

Blending Efficiency of Asphalt Mixtures Containing Recycled Asphalt Pavement and Shingle

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16. Abstract This study aims to address blending issues in warm mix asphalt (WMA) and hot mix asphalt (HMA) containing recycled asphalt pavement (RAP) and recycled asphalt shingle (RAS). Two fingerprinting methods of asphalt covered in this study are gel permeation chromatography (GPC) and atomic force microscopy (AFM). Laboratory testing methods for determining blending efficiency employed in this study include determining aged binder mobilization rate and staged extraction method. The factors affecting the blending efficiency include mixing time, mixing temperature, aged binder content and effect of WMA technology. Major conclusions from the study are summarized as follows: 1) There existed a strong correlation between the percentage of large molecular size (LMS) and the complex modulus (G^*) of asphalt binder based on the comparison of GPC and dynamic shear rheometer (DSR) test results. As mixing time and temperature increased, more blending occurred in the RAP/RAS mixture. The size of virgin aggregate did not affect the blending efficiency of RAS in pavement mixtures. 2) "Blending Charts" could be generated between the RAP/RAS binder content in the blend with the large molecular size (LMS%) defined by molecular weight and the relations were found to be linear. The mobilization rate of RAP binder decreased with the increase of the RAP percentage in the mixture. RAS binder mobilization rate increased with RAS percentage growing from 2.5% to 5%, but decreased with RAS percentage passing 5%. The highest mobilization rate was around 61% and found on 5% RAS mixture while the mobilization rate of mixture containing 10% RAS could be as low as 36%. 3) Trichloroethylene (TCE) was found to be the most effective solvent used in the study for staged extraction. The binder coating on the raw RAP and RAS aggregates was proved to be homogeneous and the layer stripping did occur in a well-controlled composite binder system. Based on well-designed staged extraction and GPC analysis, binder film coating virgin aggregates was approximately homogeneous in RAP mix, while a non-homogeneous binder was generated on RAP aggregates. A potential composite binder system was found coating the virgin aggregates in RAS mix. The diffusion study shows that within the mixture storage time, binder diffusion can be accomplished in both warm and hot mixes containing RAP, indicating old binder mobilization, rather than binder homogeneity, could be more critical in RAP mix. The binder diffusion in RAS mix was captured in a very slow rate. 4) WMA additives yielded higher blending ratio than control mix produced at 135°C, but the temperature of 165°C still produced the mix with the highest blending ratio value. This indicates that a concern still exists over asphalt blending even if WMA additives are used. Foaming technology yielded a higher blending ratio, indicating foamed WMA may yield a higher blending than regular HMA. It was also found that temperature rather than coating is more critical in RAS blending. 5) According to the observations, AFM proved to be capable of differentiating virgin binder from RAS binder in terms of microstructures. The microstructures of tear-off RAS binder was found to be temperature-dependent, but changed very little within the range from 60°C to 180°C. Virgin binders selected in this study could not blend through a RAS binder layer of 300 μm within 30 minutes at 180°C. On the basis of observations on the interfacial zone, RAS binder was found to be "mixing" but not "blending" in a mixing zone of 25 to 30 μm .					
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Executive Summary

The current tendency in paving industry is to increase the use of recycled asphalt pavement (RAP) and recycled asphalt shingle (RAS). TDOT Materials and Test Division has been collaborating with the University of Tennessee conducting studies of recycling RAP/RAS into hot-mix asphalt (HMA) or warm mix asphalt (WMA). The studies have shown that one of the big advantages of WMA is its capability of incorporation of higher percentages of RAP/RAS. However, one of the reasons that limit the high recycled amount is the unknown blending between virgin and RAP/RAS binders. This study aims to address blending issues in WMA and HMA containing RAP and RAS. Major research activities are summarized as follows:

- 1) Two fingerprinting methods of asphalt covered in this study include gel permeation chromatography (GPC) and Atomic Force Microscopy (AFM). GPC was used to determine aged binder concentration in and blend. AFM was used to directly detect the blending process between aged binder and virgin binder.
- 2) Laboratory testing methods for determining blending efficiency employed in this study include determining aged binder mobilization rate and staged extraction method. Using these testing methods, the factors affecting the blending efficiency include mixing time, mixing temperature, aged binder content and WMA technology. The effects of these factors were investigated in this study.

Based on the results from the study, the following conclusions can be drawn:

- 1) As mixing time and temperature increased, more blending occurred in the RAP/RAS mixture. The size of virgin aggregate did not affect the blending efficiency of RAS in pavement mixtures. The most efficient blending of RAS may occur at approximately 5% RAS content. There existed a strong correlation between the percentage of large molecular size (LMS) and the complex modulus

- (G*) of asphalt binder based on the comparison of GPC and the dynamic shear rheometer (DSR) test results.
- 2) A new LMS% related to molecular weight distribution derived from GPC analysis, was developed to differentiate the RAP/RAS and virgin binders as well as their blends. “Blending Charts” could be generated between the RAP/RAS binder content in the blend with the newly defined large molecular size (LMS%) and the relations were found to be linear. The results generated from “blending charts” shows that RAP binder mobilization rate decreased with the increase of the RAP percentage in the mixture with mobilization rates close to 100% at low RAP mixtures (10% and 20%), but dropping from 73% to 24% with RAP percentage varying from 30% up to 80%. RAS binder mobilization rate increased with RAS percentage growing from 2.5% to 5%, but decreased with RAS percentage passing 5%. The highest mobilization rate was around 61% and found on 5% RAS mixture while the mobilization rate of mixture containing 10% RAS could be as low as 36%.
 - 3) It was found that trichloroethylene (TCE) was the most effective solvent used in the study for staged extraction. The binder coating on the raw RAP and RAS aggregates was proved to be homogeneous and the layer stripping did occur in a well-controlled composite binder system. A well designed step-extraction method with progressive wash times could replace equal-time extraction method, and yielded better analysis. Based on well-designed staged extraction and GPC analysis, it was found that, in RAP mix, binder film coating virgin aggregates was approximately homogeneous, while a non-homogeneous binder was generated on RAP aggregates. A potential composite binder system was found coating the virgin aggregates in RAS mix. The diffusion study shows that within the mixture storage time, binder diffusion can be accomplished in both warm and hot mixes containing RAP, indicating old binder mobilization, rather than binder

homogeneity, could be more critical in RAP mix. The binder diffusion in RAS mix was captured in a very slow rate. It was suggested that old binder activation and binder homogeneity can both be critical for RAS mix.

- 4) WMA additives yielded higher blending ratio than control mix produced at 135°C, but the temperature of 165°C still produced the mix with the highest blending ratio value. Foaming technology yielded a higher blending ratio, indicating foamed WMA may yield a higher blending than regular HMA. It was also found that temperature rather than coating is more critical in RAS blending. Finally, the mix produced with coarse virgin aggregates and medium RAP may not be sensitive enough to test the effect of WMA additives on blending, while the mix with medium virgin aggregates and fine RAP was more effective.
- 5) The blending of virgin-RAS binder was first observed in this study by AFM. According to the observations, AFM proved to be capable of differentiating virgin binder from RAS binder in terms of microstructures. The microstructures of tear-off RAS binder was found to be temperature-dependent, but changed very little within the range from 60°C to 180°C. Virgin binders selected in this study could not blend through a RAS binder layer of 300 µm within 30 minutes at 180°C. On the basis of observations on the interfacial zone, RAS binder was found to be “mixing” but not “blending” in a mixing zone of 25 to 30 µm.

Recommendations

On the basis of the conclusions obtained in this study, the following recommendations can be made:

- 1) Better tracking materials, other than the round aggregate, could be used for the quantitative evaluation of the old binder mobilization rate. The texture, size and other surface properties of the tracking materials could be considered as influencing factors.

- 2) It is recommended that new methods be developed to quantify the binder homogeneity through AFM. Statistical methods could be used to track the numerical change of the domains. Layered system with well controlled binder film thickness is recommended to characterize the diffusion coefficient of the virgin binder through the old binder.
- 3) Neutron scattering are also recommended for use in blending research. Samples with different blending degrees may express different inner structural properties and might be revealed by neutron scattering detection. Additionally, neutron scattering samples will not go through any destructive damage during preparation and testing processes.
- 4) Test methods designed in this study have been proved to be useful in laboratory mixing. However, their effectiveness in plant mixtures still need to be further verified. In the follow-up study, the test methods for blending efficiency may be modified according to needs in future plant mixture study.

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CHAPTER 1 INTRODUCTION

1.1 Problem Statement

This proposed research project is the continuation of the TDOT-sponsored study entitled “Laboratory and Field Evaluation of Warm Mix Asphalt Pavement in Tennessee”. TDOT Materials and Test Division has been collaborating with the University of Tennessee conducting studies of recycling recycled asphalt pavement (RAP) and/or recycled asphalt shingle (RAS) into hot-mix asphalt (HMA) or warm mix asphalt (WMA). The studies have shown that one of the big advantages of WMA is its capability of incorporation of higher percentages of RAP/RAS. However, when RAP/RAS is recycled into WMA or HMA mixtures, one key question needs to be answered: how much of the aged asphalt binder in RAP and/or RAS can be blended into virgin asphalt? What is the role of RAP/RAS in asphalt mixtures? Do they act as black rock or the aged binder can be fully blended into virgin binder? To fully understand the role of RAP/RAS in asphalt mixtures and to maximize the use of RAP/RAS in WMA, these questions have to be answered.

In addition to blending efficiency of RAP and RAS, one particular concern regarding RAP limits in current TDOT specification will be identified and explored. Specifically, TDOT specification allows higher percentages of RAP in mixtures made with non-modified asphalt binders (PG 64-22 and PG 67-22), which are mainly used in relatively thin pavement structures in state routes, whereas higher restrictions are applied to the mixtures made with modified-asphalt binder (such as PG 76-22), which are typically used for thick pavement structures such as interstates. The performance of these two types of pavements with respect to RAP content is of great concern and interest to TDOT and will provide a sound basis for more reasonable limitations and restrictions of

RAP usage. Currently, recycle of RAS into asphalt mixtures is gaining more and more attention in asphalt paving industry. The blending efficiency issue is of paramount importance to highway agencies.

This research will significantly benefit the economy of the State of Tennessee through use of both WMA and RAP technologies in flexible pavements:

- (1) Less fuel consumption to heat aggregates due to lowered mixing and placement temperatures;
- (2) Reduced emission and improved working environments;
- (3) More RAP/RAS may be recycled into asphalt mixtures;
- (4) Significant cost saving for asphalt mixtures;
- (5) More asphalt pavements can be rehabilitated or built with the same budget;
- (6) Beneficial to the environments in Tennessee due to the use of WMA and RAP/RAS technologies.

1.2 Objectives

The objectives of the proposed research are to:

- (1) Fingerprint the liquid virgin asphalt, RAP, RAS, and recycled asphalt mixtures containing RAP/RAS using available chemical testing techniques.
- (2) Develop a laboratory testing method to determine the blending efficiency of recycled asphalt mixtures containing RAP/RAS.
- (3) Investigate the effects of different blending efficiencies on the laboratory performance of recycled asphalt mixtures containing RAP/RAS.

1.3 Scope of Study

The scope of the research work includes:

- To complete a synthesis of literature review and state DOT survey on the use of RAP and/or RAS in asphalt mixtures;
- To fingerprint the liquid virgin asphalt, RAP, RAS, and recycled asphalt mixtures used by TDOT with available chemical testing techniques;
- To develop a practical procedure to determine the blending efficiency of RAP/RAS in recycled asphalt mixtures;
- To investigate into different factors affecting blending efficiency and subsequently their effects on laboratory performance of recycled asphalt mixtures.

CHAPTER 2 LITERATURE REVIEW

2.1 Blending Efficiency Studies

A major cause of concern in the reuse of asphalt binder from a reclaimed asphalt source such as recycled asphalt pavement (RAP) and/or recycled asphalt shingle (RAS) is whether or not the reclaimed binder truly blends with the virgin binder. “Black rock” theory is based on the premise that the RAP may actually perform as nothing more than an aggregate. While this may provide some use of the RAP as a recycled aggregate, the major economic savings come from the reuse of the RAP binder. However, if the stiff, highly oxidized binder does not truly blend with the virgin binder in the mixture, the use of blending charts commonly used in pavements where RAP is included is unnecessary [1, 2].

Blending charts are commonly used in practice as a guide to safe addition of RAP. The premise of these charts is that up to a certain percentage of RAP can be added without needing to decrease or “bump” the binder performance grade in order to counteract the stiff, oxidized RAP binder [3]. Common practice is to add up to 15% RAP without changing binder grade and between 15-25% RAP by only reducing one binder grade with respect to both high and low temperatures. Beyond 25% RAP a blending chart is required to estimate the binder grade necessary to create a mixture that will perform to SuperPave standards. The use of blending charts in current practice was further supported by NCHRP 9-12 conducted by McDaniel et al. [2] which concluded that partial blending does occur to a significant extent. In order to further refute the “black rock” theory, Soleymani et al [4] simulated a “black rock” condition. The researchers created three mixtures, denoted Case A, Case B, and Case C. The black rock scenario, Case A, was created by extracting the binder from a RAP and adding only the recovered aggregate to a

new mixture of virgin aggregate and virgin binder. Case B is considered a “true” mixture, where the RAP is added directly to the mixture with the virgin aggregate and virgin binder. The “total blend”, Case C, was created by mechanically blending the virgin binder and recovered RAP binder and adding it to the virgin and RAP aggregate to make the mixture. All three cases were evaluated using the SuperPave Shear Tester (SST) with frequency sweep, simple shear, and repeated shear at a constant height testing scenarios. The researchers evaluated compared the results of the three cases statistically and found that at a 10% RAP content none of the cases were differentiable. However, at 40% RAP content, 45% of the “true” RAP mixtures (Case B) performed similarly to the 100% blend (Case C), while only 5% performed similarly to the “black rock” scenario (Case A). The remaining 50% of the mixtures didn’t not perform similarly to either Case A or Case C. This study concluded that RAP does not behave as a black rock considering at a high RAP content (40%) the mixture performed similarly to that of a 100% blend. The researchers also state conclude that at least partial blending occurs in almost all cases. Additionally, an important conclusion is that the suggestion that up to 15% RAP can be added without a need to resort to blending charts is reasonable on the basis of this study.

Other attempts to address the blending efficiency question have been made. McDaniel et al. [5] address this issue by using the “Bonaquist Approach” [6] which considers pavement volumetrics and their relationship to the dynamic modulus (E^*) of the mixture. The Hirsch Model is used to create an estimated E^* master curve. Twenty-four mixtures were considered utilizing multiple contractors. Mixtures were created mixes using a virgin Performance Grade (PG) 64-22 asphalt binder with 0%, 15%, 25%, and 40% RAP contents. Additionally, a softer PG58-28 virgin binder was used at 25% and 40% RAP content. Each of the contractors made efforts to keep the mixture gradation as close as possible to their counterparts. The binder was recovered using n-propyl bromide and the complex modulus (G^*) was investigated using the Dynamic Shear Rheometer (DSR) and low temperature performance was tested using the Bending

Beam Rheometer (BBR). These values were used in the Hirsch Model to estimate the E^* master curve on the assumption that the recovered asphalt could be considered a 100% blend between the virgin binder and RAP binder. The E^* master curve was then generated in the lab through performance testing for each of the mixtures. If the estimated E^* matched the mixtures true E^* , the mixtures were considered to be 100% blended. Out of 21 samples containing RAP only three were considered to have poor blending and one had partial blending.

A similar study was conducted by Mogawer et al. [7] looking specifically at 9.5 mm and 12.5 mm SuperPave mixtures. These mixtures comprised of PG58-22 binder containing 30% and 40% RAP, PG64-22 binder containing 0%, 20%, 30%, and 40% RAP, and PG52-34 and PG64-28 binder mixtures containing 0%, 20%, 30%, and 40% RAP. Samples were collected from New Hampshire, Vermont, and New York. The Christenson-Anderson model was used to develop a master curve for the extracted and recovered binders from each mixture. These estimated master curve was then compared to the E^* master curve of the mixture to determine the degree of blending. A conclusion of this study focused on the handling, mixing, and storage of the material in terms of its impact on the mixture stiffness and cracking properties. The authors state that blending efficiency seemed to be impacted by the discharge temperature of the mixture from the silo.

2.2 Gel Permeation Chromatography (GPC)

Many works have been conducted that show the relationship between the chemistry chemical composition and the mechanical behavior of the asphalt binder. GPC is an analytical chemistry technique that yields the molecular weight distribution of a given medium in solution. Figure 2-1 shows a simplified example of asphalt binder in solution passing through a single multi-pore GPC column.

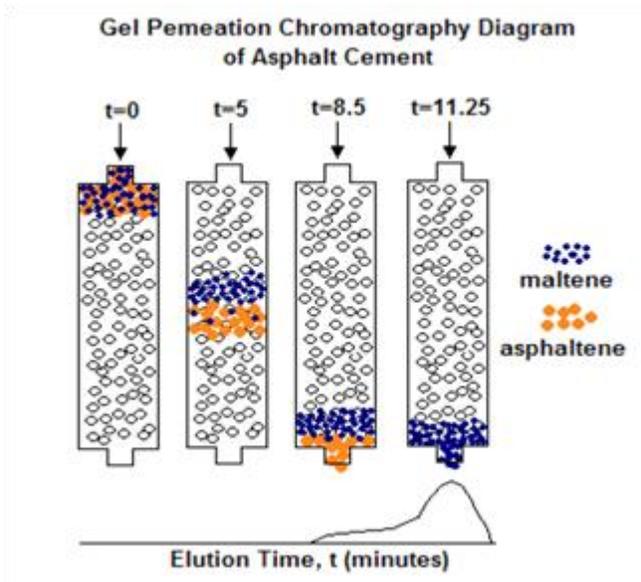


Figure 2-1 Example of Gel Permeation Chromatography

In Figure 2-1 the same column is represented four times at different elution intervals ($t = 0, 5, 8.5,$ and 11.25 minutes) as shown on the x-axis. Time can be directly correlated to specific molecular weights on the basis of polymer standards such as polystyrene. The y axis is representative of the refractive index (RI) output in mV. An increase in refractive index indicates and an increase molecules of a given size, with the maximum occurring where the most molecules of a given size are present. The example is based on the assumption that asphalt binder can be simply separated into two fractions; asphaltenes which are high in molecular weight and maltenes which are low in molecular weight. At $t=0$ the asphaltenes and maltenes are injected in one solution. However, as they pass through the column as represented by $t=5$ they begin to separate. This is due to the absorption of smaller molecules by small pores in the columns packing. Larger molecules are able to pass these small pores, thus causing separation between the different molecular sizes. At $t=8.5$ the high molecular weight asphaltenes begin to exit the column and a slight increase in the RI occurs. At $t=11.25$ the asphaltenes have completely exited the column and the maltenes begin to exit. It is important to note that the peak of the chromatogram is at $t=11.25$, indicating that there are more molecules present of the

correlating molecular size to $t=11.25$, which also corresponds to the region encapsulated by the maltenes fraction.

Much work has been conducted studying the application of GPC to asphalt binder chemistry. The following Table 2-1 outlines many uses and findings:

Table 2-1 Overview of literature involving the application of GPC to asphalt binder

Citation	GPC Application
McCann et al. (2008)[8]	Detected polymers in asphalt binders using GPC
Lu and Isacson (2002) [9] Siddiqui and Ali (1999) [10] Kim and Burati (1993) [11] Churchill et al. (1995) [12] Lee et al. (2011)[13]	Studied effects of aging on asphalt binder using GPC
Snyder (1969)[14]	Determined asphalt molecular weight distributions; based on polystyrene standard estimated between 700-2400 Daltons
Gilmore (1983)[15]	Identified the presence of antistripping agents within asphalt cement
Kim et al. (2006)[16]	Estimated RAP binder viscosity with GPC
Shen et al. (2007)[17]	Studied effect of crumb rubber modification of binders
Kim et al. (2013)[18]	Examined oxidative aging on polymer-modified asphalt mixtures made with Warm Mix Asphalt (WMA) technologies
Jennings et al. (1980, 1985)[19, 20] Yapp, Durrani, and Finn (1991)[21]	Studied pavements ranging from good to poor condition and compared the chromatogram; established a tipping point within the chromatogram at which pavement failure occurs
Zhao et al. (2013)[22]	Correlated an increase in large molecular sizes to the complex modulus (G^*) of binder

Many of the summarized works in Table 2-1 employed a measure of the Large Molecular Size (LMS%) to compare the binders. The percentage of LMS% grows as the

binder is oxidized. Kim et al [16] correlated the percentage of LMS% directly to the binder viscosity, as stated above. This important finding relates LMS% to the binder viscosity, a performance property of asphalt paving. The LMS% is defined by the first 5 slices of the GPC chromatogram if the total chromatogram was divided into 13 equal slices on the basis of elution time as shown by Figure 1.56. The LMS% is defined with the following equation:

$$LMS\% = \frac{\text{Area of frst 5 of 13 slices}}{\text{Area of ALL 13 slices}} \quad (2-1)$$

Zhao et al. [22] used LMS to estimate the complex modulus (G^*) of asphalt binder that contained RAS successfully. The researchers found that the complex modulus increased as the LMS% increased. Correlating these properties is important in further correlating the rheological properties of the asphalt binder to changes in the molecular weight distribution.

In 1980 Jennings et al. [19] conducted research identifying a number of roadways in Montana and ranking them on the basis of the amount of cracking the pavement had in certain age ranges. If a pavement was less than 10 years of age and exhibited extensive cracking it was ranked as “bad”, newer than 10 years old and only had some cracks it was listed as “poor”, newer than 14 years with few cracks was considered “good”. Pavements that were considered “excellent” were those that were 14 years or older and had little cracking. Jennings noticed that as the ranking of the pavement declined (i.e. went from “excellent” to “bad”) the LMS% of the chromatogram continued to increase. However, Jennings also realized that the performance of the pavement was not based on asphaltene content, which generally takes up most of the LMS% region.

Daly [23] fractionated asphalt binder with heptane and then tested each fraction in the GPC compared to the total chromatogram. The asphaltene fraction is heptane insoluble, while the maltene fraction is soluble. Daly found that the asphaltene fraction was responsible for the LMS% region, however it also tailed well into the maltene

fraction. The maltene fraction was responsible for the remaining portion (e.g. the distribution after the LMS) of the chromatogram. In the case that the asphaltene fraction was solely responsible for the formation of cracks (i.e. stiffening of the binder) the asphaltene fraction would not drag on into the medium and small molecular size regions.

There are some perceived limitations of this methodology. Namely, when GPC is being used to identify molecular weight distributions the molecular weights are qualitative, not quantitative. Thus, as previously shown, to quantitatively analyze data the data needs to be normalized by dividing the area of the LMS% region by the area of the total chromatogram. Furthermore, in effort to compare LMS % between samples the researcher must compare all samples with the same base limits. RAP for example typically will have more large molecules and those molecules will likely begin to elute from the column before the molecules of the virgin binder. Thus the minimum limits in which the area of the chromatogram is being analyzed need to be adjusted to meet those of the RAP (e.g. shifted from a minimum of 8.7 minutes for virgin binder to 8.5 minutes, which may be where the RAP begins to elute).

2.3 Atomic Force Microscopy (AFM)

Loeber's group [24, 25] first investigated the bitumen heat-cast film using AFM, and observed the well-known "bee" shaped microstructures with several micrometers in diameter and tens of nanometers. Several years later, Pauli et al. [26] acquired the same bee-shaped microstructures and advanced to correlate the "bees" with the amount of asphaltenes in the binder by imaging solvent-cast film. Having found the same randomly distributed bee-shaped structures, Jäger et al. [27] furthered the research and identified four phases in topographic images of the bitumen (hard-bee, soft bee, hard matrix and soft matrix), separating the higher and lower parts of the "bees" and the surrounding phase. Later on, a more extensive research including 13 bitumen was conducted by

Masson et al. [28] with phase-detection mode in AFM. The similar phases as identified in earlier research [27] were observed but named differently, with one new salt-like phase found and termed sal phase. The authors also classified bitumen in three groups: one that showed a fine dispersion (0.1 to 0.7 μm) in a homogenous matrix, one that showed domains of about 1 μm and one that showed up to the aforementioned four phases. An interesting finding in this research was that poor correlation was reported between the asphaltene content and the bee-shaped structures. This finding was subsequently verified by Pauli et al. [29], who first claimed the correlation between bee-shaped microstructures and asphaltene content. Pauli's group found 'bees' in maltenes without any asphaltenes but no similar microstructure existing in de-waxed bitumen. This observation led to a corrected statement that the microstructuring in bitumen, including well-known bee-shaped microstructures, resulted from the interaction between the crystallizing paraffin waxes.

Besides chemical composition of bitumen, temperature was another factor found responsible for its microstructural change. Das et al. [30] studied the influence of temperature on microstructures in bitumen by combining differential scanning calorimetry (DSC) and AFM. It was found that the appearance of microstructures is always in the crystallization temperature range of the same bitumen, while the dissolving of these microstructures is related with the melting temperature range. Another study addressing the similar issue was conducted by characterizing the microstructure for various thermal scenarios like cooling or heating in a fast or gradual manner [31]. The major findings of this research can be summarized as: microstructure possessed memory of its previous thermodynamic state; elliptical domains ("bees") showed the tendency to orient relative to each other with the change of temperature; the microstructural properties were found to depend on the maximum hold temperature of the bitumen.

Generally, these studies showed that AFM proved to be capable of fingerprinting bitumen from different sources under certain thermodynamic condition, although the

mechanism of the development of microstructures still needs to be answered. This motivated applying AFM to other areas of asphalt research, such as aging [32] and moisture damage [33]. These published AFM applications, together with current need of direct detection on the binder, which was previously discussed, incited using this powerful microscopic tool to research on binder blending. The authors of this paper recently evaluated the interaction and extent of blending between RAP-binder and virgin binder by studying the microstructures of the 'blending zone' by using AFM [34]. The blending zone was estimated to be about 50 μm . The blending zone can be considered to be a completely blended 'new material', having an intermediate microstructural property of the two materials. A design formula was proposed, which correlated the blending zone dimension to temperature and mixing time. Since the concern over binder homogeneity is more significant in RAS mixtures, blending between RAS binder and virgin binder was evaluated in this study.

CHAPTER 3 RESEARCH METHODOLOGY

3.1 Fingerprinting Methods

3.1.1 Gel Permeation Chromatography (GPC)

When GPC works, analytes are dissolved in the solvent, commonly tetrahydrofuran (THF), then stirred and injected into the columns that are packed with different pore sizes. It can be seen in Figure 2-1, larger molecules escape from the pores while smaller ones enter the pores easily with increased retention time. A differential refractive index (RI) is used as the detector, since it is most commonly used for asphalt chromatography.

GPC has been introduced into the blending efficiency study because it is capable of differentiating aged binder from virgin binder due to the fact that aged binder has a higher portion of large molecule than virgin binder. Figure 3-1 shows the results comparing the GPC chromatograms of one virgin binder (PG 64-22), binder extracted and recovered from one RAP and one RAS provided by TDOT, respectively. Each binder gives a different LMS% defined as the ratio of area of the large molecules to the total area. It can even be visually detected that the LMS% vary significantly from virgin binder to recycled binder. The significant change in molecular distribution is the foundation of using GPC in blending efficiency research.

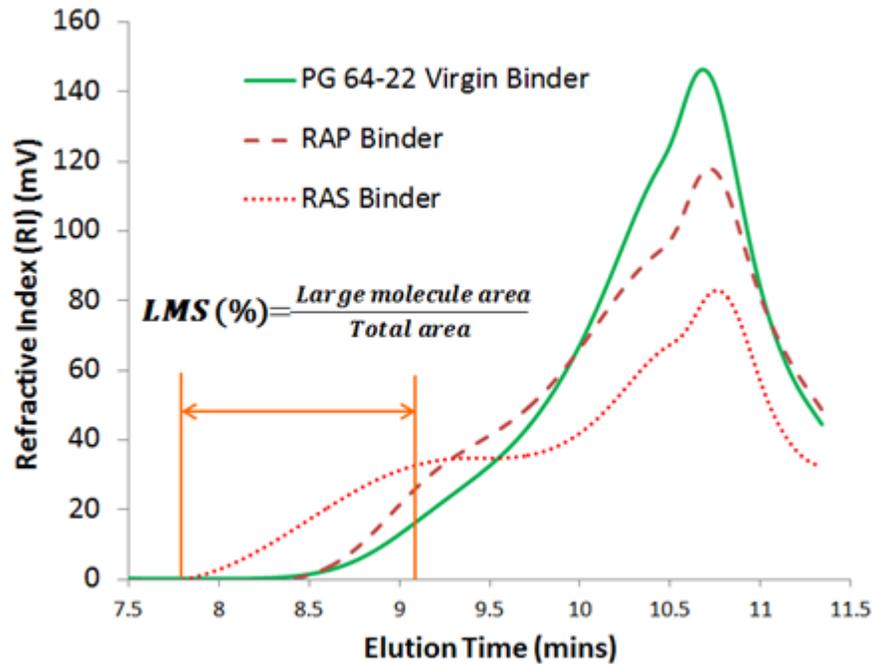


Figure 3-1. Comparison of GPC chromatograms of virgin, RAP and RAS binders

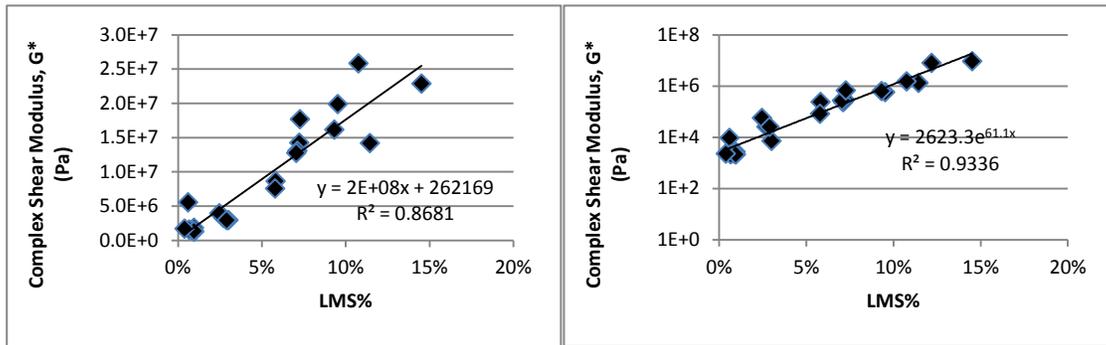
3.1.1.1 5/13 Method

The concept of LMS increase with respect to the stiffening of asphalt binder due to oxidation and aging is a popular one. The following table (Table 3-1) shows a number of the different approaches to LMS%. Each argues that the chromatogram needs to be divided into slices and then integrated, but there is variation on the number of slices that need to be used. One could theoretically use a range of molecular weights to divide the chromatogram. Evaluating the chromatogram on the basis of integration is straight forward, and a vast majority of the literature that studies similar GPC applications to the study of asphalt binder oxidation have been proven statistically significant with the use of an integrated LMS% method. Our research group correlated the complex modulus, G^* , of virgin asphalt binder blended with RAS binder to the LMS % using the “5/13 method”. “5/13 method” means the LMS% is defined by the first 5 slices of the GPC chromatogram if the total chromatogram was divided into 13 equal slices on the basis of

elution time. It was proved that “5/13 method” correlated very well with the G^* of random combination of virgin and RAS binders (Figure 3-2), which means this method can be used in further blending efficiency research.

Table 3-1. Differing opinions on LMS percentage

Researchers	# Slices	How many LMS
Asi, Al-Dubabi (1997)	12	n/a
Kim et al. (2006)	13	1-5
Churchill, Amirkhani, Burati (1995)	10	n/a
Lee, Amirkhani, Shatanawi (2006)	13	1-5
Doh, Amirkhani, Kim (2008)	13	1-5



a) Tested at 25°C

b) Tested at 64°C

Figure 3-2. The correlation between G^* and LMS%

3.1.1.2 Molecular Weight Method

Since GPC columns need to be calibrated by standard solutions, mostly polystyrene for asphalt research, the retention times in the chromatogram can be converted to molecular weights using the calibration curve obtained using polystyrene standards. Figure 3-3 shows the same chromatogram presented in Figure 3-1 but re-arranged based on polystyrene molecular weights in Daltons. The fractions generated by components with molecular weights less than 200 Daltons have been removed due to

the effects of solvent and air species. It can be found that both virgin and RAP binder components have molecular weights ranging from 20,000 to 200 Daltons, while those from RAS binder starting as high as 50,000 Daltons. Therefore, a more reasonable LMS fraction can be re-defined as the area under the curve with molecular weights higher than a specific threshold that is defined as large molecule threshold (LMT). Correspondingly, LMS% can be calculated using Eq. 3-1.

