Development of an Innovative Bio-Binder Using Asphalt-Rubber Technology

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Abstract: This research work evaluates several parameters that can affect Asphalt Rubber (AR) binder performance and applies the AR technology to the development of an innovative renewable bio-binder that can fully and cost-effectively replace asphaltic bitumen derived from petroleum in flexible pavement construction. The "Binder Accelerated Separator" method was used to divide the constituents of the Asphalt Rubber and bio-binder (residual binder and swelled rubber). The physical and chemical changes in the Asphalt Rubber and bio-binder is suitable for use in flexible pavements with properties comparable to those of conventional and Asphalt Rubber binders.

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Introduction

The new world political organization (arrangement) that mainly affects some of the greatest petroleum producing countries, is making the petroleum market unpredictable leading to record high prices of this material, which is reflected in the price of bitumen. On the other hand, there is an increasing environmental conscience pushing towards the use of renewable materials in all economic activities. In the paving industry, there is effort to develop new binders using renewable materials, usually from other productive activities such as forestry and agricultural residues, without impairing, rather improving, pavement performance.

The referenced bio-renewable materials can be used with bio-oil produced from fast-pyrolysis of biomass materials. This process can provide several chemical products such as bio-oil. Bio-oil presents many rheological and performance similarities with asphaltic bitumen, being cost effective and easy to be produced locally on a regular basis. However, in order to meet the present demands of the road industry some upgrades must be done in the bio-oil to turn it to a bio-binder that performs as well as bitumen. Therefore, it can be defined as an "asphalt binder alternative made from non-petroleum based renewable resources, which should not rival any food material, and have environmental and economical benefits" [1].

Most of the research conducted on the application of bio-oils is focused on their uses as biorenewable fuels to replace fossil fuels. However, work has been done showing that the applicability of using bio-oils as a bitumen modifier or extender is a very promising alternative for the use of bio-oils [2-4]. On the other hand, there has been no research conducted until recently that studies the applicability of bio-oils as a bitumen replacement (100% replacement) to be used in the pavement industry [5]. As a result, there is scarcity of data that illustrates the procedures for developing bio-binders from bio-oils.

One of the thermochemical processes used to produce bio-oils is fast pyrolysis. Fast pyrolysis is the rapid decomposition of organic matter (biomass) in the absence of oxygen to produce solids such as, char, pyrolysis liquid or oil (bio-oils), and gas [6, 7]. The yields from fast pyrolysis vary with the biomass feed stock and the reactor conditions [8]. The bio-oil is a high-grade liquid fuel containing lignin that can be combusted by specific engines or turbines for electricity generation [9].

In many cases, the characteristics of bituminous binders need to be changed to improve their elastic properties at low temperatures for sufficient cracking resistance, and to increase its shearing resistance during sustained loads and high temperatures for rutting resistance. The physical properties of bitumen are often modified with the addition of a polymer, styrene-butadiene-styrene (SBS), to produce an improved bitumen grade that enhances the performance of bituminous paving mixtures. A viable alternative to using SBS polymers would be the use of recycled rubber from tires.

Polystyrene (PS) is a tough hard plastic, which provides SBS its durability, while polybutadiene (PB) is a rubbery material, and gives SBS its rubber-like properties. The material has the ability to retain its shape after being stretched, and consequently SBS is an unusual type of material called a thermoplastic elastomer [10]. The vulcanized rubber of tires cannot be recycled or used for the same purpose as the unvulcanized polymer. Thus, the introduction of crumb rubber in the production of asphalt rubber (AR) mixtures for road pavements should be considered as a sustainable technology, which will transform an unwanted residue into a new mixture with a high resistance to fatigue and fracture.

Recycled tires consist mainly of natural and synthetic rubber. After grinding, this material can be reused as a constituent of

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pavements contributing for a sustainable development of road infrastructures, namely through: (i) the definition of an efficient final destination for the used tires of cars and trucks, and (ii) the improvement of the performance of the resulting material used in the pavement.

