

## POLYMER DEGRADATION OF WARM MIX ASPHALT BINDERS AT DIFFERENT AGING CONDITIONS

*Yusuf Mehta<sup>1</sup>, Luis Gaitan<sup>1</sup>, Darren Reger<sup>1</sup>, Eric Dubois<sup>1</sup>, Leslie Mccarthy<sup>2</sup>, Claude Villiers<sup>3</sup>*

*<sup>1</sup>Department of Civil and Environmental Engineering, Rowan University, Glassboro, NJ 08028*

*<sup>2</sup>Department of Civil Engineering, Villanova University, Philadelphia, PA*

*<sup>3</sup>Department of Civil and Environmental Engineering, Florida Gulf Coast University, FL*

### ABSTRACT

*Warm Mix Asphalt (WMA) has gained popularity in the past decade and a plethora of research is underway to further understand how it compares to conventional hot mix asphalt. The focus of this study is to determine if polymer degradation is significantly reduced with the lower production temperatures that WMA offers. Gel permeation chromatography was performed to quantify polymer degradation through molecular weight changes found in the polymer and organic components of asphalt binder. In regard to molecular weights, polymer degradation was decreased at lower production temperatures but greater polymer degradation occurred when WMA binders were subjected to HMA conditioning.*

**Keywords:** warm mix asphalt, binder, reclaimed asphalt pavement

## 1. INTRODUCTION

In response to the Kyoto Accord adopted in December 1997, the European Union was prompted to seek new ways to reduce carbon emissions via any median, including paving methods and practices. By 2000, the European Union (EU) had introduced various paving alternatives, one of which was warm mix asphalt (WMA) technology (1). Progress made regarding warm mix technology in European nations prompted the United States industries to make several tours and scans of the research and projects that had been implemented (1). As a result of these trips, about 25 warm mix asphalt technologies are now available in the United States and various studies exist exploring the characteristics of the various types of warm mix.

WMAT (warm mix asphalt technology) reduces the production temperature of asphalt concrete by approximately 100 °F (50 °C) to 130 °F (75 °C) (2). The decrease in production temperature decreases greenhouse gas emissions as well as health and odor problems associated with the emission (3). This drop in emission can lead to a significant cost reduction considering emission control required at asphalt plants (4). The process by which the production temperature is reduced typically varies between the various warm mix technologies that are available. Generally these processes are categorized into 4 different types (5). These include foaming agent/additives, plant foaming, viscosity reducers, and emulsions. There are more than 22 different WMA technologies currently in the United States that can be grouped into these 4 categories.

Currently on hot mix asphalt designs, design bitumen content is established by assuming that entire RAP bitumen is mobilized. In actuality, research shows that the degree of blending within a mix exhibits partial blending, which is a blending proportion in the range of 100% blending and the “black rock” effect (6, 7, 8). Therefore, the 100% assumption of mobilized RAP bitumen may result in under-asphalted mixture designs.

Since warm mix asphalt is a newer technology when compared to hot mix, little is known about the degree of blending and performance, and even less is known when RAP is added to the mixture. New Jersey Department of Transportation (NJ DOT) is currently in the preliminary steps of creating guidelines to using WMA technologies. In preparing these guidelines, a degree of blending is necessary to verify the amount of bitumen that is credited from the RAP and the degree to which it blends with the different warm mix asphalt virgin bitumens. The study will focus on quantifying how much of the RAP bitumen is actually mobilized when the pre-paving conditions such as mixing time, mixing temperature, and conditioning time are changed.

In addition to degree of blending being affected by lower temperatures, polymer degradation is also affected by lower production temperatures. Studies on polymer modified hot mix asphalt bitumens have exhibited increased stiffening as a result of aging and oxidation. (11) The purpose of the polymer degradation study will be to determine if polymer degradation is sensitive to lower production temperatures as well as WMA technologies.

## 2. OBJECTIVE

The objectives of the study is to conduct Gel Permeation Chromatography (GPC) test to determine molecular weight as a measure of polymer degradation due to short term aging, both at warm mix asphalt temperatures (133°C) and hot mix asphalt (163°C).

