Fuel Resistance Asphalt Binder: Mixing Procedure and Fuel Damage Resistance

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Abstract. Most of the biopolymers are made from animal waste. Animal waste is treated and converted in a form of glue generally known as Hide Glue or Bone Glue (BG), which is prepared from animal protein. This study focusses of developing fuel resistant asphalt using biopolymers i.e. protein based polymers. A procedure to develop fuel resistant asphalt for commercial use and its performance evaluation was conducted in this study. Mixing procedure of BG was evaluated and refined and multiple fuel resistance tests were performed to evaluate the impact of bone glue modification on resistance to fuel of neat binder. It was determined that BG-binder mixing equipment developed in earlier studies was appropriate. Optimum BG dosage to develop FRA was found to be higher than the BG dosage recommended in earlier studies to develop mechanistically better performing asphalt binder. Fuel solubility resistance test was used to select the optimum BG dosage. Fourier Transform Infrared Spectroscopy results proved that water was completely evaporated using the mixing procedure developed for the preparation of FRA. Fuel damage resistance test revealed that BG modification not only improved the intermediate to high temperature characteristics of the neat binder but outperformed the conventional polymer modified asphalt binder in resistance to fuel damage.

1 Introduction and Background

Asphalt cement is a cementitious material either naturally occurring or produced through petroleum distillation. Asphalt is a black, sticky, semisolid, and a highly viscous material at ambient temperature (Brown et al. 2009). The Asphalt binder is used in construction industry especially in road pavements. Like any other material, asphalt binder also has some limitations such as; rutting at high temperatures, brittle at lower temperatures, and soluble in hydrocarbon fuels. High and low temperature problems are controlled by improving the rut resistance and fatigue performance of the binder, respectively. However, resistance to hydrocarbon fuel solubility is not well explored. The asphalt binder chemistry i.e. carbon (>80%), hydrogen (>10%) and sulfur ($\sim$5%) makes it a viscous hydrocarbon i.e. soluble in all petroleum fuels. Therefore, asphalt

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industry uses hydrocarbon fuels to reduce the viscosity of asphalt for lower application temperatures. This phenomenon is termed as cutback asphalts.

The use of hydrocarbon fuel to develop cutback asphalts is surely an advantage; however, the solubility of asphalt binder in hydrocarbon fuel is detrimental to pavement sustainability especially where frequent oil spills occur such as: airport taxiways, aircraft hangers, aircraft gates, car parking lots, private property driveways etc. The hydrocarbon fuel damages the asphalt binder and in turn, binder loses its binding strength, which is critical for mixture stability. Resistance of asphalt binder to solubility in hydrocarbon fuel has been explored by few researchers (Shoenberger 1983; Corun et al. 2006; Rooijen et al. 2004). Till now, Fuel Resistant Asphalt (FRA) has been explored as a replacement to the conventional flexible pavement on airport pavements. A FRA binder was developed by a private firm in the name Sealoflex®SFB 5-JR-50. The specifications of the binder and development recipe has not been shared; however it is proven that they used synthetic polymers to develop this FRA (Corun et al. 2006).

This study focusses of developing FRA using biopolymers i.e. protein based polymers. Most of the biopolymers are made from animal waste (Rizvi et al. 2014, 2015). Animal waste is treated and converted in a form of glue generally known as Hide Glue or Bone Glue (BG) (Rizvi et al. 2014) (Fig. 1a), which is prepared from animal protein. The BG has been used to study the effects of BG-modification on performance characteristics of asphalt binder and it was determined that BG modification improved the mechanical and rheological properties of asphalt binder (Rizvi et al. 2014, 2015). However, Rizvi et al. did not explore the potential of BG-modified binder as FRA. The concept of using biopolymer to develop FRA is based on the fact that protein is not soluble in hydrocarbon fuels (Cecil and Louis 1970); therefore, BG-modified asphalt binder was selected to evaluate its resistance to fuel damage.

