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Rebecca M. Herndon

Jay Balasubramanian

Magdy Abdelrahman
Missouri University of Science and Technology, abdelrahmanm@mst.edu

Klaus Woelk
Missouri University of Science and Technology, woelk@mst.edu

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Asphalt-Binder Mixtures Evaluated by T_1 NMR Relaxometry

Rebecca M. Herndon [1,*], Jay Balasubramanian [2], Magdy Abdelrahman [1] and Klaus Woelk [3]

[1] Department of Civil Engineering, Missouri University of Science and Technology, Rolla, MO 65409, USA; m.abdelrahman@mst.edu
[2] Department of Chemical and Biomedical Engineering, Missouri University of Science and Technology, Rolla, MO 65409, USA; jrbnpk@umsystem.edu
[3] Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65409, USA; woelk@mst.edu
* Correspondence: rmhxkc@umsystem.edu

Abstract: Asphalt pavements make up a majority of the essential transportation systems in the US. Asphalt mixtures age and degrade over time, reducing the pavement performance. Pavement performance critically depends on the aging of asphalt binder. The aging of asphalt binder during construction is traditionally modeled by rolling thin film oven (RTFO) testing, while aging during service life is modeled by pressure aging vessel (PAV) testing. Comparing these models to the aging of binders in actual pavements is limited because, to be used for current testing, binders must be separated from the pavement's aggregate by solvent extraction. Solvent extraction will, at least in part, compromise the structural integrity of asphalt binder samples. Spin-lattice NMR relaxometry has been shown to nondestructively evaluate asphalt properties in situ through the analysis of hydrogen environments. The molecular mobility of hydrogen environments and with it the stiffness of asphalt binder samples can be determined by characteristic T_1 relaxation times, indicating the complexity of asphalt-binder aging. In this study, two laboratory-generated asphalt mixtures, a failed field sample, and several laboratory-aged binder samples are compared by NMR relaxometry. NMR relaxometry was found to be able to differentiate between asphalt samples based on their binder percentage. According to the relaxometry findings, the RTFO binder aging compared favorably to the 6% laboratory-mixed sample. The PAV aging, however, did not compare well to the relaxometry results found for the field-aged sample. The amount of aggregate was found to have an influence on the relaxation times of the binder in the mixed samples and an inverse proportionality of the binder content to the primary NMR relaxation time was detected. It is concluded that molecular water present in the pores of the aggregate material gives rise to such a relationship. The findings of this study lay the foundation for nondestructive asphalt performance evaluation by NMR relaxometry.

Keywords: nuclear magnetic resonance; relaxometry; asphalt aging; aggregate; hot mix asphalt

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1. Introduction

Asphalt pavements are critical to the world's transportation infrastructure [1–6]. As of 2020, 67% of the world's roads are paved, with a vast majority using asphalt mixtures [7]. Due to this, there are many important design considerations for these mixtures depending on the construction locale and source materials to resist weather and use effects. Water degrades aggregate properties, which allows for failures to occur in the mixture [8–11]. Therefore, it is imperative that the aggregate is coated in enough binder to resist water infiltration as well as prevent brittleness. However, too much binder is also a problem that leads to permanent deformation failures [8,9,12]. This metric is tested as an asphalt weight percentage. Aging also changes the effectiveness of a binder coating on the asphalt; as the mobile maltenes escape, the more brittle the mixtures become. This leads to water affecting the structure of the aggregates and leading to freeze-thaw failures [1,8,10,13,14]. Currently, the only conventional lab testing for Hot Mix Asphalt (HMA) samples to determine the

effectiveness of asphalt percentages as well as resistance to failures involves the destructive testing of asphalt cores [11,15–20]. However, new techniques have been developed to determine adhesion characteristics between the binder and the aggregate [1,21].

Apart from the mixtures, the performance of asphalt binders is tested by mimicking the processes that cause the most aging, construction, and service life [8,22]. Construction is mimicked with the rolling thin film oven (RTFO) test. RTFO aging heats and rotates the binder to determine the amount of volatiles that will leave the binder when mixed and paved. Service life is simulated through the Pressurized Aging Vessel (PAV) test, which heats the binder for 20 h under pressure. This process simulates the oxygenation that occurs in the field over 7–10 years. After the aging of the binder is modeled with RTFO and/or PAV testing, the viscoelastic properties are compared. These parameters are then used in mixture designs to ensure proper binder performance depending on the climate of the region. Once the asphalt is placed, it is assumed that the mixture will live through its predicted service life and that failures cannot be detected until after they occur. The current and experimental methods of asphalt pavement performance assessment are based on optical analysis of existing failures or using destructive core extraction methods [11,15–20,23–26]. Therefore, the application of a chemically non-destructive method, which has predictive power, will allow for more precise evaluation and maintenance of existing roads.

NMR relaxometry has been adapted over the years for numerous applications. From determining adsorption mechanisms to evaluating binder viscosity, NMR relaxometry has been used for various purposes with great success in asphalt research [27–33]. Relaxometry is a superior method to current physical testing since solvents and heat are not needed, preserving the molecular integrity. Additionally, smaller amounts of analytes are needed. While T_2 relaxation has been used wildly for its rapid acquisition, solvents are needed to capture the fast relaxation times of solids. Therefore, this work focuses on the lesser-used T_1 relaxation, which indicates the lattice relaxation of hydrogen environments without the need for a solvent. This lattice relaxation has been used on asphalt binder blends to show some correlation to physical properties [32,33]. Little research has been conducted on asphalt mixtures and the chemical effects of the aggregate on the asphalt binder. If correlations between field and lab-aged samples can be made through T_1 NMR relaxation times, then asphalt conditions and failures can be analyzed and predicted. Additionally, comparisons between aged binders and mixtures can evaluate the applicability of binder aging modeling.

