly increases the viscosity of both base and CRMB binders at a certain shear rate. However, organic additive dramatically increases the viscosities of base and CRMB binders, which seems contradictory to the reported viscosity-reduction effect of wax-based additive at high construction temperatures [27]. It should be noted that additive W is a synthetic wax with high molecular hydrocarbon chains ($C_{40}\sim C_{120}$), and its melting point is around 100 °C [28]. Therefore, when tested at 50 °C, additive W exists in bituminous binders as the form of microcrystalline and hence make the binders stiffer. Beyond its melting point, the wax liquefies and can be fully miscible in the binder, which significantly reduces the binder viscosity [29]. Rheological tests at temperatures around 100 °C are recommended to be carried out in the future to verify this conclusion.

3.2. Shear-Thinning Behaviors

The previous subsection has shown the shear-thinning behaviors of different bituminous binders at certain temperatures. The occurrence of shear-thinning in non-Newtonian fluids can be attributed to the changes in particle/molecular orientations and/or alignment in the direction of flow. Specifically, there are three types of mechanisms as shown in Figure 4 can explain the complex shear-thinning behaviors of the unmodified and modified binders [6]. For polymer solutions or melts, polymer entanglements or coils are formed in the polymer network at rest. When the polymer solution/melts are

subjected to shear loading, the entanglements or coils will unfold and align with the applied shear force, which in turn makes the polymer network easy to deform as shown in Figure 4a. For suspensions, solid particles in the liquid are prone to agglomerate at rest. With the applied shear loading, agglomerates tend to break up and disseminate into the matrix as shown in Figure 4b. For colloidal dispersions, when particles are introduced into a liquid at rest, they are randomly oriented to reach a thermodynamic equilibrium state (disordered state). With the applied shear force, particles will try to align themselves to the shear direction as shown in Figure 4c. In all cases, materials in a disordered state at rest will shift to an orientational ordered state with applied shear, which corresponds to a shift from high viscosity to low viscosity. This means shear-thinning behavior is an entropy-decreasing process [30,31]. Bitumen is commonly recognized as a multi-disperse colloidal system, where high molecular weight asphaltene micelles are peptized by resins in low molecular weight maltenes. For base bitumen, the asphaltene can be regarded as particles which are randomly oriented in the maltenes and have the tendency to aggregate at rest. When the bitumen is subjected to shear loading at certain temperatures, the asphaltenes which contribute mainly to the viscosity will tend to an orientational ordered state in the maltenes. Therefore, shear-thinning happens. A similar explanation which regards wax as solid particles can be applied for the shear-thinning behavior of wax-modified bitumen. In terms of rubber modified bitumen, the potential polymer entangled network formed in the bitumen microstructure due to the rubber-bitumen interaction will unfold and stretch itself to adjust with the applied shear forces. The other two types of shear-thinning mechanism may also exist in CRMB. For the rest bituminous binders, a combination of these three types of mechanism will be capable to explain the shear-thinning behavior.

