Analyzing Behavior of Polymer Modified Asphalt Using Master Curve Approach

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ABSTRACT

In Pakistan, asphalt pavements are experiencing a high rate of deterioration due to rutting and fatigue cracking. These problems arise in asphalt pavements due to the use of improper binder characterization and mix design. It is believed that polymer modification can be employed to improve binder ductility and durability. Therefore, the objective of this study is to analyze the behavior of virgin and polymer modified asphalt at a range of temperature and rate of loading. Two virgin and seven polymer modified asphalt (PMA) samples were tested using Dynamic Shear Rheometer. Master curves were developed for complex shear modulus by applying a shift factor to log of time at each temperature to the reference temperature. The major finding is that a decrease in the temperature susceptibility was observed for PMA samples; that is relatively lower stiffness at lower temperature and relatively higher stiffness at higher temperature. These polymer modification results are beneficial in improving the performance of flexible pavements.

KEYWORDS: Polymer modified asphalt, Viscosity temperature susceptibility, Master curve, Rutting, Fatigue cracking.

INTRODUCTION

Background

Rutting is a major reason of premature deterioration of asphalt pavements in warm climatic regions of Pakistan; whereas fatigue and thermal cracking is a common problem in cold regions. These problems arise in asphalt pavements due to improper mix design and lack of asphalt characterization. The average maximum temperatures lie in the range of 45 to 50 °C like in the areas of Sehwan, Sibbi, Jacobabad,… etc.; whereas the average minimum temperatures range from -10 to -15 °C in the northern part of Pakistan like in the areas of Narran, Kalam,… etc. (Mirza et al., 2011). At present in Pakistan, the asphalt binder's specifications are typically based on measurements of penetration and ductility tests. These measurements are not sufficient to completely describe viscous and elastic properties that are needed to define the performance of pavements (Javid and Rahim, 2011). It is well known that early failure of asphalt pavement, such as rutting (permanent deformation) usually results from inadequate initial mixture properties, while later-term failure can be the result of significant changes to the pavement due to fatigue (Abojaradeh 2013) and oxidative aging of the asphalt binder. Moreover, the increase in loading frequency tends to increase fatigue life (the number of cycles to fatigue failure) of asphalt concrete pavements (Al-Khateeb and Ghuzlan, 2014). Low temperature thermal cracking is mainly caused due to drop in the temperature of pavement layers to some critical temperature (Roberts et al., 1996). In order to reduce

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the deterioration and cracking of pavements that result in huge maintenance expenditures, efforts have been made to improve the properties of asphalt binders with regard to increased resistance to high-temperature rutting, fatigue and low-temperature thermal cracking. Polymer modified asphalt (PMA), which is the blending and interaction of polymers in a base asphalt binder, has been used with increasing frequency for the construction of pavements, primarily due to its ability to stiffen the binder at high temperatures, but without stiffening it at low temperatures, resulting in reduced permanent deformation without harming thermal cracking. In addition, it was found that polymer modifiers in some cases were able to decrease the deleterious impact of binder oxidative aging and thereby result in more durable pavements (Ruan et al., 2003a, b, c; Leicht et al., 2001). Polymer modification has been increasingly employed in asphalt concrete, primarily for control of short-term permanent deformation (Lu and Isacsson, 1999; Bouldin and Collins, 1992). Polymer modification typically improves binder ductility, thereby providing a binder that is more durable to pavement stress and deformation (Bahia et al., 2001). By adding polymer to conventional asphalt, the superpave performance grade span (low temperature grade plus high temperature grade, e.g. PG 64-22 span is 86) can be increased by increasing the upper grade without harming the lower grade significantly. Moreover, there is evidence that polymer modifiers may improve the aging characteristics of a binder so that the deleterious impact of oxidative aging is delayed, leading to a more durable pavement (Glover et al., 2005).

