MODIFIED ASPHALT BINDERS EVALUATION USING RHEOLOGICAL MASTER CURVES AND BLACK DIAGRAMS

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Abstract- Modified bitumen is being increasingly used to enhance performance properties of asphalt mixtures. In this research, four types of modifiers are used to modify an Iranian PG58-22 (85/100 pen) base binder. Rheological master curves of |G*| and phase angle, and the Black diagrams were generated to investigate the rheological properties of these modified binders. Improvements in the high and low temperature properties and temperature susceptibility of the majority of the modified binders were observed. A qualitative comparison of all modified binders was made based on the shape of their master curves.

Index Terms- Modified Binder, Rheological Master Curve, Black Diagram, Complex Modulus, Phase Angle.

I. INTRODUCTION

There is an ever-increasing demand to carry heavier loads on the existing roadways. New axle design and tire configurations have made it possible for trucks to carry heavier hauls that exert higher stresses on pavements, leading to different kinds of pavement distress. Bitumen modification to improve the performance of binders and asphalt mixtures so they withstand the higher applied stresses, particularly in harsh environmental conditions, has been the focus of recent research.

There are several broad classes of binder modification methods; polymers (elastomers and plastomers), acids, hydrocarbons, fibers (natural and man-made), extenders, oxidants/antioxidants, and anti-stripping agents. Among these, polymers have been the most popular over the past two decades. Crumb rubber modifier (CRM) is another popular elastomeric polymer that is also a waste material and is regarded as a modifier that can lead to sustainable pavement. Polyphosphoric acids (PPA) modification has received attention in recent years, although concerns about it remain. The present research evaluated and compared the efficacy of different modifiers used with a neat PG 58-22 binder from Iran. The rheological characteristics of modified binders are dependent on the properties of the base binder. These characteristics are evaluated by studying their master curves in this research. Rheological master curves provide a fundamental understanding of the materials since they allow an estimation of mechanical properties over a wide range of temperature and loading times (or frequencies) experienced in the field, but not readily tested or simulated in the laboratory[1]. They also offer a full view of time-temperature performance of binders and provide a good tool to compare their performance with that of an ideal binder. The type of information that can be obtained from the master curves of binders and asphalt mixtures have received particular attention in recent years because they have been used to obtain input parameters for the new MEPDG pavement design software.

II. MATERIALS

Materials used in this research include an 85/100 binder and four types of modifiers mixed in different dosages to form the PMBs. Their properties and specifications are shown in Tables 1 and 2.

TABLE I. BITUMEN SPECIFICATIONS

Classic Tests			Performance Grading (true grades)		
Viscosity @ 135°C (mPa.s)	Penetr. @ 25°C (0.1mm)	Soften. point (°C)	High temp.	Inter. temp.	Low temp.
253	86	48	58 (61.6)	22 (20.9)	-22 (-25.2)

TABLE II. MODIFIERS SPECIFICATIONS AND MIXING CONDITIONS

Modifier	Spec.	Dosage	Mixer Type	Mixer Spd. (rpm)	Mix. Dur. (min)	Temp. (°C)
EVA	19% VA	6% & 10%	High Shear	5000	120	180
SBS	31% styrene -linear struc.	4% & 7%	High Shear	5000	120	180
Crumb Rubber	12% on #30 80% on #50	9% & 18%	High Shear	5000	60	180
PPA	85% of P2O5	0.5% & 2.5%	Low Shear	350	30	165

III. EXPERIMENTALS

In order to generate the master curves for the norm of complex modulus |G*|, two different tests were conducted. The first was the frequency sweep test using a dynamic shear rheometer. The second was the bending beam rheometer (BBR) test. The frequency sweep test was performed under a constant strain

mode at frequencies between 0.01 and 40 Hz and at temperatures between 5 and 88°C. For temperatures ranging from 5 to 40°C, 8 mm plate geometry was used and 25 mm plate geometry was used for temperatures of 40 to 88°C. The temperature of 40°C was chosen as the reference temperature for the generation of master curves. The G* data at other temperatures was obtained based on the time-temperature superposition principle (TTSP) [2]. Shifting process was carried out using US200/32 V2.3 software. The absolute value of complex modulus |G*| was selected as the key parameter for shifting.