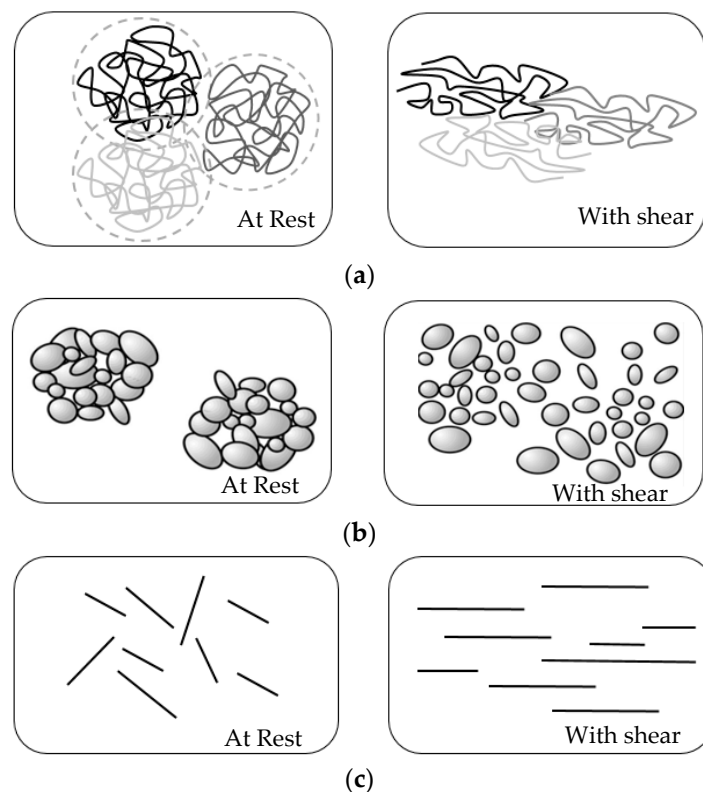


Figure 4. Schematic representation of shear-thinning mechanisms (a) polymer solutions/melts; (b) suspensions; (c) dispersions, adapted from [6].

3.3. Zero Shear Viscosity

Since bitumen viscosity at relatively low temperatures is highly shear rate dependent, directly comparing the viscosity value at a certain shear rate seems quite tedious. A parameter describing

the viscosity that independent of shear rate is plausible. At very low shear rates, Brownian motion dominates and causes all molecules or particles to be oriented randomly despite the initial effects of any applied shear stress. Under this circumstance, structured liquids behave similarly to Newtonian liquids, with a defined viscosity independent of shear rate or angular frequency. This viscosity, measured in the shear deformation when the shear rate approaches zero, is called zero shear viscosity (ZSV). ZSV is reported to be a good indicator of rutting resistance of bituminous binders [32]. Various methods were proposed to estimate the theoretical ZSV value [13]. In this study, data obtained from the frequency sweep tests were applied to the Cross model to determine the ZSV. The Cross model defined in the form of a four-parameter equation (Equation (1)) was able to fit the flow behavior of binders over a wide range of shear rates.

$$|\eta^*| = \frac{\eta_0 - \eta_\infty}{1 + (K\omega)^m} + \eta_\infty \quad (1)$$

in which η^* is the complex viscosity; η_0 is ZSV or the first Newtonian region viscosity; η_∞ is infinite shear viscosity in the second Newtonian region; ω is angular frequency (rad/s); K is a material parameter with the dimension of time; and m is a dimensionless material parameter. In the frequency range tested in this study, it is reasonable to assume that $\eta^* \gg \eta_\infty$. Therefore, the Cross model reduces to a three-parameter equation as shown in Equation (2).

$$|\eta^*| = \frac{\eta_0}{1 + (K\omega)^m} \quad (2)$$

Non-linear regression analysis was used to estimate ZSV at 50 °C with the available data. The measured viscosity and the model predicted results are plotted in Figure 5. The complex viscosities of two binders containing wax additives did not approach a plateau when the shear rate approaches zero. This was observed through the model fitting results that the solver to the solution of binder 70/100-W and CRMB-W cannot converge with defined constraints and convergence. Therefore, there are no practical ZSV values for these two binders. ZSV values and corresponding model parameters for the other four binders are summarized in Table 4. ZSV of CRMB is much higher than the base bitumen 70/100, which indicates superior high-temperature rutting resistance. Besides, ZSV also reveals the molecular weight of binders [6]. CRMB with higher ZSV possesses higher molecular weight than base bitumen due to the rubber–bitumen interaction. Both natural rubber and synthetic rubber in CRMs are macromolecules with much higher molecular weight than bitumen [33]. The formed polymer network within the bitumen matrix after rubber–bitumen interaction increases the viscosity and molecular weight of binder [34]. The addition of chemical additives increases the ZSV of both binders. From the definition of the Cross model, it can be noted that parameter m is related to shear susceptibility. Based on the data in Table 4, it is inferred that the rheological behavior of a binder with smaller m is closer to Newtonian behavior. Furthermore, the level of non-Newtonian behavior is reflected in parameter K . The higher value K is, the higher level of non-Newtonian behavior the binder has.