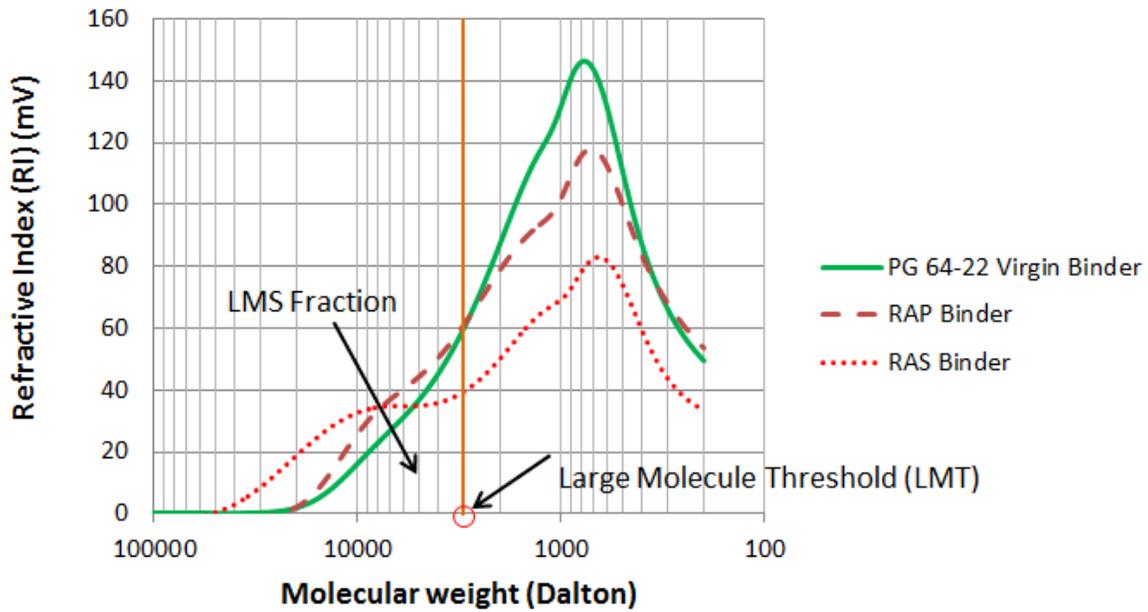


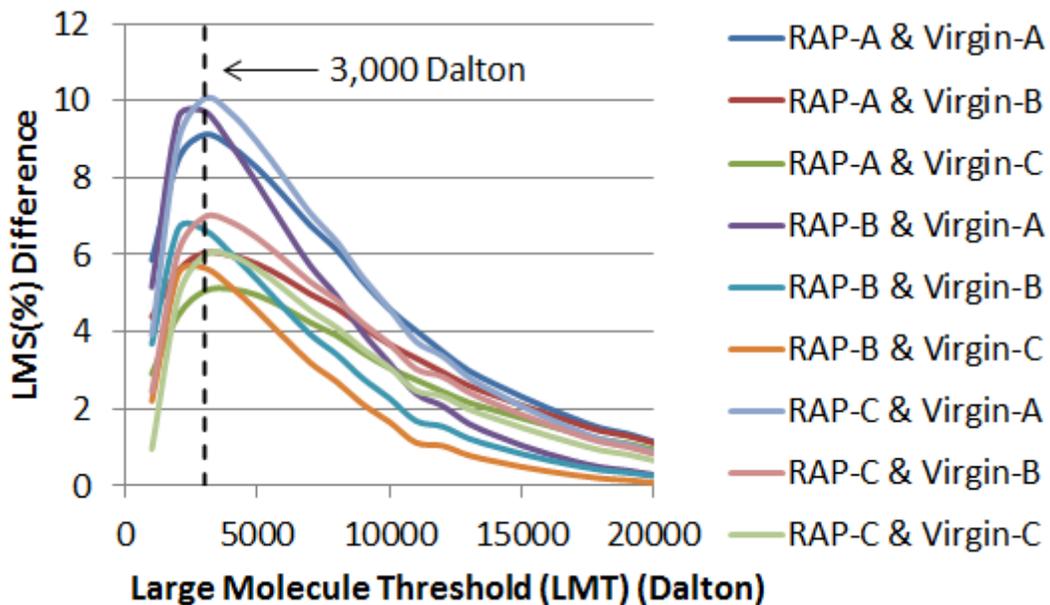
Figure 3-3. GPC Chromatograms Based on Molecular Weights

$$Redefined\ LMS\ (\%) = \frac{Curve\ Area\ (Molecular\ Weights\ Larger\ than\ LMT)}{Total\ Curve\ Area\ (from\ Beginning\ to\ 200\ Daltons)} \quad (3-1)$$

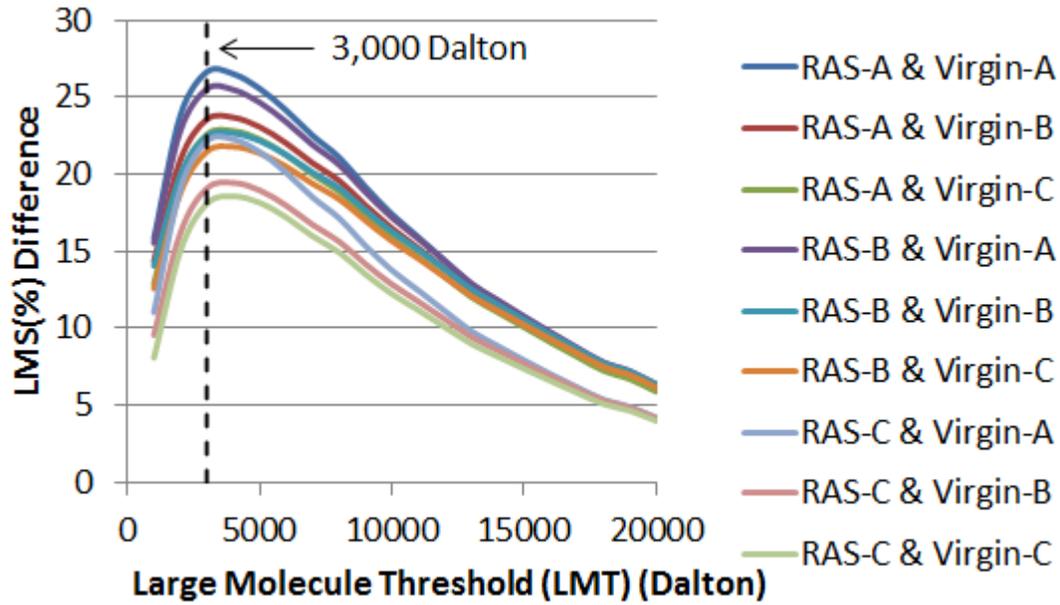
According to literature review, the only research that has addressed the binder component fractions based on molecular weight distribution, has divided the curve into three fractions including polymers (molecular weight greater than 19,000), asphaltenes (molecular weight from 19,000 to 3,000), and maltenes (molecular weight less than 3000). Since the purpose is to clearly differentiate virgin-recycled binder blend with different blending levels, the threshold that yields the most significant difference in

LMS% should be considered.

Figure 3-4 plots the relation between LMT ranging from 1,000 to 20,000 Dalton and LMS% differences between RAP/RAS and virgin binders based on the solution in concentration of 1 mg/mL. Three types of virgin binder, RAP and RAS from different sources were selected, respectively. The peak of LMS% difference is always found around 3,000 Dalton. This finding can be related to the above mentioned study that divided the molecular weight range from 3,000 to 19,000 into asphaltenes fraction, which is usually considered as the large molecular components fraction for asphalt binder. Therefore, 3,000 was selected as LMT for calculation of the newly defined LMS%.



(a) RAP-Virgin Binders



(b) RAS-Virgin Binders

Figure 3-4 Relation between LMT and LMS% Difference for RAP/RAS-virgin binders

Figure 3-5 presents LMS% values calculated with 3,000 Dalton as LMT. It can be seen that LMS% values for virgin binders selected in this study range from 10.1% to 20.5%, while those for RAP binders lie in a clearly higher range from 23.8% to 27.1%. The RAS binders yield an even higher range from 36.3% to 43.5%. The variations among triplicates are small with maximum coefficient of variation (CV) of 2.34% obtained from Tennessee RAP B binders, which validates the repeatability of this LMS% determination method.

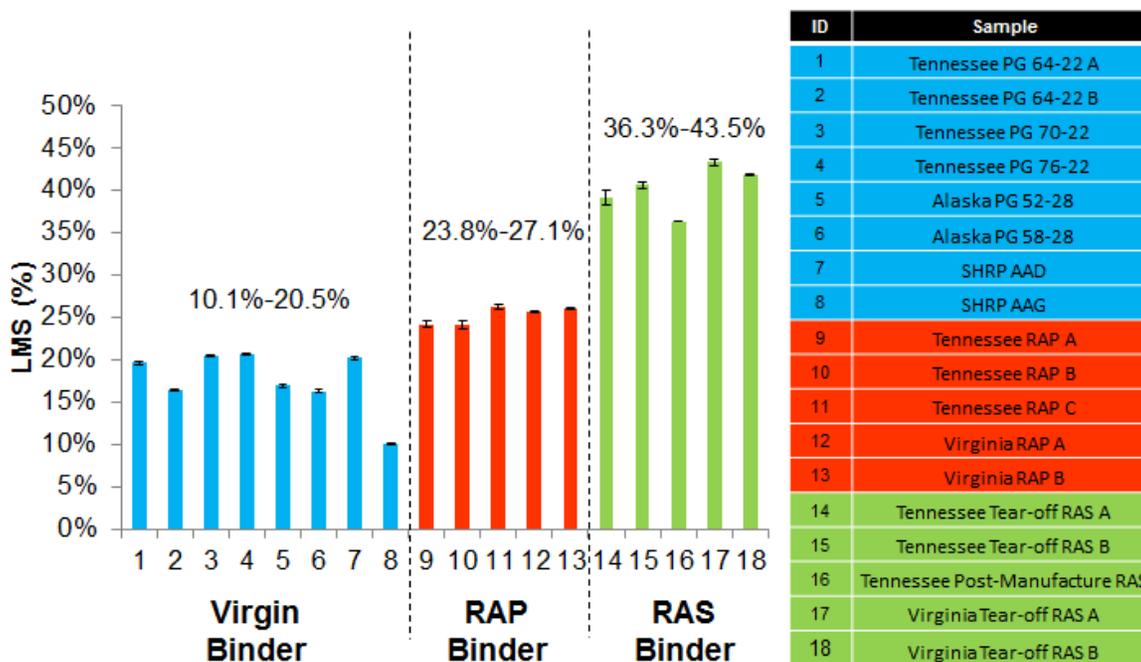


Figure 3-5. LMS% calculated with LMT of 3,000 Dalton for different binders

3.1.2 Atomic Force Microscopy (AFM)

In our study, the second question of interest is how well the aged binder blends with the virgin binder? Figure 3-6 shows the two possible scenarios for blending between the mobile aged binder and virgin binder, where either aged binder partially dissolved into the virgin binder, or a total blending into a homogeneous “new” material. Therefore, this question can be answered by investigation of the homogeneity of the blended binder.

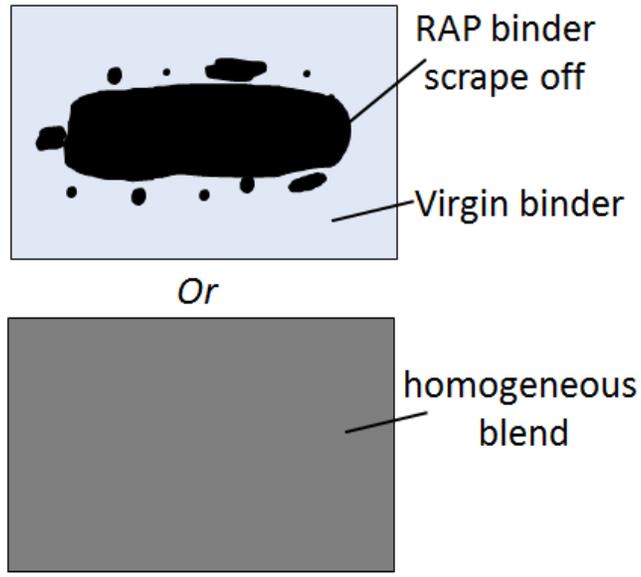


Figure 3-6. Two scenarios for blending

The two aforementioned possible scenarios in Figure 3-6 cannot be differentiated if blended binder is dissolved in solution, so the binder homogeneity defined in this research needs to be studied in solid state without extraction. The direct detection can be achieved by engaging microscopy, but due to the opacity of bitumen, higher resolution was not attainable by any traditional microscopic technique [28]. The use of atomic force microscopy (AFM) to characterize bitumen made it possible to reveal the details of the material's microstructural morphology [35].

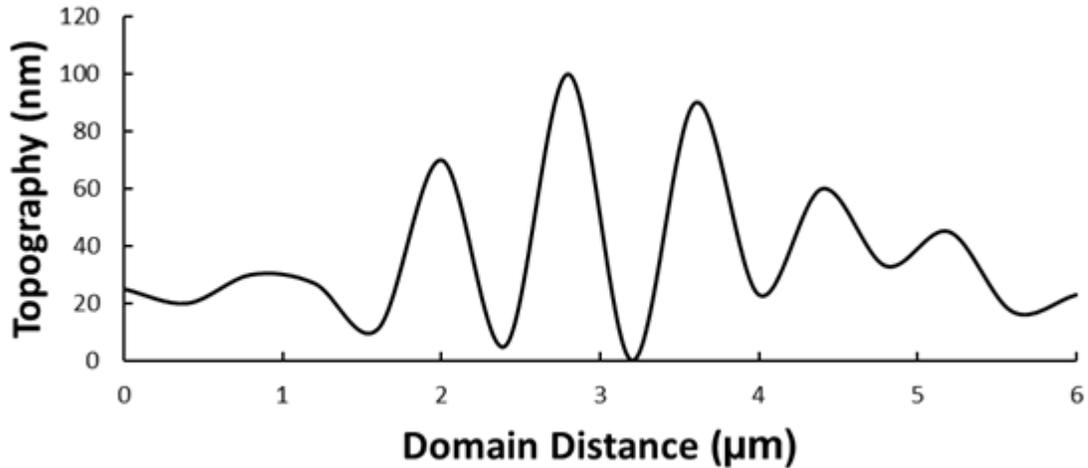


Figure 3-7. Typical topographic profile of one domain on the surface of virgin binder observed in AFM

The model of atomic force microscope used in this study was the “Multimode-V Atomic Force Microscope” from Bruker (Santa Barbara, USA), consistent with previous research [31, 34, 35]. The tapping-mode [36] was chosen because it is ideal for soft material such as bitumen [36, 37]. During imaging, a cantilever with a sharp tip was oscillated and scanned across the surface of the sample. Two types of images, topography (Figure 3-7) and phase-contrast (Figure 3-8), were acquired from a piezoelectric scanner and post-processed to be readable.

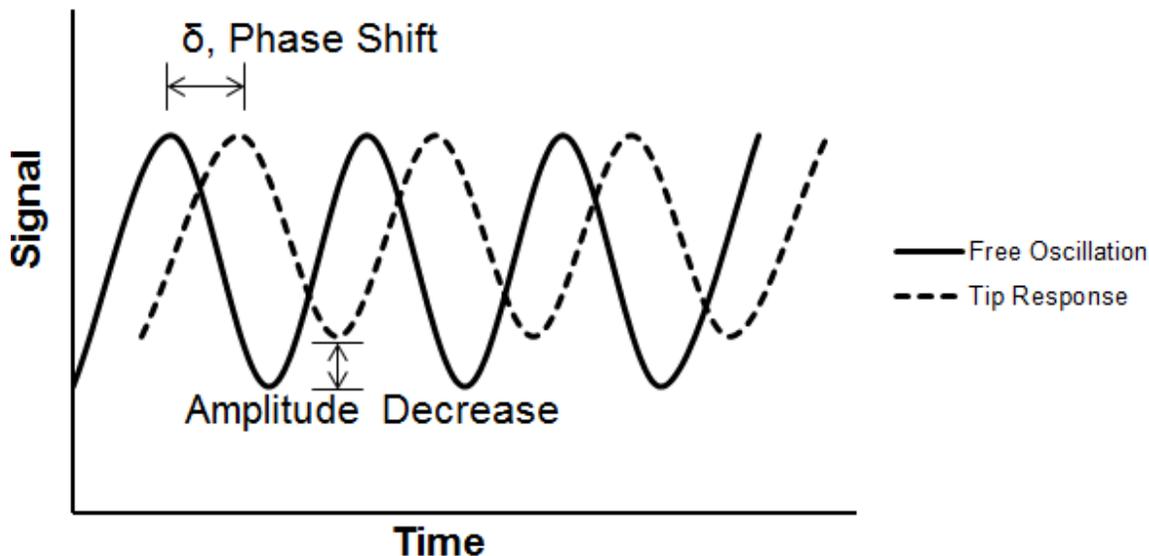


Figure 3-8. Illustration of phase lag between set signal (free oscillation) and the tip response due to sample-tip interaction (adapted from [28, 35])

The cantilevers used in this study were made from Antimony (n) doped Silicon, with nominal dimensions of $120\mu\text{m}\times 35\mu\text{m}\times 3\mu\text{m}$. The drive frequency was 330 kHz and the nominal force constant was 40 N/m. The probe rate was 1.0 Hz and the pixel resolution was 512×512 . Scan sizes were mostly $30\times 30\mu\text{m}$, with a few were $15\times 15\mu\text{m}$.

3.2 Laboratory Methods to Determine Bleeding Efficiency

3.2.1 Building “Blending Chart”

A total of 11 points, with RAP/RAS binder content increasing from 0 to 100% in 10% interval, were selected to ensure accuracy. Duplicates were made for each point. Since only 10 to 15 mg of the sample is required for GPC test, sampling after traditional mechanical blending may cause high variations thus should be avoided. The virgin binder and recovered RAP/RAS binder were first dissolved into THF to make solutions in target concentration (1 mg/mL), then 10 mL solution of the binder blend was produced by adding solutions of different binders in proportion to a 20 mL scintillation vial (e.g. 8 mL

virgin binder and 2 mL RAP/RAS binder solutions were added to produce a solution of binder blend containing 20% RAP/RAS binder. The solution was shaken in a solution shaker at high speed for 1 minute for complete dissolution, and then injected through a 0.2 μm filter to filter out the undissolved impurities. An auto-sampler was used to collect the prepared sample and then placed in the sample holder in EcoSEC GPC. 15 minutes were required for running one sample.

3.2.1 Aged Binder Mobilization Rate

Figure 3-9 illustrates two possible blending scenarios when recycled asphaltic material is used, where RAP represents both RAP and RAS hereinafter. The ideal case would be total mobilization of RAP binder and then full blending with virgin binder, which generates a homogeneous film coating both the virgin and RAP aggregates. In reality, however, part of the RAP binder remains inactive and cannot be mobilized during mixing, thus not contributing to further coating. On the other side, the mobilized RAP binder may highly interact with virgin binder, which yields a binder blend serving to coat both the virgin and RAP aggregates.

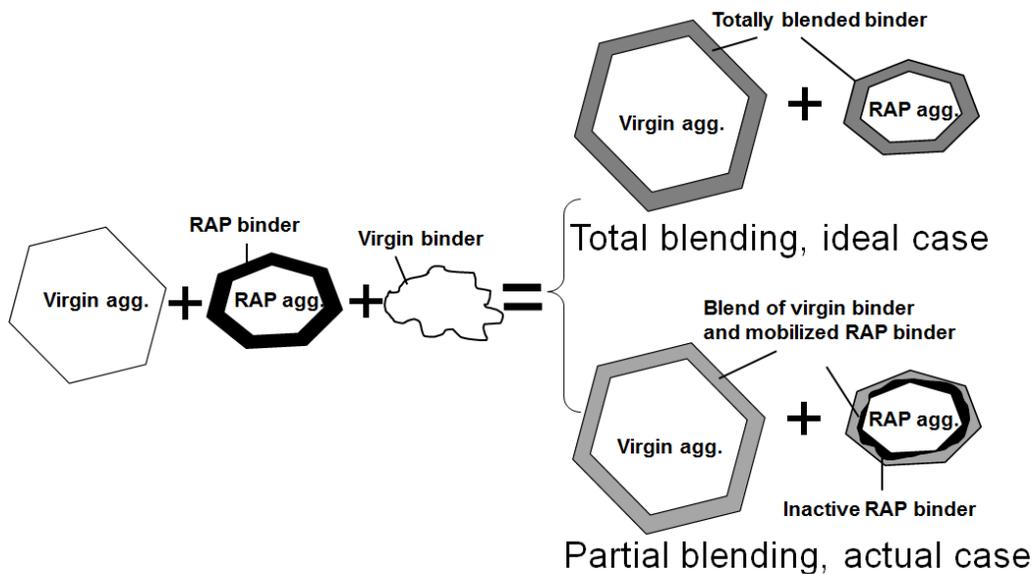


Figure 3-9 Two possible blending scenarios

The mechanical “scrape-off” has been studied as a factor to address RAP binder mobilization by researchers through “dry blending”, which is a mixing process without virgin binder addition [1, 38]. However, the authors admitted the impact of the presence of hot virgin binder cannot be captured by “dry blending”.

The actual blending process in the asphalt plant is complicated since RAP/RAS and virgin binders cannot be differentiated after mixing. According to Figure 3-9, however, the binder attached to the virgin aggregates can be evaluated in the representative of the binder blend of virgin binder and mobilized RAP binder. Therefore, the mobilized RAP binder contribution in the blend can be analyzed, if virgin aggregates can be separated after mixing. Assuming the relation between the RAP binder content and certain specific parameter is known, and this parameter of the binder blend can be measured through corresponding experiment, the RAP binder content in the blend can be quantitatively determined.

As illustrated in Figure 3-9, RAP binder content in the blend can be expressed as Eq. 3-2:

$$RAP\ Binder\ (\%)_{Blend} = \frac{W_{(Mobilized\ RAP\ Binder)}}{W_{(Mobilized\ RAP\ Binder)} + W_{(Virgin\ Binder)}} \quad (3-2)$$

RAP binder mobilization rate, denoted as α_M , is defined as

$$Mobilization\ Rate = \alpha_M = \frac{W_{(Mobilized\ RAP\ Binder)}}{W_{(Total\ RAP\ Binder)}} \quad (3-3)$$

Given percent RAP binder by total mixture as $P_{(b, RAP)}$, percent virgin binder by total mixture as $P_{(b, Virgin)}$, Eq. 3-2 can be further written as

$$RAP\ Binder\ (\%)_{Blend} = \frac{P_{(b, RAP)} \cdot \alpha_M}{P_{(b, RAP)} \cdot \alpha_M + P_{(b, Virgin)}} \quad (3-4)$$

Then α_M can be solved out as

$$\alpha_M = \frac{P_{(b, Virgin)} \cdot RAP\ Binder\ (\%)_{Blend}}{P_{(b, RAP)} \cdot (1 - RAP\ Binder\ (\%)_{Blend})} \quad (3-5)$$

Table 3-2 presents an example of α_M calculation in a real case. Assuming *RAP Binder (%) Blend* is determined in the lab as 20%, α_M can be calculated since the rest of the parameters are all given if one paving job is finalized. For this case, α_M is calculated as 75%, which means 75% of the RAP binder can be mobilized during mixing and contribute to coating the aggregates.

Table 3-2 Example of α_M calculation

Parameters	Description	Calculation	Value
RAP (%) Mixture	RAP (%) by total mix	Given	30%
RAP Binder (%) RAP	RAP binder (%) in RAP	Given	5%
P _b	Optimum binder (%) by total mix	Given	6%
P _(b, RAP)	RAP binder (%) by total mixture	[RAP (%) Mixture] · [RAP Binder (%) RAP]	1.5%
P _(b, Virgin)	virgin binder (%) by total mixture	P _b – P _(b, RAP)	4.5%
RAP Binder (%) Blend	RAP binder (%) by binder blend (after mixing)	Determined in the lab	20%
α_M	RAP binder mobilization rate	Eq. (3.2b)	75%

According to the aforementioned case, the key point of α_M calculation lies on determination of the *RAP Binder (%) Blend*. A straightforward method to determine *RAP Binder (%) Blend* is to build a “blending chart” with one certain parameter and interpolating the lab-testing result of the sample. As mentioned in “Introduction” section, a new parameter for blending research derived from GPC testing is to be developed in this study. Accordingly, this study follows the flow chart presented in Figure 3-10.

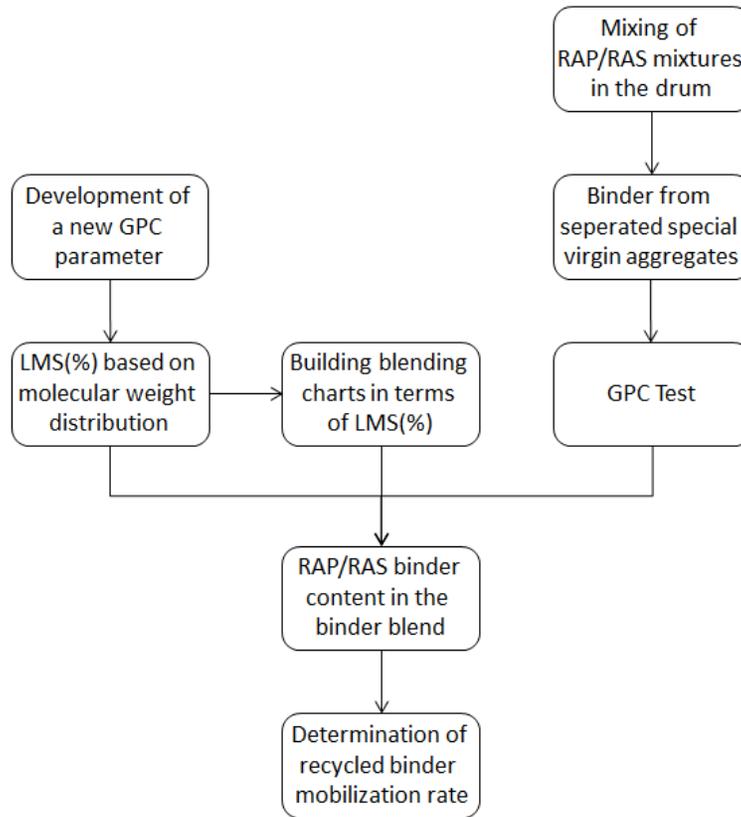


Figure 3-10 Research flow chart of this study

3.2.3 Staged Extraction Method

Researchers have used a method called staged extraction [1, 39], or progressive extraction [40], that soaks the asphalt mixture in asphalt solvent for a certain period of time so that the binder can be extracted layer by layer from the aggregate after mixing.

The previous research has yielded promising results, however, several questions still need to be answered before it can be widely used. Does the solvent affect the analysis? Do the light components in the binder tend to be extracted first, which may lead to a fake “layered structure”? Which is the best or most effective solvent? Is the RAP binder homogeneous after years’ service? This paper answered these questions by validating the staged extraction method and used it to further investigate the binder

homogeneity of RAP-virgin blend. Since RAS is similar to RAP but stiffer, the same approach validated on RAP can be extended to RAS. The binder homogeneity research on RAS-virgin blend could be even more valuable, because air-blown process and long-term aging of RAS may result in a more difficult blending potential.

3.2.3.1 Solvent Selection

Trichloroethylene (TCE) has traditionally been used for asphalt extraction and identified by Strategic Highway Research Program (SHRP) as one of the best solvents. The health and environmental concerns, however, has limited the use of TCE and attracted asphalt researchers to a less toxic solvent, the combination of toluene and ethanol (T/E) (85:15 volumetric ratio), in the past few years. The T/E blend, unfortunately, has still raised potential health concerns [2]. Recently, the need to replace chlorinated solvents led state agencies to use alternative normal propyl bromide (nPB) solvents, and it was found that nPB solvents can be used as direct replacements for the chlorinated solvent[2, 41]. Another solvent, decahydronaphthalene (decalin), was evaluated as asphalt solvent since it has similar solubility parameter and dissolution kinetics to toluene at 15 °C [42].

Most of the staged extraction studies used TCE as the solvent [1, 39, 43, 44], or the solvent type was not addressed [40]. None of the research, however, mentioned the potential effect of the solvent on the results. In this paper, the effects of different solvents on the binder were evaluated in terms of the change in molecular weight distribution obtained by gel permeation chromatography (GPC). The selected solvents included TCE, nPB, T/E (85:15 volumetric ratio) and decalin, which are the ones mentioned in the literature review.

Figure 3-11 presents the GPC results in terms of LMS%. LMS % is defined as the percentage of large molecular fraction (molecules larger than 3,000 Dalton) over the total area of the chromatogram generated by GPC [22]. 100 g of one typical PG 64-22 binder

was dissolved in solvents, recovered in a vacuum oven at 85°C for overnight, then subject to GPC test. It can be found that LMS % values for the binders extracted and recovered by the solvents selected in this study are approximately the same, indicating that there is no or limited effect of the solvent on the molecular weight distribution of the binder.

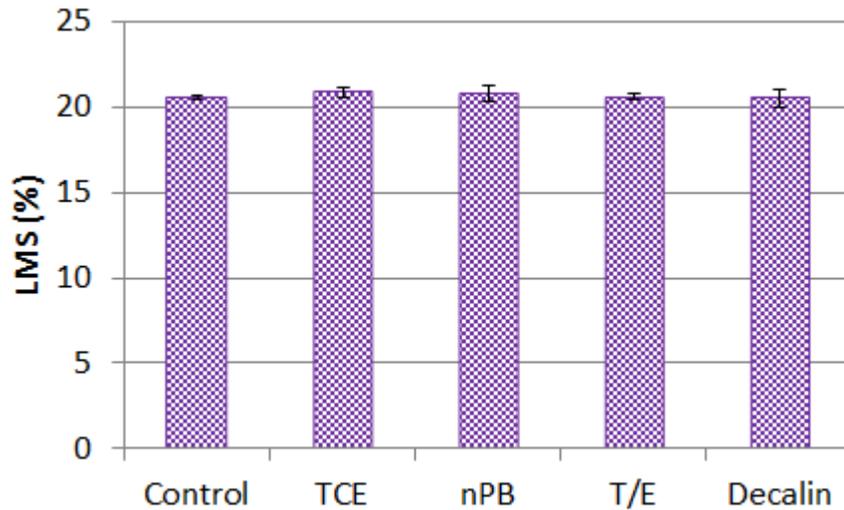


Figure 3-11 Solvent effect on GPC results

According to the selective dissolution results, TCE seems a better solvent that can be used in staged extraction research. The dissolving rate of each solvent, however, should also be checked since the more time the asphalt mixture was soaked in the solvent, the more uncertainties could be caused. The authors of this study also recorded the extracted sample weight of each layer from the samples mentioned above. Figure 3-15 shows the plot of the change in percentage of accumulative extracted binder weight over the total binder with increase of dissolving time. It can be seen that TCE dissolved the asphalt binder faster than the rest of the solvents. nPB was ranked 2nd, while T/E and decalin may extract the binder layer with a similar but slow rate. Accordingly, TCE was revealed by the dissolving rate finding as the most effective solvent that can be used with staged extraction method. NPB can be considered as the replacement if TCE is not

accessible, but may slightly affect the analysis. Therefore, TCE was used as the solvent for the rest part of the paper.

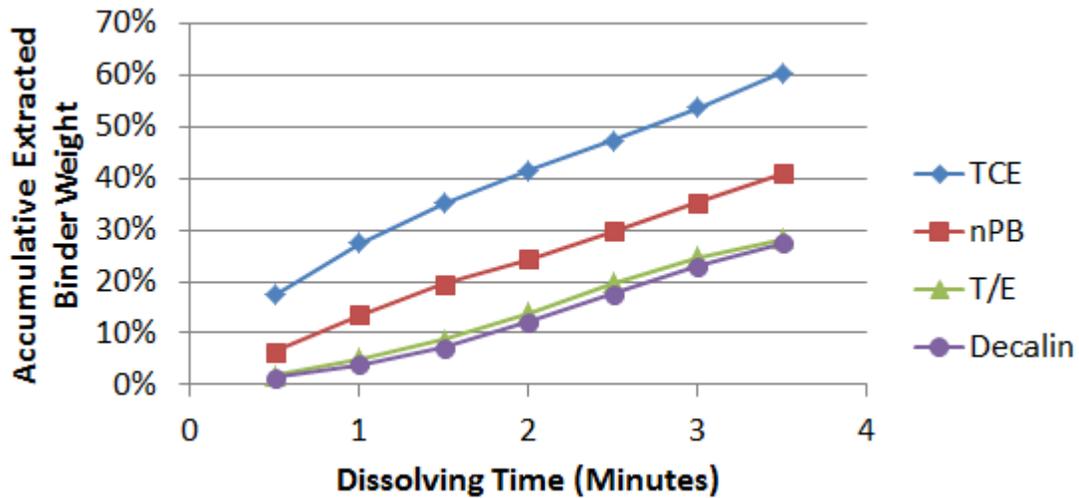


Figure 3-15 Dissolving rate of different solvents

3.2.3.2 Selective Dissolution

Staged extraction method has been used on the basis of the assumption that all the components in the asphalt binder can be extracted layer by layer in the same proportion. However, this assumption has been questioned. Since outer layers extracted from RAP aggregate were found to be softer than inner layers in plenty of studies [1, 39, 40, 43, 44], one concern has been raised that lighter maltene fraction of the binder may wash out first, then the remaining asphaltene fraction will breakdown after successive washes [42]. To address this concern, the same virgin binder was fractionated into maltene and asphaltene by soxhlet extraction, with iso-octane as the fractionation solvent (Figure 3-12).

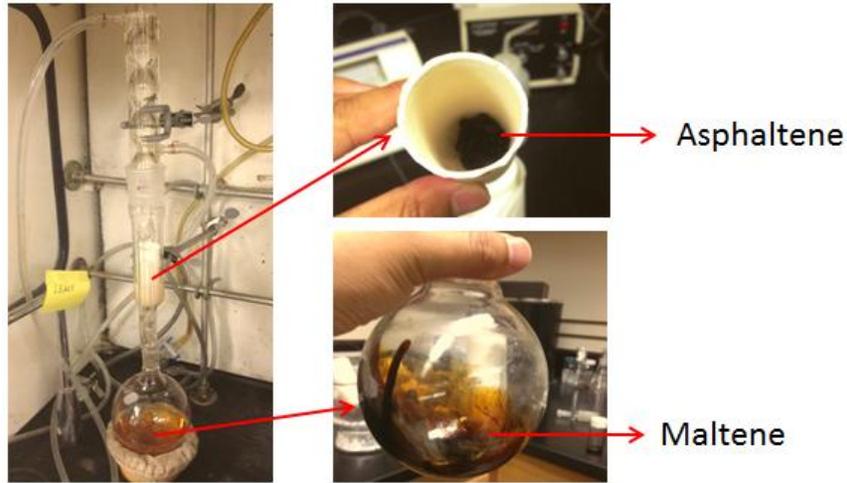
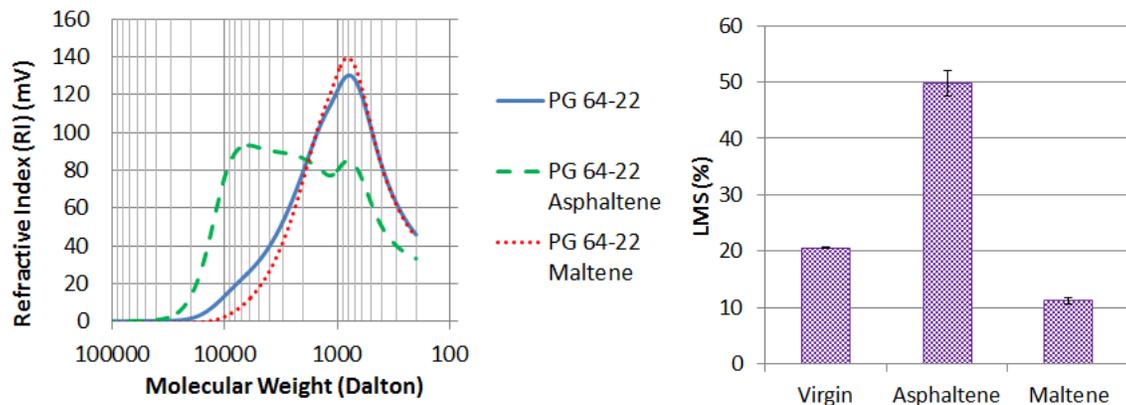


Figure 3-12 Fractionation of asphalt through soxhlet extraction method

Figure 3-13 presents the GPC results of the asphaltene and maltene from Soxhlet extraction, as well as the control virgin binder. It can be seen that asphaltene yielded significantly different chromatogram from corresponding virgin binder, while maltene followed the same shape but with smaller large molecule fraction. LMS% values can also be differentiable, with approximately 20, 50 and 11 for control binder, asphaltene and maltene, respectively. On the basis of this finding, a layered extraction design was brought up to evaluate if selective dissolution occurred.