When polymer networks are exposed to low-molecular weight liquids, the liquid molecules diffuse into networks and are absorbed within the polymer network. The liquid molecules occupy positions among the polymer molecules forcing them to move apart, which swells the polymer. This process continues until an equilibrium in the swelling is reached. Swelling of rubbers by organic liquids may also be considered to be a partial dissolution process in which there is a limited solubility of the un-vulcanized polymer in the solvent [11].

Other processes occur as the AR binder is subjected to different combinations of digestion time and temperature, i.e., once the rubber has swelled, if the temperature is maintained too high or too long, the rubber begins to disintegrate into the bitumen by partial depolymerization. When rubber particles significantly depolymerize, the liquid phase of a binder made with fine material will be stiffer than the liquid phase of a binder made with a coarse material. Using high shear rate mixers reduces the particle size of coarse crumb rubber and allows the interaction process to progress with greater speed [12].

The mutual changes between the bitumen and rubber during AR production are evident during the AR production, and the final properties of the AR binder are clearly influenced by the changes evaluated on the residual bitumens. The final properties of the AR binders are more dependent on the residual bitumen changes than on rubber changes [13].

During the AR binder production, the interaction of the crumb rubber particles with softer bitumens is clearly higher than with harder bitumens. The rubber particles saturated with bitumen molecules become a brittle gel that split by the action of stirring, heating and eventual depolymerization [14].

Therefore, the aim of this work is to understand several parameters that affect the Asphalt Rubber (AR) binder performance and apply the AR technology to the development of a renewable bio-binder that can fully and cost effectively replace asphalt bitumen derived from crude petroleum in flexible pavement construction.

Materials and Methods

Materials

The main materials used in this work were a bio-oil produced from the fast pyrolysis of red oak (Quercus rubra) (Wood Residual Solutions, LLC of Montello, WI) in the Iowa State University pyrolysis unit, and two sources of crumb rubber from used tires (GTR) from different suppliers. These were obtained using two different processing methods: i) mechanical shredding – ambient rubber (ambGTR), supplied by Seneca Petroleum (# 30 mesh) and ii) frozen and milled – cryogenic rubber (cryoGTR), supplied by



Fig. 1. "Binder Accelerated Separator" Method.

LTLehigh Technologies (# 80 - 200 mesh). Two bitumens were also chosen as controls, for comparison to the developed biobinders, a 160/220 (PG58-28) and a 50/70 (PG64-22) bitumens.

Methods

Initially, the bitumen and bio-oil properties were evaluated using conventional CEN standard tests (Penetration at 25 $^{\circ}$ C (Pen) – NP82/1964, viscosity (RV) – ASTM D4402, and ring and ball softening point (R&B) –E34/1955. After this preliminary characterization, the bitumen and bio-oil were blended with 10% and 15% of crumb rubber using a Silverstone shear mill at 125 $^{\circ}$ C and 1000 rpm for 1 hour. After blending, the "Binder Accelerated Separator" – BAS method (Fig. 1) was used to separate the constituents of the asphalt rubber (AR) and modified bio-oil (MBO) into residual and swelled rubber. The changes in the AR and MBO and in the residual binders (residual bitumen and residual MBO) were evaluated by replicating the same tests used for initial binder characterization.

Some of the ARs and the MBOs, as well as the respective residual materials, were aged by the Rolling Thin-Film Oven test (RTFO) – EN 12607-1, followed by the Pressurized Aging Vessel (PAV) – ASTM D6521-08. The rheological characteristics of the produced materials were assessed using a Dymanic Shear Rheometer (DSR) – ASTM D7175-08 and a Bending Beam Rheometer (BBR) – ASTM D6648-08.