Table 4. Zero shear viscosity (ZSV) fitting results using the Cross model.

Binder Type	70/100	70/100-C	CRMB	CRMB-C
η_0 (Pa·s)	1377	1848	1.2×10^5	3.55×10^5
K (s)	4.31	3.10	1191.18	2144.81
m	0.0644	0.0639	0.3951	0.3924

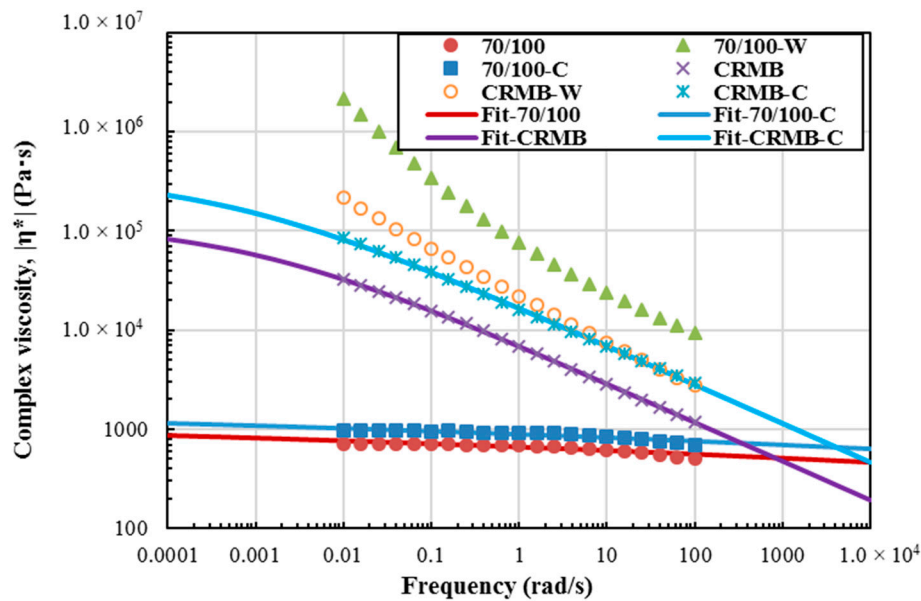


Figure 5. Measured and model predicted viscosity values for different binders at 50 °C.

3.4. Yield Stress

As observed in previous subsection, bituminous binders modified by wax additives do not show a practical or show an infinite viscosity approaching zero shear rate. The reason for this special non-Newtonian behavior can be attributed to the yield stress characteristic which is a property associated with numerous types of complex fluids. For example, paint can only flow with the help of brush, but remains fixed on a vertical wall despite the force of its own gravity. The yield stress is defined as a critical stress that must be applied to the material before flow or continuous deformation is observed [7]. Below the yield stress, the solid-like bituminous binder will deform elastically which results from elastic elements being stretched in the shear field. Above the yield stress, such elastic elements begin to break down causing shear-thinning behaviors and consequent flow. Although many researchers have doubt about whether the true yield stress exists [35], the concept of yield stress, if defined properly, is very useful in a whole range of applications, such as stirring, mixing and pumping.

To determinate the yield stress of the wax-modified bituminous binders, the Herschel–Bulkley model was applied to fit the measured data (shear stress versus shear rate) and extrapolate to a zero-shear rate. The Herschel–Bulkley model [7] describes non-Newtonian behavior after yielding and is basically composed of a power law model with a yield stress term as shown in Equation (3):

$$\sigma = \sigma_y + K\omega^n \quad (3)$$

In Equation (3) above σ is the shear stress; σ_y is the yield stress; K is the consistency; and n is the flow behavior index. The parameter n describes the material as shear thinning when $n < 1$, or shear thickening when $n > 1$, or Newtonian when $n = 1$.