(a) Chromatograms

(b) LMS%

Figure 3-13 GPC results after binder fractionation

Staged extraction by each solvent was conducted on a 500 mg sample of the same binder. The sample was rolled into the ball-shape prior to the extraction so as to avoid the potential effect of the sample geometry, and then washed by the solvent for 30 seconds for 7 times. Each washed layer was labeled as layer 1 to 7 outside in, with the remaining layer designated as layer 8. GPC test was conducted on each layer, and the results can be found in Figure 3-14. “Total” represents the binder totally dissolved in TCE and recovered afterwards, serving as the control sample. There was no appreciable difference in terms of LMS% observed on each layer extracted by TCE and the corresponding control sample. nPB did not yield much difference either, but the LMS% values of the first several layers were slightly lower than the layers extracted later and the control sample, which indicates that slight selective dissolution might occur. The average of LMS% of the layers extracted by toluene/ethanol (T/E) combination was found to be approximately equal to the control sample. However, the dissolution of the components seems unstable. This indicates that selective but non-sequential dissolution might occur when T/E combination is used as the asphalt solvent. The most significantly selective dissolution was found on samples extracted by decalin. This finding is consistent with the binder fractionation results from a previous study [42], and it can be concluded that the concern over decalin used as an asphalt solvent still stays.

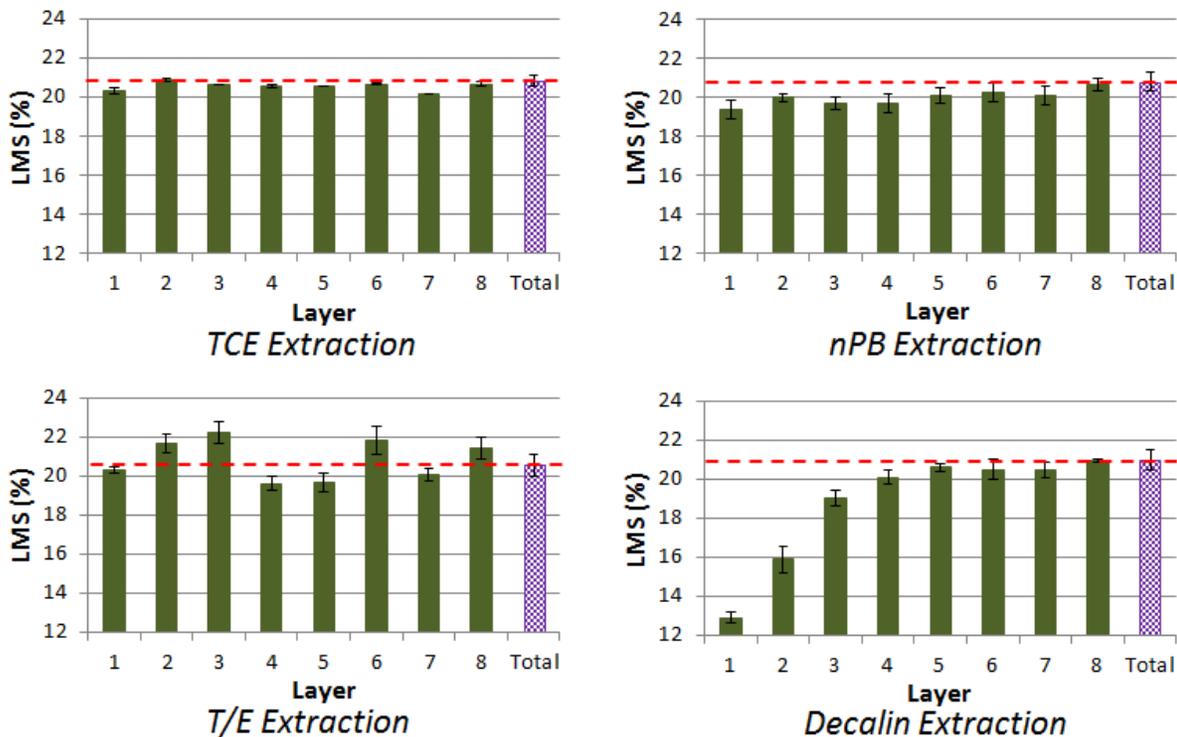


Figure 3-14 GPC results after staged extraction by different solvents

3.2.3.3 Binder Homogeneity of RAP and RAS Particles

The homogeneity of the binder covering the RAP and RAS aggregates can affect the blending process. Prior to using the staged extraction method, the binder homogeneity of the RAP and RAS materials ready for mixing should be checked. In this study, the same RAP and a locally available RAS batch were checked for corresponding homogeneity.

Two identical samples of 50 g for each were selected for each material. Each sample was soaked in TCE for 1-minute wash of three consecutive times, and then left in the 4th beaker filled with TCE for 30 minutes for a complete dissolution. The sample of each layer was then prepared into standardized sample and tested in GPC.

Figure 3-16 presents the results. There is no difference among the layers that can be detected. In addition, the LMS% of each layer was found to be equal to that of the totally extracted control sample. The similar finding can be applied to both RAP and RAS

selected in this study. This means the binder coating the RAP or RAS aggregate is homogeneous after long years' service, which enables using the staged extraction method to investigate the recycled and virgin binder blending.

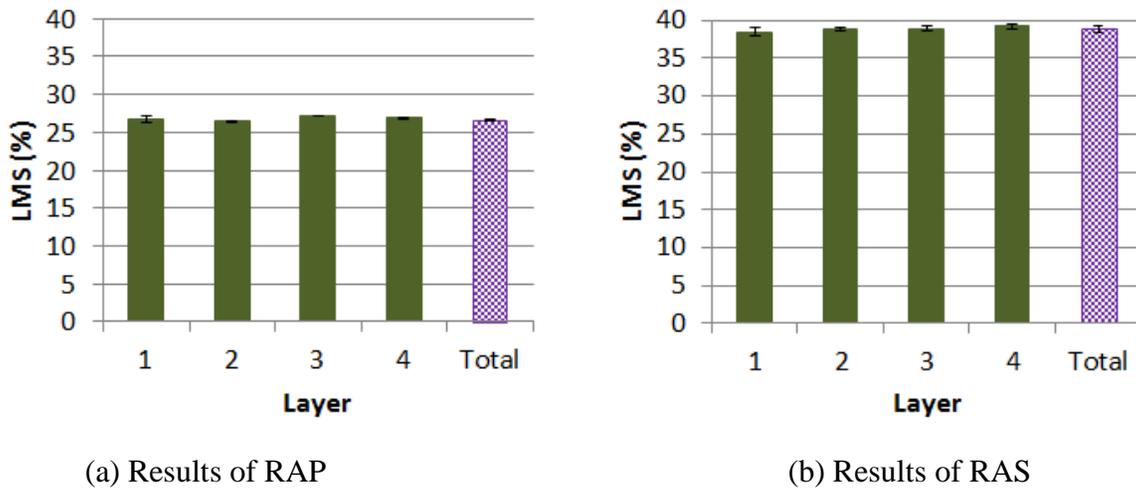


Figure 3-11 GPC results of four-layer stripping of raw RAP and RAS

3.3 Factors Affecting the Blending Efficiency

3.3.1 Mixing Factors

3.3.1.1 RAP

Materials used in the mixture were Performance Grade (PG) 64-22, RAP of an unknown source, and a virgin aggregate. The RAP was processed by first barrel rolling two minutes and then sieved eight minutes, collecting only material retained on the #4 and #8 sieves. The process was for assurance of no agglomerates and minimizing dust. An extraction and recovery of the processed RAP was performed with a resulting asphalt content of 3.24%.

The virgin aggregate was sieved and the material retained on the 1/2-inch sieve was collected. The sizes were chosen based on the ability to readily distinguish the two materials after mixing with the virgin binder. A total asphalt binder content of 3.00

percent was selected with a rap binder replacement of 2.10 percent. The percentages were selected based upon trial blending and recovery testing. Additionally, based on preliminary trials, it appeared that the smaller aggregate size of the RAP caused it to receive priority in coating due to increased surface area. The percentages of RAP, virgin binder and RAP binder replacement for the mix were selected for assurance of total virgin binder coating on the smaller RAP aggregates did not saturate the RAP to an unrealistic level and reduce the margin of the ability to distinguish virgin binder from RAP binder. The surfactant based WMA additive Evotherm and the wax based WMA additive Sasobit were additionally studied. Both additives were added to the PG64-22 binder for their respective mixtures.

The virgin binder was heated to mixing temperatures on the basis of the test matrix and the virgin aggregate was superheated to 10°C beyond the mixing temperature. The RAP was not heated so that any blending was induced by the superheated aggregates, similar to the processes that occur in the asphalt plant.

In efforts to ensure that the virgin binder coated the coarse aggregate the aggregate and binder were mixed for one minute prior to the addition of RAP. The RAP was then added and allowed to mix for the duration of mixing time provided in the experimental matrix (Table 3-3). This step was important because the RAP aggregates are smaller in size. The virgin binder was found to have a tendency to be attracted to the smaller aggregates, and coats them first. This caused an irregular amount of virgin asphalt to coat the RAP without coating the larger, virgin aggregates. A Hobart Mixer model A-120 with wire whisk was used for mixing.

Table 3-3. Experimental matrix of mixing scenarios

Mixture	Time (s)	Temperature (°C)
1	30	160
2	60	160
3	105	160
4	150	160
5	300	160

The virgin binder was heated to mixing temperatures on the basis of the test matrix and the virgin aggregate was superheated to 10°C beyond the mixing temperature. The RAP was not heated so that any blending was induced by the superheated aggregates, similar to the processes that occur in the asphalt plant.

In efforts to ensure that the virgin binder coated the coarse aggregate the aggregate and binder were mixed for one minute prior to the addition of RAP. The RAP was then added and allowed to mix for the duration of mixing time provided in the experimental matrix (Table 3-4).

Table 3-4. Experimental matrix of mixing scenarios

Mixture	Time (s)	Temperature (°C)	Additive
1	105	130	-
2	105	160	-
3	105	180	-
4	105	130	Evotherm
5	105	130	Sasobit

At the conclusion of mixing, the large, “coarse” (virgin) and small, “fine” (RAP) aggregates were separated. Upon separation, the binder was recovered from the mixtures using AASHTO T164 “Standard Method of Test for Quantitative Extraction of Asphalt Binder from Hot-Mix Asphalt (HMA)”. The solvent used for the extraction and recovery was n-propyl bromide. The recovered binders were then subject to GPC and DSR tests for evaluating the blending efficiency.

3.3.1.2 RAS

Aggregates of three different sizes that could be visually detected and separated were designed to be mixed with RAS and virgin binder to make mixtures (Figure 3-17). The small aggregates were pre-blended with RAS as mixing carriers that completely covered the RAS before blending, in order to avoid further binder loss to the mixing bucket. The change in percentages of LMS among the extracted and recovered binder

from the different types of aggregates would give a better understanding of the blending efficiency. In addition, RAS content and mixing time were considered as two parameters that affect the binder blending efficiency and would be taken into consideration in this study. Figure 3-18 shows the design parameters for the mixtures studied in this research. Altogether, seven mixtures were made in the lab and twenty-one GPC samples were evaluated (Table 3-5). Each of these mixtures is referred to as mixing binder.

Table 3-5 Differentiation between mixtures 1 through 7

	Time	Temperature (°C)	RAS Content (%)
Mixture 1	2 min	170	2.5
Mixture 2	2 min	170	5
Mixture 3	2 min	170	7.5
Mixture 4	2 min	170	10
Mixture 5	30 s	170	5
Mixture 6	1 min	170	5
Mixture 7	3 min	170	5



Figure 3-17 Aggregates and RAS used in this study (size distribution in Table 3-5)

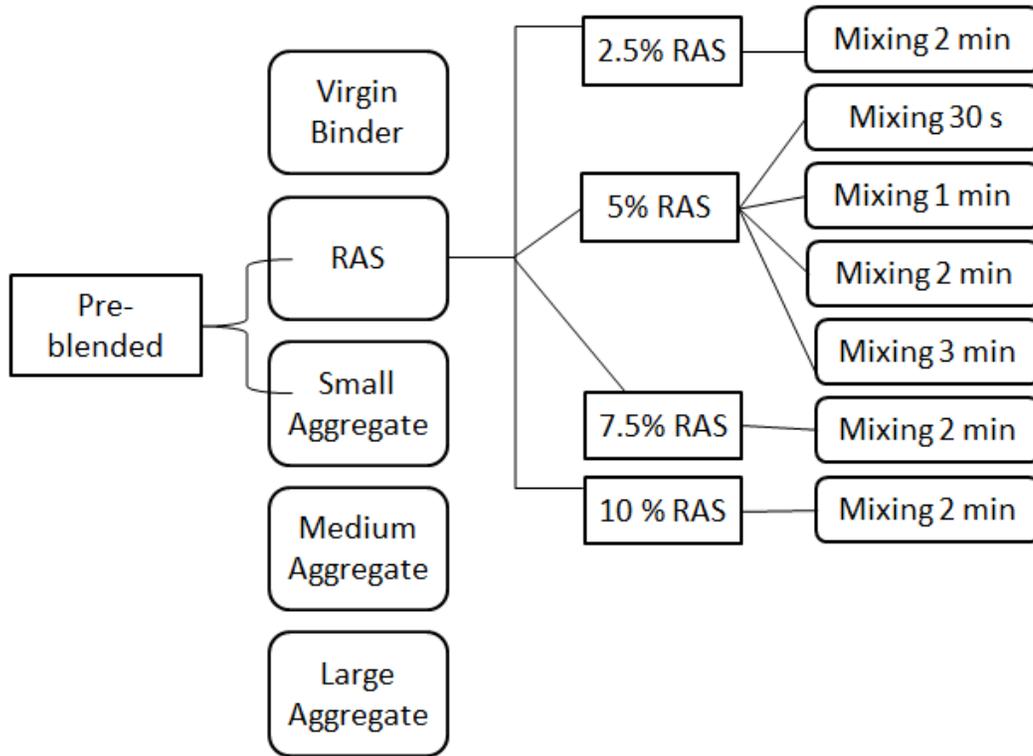


Figure 3-18 Design parameters for mixture blending

The RAS used in this study came from tear-offs, which was plant screened and passed No. 4 sieve and had an asphalt content of 19%. The virgin binder is a typical PG 64-22 binder commonly used in the United States. The aggregates utilized in this study included natural sand (referred as small) that completely passed No. 4 sieve, intermediate limestone (referred as medium) that totally passed 19 mm (¾-in.) sieve but retained on No. 4 sieve, and coarse limestone (referred as large) that retained on 19 mm (¾-in.) sieve. Table 3-6 summarized the size distribution for materials used in this study. Gradation was ignored but each component of the mixture was given specific portion by weight of total mix to make it close to a well-graded mixture (Table 3-7). Among all the mixtures, there were 10% large aggregates, 40% medium aggregates, and 36–42% small aggregates that

vary with the change of RAS content. The 5.5% optimum asphalt content was selected for all the mixtures.

Table 3-6 The size distribution of the materials

Materials	Size Distribution
RAS	Pass No.4 Sieve
Small Aggregates	Pass No.4 Sieve
Medium Aggregates	Pass 3/4 in Sieve, Retain on No.4 Sieve
Large Aggregates	Retain on 3/4 in Sieve

Table 3-7 Mix design for mixtures 1 through 7 (by weight of the total mixture)

	RAS (%)	Large Aggregate (%)	Medium Aggregate (%)	Small Aggregate (%)	Virgin Binder (%)	Total (%)
Mixture 1	2.5	10	40	42.475	5.025	100
Mixture 2	5	10	40	40.45	4.55	100
Mixture 3	7.5	10	40	38.425	4.075	100
Mixture 4	10	10	40	36.4	3.6	100
Mixture 5	5	10	40	40.45	4.55	100
Mixture 6	5	10	40	40.45	4.55	100
Mixture 7	5	10	40	40.45	4.55	100

The RAS was extracted and recovered according to the centrifuge-rotavapor recovery method [45]. The recovered RAS binder was heated up to 240°C at which the binder was flowable enough to be blended, while the virgin binder was heated up to 154°C. Then the two binders were blended by a high-performance mixing gun at 180°C

with a total weight of 100 g for 3 min. The newly blended binder was made into DSR standard samples with 8 mm diameter and GPC samples that weighed between 15 to 20 mg. The results were obtained based on the average of two duplicates.

The aggregates were heated to 180°C, 10°C higher than target mixing temperature of 170°C for more than 2 h before mixing. RAS samples were heated to 110°C for 2 h to avoid further aging. Virgin binder was heated to 170°C for 2 h. The small aggregates were pre-blended with RAS samples as RAS carriers 20 min before mixing with the larger aggregates to avoid further binder loss during mixing. The three different types of aggregates were separated immediately after mixing was complete, among which a representative (around 50 g) of each aggregate was selected to be extracted, recovered, and tested by GPC. The results were obtained based on the average of two duplicates.

3.3.2 Effect of Aged Binder Content

In this study, gravel with round and smooth surface passing 9.5 mm (3/8 in.) sieve and retained on 4.75 mm sieve (No. 4) was selected and added as part of the virgin aggregates in order for better separation. Figure 3-19 shows the round gravel separated before and after mixing.



Figure 3-19. Round-shaped gravel before and after mixing

A total of 10 mixtures with 2,000 g for each batch, covering RAP percentage up to 80% and RAS up to 10% (Table 3-8), were prepared in the lab at 165 °C with the mixing time set to 2 min. 100 g of round-shaped gravel was added as part of the virgin aggregate for each mix. The properties of RAP, RAS and virgin aggregate used in this study can be found in Table 3-9. The mix design recommended by the asphalt plant providing the materials was followed, with consideration of the total contribution of the recycled binder. The gradation and optimum asphalt content (5.7%) were hold constant for all the mixtures.

Table 3-8. Usage of recycled materials selected in this study

Recycled Material	Percentage by Weight of the Total Mix
RAP	10%, 20%, 30%, 40%, 50% and 80%
RAS	2.5%, 5%, 7.5% and 10%

Table 3-9. Properties of RAP, RAS and virgin aggregate

Properties		Mixture	Virgin Agg.	RAP	RAS
AC Content (%)		5.7	-	4.76	20.85
Gradation	Sieve (in.)	Sieve (mm)	Passing (%)		
	5/8	16	100.0	100	100
	1/2	12.5	96.0	92	100
	3/8	9.5	85.5	71	92.4
	#4	4.75	59.3	23	61.5
	#8	2.36	41.3	15	44.5
	#30	0.6	19.3	9	26.7
	#50	0.3	11.0	6	18.3
	#100	0.15	6.6	4	13
#200	0.075	4.4	2.5	8.7	

After mixing, the round-shaped gravel was picked and eluted by n-propyl bromide (nPB) for 30 min in order for complete binder extraction. Then the binder was recovered in a 20 mL vial using a water bath at 70°C in less than 15 min until solvent was non-visible, and then left in a vacuum oven at 85°C overnight for complete removal of the solvent. The relatively lower temperatures and vacuum oven were selected to reduce

the potential aging effect. The effects of mixing, nPB extraction and recovery were also checked and found to be limited or none on LMS%. Once the binder sample was ready, the GPC test was carried out following the same procedure described in “blending chart” section.

3.3.3 Effect of WMA technologies

A gap-gradation was used to design mixtures in this study in order to easily distinguish the virgin aggregates from RAP particles after mixing. Two models, coarse-virgin with medium-RAP and medium-virgin with fine-RAP, were used to design RAP mixes. The medium-virgin with fine-RAS model was used for RAS mix only, since most of the processed RAS consists of fine particles passing No.4 sieve. A No.57 limestone batch was selected as the coarse virgin aggregate and the materials retained on 1/2 in. sieve were collected only. The medium-virgin aggregates were collected from a gravel batch retained on No.4 sieve. A locally available batch of RAP passing 5/8 in. but retained on No. 8 sieves was used as medium-RAP, while the same RAP and a local RAS batch passing No.8 were used as fine-RAP and fine RAS. Two types of models were selected for RAP mix in order for consideration of size effect. Three mixtures were design to cover 50% RAP and 10% RAS. Table 3-10 presents the properties for each batch of materials, including gradation, asphalt content and average film thickness calculated following the method proposed by Asphalt Institute (1993) [3, 38]. A typical PG 64-22 binder was selected as the virgin binder.

Table 3-10 Properties of the materials used in this study

Properties	Virgin Agg. (Coarse)	Virgin Agg. (Medium)	RAP (Medium)	RAP (Fine)	RAS (Fine)
AC (%)	-	-	3.24	9.75	21.28
Film Thickness (µm)	-	-	-*	6.17	10.42

Gradation	Sieve (in.)	Sieve (mm)	Passing (%)				
	1	25.4	100	100	100	100	100
	3/4	19	64.6	100	100	100	100
	5/8	16	43.1	100	100	100	100
	1/2	12.7	0	89.6	100	100	100
	3/8	9.5	0	62.3	86.3	100	100
	#4	4.75	0	0	30.6	100	100
	#8	2.36	0	0	0	100	100
	#16	1.18	0	0	0	77.8	83.1
	#30	0.6	0	0	0	60	61.8
	#50	0.3	0	0	0	41.1	54.4
	#100	0.15	0	0	0	29.2	46.1
#200	0.075	0	0	0	19.6	35.5	

**Only the film thickness of fine particles can be calculated using this method.*

The non-foaming additives selected are presented in Table 3-11.

Table 3-11 Properties of WMA additives

Type	Products	Code	Description
Evotherm Related	Evotherm M1	Ev-M1	Chemical packages, liquid, fatty amine derivatives, 0.25 to 0.75% by weight of binder
	EvoFLEX CA	Ev-CA	Chemical packages, liquid, fatty acid derivatives, 1 to 5% by weight of binder
Rediset	Rediset LQ-1102C	Re1102	Chemical packages, liquid, proprietary alkoxyated fatty polyamines, proprietary polyamine, Glycol. 0.5% to 1% by weight asphalt cement
	Rediset LQ-1106	Re1106	Chemical packages, liquid, surfactant blend, 0.5% to 1% by weight asphalt cement
Cecabase	Cecabase RT 945	Ce	Chemical packages, liquid, fatty acid amines, 0.3% to 0.5% by weight asphalt cement
Sasobit	Sasobit	Sa	Fischer-Tropsch wax, solid, solid saturated hydrocarbons, 1% to 1.5% by weight of the binder
	Sasobit LM	Sa-LM	
	Sasobit	Sa-570	Sasol wax Slack wax blend, solid,

	GTRM570		petroleum hydrocarbon, 1% to 1.5% by weight of the binder
	Sasobit GTRM850	Sa-850	

Since the aggregate batch is gap-graded, the mix design is conducted according to trial and error in order to obtain mixtures with good coating (Table 3-12).

Table 3-12 Mix design

Mixture	RAP/ RAS (%)	Total Weight (g)	RAP/ RAS (g)	RAP/RAS AC (%)	Total AC (%)	Virgin Binder (g)	Virgin Agg. (g)
Coarse-Virgin Medium-RAP	50	2000	1000	3.24	3.00	27.6	972.4
Medium-Virgin Fine-RAP	50	2000	1000	9.75	6.66	35.7	964.3
Coarse-Virgin Medium-RAS	10	2000	200	21.28	3.29	23.2	1776.8

The foamed binder was produced at 135°C with Wirtgen model WLB 10S in the materials lab at Virginia Center for Transportation Innovation & Research (VCTIR), with water content of 2.5% and 5%, respectively. The non-foaming additives were added and blended with 100 g virgin binder in a metal container (76.2 mm (3 in.) diameter × 55.9 mm (2.2 in.) height) with a high shear-rate mixing gun at 135°C for 3 min in materials lab at University of Tennessee, Knoxville (UTK). The additive dosages selected in this study were generally based on the recommendations by the suppliers. For some additives, the increased dosage was also used by the authors to extend the testing range.

The mechanism of most WMA technologies is to reduce the viscosity of asphalt binder so as to be workable at lowered temperature. Thus, viscosity of foamed binder and binder blended with selected additives was determined, respectively. Brookfield rotational viscometer was used in accordance with AASHTO T316 to test the viscosity of the control and WMA binders at 135°C, and one control binder at 165°C.

The binder produced with different WMA technologies were mixed with virgin aggregates and virgin binder at 135°C following the mix design (Table 3-12). The control hot mix was produced at 135°C and 165°C, respectively. It should be noted that foamed WMA and corresponding control HMA were mixed with Troxler PMW high energy asphalt mixer at VCTIR, while non-foaming WMA mixes and control mixes were mixed at UTK with a Hobart Mixer model A-120 with wire whisk recommended by Asphalt Institute for laboratory mixing. Upon completion of mixing, the materials were separated into coarse and medium particles, or medium and fine particles, respectively (Figure 3-20). The separated particles were eluted with n-propyl bromide (nPB) for a complete extraction, then recovered in a 20 mL vial with a water bath of 70°C in less than 15 min until solvent was non-visible.



Figure 3-20 Separated particles after mixing

The recovered binder was made into standardized sample and subjected to gel permeation chromatography (GPC). The whole experimental plan is illustrated in Figure

3-20.

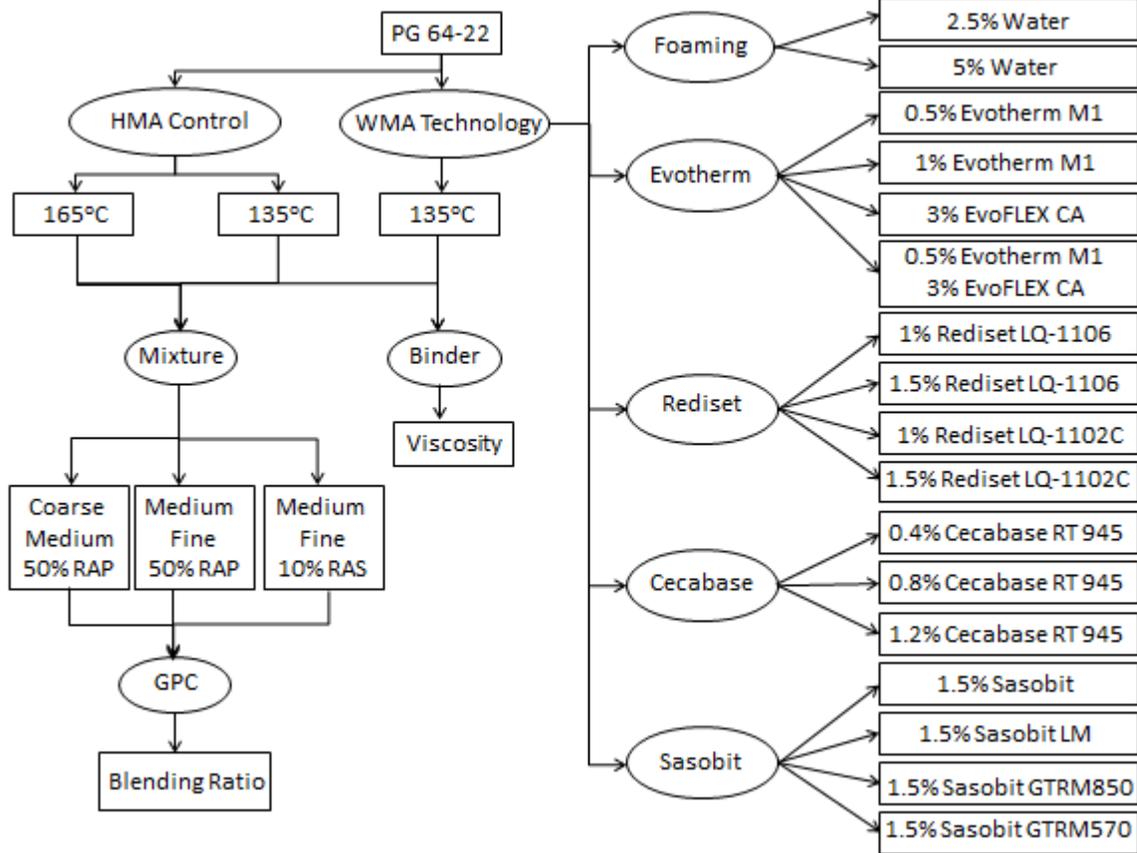


Figure 3-20 Flow chart of the experimental design

3.3.3 Stage Extraction Method

3.3.3.1 Effect of Extraction Time

Two mixtures, one containing 50% RAP and the other one containing 10% RAS, were prepared to fulfill the current tendency of incorporating high amount of the recycled materials. During the asphalt mixture production, the virgin binder may fully blend with the activated recycled binder and re-coat the virgin aggregates and recycled aggregates with un-mobilized old binder still remaining. Therefore, the blending occurring on RAP/RAS aggregates are of higher significance. In order to visually and easily distinguish the RAP/RAS aggregates from the virgin ones, a gap-gradation was used to

design the two mixtures.

The RAP and RAS used in this study were sieved prior to mixing, and only the materials passing No. 8 (2.36 mm) sieve were collected. The virgin aggregates were from a gravel batch that is locally available for surface mixture, and sieved for collecting the part retaining on sieve No. 4 (4.75 mm). The aggregate gradation of the mixture, as well as the job mix formula (JMF) from the same asphalt plant that provided all the materials, can be seen in Figure 3-22. The asphalt content of the recycled materials and the mix design are arranged in Table 5.1. 5.5% was provided by the asphalt plant as the optimum asphalt content (AC) for the mixture of which the JMF was also provided in Figure 3-21. The same optimum AC was selected for the 50% RAP mixture since its gradation was similar. 3.5% was selected for 10% RAS mixture based on trial and error, in order for a mixture with good coating by visual judgment.

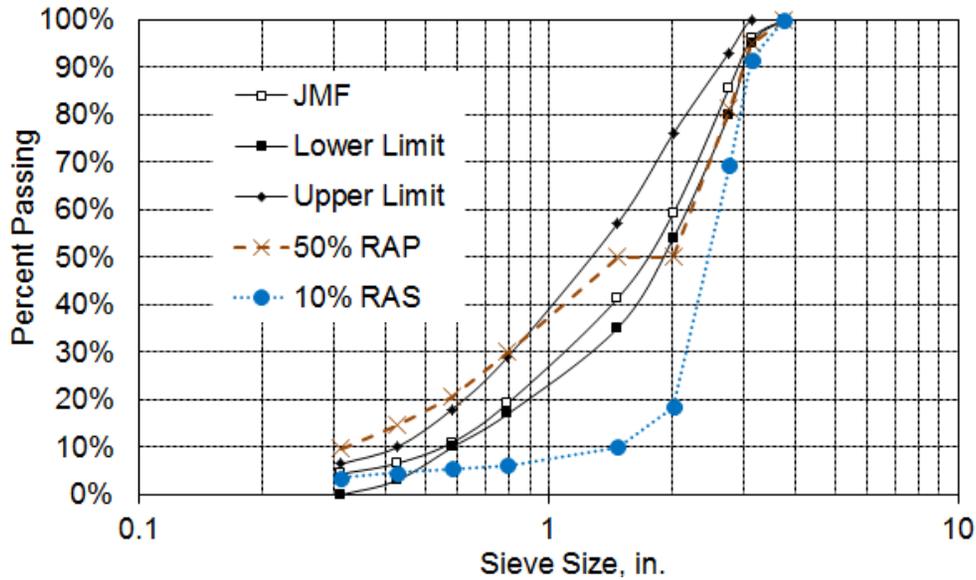


Figure 3-21 Aggregate gradation

Table 3-13 Mix design of the mixtures used in this study

Mixture	Total	RAP/RAS	RAP/RAS	Optimum	Virgin	Virgin
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	Weight (g)	(g)	AC (%)	AC (%)	Binder (g)	Aggregate (g)
50% RAP	2000	1000	5.71	5.5	52.9	947.1
10% RAS	2000	200	20.85	3.5	28.3	1771.7

The virgin aggregates were pre-heated at 175°C two hours prior to the mixing, while the RAP and RAS were heated at 110°C 30 minutes earlier to gain some workability. Note that the heating for RAP/RAS should be limited to maximum of 30 minutes to avoid further aging [2]. The virgin binder was heated at 165°C for a minimum of one hour with the cap tight. A Hobart Mixer model A-120 with wire whisk recommended by Asphalt Institute for laboratory mixing was used to make mixtures in this study. A 2-minute mixing was conducted to ensure a better coating. Upon completion of mixing, the coarse virgin and fine RAP/RAS aggregates were manually separated. Figure 3-22 presents fine RAP aggregates and coarse virgin aggregates separated after mixing.



Figure 3-22 Separated fine RAP and coarse virgin aggregates

The equal time interval was commonly used for staged extraction by researchers. 30 seconds, 1 minute [39] and 3 minutes [1] were tried in different studies. However,

based on the plenty of trials, the authors of this study found the binder layers extracted with equal-time extraction may not accurately represent the actual layers. According to trial and error, a new procedure, named as “Step-Extraction”, was used to strip the binder layers from RAP/RAS aggregates. The step-extraction included six TCE washes that yielded six layers for analysis. The time was 5, 10, 15, 20 and 120 seconds for the first 5 washes, respectively. The remaining binder was soaked in TCE for 30 minutes for complete dissolution, generating the 6th layer. Figure 3-23 shows the percent weight of each layer based on a 1-minute equal extraction and re-designed step-extraction. It can be found that the percent weight of each layer by step-extraction can reach an approximately equal distribution. For comparison purpose, the 1-minute extraction was also conducted. A sample of 10 g was used so as to fit a 50 mL beaker. Upon completion of stripping the binder from RAP/RAS aggregates, each layer was made into standardized GPC sample as mentioned above.