Time-Temperature Superposition and Master Curve

Many researchers have used time temperature superposition approach to develop a master curve for characterizing asphalt binder and asphalt concrete mixtures (Rowe et al., 2008; Rowe and Sharrock 2000; Al-Khateeb et al., 2006). Master curves are constructed using the principle of time-temperature superposition as shown in Figure 1. The data at various temperatures should be shifted with respect to log of time until the curves merge into a single smooth function. The resulting master curve of the modulus, as a function of time, formed in this manner describes the time dependency of the material. The amount of shift required at each temperature to form the master curve describes the temperature dependency of the material (Rowe et al., 2008). Due to the importance of this method and its application in this research, a review of the method is given below. Theoretical and experimental results indicate that for an asphalt binder, the effect due to temperature and time can be combined into a single parameter. This can be obtained through the concept of time-temperature superposition principle which implies the following equation:

$$G(T,t)=G(T_0,\varsigma) \tag{1}$$

where '*t*' is the actual time of observation measured from first application of load, T is the actual temperature, T_0 is the reference temperature, and ζ is reduced time which is related to the real time t by a temperature shift factor a (T).

According to time temperature superposition principle, the effect of temperature on the time dependent material behavior is equivalent to stretching or shrinking of the real time for temperature above or below the reference temperature. In other words, the behavior of the material at high temperature is equivalent to low temperature with reduced time. There are various mathematical forms of master curve functions developed by different researchers. The master curve within the MEPDG (Mechanistic Empirical Pavement Design Guide) is of a standard sigmoid form which is referenced as Witczak's (symmetrical or standard logistic) Sigmoid, as follows in Equation 2 (Witczak and Pellinen, 2000).

$$Log\left|G^*\right| = \delta + \frac{\alpha}{1+e^{\beta+\gamma(\log t_r)}} \tag{2}$$

An alternate sigmoid function that can be used is the Richard's (non-symmetrical or generalized logistic) Sigmoid function as follows in Equation 3 (Row et al., 2009). The principle advantage of Richard's function over the standard logistic is that greater flexibility exists in fitting non-symmetrical master curve data. The non-symmetrical behavior is evidenced by an inflation point that is not half the distance between the maximum and minimum dynamic complex modulus (Row et al., 2009).

$$Log|G^*| = \delta + \frac{\alpha}{\left[1+\lambda e^{\beta+\gamma(\log t_r)}\right]^{\frac{1}{\lambda}}} \tag{3}$$

where $|G^*|$ is the dynamic complex modulus (KPa), δ is the lower asymptote limit for $|G^*|$ at long loading times and high temperatures, α describes upper asymptote, $(\delta+\alpha)$ gives limit for $|G^*|$ at short loading times and low temperatures, t_r is reduced time (sec); β, γ, λ are curve fitting parameters. It is well known that the ratio between the original time (t) and the shifted time (t') is mainly a function of temperature for many polymeric materials, and is called a time-temperature shift factor. The distance of the shift is referred to as the time–temperature superposition shift factor. The time–temperature shift factor is described in terms of the activation energy (E_a) as expressed in Equation 4.

$$Loga(T) = \frac{\Delta E_a}{\mathbf{19.14}\left[\frac{\mathbf{1}}{T} - \frac{\mathbf{1}}{T_r}\right]} \tag{4}$$

where $a(T)$ is the shift factor in time at temperature T, T_r is the reference temperature (^{0}K) for time-temperature superposition, T is the test temperature (^{0}K) *and* ΔE_a is the activation energy.

Objective and Outline of the Paper

The objective of this paper is to determine the principal characteristics of polymer-modified asphalts and available virgin asphalts typically used in Pakistan for asphalt pavement construction. In addition, this research is conducted to determine the optimum content of polymer for polymer modification. The polymer modified asphalt can use to control rutting in warmer regions of Pakistan as well as to control fatigue and low temperature cracking in cold regions. Master curve development technique has been used to evaluate the rheological behavior of virgin and polymer modified asphalt. One polymer modified asphalt sample was obtained from the Attock oil refinery, and six polymer modified asphalt samples were prepared in the laboratory by blending two virgin grades with three values of polymer as presented in Table 1. All asphalt samples were tested using Dynamic Shear Rheometer (DSR) setup. This paper is organized in the following manner; the next section describes the details of materials and experimental setup, then results and analysis are reported. Last section elaborates main findings and research implications.

