

Development of Rubber-Modified Fractionated Bio-Oil for Use as Noncrude Petroleum Binder in Flexible Pavements

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The increasing demand for petroleum-derived products coupled with decreasing world crude reserves has led to substantial increases in asphalt pricing. Society's additional interest in energy independence and use of renewable sources of energy is also a motivation for developing and using more sustainable materials such as binders derived from noncrude petroleum sources for use in highway applications. Iowa State University has been developing noncrude petroleum binders derived from the production of bio-oil via fast pyrolysis of non-food source bio-renewable residues. Currently, research has demonstrated that bioasphalt can be used as a modifier, extender, or even as an antioxidant when added to petroleum asphalt. Previous research illustrated concerns with low-temperature cracking and the ability to produce typical binder grades used in the United States. This work aims to develop a biobinder that can replace 100% of the petroleum derived asphalt used in constructing flexible pavements utilizing bio-oil and crumb rubber. Both ambient and cryogenic crumb rubber were used in the research. The outcomes of the processes and formulations illustrates that noncrude petroleum binders can be developed effectively to replace typical paving grades of asphalt such as a PG 64-22 binder.

INTRODUCTION

The United States has numerous efforts under way working to establish a bio-based economy which generates energy from renewable organic matter rather than fossil fuels (1). The substantial increase in asphalt pricing in the past 8 years coupled with the installation of coking facilities at many refineries, which can reduce the supply of asphalt, is also creating an impetus for alternative nonpetroleum binders.

Most bituminous binders that are used for pavement materials are derived primarily from fossil fuels. With petroleum oil reserves becoming depleted and the drive to establish a bio-based economy, there is a push to produce binders from alternative sources, particularly from bio-renewable resources.

A biobinder is an asphalt binder alternative made from nonpetroleum-based renewable resources, which should not rival any food material, and have environmental and economical benefits. Presently, biobinders are produced by upgrading bio-oils produced from the rapid heating of biomass in a vacuum condition. Bio-oils are produced from plant matter and residues, such as agricultural crops, municipal wastes, and agricultural and forestry byproducts (1, 2).

Currently, the state of the art for the utilization of bio-oils is concentrated on its use as biorenewable fuels to replace fossil fuels. However, there has been a limited amount of research

investigating the applicability of bio-oils as a bitumen modifier or extender. Williams et al. conducted research on the usage of bio-oils fractions as an extender in original and polymer modified asphalt binders (3). They reported that the bio-oils can considerably increase the performance grade of polymer-modified asphalt binders by nearly 6°C (3). In addition, it was concluded that the effect of bio-oils was dependent upon many factors including the base asphalt, source of the biomass from which the bio-oils were derived, and the percentage of bio-oils blended with asphalt binders (3). Moreover, Williams et al. reported that up to 9% of a bio-oil could be blended with asphalt binders with significant improvement in the performance grade of the bio-oil modified asphalt binder. Concurrently, Fini and others have found that the use of swine manure-based biobinder as an asphalt modifier can enhance the asphalt low-temperature performance (4, 5). Based on the conclusions of these investigations, the utilization of bio-oils as a bitumen modifier is very promising. Nevertheless, there has been no research conducted until recently that studies the applicability of using bio-oils as a bitumen substitute (100% replacement) to be used in the paving industry.

One of the thermochemical processes used to produce bio-oils is fast pyrolysis. The yields from fast pyrolysis vary with the biomass feed stock and the reactor conditions (6). Generally, this process generates bio-oil, biochar, gases, and moisture. The biochar can be used for carbon sequestration as a soil modifier by improving the soil's ability to retain liquid fertilizers and thus reducing liquid fertilizer application rates. The bio-oil is a liquid fuel containing lignin that can be combusted by some engines or turbines for electricity generation (7).

Fast pyrolysis is a thermal decomposition process that requires a high heat transfer rate to the biomass particles and a short vapor residence time in the reaction zone (8). In other words, 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 (9, 10).

Generally, fast pyrolysis is used to obtain high-grade bio-oil. Organic biomass consists of biopolymers, such as cellulose, hemicelluloses, and lignin. Because of the different sources of biomass, the amount of production of the liquid bio-oils, solid char, and noncondensable gases varies. For example, fast pyrolysis processes produce about 60 to 75 wt% of liquid bio-oil, 15 to 25 wt% of solid char, and 10 to 20 wt% of noncondensable gases (2).

Figure 1 shows the 25 kWt fast pyrolysis system developed at Iowa State University by the Center for Sustainable Environmental Technology where bio-oils are produced from different biomass materials.

The pilot unit consists of a 16.2-cm diameter fluidized bed reactor, a burner to externally heat the reactor, a two-stage auger to feed the solid, two cyclones to remove particulate matter, and a vapor-condensing system consisting of four condensers and an electrostatic precipitator. The system can process 6 to 10 kg/h of solid feed. The separation of bio-oils into multiple fractions was conducted using a fractionation condenser system which facilitated the selection of bio-oil fractions that would be optimal for being used as a pavement binder. However, bio-oils cannot be used as biobinders–pavement materials without any heat pre-treatment, since an upgrading procedure is required (11).