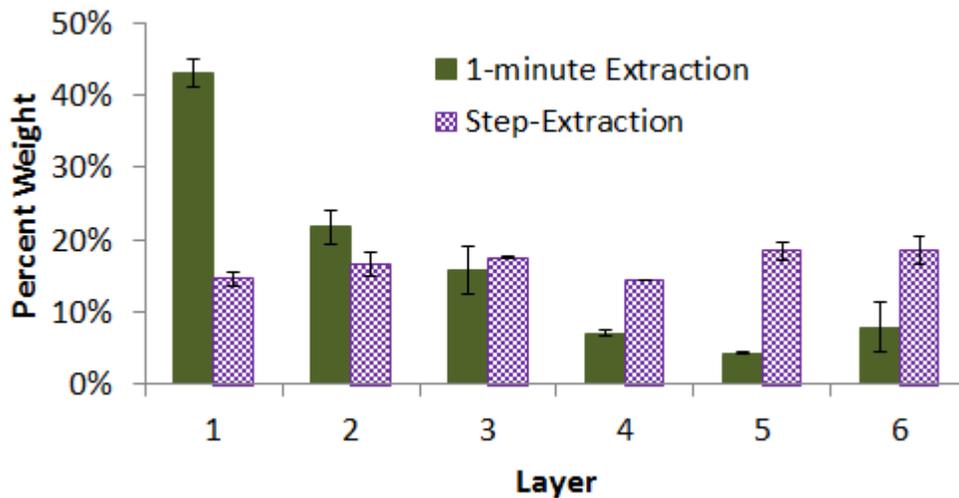


Figure 3-23 Layer weight distribution caused by different extraction methods

3.3.3.2 Diffusion Studies

A locally available PG 64-22 binder was selected as virgin binder in this study.

One gravel batch specified for surface mixture was used as virgin aggregates. One locally available RAP and one RAS were selected as the recycled materials. As illustrated in Figure 3-25, the binder distribution on virgin aggregates and RAP/RAS aggregates may be highly different, so a better analysis can be achieved by evaluating the blending status on virgin and RAP/RAS aggregates, respectively. Thus, a gap-gradation was selected in this study in order to easily distinguish the RAP/RAS aggregates from the virgin ones upon completion of mixing. The virgin aggregates retained on No. 4 (4.75 mm) sieve and the recycled materials passing No. 8 (2.36 mm) sieve were collected for use in this study. The basic information of the raw and sieved materials can be found in Table 3-14.

Table 3-14 Properties of materials selected in this study

Properties			Virgin Agg.	Virgin Agg. (+ No.4)	RAP	RAP (- No.8)	RAS	RAS (- No.8)
AC (%)			-	-	4.76	9.75	20.85	21.28
Gradation	Sieve (in.)	Sieve (mm)	Passing (%)					
	5/8	16	100	100	100	100	100	100
	1/2	12.5	92	89.6	100	100	100	100
	3/8	9.5	71	62.3	92.4	100	100	100
	#4	4.75	23	0	61.5	100	99.2	100
	#8	2.36	15	0	44.5	100	97.4	100
	#16	1.18	12	0	34.6	77.8	80.9	83.1
	#30	0.6	9	0	26.7	60	60.2	61.8
	#50	0.3	6	0	18.3	41.1	53	54.4
	#100	0.15	4	0	13	29.2	44.9	46.1
	#200	0.075	2.5	0	8.7	19.6	34.6	35.5

Two mixtures, one containing 50% RAP and one with 10% RAS, were prepared to meet the current tendency of using high amount of recycled materials. Mix design was adjusted to pursue mixtures with good coating based on visual judgment. The mix design parameters and other useful properties of mixtures are presented in Table 3-15.

Table 3-15 Mix design and other properties of mixtures

Mix	Total Weight (g)	RAP/RAS (g)	RAP/RAS AC (%)	Mix AC (%)	Virgin Binder (g)	Virgin Aggregate (g)
50% RAP	2000	1000	9.75	6.66	35.7	964.3
10% RAS	2000	200	21.28	3.29	23.2	1776.8

Mixing was conducted at 165°C for 2 minutes with a Hobart Mixer model A-120 with wire whisk recommended by Asphalt Institute for laboratory mixing. Upon completion, the coarse virgin and fine RAP/RAS aggregates were separated for staged extraction, respectively. Figure 3-24 presents the separated coarse virgin and fine RAP particles for 50% RAP mix. Trichloroethylene (TCE) was used as the extraction solvent since it was found to be the most effective binder solvent used for staged extraction analysis [42]. A step-extraction was selected to generate binder layers with similar thicknesses based on trial and error (Table 3-16). A total of four layers and six layers were obtained from coarse virgin aggregates and fine RAP/RAS aggregates, respectively. Samples of 25 g and 10 g were used for extraction of fine particles and coarse particles, respectively, to fit the dimension of a 50 mL beaker. The same aforementioned GPC testing procedures were conducted on each extracted binder layer.



Figure 3-24 Separated coarse and fine particles for 50% RAP mixture

Table 3-16 Step-extraction procedure

Layer No.		1	2	3	4	5	6
Wash Time	Coarse	10 s	20 s	30 s	30 minutes	-	-
	Fine	5 s	10 s	15 s	20 s	2 minutes	30 minutes

Figure 3-25 presents the temperature change of hot and warm mix from production to placement. Since diffusion is highly dependent on temperature [46-48], diffusion may mostly occur at mixture storage period at higher temperature after the mixture is produced. In order to evaluate the diffusion at this stage, the fine particles obtained in “blending” study were left in the vacuum oven for 1 hr at target temperature for HMA and WMA respectively, and then subjected to staged extraction and GPC testing. The vacuum oven was used to avoid the effect of aging. The experimental design was organized in Table 3-17.

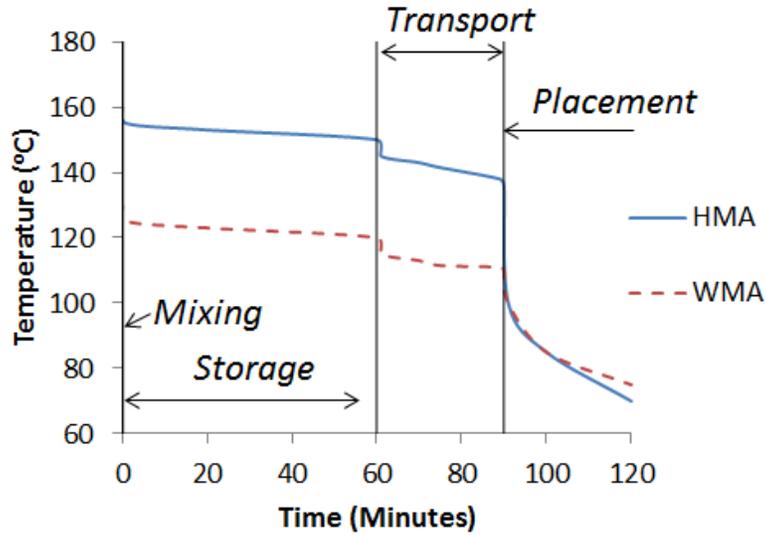


Figure 3-25 Temperature profile for mix production, storage, transportation and placement (adapted from [48])

Table 3-17 Experimental plan for diffusion study

ID	Materials	Treatment	Method
1	Coarse particles from 50% RAP mix	125°C for 1 hr	4-layer staged extraction
2	Fine particles from 50% RAP mix	125°C for 1 hr	6-layer staged extraction
3	Fine particles from 50% RAP mix	155°C for 1 hr	6-layer staged extraction
4	Coarse particles from 10% RAS mix	125°C for 1 hr	4-layer staged extraction
5	Coarse particles from 10% RAS mix	155°C for 1 hr	4-layer staged extraction
6	Fine particles from 10% RAS mix	125°C for 1 hr	6-layer staged extraction
7	Fine particles from 10% RAS mix	155°C for 1 hr	6-layer staged extraction

CHAPTER 4 LABORATORY TEST RESULTS AND DISCUSSION

4.1 Blending Chart

Figure 4-1 presents the “blending charts” generated by blending one typical PG 64-22 binder with recycles asphalt pavement (RAP) and/or recycled asphalt shingle (RAS) binder. All three materials are typical materials and locally available in Tennessee. Linear correlations between recycled binder content and LMS% are revealed on both virgin-RAP blend and virgin-RAS blend with high “R²” values (both over 0.98). Accordingly, the following equations can be derived, for determination of *RAP Binder (%) Blend* [Eq. (4-1)] and *RAS Binder (%) Blend* [Eq. (4-2)], respectively.

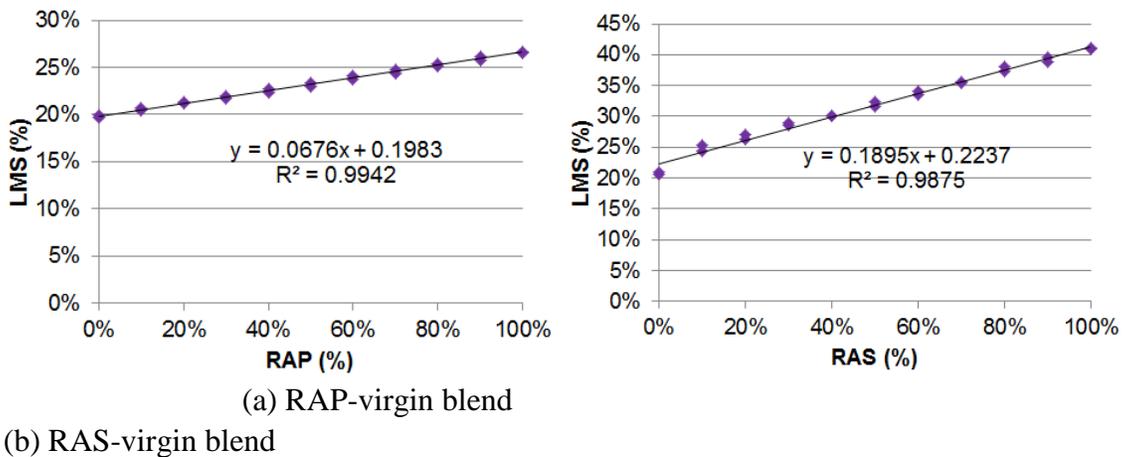


Figure 4-1. “Blending Chart” generated with LMS%

$$RAP\ Binder\ (\%)_{Blend} = \frac{LMS\ (\%)_{Blend} - 0.1983}{0.0676} \quad (4-1)$$

$$RAS\ Binder\ (\%)_{Blend} = \frac{LMS\ (\%)_{Blend} - 0.2237}{0.1895} \quad (4-2)$$

It should also be noted that the proposed idea of using LMS% to build the “blending charts” between recycled and virgin binders can be extended to other multi-binder involved studies. Its further application is not discussed in this paper, but can be valuable for future research.

4.2 Factors Affecting the Blending Efficiency

4.2.1 Effect of Mixing Factors

4.2.1.1 RAP

The recovered binders from the coarse and fine aggregates were tested for their rheological properties. In a poor mixing condition the fine (RAP) aggregate is expected to exhibit stiff rheological properties due to the presence of the RAP binder, while the coarse aggregate is expected to exhibit soft rheological properties since it was mixed with virgin binder prior to RAP inclusion.

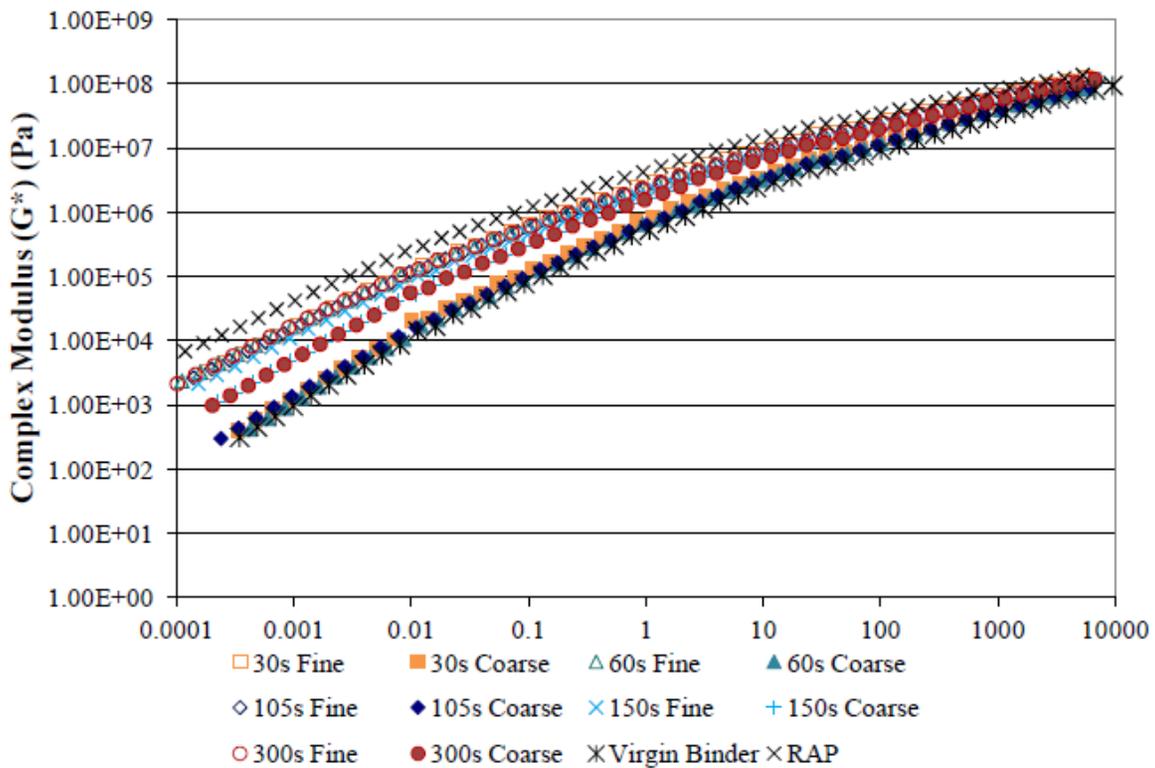


Figure 4-2. Master curve of the Complex Modulus (G^*) for changing mix times

The master curve data (Figure 4-2) shows that there is a large gap between the virgin binder and RAP binder curves. In the case of the virgin binder curve, the binder was recovered from a coarse mixture that contained no RAP. At 30, 60, and 105 seconds, there is no noticeable differentiation between the coarse master curves. However, when the mixing time reaches 150 seconds there is an evident increase in the complex modulus at the lower frequencies. This indicates that there is an increase in the presence of RAP binder in the binder recovered from the coarse aggregate.

A ratio for the LMS% of the coarse aggregate to the fine aggregate was considered for an estimation of the efficiency of blending. The RAP binder exhibits a significantly higher LMS% than virgin binder. Thus, if RAP binder blends with the virgin binder on the coarse, virgin aggregate, the LMS% should increase. Likewise, as the virgin

binder blends or diffuses into the RAP binder on the fine aggregate, the LMS of the fine aggregate should decrease. If the LMS% for the binder recovered from the coarse aggregate, which has been increasing in the number of large molecules present, is equivalent to that of the binder recovered from the fine aggregate which is decreasing in large molecules as the virgin binder blends and/or diffuses into the RAP binder, then a complete blend will have been achieved. The blend ratio is computed as follows:

$$\text{Blending ratio} = \frac{\text{Coarse LMS}\%}{\text{Fine LMS}\%} \quad (4-3)$$

At a typical mixing temperature of 160°C the times were increased from 30 seconds to 150 seconds. The blending ratio gradually increased from just over 55% at 30 seconds of blending to nearly 80% after 150 seconds. . This data was plotted and regressed as shown in Figure 5, to estimate the total time, assuming linearity, to achieve a 100% blend. A linear regression was performed on the data, which yielded the following equation for the estimation of the blending percentage with respect to time:

$$\text{Blending Ratio} = 0.1591(\text{Seconds of Mixing}) + 49.73 \quad (4-4)$$

The basis of the regression equation, it would take over 5 minutes to achieve a 100% blend. That is not a realistic time frame for mixing in a practical field application. A 5 minute mixing time was attempted, as shown in Figure 4-3.

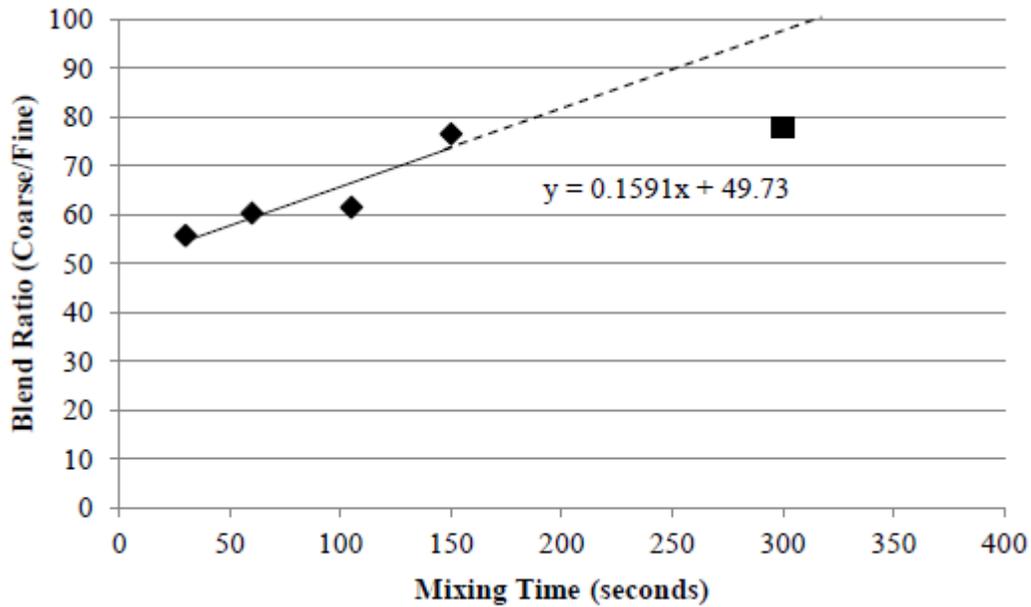


Figure 4-3. Regression of 30, 60, 105, and 150 second blending ratio results to calculate 100% blend ratio. Blending ratio at 300 seconds also presented.

An important finding as noted in Figure 4-3 is that doubling the mix time beyond 150 seconds to 300 seconds (indicated by square in Figure 4-3) only achieved a one percent increase in blend ratio from 77% to 78%. In this mixing scenario it can be concluded that an increase in mixing time is not helpful in creating an increase in blend ratio, and the trend is certainly not linear beyond 150 seconds.

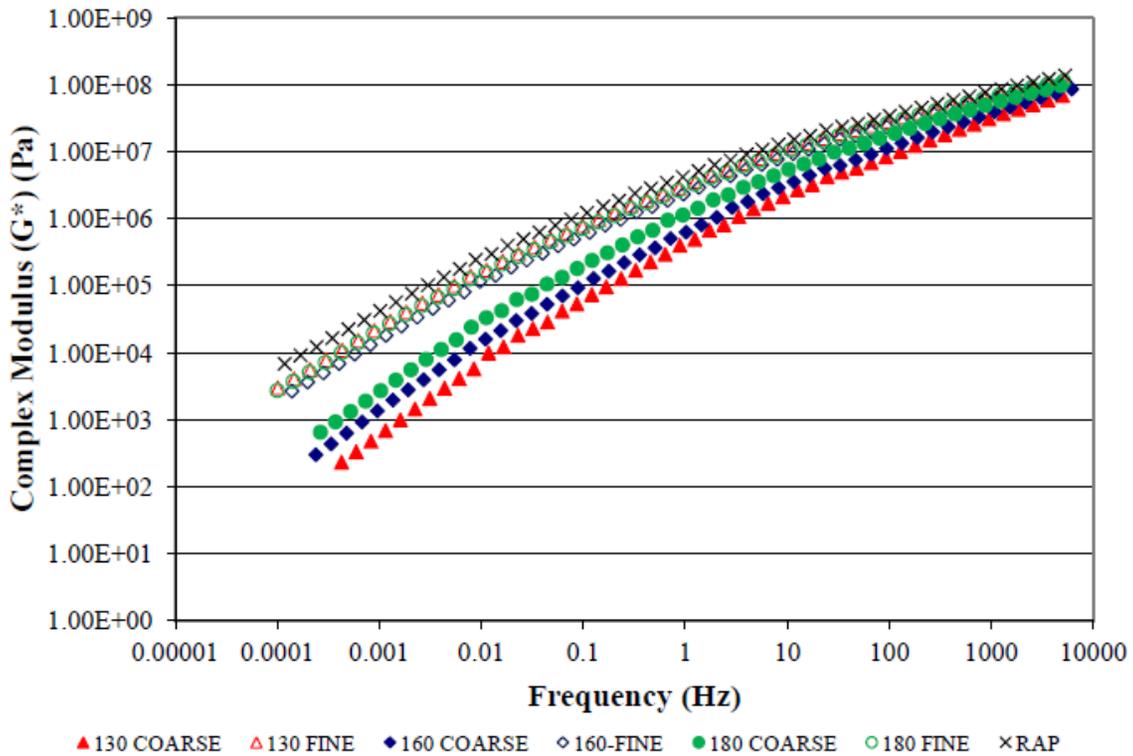


Figure 4-4. Master curve of the Complex Modulus (G^*) for changing temperatures

The master curve shown in Figure 4-4 reveals the influence of mixing temperature on the blending of the binders. The coarse aggregate clearly increases in complex modulus as the mixing temperature increases from 130°C to 160°C and from 160°C to 180°C. Furthermore the fine aggregate master curves never have any clear separation, indicating that the fine aggregate, originally coated in RAP binder, is not further oxidized even at higher temperatures. This is further supported when examining Figure 4-5 which shows the average LMS% and standard deviation for both the recovered fine and coarse binders.

The data presented in Figure 4-6 shows that there is an increase in blend ratio as the mixing temperature increases. This is to be expected, however there it should be noted that since there is no increase in the LMS% for the fine aggregate, it is clear that the binder on the coarse aggregate is indeed receiving some of the effective RAP binder. This

is likely because the hot virgin aggregates and the hot virgin binder can assist in melting the RAP binder, allowing for further diffusion of the two binders into one another.

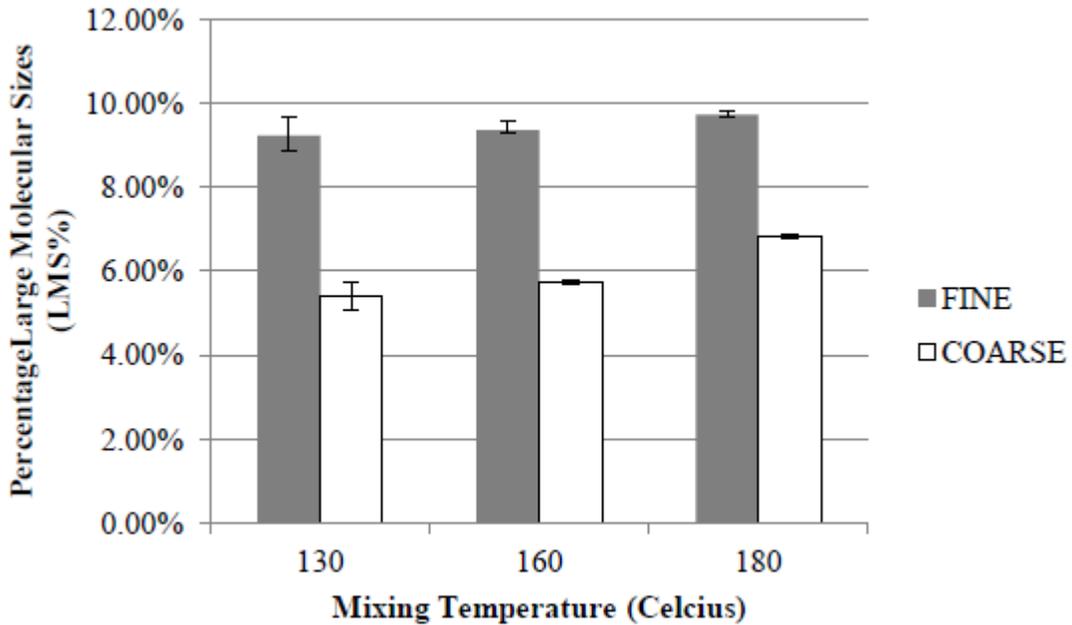


Figure 4-5. Course and fine LMS% for mixing times at varying temperatures at a 105 second mix time

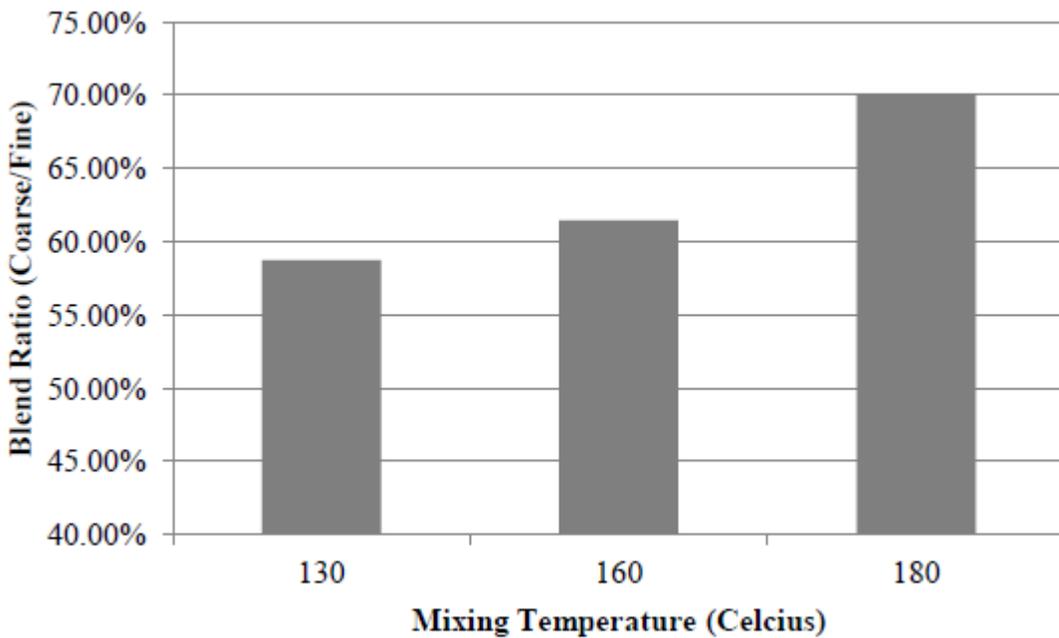


Figure 4-6. Blend ratio for varying mix temperature at a 105 second mix time

The evaluation of WMA additives compared to a control mixture yielded interesting results. In both cases, the WMA additive showed to increase the blend ratio. However, as seen both by the master curve in Figure 4-7 and the blend ratio in Figure 4-8 the Evotherm WMA additive induced better blending than either the Sasobit mixture or the control mixture. The Evotherm mixture had a blend ratio equivalent to that of the 160°C, 150 second mixture even though it was mixed for less time and at a lower temperature. This indicates that Evotherm actually does assist in the blending of RAP and virgin binders. The researchers did notice that Sasobit seemed to increase the workability and more easily coated the RAP when the coarse aggregates with virgin binder were mixed together. Further investigation into the use of Sasobit at a longer mix time (150 seconds) or a higher temperature (160°C) may be worth investigating to see if these two variables play a significant impact in Sasobit's ability to increase RAP blending efficiency.

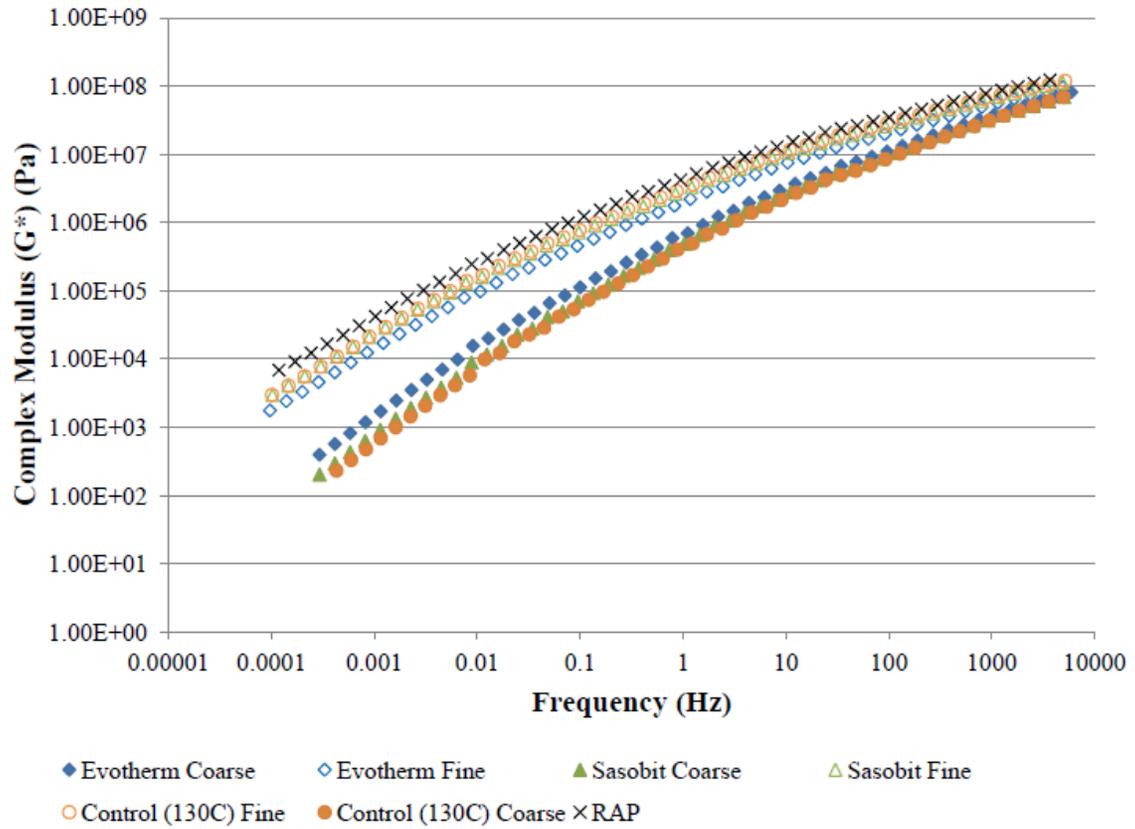


Figure 4-7. Master curve of the complex modulus (G^*) for different WMA additives and a control mixture

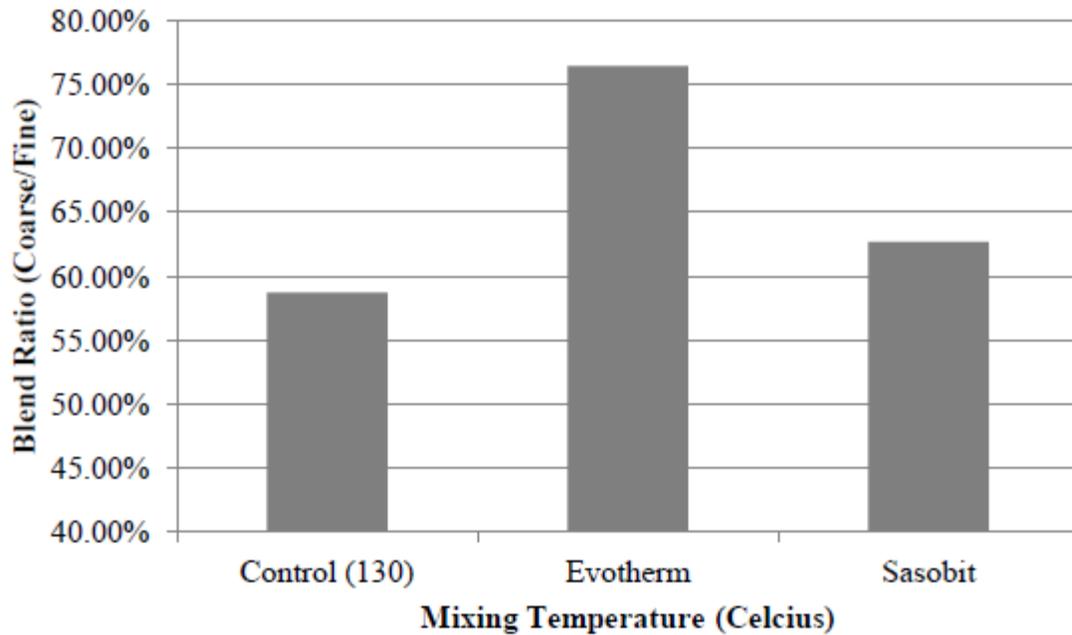


Figure 4-8. Blend ratio for the 130°C control and WMA additives at 105 seconds of mixing

4.2.1.2 RAS

Binders of mixtures containing 5% RAS were selected to evaluate the effect of mixing time. It can be seen from Figure 4-9 that both the LMS% of binders on medium and large aggregates expressed upward trends with the increase in mixing time. Unlike binders on small aggregates, the medium and large ones had not been pre-blended with RAS prior to laboratory mixing. This means the increase in LMS levels of these two aggregates reflects an increase in blending with the RAS binder. The larger the percentage of LMS, the more RAS binder the carriers contributed to the blending. The small aggregates, on the contrary, didn't show any apparent trend with the change of mixing time. As the RAS carrier, small aggregates hold a large amount of RAS binder, which made it difficult to detect the percentage change in LMS, even if the change in blending efficiency did occur.

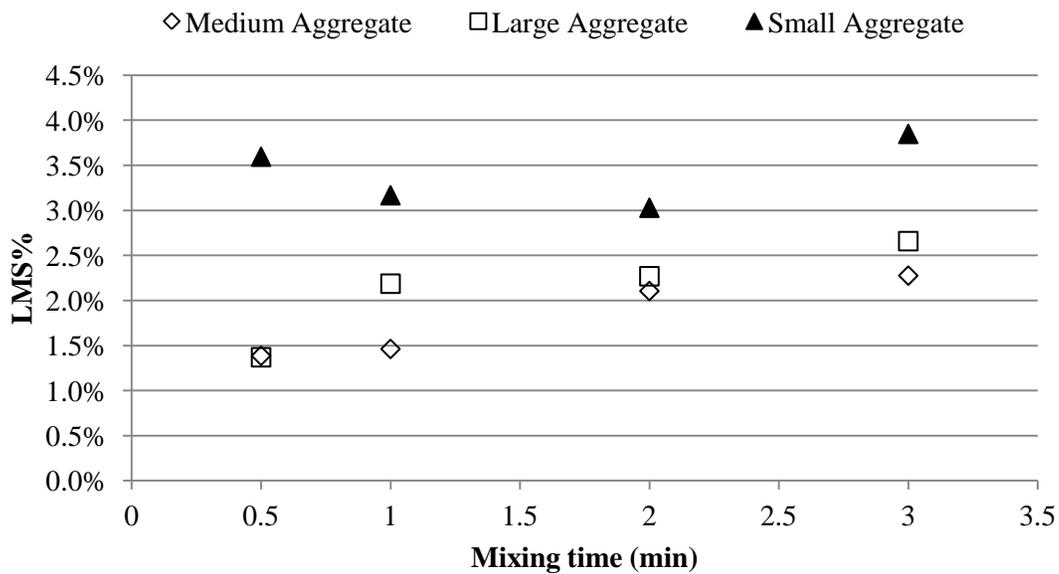


Figure 4-9 The relation between mixing time and percentage of LMS

The effect of aggregate size was evaluated using GPC to investigate the blending efficiency of the RAS binder within a mixture. Figure 4-10 represents seven mixtures, which have different RAS contents or mixing times. The differences between mixtures 1 through 7 were previously defined in Table 3-6 and 3-7. Though each mixing case was different, the small carrier aggregates always had a higher LMS content than that of the medium and large aggregates. Furthermore, the medium and large aggregates always maintained nearly the same percent LMS which indicates that they had a similar binder molecular weight distribution, which correlates to G^* and further performance. The similar LMS% result for the Medium and Large aggregates indicates that the size of the virgin aggregate does not alter the blending efficiency.