Table 1. Test Samples

Sr. #	Samples	PG-grade [a]
1	Attock 60/70	PG 58-12
2	Attock 60/70PMA (prepared @1.35% of polymer in Attock oil refinery)	PG 76-06
3	Attock 60/70+1.35% Elvaloy® RET (Laboratory)	PG 64-12
4	Attock 60/70+1.7% Elvaloy® RET (Laboratory)	PG 70-12
5	Attock 60/70+2.0% Elvaloy® RET (Laboratory)	PG 70-12
6	Attock 80/100	PG 58-12
7	Attock 80/100+1.35% Elvaloy® RET (Laboratory)	PG 64-12
8	Attock 80/100+1.7% Elvaloy® RET (Laboratory)	PG 70-12
9	Attock 80/100+2.0% Elvaloy® RET (Laboratory)	PG 70-12

Note: [a]Mirza *et al.* (2011).

Experimental Setup

Material Collection and Preparation

This comprehensive research includes laboratory testing to study the effect of polymer modification on the rheological properties of asphalt. For this objective, two virgin asphalt samples and one PMA (polymer-modified asphalt) obtained from Attock oil refinery and then six polymer modified asphalt (PMA) samples were prepared in the laboratory by using standard procedure of modification. Virgin asphalt samples selected for investigation cover a wide range of practical usage for pavement construction that serves in hot and cold climates of Pakistan. These asphalts include three grades of Attock Oil Refinery that are 60/70, 60/70P (polymer modified asphalt prepared in Attock Oil Refinery @ 1.35% of polymer) and 80/100. PMA samples were prepared in the laboratory by blending 1.35%, 1.7% and 2 % of Elvaloy® RET polymer with 2 virgin grades of Attock oil refinery; i.e. 60/70 and 80/100 as presented in Table 1. The performance grades (PG) of all samples are also given in Table 1 (Mirza et al., 2011). These nine samples were tested in the laboratory using dynamic shear rheometer (DSR) to examine complex shear modulus and phase angle.

Preparation of Polymer Modified Asphalt

Sufficient amount of virgin asphalt (700 to 800 grams) was taken. This quantity of asphalt samples was decided so that the sample is enough to perform different tests on it. Asphalt sample was heated in an oven at a temperature of 165 °C for about twenty minutes so that it can easily be worked. Then, this sample was placed on a hot plate at 165 °C and the blades of the stirrer were dipped into the sample up to the middle of its depth. The mechanical stirrer was rotated at 100 rpm for about twenty minutes so that the temperature of the sample becomes uniform. Then, the required amount (1.35%, 1.7% and 2% of asphalt sample) of Elvaloy® RET polymer was taken and added, at a very slow rate, into the virgin asphalt with the continuous mixing at a speed of 120 rpm. It was insured that there should not be any formation of clogs while adding the polymer into the asphalt. After the addition of whole polymer, the asphalt was kept on agitating for further half an hour to insure the proper mixing of polymer. While the mixing of asphalt at 165°C was continuous, 1.4 gram of Super Phosphoric Acid (SPA) was added into the asphalt as a catalyst. After the addition of SPA, the viscosity was measured at 165 °C while the mixing was continuous. Another reading of viscosity was taken after 30 minutes and this process remained continuous until the viscosity became constant. After that, the asphalt sample was kept for two hours in the oven for curing.

Equipment and Testing Setup

All the asphalt samples were investigated in the laboratory by using Dynamic Shear Rheometer apparatus. In DSR test operation, the asphalt sample was sandwiched between two parallel plates, one of which is fixed and the other one is moveable (SUPERPAVE Asphalt Mixture Design Lecture Notes, 1994). The tests were conducted on each asphalt sample at 46, 52, 58, 64, 70, 76 and 82 °C by using a 25 mm diameter plate with 1 mm gap at a frequency range of 1 to 100 radian/sec and at 7, 13, 19, 25, 31 and 37 °C by using an 8 mm diameter plate with 2 mm gap at a frequency range of 0.1 to 100 radian/sec (AASHTO TP5[1], 1994).