Additionally, the chemical analysis of the materials was made using Fourier Transform Infrared Spectroscopy (FTIR), a Thermo Scientific Nicolet iS10 (Thermo Scientific®, Hanover Park, IL) equipped with a Smart iTR accessory, utilizing OMNIC Software (Thermo Scientific®, Hanover Park, IL) operating system. Background was collected before every sample and attenuated total reflectance (ATR) correction was used with 4 wavenumber resolution. Spectra were obtained by averaging 32 scans in the range of 4000-650 cm-1. The solid samples were placed on the diamond

| Table 1. Materials | s and Tests Used | III UIIS WOIF | | | | | | | | |
|-------------------------------|------------------|---------------|-------------------|------|-------|----|-----|---------------------|-----|-----|
| Materials | | | | | Tests | DU | | D (D | DCD | |
| C CTD | | | | | FIIK | RV | Pen | R&B | DSR | BBK |
| CryoGIR | | | | | X | | | | | |
| AmbGIR | | | | | X | 37 | 37 | 37 | 37 | |
| | · · · · · · | | | | X | X | X | Х | X | |
| | Aged bio-oil | | | | X | X | 37 | 37 | | V |
| | CryoGTR | 10% | | | X | Х | Х | Х | | Х |
| | | | | RTFO | Х | | | | | |
| | | | | PAV | X | | | | | |
| | | | | | Х | Х | Х | Х | Х | |
| | | | Residual | RTFO | Х | | | | Х | |
| | | | | PAV | Х | | | | Х | |
| Bio-oil | | 15% | | | Х | Х | Х | Х | | Х |
| | | | | RTFO | Х | | | | | |
| | | | | PAV | Х | | | | | |
| | | | | | Х | Х | Х | Х | Х | |
| | | | Residual | RTFO | Х | | | | Х | |
| | | | | PAV | Х | | | | Х | |
| | AmbGTR | 10% | | | Х | Х | Х | Х | | Х |
| | | | | RTFO | Х | | | | | |
| | | | | PAV | Х | | | | | |
| | | | | | Х | Х | Х | Х | Х | |
| | | | Residual | RTFO | Х | | | | Х | |
| | | | | PAV | Х | | | | Х | |
| | | 15% | | | Х | Х | Х | Х | | Х |
| | | | | RTFO | Х | | | | | |
| | | | | PAV | Х | | | | | |
| | | | | | Х | Х | Х | Х | Х | |
| | | | Residual | RTFO | Х | | | | Х | |
| | | | | PAV | Х | | | | Х | |
| 160/220 (PG58-28) | | | | | | Х | Х | Х | | |
| | CryoGTR | 10% | | | | | | | Х | |
| | | | Residual | | | Х | Х | Х | | |
| | | 15% | | | | | | | | Х |
| | | | | | | Х | Х | Х | | X |
| | | | Residual | RTFO | | | | | х | |
| | | | | PAV | | | | | X | |
| | AmbGTR | 10% | Residual | 1111 | | X | X | X | | |
| | | 15% | | | | X | X | X | x | |
| | CryoGTR | 1.5 /0 | | | | x | x | X | X | |
| | | 10% | | | | X | X | X | Δ | |
| 50/70 (DC-64 22) | | 15% | Residual | | | X | X | X | | |
| 50,70 (1 00+ ³ 22) | AmbGTR | 10% | 0% 5% Residual | | | X | X | X | | |
| | | 15% | | | | X | X | X | | |
| | | 1.5 /0 | | | | 11 | 11 | 11 | | |

Table 1. Materials and Tests Used in this Work.¹

¹Rheological testing (RV, DSR and BBR) will be done in triplicate.

crystal plate and prepared for analysis with an equipped constant pressure press.

TQ Analyst software was used to obtain the similarity matches used in this research. The regions used for the similarity matches included 3500-3100 cm-1, 3000-2800 cm-1, 1500-1200 cm-1, and 1150-800 cm-1.

The materials and test matrix is presented in Table 1.

Results and Discussion

The feedstock materials, initial bio-oils and rubbers, and those after the bio-binder production and the application of the BAS method, namely the MBO and the residual MBO that result from the separation of the bio-binder were analyzed. The analysis of these materials provides very important information about interactions between the bio-oil and the crumb rubber. Therefore, the FTIR



Fig. 2. FTIR Spectra of the Materials Related with the Use of 15% ambMBO.

spectra of the reference materials, as an example, are compared in Fig. 2.

By spectra comparison, it can be observed that the bio-oil did not have significant changes due to aging during bio-binder production. To confirm these observations, a similarity match was done, namely match values from the base bio-oil with the aged bio-oil were computed and compared.

