

The Thermo-Rheological Behavior of Bitumen

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ABSTRACT

As a very important coating material in different applications, bitumen is a complex mixture of different chemicals. It is generally accepted that the principle of time-temperature superposition (TTS) holds for this material. In this study rheological measurements were carried out on four different bitumens. Different representations of the experimental data were examined to check failure or holding of TTS for this complex system. Due to differences in dynamics of components, discontinuities were observed in δ versus G^* curves for all four bitumens. It was concluded that the TTS fails to be applied for the studied bitumens. Prog. Color Colorants Coat. 1(2008) 45-55. © Institute for Colorants, Paint and Coatings.

1. Introduction

Bitumen is a complex material, which is composed of a vast range of molecular weights and chemical structures. This complex mixture leads to formation of a very complicated nano-scale suspension or composite, where its structure is very temperature sensitive. The corresponding gel structure transforms into a sol structure at high temperatures [1].

Solubility of the isolated bitumen fractions are as follows:

- Asphaltenes: Insoluble in low boiling saturated hydrocarbons (e.g. pentane), soluble in carbon tetrachloride.
- Maltenes: Soluble in low boiling saturated hydrocarbons.

The quantity and nature of the asphaltenes and maltenes fractions largely affect the quality of bitumen. Some workers have further fractionated bitumen to hard bitumen, bitumen resin, oil resin and oily constituents [2]. The percentage of bitumen fractions changes from

crude to crude, from bitumen to bitumen and even from process to process: For example, the maltenes and asphaltenes contents range from 70 to 95 and from 5 to 30, respectively.

The maltenes are a mixture of oils and resins. The molecular weight of the maltenes' constituents lies between 250 and 1250 g/mol. The oils and resins are described as following:

- Oil molecules from 40 to 60 weight percent of bitumen constituents are essentially composed of mono and polycyclic naphthenic and aromatic hydrocarbons. The oil fraction also contains variable quantities of sulfur compounds such as thionaphthenes, cyclic sulfurs and mono and dibenzo-thiophene derivatives [3].
- Resin molecules are polycyclic compounds, which can be saturated, aromatic or heterocyclic (sulfur, nitrogen and oxygen). There are some organic chemical functional groups in resins such as carboxylic and phenolic acids and nitrogen bases. The chemical

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structure of resins is similar to that of asphaltenes. Their structural units are the same and their differences lie in their molecular weights (which are less than those of asphaltenes) and in their H/C ratio (which is higher than that of asphaltenes, maltenes, i.e.: 1.41 to 1.66, and asphaltenes, i.e.: 0.98 to 1.25) [4]. During the process of air blowing and the aging period, the polycyclic compounds of resins undergo polycondensation reactions to form asphaltenes. Maltenes can be fractionated into their components by sensitive separation methods, e.g. GPC [5]. Some known maltene structures are shown in Figure 1 [6]. Some other workers have characterized bitumen molecular weight distribution (MWD) via rheological techniques [7, 8].

Asphaltenes are the n-alkane insoluble fractions that form 5-30% of bitumen. The asphaltene content greatly affects the physical properties of bitumen. A higher asphaltene content leads to a stiffer bitumen. It changes

the colloidal structure of bitumen. The insolubility of asphaltenes in n-alkanes results from their aromaticity and very high molecular weights. The details of structure and properties of asphaltenes are discussed elsewhere [9]. The typical molecular weight of asphaltenes ranges from 10^3 to 10^4 g/mol. The asphaltene molecules tend to associate and form molecular associations (micelles) [10]. The recent research data based on NMR technique revealed 10 times decrease in asphaltenes' molecular weight, i.e.: 1000-2000 g/mol [11]. This arises controversy which can be overcome via obtaining data on asphaltenes' aggregations (micelles). These micelles are responsible for the formation of the colloidal structure observed in bitumen. Asphaltenes can be considered as a mixture of polymers obtained from polycondensation of carbon skeletons that contain heteroatoms (sulfur and nitrogen) and chemical functional groups such as: hydroxyl and carboxyl groups. A hypothetical structure for asphaltenes is shown in Figure 2 [6].