The yield stress determined through the Herschel–Bulkley model was shown in Figure 6. As analyzed before, for bituminous binders having practical ZSV do not have a yield stress. This is also verified in Figure 6a as the fitted equations do not have the yield stress term. The yield stresses of wax modified binder 70/100-W and CRMB-W are clearly plotted in Figure 6b with the values of 190.60 Pa and 4.22 Pa, respectively. The significant difference between the yield stresses shows additive W has different extents of effect on the base bitumen and CRMB. This is possibly due to the different microstructures of these two binders which stem from the potentially complex interaction between bitumen, rubber and warm mix additives. Generally, larger yield stress indicates more stable internal structure of the material [35]. The yield stress brings both positive and negative effects to the material

depending on the application conditions. For instance, higher yield stress can be a hindrance if the binder is being pumped or mixed while it will benefit the binder making it more stable during the service stage on the pavement. One also should note that the predicted yield stress is highly dependent on the instrument resolution, measuring conditions and analysis method.

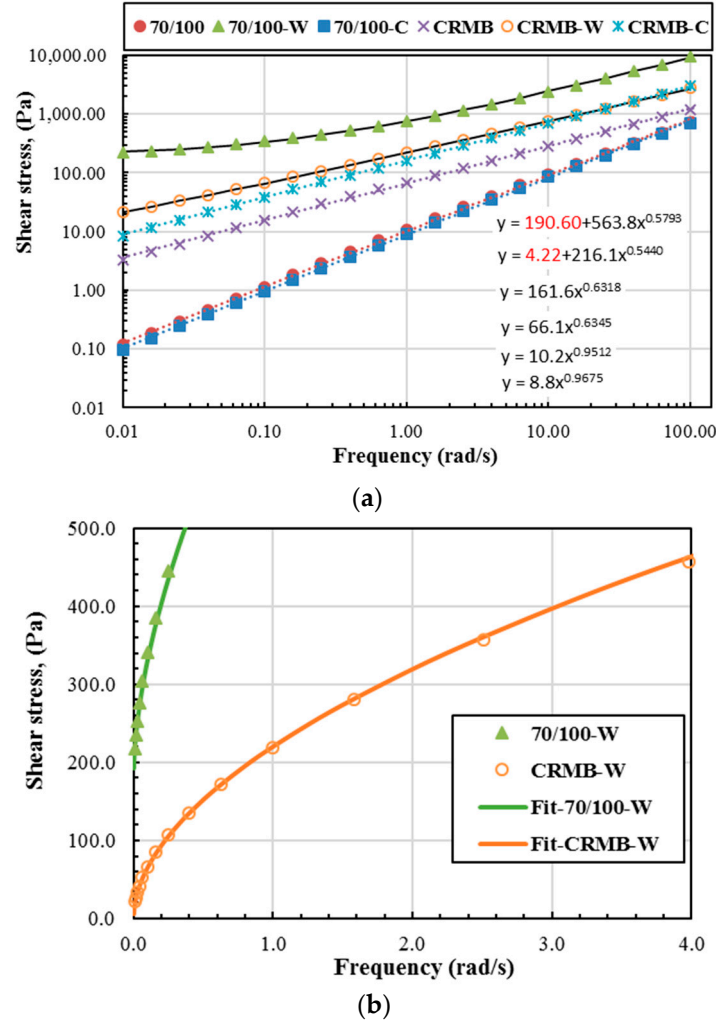


Figure 6. Yield stress calculation of different binders at 50 °C (a) entire curve; (b) partial curve.