The difference in percentage of LMS for the larger aggregates (large and medium) as compared to the carrier aggregates (small) is an important finding. The increased RAS content shown in Mixes 1 through 4 resulted in an increase in percentage of LMS in both medium and large aggregates in all mixes, indicating that the RAS binder is in fact

blending with the virgin binder when the mixing process is occurring. The difference of percentage of LMS between small carriers and larger aggregates indicates that a complete blend is not occurring between the small carrier aggregate binder and the larger aggregate binder. Thus it can be concluded that for this mixing case only partial blending commences.

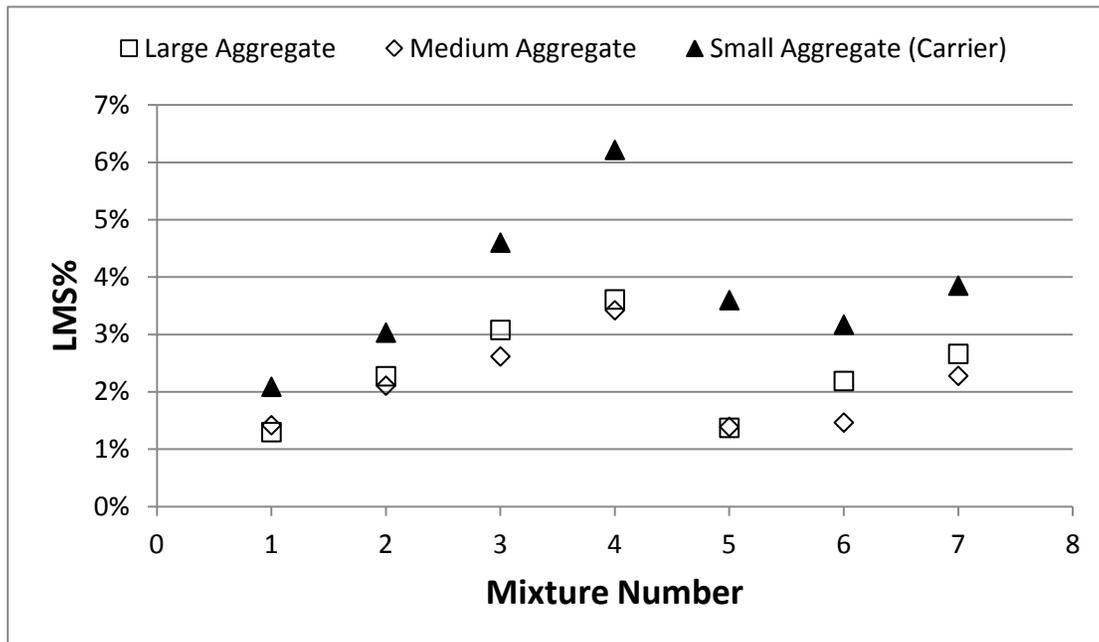


Figure 4-10 The comparison of small “carrier” aggregates to medium and large aggregates

The small carrier aggregate binder contained a higher LMS and thus was believed to have a higher RAS content than the larger aggregates (large and medium). When evaluating the percentage of LMS for the larger aggregates and comparing it to the small carrier aggregates an interesting conclusion could be reached. Based on the limited data provided by the large and medium aggregate tests, the ratio of percentages of LMS of larger aggregates to small aggregates increased up to 5% RAS and then decreased, as shown in Figures 4-11 and 4-12. The increase in the ratio indicates that blending is occurring because the larger aggregate binder LMS percentage is moving closer to that of

the small carrier aggregate binder. This finding is interesting when compared to past literature which states that a maximum recommended RAS content is 5% [49].

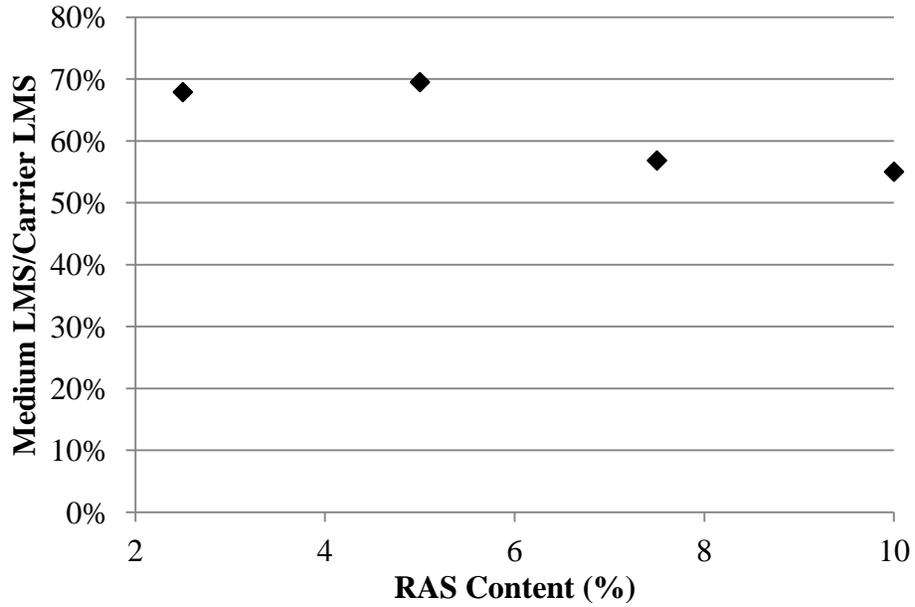


Figure 4-11 Relationship between the medium aggregate LMS and carrier (small aggregate) LMS when compared to RAS content

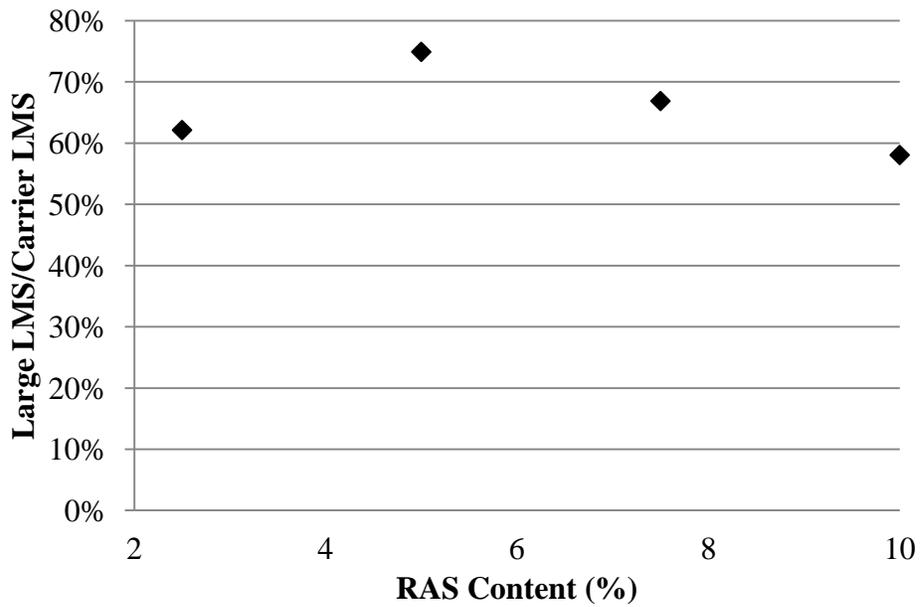


Figure 4-12 Relationship between the large aggregate LMS and carrier (small aggregate) LMS when compared to RAS content

4.2.2 Effect of Aged Binder Content

Figure 4-13 presents the results of LMS% obtained from GPC. It can be seen, for both RAP and RAS, that LMS% of the binder blend increases with the increase of RAP/RAS content in the mixture.

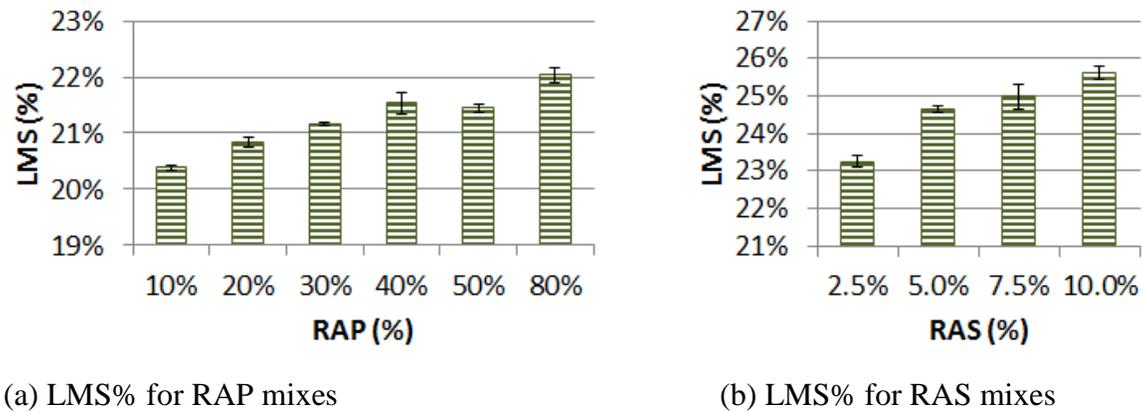
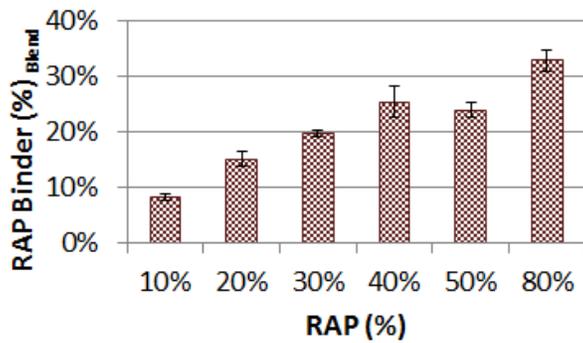
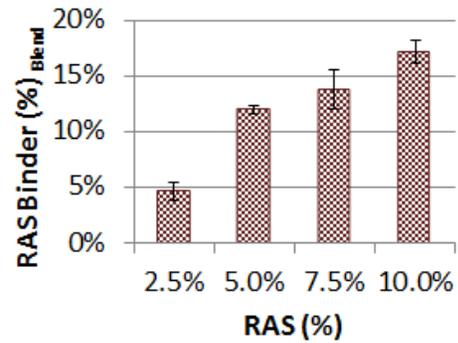


Figure 4-13. LMS% results

Figure 4-14 presents the *RAP/RAS Binder (%) Blend* values. As expected, the trend is consistent with that of LMS%. The increase of recycled binder content in the blend can be attributed to the increase of potentially workable RAP binder in the mixture and less addition of virgin binder, when RAP/RAS percentage is increased.



(a) RAP Binder (%) Blend



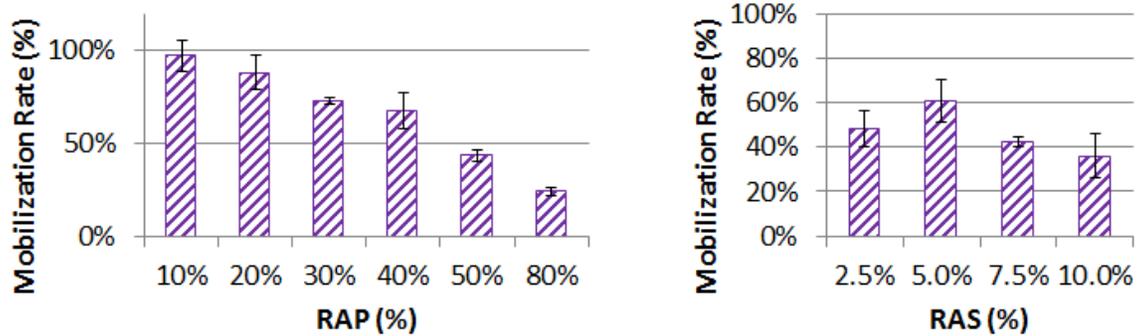
(b) RAS Binder (%) Blend

Figure 4-14. LMS% results

Figure 4-15 shows recycled binder mobilization rates for the mixtures selected in this study. It is found in Figure 4-15 (a) that the mobilization rate decreases if more RAP is added, which indicates lower ratio of the available RAP binder by total will be incurred with increase of RAP addition. For low RAP mixtures (10% and 20%), the mobilization rates are fairly close to 100%, which indicates an approximately complete mobilization of the RAP binder during mixing. However, the mobilization rate drops from 73% to 24% with RAP percentage varying from 30% up to 80%. This finding may lead to an assumption that the fatigue and cracking resistance of HMA containing high RAP (30% or over) is reduced not just because the high stiffness of the recycled binder, but also due to its lower mobilization rate that may cause an under-asphalt mixture or heterogeneous blending. This assumption should be validated in future research.

Unlike RAP, the mobilization rates of RAS mixtures are comparatively low, even at low RAS content. This can be explained by the highly aged nature of RAS binder, which limits the RAS binder from being mobilized at normal mixing temperature. It can also be seen that the mobilization rates of low RAS mixtures (2.5% and 5%) stay around 50% to 60%, which are close to 66.7%, an engineering estimation that has been used by several state agencies as the RAS binder contribution factor. The mobilization rate for 10% RAS mixture can be as low as 36%, which may also account for the restriction of maximum usage of RAS to 3% to 5% in several states. The interesting finding is that the

optimum mobilization rate is found on 5% RAS mixture. This may be explained by the assumption that RAS particles tend to be coated by virgin binder at a low RAS percentage (2.5%), thus could be limited from providing binder to coat virgin aggregate. Meanwhile, RAS particles tend to agglomerate with increased percentage (over 5%) thus leading to less exposure to the binder blend. In addition, the 5% optimum mobilization rate is consistent with the blending ratio results addressed in a previous study by the authors [22].



(a) Mobilization rates for RAP mixes

(b) Mobilization rates for RAS mixes

Figure 4-15. Calculated mobilization rates for mixes selected

4.2.3 Effect of WMA technology

The viscosity of the asphalt binder is used to reveal its flow characteristics to ensure that the binder can be pumped and handled on site and also to determine the mixing and compacting temperature of the mixture [50].

During viscosity testing for foamed asphalt, it was noticed that the reading was not stable even after 30 minutes, thus, the results cannot be used. This can be explained by the water trapped in the binder tending to evaporate at testing temperature of 135°C, so the whole binder system was not in equilibrium. However, the workability of WMA

produced with foamed asphalt was fairly good based on visual judgment.

Figure 4-16 presents the results of binder blended with additives and tested at 135°C as well as control binder tested at 135°C and 165°C. As expected, the viscosity values of WMA binders slightly decreased with addition of additives, as compared to control binder tested at the same temperature (135°C). This indicates that the WMA additives selected in this study can help reduce the mixing and compaction temperatures. However, it can also be found that all the viscosity values of WMA binders are significantly higher than that of control binder tested at regular mixing temperature for hot mix (165°C). This means the WMA produced by adding additives may not be as workable as the regular HMA, although it may improve the workability of mixture produced at the same temperature without any additives. Therefore, the potential old binder mobilization could be limited if the WMA binders were used.

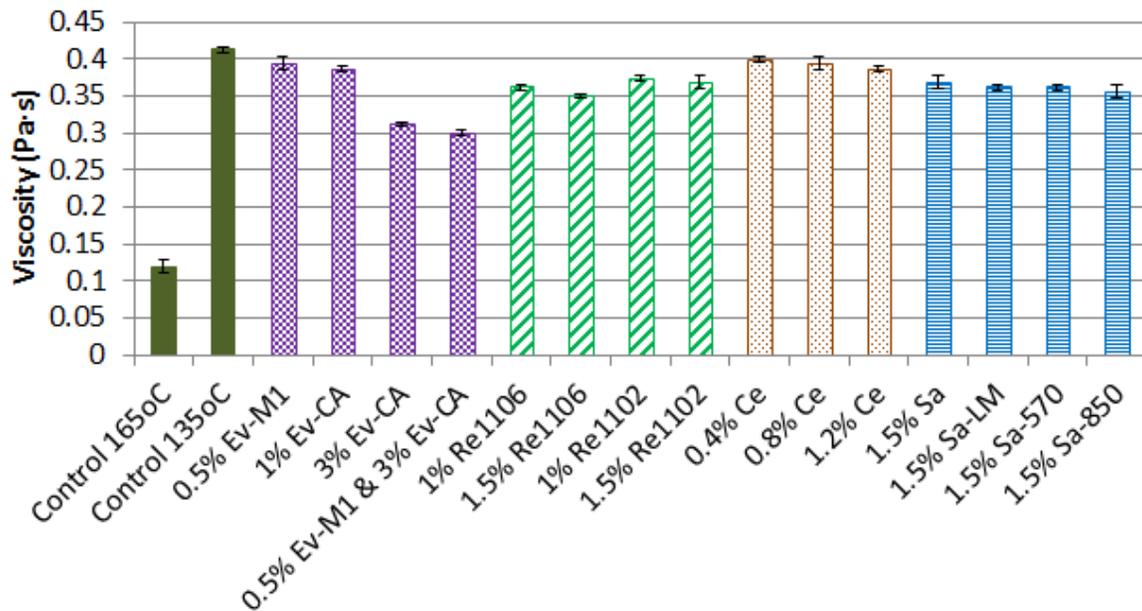


Figure 4-16 Viscosity testing results

Among the additives, EvoFLEX CA seems more capable of reducing the binder

viscosity and the lowest viscosity occurred to binder blended with the combination of 3% EvoFLEX CA and 0.5 % Evotherm M1. This dosage was recommended by the additive supplier as the most effective one used for high RAP/RAS mixtures. However, it should be noted that the EvoFLEX CA addition was 3%, comparatively higher than other additive addition dosage. The clear reduction in viscosity may be attributed to its high dosage rate.

Rediset and Sasobit yielded relatively low values of viscosity than Evotherm M1 and Cacebase regardless the product type, but this reduction was very limited. The different products of the same type of additive did not generate any differences. It was also noticed that increasing the additive dosage slightly decrease the viscosity level.

Since WMA additive was injected into the GPC system with the binder, the effect of additive on the GPC results were checked prior to the blending test. The heating effect was also checked. Figure 4-17 presents the GPC results of binders blended with several additives as well as the control binder heated at 135°C and 165°C with tight cap. It can be seen that GPC testing was not sensitive to the effect of additive or heating for a short period of time. A one-way ANOVA test was also conducted on the results and the p-value with α of 0.05 is 0.88. This indicates that no statistical difference can be found within this group of samples. The limited effect of additive may be attributed to the relatively low adding dosage.

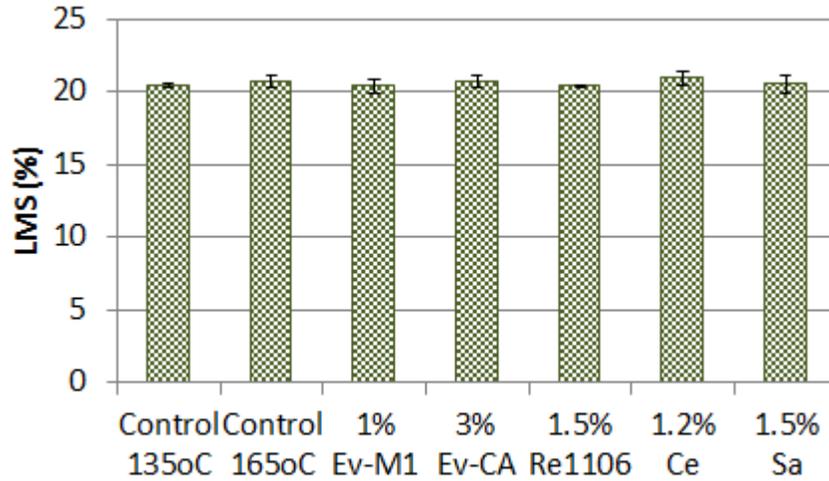
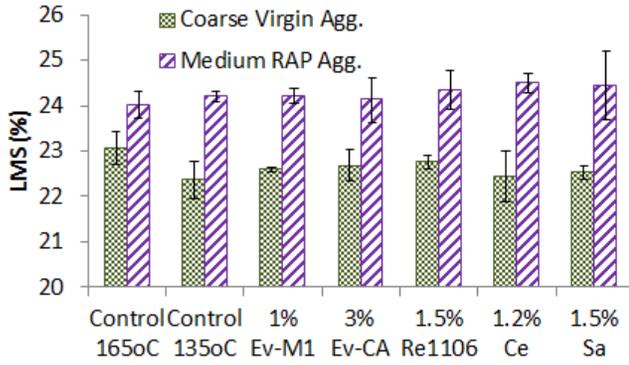


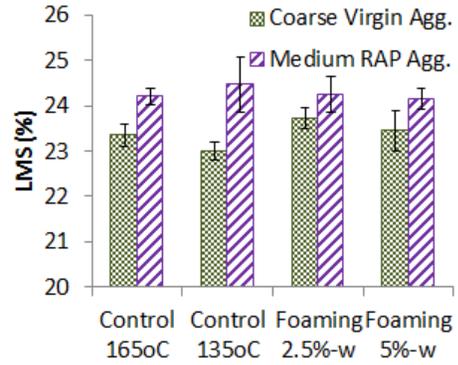
Figure 4-17 Effect of WMA additive or short period heating on GPC results

4.2.3.1 RAP

Figure 4-18 shows the GPC results of binders extracted from coarse virgin aggregates and medium RAP aggregates. Control samples were prepared for both foaming and non-foaming mixtures since they were produced with different mixers at different labs. Only one representative of the same type of additive was reported for general analysis, since the difference within the same additives was very limited. As expected, LMS% values of binders extracted from coarse virgin aggregates were lower than those from medium RAP aggregates, indicating lower RAP binder concentration on virgin aggregates.



(a) GPC results of non-foaming mix



(b) GPC results of foaming mix

Figure 4-18 GPC results of coarse-medium RAP mix

According to previous research, a parameter called “blending ratio” was used to quantify the blending degree, defined as the LMS% ratio of the two binders [22, 39] [Eq. (4-5)].

$$\text{Blending Ratio} = \frac{\text{Coarse LMS (\%)}}{\text{Fine LMS (\%)}} \quad (4-5)$$

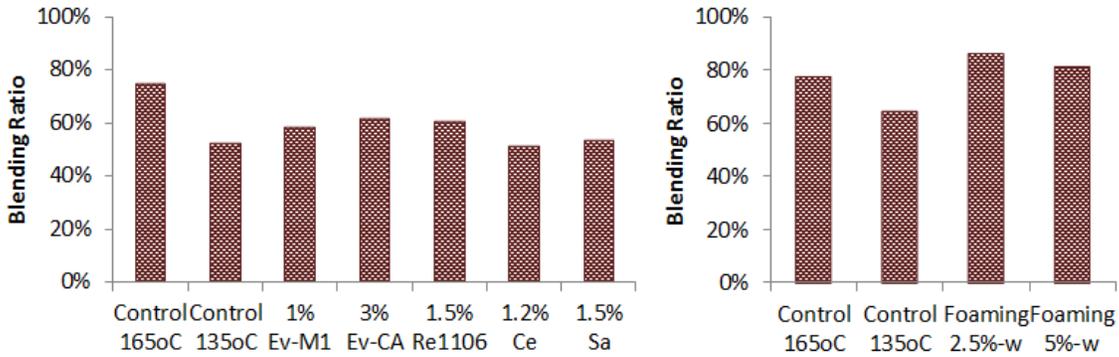
The blending ratio proved to be able to quantify the blending level, however, could be controversial. Imagining there is no blending, the binder coating the virgin aggregate should be totally from virgin binder. Then the blending ratio can be calculated as the ratio of LMS% of virgin binder over LMS% of blend of virgin and RAP binders coating the RAP aggregates. Therefore, the blending ratio is calculated as a non-zero number under no-blending case. If the similar idea is still used, a more reasonable calculation method should take out the LMS% of virgin on both sides, which is expressed as Eq. (4-6).

$$\text{Blending Ratio} = \frac{\text{Coarse LMS (\%)} - \text{LMS (\%)}_{\text{virgin binder}}}{\text{Fine LMS (\%)} - \text{LMS (\%)}_{\text{virgin binder}}} \quad (4-6)$$

In this study, the LMS% for virgin binder was obtained as 20.337, thus Eq. (4-6) in this study can be written as Eq. (4-7).

$$\text{Blending Ratio} = \frac{\text{Coarse LMS (\%)} - 20.337}{\text{Fine LMS (\%)} - 20.337} \quad (4-7)$$

Using Eq. (4-7), the blending ratio for the mixes reported in Figure 4-18 can be calculated and presented in Figure 4-19. Generally, the blending ratio of non-foaming WMA is slightly higher than control mix produced at 135°C, but lower than the 165°C mix. The foaming mix exhibited higher blending ratio than both control mixes. However, the difference is not appreciable, especially among WMA mixes.



(a) GPC results of non-foaming mix

(b) GPC results of foaming mix

Figure 4-19 Blending ratio of coarse-medium RAP mix

Figure 4-20 and Figure 4-21 present the GPC results of non-foaming and foaming WMA mix with medium-fine design. Using Eq. (4-7), blending ratio was calculated and presented in Figure 4-22 and Figure 4-23.

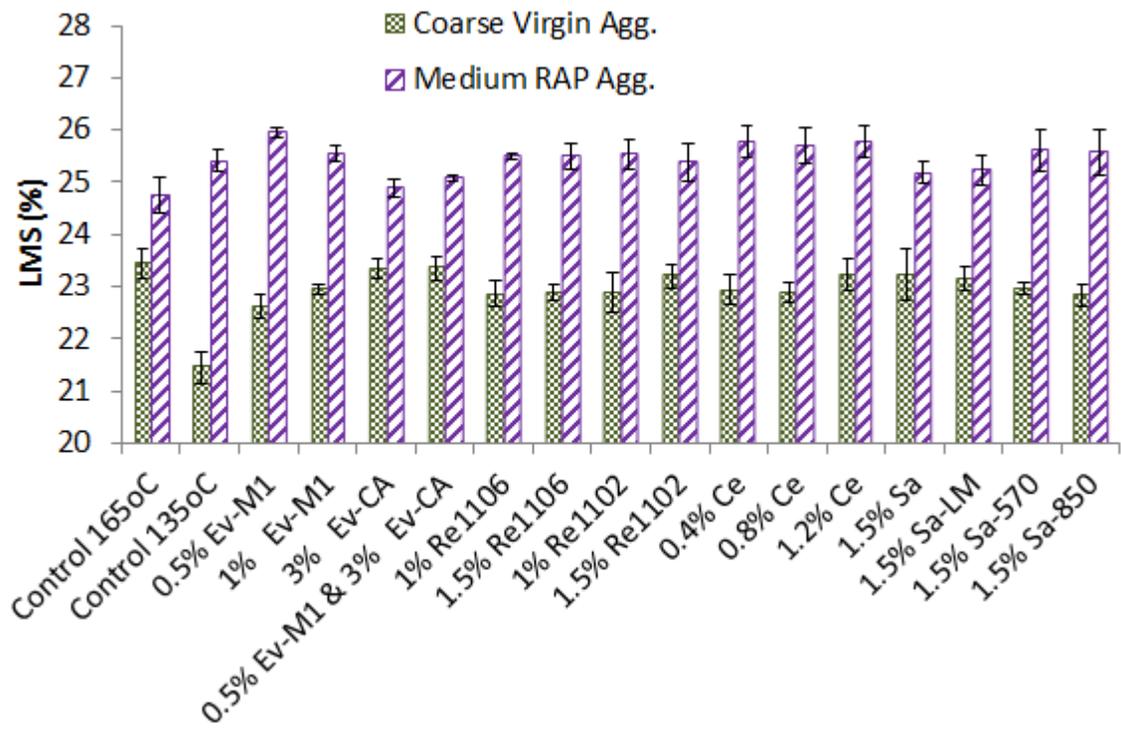


Figure 4-20 GPC results of non-foaming medium-fine RAP mix

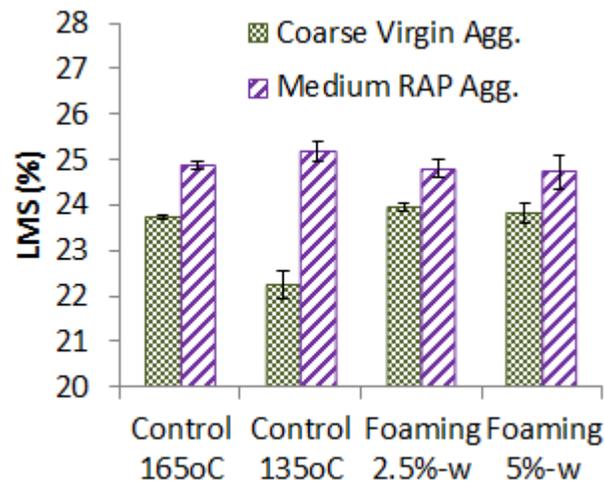


Figure 4-21 GPC results of foaming medium-fine RAP mix

Figure 4-22 presents the blending ratio of non-foaming medium-fine RAP mix.

The effect of the products within the same type of additive was observable, so the figure was processed with the additives of the same type in the same group. Generally, the WMA mixes yield blending ratios obviously higher than control mix produced at 135°C, but still lower than control mix made at 165°C. This finding is consistent with that obtained from the coarse-medium mixes.

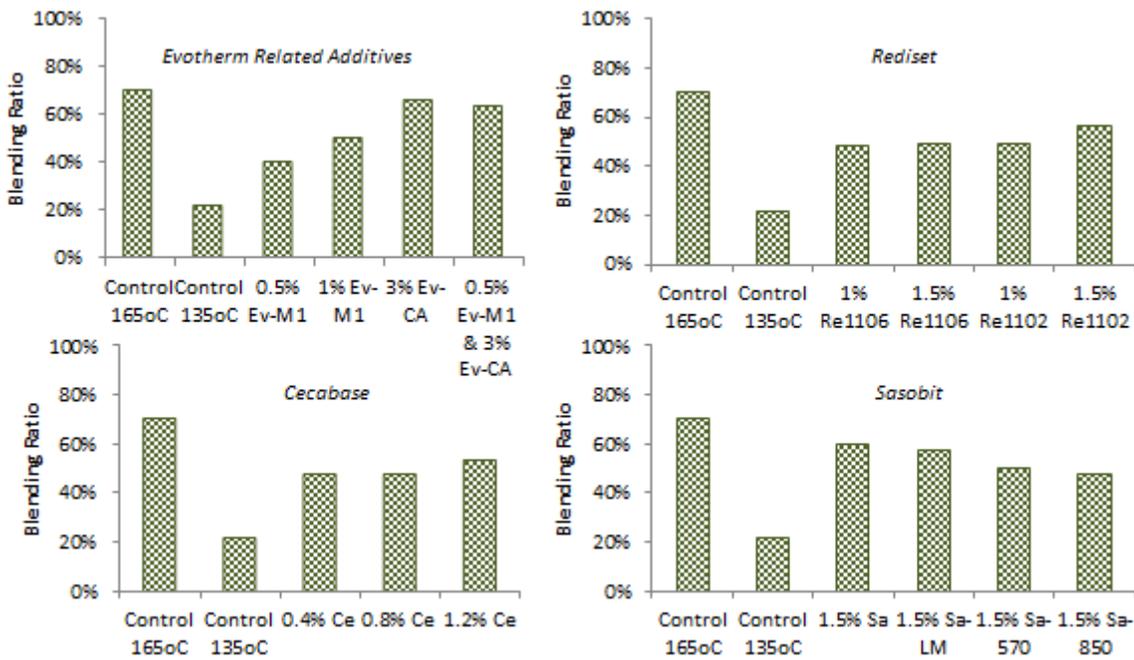


Figure 4-22 Blending ratio of non-foaming medium-fine RAP mix

For Evotherm related additives, adding 3% EvoFLEX CA with or without Evotherm yielded a blending ratio close to the 165°C control mix. Blending ratio increased when adding higher dosage of Evotherm. Rediset 1102C mix exhibited a higher blending ratio than another product 1106 at a dosage of 1.5%. Cecabase with higher dosage rate also improved blending. Among the four sasobit additives, sasobit yielded the highest blending ratio. It seems the results from different type of additive agreed on a trend that increasing the WMA additive increased the blending ratio. Among various

products from the same company, no appreciable difference can be found. All these findings mentioned above indicate that blending remains a critical question over non-foaming WMA.