In this study, ^{1}H NMR relaxometry was used to determine T_1 times for binders and mixtures to quantify a relationship between laboratory testing of binders with real-world aging. Evaluation of the aggregate's effects on the binder and mixture parameters were also considered and tested. This is wholly new research in the asphalt and NMR fields and could provide useful information regarding the effectiveness of current aging simulation parameters, as well as provide information on the chemical environments of asphalt mixtures.

2. Materials and Methods

Mixtures of 4.5%, 5.5%, and 6% PG 64-22 were obtained from the Missouri University of Science Department of Civil Engineering, Rolla, MO, USA. PG 64-22 was chosen since it is a preferred binder used in the Midwest area [34–37]. The asphalt content of 4.5%, 5.5%, and 6% were noted as low, optimal, and high asphalt percentages, respectively. The 9/16″ coarse aggregate used in these samples was also obtained and listed as Agg. A failed 18-year-old field-aged sample was gathered from the City of Rolla, MO, USA and listed as Field. The mixtures were ground to fit into a 5 mm NMR tube. Additional preparations of the aggregate included heating the samples at 163 °C in a standard lab oven for 3 days to remove excess moisture and submerging them in de-ionized water for 3 days to maximize moisture content. The dried and submerged aggregates were labeled as Agg_d and Agg_w, respectively. Holmes-sourced PG 64-22 asphalt binder was aged by RTFO (AASHTO T240-21) and PAV (AASHTO R28-21) standards. Three samples of each type of

material were obtained. In total, 12 mixture samples along with 9 binder and 9 aggregate samples were tested. The material preparation is summarized in Figure 1; arrows indicate chronological progression and dashes indicate expected similarities between binder models and mixture samples.

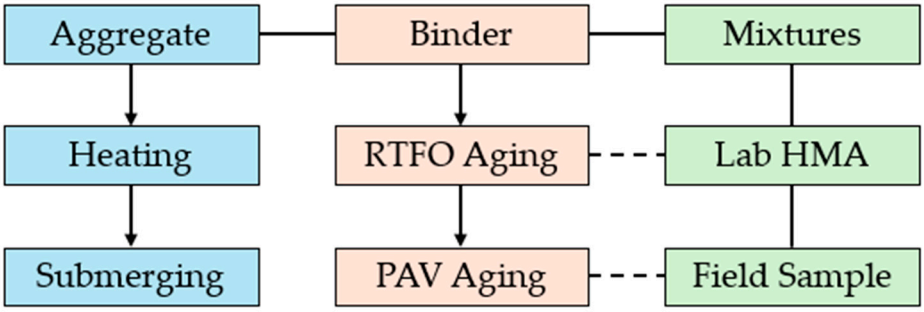
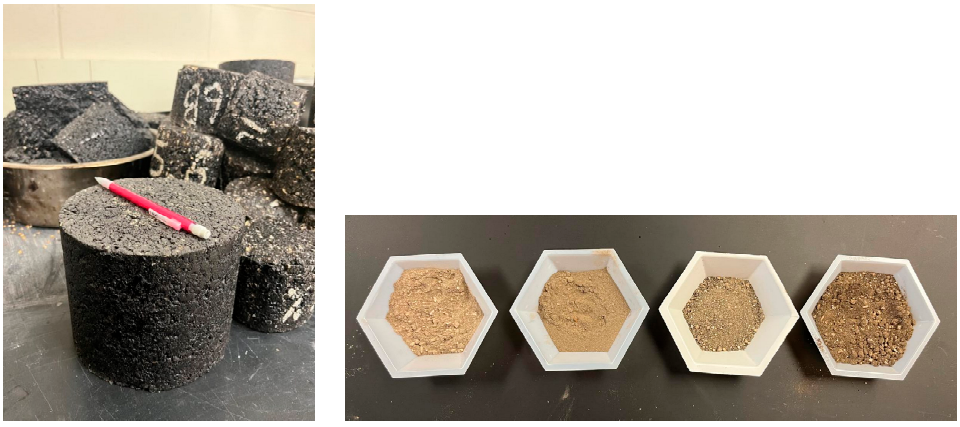


Figure 1. Research methodology.

A Bruker Avance DRX 200-MHz spectrometer was used to collect the ^{1}H NMR T_1 relaxation data. Relaxation curves were acquired at room temperature without a solvent, preserving the microstructural integrity of the binder. The SIP-R pulse sequence was used to obtain exponential decay to zero [38]. The recovery delays were equally spaced on a logarithmic scale to determine the shape of the exponential decay. Other processing variables entailed using 4 scans, 5 s pre-delay, and 100 µs dead time. The delay-dependent signals were evaluated through SigmaPlot 11's mono-, bi-, and tri-exponential decay regressions. The primary relaxation times along with the standard deviation of three samples were compared in all samples. Pictures of the compacted and crushed samples are provided in Figure 2.