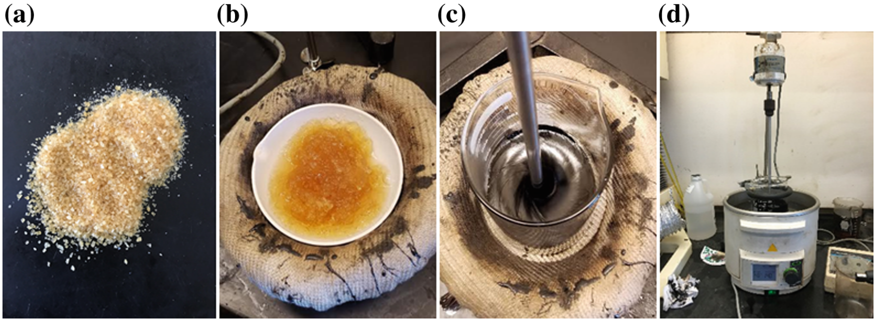


Fig. 1. **a** Bone glue **b** BGW mixture heating and **c** heating mantle **d** oil bath

It has been a known fact that protein is soluble in aqueous solutions (i.e. based on water) (Nick et al. 2004). Therefore, the water was used to achieve the homogeneous mixing of asphalt binder and BG. Rizvi et al. (2014) developed a mixing procedure; however various equipment, temperature, and mixing times may be explored to determine the optimum mixing conditions for BG mixing. Moreover, fuel damage resistance of the BG modified asphalt binder was also explored to determine the resistance to fuel capability of BG modified binder. In summary, this study explored optimum mixing conditions, equipment, and fuel damage resistance capabilities of BG-modified binder.

2 Objectives

The objective of this study is to optimize the mixing procedure of BG and explore the fuel damage resistance capabilities of BG modified binder.

3 Materials and Testing

Two frequently used binders i.e. PG 64-22 (Un-modified Binder (Neat)), and PG 76-22 (Polymer Modified Binder (PMB)), were selected to be used for this study. The BG was purchased from local vendor in finely ground form. The fuel used for this study was automobile 87 octane gasoline (AKI rating 87-Octane).

The mixing procedure was adopted from the Rizvi et al. (2014) and heating equipment, temperature and mixing time was altered to achieve the optimum mixing conditions and BG dosage. Procedure developed by Rizvi et al. and alterations to the procedure are provided in Table 1. The lower BG dosage i.e. 2.5% was eliminated and 30% was added to explore the optimum resistance to fuel damage. Intermediate dosage was also eliminated i.e. 7.5% because Rizvi et al. proved that 10% was the optimum dosage to develop BG modified asphalt binder. Mixing equipment was also changed to determine the effect of equipment. Heating mantle was selected because heating mantle is simple and easy to use in comparison to oil bath i.e. more expensive, cumbersome and energy consuming (as it take some time to heat up the oil). Three Mixing temperatures were used: one for heating mantle i.e. 180 °C; two for the oil bath i.e. 140 and 175 °C. The objective of changing the temperature was to reduce the mixing time. Lastly, two mixing times were selected to determine the optimum time. Rizvi et al. selected 70 min for 10% and reported that BG dosage and mixing time are directly proportional to each other. In this study, consistent time was used for all BG dosages and the temperature was increased and mixing time was reduced to study the effect. Rest of the mixing procedure parameters were not altered.

Optimum BG dosage was based upon the maximum resistance to fuel solubility resistance. A fuel solubility resistance test was developed in this study to determine the optimum BG dosage for fuel solubility resistance by calculating the percentage of binder lost due to fuel exposure in 3, 6 and 24 h (Table 2). The details of the test are provided as follows:

- Neat and BG modified binders were heated, poured into sealable pans, and allowed to cool to room temperature (25 ± 5 °C). Fuel, equal in mass of binder, was added to the binder and the pan was sealed, weighed, and placed in an environmental chamber at 25 ± 5 °C. The pans were taken out of the environmental chamber after 3, 6, and 24 h and the liquid (i.e. fuel-binder mixture) was poured. Shaking and jolting were avoided to minimize variability. A flame-ignition was applied (i.e. not