3.5. Complex Viscosity as a Function of Temperature

The viscosity of bituminous binders is highly temperature-dependent. Generally, there are two common equations to evaluate the viscosity-temperature characteristics of binders, namely the William–Landel–Ferry (WLF) function based on the free volume theory and the Arrhenius-type equation based on the absolute theory of reaction rate [36]. These two equations correspond to two temperature regions. At temperatures well above the glass transition temperature T_g , i.e., $T_g + 100$ °C or $\sim 1.3T_g$, the viscosity follows the Arrhenius equation:

$$\eta^* = Ae^{\frac{E_a}{RT}} \quad (4)$$

where A is a pre-exponential parameter; R is the universal gas constant (8.314 J/(mol·K)); and E_a is the flow activation energy (J/mol). T is temperature (K). At lower temperatures ranging from T_g to

$T_g + 100$ °C, the WLF function should be used instead. A strictly equivalent form to the WLF function is described by the Vogel-Fulcher-Tammann (VFT) expression:

$$\eta^* = A_0 e^{\frac{E_0}{R(T-T_0)}} \quad (5)$$

where A_0 , E_0 , and T_0 are material constants. Apart from these two common equations, a number of empirical expressions have been proposed to represent the viscosity-temperature dependence based on available experimental data. The proposed equations of viscosity-temperature characteristics have the following general form [8,37]:

$$\ln \eta^* = A + \frac{B}{T+C} + a \ln T + bT + cT^2 + \frac{D}{T^2} \quad (6)$$

where A , B , C , D , a , b , c are fitting constants. It is possible to add more power-law terms of T into the above empirical equation.

Figure 7 presents the plot of logarithmic viscosity as a function of the reciprocal of temperature ranging from 283.15 K to 323.15 K at two extreme shear rates. At a low shear rate of 0.01 rad/s, the viscosity-temperature curve can be fitted by a linear line, which is an Arrhenius-type equation. The reason that Arrhenius equation requires elevated-temperature condition is to guarantee the material is in the Newtonian state. Based on the time-temperature superposition principle as well as the test results in this study, bituminous binders can be regarded as Newtonian-like fluids at a low shear rate of 0.01 rad/s, so that Arrhenius equation is applicable. However, this observation is invalid at a high shear rate of 100 rad/s, under which bituminous binders exhibit apparent non-Newtonian behaviors. The viscosity-temperature curve at the higher shear rate of 100 rad/s can be fitted by a second-order polynomial equation with enough high correlation degree instead of a linear one. Based on the above findings, it is not reasonable to fit the viscosity-temperature curve with only an Arrhenius equation over a wide range of temperatures or shear rates.

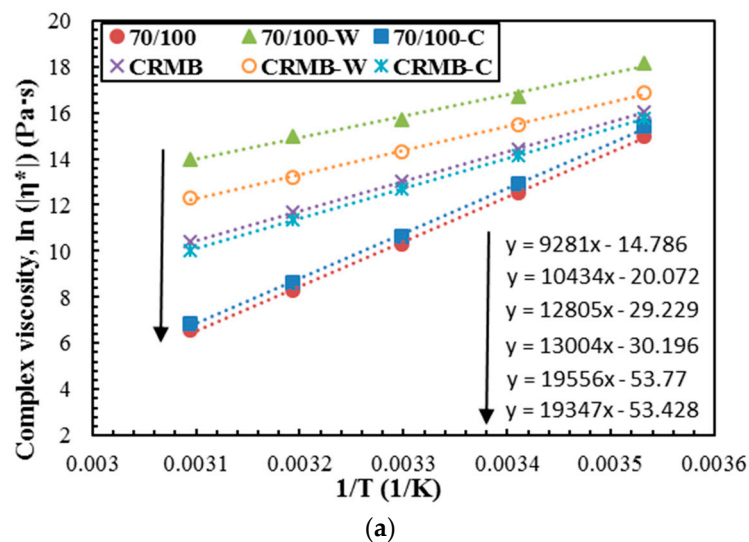


Figure 7. Cont.