Raouf (11) also found that the biobinders developed from oakwood, switchgrass, and corn stover bio-oils cannot be treated at temperatures higher than 120°C because of the volatilization of some bio-oil compounds. Raouf (11) further found considerable differences between the properties of the bio-oils and asphalt at the same temperatures, and thus the Superpave test criterion should be modified to comply with the biobinders properties, namely the Superpave specifications for the rolling thin film oven test (RTFOT) and the pressure aging

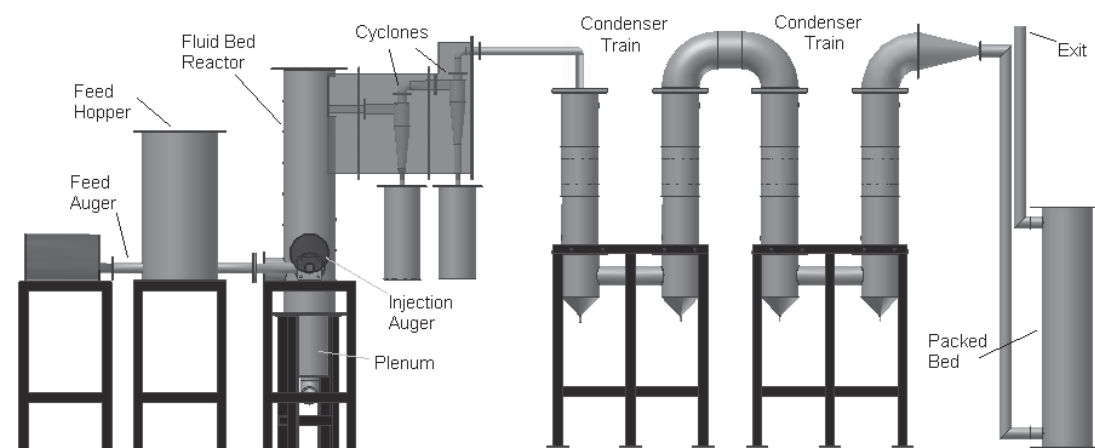


FIGURE 1 Bio-oil fast-pyrolysis pilot plant. (Source: Iowa State University.)

vessel (PAV) procedures. Longer in-situ aging studies would need to be done to understand the aging mechanisms of biobinders such that simulative laboratory criteria can be established.

Based on the tested bio-oils, the following suggestions were made (11). First, the RTFOT temperature should be modified to 110°C to 120°C instead of 163°C to be consistent with the intended mixture production temperature. Also, a period of 20 min was established to be the duration that resembles the mixing duration. Second, the aging duration in the PAV should be shortened to 2.5 h instead of 20 h and the temperature of the degassing container should be lowered to 120°C instead of 170°C. Raouf found that it was difficult to reach low-temperature grades of binders when attaining the appropriate high-temperature grades (11).

In many cases, the characteristics of asphalt 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 typically modified with the addition of styrene-butadiene-styrene (SBS) polymers to produce an improved asphalt grade that enhances the performance of asphalt paving mixtures. A viable alternative to using SBS polymers would be the use of recycled rubber from tires.

According to ASTM D 6814-02, rubber is a natural or synthetic elastomer that can be chemically cross linked or vulcanized to enhance its useful properties. Cross-linked rubbers or elastomers are three-dimensional molecular networks with the long molecules held together by chemical bonds. They absorb solvent and swell but do not dissolve. The glass transition temperature, T_g , of natural rubber is about -70°C . Furthermore, they cannot be reprocessed simply by heating (12).

Gawel et al. (13) also found that, of the nonpolar components, the n-alkanes and n-alkylbenzenes possess the highest propensity to penetrate into rubber particles. Preferential absorption of the compounds with linear aliphatic chains into the rubber suggests that these components have better skeletal compatibility with the linear polymeric skeleton of the rubber.

Despite natural rubber being a constituent of tires, because of its vulcanization, they cannot be easily recycled. Every year approximately 9 to 10 kg of rubber tires per inhabitant are discarded in industrialized countries. Although tires are not regarded as a dangerous residue, their hollow shape usually creates sanitary problems and difficulties in their final disposal. A

technical challenge is the vulcanized rubber of tires cannot be recycled or used for the same purpose as the unvulcanized polymer. Furthermore, society is not utilizing the valuable materials that exist in tires, namely its main constituent, the vulcanized natural and synthetic rubbers.

Therefore, the main objective of this work is the development of a biobinder capable of fully replacing conventional asphalt in flexible pavements. The utilization of recycled tires blended with bio-oil is examined to determine if the materials are chemically compatible as well as the recycled tires can enhance the low-temperature properties of biobinders.

EXPERIMENTAL PLAN

The experimental plan consists of a description of the materials, including the production of the biobinders, and the chemical and rheological testing. The specific components of the experimental plan are discussed in the following subsections.

Materials

The main material used in this work was the bio-oil derived from the fast pyrolysis of red oak wood residues in the Iowa State University pyrolysis unit (Figure 1) and two sources of crumb rubber from used tires from different suppliers that were obtained using two different processing methods: (a) mechanical-shredding ambient rubber and (b) and cryogenic-milled rubber.

The asphalt binder chosen as control for this study, for comparison to the developed biobinders, is AAM-1 from FHWA's Materials Reference Library. AAM-1 is a PG 64-16 and is from a west Texas crude source.