Table 1. Mixing procedure comparison for BG and asphalt binder

Mixing procedure to make BG-modified binder	
Rizvi et al. (2014)	Variations in this study
BG submerged in water for 15 min	–
Water quantity was two times the weight of BG	–
BG-water mixture was heated for 10 min (continuous stir to prevent burning) (Fig. 1b)	–
BG poured in preheated asphalt binder at 150 °C	–
BG dosage (2.5, 5, 7.5, 10 and 20%)	5, 10, 15, 20, 30%
Mixing conducted using oil bath	Heating mantle (Fig. 1c) and oil bath (Fig. 1d)
Mixing temperature 130 °C	180 °C for heating mantle 145 and 175 °C for oil bath
Mixing times 70 min	40 and 60 min

Table 2. Types of test and respective parameters

Description	Parameters
Fuel solubility resistance	Dissolved percentage of the binder in fuel in 3, 6 and 24 h
FTIR spectroscopy	Water peaks
G*-master curve	Rheological index (R); cross-over frequency (ω_c)

touching the surface of the binder) to let the trapped fuel burn. It was observed that a very weak flame lasted from two to three seconds on the top of the mixture in pan. Two consecutive flames-ignitions were introduced in intervals enough to let the mixture cool down to room temperature (i.e. approximately two minutes). For each trial, 40 g of binder was used for FSR test because anything greater than 40 g of mixture combined with the fuel would not fit in the testing tins. The testing temperature was 25 ± 5 °C because it was easy to manage the binder storage and testing. Furthermore, higher temperatures might be hazardous due to flammable materials. The pan containing the binder was weighed after the fuel-binder mixture was spilled to analyze the binder's resistance to fuel. The fuel solubility resistance results are measured in terms of percent binder mass loss and are calculated by the following equation:

$$P_L = \frac{B_i - B_f}{B_i} * 100 \tag{1}$$

where

P_L = Binder loss, %
B_i = Initial binder mass, g
B_f = Final binder mass after testing, g

The optimum mixing conditions were based on the complete or maximum evaporation of water from the mixture; therefore, Fourier Transform Infrared (FTIR) spectroscopy was used to trace the presence of water in mixture (Table 2). FTIR test was conducted using Perkin Elmer Frontier FTIR Spectrometer. The FTIR spectrum of asphalt composite shows Carbon-Hydrogen stretching and bending frequencies characteristic of a hydrocarbon (Rizvi et al. 2014).

The damage caused by fuel on asphalt was evaluated based on: (1) Comparison of parameters determined using the G*-master curve of un-soaked and fuel soaked binders developed using time-temperature superposition methodology; and (2) Comparison of Fourier Transform Infrared (FTIR) spectroscopy of hydrocarbon fuel peaks between un-soaked and fuel soaked binder. The concept of fuel damage resistance test was adopted from Rooijen et al. (2004). However, details and quantities of material and procedure is provided as follows:

- A 40 g sample of binder was poured into a pan followed by a 40 g sample of fuel, completely soaking the binder in fuel. The fuel quantity was determined by trial and error method so that fuel would be sufficient to soak the binder completely. The pans containing binder-fuel mixture were left unsealed in an environmentally controlled chamber to let the fuel evaporate at room temperature for five days. Dynamic Shear Rheometer (DSR) was used to conducted frequency sweep tests at six frequencies and five temperatures i.e. (0.1, 0.5, 1, 5, 10, 25 Hz & 4, 10, 20, 35, 50 °C). G*-master curves of fuel damaged and undamaged binders were developed and curve shape, rheological index (R) and crossover frequency (ω_c) were discussed to evaluate the effects of fuel damage on performance of asphalt binders (Table 2).

4 Results and Discussion

4.1 Mixing Procedure

Mixing procedure of BG and asphalt binder results proved that due to high stiffness at 20 and 30% dosages, the 20% BG dosage was not workable. Furthermore, at 30% dosage, binder was not mixable. Therefore, no further mixing trials or testing was performed using more than 15% of BG dosage and three dosages were experimented further i.e. 5, 10 and 15%.