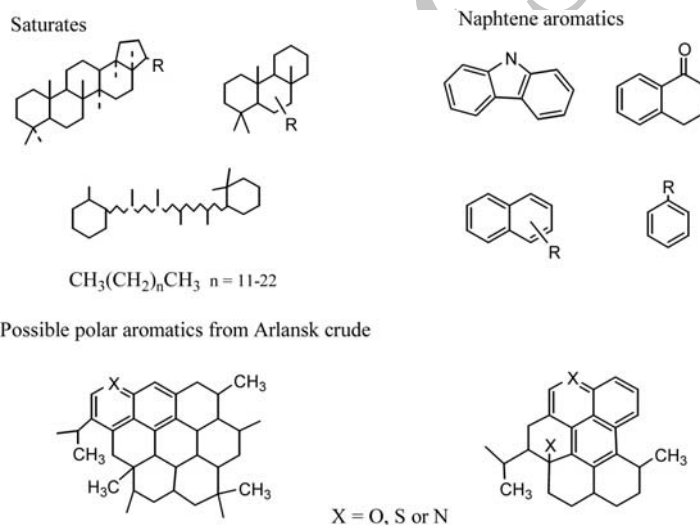
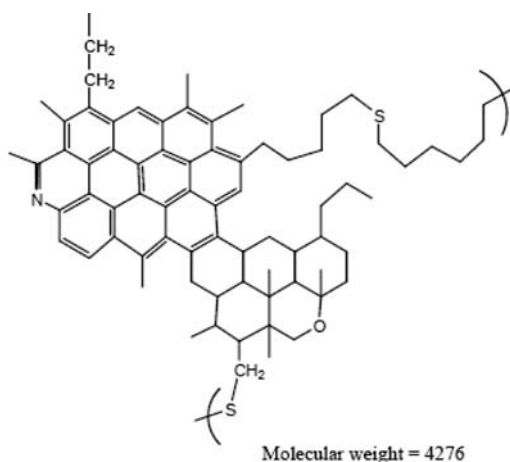


Figure 1: Various maltenes constituents [6, 7].



Molecular weight = 4276

Figure 2: The hypothetical structure of asphaltenes [6, 7].

As mentioned, bitumen is composed of saturates (17.4-20), aromatics (19-22.5), polar aromatics (21.9-26.6) and asphaltenes (25-33). The numbers between parenthesis indicate the range of the solubility parameters of these materials in (MPa)^{0.5}[12]. From a physical point of view, they are in liquid-state to solid-state at room temperature, respectively. As seen, the solubility parameters of the bitumen components overlap. Consequently, the nano-size asphaltene particles are very well dispersed in liquid and/or greasy glass-forming phase of maltenes (saturates, aromatics and polar aromatic components). It should be noted that depending on the parent crude oil and the process by which bitumen is produced the percentage and nature of bitumen components are different [7, 13, 14]. A picture of isolated bitumen components is reported in [15].

Many ambiguities in understanding rheological and thermo-rheological behavior of bitumen have been resulted for such a complicated structure. Some workers have assumed the bitumen's thermo-rheological behavior to be simple and they have employed the time-temperature superposition (TTS) for bitumen [16]. Some others have found bitumen complex and ruled the failure of TTS. Surprisingly, some researchers have applied TTS for polymer-modified bitumen and constructed master curves of rheological material functions [7, 8, 17].

There is a wealth of literature on the heterogeneity, thermo-rheological behavior and dynamics of amorphous miscible polymer blends [18-28]. In case of polymer blends the chain connectivity is an intrinsic character of polymer molecules, which dictates the effect of self-concentration. This effect can be simply explained as following; the effect that intra-molecular connectivity has on the local concentration of the polymeric components of a miscible blend, which is a segment of polymer "A" in the middle of the chain is attached to other "A" segments at both of its ends. The net effect of this phenomenon is that the segment "A" generally finds itself in an environment, which is richer in "A" as being compared with the blend of overall composition. Consequently, the dynamics of the segment "A" is very biased to those of pure "A" polymer segments. This results in an effective local volume fraction (effective concentration, ϕ_{eff}) which can be calculated by the following type of addition of self-concentration (ϕ_{self}) and bulk concentration (ϕ_b):

$$\phi_{eff} = \phi_{self} + (1 - \phi_{self})\phi_b \quad (1)$$

In dilute polymer solutions the dynamics of diluted polymer chain is slaved by the dynamics of the glass-forming host (solvent or polymer) [29]. This situation is very similar to the case of dilution of asphaltenes and other heavy components of bitumen in low molecular weight components of bitumen.