(**a**) (**b**)

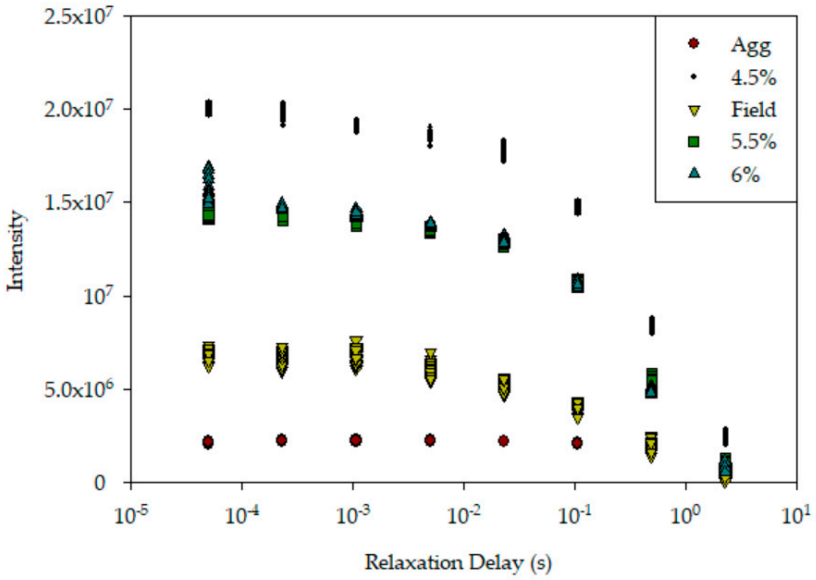
Figure 2. (**a**). Compacted HMA (**b**). Crushed HMA increasing in asphalt percent from left to right (4.5, field, 5.5, 6%).

3. Results

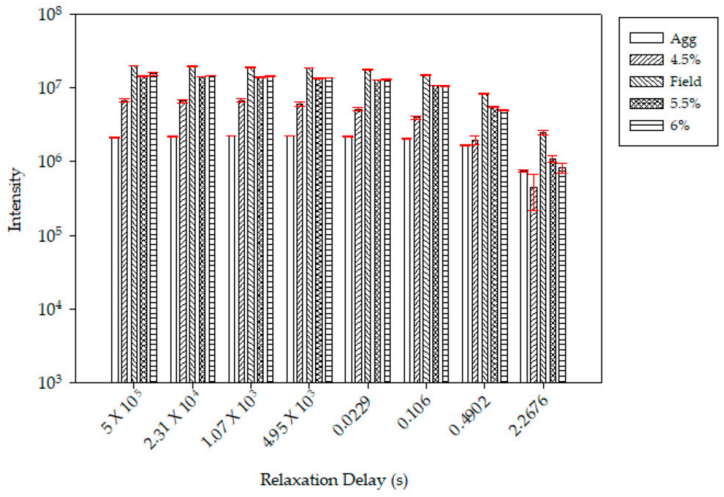
3.1. Noise

Since asphalt is not a traditional type of sample for NMR testing and because the mixtures contain paramagnetic materials, the noise of each mixture was determined as displayed in Figure 3. If the noise was high, then variation in relaxation times could be attributed to the NMR device noise. Eight logarithmically equidistant points were chosen and repeatedly tested 32 times to develop an average value for the signal intensity. The standard deviation is shown in each sample as the error bars. Each sample had a different signal intensity depending on the device parameters and concentration of hydrogen atoms. The field sample had the most error/noise. The other samples had small amounts of noise.

All samples contained higher amounts of noise at 2.2676 s since most of the signal was decayed and most noise remained. Since the aggregate had longer relaxation times, it had more signal at 2.267 s, which reduced the amount of noise. The combination of aggregate and binder did result in some noise but the impurities found in the field were most likely responsible for the high variation in signal intensity. While there were detectable levels of noise due to the NMR device, it was not enough to drastically change the shape of the relaxation curve. Any drastic changes in the average relaxation times were concluded to result from the variability of the samples, not the noise of the device.



(**a**)



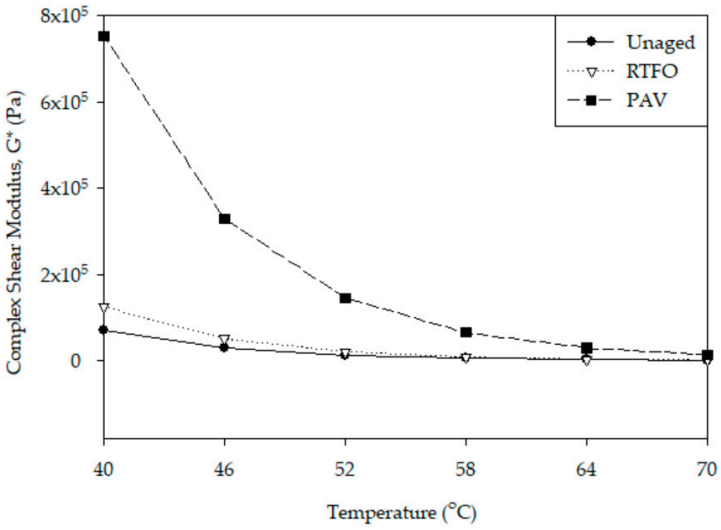
(**b**)

Figure 3. (**a**). Scatter plot of repeated 8 points (**b**). Device noise is the standard deviation (red bars) in mixtures and aggregate samples.