Biobinder Production

In order to obtain a biobinder with the suitable characteristics to be used as a comparable replacement of the conventional petroleum derived asphalt, the bio-oil produced from the fast pyrolysis unit needs to be upgraded. According to previous studies the bio-oil by itself possesses very good characteristics, similar to asphalt, at high and medium temperatures (11). However, the performance at low temperatures was not acceptable for the use in the majority of the United States as they were too stiff at low temperatures and susceptible to low-temperature cracking. The approach to try to solve this issue was to add rubber to the bio-oil.

Rubber swells in contact with some solvents and is time-temperature dependent. Additionally, the characteristics of the final binder also depend on the concentration and properties of the rubber. Therefore, the first approach to this concept was to determine whether the rubber swells or not in contact with bio-oil. Since the swelling rate directly depends on the interaction temperature, the temperature used for the biobinder production was maximum possible that minimizes the degradation of the bio-oil, i.e., 125°C. The selected concentration of rubber for the first test was 15%. The rubber was allowed to interact with the biobinder in a mechanical (Figure 2) at 1,000 rpm and small samples of the material were collected every 30 min (interaction times: 30 min, 1 h, 1 h 30 min, 2 h, 2 h 30 min, and 3 h) for visual and physical inspection. As a result, an interaction time of 1 h 30 min was initially considered adequate.

In order to determine the parameters that would produce a biobinder with the adequate characteristics, the two sources of rubber were used in two different percentages, 10% and 15%, for blending with the bio-oil.

Applying the aforementioned parameters, four biobinders were produced:

- A: 90% bio-oil plus 10% cryo rubber;
- B: 85% bio-oil plus 15% cryo rubber;
- D: 90% bio-oil plus 10% amb rubber; and
- E: 85% bio-oil plus 15% amb rubber.

Additionally, to assess the changes that occur in the bio-oil that were independent from the interaction with the rubber particles, the bio-oil was heated with agitation for 1.5 h at 125°C to obtain the aged bio-oil.

After the biobinder production, a sample was taken for subsequent analysis and testing. The remaining biobinder was separated using a centrifuge consisting of a cylindrical cage with a fine meshed wire and a cloth filter (Figure 2). The binder accelerated separation (BAS) method was developed to separate the two phases of the biobinder, namely, the residual bio-oil (Res) and the swelled rubber.

The main constituents of the separation equipment are the aforementioned filter and the centrifuge. The method consists in introducing the biobinder in the filter, place the filter in the heated residual bio-oil receptacle and centrifuge at a velocity about 2,000 rpm for 3 min. The centrifuged material (Res) could then be rheologically tested as well as a chemical analysis done and the retained material weighed to determine the rubber swelling.

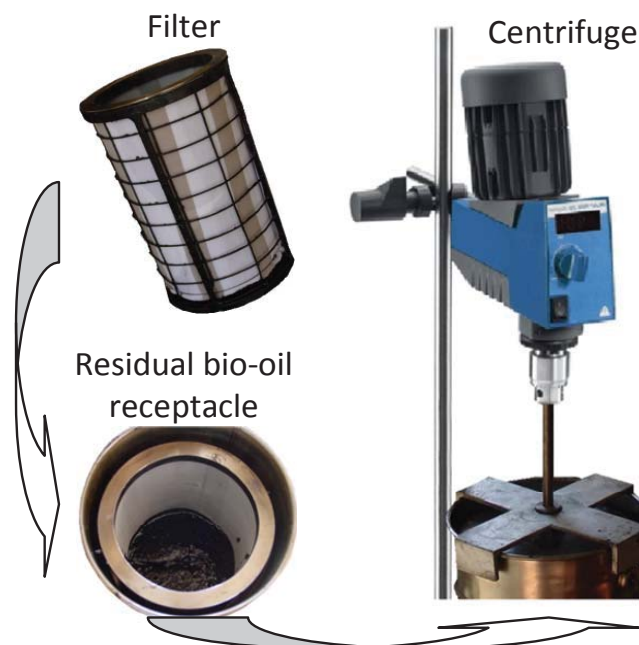


FIGURE 2 BAS method.

Chemical Analysis and Performance Grading of the Biobinders

The Res bio-oil was subjected to two aging methods in order to be possible to evaluate its grade. Therefore, first the Res bio-oil was aged by the aforementioned modified RTFOT that was performed at 120°C for 20 min. After taking a sample for analysis, the remaining material was aged using the PAV at 100°C for 2.5 h. The degassing was performed at 120°C for 30 min.

The chemical analysis of the materials was made using the Fourier transform infrared spectroscopy (FTIR) method and the resulting spectra were compared. Thus the characterized materials were: (a) the base bio-oil; (b) the aged bio-oil; (c) the ambient and cryogenic rubbers; (d) the four biobinders; and (e) the four Res bio-oils that resulted from the BAS method.

The evaluation of the critical temperatures (T_c) of the materials was performed using a dynamic shear rheometer (DSR) for high and intermediate temperatures and using a bending beam rheometer (BBR) for low temperatures.

The materials characterized in the DSR were the base bio-oil, the aged bio-oil, the four Res bio-oils (two each for each type of rubber at the two different percentages), the four RTFOT Res bio-oils, and the four PAV Res bio-oils. The BBR testing was performed only on the four biobinders.