RESULTS AND ANALYSIS

Testing Results

The complex shear modulus (G^*) and phase angle (δ) were obtained by testing all virgin and polymer modified samples in the laboratory using dynamic shear rheometer. The results of complex shear modulus for one sample are presented in Fig. 1. These results show that the value of complex shear modulus decreases with the increase of temperature which is obvious. Similarly, the complex shear modulus decreases with the increase of loading time. These results are true for all asphalt samples including polymer modified asphalt (PMA).

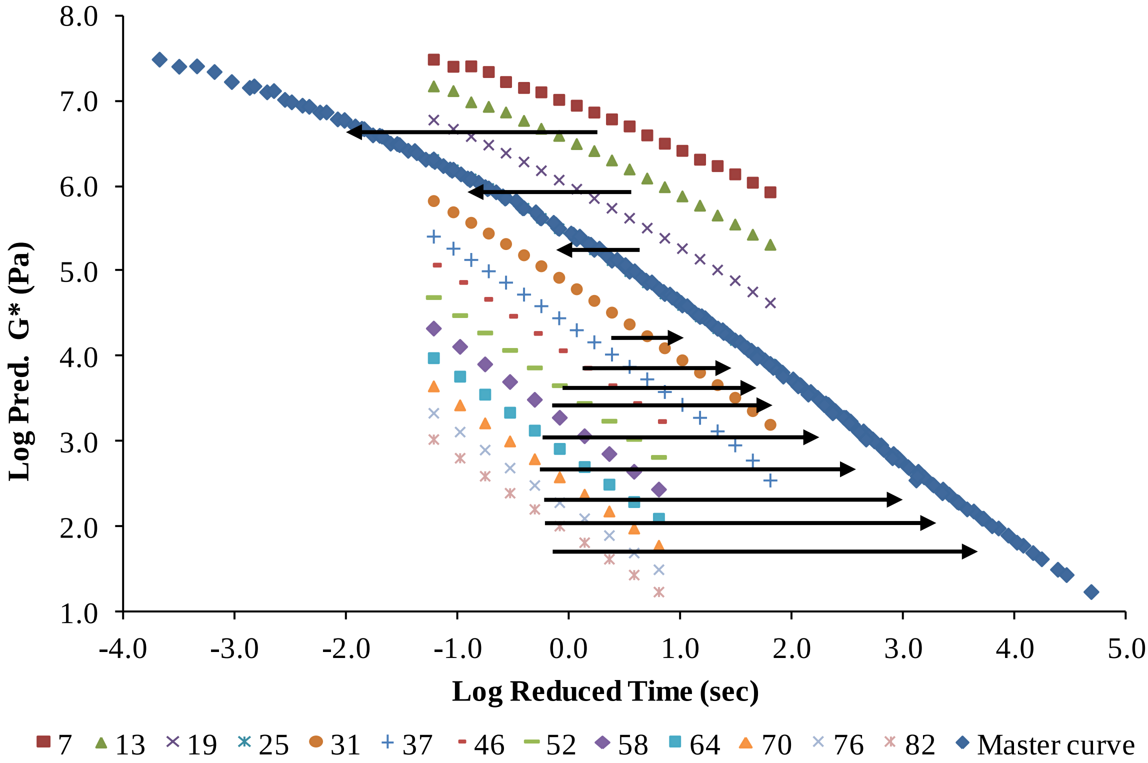

Figure (1): Master curve construction in reduced time format at a reference temperature of 25 °C

Table 2. Witczak Parameters for Dynamic Modulus Master Curve Computed Using Excel and Solver

Asphalt type	δ	α	β	γ	ΔE
60/70	-2.60643	11.23024	-0.93091	0.340088	209.5
60/70PMA	-0.82175	9.952026	-0.91462	0.320596	246.4
60/70+1.35%Polymer	-2.17496	12.03413	-0.56939	0.254389	213.7
60/70+1.70%Polymer	-1.6926	12.22744	-0.45255	0.238885	231.7
60/70+2.0%Polymer	-0.53011	10.41951	-0.45068	0.283281	239.8
80/100	-2.48201	11.00814	-0.82383	0.342291	200.4
80/100+1.35%Polymer	-1.42975	11.41557	-0.45582	0.267462	228.3
80/100+1.70%Polymer	-0.8348	10.96434	-0.31341	0.262301	222.4
80/100+2.0%Polymer	-0.71129	10.99759	-0.31866	0.256589	246.4