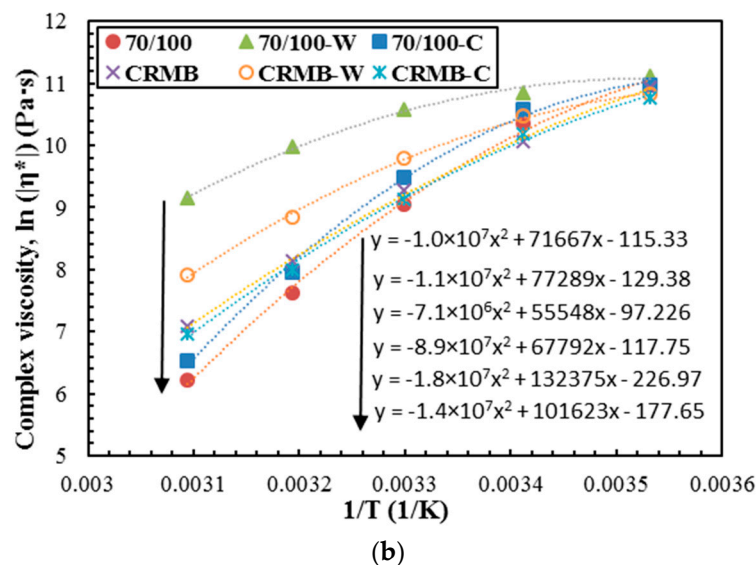


Figure 7. Logarithmic complex viscosity as a function of the reciprocal of temperature (a) at shear rate of 0.01 rad/s; (b) at shear rate of 100 rad/s.

4. Conclusions

Non-Newtonian behaviors of highly modified bituminous binders challenge the traditional interpretation of viscosity measurements of blends. Crumb rubber modified bitumen and binders with wax additives show apparent shear-thinning behaviors at certain temperatures. The shear-thinning mechanisms of different binders can be attributed to three types: polymer solutions/melts, suspensions and dispersions. Zero shear viscosity of different binders calculated using the Cross model and yield stresses derived based on the Herschel–Bulkley model are two important parameters to characterize the non-Newtonian behaviors of bitumen. It is emphasized that characteristics of zero shear viscosity and yield stress are highly temperature-dependent. The Arrhenius equation is only valid to model the temperature dependence of viscosity in the Newtonian region. The viscosity-temperature dependence of bitumen should be described with distinct equations in different temperature regions, namely Newtonian and non-Newtonian regions.

The testing temperature range in this study covers the average pavement temperature and high pavement temperature. For further research, viscosities of different bituminous binders tested at a wider temperature range (including mixing temperatures around 135 °C) and using different measuring systems (e.g., concentric cylinder, cone-plate) in DSR (Dynamic Shear Rheometer) are needed to examine the repeatability and accuracy of the model predictions. Systematic approaches to measure the yield stress of bituminous binders can be developed to compare with that predicted by the model.

Author Contributions: Conceptualization, X.L.; Formal analysis, H.W.; Methodology, P.A. and T.S.; Project administration, T.S.; Supervision, X.L. and T.S.; Writing—original draft, H.W.; Writing—review and editing, H.W. and X.L.

Funding: This research received no external funding.