BBR tests at temperatures of -12, -18, -24, and -30°C (or just three of them) were also conducted to obtain a wide range of low temperature creep stiffness modulus data in addition to the DSR data. The absolute value of the complex shear modulus was determined from the creep stiffness data from 8 to 240 sec of loading time using the following equation proposed by Marasteanu and Anderson [3]:

$$|G^*| = \frac{S(t)}{2(1+\mu)} \frac{\sin[(0.5m+0.5b)\pi]}{(0.5m+0.5b)\pi} \frac{1}{\cos[\arctg(m\pi/2)]} \quad (1)$$

where b comes from $log(S(t))=a+b[log(t)]+c[log(t)]^2$, and m is the slope of log(S(t)) over log(t) that can be calculated from $m=b+2\times c\ [log(t)]$ [4]. A constant value of 0.5 was used for μ. The shift factors determined for the *G** master curves were also used for the phase angle.

A secondary function was also used to estimate the phase angles from the BBR test results. This was a Kramers-Kronig equation as presented by Booij and Thoone [5]:

$$\delta(\omega) \cong 90 \times \frac{dlog(G^*(\omega))}{dlog\omega} \quad (2)$$

A second order polynomial fit is made of $|G^*(\omega)|$ and the slope of the curve is used to calculate the phase angle values. Notice that the Kramers-Kronig method is not a precise approach and the curves obtained from this method are used to present an initial estimate of the phase angle master curves in the same frequency range of |*G**| master curves. Therefore, in this region, analysis of the phase angle master curves was not performed.

IV. RESULTS

A. SBS Modification

The neat asphalt and SBS PMBs Black diagrams are shown in Fig. 1a. Black diagrams can be used to differentiate between thermorheologically simple and complex materials [6] The neat binder Black diagram in Fig. 1a shows a very smooth curve, which indicates time–temperature equivalency for this binder (thermorheologically simple). The return of the Black diagrams toward lower phase angles (marked with a dashed rectangle) for both PMBs shows breakdown of TTSP and presence of a high polymer modification for these binders (thermorheologically complex) [6]. Although the Black diagrams for both SBS PMBs in Fig. 1a are not unique, it is still possible to make smooth |G*|