Here, I tried to find a way to precisely specify the reason for the failure of TTS in case of bitumen. Some researchers have reported that the TTS holds for bitumen at low temperatures, whereas it fails at high temperatures. The correctness of this point have been checked for bitumens of different sources. It is believed that the answer lies in the differences between the dynamics of bitumen components. At low temperatures almost all materials in bitumen are glassy and the system shows a solid-like behavior, but upon heating the maltenes start to melt and their dynamics become faster than those of large solid asphaltene molecules. At moderate and high temperatures the bituminous system behaves like a viscoelastic material. Due to the infusible character of asphaltenes, the differences in the dynamics increase as temperature increases.

The objective of this paper is to report on the distinct dynamics of bitumen components using dynamic rheological measurements at low, moderate and high temperatures in the linear viscoelastic zone of the studied bitumens. At the end, a conclusion about the failure of TTS in bitumen case is drawn.

2. Experimental

2.1. Materials

Four different bitumens were used one from Shell Canada (Shell PG grade 52-34), two from Ultramar Co. (150/200 penetration grade and 58-28 performance grade, PG) one from Tehran refinery (60/70 penetration grade) acronymed as TR60/70.

2.2. Procedures

Rheological measurements were carried out on two rheometers. The first three bitumens [7] were analyzed using a Bohlin CVO and the forth one (TR60/70) was analyzed using a Paar Physica MCR 300. All rheological measurements were carried out using 8 (at -15, 0 and 15 °C), 25 (30 °C) and 60mm (60 and 90 °C) in diameter parallel-plates geometry in the linear viscoelastic (LVE) zone of bitumens rheological behaviour. The LVE zones were inferred from strain sweep tests. At high

temperatures 10% strain and 1-2% strain were applied at low temperatures. Then, frequency sweep tests were performed in 0.005 to 100 rad/s frequency range and the temperature range of -15 to 90°C by 15 and/or 30-degree steps at low and high temperatures, respectively.

3. Results and discussion

The dynamic shear storage (G') and loss (G'') moduli master curves of the studied bitumens are presented in Figures 3.a to 3.d. These master curves are constructed using the well-known time-temperature superposition (TTS) principle and the corresponding horizontal shift factors are compiled in Table 1. As seen, fairly good matches of G' and G'' data are observable in master curves. This seems to be correct at first glance, but it is very tricky. Once we try to construct the master curves of dynamic complex viscosity and loss angle versus the reduced frequency ($a_T^* \omega$) using the same horizontal shift factors, the discontinuous master curves will be

resulted. Usually, the care is not taken and the master curves are used without any precautions even for more complicated systems such as polymer-modified bitumens [1, 7, 8, 17, 30, 31]. Here, care has been taken that bitumen is a complex mixture of materials of different temperature sensitivity and thermo-rheological behavior. All these mean that different components of bitumen are of different dynamics at the test temperature. Apart from these observations, in Figure 3.d a plateau is observed at low frequency zone (10^{-3} - 10^{-5} s^{-1}). This confirms existence of a two-phase system. This type of plateau is already predicted by Palirene's model for a blend of two different fluids [33]. As a matter of fact, bitumen is a nano-composite filled with the nano-particles and associations of the asphaltene's molecules. Due to contribution of these asphaltene inclusions in the elasticity of the bitumen a delay (plateau) is observed as frequency decreases.

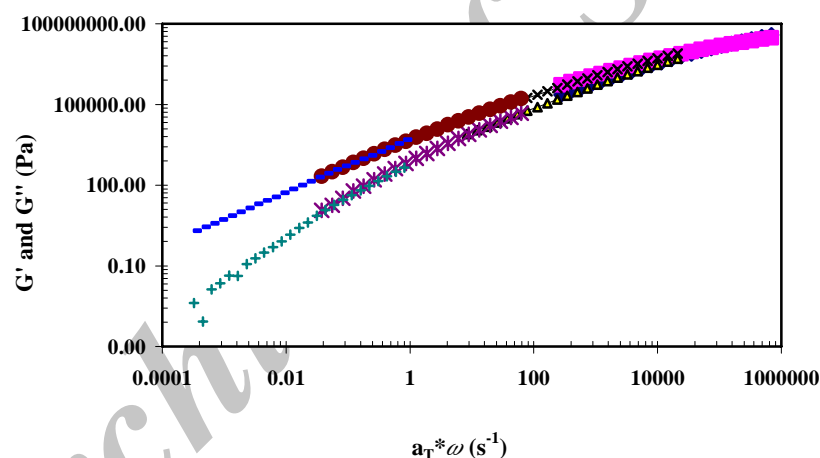


Figure 3.a: Master curves of Shell 52-34 at 30°C .