RESULTS AND DISCUSSIONS

The results and subsequent discussion are presented in three sections: physical characteristics of the blended rubber (swelling), chemical analysis using FTIR, and performance grading of the biobinders.

Physical Characteristics of Rubber

The first important result obtained from the application of the BAS method was the amount of rubber swelling. Despite of the accepted knowledge that rubber only swells at high temperature and in the presence of solvents derived from petroleum, both crumb rubber samples swelled significantly (Table 1).

At the selected interaction temperature (125°C) for a reduced time of interaction (1.5 h), the rubber swelled an average of nearly 300% of its initial weight. The rubber swelling in the bio-oil is similar to that observed in the conventional asphalt (14, 15), been higher for the lower concentration of crumb rubber. Despite the small differences between the two types of rubber, the cryogenic rubber swelled more than the ambient one.

TABLE 1 Amount of Rubber Swelling

Samples	Crumb Rubber	% Rubber	Swelling (% of the initial crumb rubber weight)
A	Cryogenic	10	351
B		15	270
D	Ambient	10	325
E		15	228

As previously described, the biobinder production process consists of a blending and heating process, during which two phenomena occur simultaneously: (a) the diffusion of parts of the bio-oil causes the rubber to swell and (b) the volatilization of some molecules of the bio-oil increases its stiffness.

Chemical Analysis of the Biobinders

To understand the relative effects of the chemistry, FTIR of the base bio-oil was compared with that of the bio-oil aged at 125°C with agitation, mimicking the biobinder production, but without the addition of rubber (Figure 3).

The bio-oil chemical composition can be determined from a qualitative point of view by assessing Figure 3. By observing the comparative spectra, the bio-oil did not have significant changes because of aging during biobinder 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.

The match value of the base bio-oil compared with the aged bio-oil was about 0.30, which shows that there were almost no changes in the chemical composition of the bio-oil during the bio-oil to biobinder production.

Additionally, since the cryogenic and ambient rubber were provided by two different companies (one in the Chicago metropolitan area and the second in the Atlanta metropolitan area), the spectra of the two crumb rubbers were also compared (Figure 4).

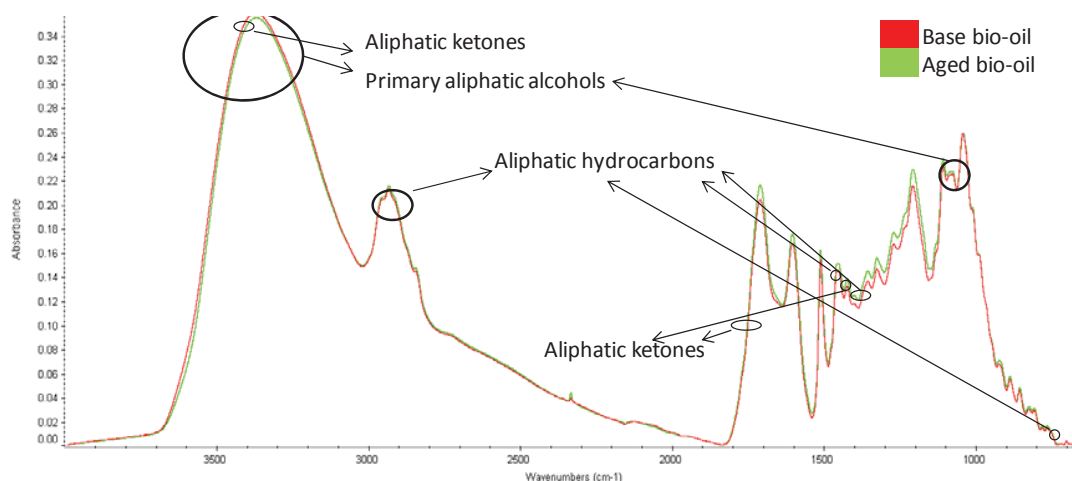


FIGURE 3 Comparative FTIR spectra of the base and aged bio-oils.

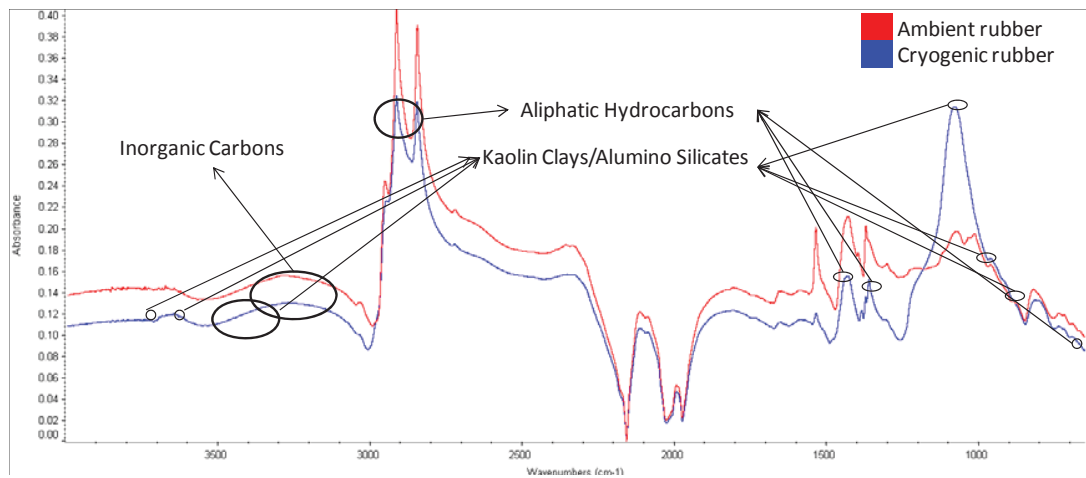


FIGURE 4 Comparative FTIR spectra of the cryogenic and ambient crumb rubbers.