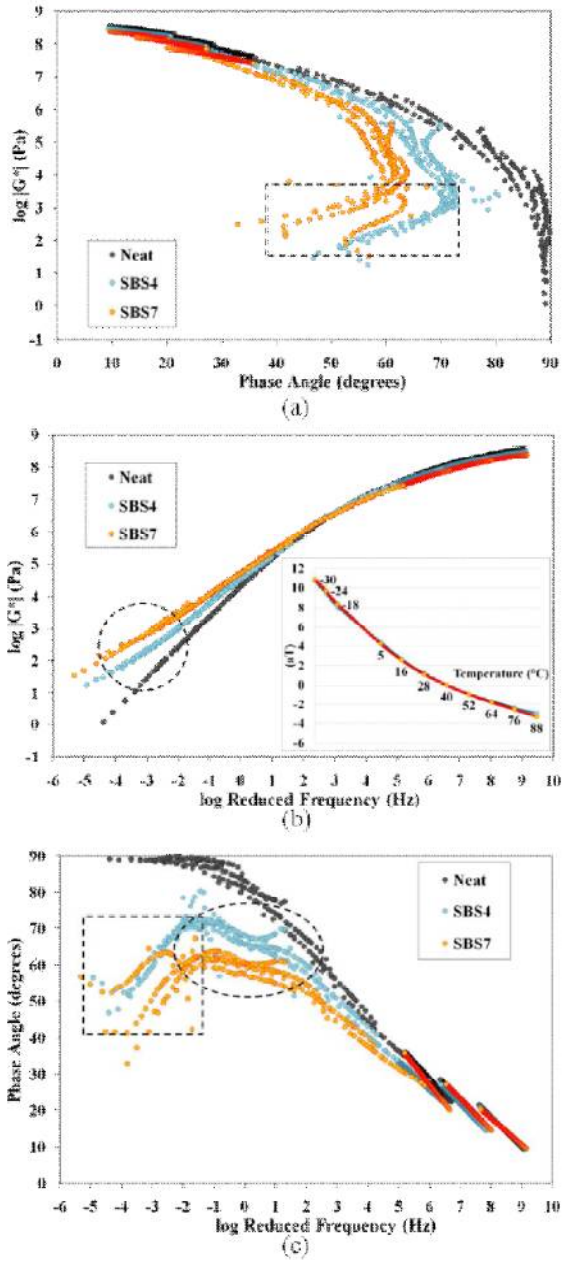


Figure 1. (a) Black diagrams, (b) |G*| master curves and (c) Phase angle master curves of neat and SBS modified binders.

master curves based on a partial time temperature superposition principle (PTTSP) [7] as shown in Fig. 1b.

The |G*| master curves for both PMBs show considerable increase in the low frequency (high temperature) range and some decrease in the high frequency (low temperature) range. The temperature susceptibility of the PMBs shows considerable improvement compared to the neat binder. The

increase in |G*| in the low frequency range is quite common in the polymer modification of binders. The slight decrease in the slope of the PMBs in the low frequency region (marked with a dashed circle) in Fig. 1a is attributed to molecular interaction, dispersion, swelling and compatibility of the neat binder and SBS as reported by other researchers [8, 9]. Where compatibility is good, the elastomeric part of SBS absorbs the aromatic oils or maltene fractions from the binder and swells [10]. This is a binder dependent behavior that cannot be found for all SBS PMBs in the literature [8, 9, 11]. The binder used in this research had high aromaticity (44.6% wt. of naphtenearomatics and 33.6% wt. of polar aromatics) and enjoyed good polymer compatibility which resulted in a strong polymer-rich network in the low frequency and high temperature range of the master curve. The formation of an elastic polymer-rich network is also dependent on the polymer content [10, 12, 13]. In the present research, it appeared that, for both 4% and 7% modification, strong polymer networks were formed.

The phase angle master curve in Fig. 1c shows a reduction in the phase angle in the entire frequency region. This reduction means there was more elastic behavior for the SBS modified binders than the neat binder. This reduction led to formation of a plateau in the intermediate frequency range (marked with a dashed ellipse) of the phase angle master curves, especially for a high level of modification, and a sudden decrease in the phase angle accompanied by a reverse slope in the low frequency range (marked with a dashed square). The plateau in the phase angle master curve (marked with a dashed ellipse) arises either from physical cross-linking of polystyrene blocks or because of entanglements in the modified binder [8, 14]. The considerable reduction of phase angle (marked with a dashed square) is also a result of the described mentioned polymer swelling and polymer-rich elastic network [8, 9].

B. EVAModification

EVA is a plastomer that improves the physical properties of the binder through formation of a tough, rigid three-dimensional network that is plastomer-specific [15]. The Black diagrams, |G*| isotherms, |G*| master curves and phase angle master curves of the neat binder and 6% and 10% EVA modified binders are shown in Fig. 2. The PMB Black diagrams in Fig. 2a show thermorheologically complex behavior as seen for the SBS PMBs. Shifting of the rheological data toward a lower phase angle in the |G*| middle range (marked with a dashed rectangle) and a completely separate two-phase data set as a result of a structural change or a bitumen phase transition [6] is clear in the figure.