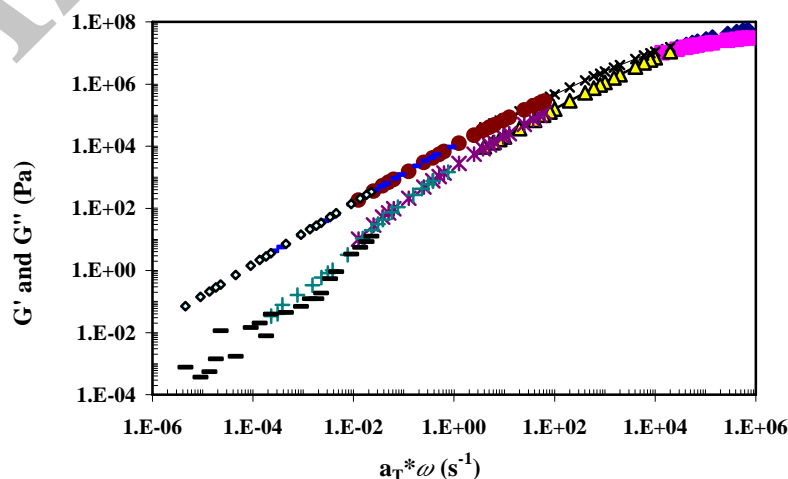


Figure 3.b: Master curves of Ultramar 150/200 at 30°C .

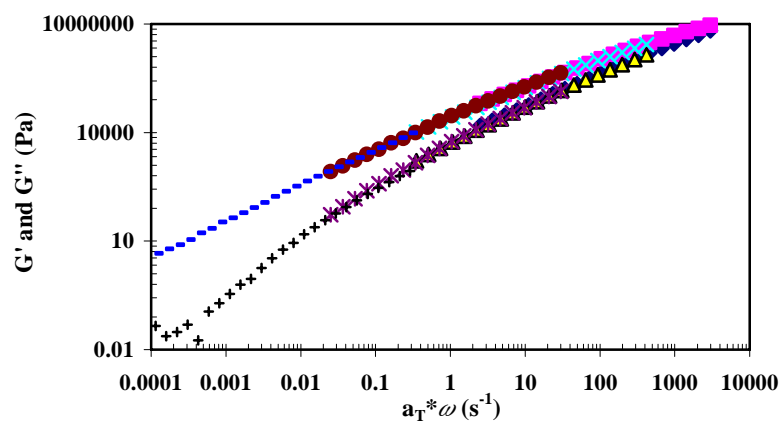


Figure 3.c: Master curves of Ultramar 58-28 at 30°C.

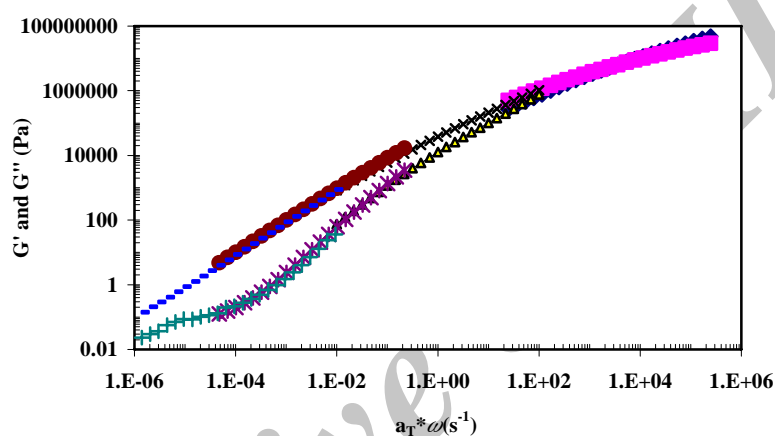


Figure 3.d: Master curves of TR60/70 at 30°C.

Table 1: Shift factors for shifting rheological material functions of bitumens.