## 3. POLYMER DEGRADATION

In regard to polymer degradation, Lu and Isaccson (1998, 2000) concluded that the rheological properties of asphalt bitumen were adversely affected by oxidation and styrene-butadiene-styrene (SBS) degradation in SBS modified bitumens. Gel permeation chromatography (GPC) was used to measure the molecular weights of the bitumen and polymer components of the bitumen (9, 10). Results showed that as heat and oxidation increased, polymer molecular weight decreased indicating polymer degradation as a result of stabilization with chemical constituents within the bitumen. Unlike the polymer, the bitumen increased in molecular weight as a result of the increase of the high molecular weight bitumen constituent known as asphaltenes. (11)

## 4. EXPERIMENTAL PROCEDURE

### 4.1 Materials and Scope

In this study, the base bitumen consisting of a SBS-modified PG76-22 was modified with two warm mix bitumen additives, totaling two bitumens for the degree of blending study. One RAP source was used for the RAP bitumen and RAP aggregate portion of the study. A controlled gradation containing two aggregates and RAP was used.

WMAT 1 and WMAT 2 were the two warm mix bitumen additives selected for this study. Currently WMAT 1 and WMAT 2 are some of the most widely used warm mix asphalt bitumen additives in the paving industry and thus the reason for their selection in this study. A brief overview of these additives and how they operate will be provided.

WMAT 1 is categorized as a synthetic emulsifier in that it chemically reacts to blend two previously immiscible products which are the asphalt and aggregate. Typical hot mix asphalt uses higher temperatures to reduce viscosity and promote coating. WMAT 1 reduces the heat energy required and uses chemical energy to promote coating. WMAT 1 is comprised of surface active agents (surfactants), which have polar and non-polar properties. These surfactants are able to react with the non-polar asphalt and polar aggregate bringing the two together at a lower temperature. (12)

WMAT 2 is categorized as a viscosity reducer of both mixing and compaction temperature. WMAT 2 is long chain aliphatic polymethylene hydrocarbon crystalline that originates from byproducts of the Fischer-Tropsch process on natural gases or coal. The byproducts of interest are the Fischer-Tropsch waxes which have long hydrocarbon chains which lead to higher melting points. WMAT 2 is completely soluble in asphalt bitumen at temperatures higher than 248°F (120°C) and will not separate in storage. The crystalline properties at lower temperatures of asphalt provide rut resistance and can be considered an alternative to SBS modification (13).

## 4.2 Testing Matrices

The polymer degradation testing regimen is presented in Table 1. A uniform set of the three bitumens were created using the rolling thin film oven (RTFO) procedure AASHTO T-240. (21) The three bitumens were tested at three of the following aging conditions: Original bitumen with no aging; RTFO aging at 133°C to simulate short term aging at warm mix plant conditions; and RTFO aging at 163°C to simulate short term aging at hot mix plant conditions. The time in the RTFO was controlled at 1 hour and 25 minutes in accordance to specification. The number average molecular weight ( $M_n$ ) and molecular weight ( $M_w$ ) were measured from the gel permeation chromatography test.

**Table 1 Testing Matrix for Polymer Degradation**

WMAT 1	Polymer Peak		Bitumen Peak	
	$M_n$	$M_w$	$M_n$	$M_w$
Original	2	2	2	2
RTFO at 133°C	2	2	2	2
RTFO at 163°C	2	2	2	2
WMAT 2	Polymer Peak		Bitumen Peak	
	$M_n$	$M_w$	$M_n$	$M_w$
Original	2	2	2	2
RTFO at 133°C	2	2	2	2
RTFO at 163°C	2	2	2	2
PG 76-22 (Control)	Polymer Peak		Bitumen Peak	
	$M_n$	$M_w$	$M_n$	$M_w$
Original	2	2	2	2
RTFO at 133°C	2	2	2	2
RTFO at 163°C	2	2	2	2

## 4.3 Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) was used to determine the molecular weight distribution of all of the components of asphalt bitumens. The sample runs through a column capable of handling a wide range of molecular weights so that all asphalt components can be captured. Since samples must be in the liquid phase for testing, asphalt is diluted in tetrahydrofuran (THF) before running through the test column.

The membrane has a certain pore size which only certain sized molecules can pass through. Therefore, the larger molecules that cannot pass through must go around the membrane. These move at a faster rate than the smaller

molecules, and thus pass through first. The smaller molecules must pass through the membrane pores and take longer to get through.

To analyze the data, a diode array detector (DAD) is set to read at a wavelength of 254 nm. GPC gives peak readings for each molecular weight found within a sample. Using a computer program these peaks are integrated and analyzed to obtain the average and peak molecular weights. An example of the auto-integrated chromatograph is provided in Figure 2. The parameters of interest are  $M_w$   $M_n$ , and are the mean of molecular weights within the selected region. An example of this method is presented in Figure 3. The peaks of interest for this study were the polymer and bitumen peaks which are typically the first and second peaks of the chromatograph.