As expected, the FTIR spectra of the two crumb rubbers (Figure 4) present the peaks in the same wave numbers, showing very similar constitutions. The higher difference is observed at a wave number around $1,000\text{ cm}^{-1}$ that can be identified as aliphatic hydrocarbons. The match number computed for the comparison between cryogenic and ambient crumb rubbers is around 1.0 reflecting the small differences between the two materials.

Several materials, including the swelled rubber, were obtained after the biobinder production and the application of the BAS method, namely the biobinder and the Res biobinder that result from the separation of the biobinder. The analysis of these materials can provide very important information about the way that the bio-oil and the different crumb rubber samples interact. Thus, the FTIR spectra of the referred materials were also compared (Figures 5 and 6).

In Figure 5 the spectra of the base bio-oil and the cryogenic crumb rubber were compared with the biobinder B (15% of cryogenic rubber), and Res bio-oil B.

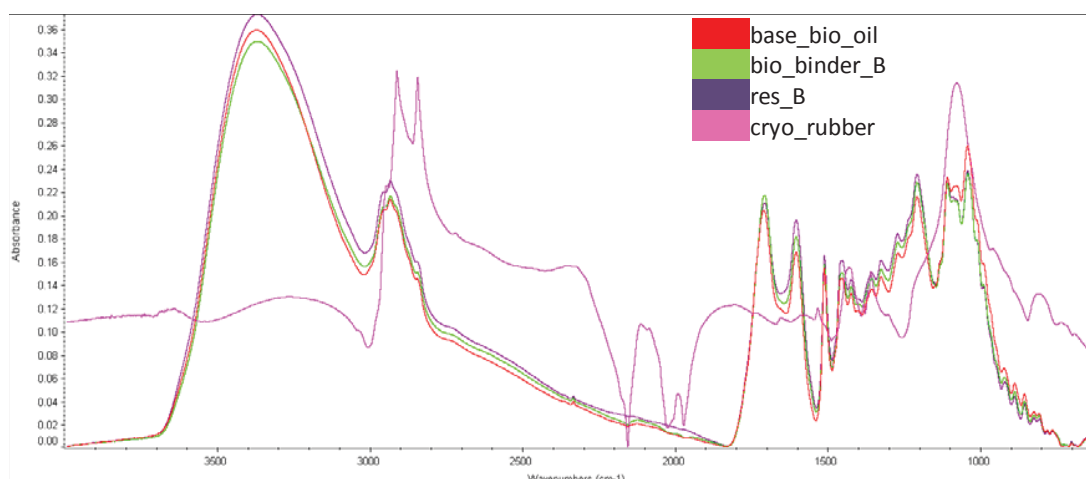


FIGURE 5 Comparative FTIR spectra of the base bio-oil, cryogenic crumb rubber, biobinder B (15% of cryogenic rubber), and Res bio-oil B.

From the analysis of the spectra presented in Figure 5, it is noticeable the transferences of parts of rubber to the bio-oil and from the bio-oil to the rubber.

Between wave numbers 800 and 1,150 cm^{-1} it is clear that some molecules disappear from the bio-oil (this is not because of volatilization as previously observed in Figure 3) meaning that these molecules are most probably diffusing into the rubber particles making them to swell. This region of the spectra can be correlated to the aliphatic hydrocarbons from the rubber, but can also be related to primary aliphatic alcohols from the bio-oil. Since these molecules decreased from the base bio-oil to the biobinder and the residual bio-oil, they are probably the molecules that facilitate the swelling process in the rubber.

These observations are consistent with the results previously reported by Gawel et al. (13), that refers 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.

Besides the movement of material from the bio-oil to the rubber, there are also many different molecules that migrate from the rubber to the bio-oil, namely the ones between wave numbers 2,800 and 3,000 cm^{-1} , that correspond to aliphatic hydrocarbons that can result from the depolymerization of the unvulcanized rubber. In the regions between 1,200 and 1,500 cm^{-1} and 3,100 and 3,500 cm^{-1} , it is obvious the transfer of some kaolin clays–alumino silicates and inorganic carbon, carbon black, from the rubber to the bio-oil, and this is an expected result since these materials represent about 30% of the tire rubber.

The same approach was adopted to assess the changes in the base bio-oil and the cryogenic crumb rubber reflected in biobinder E (15% of ambient rubber) and Res bio-oil E (Figure 6).

Comparing Figures 5 and 6 it is clear that the interaction between both types of rubber with the bio-oil is similar in all the study regions. Nevertheless, the extension of the transference between the rubber and the bio-oil is more effective when the cryogenic rubber is used.