Temperature (°C)	Shell 52-34	Ultramar 150/200	Ultramar 58-28	Tehran 60/70
-15	11000	40000	1643	----
0	335	60	100	2470
30	1	1	1	1
60	0.01297	0.0069	0.00459	0.0022
90	----	0.00006	----	0.000095

Table 2: Glass transition of different bitumen components [12].

Bitumen component	Saturates	Aromatics	Asphaltenes
Glass transition temperature (°C)	-142 to -152	53 to 73	~70

In order to clearly present the breakdown of TTS, in the case of bitumen, the standard procedure reported in the literature was used [18, 32]. The semi-logarithmic master curves of G'' versus frequency are formed in Figure 4. This type of data representation helps to detect any TTS failure. However, no discontinuity is observed in this figure with an exception for Ultramar 150/200. This leads us to this preliminary conclusion that the TTS holds for three out of four studied bitumens.

An alternative representation of rheological data is $\tan \delta$ versus reduced frequency master curves (Figures 5.a to 5.d). As seen, none of bitumens shows good superposition data in the master curves, especially at low frequencies, which correspond to high temperatures. The same results can be obtained by tracing loss tangent ($\tan \delta$ versus G^* (the curves are not reported for the sake of brevity)). To discover more about the thermo-rheological behavior of bitumens, the loss angle was plotted against complex modulus (δ - G^* curves, Figures 6.a to 6.d). This method of presentation of rheological data bypasses the superposition. In the figures, one clearly observes existence of the discontinuity for all four bitumens. This means that the TTS does not hold for bitumen. The question that must be answered is: "How can we account for the failure of TTS in the case of pure bitumens?" The answer lies in the chemical structure of bitumen's components and their different dynamics and temperature sensitivity. Using the results of the similar systems in the literature leads us to the answer. The following paragraph describes the chosen path to the answer.

Ediger et al in their work [29] treated a system which was structurally very similar to bitumen. In their work, the dynamics of polymers like polystyrene (PS) and polyisobutylene (PI) were diluted in relatively small molecules like tetracene and rubrene was reported. It was very interesting to note that the structures of these molecules were very close to those of bitumen components. They concluded that:

- *Self-concentration plays little or no role in determining the dynamics of small dilute molecules in*

a glass-forming matrix, thus Lodge-McLeish model is not to be used.

- *The motion of molecules smaller than the necessary size for formation of entanglement of matrix is not governed by the matrix viscosity. Under these conditions the motion of small molecules is decoupled from the motion of matrix.*

Both above-mentioned findings are to say that bitumen is a non-phase separated system in which small and large molecules (Figures 1 and 2 and [13-15]) co-exist and thermo-rheologically behave independently and differently. Unfortunately, the brittleness of pure bitumen at low temperatures makes dynamic-mechanical thermal measurements very difficult or non-reliable for this material [7, 34-35]. However, DSC measurements show some separated T_g s for bitumen [9, 11] (Table 2). The observation of separated glass transitions, which can be interpreted as distinct dynamics of bitumen components, is consistent with the findings of other workers about miscible polymer blends [15, 24]. Otherwise, a phase-separated morphology should be considered for bitumen. Experimentally (AFM method), it is proved that nano-size domains of asphaltenes are distributed throughout maltenes (the matrix) [10]. These domain sizes are very close to the molecular scale sizes and one may consider bitumen as a one-phase material despite flocculation and phase separation under different conditions [36-37].

As a matter of fact, at high temperatures the dynamics of different bitumen components (fractions) becomes independent where this type of master curves becomes discontinuous. According to presented curves (Figures 5 and 6), at low temperatures (high frequencies) the dynamics of fast moving bitumen components are slaved by the slow moving components. Meanwhile, this is not the case at high temperatures (low frequencies) and the dynamics of components are decoupled. This might stem from similar chemical structures but very different molecular weights of the bitumen components. Finally, it is concluded that whenever the superposition artifacts are removed or bypassed, the failure of TTS becomes evident for the bituminous systems.

4. Conclusions

Bitumen is a very complex set of chemicals, that has more than one T_g and its components are of different dynamics. These different dynamics cannot be detected by some characterization techniques. Rheological measurements provide information about dynamics of materials. Construction of the master curves of rheological data using the well-known shift factors does not clearly show the failure of time-temperature superposition principle (TTS) for bitumen. Meanwhile, other methods of data presentation, in which superposition is bypassed ($\delta - G^*$, $\tan \delta - G^*$ curves) show that TTS fails to hold for bitumen in the whole range of

studied temperatures. According to the results of the researches on the similar works, it was concluded that the main reason for the failure of TTS principle in case of bitumen is due to the differences in chemical structures and consequently the dynamics of the bitumen components.