The |G*| isotherms diagram in Fig. 2b shows that the isotherms at 64°C and lower have different slopes from isotherms at 76°C and 88°C. As a result, the shape of the master curves for the EVA modified binders is somewhat different from that of neat asphalt in Fig. 2c. This is clear in the low frequency range (the circled area of Fig. 2c) that a break in the slope exists. For temperatures greater than the breaking point temperature (or lower frequencies), a constant slope of isotherms can be seen. At temperatures lower than the breaking point temperature (or higher frequencies), branching of the curve is more pronounced. It has been postulated that the main reason behind this phenomenon is melting of semi-crystalline EVA copolymers at temperatures in this range [15, 16].

In the phase angle diagram, a broken up plateau region can be seen at the phase angles of 30 to 50°C for both modified binders (marked with a dashed rectangle). This shows reduced temperature susceptibility of the binders

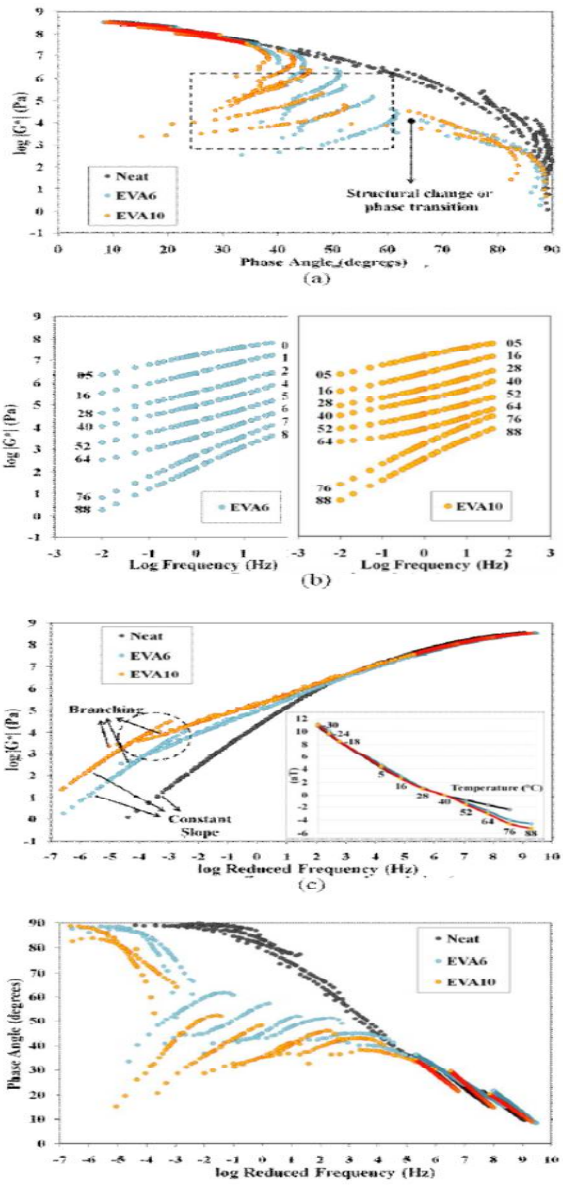


Figure 2. (a) Black diagram, (b) |G*| isotherms, (c) |G*| master curves and (d) Phase angle master curves of neat and EVA modified binders.

and may be indicative of a more rubber-like behavior of the PMBs. The presence of a wide plateau has been contributed to better compatibility between the neat binder and the polymer [17]. The discontinuous shape of the isotherms resembles a series of waves. Researchers have attributed this discontinuity to the presence of crystalline structures at different temperatures within the EVA PMBs [15]. Differential scanning calorimetric (DSC) measurements on the EVA copolymer (Fig. 3a) and EVA PMBs (Fig. 3b) were carried out to precisely investigate this behavior. The DSC on the EVA copolymer was performed using a Netzsch 200 F3 on an 11.59 mg EVA sample sealed in an aluminum pan and purged with nitrogen. Three consecutive scans were made in accordance with ASTM D3418 at a heating rate of 10°C/min at -30 to 150°C, 150 to -30°C and again at -30 to 150°C to acquire the transition temperatures. As shown in Fig. 3a, the first DSC run exhibited two endothermic peaks, which is a common EVA signature [18-21]. The first small endothermic peak occurred at about 59°C, is attributed to the melting of the smaller imperfect crystallite structures. The second endothermic peak, at about 89°C, is attributed to the melting of larger and more regularly formed structures [18, 19]. The melting point of EVA, as extracted from the second endothermic run, is 88.5°C, which is very close to the first run value.