Master Curve Development

In order to develop a master curve by using time temperature superposition, first data is collected over a range of temperature and frequency (time). Complex shear modulus values measured at various temperatures are plotted as the logarithm of the modulus *vs.* the log of time. A reference temperature of 25 °C is selected considering average pavement temperature in Pakistan and a horizontal shift is applied to the data at all temperatures to develop a master curve. Figure 1 shows the master curve development procedure by applying a shift factor to time at a given temperature to the reference temperature. The shifting may also be done for the other visco-elastic parameter δ. Excel-Solver analysis was used to obtain a master curve that fits Witczak sigmoid function. The Witczak sigmoid function parameters and activation energy were calculated for all asphalt samples by following the same procedure. The parameters of Richard's sigmoid function were also calculated and compared with Witczak parameter values. The values of parameters for both models are presented in Table 2 and Table 3, respectively.

Table 3. Richard's Parameters for Dynamic Modulus Master Curve Computed Using Excel and Solver

Asphalt type	δ	α	β	γ	λ
60/70	0.231091	8.813365	-0.70456	0.263866	-0.22597
60/70PMA	1.218227	8.440313	-0.71269	0.238121	-0.16686
60/70+1.35%Polymer	-0.83764	11.91334	-0.46682	0.173837	-0.01583
60/70+1.70%Polymer	-0.29886	11.96677	-0.36635	0.171473	0.068731
60/70+2.0%Polymer	0.438547	10.4084	-0.38341	0.202276	0.109217
80/100	0.243786	8.746618	-0.62146	0.261348	-0.23306
80/100+1.35%Polymer	-0.3299	11.10296	-0.39674	0.203409	0.178556
80/100+1.70%Polymer	-0.01553	10.95814	-0.27756	0.202104	0.281487
80/100+2.0%Polymer	-0.00015	11.00204	-0.28549	0.204137	0.358297