In addition, a plateau was observed in the elastic modulus master curve (G') of one of the bitumen which shows a two-phase system, in which the dispersed phase actively contributes in the elasticity of the system at low-frequency region. This also is an indication of the difference in the rheological behavior of the bitumen components which results in TTS failure in its case.

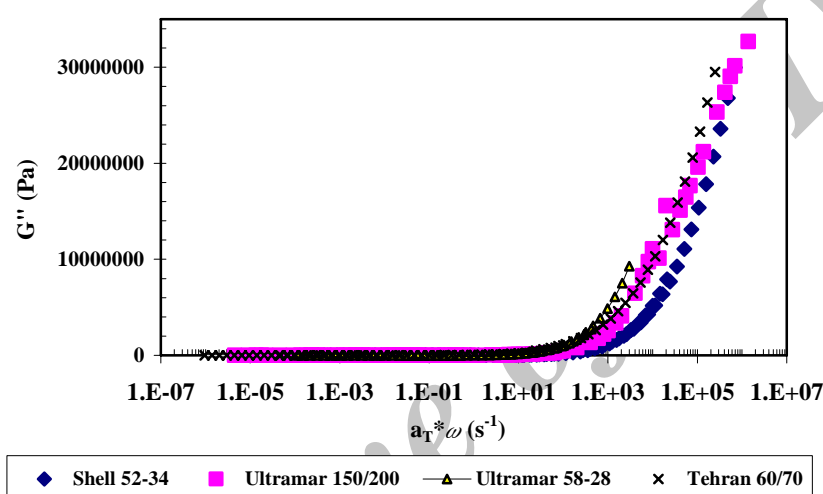


Figure 4: Dynamic loss modulus versus reduced frequency shifted to 30 °C for different bitumens.

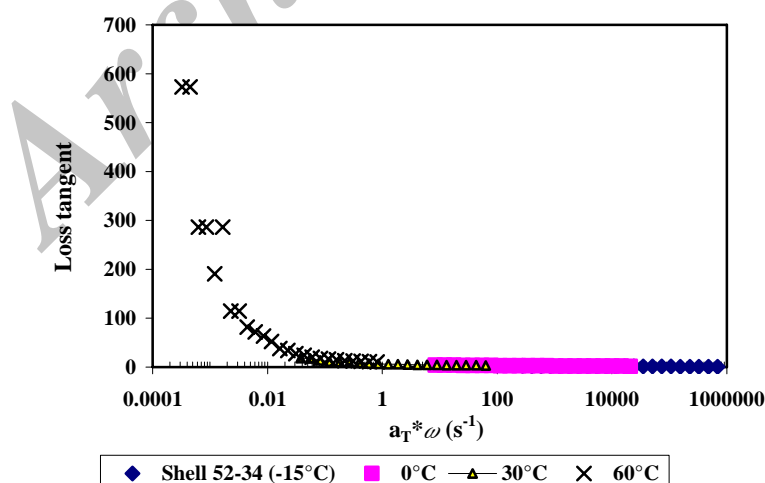


Figure 5.a: Master curves of loss tangent versus frequency for Shell 52-34 ($T_{ref}=30^{\circ}\text{C}$).