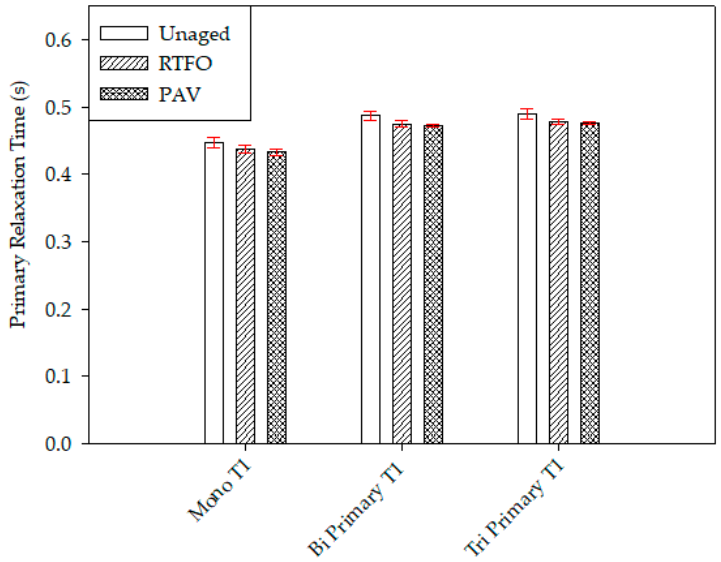
3.2. Binder Comparison

Asphalt binder was expected to have the highest density of hydrogen environments in the mixture. For comparison, laboratory-modeled binders were tested and compared. In a previous study, stiffer binders had longer relaxation times and/or more hydrogen environments [33]. In this study, the stiffnesses of the binders were different as shown in Figure 4a but their hydrogen environments were very similar, as displayed in Figure 4b.

While the binder may be stiffer, the chemical structure still contains complex hydrocarbons as described by NMR. While these structures may interact differently to cause an increase in stiffness, the hydrogen environments are similar. The binders could not be differentiated using a mono-, bi-, or tri-exponential fit due to the overlapping of standard deviations as seen in Figure 4b. While other environments could have formed, the relaxation times of the RTFO and PAV-aged samples were very similar despite having different viscoelastic properties. The major pattern detected between these asphalt binder samples was the standard deviation; as the samples were aged, the sample variability decreased.



(**a**)



(**b**)

Figure 4. (**a**). Viscoelastic comparison of binders (**b**). Primary T_1 relaxation time comparison of binders with standard deviation (red bars).

3.3. Mixture Comparison

After the primary relaxation times of the modeled binder aging were determined, the mixtures were tested. Three hot mix asphalt samples were compared by mono-, bi-, and tri-exponential fits, as shown in Figure 5. The main difference between the mixtures was the age of the sample and the asphalt binder content. The field sample came from an 18-year-old pavement while the 4.5% and 6% binder content samples were mixed in a lab

at the same time. While the field sample is aged much more than the lab mixes, the asphalt content is shown to have a large impact on the hydrogen environments of the sample. Each exponential fit changed the relation of the mixtures due to the number and intensity of hydrogen environments present. In the monoexponential fit, all hydrogen environments were summarized with one value. According to Figure 5, a monoexponential fit is insufficient while a tri-exponential fit is too much for a meaningful analysis. Since HMAs have many variable hydrogen environments, the number of relaxation times evaluated can drastically change the comparison. A clear differentiation was seen using the biexponential fit. Using this fit, the relaxation time was concluded to be inversely proportional to the amount of binder in the sample.

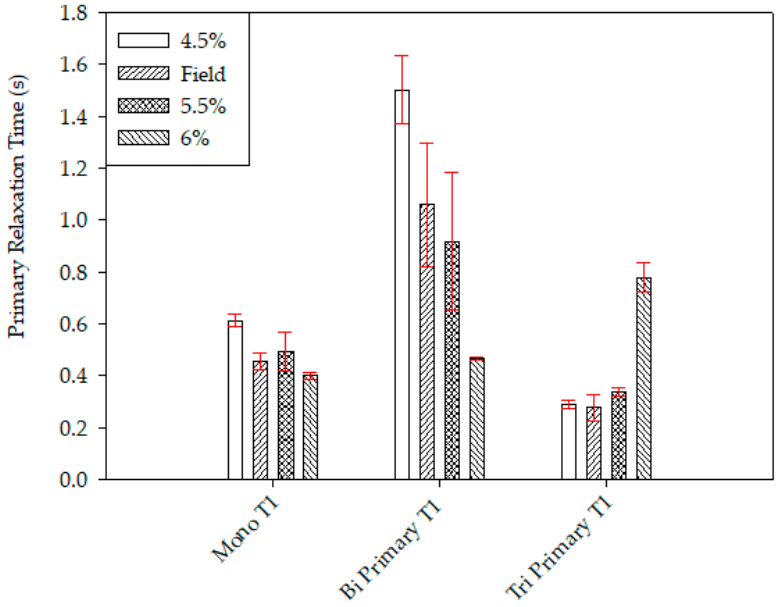


Figure 5. Comparison of the 4.5%, field, 5.5%, and 6% HMA samples with standard deviation (red bars).