DSC measurements on the neat and EVA modified binders were performed using a DSC8000 PerkinElmer device. A first endothermic run, a quench cooling and a second endothermic run were carried out. The first endothermic run is shown in Fig. 3b. Small peaks in the DSC results of the EVA PMBs represent the melting of crystalline structures in the PMBs. The melting temperatures for the EVA PMBs is 72°C for EVA6 (74°C for the second run) and 74°C for EVA10 (75°C for the second run). It is believed that the polymer content does not change the melting temperature significantly[22], so the small differences in the results were likely measuring and testing errors. The melting temperature for the PMBs (about 74°C) is less than that of pure EVA polymer (89°C). This is a result of the swelling effect of bitumen on EVA. During swelling, bitumen disrupts the crystalline component of the polymer and yields crystallites with a distribution of smaller sizes [22] leading to a decrease in melting temperature. The PMB melting temperature agrees with the temperature corresponding to the change of slope in the |G*| isotherms (between 64°C and 76°C).

It was noticed that the polymer-type modification of the EVA PMBs at temperatures below the melting point shifted to a simple filler-type modification at higher temperatures [15] with less impact on binder properties. This phenomenon depends on the asphalt binder [15] and the type of EVA [16, 23].

C. PPAModification

PPA has been employed to catalyze the air blowing process and used as an independent modifier without the need for air blowing to achieve the desired binder grades [24, 25].

The Black diagram and master curves of the neat and PPA modified binders are shown in Fig. 4. The Black diagram for 0.5% PPA is slightly different from that of the neat binder, whereas the 2.5% PPA modification

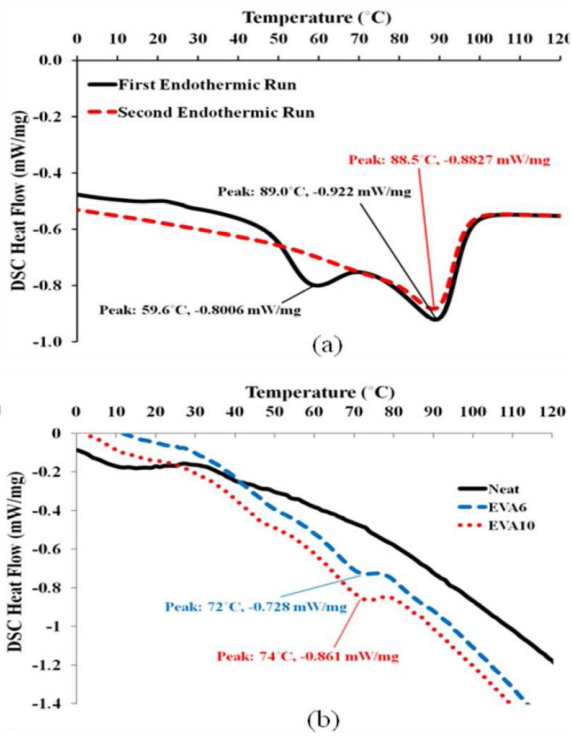


Figure 3. (a) DSC results of EVA copolymer in two different runs (b) DSC results of neat, 6% EVA and 10% EVA modified binders.

shows a distinctly different behavior. This difference stems from the formation of different colloidal structures within the binders [26]. The reduced length of the curve for 2.5% PPA indicates that very small changes occurred across all testing temperatures. This indicates the lower temperature susceptibility of PMB compared to the neat binder.