4.2 Fuel Solubility Resistance Test

The results of FSR test are provided in Fig. 2. It can be observed that BG15% showed least binder loss among all dosages of BG proving that 15% is the optimum dosage to develop FRA. BG modification reduced the binder loss due to solubility in hydrocarbon fuel up to 41.6% after exposure of 24 h. The percent binder loss of BG15% was less than neat binder by 20.5, 21 and 41.6% after 3, 6 and 24 h of fuel exposure, respectively. These results proved that 15% BG dosage approximately doubled the FSR capabilities of the neat binder after 24 h of fuel exposure. As the time of soaking increases, the fuel diffuses into the binder and breaks carbon chains causing it to dissolve. This process of diffusion may take hours to complete. It is evident from FSR test results that initially the diffusion might not be complete; therefore the results show that after 3 and 6 h, the FSR enhancement is approximately 20%. On the other hand, when diffusion process was given time, as observed in case of neat binder, where approximately 90% of the binder was lost after 24 h, the BG modification showed its real impact and resulted in a two-fold improvement in FSR capability of neat binders.

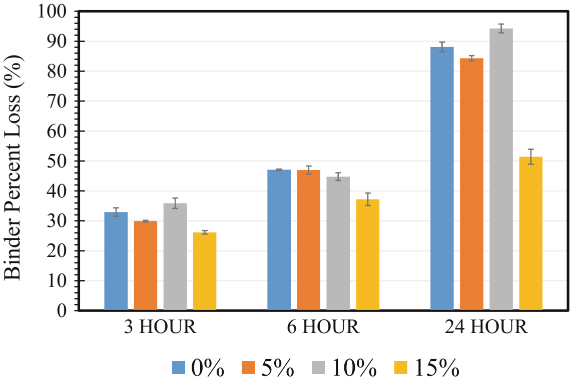


Fig. 2. Fuel solubility resistance test results at different dosages of bone glue modified binder

Figure 2 also showed that 5 and 10% BG dosages did not significantly impact the FSR capabilities of the neat binder. In order to determine the statistical significance of the mean differences of the results of three replicates, T-test between neat, 5 and 10% results were conducted and it was found that all *p*-values were higher than 0.05, proving that the mean difference between neat and 5%, and neat and 10% is not statistically significant. However, the t-test between neat and 15% BGB showed *p*-value 0.001, proving that FSR of 15% bone glue modified binder was statistically greater than neat binder. In summary, the results of FSR test proved that minimum dosage to observe fuel resistance capabilities is 15%; therefore only 15% BG dosage was selected for further testing.

4.3 Fourier Transform Infrared (FTIR) Spectroscopy

As mentioned above, 15% BG dosage was selected for further testing; therefore, FTIR spectroscopy (Fig. 2) was conducted on neat and 15% BGB binders to determine optimum mixing conditions for BG and binder. Generally, IR spectrum covers a range of wavelengths from 650 to 4000 cm^{-1}. Peaks in IR spectrum show the stretching and bending frequencies of different chemical compounds in specific range such as water–O–H can be observed in a range of 3100–3700 cm^{-1} (Rizvi et al. 2014) and IR stretch from 1500 to 1750 cm^{-1} shows C=O bonding that covers anhydrides, ketones, amides and. ester. It is essential to note that excess of the C=O bond shows oxidative aging of asphalt binder (Li et al. 2016). The thermo-oxidative aging decreases the content of small molecules and increases the content of large asphalt molecules; thus, leading to an increase in the average molecular weight and size of the asphalt binders (Li et al. 2016; Dehouche et al. 2012).