The relaxation times of the 4.5%, field, and 5.5% mixtures were much longer than pure binder (0.5 s). The 4.5% and 6% binder mixtures were less than and greater than the optimum amount of binder, respectively. The field and 5.5% samples were comparable to the optimum amount of asphalt binder. Since the major difference between the mixtures was the amount of binder, the aggregate was determined to be responsible for the large increase in relaxation times. Therefore, the aggregate was also evaluated.

3.4. Aggregate Comparison

While the asphalt binder had primary relaxation times closer to 0.5 s, the mixtures contained hydrogen environments with relaxation times above 1 s. While impurities in the environment may explain the field sample, the only other component to the 4.5% and 6% samples was the aggregate. Aggregate samples were tested in normal conditions, after 72 h of drying (Agg_d), and after 72 h of submerging (Agg_w). The results are summarized in Figure 6. These hydrogen environments were expected and concluded to most likely be water. While none of the fits could differentiate between all the samples, the submerged sample could be differentiated in all fits. Since the dried aggregate cannot be differentiated from the room temperature aggregate, more intense heating may be needed. Alternatively, the water was in a stable crystalline form, resulting in a longer relaxation time.

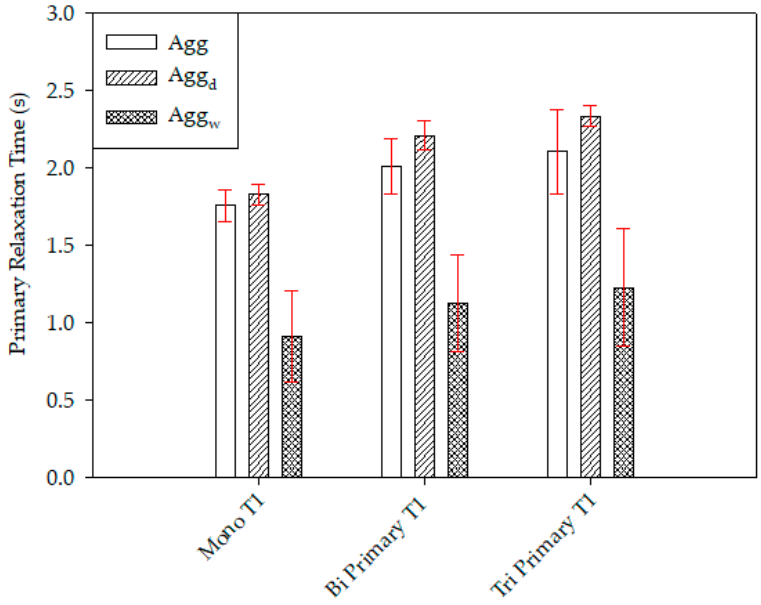


Figure 6. T_1 comparison of the aggregate in normal, dry, and wet conditions with standard deviation (red bars).

4. Discussion

The device noise of the mixtures was determined to not have a large impact on the variability of the samples. Instead, the impurities and differences between the samples impacted the larger standard deviations. Distinct and changing hydrogen environments were represented by NMR T_1 relaxation times as displayed in Figure 7. To differentiate between the asphalt mixtures, asphalt binders, and aggregates, a biexponential was chosen as the best fit. Biexponential fits have been shown previously to be the best fit for mixture samples [27].

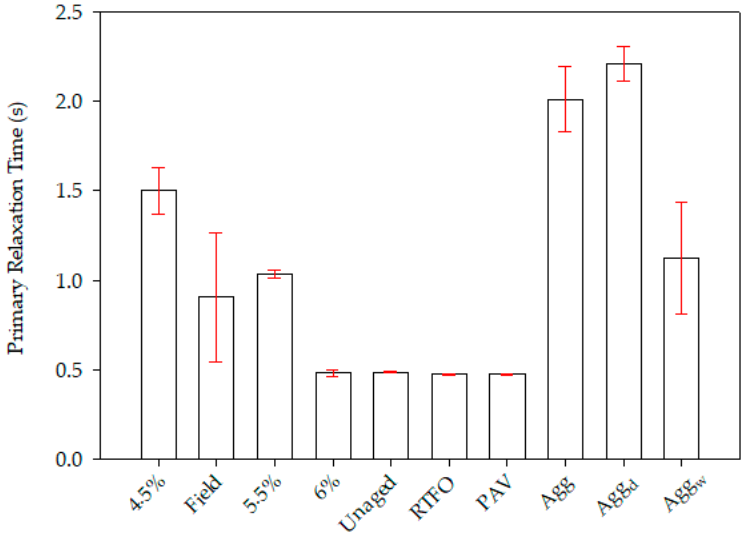


Figure 7. T_1 relaxation times from the biexponential fit of field HMA, lab HMA (4.5%, 5.5 6%), unaged binder, aged binders (PAV, RTFO), and aggregate (normal, dry, wet) with standard deviation (red bars).