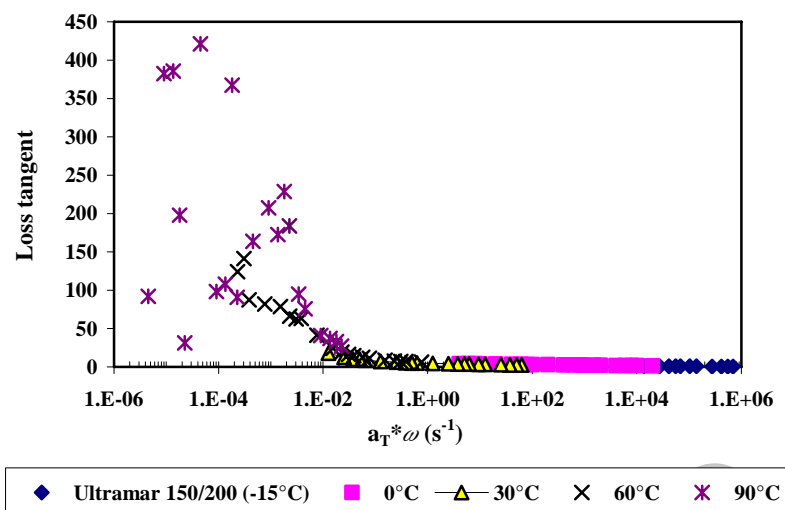


Figure 5.b: Master curves of loss tangent versus frequency for Ultramar 150/200 ($T_{ref}=30^{\circ}\text{C}$).

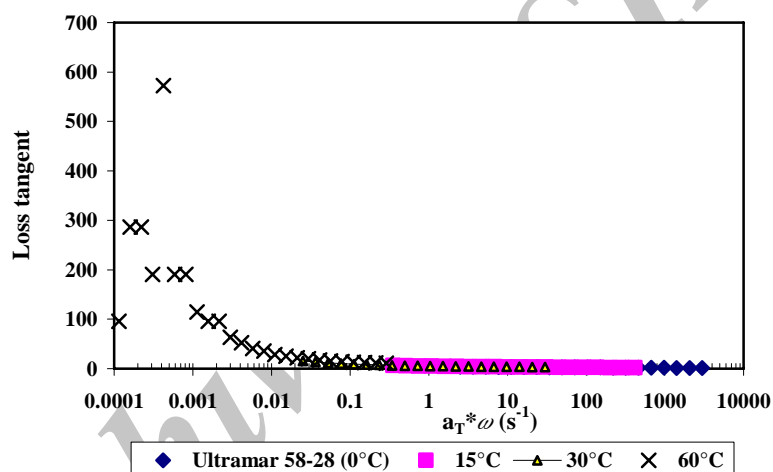


Figure 5.c: Master curves of loss tangent versus frequency for Ultramar 58-28 ($T_{ref}=30^{\circ}\text{C}$).

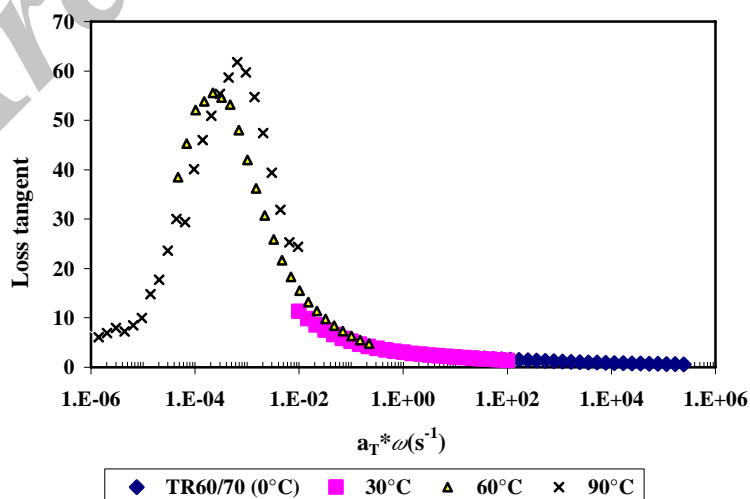


Figure 5.d: Master curves of loss tangent versus frequency for TR60/70 ($T_{ref}=30^{\circ}\text{C}$).

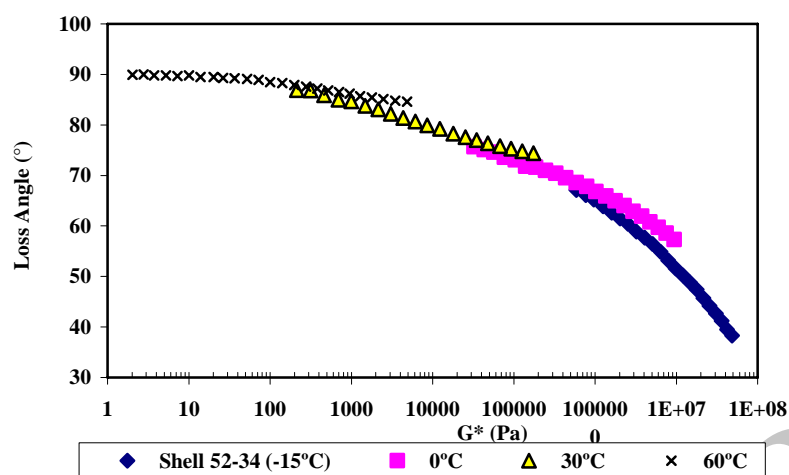


Figure 6.a: Loss angle versus G^* for Shell 52-34.

