Effect of Heat on Virgin and UV-Aged Asphalt Binders Determined by Nuclear Magnetic Resonance Relaxometry

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Abstract

Nuclear Magnetic Resonance (NMR) spectroscopy is a well-known analytical technique that uses the excitation of nuclear spins for solving chemical structures and conformations. Relaxometry is a special field of NMR spectroscopy where information is gained about interactions of nuclear spins with their molecular surroundings. The deterioration of asphalt is a major infrastructure problem, and its rejuvenation back toward its original virgin state is an important field of research and development. The current asphalt industry relies on visual inspection on site and invasive or destructive physical methods to assess emerging asphalt failures. This study examines the chemical changes environmental factors have on asphalt binders by using NMR relaxometry. The effects heat treatments have on virgin and UV aged binder samples are quantified by the relaxation times of the organic hydrogen atoms in bituminous asphalt-binder samples. The research is aimed at providing insight into the integrity of asphalt before failures become apparent.

Introduction

The aging of asphalt is a problem that affects anyone using the roads. It especially affects those in impoverished areas where funding for road repair is lacking. Because of this many companies have tried to figure out methods to either reverse the aging, determine how far along the aging is, or slow the aging down. For example, one method proposed to reverse the effect of asphalt binder aging is the application of pyrolysis oil obtained from used car tires. Pyrolysis oil from car tires is yielded from thermal processing of tires in an anaerobic environment at temperatures between 300 °C and 1000 °C. If car tire pyrolysis oil proves to be an effective method asphalt binder rejuvenation, it would not only allow for an extended lifespan of road pavements, but also provide a valuable end-of-life solution for vast amounts of used car tires that otherwise would take up space in landfills. Inspired by a collaboration with a company providing car tire pyrolysis oil, we developed a Nuclear Magnetic Resonance (NMR) project that uses the relaxation of excited nuclear spins to thermodynamic equilibrium as a performance measure for the aging of asphalt binder. Traditional performance measures for the aging of asphalt binder include kinematic stress tests that do not consider the effects of chemical changes in the molecular structure of the binder. On the contrary, NMR relaxometry is a technique that allows for the detection of changes in the immediate chemical environment and thus can determine changes in the performance of asphalt based on chemical reactions that contribute to the aging of the binder. However, after trials with pyrolysis oil it was determined that trials with environmental factors should be considered. Common environmental factors that may initiate chemical reactions in asphalt binders are ultraviolet (UV) radiation, heat, and oxygen. For example, it is known that the oxidation of asphalt binder leads to an increased brittleness of road pavements, which in turn may cause cracking and the formation of potholes. One of these environmental factors is heat aging/rejuvenation.
Background

Other experiments have been done to try to help delay the aging of asphalt or to find ways to reverse the effects of aging on the asphalt. For example, research done by the National Institute of Technology Karnataka [1] described how they were experimenting in the upgrading of already existing tire pyrolysis oil. They did this by involving silica gel into the pyrolysis oil. Their results concluded that a different use of pyrolysis oil was improved through their testing. Another example is the research discussed by researchers at the Federal University of Ceara [2] about the use of palm oil in asphalt binders as a possible rejuvenator in asphalt. This article’s results concluded the use of palm oil in asphalt binders did have rejuvenating effects in comparison to their original asphalt binder. These articles’ conclusions show that there is the possibility of asphalt binders having rejuvenating effects as well as for the possibility of asphalt to be rejuvenated. Therefore, our research done this summer could help aid with these researchers’ research.

The NMR testing that these samples underwent is utilizing an NMR technique called relaxometry. Relaxometry is a method of NMR characterization that is nondestructive, can be used to simplify chemically dense material, and shows different hydrogen environments. Analyzing the spectra from this analytical technique will allow for insight into the chemical composition of the samples and to see how UV, heat, and oxygen aging effect the samples. This knowledge will aid in determining if pyrolysis oil can be used as a rejuvenator and if so, how effective it is. The type of relaxation utilized consists of a pulse sequence that is performed in the NMR machine. NMR relaxation consists of sending different magnetic pulses to the sample which switches the magnetic field of the sample, and it repeatedly does this until it is back in its original orientation (Figure 1). From this data we can get a better understanding of the chemical makeup of the samples analyzed.

Methodology

The samples used were prepared in a lab in Schrenk Hall at Missouri University of Science and Technology. Utilizing a lab grade oven and a heat gun, the asphalt binder was heated in a runny liquid. This allowed for a small glass rod to be stuck in the sample, this rod was then placed in a 5 mm tube. The reason for using a glass rod is because that in an NMR spectrometer, the glass will not give a signal strong enough to be picked up by the spectrometer. This will allow for the results of just the sample to be picked up. In order to get the results of the samples, macros were utilized on the NMR computer that is linked to the spectrometer. The macros used were created by prior researchers and allow for the 256 scans to be taken of the sample. Before samples were
exposed to UV, heat, and oxygen, the results of the unchanged samples were reviewed. At first some of the samples had inconsistent results, but after changing a few parameters with the inverse LaPlace transformation (ITL). The samples data points did not fit along the relaxation curve (Graph 1), but after the few adjustments made the data points fit well along the curve (Graph 2).