4.1. Binder Aging

Traditional aging of the binder did not correlate to a significant difference in hydrogen environments. If stiffer binders are expected to have longer T_1 times, the field sample should have had the longest relaxation time. However, the 4.5% HMA sample had the

longest relaxation time around 1.5 s, then the field around 1.06 s, then the 5.5% around 0.92, and finally the 6% HMA sample around 0.47 s. The field sample may have extra hydrogen environments that better describe the aging occurring in the field but, due to sample variability, these smaller hydrogen environments have large standard deviations. There were slight differences between the binders but these differences do not account for the changes seen in the mixtures. Asphalt mixtures rely on the proper coating of aggregate. While each mixture is created by standard procedures, the aggregate may differ slightly when mixing, leading to sample variability. Sampling variability also occurs when crushing the mixture since some aggregate may be easier to breakdown than others.

Hot mixture asphalt (HMA) samples were compared with PAV- and RTFO-aged asphalt binder. The PAV-aged sample should be comparable to the field-aged sample while the RTFO-aged sample should mimic the 4.5% and 6% lab mixes. Using a biexponential fit, the T_1 times of the PAV-aged samples are incomparable with those of the field-aged sample as seen in Figure 7. This could be a result of or be in conjunction with the field sample being older than what PAV testing simulates. Additionally, the relaxation times of the field mixture were longer than the pure binder and shorter than the pure aggregate. This intermediary relaxation time could be related to the asphalt–aggregate interaction that would degrade over time from moisture damage. The RTFO-aged binder closely modeled the hydrogen environments of the 6% HMA sample but the 4.5% HMA sample was more similar to the aggregate. When a mono-exponential fit was used, the PAV binder better represented the field sample, as shown in Figure 7. Summarizing the variability of hydrogen environments with one relaxation time was more effective for some comparisons. This one relaxation time was determined by the most influential relaxation times. However, when considering the mixtures, the mono-exponential fit was not sufficient for comparison.

4.2. Hot Mix Asphalt

A bi-exponential fit could be used to compare binder content but not the age of the mixture samples. When comparing the HMA samples, the primary T_1 relaxation time was related to the amount of binder in the mixture, not the age of the sample. The 4.5% sample had the longest primary relaxation time and was designed below the optimum asphalt content. The 6% sample had the shortest primary relaxation time and was above the optimum asphalt content. The field sample would be comparable to the optimum asphalt content to meet design specifications, though a mixture design could not be obtained from the City of Rolla. The field sample relaxation time landed in the middle of the 4.5% and 6% HMA lab samples, indicating a correlation between asphalt percentage and T_1 relaxation time. The 4.5% T_1 time was closer to the time of the pure aggregate and the 6% T_1 time was closer to the pure binder samples.

The samples with aggregate, excluding the 6% HMA, had larger ranges of standard deviation. The 6% sample had a smaller standard deviation due to the excess of binder that completely filled the aggregate pores and enhanced the hydrogen signal. The other HMA samples had more variability due to the impurities in the aggregate pores. The field sample had the largest standard deviation due to the aggregate and other potential impurities such as oils, organics, and tire rubbers.

4.3. Aggregate

The aggregate was shown to have a large impact on the major hydrogen environment of the mixtures. This hydrogen environment is most likely from water, as some components of aggregates contain or easily absorb water [39,40]. While heating the aggregate did not drastically change the primary relaxation time, submerging the sample did. When submerged in water, the relaxation time was reduced. A longer relaxation may indicate a more crystalline water environment, while a shorter relaxation reflects a more mobile phase of water. This could be the difference between water trapped in the aggregate and surface moisture. The exact absorbance depends on the components in each aggregate sample, which explains the larger standard deviations of the aggregate-containing samples.

5. Conclusions

Asphalt mixtures are a necessary part of pavement infrastructure. The aging properties of asphalt mixtures are difficult to detect and predict due to traditional destructive testing methods. A nondestructive method that has indicated binder and aggregate properties is NMR relaxometry.

- NMR relaxometry was shown to be able to differentiate asphalt mixtures based on asphalt content. The average primary relaxation times of the 4.5%, field, 5.5%, and 6% HMA were 1.5, 1.06, 0.92, and 0.47 s, respectively;
- The hydrogen environments of aggregate were concluded to be from moisture in adsorbed and crystalline states. The average relaxation time of regular, dry, and wet aggregate was 2.01, 2.21, and 1.13, respectively;
- In relation to the asphalt mixtures, these water environments indicate the susceptibility to water damage and are expected to be the reason for the differences between the mixture samples as detected by NMR;
- While large differences between unaged, RTFO, and PAV binders were not detected with NMR relaxometry, asphalt mixtures, binders, and aggregates could be differentiated. When the aggregate was more prevalent, the primary relaxation time was closer to 1 s; otherwise, the primary relaxation time was close to 0.5 s.

In engineering applications, quality assurance procedures rely on optimum parameters. NMR relaxometry was found to indicate and differentiate the optimum asphalt binder in mixtures. While traditional testing would require hours of labor and large sample sizes, NMR relaxometry could save time, money, and resources. It is recommended to utilize NMR relaxometry as an innovative quality assurance method.

While this study suggests some exciting applications of NMR relaxometry for asphalt quality assurance, an in-depth analysis of HMAs and aggregate samples should be considered for further research. A limited number of binders and mixtures were considered for this study. Therefore, future studies should also use this methodology to dive further into mixture additives and aggregate impact. Quantifying the relationship between asphalt aging and T_1 relaxation times could be a possible breakthrough for monitoring and enhancing the service life of pavements by preventative detection through NMR relaxometry.