The phase angle master curve of the 2.5% PPA in Fig. 4c shows a flat region for a wide range of intermediate frequencies. It appears that each isotherm was independent of frequency changes and small vertical shifts occurred from one isotherm to the other at the intermediate frequency range (marked with a dashed rectangle). This type of behavior shows the transformation of binder properties from sol-like at high temperature to gel-like at intermediate temperatures [26]. Conversion of aromatics to resins and resins to asphaltenes takes place during PPA modification, leading to an increased asphaltene content [27, 28] or asphaltene swelling of the PMBs and a corresponding decrease in the resin fraction

[29]. This effect is comparable to a mild oxidationor blowing process that increases the peptized material and decreases peptizing material with a shift toward a gel structure [28].

D. CRModification

The Black diagrams, |G*| and phase angle master curves of crumb rubber modified benders are shown in Fig. 5. The viscoelastic response of CR modified binders depends on the asphalt source, CR production process, particle size and content as well as the mixing conditions [30-33]. The Black diagram for 9% CR in Fig. 6a shows

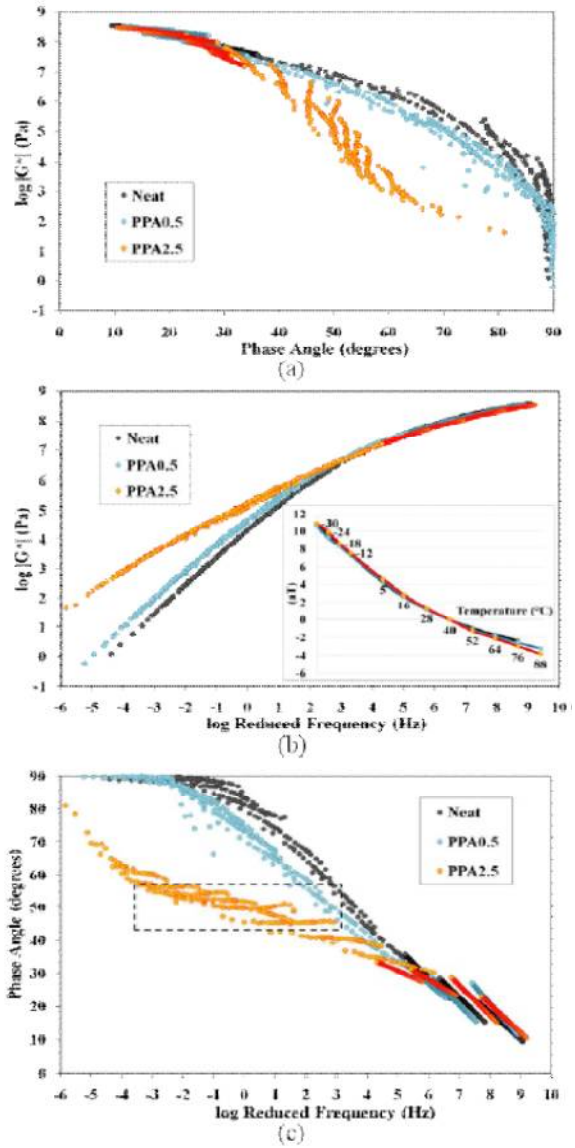


Figure 4. (a) Black diagrams, (b) |G*| master curves and (c) Phase angle master curves of neat and PPA modified binders.

no complexity, but the 18% curve shows a characteristic plateau region at phase angle values of about 55 degrees (marked with a dashed rectangle), corresponding to the partly elastomeric behavior of PMB. A return of the phase angle to lower values can also be seen (marked with a dashed circle). This is caused by the swelling of the CR particles after absorbing components of the bitumen, as occurred for the SBS PMBs. It appears that 9% CR content is not sufficient to cause a noticeable change in the neat binder, while the addition of18%CR to the neat binder (with high aromaticity) significantly influenced its behavior.