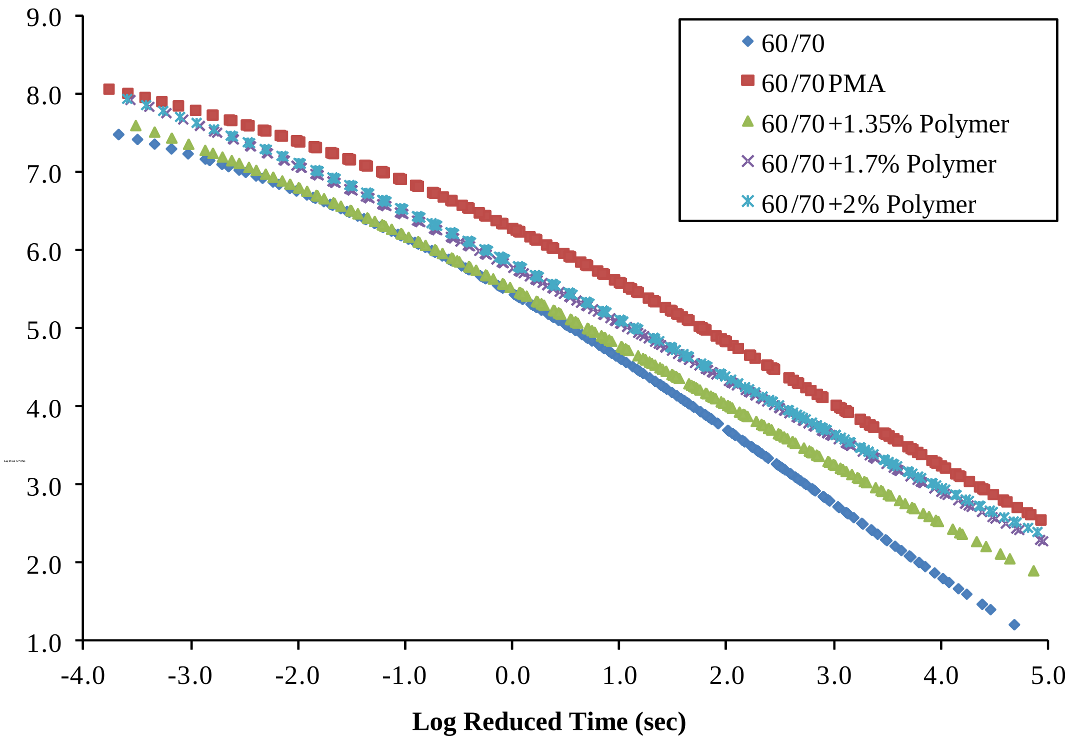

Figure (2): Master curves for Attock 60/70 and its PMA samples using Witczak sigmoid function

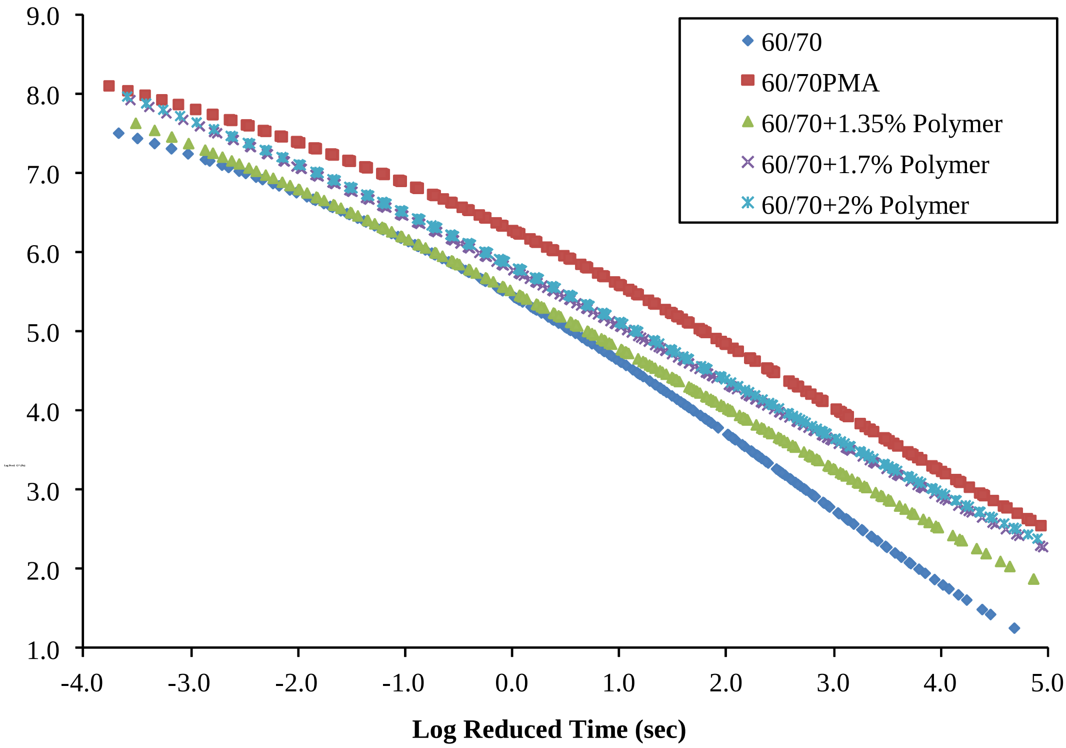

Figure (3): Master curves for Attock 60/70 and its PMA samples using Richard's sigmoid function