IR spectrum results are provided in Fig. 3. The figure is divided in four sections A, B, C and D representing combined, equipment, temperature and time effects on composition of binder, respectively. The water–O–H (3100–3700 cm^{-1}) and C=O (1500–1700 cm^{-1}) frequency stretch in IR spectrum (highlighted in A) were used to compare different mixing procedures. Combined spectrum (A) results proved that all the procedures successfully evaporated up to 99% of water because significantly bigger peaks cannot be observed in the water–O–H bonding range except B-HM-40 mix, which represents mix prepared in heating mantle for 40 min. However, significant peaks were observed in C=O bonding range showing oxidative aging of binder due to mixing procedure (Fig. 2a; C=O Bonding Zone).

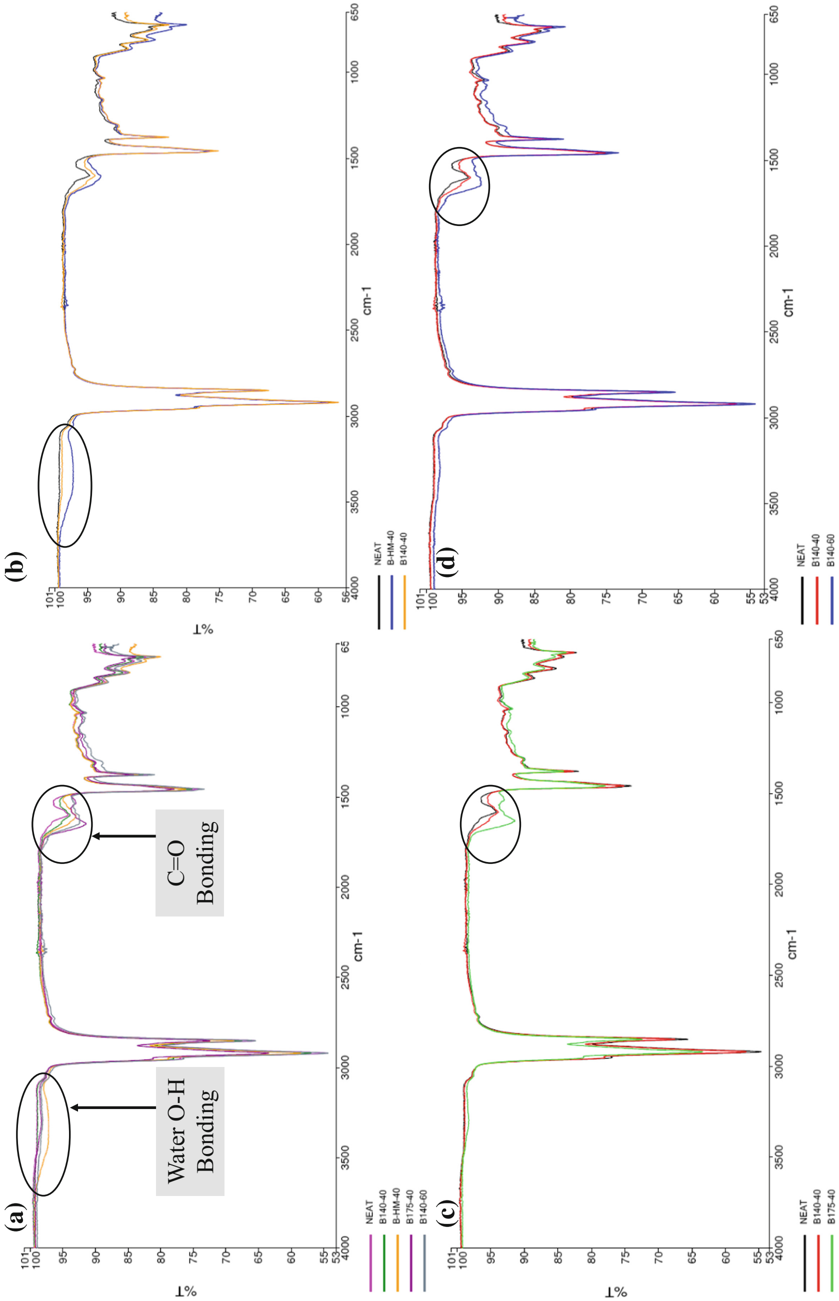
Spectrum B shows that the heating mantle could not completely evaporate the water at 185 °C in 70 min (blue) as a water peak was found in case of B-HM-40 mix, as opposed to the B140-40 (mustard),which was prepared using an oil bath. The reason for this seems to be limited heating zone i.e. only bottom of the beaker was being heated; whereas the rest of the beaker was exposed to the room temperature. On the other hand, in the oil bath the beaker was fully submerged in preheated oil providing direct heating not only to the bottom but also to the sides. This result proved that using an oil bath is more appropriate a wet mixing procedure.