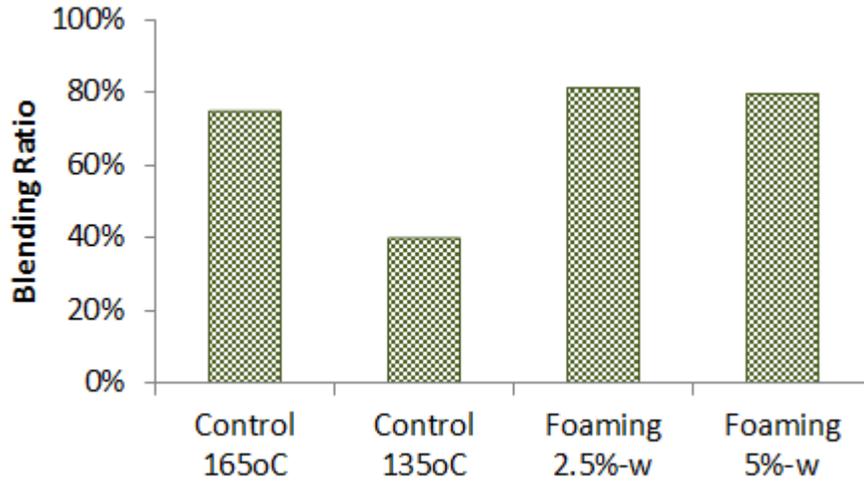
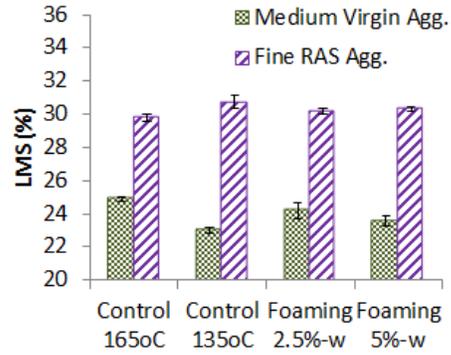
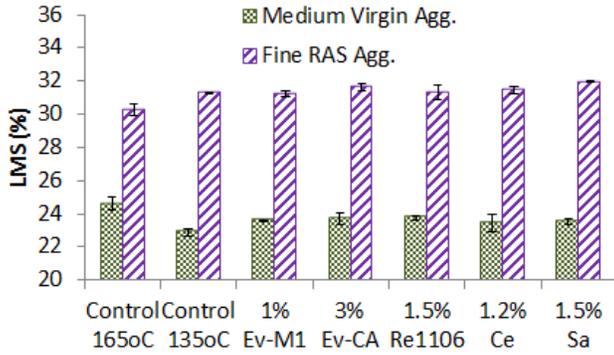


Figure 4-23 Blending ratio of foaming medium-fine RAP mix

Unlike the non-foaming additives, the foaming technology was found to increase the blending ratio of the RAP mix (Figure 4-23). The water content seems have very little effect. This indicates that foaming WMA may improve the blending between the virgin and old binder in RAP mix.

4.2.3.2 RAS

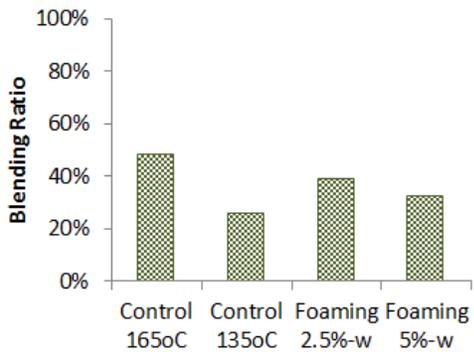
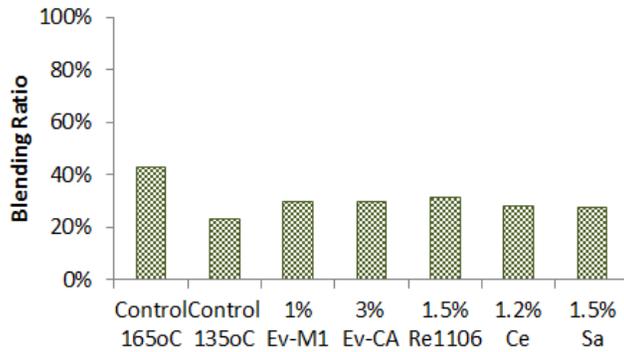
Figure 4-24 presents the GPC results of the binders extracted from medium-fine RAS mix. The blending ratio can be seen in Figure 4-25.



(a) GPC results of non-foaming mix

(b) GPC results of foaming mix

Figure 4-24 GPC results of medium-fine RAS mix



(a) GPC results of non-foaming mix

(b) GPC results of foaming mix

Figure 4-25 Blending ratio of coarse-medium RAP mix

When it comes to RAS, the highest blending ratio was found at 165°C control mix, with a value merely over 40%. This supports the concern that RAS is very stiff at normal mixing temperatures and difficult to be mobilized. Only one additive of the same type was selected to report herein, since the results were fairly close. The mixtures produced with foaming technology showed lower blending ratios than the control mix, which is contradicting the finding obtained from RAP mix. This may indicate that temperature is more important than coating when RAS is used. 135°C seems to be too low to handle the RAS materials. The blending in WMA-RAS mixtures should be further evaluated.

4.3 Results from Extraction Method

4.3.1 Validation Results of Staged Extraction

Figure 4-26 shows the steel-ball testing results. It can be seen from Figure 4-26 that the percent weight of each layer was controlled within the range 13% to 18%. The 1 minute interval was determined by several trials. According to the GPC testing results [Figure 4-26(b)], it was found LMS% values of first two layers were approximately the same with that of virgin binder. The LMS% increased from layer three to inner layers, with LMS% of last layer close but not exceeding the level of RAP binder. This finding clearly shows that the composite binder film coating the steel ball was stripped by the solvent layer by layer. Although this is an ideal and well controlled composite system, the staged extraction method can be validated.

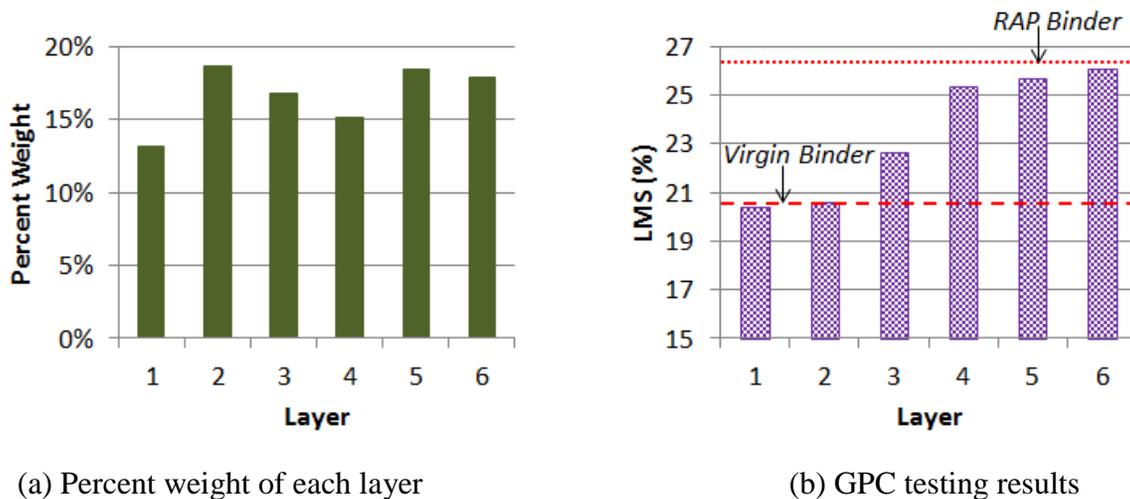


Figure 4-26 Steel-ball testing results

4.3.2 Effect of Extraction Time

Figure 4-27 presents the GPC results of 1-minute extraction and step-extraction described above on RAP particles. LMS% values of all the samples are found to be within the range generated by virgin binder and RAP binder, which follows the common sense that each layer is a combination of virgin and RAP binders. It can be seen that LMS% tends to increase from the outmost layer (layer 1) to the innermost layer (layer 6), regardless of the extraction methods. However, the variation among the layers generated by 1-minute extraction was relatively smaller, while the step-extraction yields a more differentiable LMS% distribution. In conjunction with the weight distribution presented in Figure 5.9, the step-extraction presented in this study seems to generate a more favorable evaluating system and should be used for further research.

According to the results of step-extraction, it can be found that the first layer is close to the virgin binder, while the last two layers are similar to the RAP binder. The LMS% values of layer 2, 3 and 4 stand in the middle, serving as the blending zone with unknown blending level.

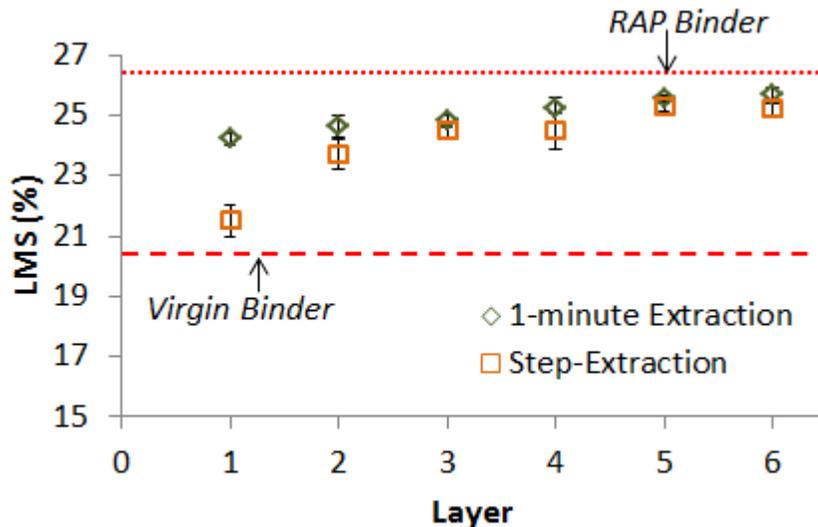


Figure 4-27 GPC results of RAP samples

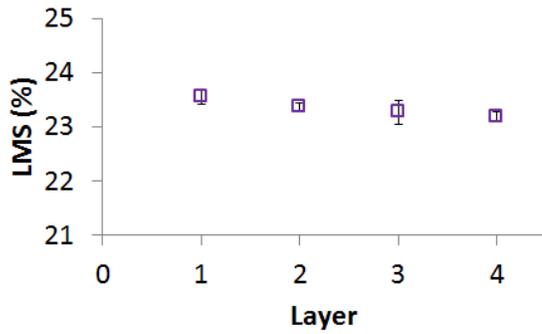
Figure 4-27 presents the GPC results obtained from extraction of RAS particles.

The same finding was observed as that of RAP extraction. This means the step-extraction proposed in this study can also be extended to RAS blending research.

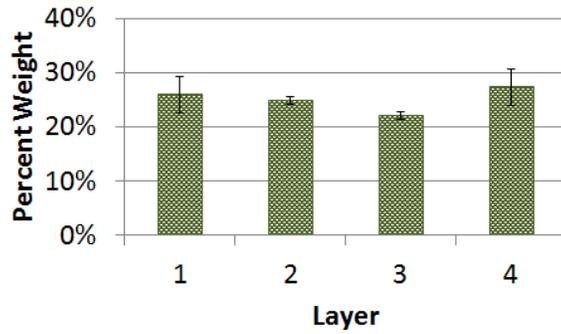
It is noted that the LMS% of the innermost layer is not very close to the RAS binder level. This does not mean the virgin binder could blend into the inner layer of RAS binder, since the fine particles passed No. 8 sieve were RAS particles only and a large amount of virgin binder might coat the RAS particles with a heavy film. The thick coating may have brought uncertainties to the system. Further research with more reasonable design should be conducted to validate this assumption.

4.3.3 Diffusion Studies

Figure 4-28 presents the staged extraction results of coarse aggregates separated from 50% RAP mixture. According to Figure 4-28(b), the weight of each stripped layer was similar, indicating the layers may be extracted in the similar film thickness. Figure 4-28(a) shows the LMS% of each layer. There is a slight decrease of LMS% from outmost layer (1st layer) to 2nd layer, and LMS% changes very little from 2nd to the innermost layer. This may suggest an approximately homogeneous film coating the virgin aggregates. A one-way ANOVA test was conducted on the data and a p-value of 0.184 was obtained with α of 0.5, which means no significant difference was found within the 4 layers. It is reasonable that the outmost layer exhibited a slightly higher LMS% since it was exposed to RAP particles.



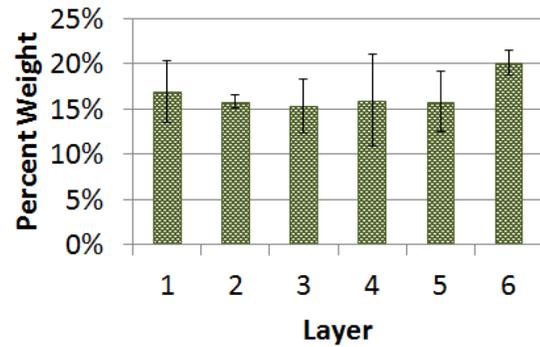
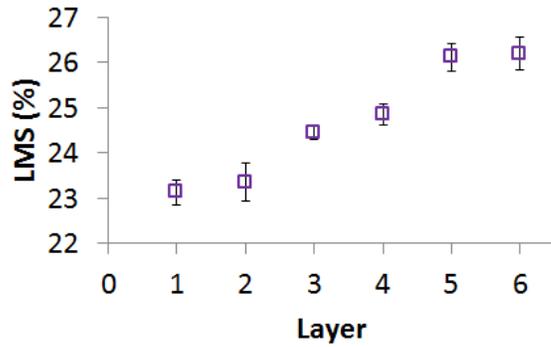
(a) GPC results in terms LMS%



(b) Percent weight of each layer

Figure 4-28 Results of staged extraction on coarse virgin aggregates in RAP mix

Figure 4-29 presents the results of fine particles separated from the RAP mix. It can be seen from Figure 4-29(b) that the extracted layer was well-controlled in similar film thickness. As expected, the LMS% of the binder layers increased from the outmost layer to the innermost layer, since the un-mobilized old binder coating the RAP aggregate considerably contributed to formation of inner layers. However, the interesting finding is that the first two layers exhibited similar LMS% values to those coating the virgin aggregates. One-way ANOVA test was conducted on the LMS% of the six layers, including two outmost layers coating RAP aggregates and all the four layers coating virgin aggregates. A p-value of 0.56 was obtained, which indicates no significant difference among the six layers. This finding may support the blending scenario proposed in Figure 6.3. The virgin binder and mobilized RAP binder may be well blend during mixing and generate a relatively homogeneous film that subsequently coats the virgin aggregates or RAP aggregates with some un-mobilized old binder still attaching. According to Figure 6.10(b), the approximately homogeneous blend film accounted for around 30% to 35% of the total binder coating the RAP aggregates.

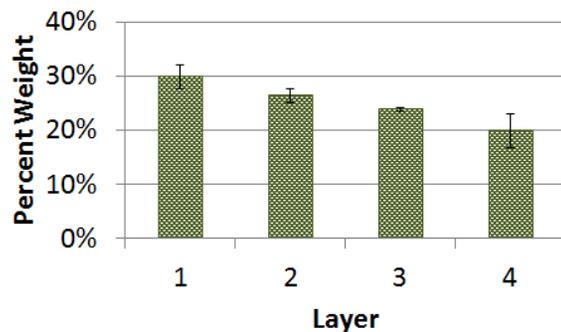
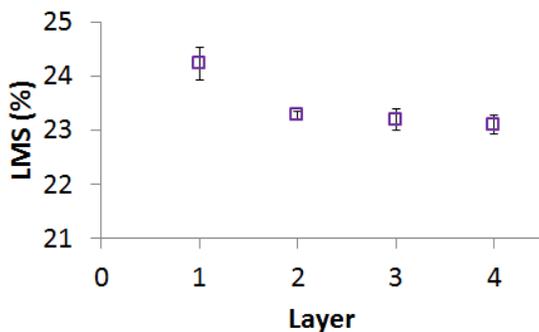


(a) GPC results in terms LMS%

(b) Percent weight of each layer

Figure 4-29 Results of staged extraction on fine RAP aggregates

Figure 4-30 shows the testing results of binders coating the virgin coarse aggregates. Unlike the RAP mixture, the binder on virgin aggregates was extracted in an uneven rate but still within a 10% range. It was also found that LMS% of the outermost layer was a little higher than the other three that showed similar LMS% values. This may be because the mobilized RAS binder did not blend well with the virgin binder, thus attached onto the outmost layer of binder coating virgin aggregates.



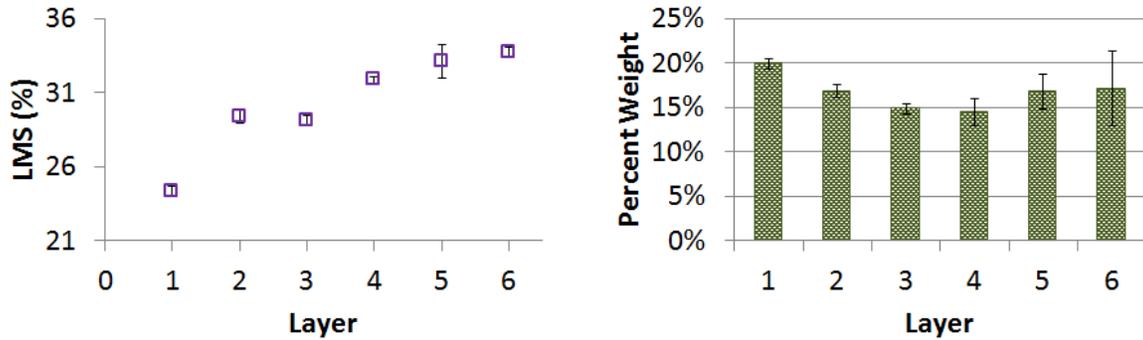
(a) GPC results in terms LMS%

(b) Percent weight of each layer

Figure 4-30 Results of staged extraction on coarse virgin aggregates in RAS mix

Figure 4-31 presents the results obtained from testing on fine RAS particles. The average LMS% of the outmost layer that accounts for approximately 20% of the binder was 24.35, close to the average LMS% of the outmost layer on virgin aggregates, 24.23.

Starting from the second layer, the LMS% of the binder was significantly higher. This finding shows that the binder distribution in RAS mixture may be different from the RAP mixture. The new blending scenario was proposed and illustrated in Figure 4-32.



(a) GPC results in terms LMS%

(b) Percent weight of each layer

Figure 4-31 Results of staged extraction on fine RAS aggregates

Figure 4-32 illustrates different blending scenarios of RAP and RAS mixes. The blending scenario of RAP was validated, to some extent, by the staged extraction results of RAP mix. Unlike RAP, the staged extraction results on RAS mix suggested a composite structure of binder coating the virgin aggregates after mixing. The virgin aggregate was coated by virgin binder first, then the blend of virgin binder and RAS binder mobilized during mixing re-coated the virgin and RAS aggregates. Due to the reduction in temperature or intrinsic difference between RAS and virgin binders, the binder blend could not enter through the virgin binder layer, thus developing a composite binder system on virgin aggregates. Since RAS was extremely aged during production process and service life, only a small portion of RAS binder could be mobilized, therefore a thick inactive RAS binder layer was left remaining coating the RAS aggregates. The blending process does not stop when mixing is completed. As shown in Figure 6.7, the mixture is generally kept at relatively high temperature up to several hours, thus diffusion starts to occur upon completion of mixing process.

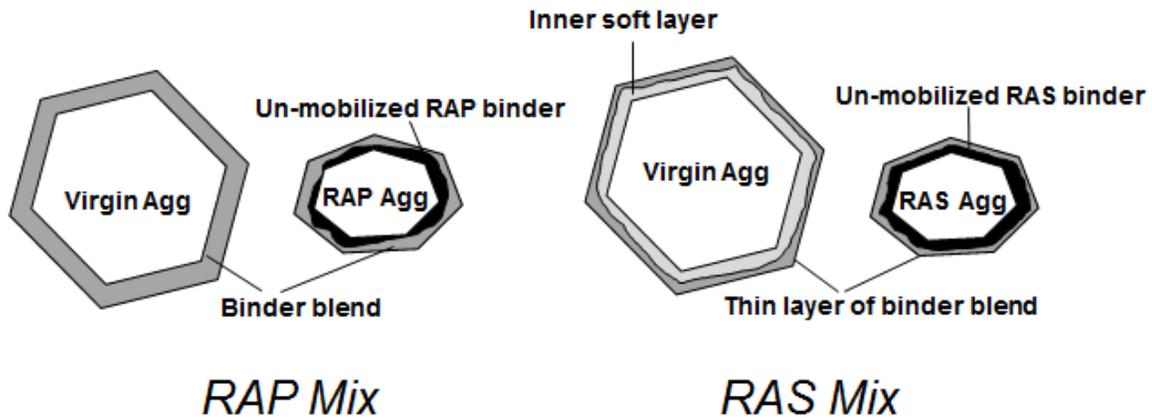
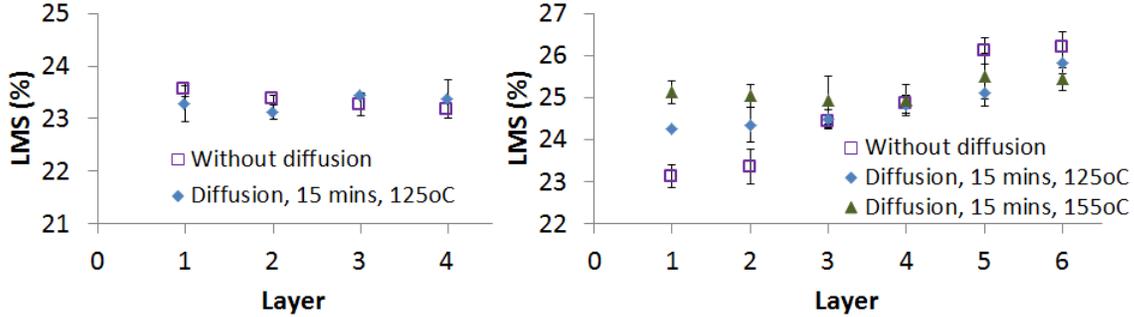


Figure 4-32 Different blending scenarios of RAP and RAS mixes

The same materials used in blending study were also used in diffusion study for comparison purpose. According to description of sample 1 to 3 in Table 3-17, the coarse and fine particles from RAP mix were conditioned in a vacuum oven at 125°C or 155°C for 1 hr to simulate the storage temperature and time for WMA and HMA, respectively. The lab testing results showed statistically the same LMS% values for binder layers extracted from the same batch of particles. The authors of this study shortened the testing time to 15 minutes and the testing results were arranged in Figure 4-33. After conditioned at 125°C for 15 minutes, the binder on virgin aggregate tended to be more homogeneous, with a p-value of 0.636 from one-way ANOVA test, compared to a p-value of 0.184 without diffusion.

On the RAP aggregates, a fairly homogeneous binder system was generated after conditioned at 155°C for 15 minutes, with a one-way ANOVA p-value of 0.604. The binder exhibited a tendency of being more evenly distributed after treated at 125°C for 15 minutes, although the p-value of 0.008 indicates that LMS% of all layers were not statistically the same. This indicates that binder diffusion can be completed during the mixture storage time for HMA and approximately completed for WMA mixes.

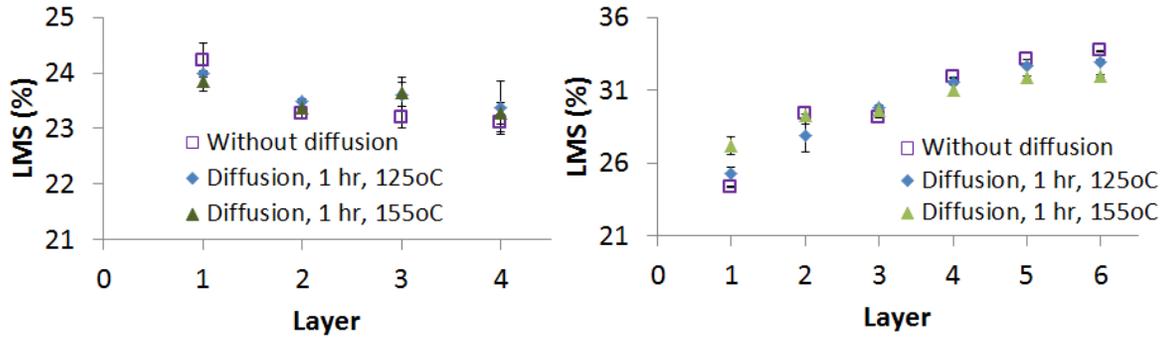


(a) Staged extraction on coarse virgin aggregates (b) Staged extraction on fine RAP aggregates

Figure 4-33 Diffusion results of RAP mix

Figure 4-34 presents the diffusion testing results for 10% RAS mix. On the virgin aggregates, it seems binder diffusion occurred but not in an appreciable level. However, one-way ANOVA test results show that p-value increased from 0.0149 for sample without diffusion, up to 0.249 for 125°C conditioning and 0.119 for 155°C conditioning. This may indicate that diffusion occurred, but very slowly. Since the original differences in LMS% among layers were not significant, the binder on virgin aggregates may be considered as approximately homogeneous after storage diffusion.

The diffusion concern was noticed on RAS particles. According to the LMS% results, the homogenization process, especially at higher temperature, could be noticed. However, the variation of LMS% obtained from the outermost layer to the innermost layer stayed at a high level. This finding confirmed the concern over binder homogeneity in RAS mixtures. Since diffusion is highly dependent on temperature, the long-term diffusion between the virgin and RAS binder at lowered temperature may not be promising. Therefore, the diffusion homogeneity may remain an issue for RAS mix.



(a) Staged extraction on coarse virgin aggregates (b) Staged extraction on fine RAS aggregates

Figure 4-34 Diffusion results of RAS mix

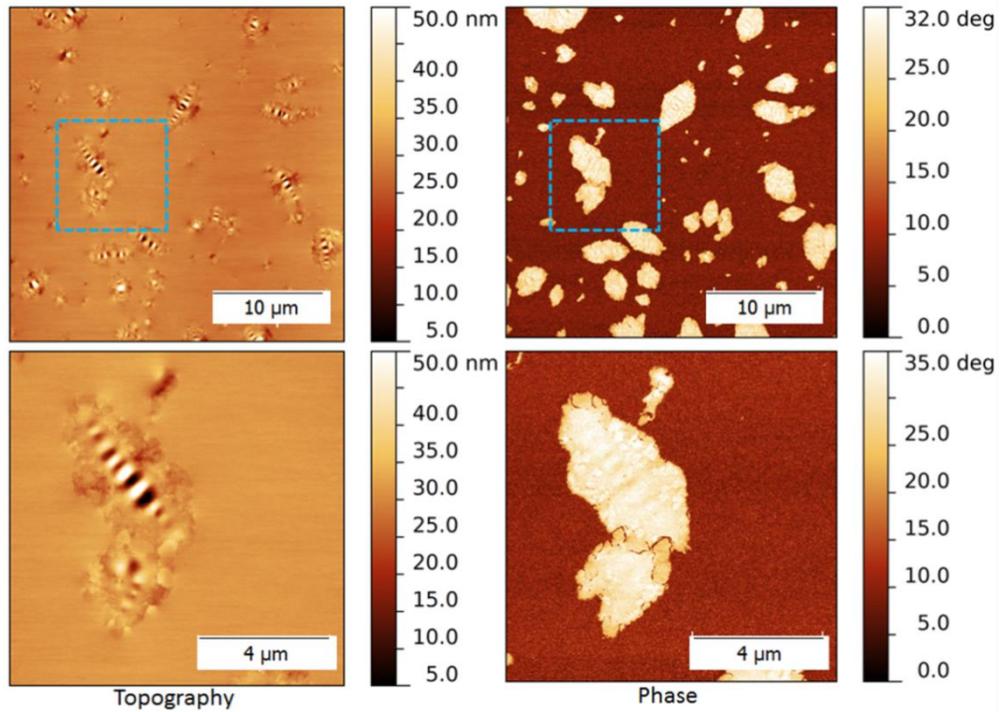
4.4 AFM

AFM imaging was conducted on previously prepared samples made from all the five binders at 25 °C. The results are shown in Figure 4-35 to 4-37. According to the results of topography, the characteristic bee-shaped microstructures can be observed in both two virgin binders and are found in larger size in binder with lower PG grade. These bee-shaped microstructures are similar to those found in previous research [31, 34, 35]. On the contrary, no “bees” are found existing in the two tear-off binders, VT and TT. Both of them show similar topographic images with domains with the size of 1 to 2 μm, which is largely different from the topography of virgin binder. From the perspective of profile, these domains look like plenty of round or elliptical “humps” dispersed onto the surface of a lower homogeneous matrix. It should also be brought into attention that the topography of binders extracted from tear-offs is significantly rougher than virgin ones. These observations validate the feasibility of using AFM to differentiate aged RAS binder and virgin binder through direct detection in solid state. The hump-shaped microstructures can be seen as the fingerprint of the RAS binder under AFM. These changes in topography can be attributed to either the polymer added during the shingle production or significant aging in the air-blown process or after years’ service life.

The interesting finding is the typical bee-shaped domains can also be observed in the topographic images of TM binder, which has gone through the air-blown process for production. Meanwhile, the roughness of TM binder is also found in between the tear-off binders and virgin ones. This indicates that post-manufactured RAS binder, in the microstructural view, behaves like a transition from virgin binder to further aged tear-off binder. This finding supports the assumption that the microstructural changes, for the most part, result from aging rather than interaction between polymer and asphalt binder.

Similar to the topography, the phase image of each binder selected in this study also shows its uniqueness. The phase change transforms from virgin binder to most aged tear-off binder in the order from simplicity to complexity. Only two apparent phases can be detected in softest PG 52-58 binder, which is similar to the image of AAN binder observed by Mason et al. [28]. A third phase is found in PG 64-22 binder, consisting of flake-like domains [28] separating the dark and light phases. The TM binder shows less comparable domains than virgin one, while the dark phase is almost invisible in morphological images in both two tear-off binders. The phase images, therefore, proved to provide an alternative to fingerprint the RAS and virgin binders.

(a) Virgin bitumen PG5228



(b) Virgin bitumen PG6422

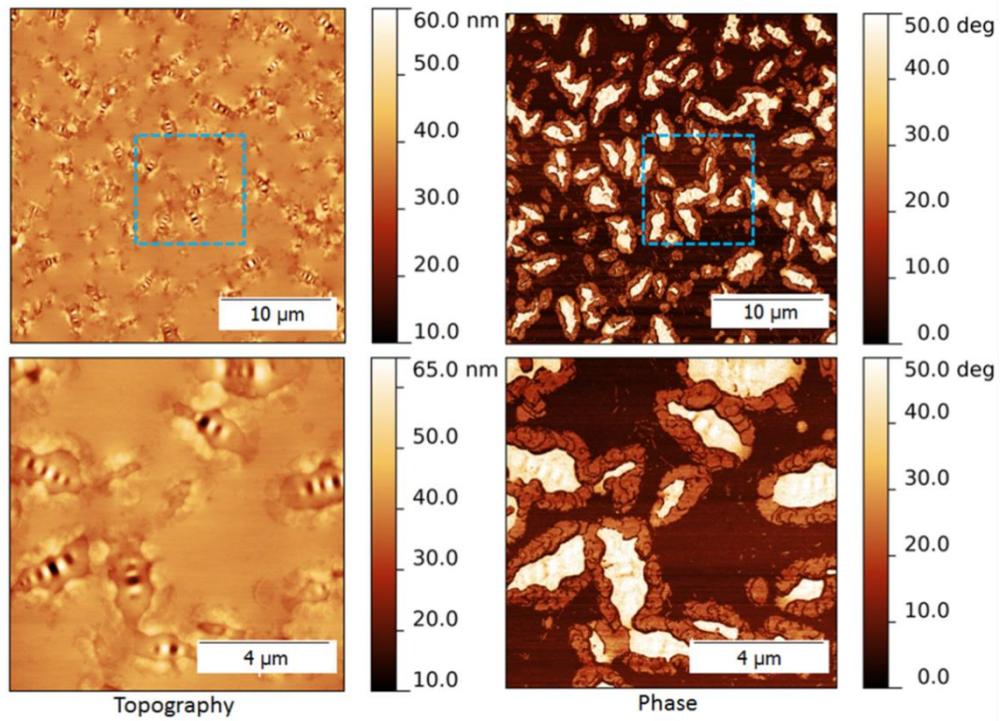


Figure 4-35 Topography and phase images of PG 52-28 and PG 64-22 virgin binder

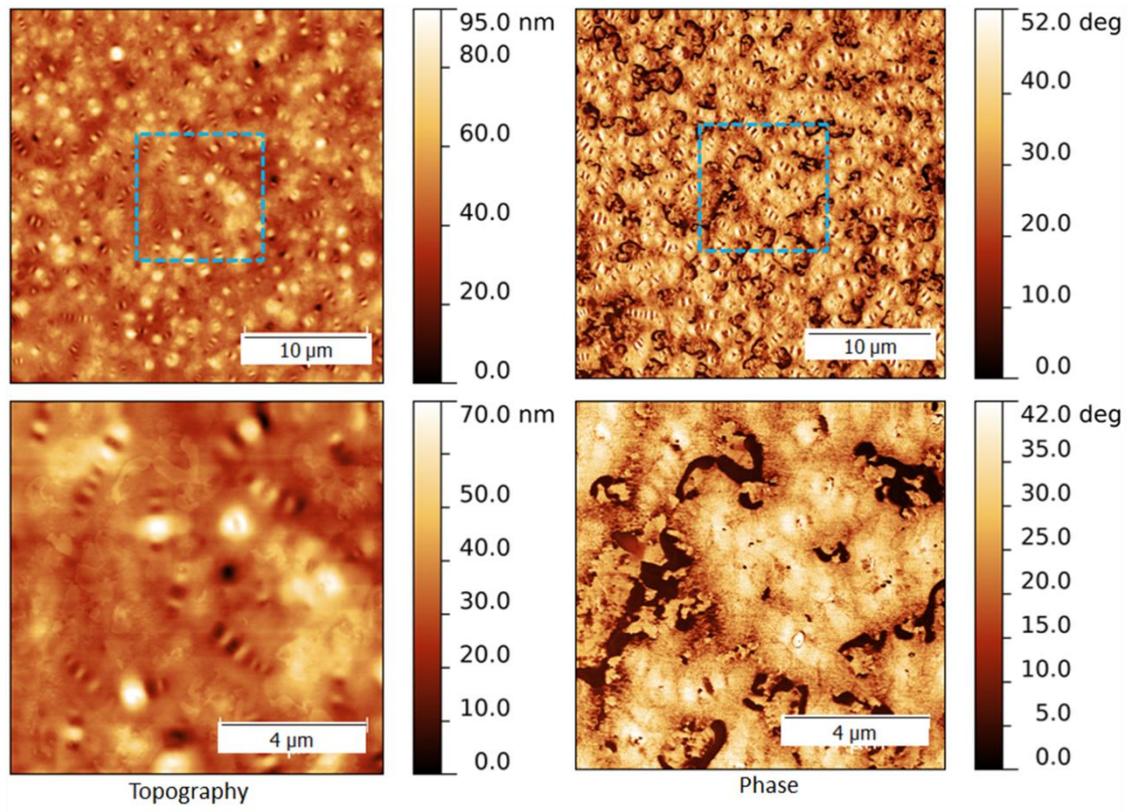
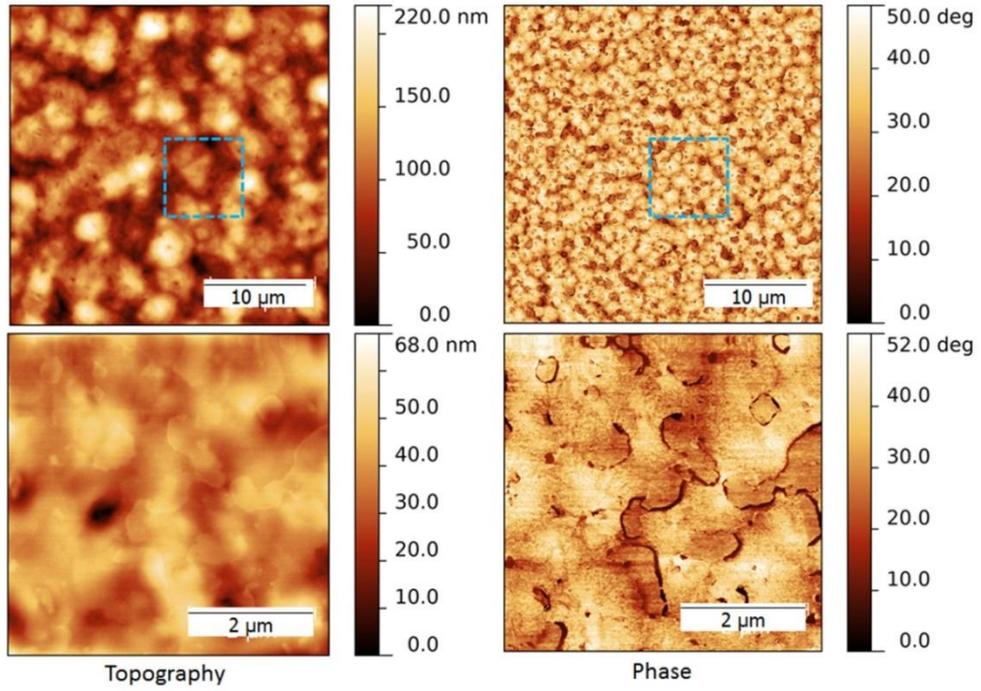


Figure 4-36 Topography and phase images of TM binder

(a) Tennessee tear off bitumen (TT)



(b) Virginia tear off bitumen (VT)

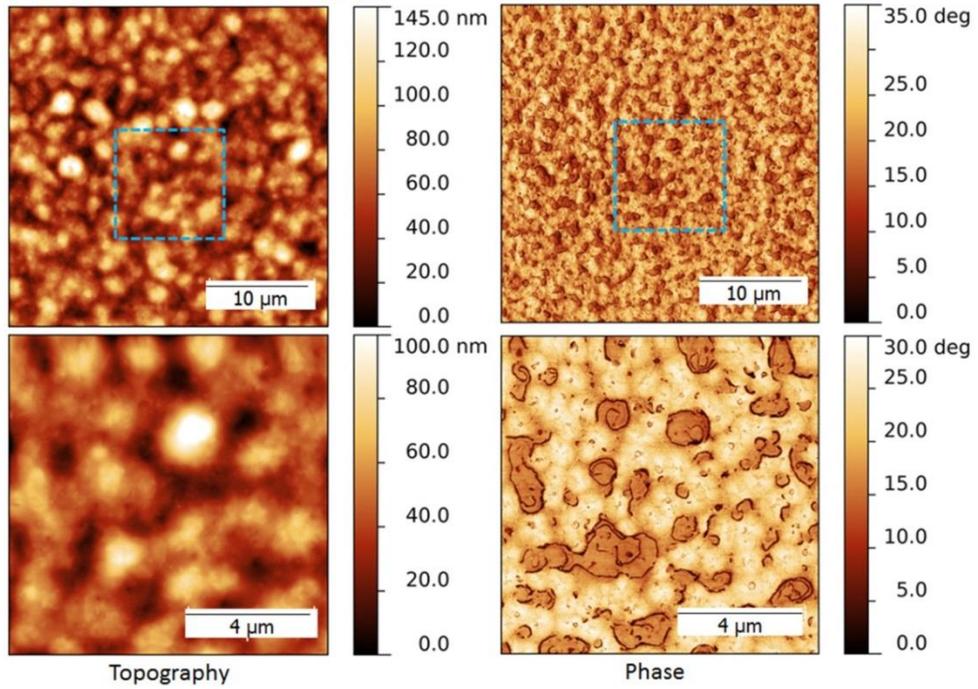


Figure 4-37 Topography and phase images of TT and VT binder

4.4.1 Temperature Dependence of Microstructures in RAS Binder

One type of tear-off binder (TT) was made into samples and scanned through AFM after treatment in different temperature. As can be seen in Figure 4-38, the sample was heated to different target temperature in a 20 °C step, hold for 5 minutes, and then cooled to 25 °C for AFM imaging. The maximum temperature was set at 180 °C that is the highest temperature most asphalt plants can reach. The observations at 120 °C and 180 °C are reported only in this study for better analysis.