Acknowledgments: The authors acknowledge RUMAL for providing testing materials. The first author would like to thank the China Scholarship Council for financial support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Lesueur, D. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Adv. Colloid Interface Sci.* **2009**, *145*, 42–82. [[CrossRef](#)] [[PubMed](#)]
2. Polacco, G.; Filippi, S.; Merusi, F.; Stastna, G. A review of the fundamentals of polymer-modified asphalts: Asphalt/polymer interactions and principles of compatibility. *Adv. Colloid Interface Sci.* **2015**, *224*, 72–112. [[CrossRef](#)] [[PubMed](#)]
3. Wang, H.; Yang, J.; Gong, M. *Rheological Characterization of Asphalt Binders and Mixtures Modified with Carbon Nanotubes*; Rilem Bookser; Springer: Berlin, Germany, 2016; pp. 141–150.
4. Wang, H.; You, Z.; Mills-Beale, J.; Hao, P. Laboratory evaluation on high temperature viscosity and low temperature stiffness of asphalt binder with high percent scrap tire rubber. *Constr. Build. Mater.* **2012**, *26*, 583–590. [[CrossRef](#)]
5. Sybilski, D. Non-newtonian viscosity of polymer-modified bitumens. *Mater. Struct.* **1993**, *26*, 15–23. [[CrossRef](#)]
6. Barnes, H.A.; Hutton, J.F.; Walters, K. *An Introduction to Rheology*; Elsevier: New York, NY, USA, 1989; Volume 3.
7. Larson, R.G. *The Structure and Rheology of Complex Fluids*; Oxford University Press: New York, NY, USA, 1999; Volume 150.
8. Haj-Kacem, R.B.; Ouerfelli, N.; Herráez, J.V.; Guettari, M.; Hamda, H.; Dallel, M. Contribution to modeling the viscosity arrhenius-type equation for some solvents by statistical correlations analysis. *Fluid Phase Equilib.* **2014**, *383*, 11–20. [[CrossRef](#)]
9. Jamshidi, A.; Hamzah, M.O.; Shahadan, Z.; Yahaya, A.S. Evaluation of the rheological properties and activation energy of virgin and recovered asphalt binder blends. *J. Mater. Civ. Eng.* **2015**, *27*, 04014135. [[CrossRef](#)]
10. Bahia, H.; Anderson, D. The new proposed rheological properties of asphalt binders: Why are they required and how do they compare to conventional properties. In *Physical Properties of Asphalt Cement Binders*; ASTM International: West Conshohocken, PA, USA, 1995.
11. Zoorob, S.E.; Castro-Gomes, J.P.; Pereira Oliveira, L.A. Assessing low shear viscosity as the new bitumen softening point test. *Constr. Build. Mater.* **2012**, *27*, 357–367. [[CrossRef](#)]
12. Sybilski, D. Zero-shear viscosity of bituminous binder and its relation to bituminous mixture's rutting resistance. *Transp. Res. Rec. J. Transp. Res. Board* **1996**, *1535*, 15–21. [[CrossRef](#)]
13. Anderson, D.; Le Hir, Y.; Planche, J.-P.; Martin, D.; Shenoy, A. Zero shear viscosity of asphalt binders. *Transp. Res. Rec. J. Transp. Res. Board* **2002**, *1810*, 54–62. [[CrossRef](#)]
14. Wang, H.; Liu, X.; Apostolidis, P.; Scarpas, T. Review of warm mix rubberized asphalt concrete: Towards a sustainable paving technology. *J. Clean. Prod.* **2018**, *177*, 302–314. [[CrossRef](#)]
15. Lo Presti, D. Recycled tyre rubber modified bitumens for road asphalt mixtures: A literature review. *Constr. Build. Mater.* **2013**, *49*, 863–881. [[CrossRef](#)]
16. Heitzman, M. Design and construction of asphalt paving materials with crumb rubber modifier. *Transp. Res. Rec.* **1992**, *1339*, 1–44.
17. Abdelrahman, M. Controlling performance of crumb rubber-modified binders through addition of polymer modifiers. *Transp. Res. Rec. J. Transp. Res. Board* **2006**, *1962*, 64–70.
18. Shen, J.; Amirkhanian, S.; Xiao, F.; Tang, B. Influence of surface area and size of crumb rubber on high temperature properties of crumb rubber modified binders. *Constr. Build. Mater.* **2009**, *23*, 304–310. [[CrossRef](#)]
19. Tang, N.; Huang, W.; Xiao, F. Chemical and rheological investigation of high-cured crumb rubber-modified asphalt. *Constr. Build. Mater.* **2016**, *123*, 847–854. [[CrossRef](#)]
20. Ragab, M.; Abdelrahman, M.; Ghavibazoo, A. Performance enhancement of crumb rubber-modified asphalts through control of the developed internal network structure. *Transp. Res. Rec. J. Transp. Res. Board* **2013**, *2371*, 96–104. [[CrossRef](#)]
21. Hajj, E.Y.; Sebaaly, P.E.; Hitti, E.; Borroel, C. Performance evaluation of terminal blend tire rubber hma and wma mixtures—Case studies. *J. Assoc. Asph. Paving Technol.* **2011**, *80*, 665–696.
22. Zhang, W.; Shen, S.; Wu, S.; Mohammad, L.N. Long-term field aging of warm-mix and hot-mix asphalt binders. *Transp. Res. Rec. J. Transp. Res. Board* **2017**, *2632*, 140–149. [[CrossRef](#)]