The comparison between the FTIR spectra is a preliminary approach to the chemical transformations that occur during the biobinder production, and a more profound study is needed. However, the FTIR results are a very useful tool to show that chemical interactions are

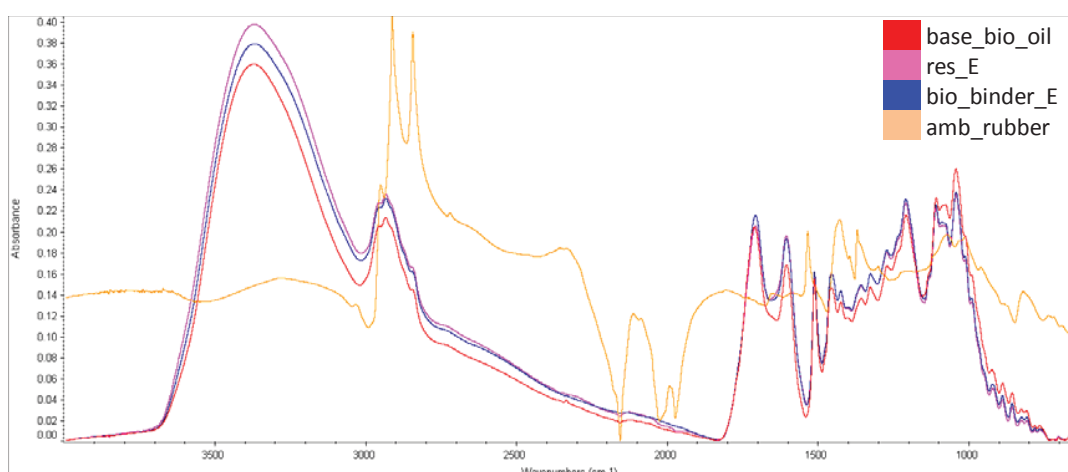


FIGURE 6 Comparative FTIR spectra of base bio-oil, ambient crumb rubber, biobinder E (15% of ambient rubber), and Res bio-oil E.

occurring and contribute to explain the results from the performance grading of the materials presented in the subsequent subsection.

The difference between the materials occurred during the biobinder production, that can be observed in their spectra, were also quantified using the similarity match method. The resulting match values, evaluated as being the variation in the spectrum of the materials compared to the bio-oil, are presented in Figure 7.

The match values presented in Figure 7 show a noticeable difference between the aged bio-oil and the Res bio-oil, demonstrating the chemical changes related to its 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 biobinder, since the rubber is still present in this material.

The match values also show that, as observed in the spectra, 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 with the rubber concentration in the biobinder, since the materials produced with a lower content of rubber are more similar. These results confirm those of the rubber swelling.

Performance Grade of Biobinders

Since the objective of this work is to develop a biobinder capable of replacing traditional asphalt derived from crude oil, it is necessary to assess the biobinder performance grade and compare it with known paving asphalt. As mentioned previously, the asphalt binder chosen as a control for this study was AAM-1 from the FHWA's Materials Reference Library. AAM-1 is a PG 64-16 and is obtained from a west Texas crude source.

The DSR critical temperatures of the AAM-1 and the biobinders at the various stages of aging used for grading paving asphalt are presented in Table 2.

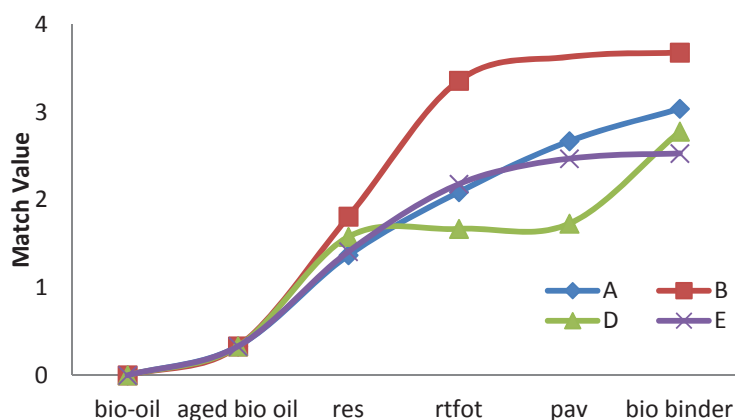


FIGURE 7 Comparative evolution of the match value between the bio-oil and the different materials assessed in this study.

TABLE 2 Critical Temperatures— T_c (°C) for Asphalt AAM-1 and the Biobinders

Bio-Oils	Control	Biobinder			
	AAM-1	A	B	D	E
Base	67.77	47.87	47.87	47.87	47.87
Aged		49.20	49.20	49.20	49.20
Res		60.51	67.50	62.58	68.12
RTFOT Res	66.68	67.76	70.66	68.06	71.57
PAV Res	20.26	22.43	30.35	26.71	32.60

The performance grade of the biobinder was determined indirectly by the analysis of the Res bio-oil, since that in the biobinder the material that effectively behaves as binder is the Res bio-oil (the swelled rubber particles provide elasticity and toughness at low temperatures but do not have binding characteristics). Furthermore, the difficulties and errors associated with the rheological analysis of heterogeneous materials are known, such as the biobinder or asphalt rubber binders with high volumetric fractions of rubber particles. In fact, the T_c determination is made using parallel plate geometry consisting of a 1- and 2-mm gap, and the particles in those binders would interfere with the movement of the plates because of their size and swelling, thus producing variability in the results. Therefore, the materials presented in Table 2 are the base and aged bio-oils before the biobinder production and the Res bio-oil separated from the biobinder by the BAS method, which was sequentially aged by the RTFOT and PAV methods.