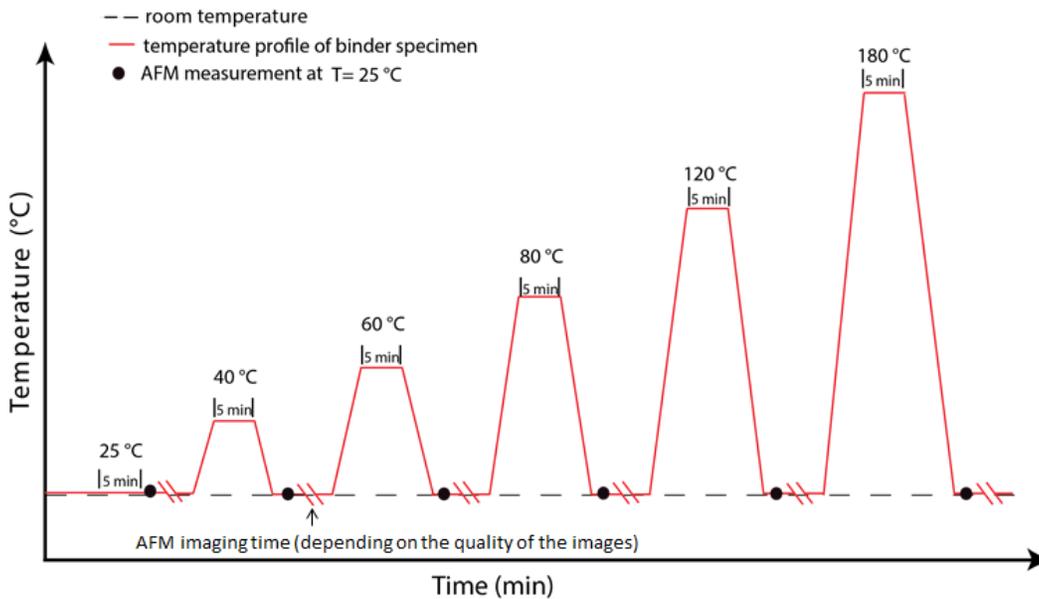


Figure 4-38 Schematic of thermal conditioning of TT binder

Figure 4-39 demonstrates the topographic images of TT binder after treatment at selected temperatures. The bright hump-shaped microstructures diminish in size with the treating temperature increasing up to 80 °C. The most dramatic change occurs from 40 °C to 60 °C. The topography of this specific binder changes very little after the temperature exceeds 80 °C, where the hump-shaped microstructures are found to “melt” with small light nuclei still remaining dispersed in the melted phase. The images vary little from 80 °C to 180 °C.

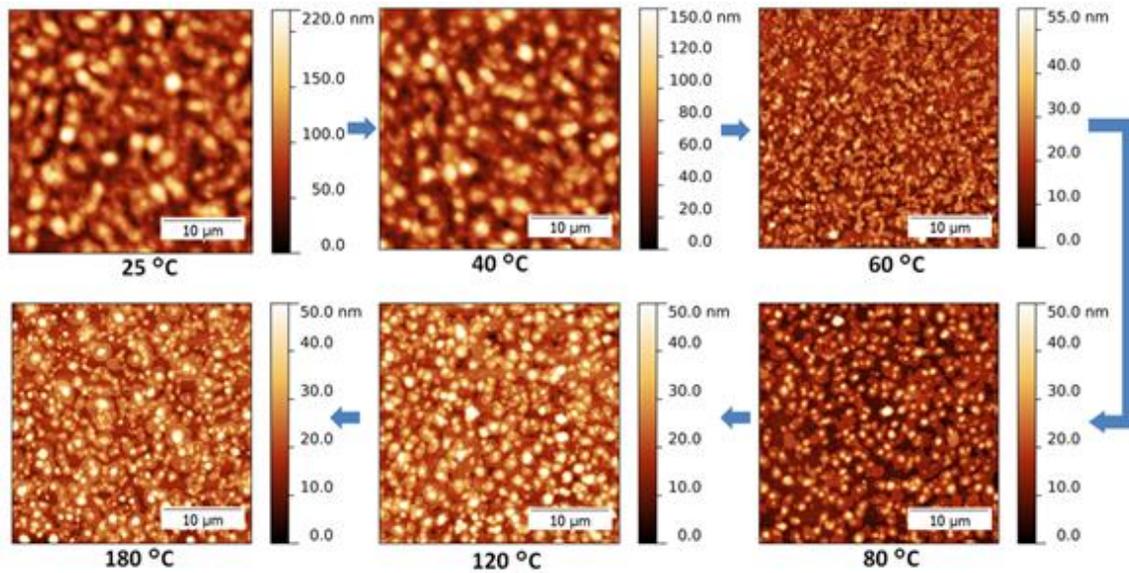
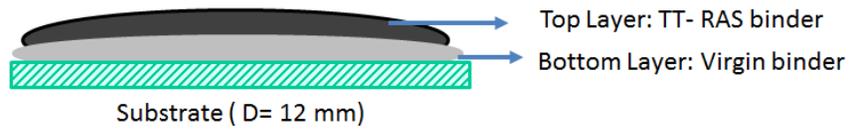


Figure 4-39 Topographic images of TT binder after temperature treatment

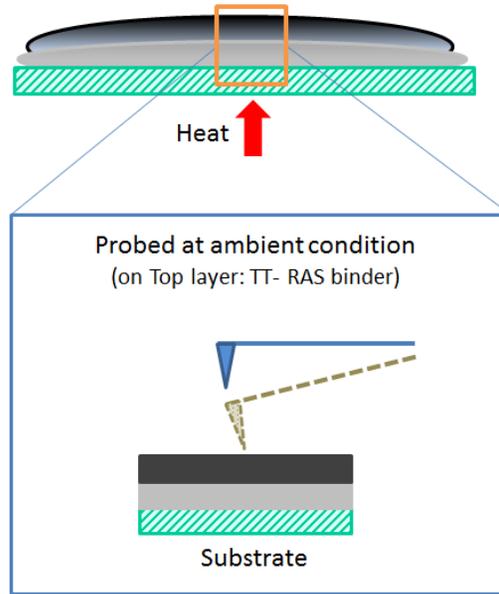
4.4.2 Blending Degree between RAS and Virgin Binder

A two-layered sample sketched in Figure 4-40 was designed to evaluate the blending degree between RAS and virgin binder. AFM images acquired from locations on the top of the sample were used to investigate whether virgin binder from the bottom layer could blend through to the surface of the upper layer of RAS binder, after being treated under certain time and temperature correlated to plant production. The RAS layer was designed to be smaller in size to intentionally make an interfacial zone that was also scanned in this study, in order for better understanding on blending.

(a) Two-layer binder specimen



(b) Thermal treatment



(c) Binder interaction scenarios

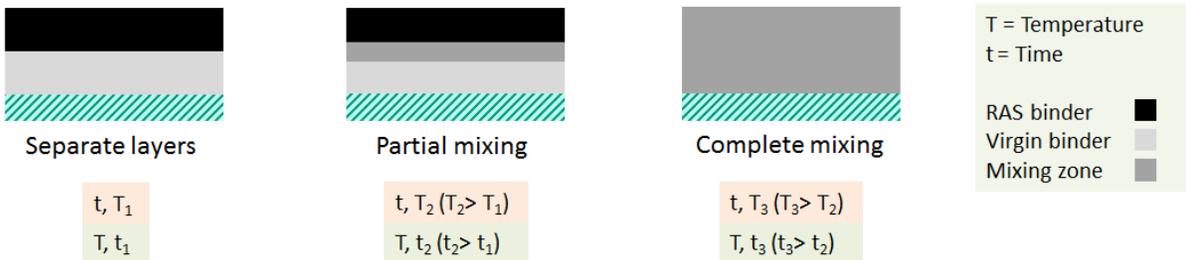
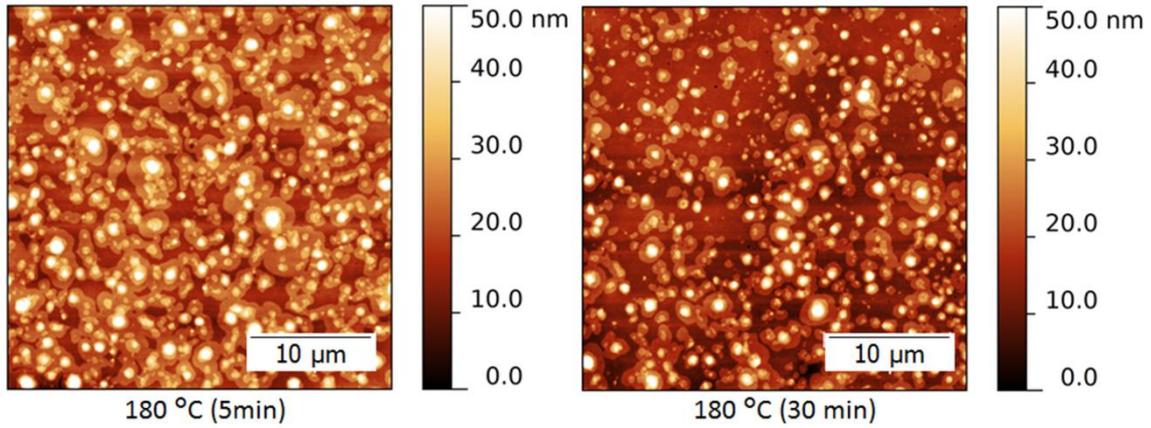


Figure 4-40 Experimental design of observing the blending degree between RAS and virgin binder

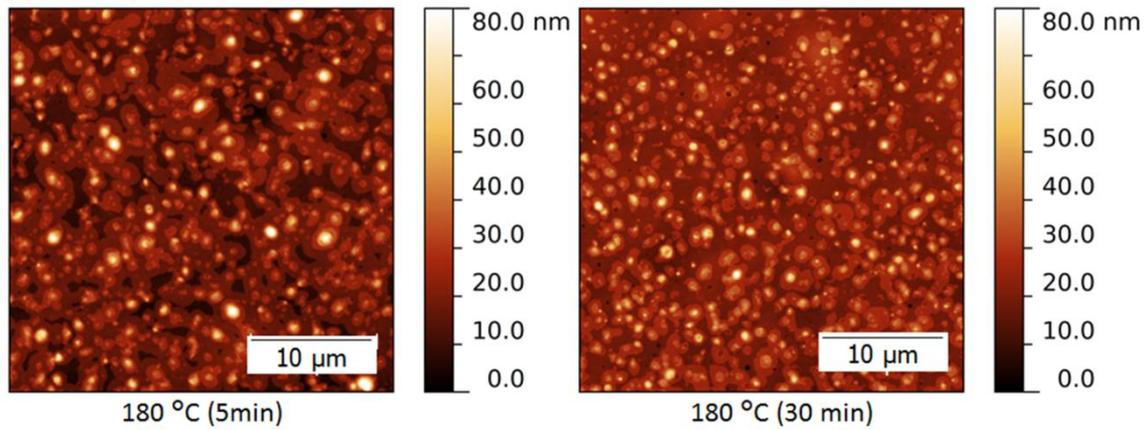
Figure 4-41 presents the representative topographic AFM images acquired from scanning on the top of the sample. The sample was treated at 180 °C for 5 minutes, which is theoretically long enough to ensure complete blending occurring. It can be seen that the topography on the surface of the layered sample is nothing different from the TT RAS

binder, regardless of the binder grade of the bottom virgin layer. This indicates that the virgin binder selected in this study could not blend through to the surface of the tear-off RAS binder layer around 300 μm in thickness. Since blending between virgin and aged binder was found to be a function of treating temperature and time, the observation of no-blending may be attributed to limited time. This assumption motivated increasing the treating time to a fairly long 30 minutes. The topography of the layered samples, however, changed very little. Accordingly, it seems of significance to detect what happens on the interfacial zone for a deeper understanding of blending between RAS and virgin binder.

(a) Two-layered specimen 1



(b) Two-layered specimen 2



(c) Single layer TT binder specimen (Control)

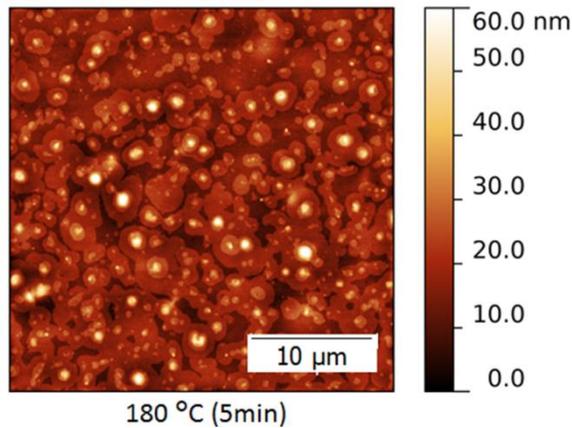


Figure 4-41 Comparison of scanning results on the top of the layered sample
: (a) Top layer TT binder and bottom layer virgin bitumen PG6422; (b) Top layer TT binder and bottom layer virgin bitumen PG5228; (c) Control TT binder

4.4.3 Scanning on the Interfacial Zone

As can be seen in Figure 4-42, the TT-RAS layer was made smaller in diameter and spread onto the bottom virgin binder at ambient temperature. The probing was conducted alongside the interfacial zone that can be easily differentiated by the optical microscope installed in AFM.

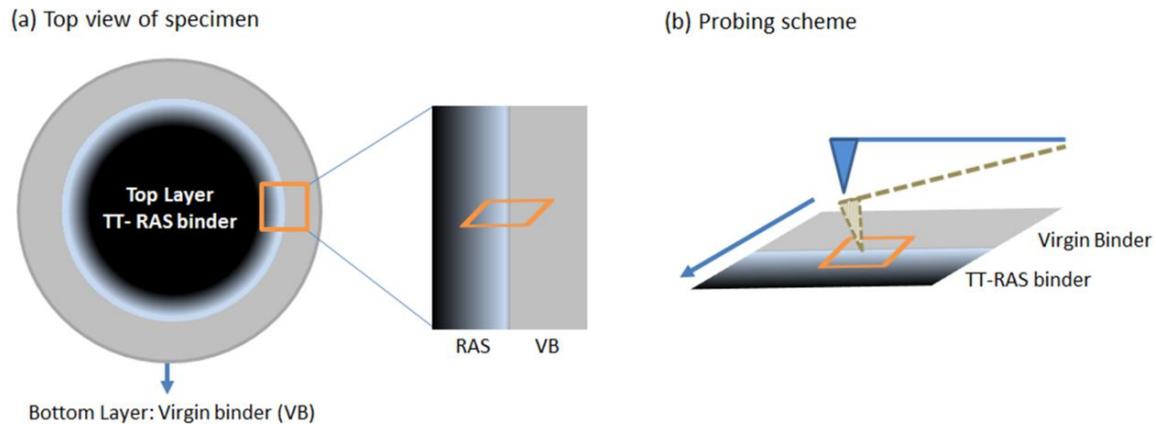


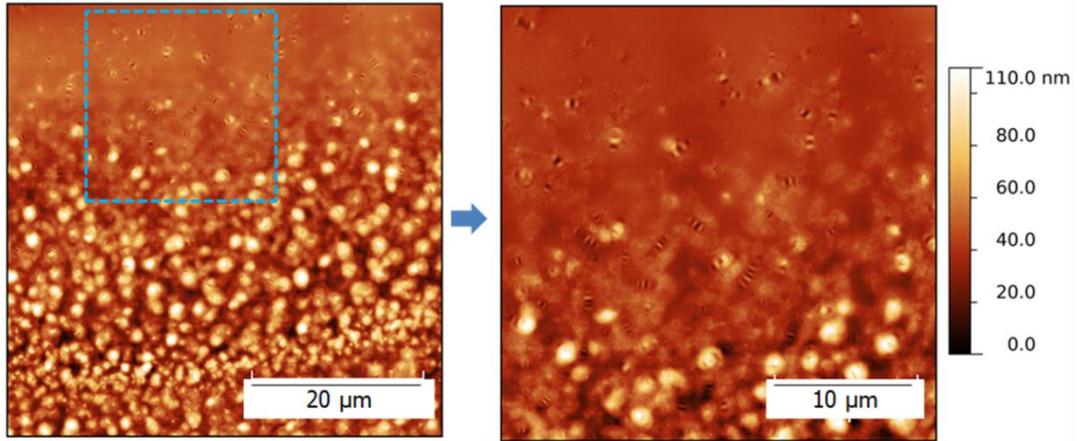
Figure 4-42 Probing the interfacial zone

In this paper, the AFM images acquired from scanning on the interfacial zone between TT RAS and PG 52-28 binder were reported to address the detailed observation on blending. As can be seen in Figure 4-43, both “bees” and “humps” can be found in topographic images of the interfacial zone, which are typical microstructures representing virgin binder and RAS binder, respectively. It seems the two binders were mixed but not blended into one ‘new’ material, indicating a poor compatibility between the virgin binder and significantly aged tear-off RAS binder. The mixing may be attributed to either upward or lateral movement of the virgin binder.

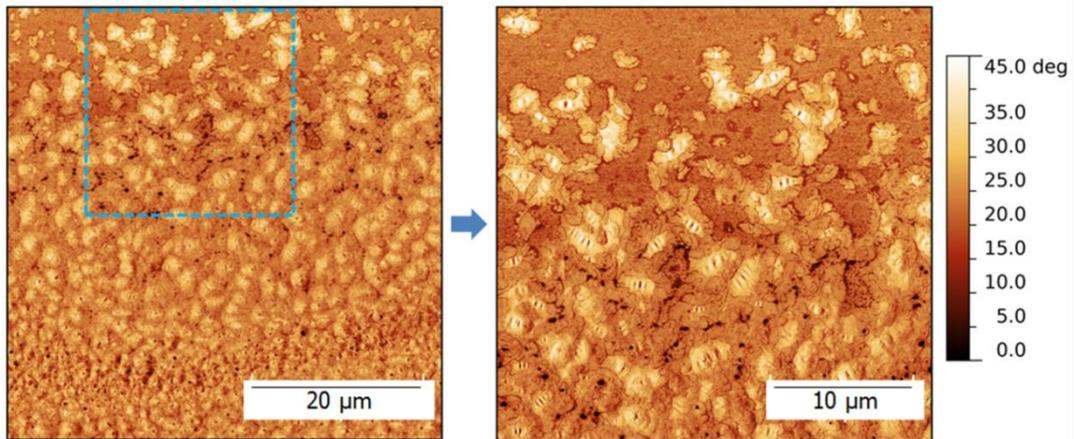
The mixing zone is found to be around 25 to 30 μm . However, the size of the mixing zone observed in this study does not indicate the real mixing scale occurring in the drum, since the film thickness on the edge of the top RAS layer was not precisely

determined.

(a) Topography



(b) Phase



(c) Contour of interfacial zone

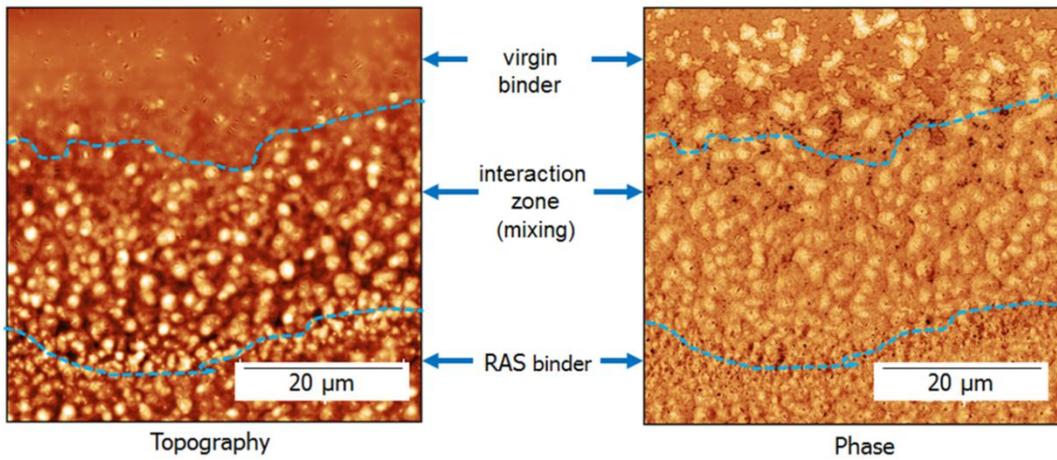


Figure 4-43 Comparison of scanning results on the interfacial zone of the layered sample and detailed description of mixing zone

The co-authors of this paper recently published a study to address the RAP-virgin blending under AFM for the first time [31]. Two blending scenarios were proposed in terms of microstructural properties (Figure 4-44). Scenario A refers to a merely mixing of two distinct colloidal fluids, according to which both the colloidal particles can be found in the mix. On the contrary, a complete blending that generates a new “colloidal” material is also possible and illustrated as scenario B.

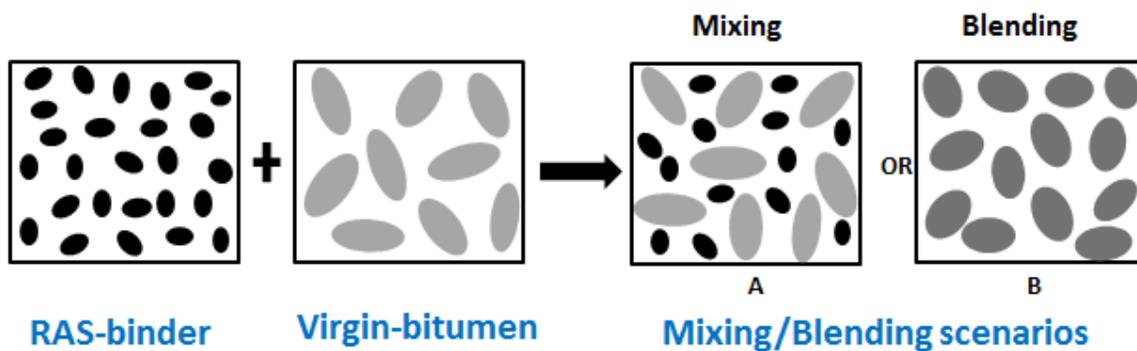


Figure 4-44 Blending scenarios (adapted from [31])

On the basis of the observation of RAP-virgin blending, as illustrated in Figure 4-45, the authors [31] concluded that “obviously scenario B is closest to the observations, hence one should speak about blending rather than mixing”.

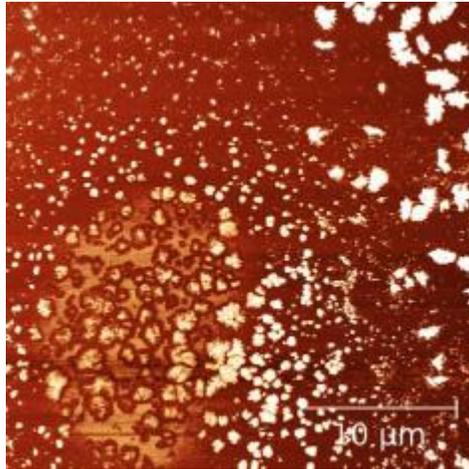


Figure 4-45 Phase image of RAP-virgin binder blending (adapted from [31])

The observations of RAS-virgin binder blending obtained in this study (Figure 4-43), interestingly, are more likely to correspond to scenario A, which is mixing rather than blending. This observation may lead to concerns over the binder segregation of RAS mixtures. Meanwhile, not all the characterizing tools used for RAP binder/mixture can be easily extended to RAS, due to the difference in nature between RAS-virgin blending and RAP-virgin blending.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

A series of studies were conducted to address the blending issues in warm and hot mix asphalt containing recycled asphalt pavement (RAP) and recycled asphalt shingle (RAS). The blending was evaluated in terms of analysis on old binder mobilization, binder homogeneity and diffusion. Several new methods were developed to characterize the blending process. Based on the results obtained from the aforementioned studies, the following recommendations can be made:

- 1) A strong correlation existed between the percentage of LMS and G^* of asphalt binder based on the comparison of GPC and DSR test results. As mixing time and temperature increased, more blending occurred in the RAP/RAS mixture. The size of virgin aggregate did not affect the blending efficiency of RAS in pavement mixtures. The most efficient blending of RAS may occur at approximately 5% RAS content.
- 2) A new parameter, large molecular size percentage (LMS%) related to molecular weight distribution derived from gel permeation chromatography (GPC) analysis, was developed to differentiate the RAP/RAS and virgin binders as well as their blends. “Blending Charts” could be generated between the RAP/RAS binder content in the blend with the newly defined LMS% and the relations were found to be linear. The RAP/RAS binder mobilization rate defined in this study could be determined by LMS% analysis of binders extracted and recovered from the virgin aggregates after mixing in the laboratory, with the use of the “Blending Charts”. The results show that RAP binder mobilization rate decreased with the increase of the RAP percentage in the mixture with mobilization rates close to 100% at low RAP mixtures (10% and 20%), but dropping from 73% to 24% with RAP percentage varying from

30% up to 80%. RAS binder mobilization rate increased with RAS percentage growing from 2.5% to 5%, but decreased with RAS percentage passing 5%. The highest mobilization rate was around 61% and found on 5% RAS mixture while the mobilization rate of mixture containing 10% RAS could be as low as 36%.

- 3) The feasibility of using staged extraction was validated in this study. It was found TCE was the most effective solvent used in the study for staged extraction that dissolved the asphalt binder without preferential dissolution. Meanwhile, TCE was found to have the highest dissolving rate. The binder coating on the raw RAP and RAS aggregates was proved to be homogeneous and the layer stripping did occur in a well-controlled composite binder system. A well designed step-extraction method with progressive wash times could replace equal-time extraction method, and yielded better analysis. Partial blending was observed within the coating of RAP particles, while the RAS-virgin blending on RAS aggregates should be further evaluated.
- 4) Based on well-designed staged extraction and GPC analysis, it was found that, in RAP mix, binder film coating virgin aggregates was approximately homogeneous, while a non-homogeneous binder was generated on RAP aggregates. The model of binder blend coating the virgin and RAP aggregates with inactive RAP binder still attaching was validated in this study. A potential composite binder system was found coating the virgin aggregates in RAS mix. The diffusion study shows that within the mixture storage time, binder diffusion can be accomplished in both warm and hot mixes containing RAP, indicating old binder mobilization, rather than binder homogeneity, could be more critical in RAP mix. The binder diffusion in RAS mix was captured in a very slow rate. It was suggested that old binder activation and binder homogeneity can both be critical for RAS mix.

- 5) WMA additives slightly decreased the viscosity of the asphalt binder at 135°C. However, Binder tested at 165°C showed significantly lower viscosity than WMA binders. This may raise the concern over workability of the WMA mix. WMA additives yielded higher blending ratio than control mix produced at 135°C, but the temperature of 165°C still produced the mix with the highest blending ratio value. This indicates that a concern still exists over asphalt blending even if WMA additives are used. Foaming technology yielded a higher blending ratio, indicating foamed WMA may yield a higher blending than regular HMA. It was also found that temperature rather than coating is more critical in RAS blending. Finally, the mix produced with coarse virgin aggregates and medium RAP may not be sensitive enough to test the effect of WMA additives on blending, while the mix with medium virgin aggregates and fine RAP was more effective.
- 6) AFM could be used to characterize microstructural properties of the selected virgin, post-manufactured RAS and post-consumer RAS (tear-off) binders, as well as the temperature dependence of microstructures in one type of tear-off RAS binder. The blending of virgin-RAS binder was first observed in this study. According to the observations, AFM proved to be capable of differentiating virgin binder from RAS binder in terms of microstructures. The microstructures of tear-off RAS binder was found to be temperature-dependent, but changed very little within the range from 60oC to 180oC. Virgin binders selected in this study could not blend through a RAS binder layer of 300 μm within 30 minutes at 180oC. On the basis of observations on the interfacial zone, RAS binder was found to be “mixing” but not “blending” in a mixing zone of 25 to 30 μm.