It can be observed in spectrum C that B175-40 mix, prepared in oil bath at 175 °C for 40 min, showed a stronger peak in the C=O bonding range in comparison to B140-40 mix, which was prepared in oil bath at 140 °C for 40 min. IR spectrum analysis proved the occurrence of extensive oxidative aging at 175 °C, represented by a green line in the spectrum. However, mix prepared at 140 °C (red) showed no peak in comparison to Neat binder (black). It was determined that evaporation of total water content remained consistent at both temperatures; therefore, to achieve the goal of complete water evaporation while simultaneously avoiding unnecessary oxidative aging, a 140 °C mixing temperature is optimum for BGB. Effect of mixing time i.e. spectrum D shows results of neat (black) and two mixes B140-40 (red) and B140-60 (blue), prepared at 140 °C for 40 and 60 min, respectively. Significant peaks observed for B140-60 in C=O bonding range proved that extended mixing time induced oxidative aging; whereas, B140-40 did not show any peak in C=O bonding range. This proved that even a 20 min difference could be significant for oxidative aging. It is evident from these results that BG should be mixed in oil bath at 140 °C for 40 min.

Fuel Damage Resistance Evaluation

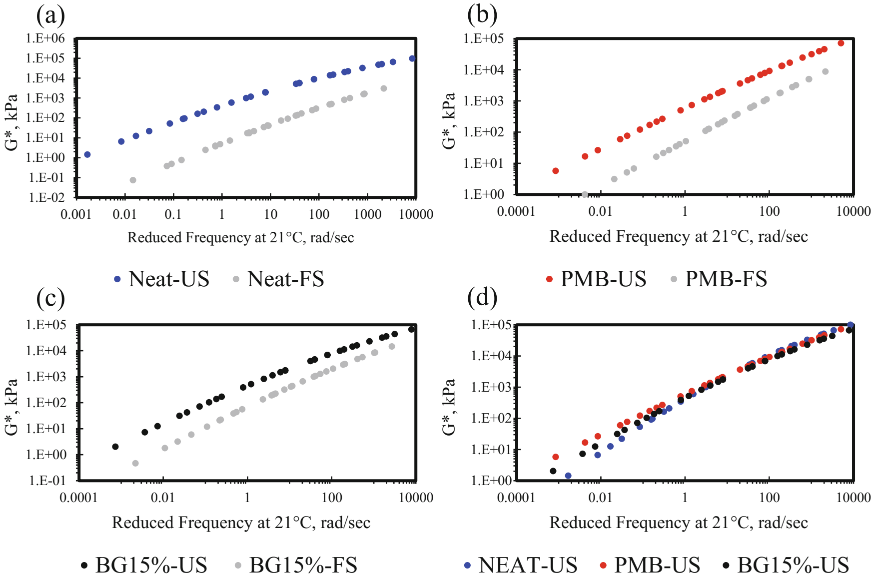
The master curves were developed using the frequency sweep test data and shown in Fig. 4. The average percentage difference in stiffness over the broad range of frequencies between a pair of unsoaked and fuel-soaked neat, PMB and BG15% binders was found to be 97, 88 and 76%, respectively. Therefore, the stiffness reduction from fuel exposure was 30 and 20% lower in BG15% binder in comparison to neat and PMB binders, respectively. The BG modification enhanced the fuel resistance of neat binder and showed even better performance than a conventional PMB modified with SBS.