![Graph 1: Data Before Parameter Changes](image1.png) ![Graph 2: Data After Parameter Changes](image2.png)

The purpose of testing with different environments is to investigate if NMR relaxometry can be utilized to determine the aging of asphalt binds. The environmental affect that was tested in this research was going to be heat on virgin and UV-aged samples.

For the heat aged samples there were different methods that were tested for this. These different kinds of aging include Pressure Aging Vessel (PAV) and Rolling Thin Film Oven (RTFO). PAV testing is done to simulate use of 7-10 years with oxidation. The way this was carried out was by heating a sample of the asphalt binder in an oven for 20 hours at 100°C and 2.1 MPa pressure. RTFO testing is done to simulate mixing and compaction rather than prolonged exposure. The way this testing was done was by heating the sample in an oven for 85 minutes at 163°C. After these samples underwent heating, they were then put into the NMR machine for testing. The graphs shown below show the different relaxation curves of the samples from the RTFO testing (Graph 3) and the RTFO testing with oxygen introduced (Graph 4). The use of samples with no oxygen and with oxygen is to determine if the addition of oxygen to the heated samples changes the relaxation times for the samples.
During the testing for this experiment there were some complications that hindered the ability to gather more data. Some of these complications included issues with the NMR spectrometer. One of the issues with the spectrometer included the spectrometer overheating when samples were heated. One of the methods that was going to be tested was by heating asphalt binder samples in different heat ranges to test the relaxation curves of the samples. The way this was going to be achieved was by heating the sample in the spectrometer and then running a sample on it at the designated heat. Another method that was going to be tested was heating the sample in an industrial oven for 30 minutes at the set time and then running tests on it, but this unfortunately couldn’t happen just yet. The NMR spectrometer after trying to heat the samples then overheated and was out of commission for a while, and once it was back would not allow for samples to be heated in it.

There was also difficulty in deciding what research was going to take place and how it would be continued. There are multiple people working in this lab and it was difficult to determine who was going to do what part of the project and difficulties kept arising which caused this to go on for a few months. This caused less research to be accomplished this year than was planned, but there are plans to continue research and gather more data.

Further Research

There is more research still being done with heat tests to determine if there is an effect on asphalt binder samples. More research includes testing different heat gradients on samples where the effectiveness is different ranges. Research will also be continued by testing heat on samples that have been UV-aged, as well as more research on virgin samples with heat aging. Different methods for sample preparation will also be experimented with to determine the best method to get consistent results.

This research has proved that there is a relationship between heat and the relaxation times of asphalt binder samples. More research will be done to further develop what the relationship
between heat and the relaxation times of asphalt binders is. When this is further developed it will allow for more testing with the rejuvenation of asphalt to be determined. This is because once there is a better understanding of environmental effects on asphalt then there can be further research into how aging can be reversed. This would be beneficial because it could lead to less resources, faster road repair, and impoverished areas being able to get improved roads.

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References


Reflection

1. Describe your foundational understanding of how research is conducted in your discipline.
   a. My foundational understanding of how research in chemistry is conducted includes laboratory testing, analytical analysis, and reading articles. I knew that there were procedures needed and a lot of trial and error when conducting experiments and that it is a long and arduous process. I also understood that before you could fully know what to research that reading articles about other areas of research like what you want to research is helpful.

2. How have you expanded your understanding of the informational resources available and how to best use these resources?
   a. I know how to more thoroughly research topics to better my research and understanding of the topic I want to research. I know more sources to utilize when researching topics as well as how to use key terms to further home in on the topic I want to research.

3. Describe the knowledge you have gained regarding the fundamentals of experimental design.
   a. The knowledge I have gained includes how to formulate a course of action to research to try to keep on track. I have also gained the knowledge of how to write research papers and how to structure them. As well as creating a presentation that thoroughly explains the research I have performed and be able to explain said research in a way that is easy to understand.

4. Describe how you have learned to interpret the results of your research project.
   a. I have learned how to extract my data and plot it so that I can interpret the data. I can then determine whether the data supports my hypothesis or if it results in inconclusive areas. I have also learned what different aspects of my results mean and whether they encourage my hypothesis or not. This experience has allowed me to be more resilient when my research doesn’t go the way that I planned and has allowed me to understand the data I am collecting more.