DISCUSSION

The master curves for Attock 60/70 and its laboratory polymer modified samples are presented in Figures 2 and 3. The results show that with the addition of polymer at 1.35%, there is a slight increase in complex shear modulus for smaller loading time, whereas resistance to deformation (G*) increases rapidly with the increase of loading time. This change in asphalt properties with polymer modification makes asphalt more suitable in controlling rutting in flexible pavements. The complex shear modulus increases enormously at 1.7% of polymer content. However, complex shear modulus increases a little with further increase of polymer content; i.e. 2%. It can be said that a regression curve among master curves of three selected polymer values would give optimum content of polymer for modification. The master curve of Attock 60/70P almost lies parallel to Attock 60/70, which shows that the addition of polymer only hardened the asphalt with no decrease in viscosity temperature susceptibility. In case of laboratory PMB samples, there is reasonable reduction in viscosity temperature susceptibility, which can be observed from the change of trend of the master curve. This makes laboratory PMBs more suitable to control rutting at higher temperatures and fatigue cracking at lower temperatures. Similarly, there is enormous increase in resistance to deformation or complex shear modulus with the addition of polymer for Attock 80/100 PMB samples both at lower and higher loading rates as shown in Figures 4 and 5. This depicts that polymer modified asphalt prepared in the laboratory can be used in extreme climatic conditions to control rutting and fatigue cracking. In addition, it can be said that the optimum polymer content for modification again lies among the mentioned three values of polymer; i.e. 1.35%, 1.7% and 2%. The values of activation energy also show that there is a significant change in visco-elastic behavior of asphalt due to polymer modification as the amount of activation energy increases with the increase of polymer content. The values of Witczak model parameters are presented in Table 2 and Richard's model parameters in Table 3. The master curves developed using Richard's curve fitting explain the rheological behavior in a better way of virgin and polymer modified asphalt. The predicted values of *G** with Richard's sigmoid fitting model are slightly higher than those predicted using Witczak sigmoid model. The master curves of predicted *G** for both models are given in Figures 2-5.

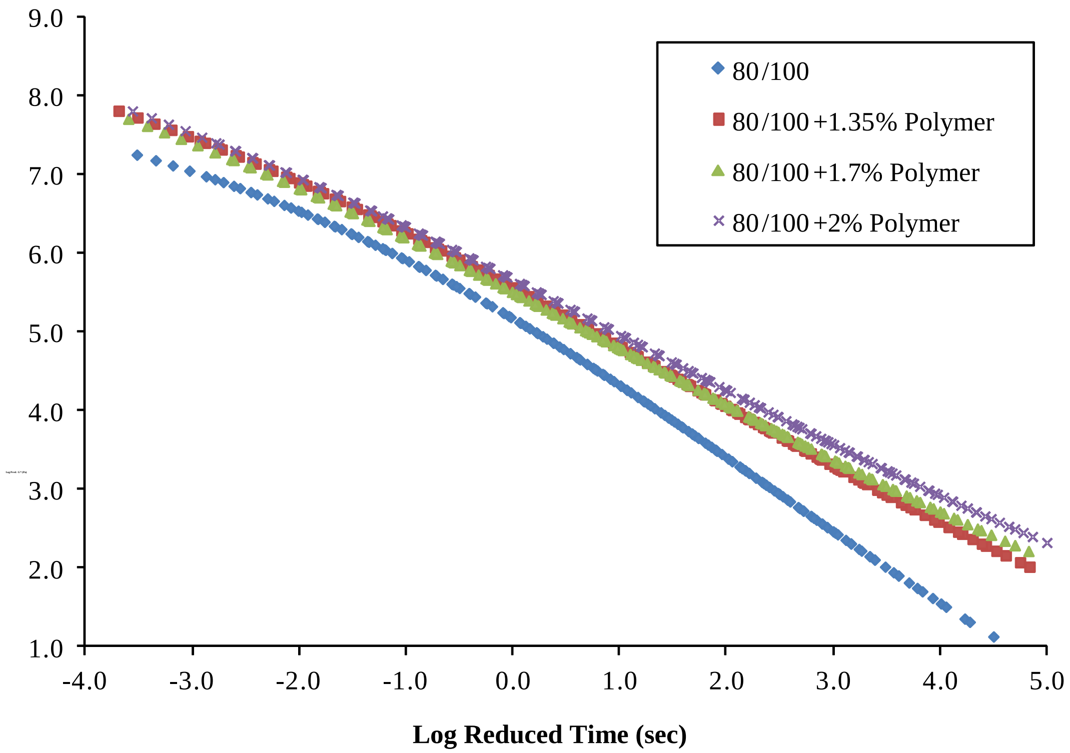

Figure (4): Master curves for Attock 80/100 and its PMA samples using Witczak sigmoid function