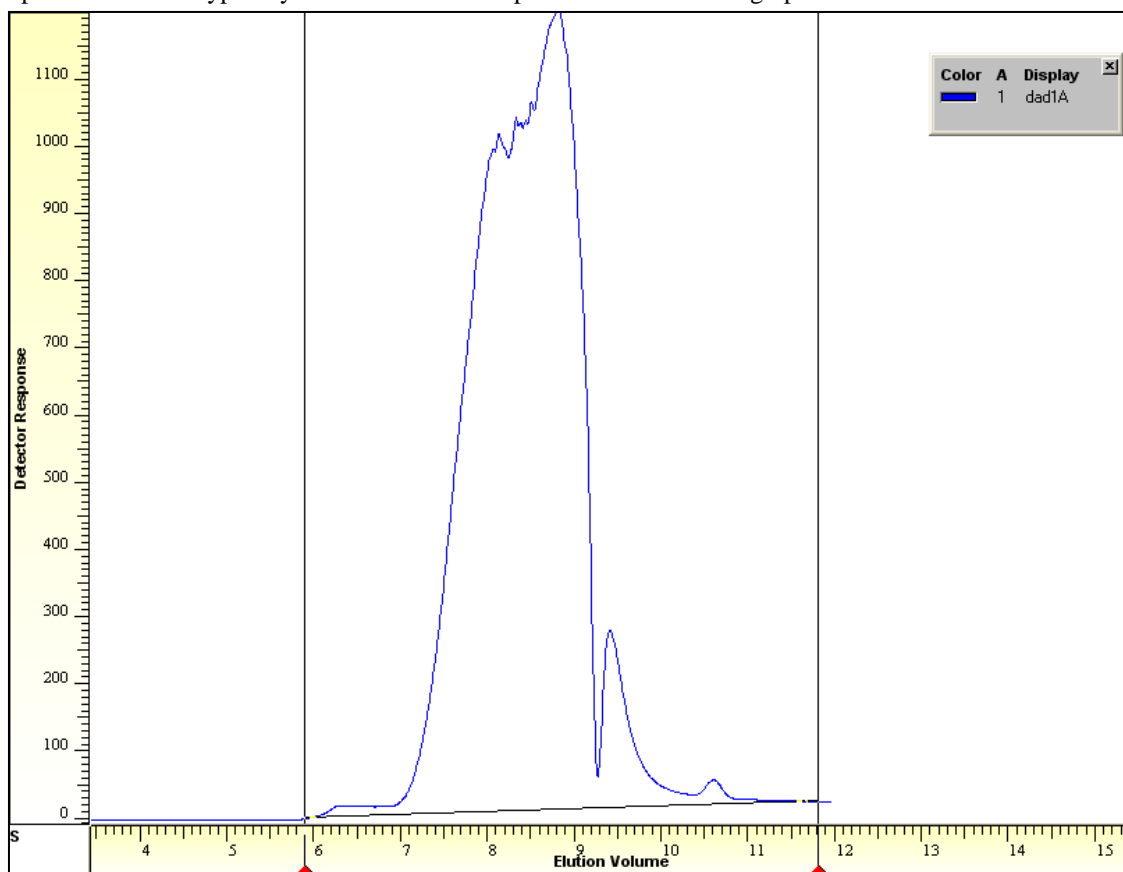


Figure 2 : Example of typical asphalt chromatograph

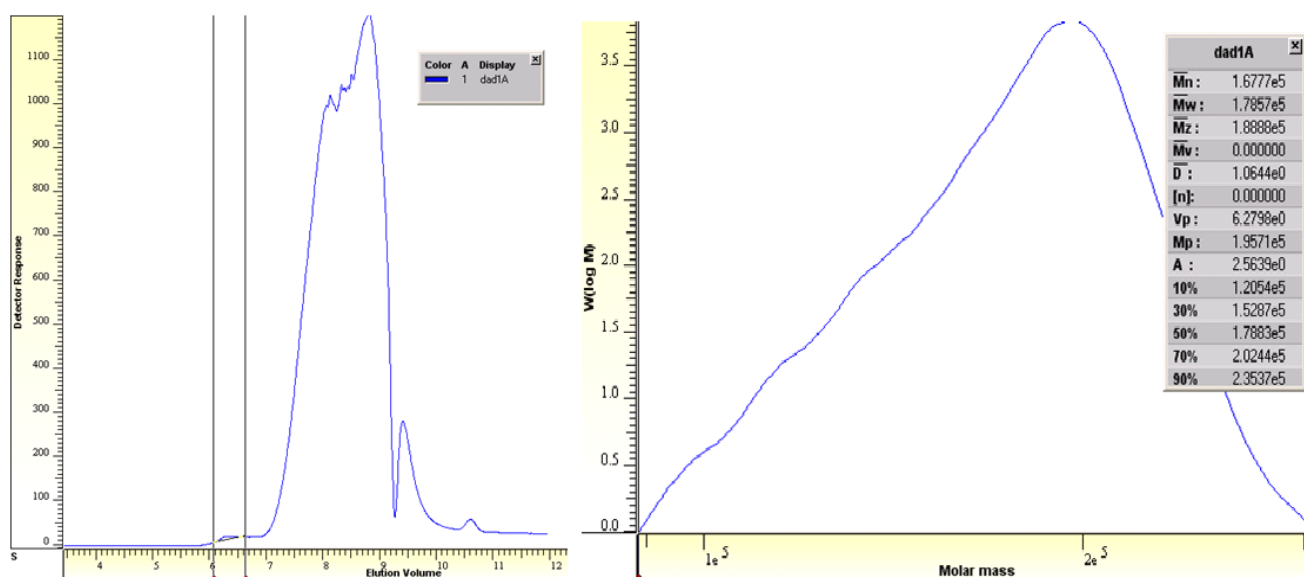


Figure 3 : a) Chromatograph with the selection of the polymer peak. b) Zoomed in chromatograph with a table providing  $M_n$  and  $M_w$  of the selected portion of the chromatograph.

## 5. GEL PERMEATION CHROMATOGRAPHY RESULTS

### 5.1 Polymer Peak

The average polymer peak molecular weights are provided in Figure 4 and 5. The WMAT 1® modified binder experienced a 16% and 13% drop in  $M_n$  and  $M_w$ , respectively, at 133°C RTFO. At a 163°C RTFO the polymer peaks fell further by 15% and 18% in  $M_n$  and  $M_w$ , respectively. Overall, WMAT 1® showed a 28% drop in both  $M_n$  and  $M_w$  when original and 163°C RTFO samples were compared.

The WMAT 2® modified binder experienced a 7% and 6% drop in  $M_n$  and  $M_w$ , respectively, at 133°C RTFO. At a 163°C RTFO the polymer peaks fell further by 9% in both  $M_n$  and  $M_w$ . Overall, WMAT 2® showed a 15% drop in both  $M_n$  and  $M_w$  when original and 163°C RTFO samples were compared.

The control showed an anomaly with increasing polymer peak molecular weight with 133°C RTFO aging. Polymer peak increased in this case by 12% and 9% in  $M_n$  and  $M_w$ , respectively, at 133°C RTFO. The 163°C RTFO samples produced an overall polymer peak drop of about 12% and 10%, maintaining the general trend.

In WMA binders, polymer peak molecular weights steadily fell from virgin condition, to RTFO condition at 133°C, and then to RTFO at 163°C. However, the average polymer peak molecular weights of control binder increased from virgin condition to RTFO at 133°C, and then decreased at RTFO condition at 163°C, before returning to its original molecular weight.