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Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Li, B.; Han, J.; Nan, X.; Li, X.; Li, X.; Zhang, P. Adhesion Characteristics and Spectroscopic Analysis of Regenerated Ultraviolet Aged Asphalt Binder Using Waste Vegetable Oil. *Case Stud. Constr. Mater.* **2023**, *18*, e01853. [CrossRef]
2. Niu, D.; Xie, X.; Zhang, Z.; Niu, Y.; Yang, Z. Influence of Binary Waste Mixtures on Road Performance of Asphalt and Asphalt Mixture. *J. Clean. Prod.* **2021**, *298*, 126842. [CrossRef]
3. Sharma, A.; Rongmei Naga, G.R.; Kumar, P.; Rai, P. Mix Design, Development, Production and Policies of Recycled Hot Mix Asphalt: A Review. *J. Traffic Transp. Eng. (Engl. Ed.)* **2022**, *9*, 765–794. [CrossRef]
4. Zahoor, M.; Nizamuddin, S.; Madapusi, S.; Giustozzi, F. Sustainable Asphalt Rejuvenation Using Waste Cooking Oil: A Comprehensive Review. *J. Clean. Prod.* **2021**, *278*, 123304. [CrossRef]
5. Fang, Y.; Zhang, Z.; Yang, J.; Li, X. Comprehensive Review on the Application of Bio-Rejuvenator in the Regeneration of Waste Asphalt Materials. *Constr. Build. Mater.* **2021**, *295*, 123631. [CrossRef]

6. Kumar, A.; Choudhary, R.; Kumar, A. Evaluation of Waste Tire Pyrolytic Oil as a Rejuvenation Agent for Unmodified, Polymer-Modified, and Rubber-Modified Aged Asphalt Binders. *J. Mater. Civ. Eng.* **2022**, *34*, 04022246. [CrossRef]
7. International Road Federation Total Road Network (by Paved and Unpaved). Available online: https://datawarehouse.worldroadstatistics.org/dashboard/checksumgraph (accessed on 20 June 2024).
8. Scholz, T. Durability of Bituminous Paving Mixtures. Ph.D. Thesis, University of Nottingham, Nottignham, UK, 1995.
9. Zaumanis, M.; Poulikakos, L.D.; Partl, M.N. Performance-Based Design of Asphalt Mixtures and Review of Key Parameters. *Mater. Des.* **2018**, *141*, 185–201. [CrossRef]
10. Yaro, N.S.A.; Sutanto, M.H.; Habib, N.Z.; Napiah, M.; Usman, A.; Al-Sabaeei, A.M.; Rafiq, W. Mixture Design-Based Performance Optimization via Response Surface Methodology and Moisture Durability Study for Palm Oil Clinker Fine Modified Bitumen Asphalt Mixtures. *Int. J. Pavement Res. Technol.* **2024**, *17*, 123–150. [CrossRef]
11. Yousefi, A.A.; Haghshenas, H.F.; Shane Underwood, B.; Harvey, J.; Blankenship, P. Performance of Warm Asphalt Mixtures Containing Reclaimed Asphalt Pavement, an Anti-Stripping Agent, and Recycling Agents: A Study Using a Balanced Mix Design Approach. *Constr. Build. Mater.* **2023**, *363*, 129633. [CrossRef]
12. Airey, G.D. Fundamental Binder and Practical Mixture Evaluation of Polymer Modified Bituminous Materials. *Int. J. Pavement Eng.* **2004**, *5*, 137–151. [CrossRef]
13. Xu, H.; Guo, W.; Tan, Y. Permeability of Asphalt Mixtures Exposed to Freeze-Thaw Cycles. *Cold Reg. Sci. Technol.* **2016**, *123*, 99–106. [CrossRef]
14. Rajib, A.I.; Samieadel, A.; Zalghout, A.; Kaloush, K.E.; Sharma, B.K.; Fini, E.H. Do All Rejuvenators Improve Asphalt Performance? *Road Mater. Pavement Des.* **2022**, *23*, 358–376. [CrossRef]
15. Xu, T.; Huang, X. Investigation into Causes of In-Place Rutting in Asphalt Pavement. *Constr. Build. Mater.* **2012**, *28*, 525–530. [CrossRef]
16. Du, H.; Ni, F.; Ma, X. Crack Resistance Evaluation for In-Service Asphalt Pavements by Using SCB Tests of Layer-Core Samples. *J. Mater. Civ. Eng.* **2021**, *33*, 04020418. [CrossRef]
17. Shen, S.; Lu, X.; Liu, L.; Zhang, C. Investigation of the Influence of Crack Width on Healing Properties of Asphalt Binders at Multi-Scale Levels. *Constr. Build. Mater.* **2016**, *126*, 197–205. [CrossRef]
18. Zhang, K.; Zhang, Z.; Luo, Y. Inspection Method and Evaluation Standard Based on Cylindrical Core Sample for Rutting Resistance of Asphalt Pavement. *Measurement* **2018**, *117*, 241–251. [CrossRef]
19. Yan, C.; Zhang, Y.; Bahia, H.U. Predicting Rutting Performance of Asphalt Mixture from Binder Properties and Mixture Design Variables. *Road Mater. Pavement Des.* **2022**, *23*, 62–79. [CrossRef]
20. Heydari, S.; Hajimohammadi, A.; Haji Seyed Javadi, N.; Jeremy Kien Chung Ng, J.; Emmanuel Kypreos, J.; Khalili, N. Modified Asphalt by Coffee Cup Fibres: An Optimum Mix Design Using Response Surface Method. *Constr. Build. Mater.* **2023**, *401*, 133005. [CrossRef]
21. Tan, Y.; Guo, M. Using Surface Free Energy Method to Study the Cohesion and Adhesion of Asphalt Mastic. *Constr. Build. Mater.* **2013**, *47*, 254–260. [CrossRef]
22. Kliewer, J.E.; Bell, C.A.; Sosnovske, D.A. *Investigation of the Relationship between Field Performance and Laboratory Aging Properties of Asphalt Mixtures*; ASTM International: West Conshohocken, PA, USA, 1995. [CrossRef]
23. Chen, D. Evaluating Asphalt Pavement Surface Texture Using 3D Digital Imaging. *Int. J. Pavement Eng.* **2020**, *21*, 416–427. [CrossRef]
24. Miller, T.; Swiertz, D.; Tashman, L.; Tabatabaee, N.; Bahia, H.U. Characterization of Asphalt Pavement Surface Texture. *Transp. Res. Rec.* **2012**, *2295*, 19–26. [CrossRef]
25. Chen, D.; Roohi Sefidmazgi, N.; Bahia, H. Exploring the Feasibility of Evaluating Asphalt Pavement Surface Macro-Texture Using Image-Based Texture Analysis Method. *Road Mater. Pavement Des.* **2015**, *16*, 405–420. [CrossRef]
26. Hu, J.; Qian, Z.; Liu, Y.; Zhang, M. Higherature Failure in Asphalt Mixtures Using Micro-Structural Investigation and Image Analysis. *Constr. Build. Mater.* **2015**, *84*, 136–145. [CrossRef]
27. Blümich, B.; Teymouri, Y.; Clark, R. NMR on the Road: Non-Destructive Characterization of the Crumb-Rubber Fraction in Asphalt. *Appl. Magn. Reson.* **2019**, *50*, 497–509. [CrossRef]
28. Shikhov, I.; Thomas, D.S.; Arns, C.H. On the Optimum Aging Time: Magnetic Resonance Study of Asphaltene Adsorption Dynamics in Sandstone Rock. *Energy Fuels* **2019**, *33*, 8184–8201. [CrossRef]
29. Menapace, I.; Garcia Cucalon, L.; Kaseer, F.; Masad, E.; Epps Martin, A. Application of Low Field Nuclear Magnetic Resonance to Evaluate Asphalt Binder Viscosity in Recycled Mixes. *Constr. Build. Mater.* **2018**, *170*, 725–736. [CrossRef]
30. Wang, Y.; Yuan, Q.; Deng, D.; Ye, T.; Fang, L. Measuring the Pore Structure of Cement Asphalt Mortar by Nuclear Magnetic Resonance. *Constr. Build. Mater.* **2017**, *137*, 450–458. [CrossRef]
31. Loise, V.; Caputo, P.; Porto, M.; Teltayev, B.; Angelico, R.; Oliviero Rossi, C. Unravelling the Role of a Green Rejuvenator Agent in Contrasting the Aging Effect on Bitumen: A Dynamics Rheology, Nuclear Magnetic Relaxometry and Self-Diffusion Study. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *603*, 125182. [CrossRef]
32. Herndon, R.; Balasubramanian, J.; Woelk, K.; Abdelrahman, M. Investigating the Physical and Chemical Effects of UV Aging on TPO-Modified Asphalt Binder. *Mod. Concepts Mater. Sci.* **2024**, *6*. [CrossRef]
33. Herndon, R.M.; Balasubramanian, J.; Woelk, K.; Abdelrahman, M. Physical and Chemical Methods to Assess Performance of TPO-Modified Asphalt Binder. *Appl. Sci.* **2024**, *14*, 3300. [CrossRef]