The similarity match is a spectral classification technique that indicates how closely an unknown material matches a known material. The similarity match method compares the spectral information in the specified region or regions of an unknown sample spectrum with that of a known set of standard spectra to determine how closely the sample matches the standards. The result of this comparison is called a match value. The match value represents the unexplained variation in the spectrum of the unknown sample; the maximum similarity is indicated by a match value equal to zero (0), and the complete dissimilarity is indicated by a match value equal to one hundred (100).

From the analysis of the spectra presented in Fig. 2, it is noticeable the transferences of parts of rubber to the bio-oil and from the bio-oil to the rubber. Between wavenumbers 800 and 1150 cm-1 it is clear that some molecules disappear from the bio-oil (this is not due to volatilization, as previously observed in aged bio-oil). Probably these molecules diffused into the rubber particles causing them to swell. This region of the spectra can be correlated to the aliphatic hydrocarbon region from the rubber, but it can also be related to primary aliphatic alcohols from the bio-oil. Since these molecules decreased from the base bio-oil to the bio-binder and the residual bio-oil, they are most likely the molecules that facilitate the swelling process in the rubber. These observations are consistent with the results previously reported [15], that mention a preferential absorption of the compounds with linear aliphatic chains into the rubber and suggests that these components have better skeletal compatibility with the linear polymeric skeleton of the rubber.

The comparison between the FTIR spectra is a preliminary approach to the chemical changes that occur during the bio-binder production, but a more in-depth study is necessary. However, the FTIR results are a very useful tool to show that chemical interactions are occurring and contribute to changes in the materials' consistency.

The spectral differences between the materials that occurred during bio-binder production were also quantified using the similarity match method, as previously mentioned. The resulting match values, evaluated as being the variation in the spectrum of the materials compared to the bio-oil, are presented in Fig. 3.

The comparative spectra do not indicate significant changes due to aging during bio-binder production. To confirm these observations, a similarity match was performed at the specified spectral regions. The similarity matched values from the base bio-oil and the aged bio-oil were computed and compared.

The match value of the base bio-oil in comparison to the aged bio-oil was about 0.28%, which indicates minimal changes in the chemical composition of the bio-oil during the bio-oil to bio-binder production. Additionally, since the cryogenic and ambient rubber were provided by two different companies (one in the Chicago metropolitan area – ambGTR, and the second in the Atlanta metropolitan area - cryoGTR), the spectra of the two crumb rubbers were also compared. The match number computed for the comparison between cryogenic and ambient crumb rubbers is 1.15% reflecting minor differences between the two rubbers.



Fig. 3. Comparison Among the Match Values for Four Types of Bio-oil Based Materials.



Fig. 4. Changes in the Viscosity of the MBOs and in the Residual MBO at 100 $^{\circ}$ C.

The different bio-oil base materials were compared among them generating a series of match values. Fig. 3 displays how the different materials differ.

The match values presented in Fig. 3 show obvious differences between the bio-oil and the MBO, demonstrating chemical changes related to interaction with the two types of rubber. Other noticeable changes are caused by the RTFO aging test and the PAV test. The greatest dissimilarity is measured in relation to the PAV material, since it is the more aged material and the rubber is still present.

The most important observation is the difference between the bio-oil and the ResMBO, which reflects the changes caused by the interaction with the rubber. The smallest match number was 1.86%, observed for the Res[10% ambMBO], which subtracting the 0.28% difference due to aging results in a difference of around 1.58% that can be attributed solely to the rubber interaction. The match values also show, as seen in the spectra, that the similarity is lower when cryogenic rubber is used, and thus indicates a higher interaction between this material and the bio-oil than that observed with the ambient rubber. In addition, the similarity is also related to the rubber concentration in the bio-binder, since the materials produced with a lower content of rubber are more similar.

The results of physical characterization of the bio-oil based materials using conventional European standards are presented in Figs. 4 to 9. The viscosity of the cryo and amb MBOs, and correspondent residual materials was measured at 100 ℃ for both percentages of rubber used. Fig. 4 depicts the comparative results.