The plateau in the intermediate frequency region of Fig. 5c for 18% CR (marked with a dashed ellipse) is in accordance with the observations of other researchers [30, 31]. This plateau was caused by entanglement in the network of the 18% CR. The end reduction of the phase angle (marked with a dashed square) was also as a result of the swelling of CR particles at very high temperatures. The last phenomenon was not observed for 9% CR binder, but the plateau formation is about to take place.

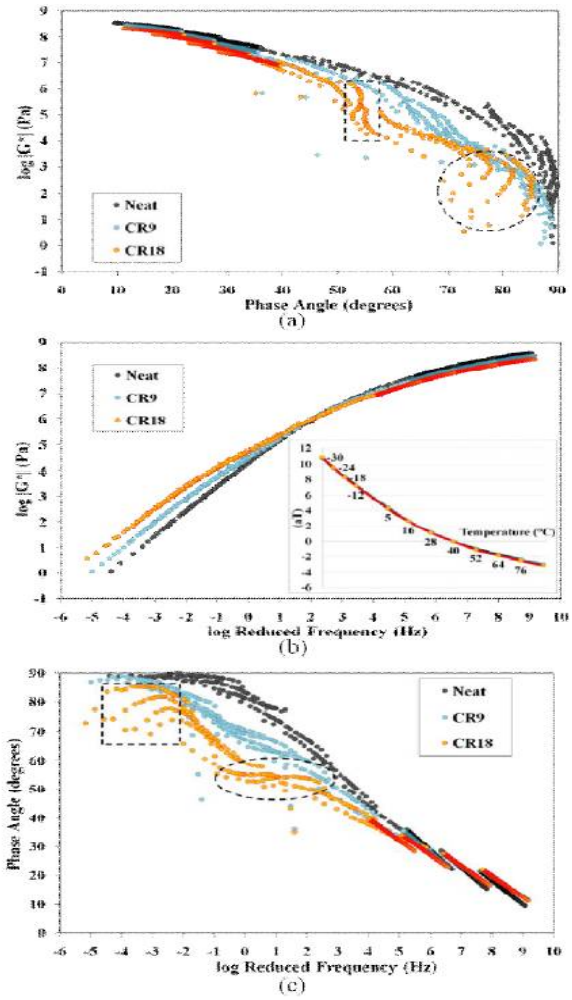


Figure 5. (a) Black diagrams, (b) |G*| master curves and (c) Phase angle master curves of neat and CR modified binders.

CONCLUSIONS

In this research, a PG58-22 Iranian neat binder was modified with two different dosages of four types of modifiers. Based on evaluations of the rheological properties of the unaged modified binders, their

master curves and Black diagrams, it can be concluded that good compatibility between the neat binder and all tested modifiers exists, and the modified binders possess lower temperature susceptibility compared to the neat binder. Table 3 summarizes the rheological interpretation of modified binders, and their performance evaluation based on a visual comparison of the master curves. As can be seen in this table CR18 and SBS7 has shown the best performance improvements in all three temperature ranges. EVA and PPA could not improve the low temperature properties of the binder at none of the selected dosages while the high temperature properties of all modified binders have shown more or less some improvements. It can be concluded that among the modified binders with similar high temperature properties SBS and CR can be selected as the best because of their low temperature advantages.

TABLE III. RHEOLOGICAL FEATURES AND EXPECTED PERFORMANCE OF ALL PMBS.

Binder	Rheological interpretation	High Temp.	Inter. Temp.	Low Temp.
SBS4	polymer swelling, physical cross-linking of polystyrene blocks, entanglements	+	+	+
SBS7		++	++	++
EVA6	presence of different crystalline structures at different temperatures, melting of EVA copolymers	++	x	-
EVA10		++	x	-
PPA0.5	No major rheological specialty	+	x	-
PPA2.5	transition from sol-like to gel-like behavior	++	x	-
CR9	No major rheological specialty	+	x	+
CR18	polymer swelling, physical cross-linking, entanglements	++	++	++
(-) No major changes (+) Slight improvement (++) Considerable improvement (x) No comment				

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