CONCLUSIONS

This comprehensive study comprises an investigation of the behavior of virgin and polymer modified asphalt through master curve development techniques. Virgin and polymer modified asphalt samples were tested using dynamic shear rheometer. The modification results reveal that the optimum polymer content for modification lies between 1.7% and 2.0% for both grades of Attock; i.e. 60/70 and 80/100, because there is only a slight change in properties of asphalt with the addition of polymer after 1.7%. The analysis results also depict that polymer modification is significantly effective in enhancing the elastic and resistance properties of asphalt binder. It can be argued that developed polymer modified asphalt samples can be utilized for control of rutting in warmer regions and fatigue cracking in colder regions in flexible pavements. The results of master curve development showed a decrease in the temperature susceptibility for PMA samples; that is relatively lower stiffness at cooler temperatures and relatively higher stiffness at warmer temperatures. This makes asphalt binder suitable to use in extreme climatic conditions. However, additional testing is required to confirm short and long term aging behavior of polymer modified asphalt. In addition, bending beam rheometer tests need to be conducted in order to evaluate the behavior against low temperature cracking.

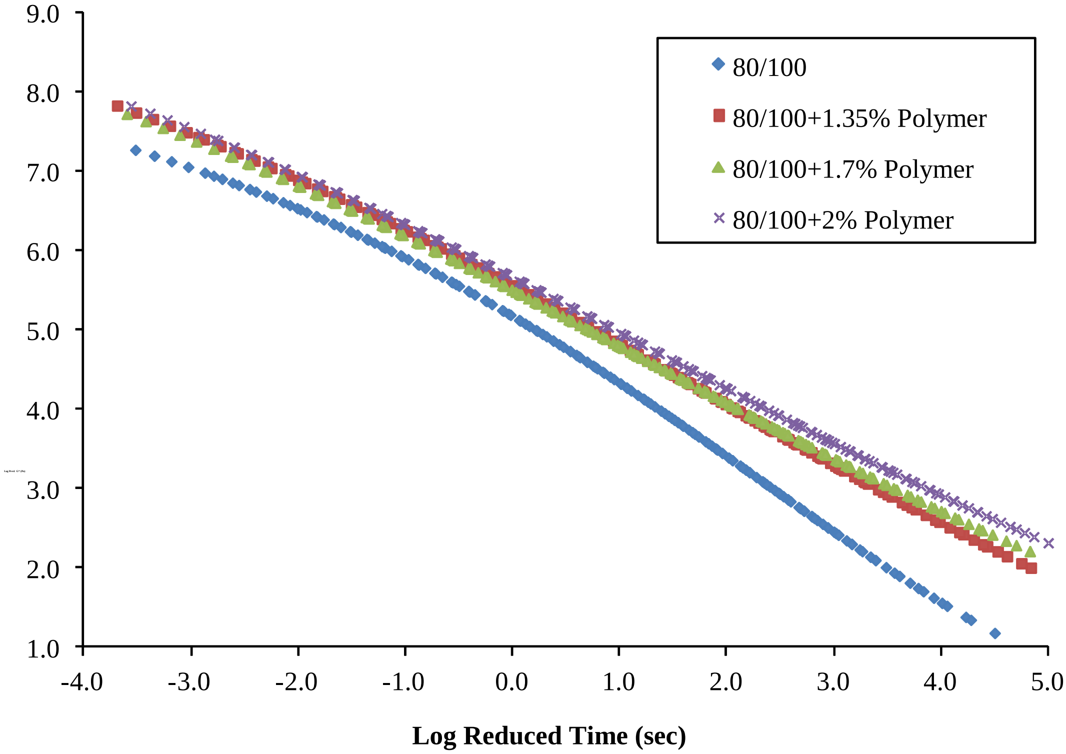

Figure (5): Master curves for Attock 80/100 and its PMA samples using Richard's sigmoid function

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