The results presented in Fig. 4 show significant changes in the viscosity of the biobinder after interaction with rubber, demonstrating the good interaction between these materials. The lines describing the changes in the viscosity of the MBO start at the viscosity of the un-aged bio-oil. According to the presented results, the ambGTR has more effect on the viscosity of the MBO than the cryoMBO. This is mainly caused by the roughness and bigger dimension of the particles of this type of rubber, when compared to the cryoGTR particles.

The starting point of the lines representing the resMBO corresponds to the viscosity of the aged bio-oil. These lines show the difference in the viscosity of the residual materials caused by the interaction with the different GTR.

The most relevant information that can be derived from the viscosity results is that despite the higher particle effect of the ambGTR in the MBO, it seems that some chemical constituents of

the GTR are migrating to the liquid bio-oil, and this phenomenon is more evident when using the cryogenic rubber to produce the cryoMBO.

When mixtures for flexible pavements are produced, the most important information needed are the mixing and compacting temperatures. This information can usually be obtained from the analysis of the binder viscosity. In order to understand how of the bio-oil derived binders behave in comparison to the AR binders (produced with bituminous binder), the viscosities of those materials at different temperatures were compared (Fig. 5).

Fig. 5 presents the changes in the viscosity with the test temperature. When bio-oil and aged bio-oil are compared with the 50/70 and 160/220 bitumens, the aged and un-aged bio-oil at temperatures ranging from 90 to 120 °C behave similarly to the 50/70 and 160/220 bitumens at temperatures ranging from 140 to 170 °C.



Fig. 5. Comparison between the Viscosities of the Bio-oil and the Bitumen Base Materials Modified with Ambient and Cryogenic Crumb Rubber.

The addition of GTR, with posterior centrifugation of the rubber binders (AR and MBO) shows an increase in viscosity, that is more noticeable when bio-oil was used. Thus, in order to obtain residual materials with a viscosity around 1000 cP lower temperatures for the MBO binders are needed when compared with AR binders. These differences in temperature are nearly less than 11 and 3°C for the 10 and 15% cryoMBO, respectively, than for the 10 and 15% cryoAR160/220. On the other hand, for the ambMBO binders the reduction in the required temperatures would be around 14 and 10 °C for the 10 and 15% ambMBO, respectively, when compared with the 10 and 15% ambAR160/220.

Most importantly, as the 50/70 bitumen is the most common bitumen used in the production of AR binders, the reduction in the temperature necessary to obtain residual binders with the same viscosity is around 26 and 19°C when 10% and 15% cryoGTR is used with bio-oil, and 29 and 23°C for the 10 and 15% Res(ambMBO). Disregarding the type and amount of GTR, this technology requires on average 24°C less to obtain the same viscosity in the resMBO than in the resAR50/70 bitumen, and a reduction, on average, of 10°C in comparison to the resAR160/220 bitumen. Thus the reduced temperatures for the bio bitumens as compared to equiviscous bitumen (from crude petroleum) would result in reduced production temperatures and thus savings in plant fuel consumption and reduced emissions.

The needle penetration test is one of the most important characterization used to evaluate the consistency of bitumen binders, and is broadly used to grade these materials. Therefore, the penetration values of the AR materials are presented in Fig. 7.



Fig. 6. Changes in the Penetration of the MBOs and in the Residual MBO.

Analyzing the variation of the penetration of the MBOs and their respective residuals, it is clear that there is a decrease in the penetration value when the content of rubber increases. The residual binders of both the cryoMBOs and ambMBOs present a very similar variation of the penetration. Interestingly, the line defining the changes in the penetration of the ambMBO is almost parallel to the respective residual. In contrast, the changes in the penetration of the cryoMBO are less affected by the content of cryoGTR than its residual.

The comparison between rubberized bio-oils and asphalt rubber show that even though bio-oil is softer than most of the bitumens



Fig. 7. Comparison between the Penetrations of the Bio-oil and the Bitumen Base Materials Modified with Ambient and Cryogenic Crumb Rubber.

currently used in paving mixtures, after being modified with around 15% of rubber, the latter is able to present penetrations equivalent to those of bitumen rubberized materials with the same rubber content. The exception is the bio-oil modified with cryoGTR, that follows the same trend as cryoARs, which is a very good tendency, as it is softer as a base material, but the effective binder (res cryoMBO) has a lower penetration, indicating a good performance regarding both stiffness and fatigue cracking resistance.