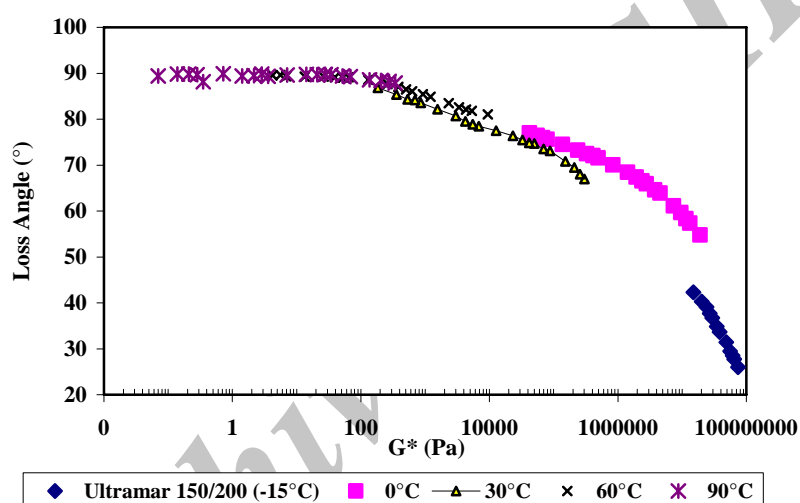


Figure 6.b: Loss angle versus G^* for Ultramar 150/200.

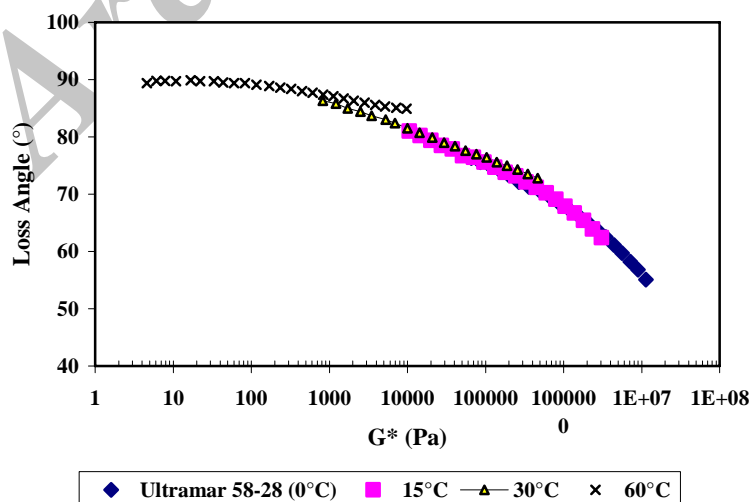


Figure 6.c: Loss angle versus G^* for Ultramar 58-28.

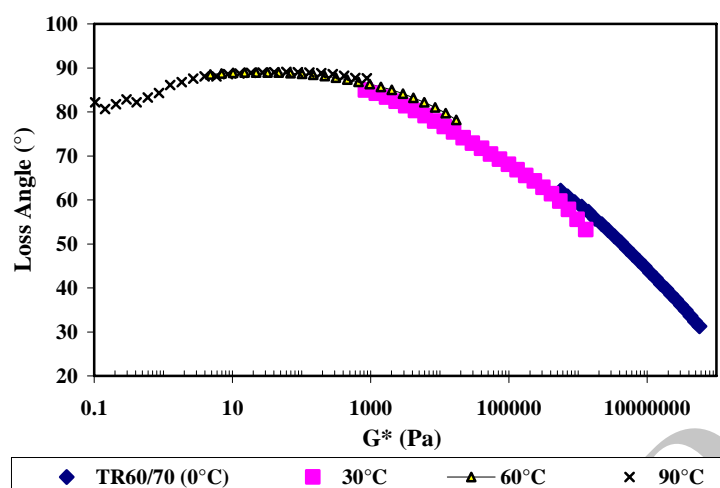


Figure 6.d: Loss angle versus G^* for TR60/70.

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