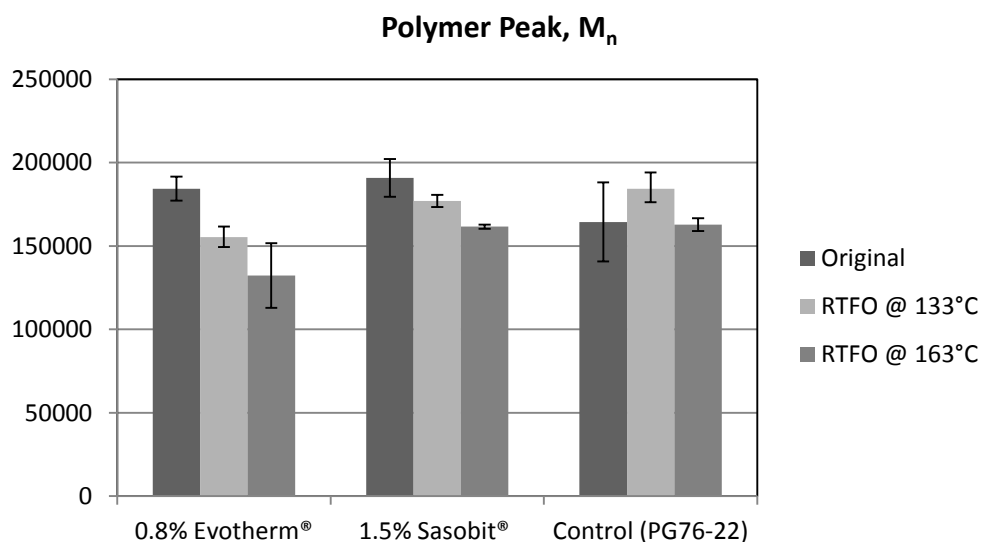


Figure 4 Polymer Peak  $M_n$  at original, RTFO 133°C and RTFO 163°C

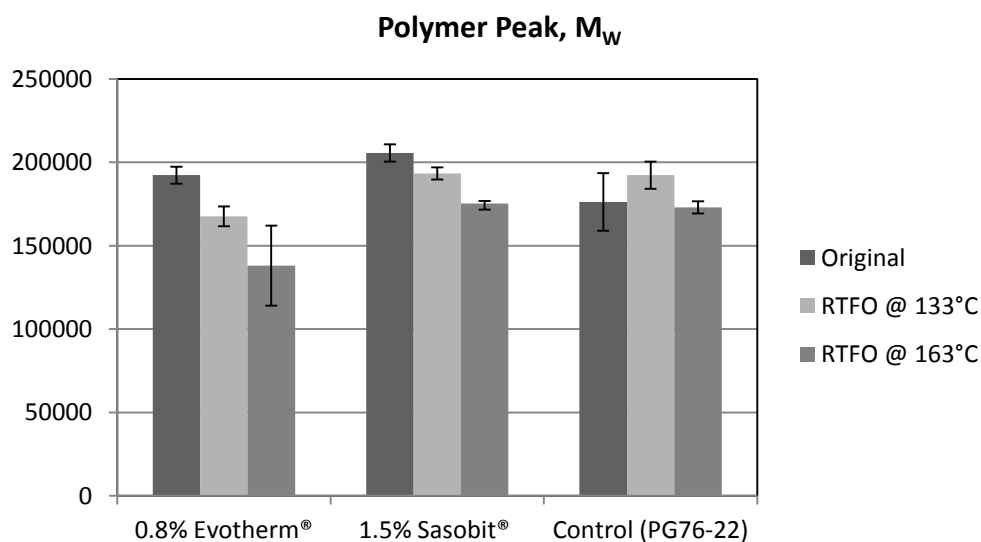


Figure 0 Polymer Peak  $M_w$  at original, RTFO 133°C and RTFO 163°C

## 5.2 Binder Distribution

The average binder molecular weights are presented in Figure 6 and 7. The binder peaks from the same molecular weight data exhibited a general increase in molecular weight although a higher degree of anomalies were apparent. WMAT 1® had greatest sensitivity while WMAT 2® exhibited the greatest anomaly.