The ring and ball softening temperatures provide some important information about the workability and rutting resistance of the mixture where the binder will be used. This characteristic was evaluated and compared among the different tested materials (Figs. 8 and 9).

Although the two residual MBOs show very similar trends for the variation of the softening temperatures with the content of both types of rubber, the ambMBO has higher softening point temperatures. On the other hand, the softening temperatures of the cryoMBOs have a very small response to the increase of the rubber content, with quite low softening temperatures. The softening point results also show very similar residual binders obtained with both types of rubber, although the cryoMBO residual binder is more workable than that of the ambMBO binder.

Concerning the residual materials, and when compared with conventional ARs, the MBO presents similar R&B temperatures for rubber contents around 10%. Nevertheless, the residual materials of the MBO seem to be more workable than those of conventional ARs, because the MBOs are less susceptible to performance changes when the GTR content varies, thus maintaining low R&B temperatures for different rubber contents.



Fig. 8. Changes in the Ring and Ball Softening Points of the MBOs and Their Residual Binders.

The master curves and the performance grade (PG) of the binders (MBOs and AR) were determined indirectly by the analysis of the residual materials, because the residual materials are the ones that effectively behave as binder. Although the swelled rubber particles provide elasticity and toughness at low temperatures, they do not have binding characteristics. Furthermore, there are significant errors associated with the rheological analysis of heterogeneous materials, such as, the MBO or AR binders, which contain high volumetric fractions of rubber particles with particle sizes higher than 300 μ m (after swelling). In fact, most of the rheological determinations were made using parallel plate geometry consisting of a 1 mm gap, therefore the probability of the rubber particles in those binders interfere with the movement of the plates is very high,



Fig. 9. Comparison between the Ring and Ball Softening Temperatures of the Bio-oil and the Bitumen Base Materials Modified with Ambient and Cryogenic Crumb Rubber.



Fig. 10. Comparison between the Master Curves (Tref. = 20 ° C) of the Un-aged Bio-oil and Residual MBOs with a (Pen)50/70 (PG64-22) Bitumen.

producing variability in the results. Therefore, the materials presented in Fig. 10 and Table 2 are the base and aged bio-oils before the bio-binder production and the residual bio-oil separated from the bio-binder by the BAS method, which was sequentially aged by the RTFO and PAV methods.

Assessing the master curves of the unmodified and unaged materials (bitumen and bio-oil), they illustrate different trends, as the bio-oil is stiffer than the bitumen at low temperatures (high frequencies). At high temperatures (low frequencies), bitumen and bio-oil show similar rheological behavior. The change on the shape of the curves of residual MBOs is evident: although the shape of the master curve of the bio-oil differs from that of the bitumen, that difference reduces with the increase in the content of GTR, as the master curves of residual MBOs assume the same shape as that of the bitumen after interacting with 15% of GTR. In terms of modulus, the difference between the MBOs and bitumen is that the increase in the rubber content shifts the MBOs master curves towards higher modulus values. Another interesting observation is that for a content of 15% of both types of rubbers, the residuals of the MBO are very similar in terms of rheological behavior at in-service temperatures (the cryoMBO and anmMBO mastercurves are almost totally overlapping).

The DSR critical temperatures of the ResAR160/220 and the ResMBOs binders at the various stages of aging used for grading paving bitumen are presented in Table 2.

Based on the results presented in Table 2 it is possible to infer that the bio-oil presents very similar values in comparison to the control bitumen after interacting with rubber, namely at high and medium test temperatures. Considering the high temperature results for the residual bio-oils, it can be assumed that the high temperature binder grades are of at least PG 58 and PG 64 for the bio-binders containing 10 and 15% cryogenic rubber, respectively. Simultaneously, the bio-binders containing 10 and 15% ambient rubber originated high temperature binder grades of at least PG 58 and 64, respectively. These results suggest that the developed material is adequate to be used as a binder in the construction of flexible pavements.