From the results presented in Table 2 is possible infer that the bio-oil presents very similar results to the control asphalt after interacting with rubber, namely at high and medium test temperatures. Considering the high-temperature results for the Res bio-oils, it can be inferred that the high-temperature binder grades are of at least PG 58 and PG 64 for the biobinders containing 10% and 15% cryogenic rubber, respectively, whereas the biobinders containing 10% and 15% ambient rubber produced 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 to use bio-oils as binders is their behavior at low temperatures (11). Figures 8 and 9 present the results from the BBR testing of the four studied biobinders.

The different biobinders were tested in the BBR between -6°C and -24°C or at a performance criteria ranging from -16°C to -34°C . The stiffness values obtained were plotted against the test temperatures for the different binders, as shown in Figure 8. The best performance results at low temperatures were surprisingly obtained for the biobinders produced with the lower percent of rubber (10%), and the binder produced with the cryogenic rubber was better than that obtained with the ambient rubber. The performance of all binders was very good, always below a test temperature of -10°C , which corresponds to a field temperature of -20°C . The biobinder consisting of 10% cryogenic rubber has a low-temperature grade around -34°C .

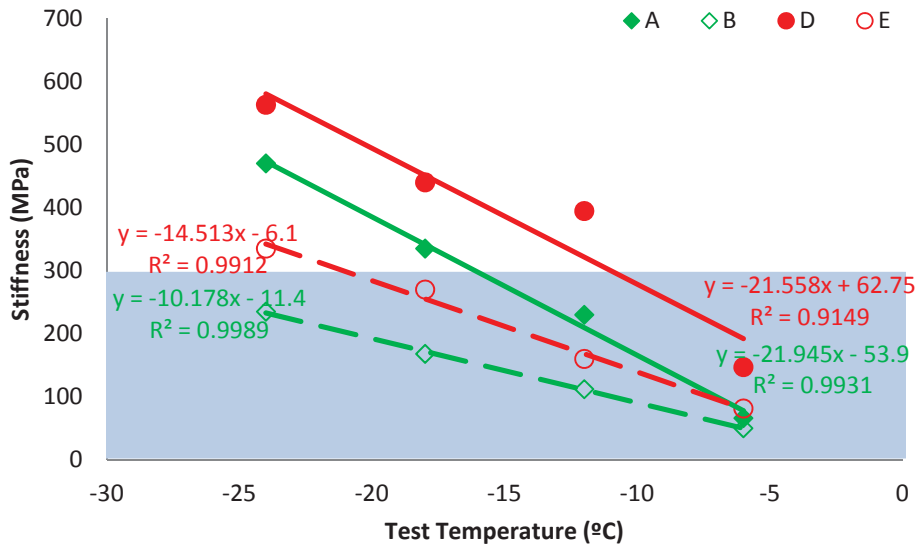


FIGURE 8 Evolution of the stiffness in the BBR test of the four biobinders with the test temperature.

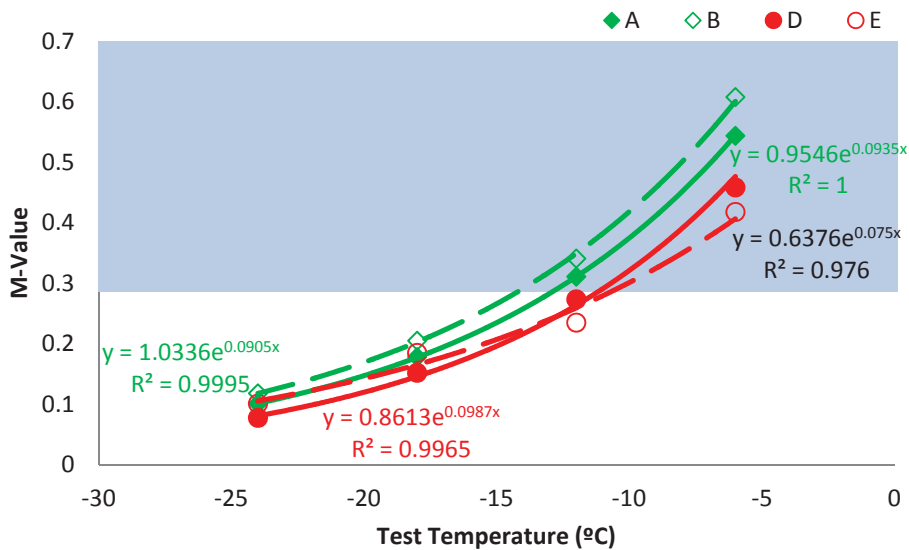


FIGURE 9 The BBR *m*-values of the four biobinders with the test temperature.