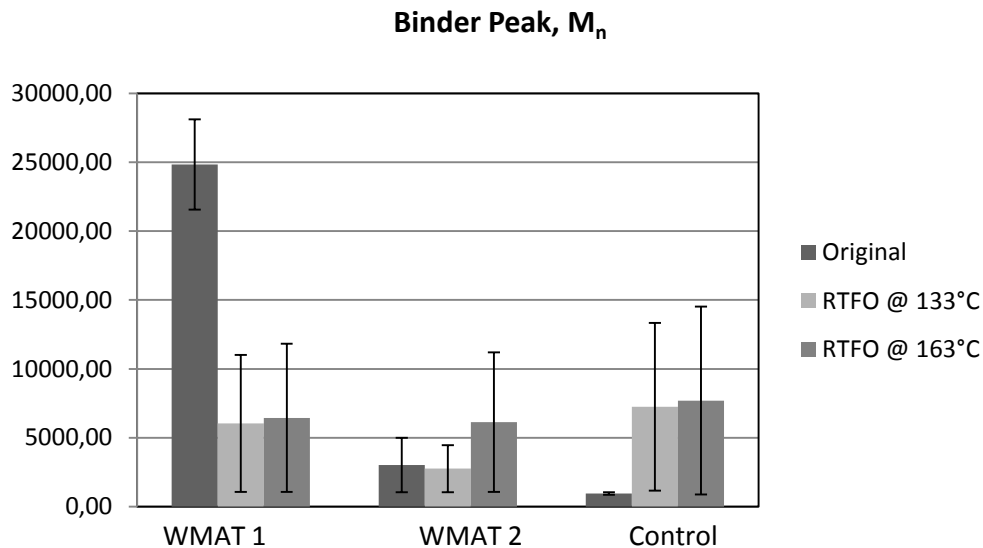


Figure 6 Binder Peak  $M_n$  at original, RTFO 133°C and RTFO 163°C

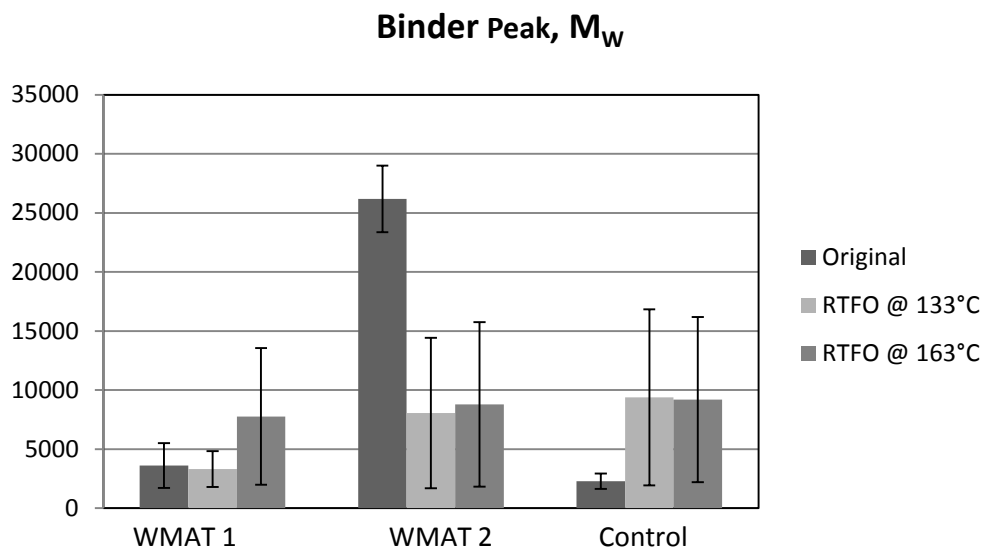


Figure 7 Binder Peak  $M_w$  at original, RTFO 133°C and RTFO 163°C

## 5.3 Statistical Analysis

In order to confirm trends, a statistical analysis was performed through SPSS 19. The main statistical function to quantify significance was the pairwise comparison which compared condition temperature (Original, 133°C, 163°C) and binder type (WMAT 2®, WMAT 1®, Control) at a 95% confidence interval.

In regard to binder type, the polymer peaks  $M_n$  exhibited no statistical differences when comparing  $M_n$ 's of all three binders. In terms of  $M_w$  a statistical difference was observed between WMAT 1® and WMAT 2® when observing polymer peaks. Another difference was seen between WMAT 1® and WMAT 2® in  $M_n$  when comparing binder peaks.

When comparing temperatures, differences were calculated between original and RTFO 163°C samples in both  $M_n$  and  $M_w$  measurements while no differences were observed between original and RTFO 133°C samples. The binder peaks of these these varying aging conditions exhibited no significant differences.

## 6. DISCUSSION

The binder peak showed a general increase in molecular weight which is a result of the aging process which increases the asphaltene content of the binder (Sugano, 2009). It can be seen that WMA conditioning temperatures resulted in less binder aging and stiffening which is an ideal paving condition and lowers the possibility of fatigue cracking. In the WMAT 2® binder, a high molecular weight value was observed which can likely be attributed to the wax composition of the binder in its original state. Further information would lie out of the scope of this study. Overall, no significant differences were apparent in binder peaks in most cases.

In considering the statistical analysis, it was observed that original state and RTFO aged at 133°C binders were not statistically different which would indicate that the lower production temperature simulated in the lab reduced polymer degradation and was able to maintain an original state better.

## 7. CONCLUSIONS

The conclusions of the study follow:

1. WMA is a viable option for asphalt pavement in trying to reduce the degree of polymer degradation.
2. Original state and RTFO 133°C results conclude that WMA production temperatures maintain the original state of binders.
3. WMAT 2® modified WMA binders are more resistant to polymer degradation than WMAT 1® binder.
4. Non WMA modified binders are more resistant to polymer degradation.

## 8. ACKNOWLEDGEMENTS

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