Previous studies pointed out that the principal difficulty in using bio-oils as binders is their behavior at low temperatures [16]. Table 3 presents the results from the Bending Beam Rheometer (BBR) testing of the four studied bio-binders and a 15% ambAR160/220 binder.

The different bio-binders were tested in the BBR at -12°C and -18°C, corresponding to performance criteria of -22°C to -28°C, respectively. Assessing the m-values of the several binders, a very good behavior of the bio-binders can be observed at low temperatures. The best performance in respect to this parameter was the one of the two bio-binders produced with the cryogenic rubber. Overall, the m-value clearly dominates the low temperature grade of the bio binders. The performance of all binders was very good, with just one performance grade bellow for the binder 15% ambAR160/220 binder.

Contrarily to the previous tests, the presence of the rubber particles do not impair the accuracy of the results in this test, as the test consists in loading a beam under flexural tension, and in this case the rubber particles do not interfere with the equipment. Thus, this test is able to successfully access the effect of the rubber in the binder performance at low temperatures without the need of using separation methods to test the residuals. At low temperatures the bio-oil by itself is too brittle, thus justifying the use of GTR because this material has a very low freezing temperature (Tg = -80°C). This fact is evident in the obtained results, as an increase in the GTR content reduces significantly the stiffness of the binder, which reflects the softness of the rubber at this temperature.

Summarizing the behavior of the bio-binders at low temperatures, it can be stated that all the materials fulfill the specifications for temperatures equal or superior to a field temperature of -20 °C. The continuous grades for the bio-binder produced with the ambient rubber are 62.6-20.7 and 68.1-20.1 for 10% and 15%, respectively. Similarly, 60.5-22.4 and 67.5-23.7 were the continuous grades obtained for the bio-binder produced with 10% and 15% of cryogenic rubber, respectively. Therefore, the overall binder grades of PG 58-22 and PG 64-22 were obtained for the bio-binders

Table 2. High and Intermediate Continuous PG from the DSR Test.

| | | CryoGTR | | AmbGTR | |
|------------|-------------------|---------|---|--------|-------|
| | | 10% | 15% | 10% | 15% |
| | Bio-oil | 60.51 | 67.50 | 62.58 | 68.12 |
| res | 160/220 (PG58-28) | | | | 72.69 |
| DTEOT(D) | Bio-oil | 67.76 | 70.66 | 68.06 | 71.57 |
| KIFUI(Kes) | 160/220 (PG58-28) | | 67.50 62.58 68.12 72.69 72.69 70.66 68.06 71.57 69.74 69.74 30.35 26.71 32.60 21.43 21.43 | | |
| PAV(Res) | Bio-oil | 22.43 | 30.35 | 26.71 | 32.60 |
| | 160/220 (PG58-28) | | | | 21.43 |
| | | | | | |

| | Test Temperature | Stiffness | m-value | |
|-------------------|------------------|-----------|---------|--|
| | (°C) | (MPa) | | |
| 15% cryoAR160/220 | -18 | 117 | 0.317 | |
| 10% cryoMBO | -12 | 230 | 0.311 | |
| 15% cryoMBO | -12 | 112 | 0.341 | |
| 10% ambMBO | -12 | 395 | 0.274 | |
| 15% ambMBO | -12 | 160 | 0.235 | |

Table 3. Parameters from the BBR Test of the Binders at LowTemperatures.

containing 10 and 15% cryogenic rubber, respectively. The bio-binders containing 10 and 15% ambient rubber produced binder grades of PG 58-16 and 64-16, respectively.

Conclusions

The main conclusions drawn from this study are the following:

- The bio-oil can be successfully reacted with crumb rubber at 125℃;
- The rubber from the used tires is likely migrating and combining with the bio-oil; and
- A bio binder consisting of bio-oil reacted with crumb rubber can produce a binder that is comparable to bitumen binders derived from crude petroleum.

This work demonstrates the successful development of a bio-binder that is derived from a renewable source of material and represents a green technology. Additional work needs to be carried out using field trials. This will best assist in understanding the oxidative aging mechanisms of these new materials as well as their field performance. Laboratory performance testing of mixtures containing the bio-binders is underway and subsequent reporting of these results is anticipated.

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