The drop in stiffness due to soaking in fuel is more significant at lower frequency/higher temperature zone than at higher frequency/low temperature zone



Note: B refers to 15% BGB; HM represents Heating Mantle

Fig. 3. FTIR spectroscopy of various BGB mixes



Legend: US=Unsoaked; FS=Fuel Soaked

Fig. 4. G* master curve comparison of all binders

(Fig. 4a–c). This was due to effect of high temperature on viscosity of the binder providing conducive environment for fuel damage. On the contrary, higher frequency/low temperature zone is where binder behaves as a solid therefore less reduction in stiffness was observed due to fuel exposure in all binders. The reduction in stiffness of the BG15% fuel-soaked binder was found to 11 and 5% less than the fuel-soaked neat and PMB binders, respectively. Generally, intermediate to high temperature zone is more critical in terms of fuel damage due to softening of binder and it was observed that BG modification offered 30% higher resistance to fuel damage. Nevertheless, bio-polymer showed better fuel resistance in comparison to the conventional synthetic polymers in both high and low frequency zones.

Although PMB showed that fuel damage resistance can also be achieved through synthetic polymer modification, BG modification surpassed the conventional polymer modification impact on fuel damage resistance. A possible reason for this is that the protein based bio-polymer chains are more fuel resistant in nature. The insolubility of protein-fibrous chains in petroleum fuels provided better resistance to fuel damage in comparison to conventional synthetic polymer chains.

The master curves of un-soaked binders showed that BG modification showed approximately 70% increase in stiffness of neat binder at lower frequency and high temperatures, hence improving rutting performance. The stiffness of BG modified binders were found to be approximately 30% lower than the neat and PMB binders at higher frequencies and lower temperatures. Therefore, master curve data proved that the BG modification did not show improvement in binder properties of neat binder at lower temperatures. Rheological index (R) and cross-over frequency (ω_c) were also calculated from fuel soaked master curves of the respective binders using the Christensen-Anderson (CA) model (Christensen and Anderson 1992). The BG modification enhanced the R value of neat binder approximately ten times i.e. 40–390 kPa. This shows significant improvement in rut resistance on the neat binder. Please note that BG15% showed higher R-value than that of the PMB by approximately four times, which proved that BG15% performed better than the conventional PMB in rut resistance.

The Cross-Over frequency (ω_c) represents hardness parameter. BG modification exhibited more stiffening effect in comparison to neat binder i.e. neat and BG15% cross-over frequency values were found to be 30 and 17 rad/s, respectively. Therefore, fuel soaked BG15% was found to be harder than the fuel soaked neat binder. However, calculated cross-over frequency value of fuel soaked PMB was 12 rad/s. This results shows that performance of fuel soaked BG15% is better than the fuel soaked PMB at lower temperature. This shows that fuel soaking has larger negative impact on low temperature performance of PMB than on 15% bone glue modified binder.

5 Conclusions

This study was focused on developing fuel resistant asphalt for commercial use. Animal waste, Bone Glue, was selected to be used for this purpose and multiple fuel resistance tests were performed to evaluate the impact of bone glue modification on resistance to fuel of neat binder. In conclusion;

1. Optimum bone glue dosage in asphalt binder was found to be 15% to develop fuel resistant asphalt binder.
2. Mixing procedure developed by Rizvi et al. was found to be viable except change in mixing time and temperature. It was determined that an increment of 10 °C in mixing temperature reduced the mixing time to approximately half of the recommended time of 70 min.
3. Oil bath was found to be appropriate mixing equipment for BG and binder mixing process. Heating mantle was easy to use but the results proved that BG and binder mixture was not homogeneous and it could also not evaporate the water from the mix.
4. Fuel solubility resistance was significantly improved by BG modification.
5. It was also proven that BG modification outperformed the conventional synthetic polymer modification by showing higher resistance to fuel damage. It can be concluded that BG modification can transform neat binder into a FRA.
6. It was determined that low temperature characteristics of PMB were more affected by the fuel soaking in comparison to BG modified binder.
7. Master curve results also proved that BG modification significantly improved high temperature characteristics of the neat binder such as the rut resistance and the elastic behavior of the binder.

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