Assessing the *m*-values (Figure 9), the very good behavior of the biobinders at low temperatures maintains below the test temperature of -10°C . However, by using this parameter the specifications for the biobinder B are achieved at a maximum test temperature around -15°C (specification temperature of below -22°C). The materials with the best performance in relation to this parameter were the two biobinders produced with the cryogenic rubber. Overall, the *m*-value clearly dominates the low-temperature grade of the biobinders

Summarizing the behavior of the biobinders 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 biobinder produced with the ambient rubber are 62.6 to 20.7 and 68.1 to 20.1 for 10% and 15%, respectively. The continuous grades obtained for the biobinder produced with 10% and 15% of cryogenic rubber were 60.5 to 22.4 and 67.5 to 23.7, respectively. Therefore, the overall binder grades of PG 58-22 and PG 64-22 were obtained for the biobinders containing 10% and 15% cryogenic rubber, respectively, whereas the biobinders 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

- A biobinder consisting of fractionated bio-oil reacted with crumb rubber can produce a binder that is comparable to asphalt binders derived from crude petroleum.
- The bio-oil can successfully react with crumb rubber at 125°C , which is a substantially lower temperature than that used in normal asphalt binders, typically around 185°C .
- The rubber swells approximately three times its weight.
- The cryogenic rubber is more effective than the ambient ground rubber at producing lower temperature grades—the stiffness of the biobinders containing the cryogenic rubber is lower than that of the environmental rubber at low temperatures.
- The FTIR results indicate that the styrene-butadiene rubber from the tire rubber is likely migrating and chemically combining with the fractionated bio-oil.

This paper summarizes the successful development of a biobinder that is derived from a renewable source of material and represents a green technology. Additional work needs to be done using field trials and 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 biobinders is under way and subsequent reporting of these results is anticipated.

REFERENCES

1. Demirbas, M. F., and M. Balat. Recent Advances on the Production and Utilization Trends of Bio-fuels: A Global Perspective. *Energy Conservation and Management*, Vol. 47, 2006, pp. 2371–2381.
2. Mohan, D., C. U. Pittman, and P. H. Steele. Pyrolysis of Wood/Biomass for Bio-Oil: A Critical Review. *Energy and Fuels*, Vol. 20, No. 3, 2006, pp. 848–889.
3. Williams, R. C., J. Satrio, M. Rover, R. C. Brown, and S. Teng. Utilization of Fractionated Bio-Oil in Asphalt. Presented at 88th Annual Meeting of the Transportation Research Board, Washington, D.C., 2009.
4. Fini, E. H., S.-H. Yang, and S. Xiu. Characterization and Application of Manure-Based Biobinder in Asphalt Industry. Presented at the 89th Annual Meeting of the Transportation Research Board, Washington, D.C., 2010.

5. You, Z., J. M. Beale, H. E. Fini, S. W. Goh, and B. Colbert. Evaluation of Low Temperature Binder Properties of Warm Mix Asphalt, Extracted and Recovery RAP and RAS, and Bioasphalt. *Journal of Materials in Civil Engineering*, 2011.
6. Diebold, J. P., A. Lilley, K. Browne, R. R. Walt, D. Duncan, M. Walker, J. Steele, M. Fields, and T. Smith. Method and Apparatus for Automated, Modular, Biomass Power Generation. Community Power Corporation, EP1896368, Patent, 2008. Available at <http://www.freepatentsonline.com/EP1896368A2.html>. Accessed June 26, 2009.
7. Bridgwater, A. V., and M. L. Cottam. Opportunities for Biomass Pyrolysis Liquids Production and Upgrading. *Energy Fuels*, Vol. 6, No. 2, 1992, pp.113–120.
8. Oasmaa, A., S. Czernik, D. K. Johnson, and S. Black. Stability of Wood Fast Pyrolysis Oil. *Biomass Bioenergy*, Vol. 7, 1999, pp.187–192.
9. Demirbas, A. Conversion of Cornstover to Chemicals and Fuels. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, Vol. 30, No. 9, 2008, pp. 788–796.
10. Mullen, C. A., and A. A. Boateng. Chemical Composition of Bio-Oils Produced by Fast Pyrolysis of Two Energy Crops. *Energy Fuels*, Vol. 22, No. 3, 2008, pp. 2104–2109.
11. Raouf, M. A. Development of Non-Petroleum Binders Derived from Fast Pyrolysis Bio-Oils for Use in Flexible Pavement. PhD thesis. Iowa State University, 2010.
12. Hamed, G. R. *Materials and Compounds. Engineering with Rubber: How to Design Rubber Components*. Alan N. Gent, Hanser Publishers, Germany, 1992.
13. Gawel, I., R. Stepkowski, and F. Czechowski. Molecular Interactions Between Rubber and Asphalt. *Industrial & Engineering Chemistry Research*, Vol. 45, No. 9, 2006, pp. 3044–3049.
14. Airey, G. D., M. M. Rahman, and A. C. Collop. Absorption of Bitumen into Crumb Rubber Using the Basket Drainage Method. *International Journal of Pavement Engineering*, Vol. 4, No. 2, 2003, pp. 105–119.
15. Peralta, J., H. M. R. D. Silva, A. V. Machado, J. C. Pais, P. A. A. Pereira, and J. B. Sousa. Changes in Rubber Due to its Interaction with Bitumen When Producing Asphalt Rubber. *International Journal of Road Materials and Pavement Design*, Vol. 11, No. 4, 2010, pp. 1010–1031.