23. Huang, S.C. Rubber concentrations on rheology of aged asphalt binders. *J. Mater. Civ. Eng.* **2008**, *20*, 221–229. [[CrossRef](#)]
24. Abdelrahman, M.A.; Carpenter, S.H. Mechanism of the interaction of asphalt cement with crumb rubber modifier. *Transp. Res. Rec. J. Transp. Res. Board* **1999**, *1661*, 106–113. [[CrossRef](#)]
25. Airey, G.D.; Rahimzadeh, B.; Collop, A.C. Linear viscoelastic limits of bituminous binders. *J. Assoc. Asph. Paving Technol.* **2002**, *71*, 89–115.
26. Shan, L.; Tan, Y.; Richard Kim, Y. Applicability of the cox–merz relationship for asphalt binder. *Constr. Build. Mater.* **2012**, *37*, 716–722. [[CrossRef](#)]
27. Baumgardner, G.L.; Reinke, G.R. Binder additives for warm mix asphalt technology. *J. Assoc. Asph. Paving Technol.* **2013**, 685–709.
28. Wang, H.; Liu, X.; Apostolidis, P.; Scarpas, T. Rheological behavior and its chemical interpretation of crumb rubber modified asphalt containing warm-mix additives. *Transp. Res. Rec. J. Transp. Res. Board* **2018**. [[CrossRef](#)]
29. Jamshidi, A.; Hamzah, M.O.; You, Z. Performance of warm mix asphalt containing sasobit®: State-of-the-art. *Constr. Build. Mater.* **2013**, *38*, 530–553. [[CrossRef](#)]
30. Angelico, R.; Burgemeister, D.; Ceglie, A.; Olsson, U.; Palazzo, G.; Schmidt, C. Deuterium nmr study of slow relaxation dynamics in a polymer-like micelles system after flow-induced orientation. *J. Phys. Chem. B* **2003**, *107*, 10325–10328. [[CrossRef](#)]
31. Angelico, R.; Rossi, C.O.; Ambrosone, L.; Palazzo, G.; Mortensen, K.; Olsson, U. Ordering fluctuations in a shear-banding wormlike micellar system. *Phys. Chem. Chem. Phys.* **2010**, *12*, 8856–8862. [[CrossRef](#)] [[PubMed](#)]
32. Morea, F.; Agnusdei, J.O.; Zerbino, R. Comparison of methods for measuring zero shear viscosity in asphalts. *Mater. Struct.* **2009**, *43*, 499–507. [[CrossRef](#)]
33. Mark, J.E.; Erman, B.; Roland, M. *The Science and Technology of Rubber*; Academic Press: Cambridge, MA, USA, 2013.
34. Ragab, M.; Abdelrahman, M. Effects of interaction conditions on internal network structure of crumb rubber-modified asphalts. *Transp. Res. Rec. J. Transp. Res. Board* **2014**, *2444*, 130–141. [[CrossRef](#)]
35. Barnes, H.A. The yield stress—A review or ‘ $\pi\alpha\nu\tau\alpha\ \rho\epsilon\iota$ ’—Everything flows? *J. Non-Newton. Fluid Mech.* **1999**, *81*, 133–178. [[CrossRef](#)]
36. Saini, D.; Shenoy, A. A new method for the determination of flow activation energy of polymer melt. *J. Macromol. Sci. Part B Phys.* **1983**, *22*, 437–449. [[CrossRef](#)]
37. Messaâdi, A.; Dhoubi, N.; Hamda, H.; Belgacem, F.B.M.; Adbelkader, Y.H.; Ouerfelli, N.; Hamzaoui, A.H. A new equation relating the viscosity arrhenius temperature and the activation energy for some newtonian classical solvents. *J. Chem.* **2015**, *2015*. [[CrossRef](#)]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).