34. Missouri Department of Transportation EPG 450.1 Asphalt Binder. Available online: https://epg.modot.org/index.php/Category:450_Bituminous_Pavement_Design (accessed on 23 July 2024).
35. Indiana Department of Transportation. *Section 902—Asphalt Materials*; Indiana Department of Transportation: Indianapolis, IN, USA, 2024.
36. Illinois Department of Transportation. *Section 1032, Bituminous Materials*; Illinois Department of Transportation: Springfield, IL, USA, 2024.
37. Iowa Department of Transportation. *Section 4137 Asphalt Binder*; Iowa Department of Transportation: Ames, IA, USA, 2020.
38. Mayes, Z.G.; Rice, W.H.; Chi, L.; Woelk, K.H. A Robust Freeman-Hill-Inspired Pulse Protocol for Ringdown-Free T 1 Relaxation Measurements. *J. Magn. Reson.* **2023**, *352*, 107490. [CrossRef]
39. Noiriel, C.; Gouze, P.; Bernard, D. Investigation of Porosity and Permeability Effects from Microstructure Changes during Limestone Dissolution. *Geophys. Res. Lett.* **2004**, *31*, 1–4. [CrossRef]
40. Cherblanc, F.; Berthonneau, J.; Bromblet, P.; Huon, V. Influence of Water Content on the Mechanical Behaviour of Limestone: Role of the Clay Minerals Content. *Rock Mech. Rock Eng.* **2016**, *49*, 2033–2042. [CrossRef]