Recommendations

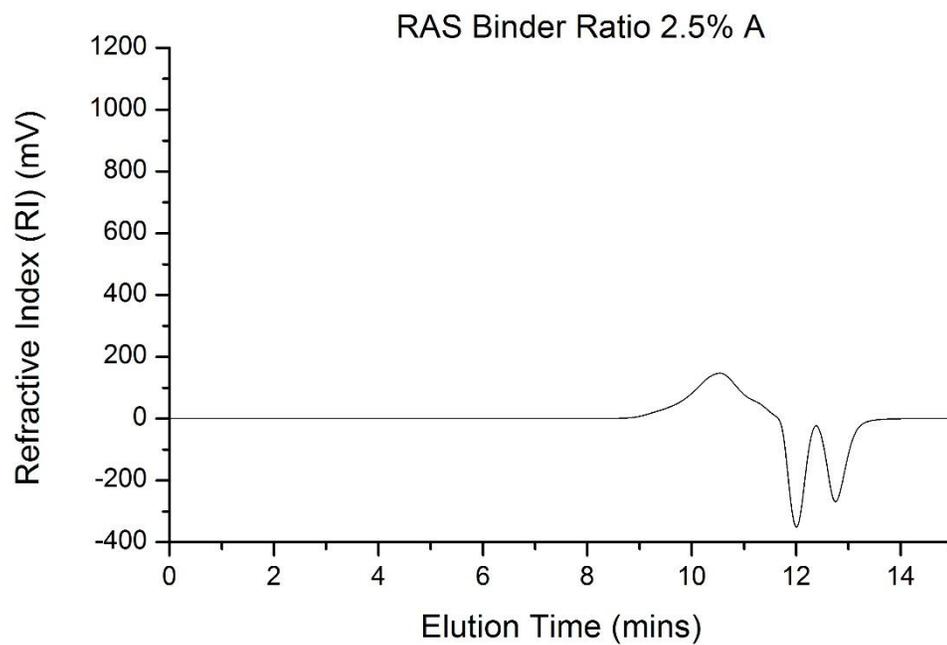
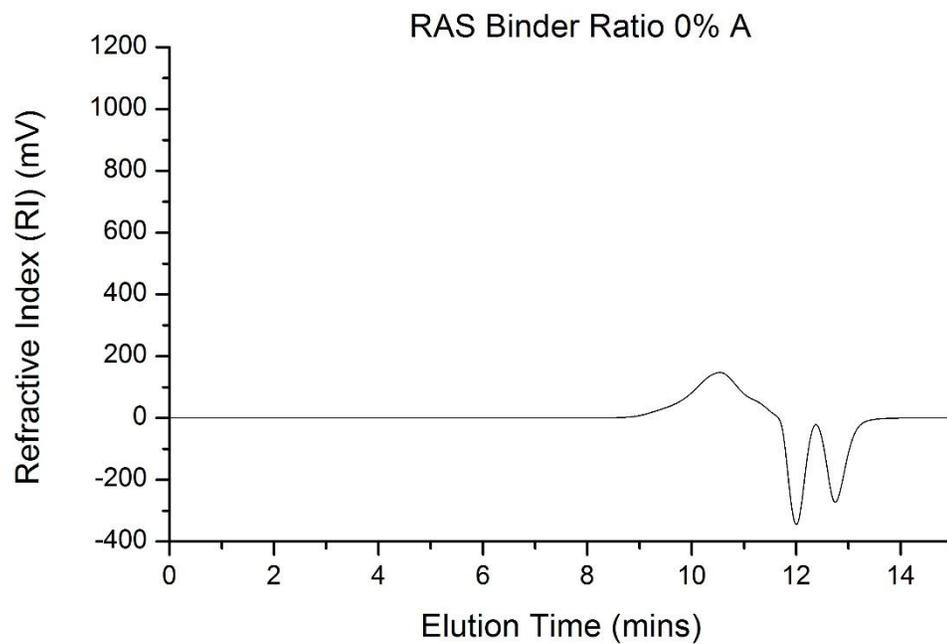
On the basis of the conclusions obtained in this study, the following recommendations can be made:

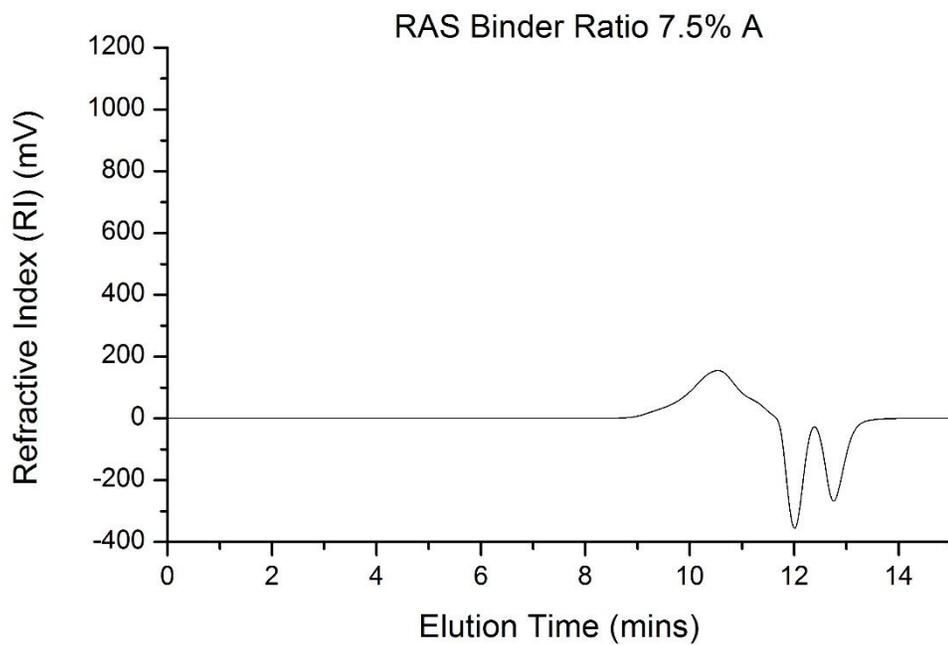
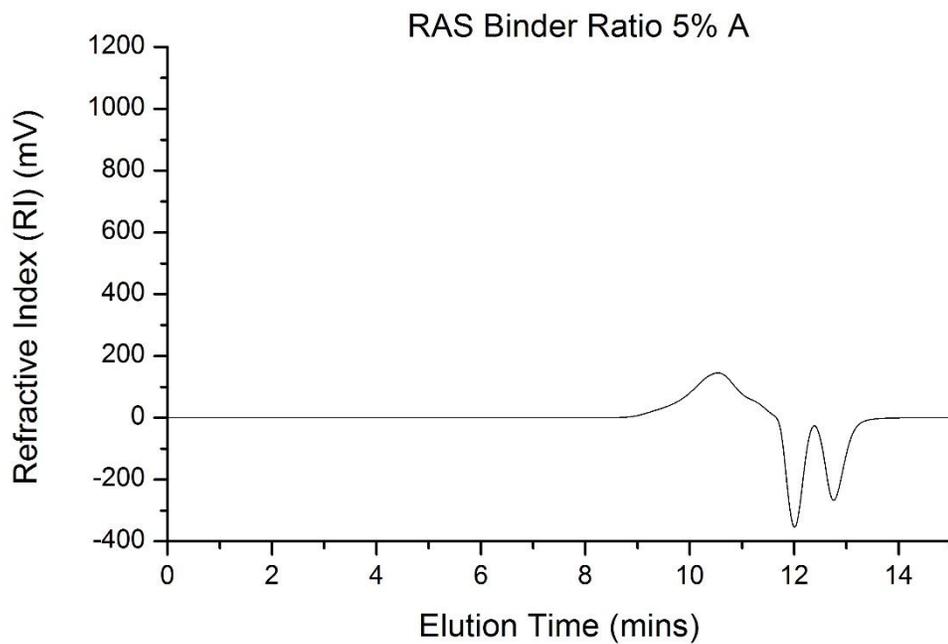
- 1) Better tracking materials, other than the round aggregate could be used for the quantitative evaluation of the old binder mobilization rate. The texture, size and other surface properties of the tracking materials could be considered as influence factors.
- 2) It is recommended to develop new methods to quantify the binder homogeneity through AFM. Statistical methods could be used to track the numerical change of the domains. Layered system with well controlled binder film thickness is recommended to characterize the diffusion coefficient of the virgin binder through the old binder.
- 3) Neutron scattering are also recommended for use in blending research. Samples with different blending degrees may express different inner structural properties and might be revealed by neutron scattering detection. Additionally, neutron scattering samples will not go through any destructive damage during preparation and testing processes.
- 4) Test methods designed in this research have been proved to be useful in laboratory research. However, their effectiveness in field research still need

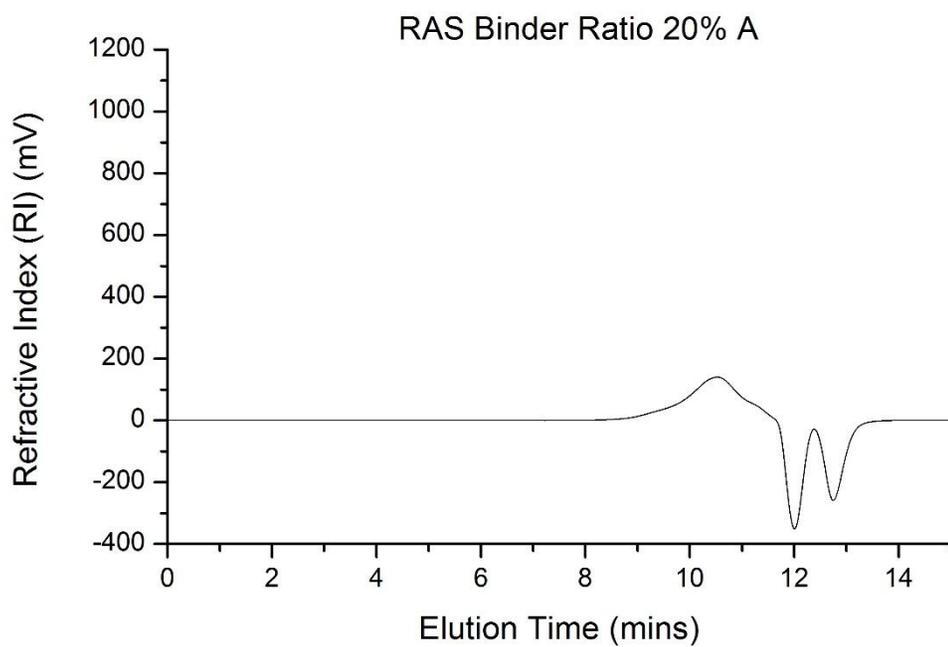
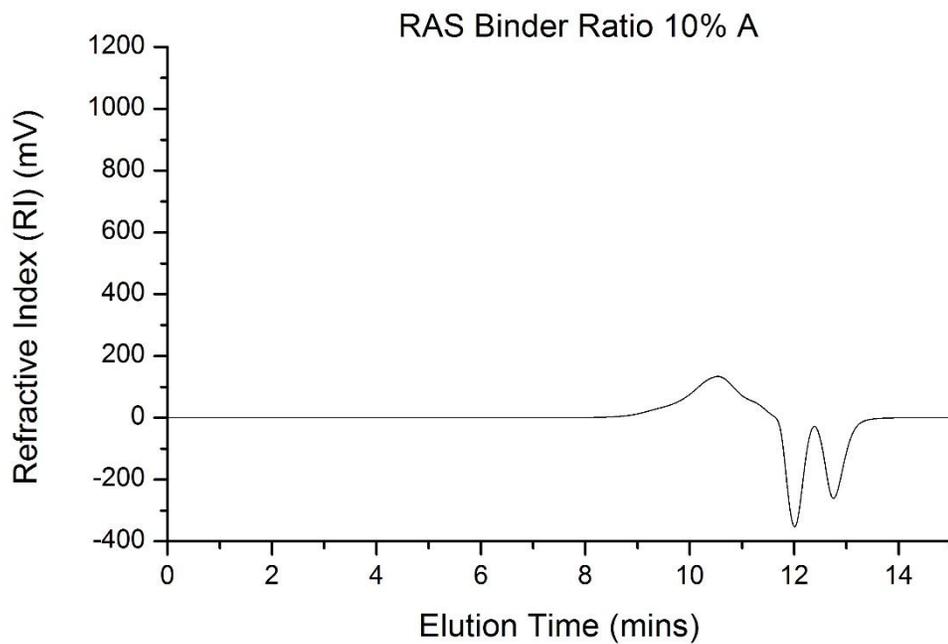
to be further verified. In the follow-up study, the test methods for blending efficiency need to be modified based on the requirement of field research.

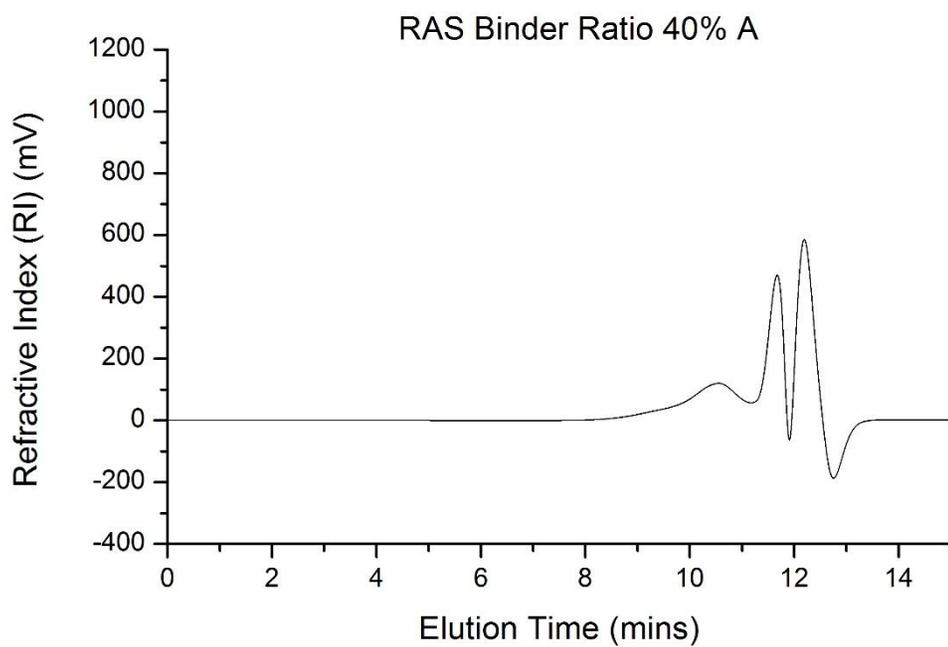
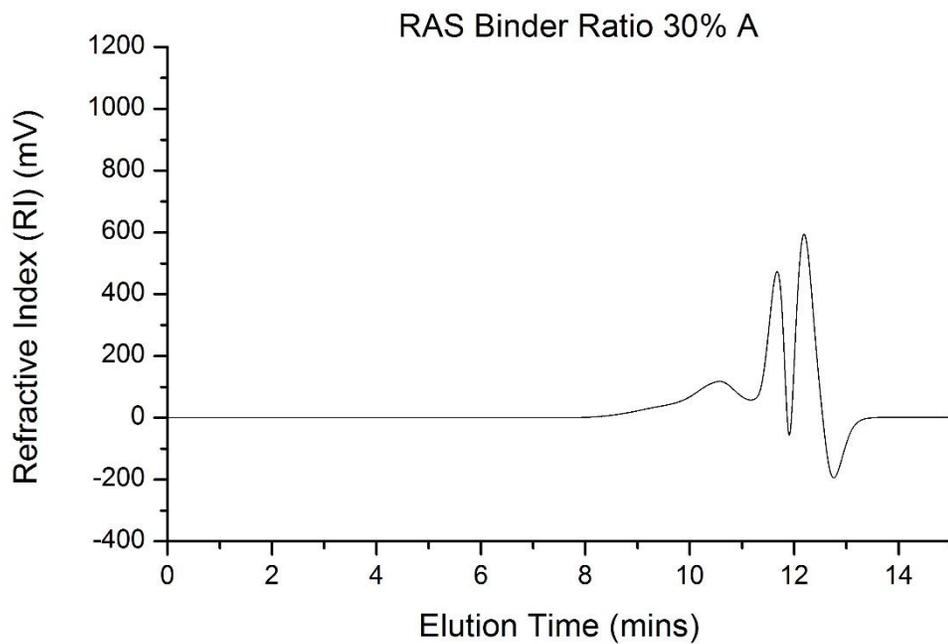
APPENDICES

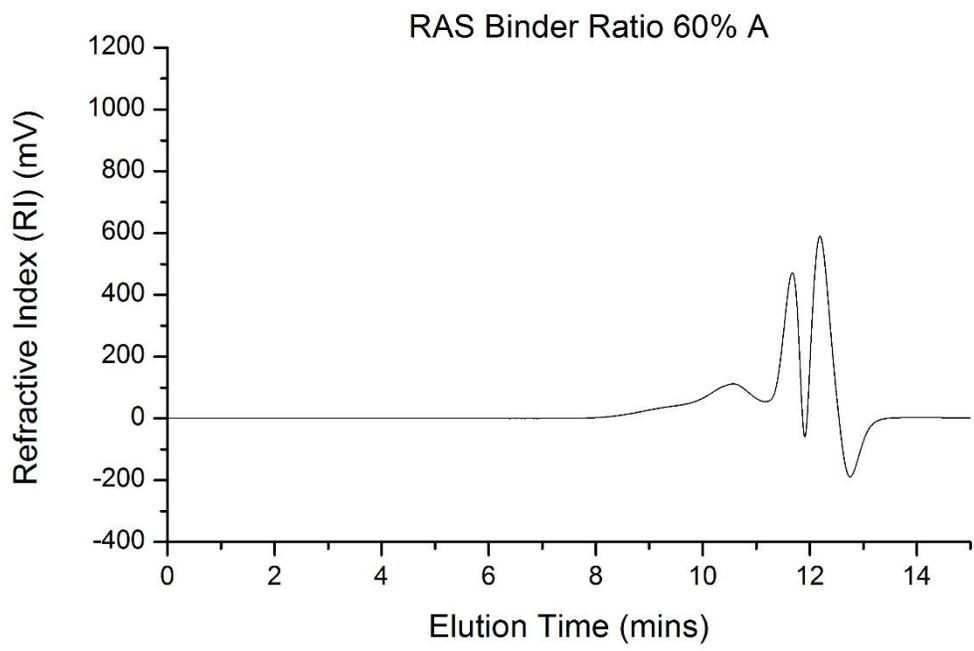
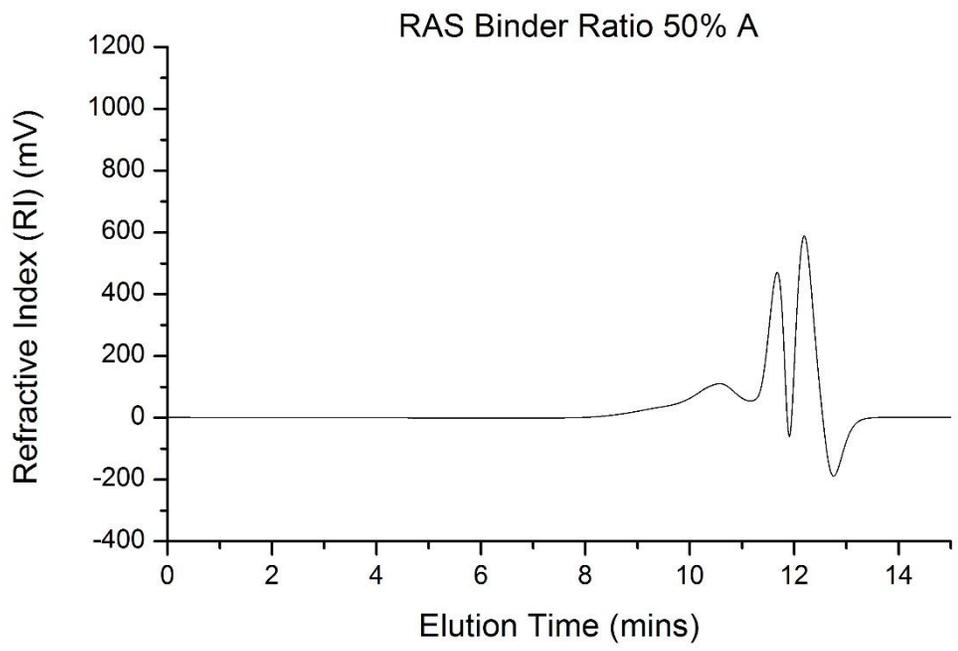
APPENDIX A: GPC Chromatograms of Test in Figure 3-2

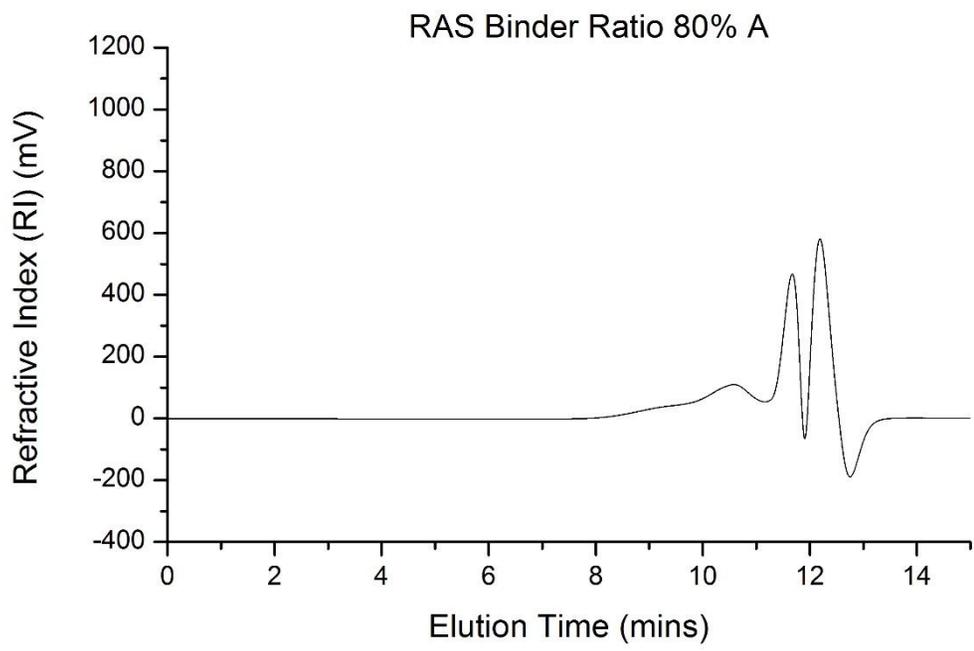
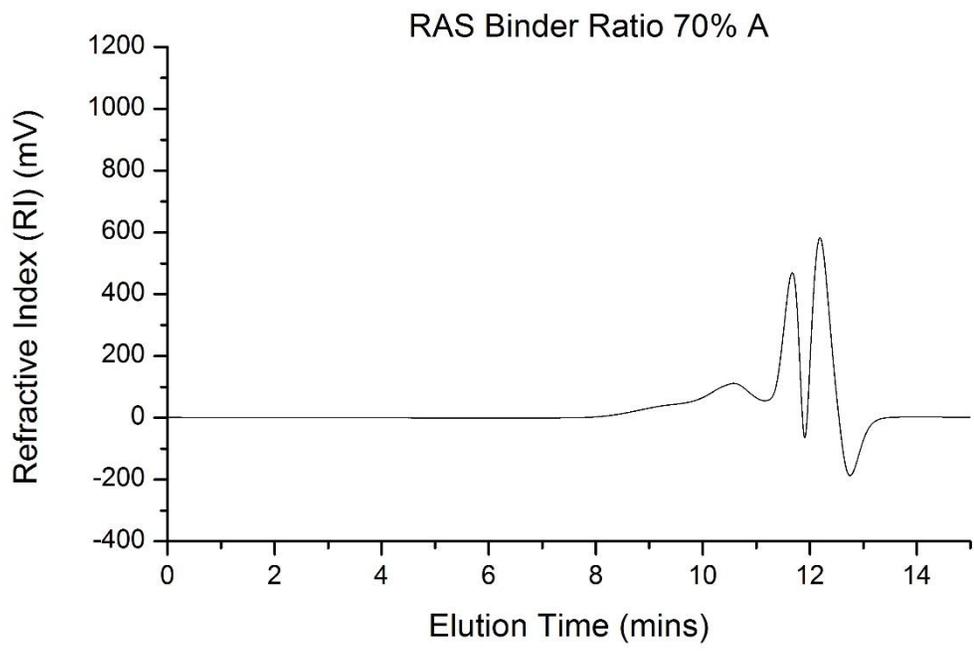


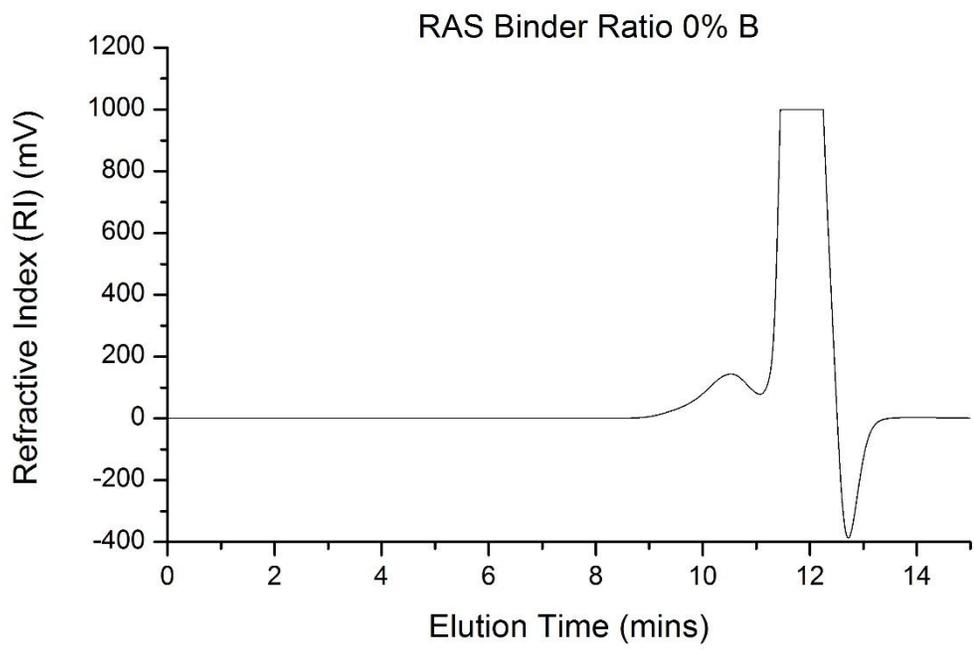
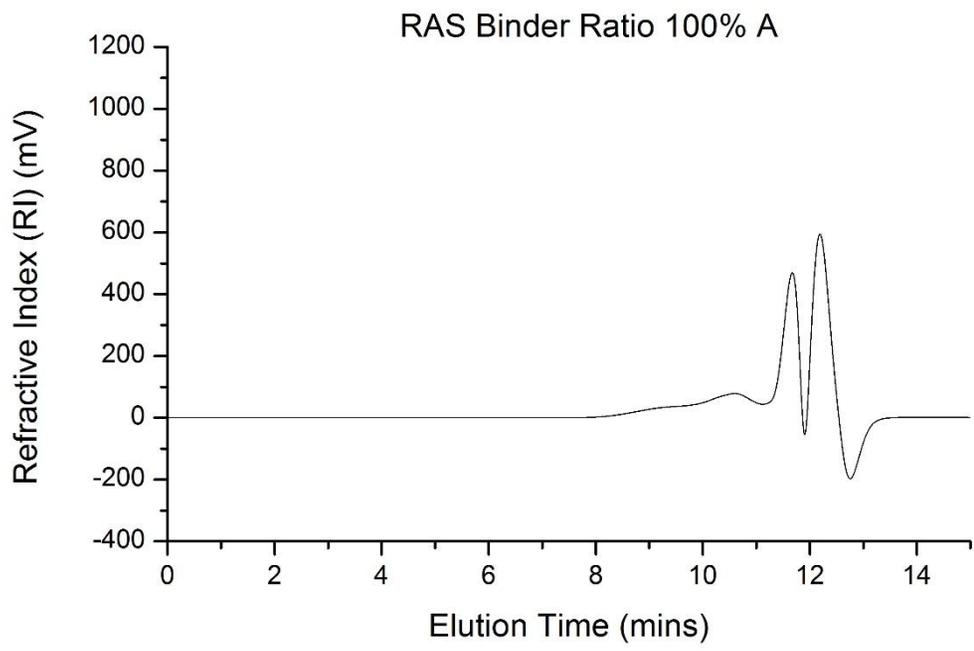


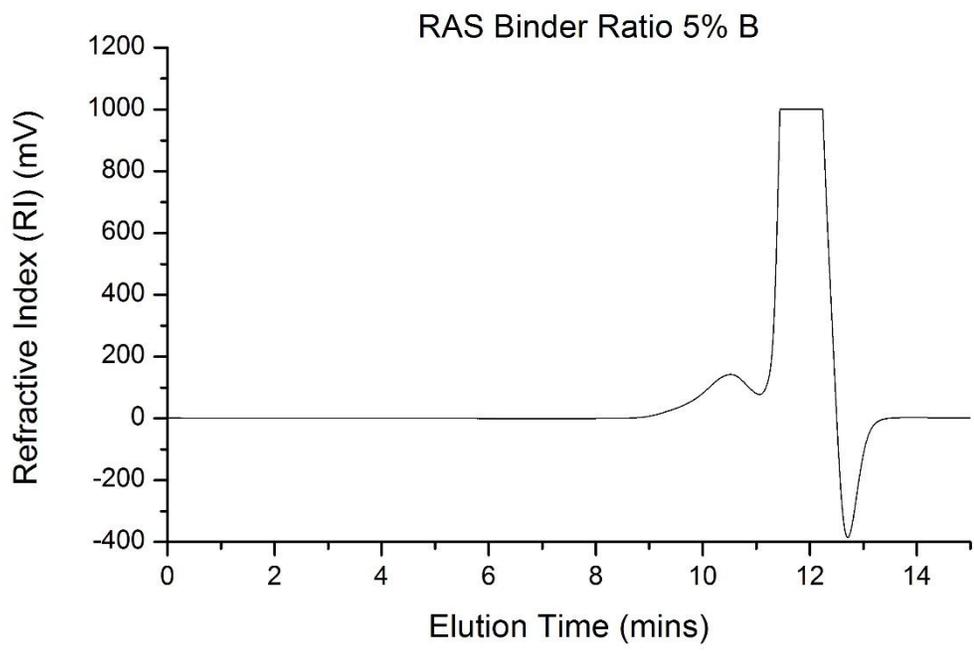
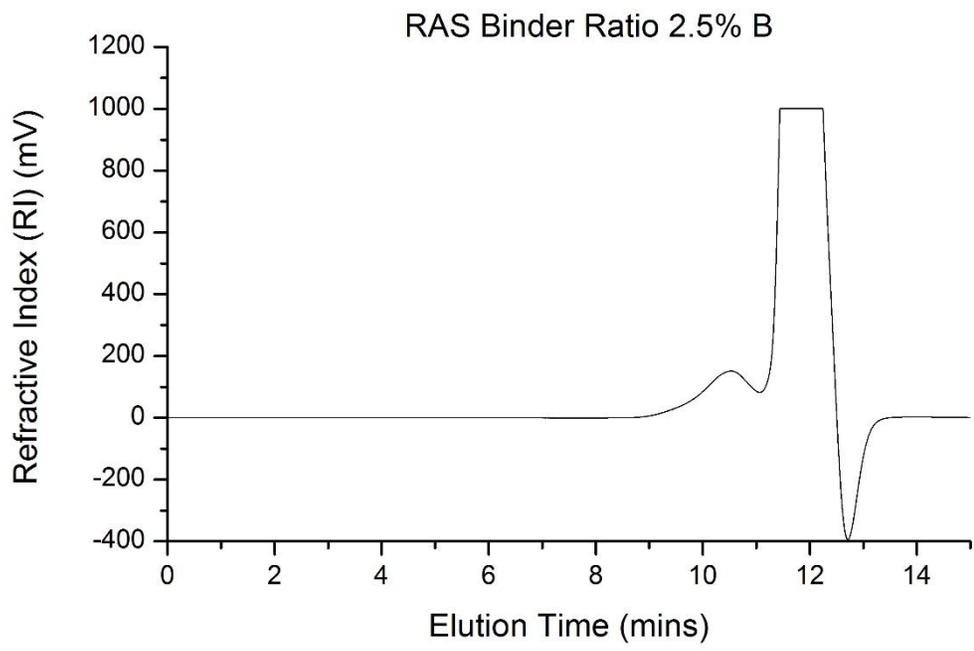


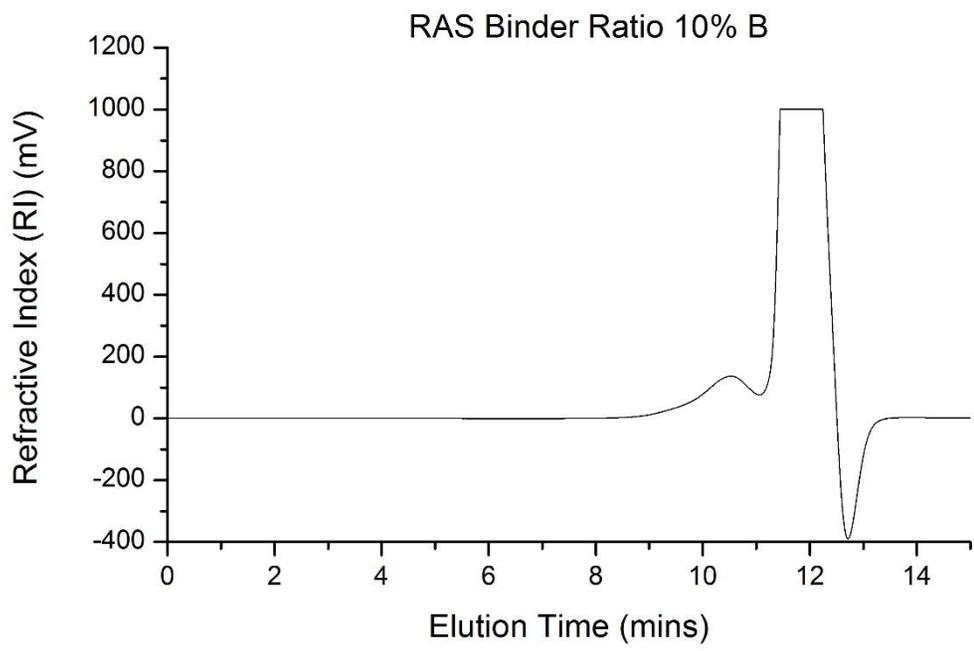
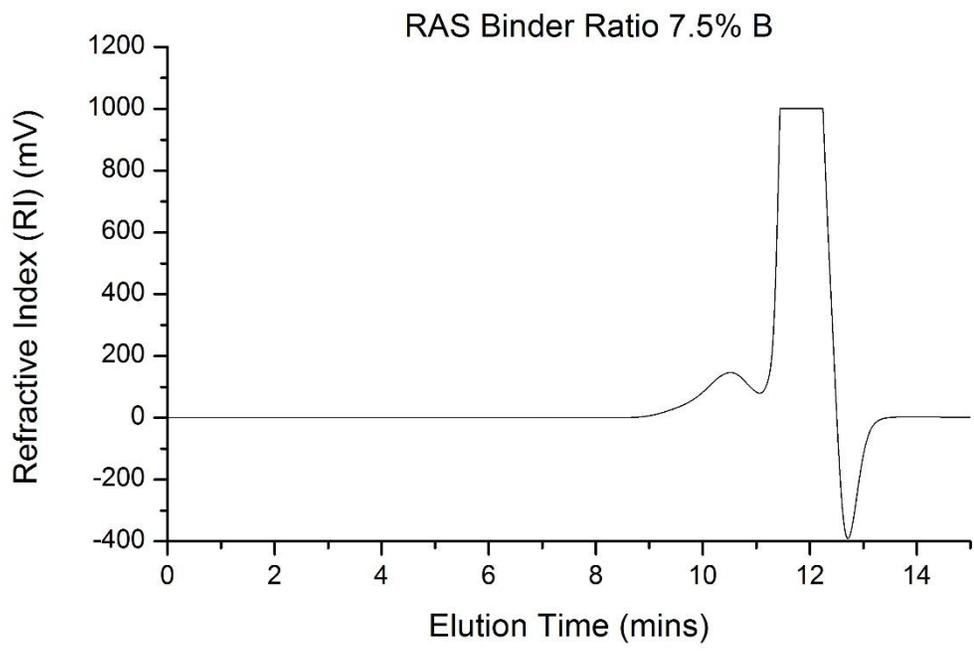


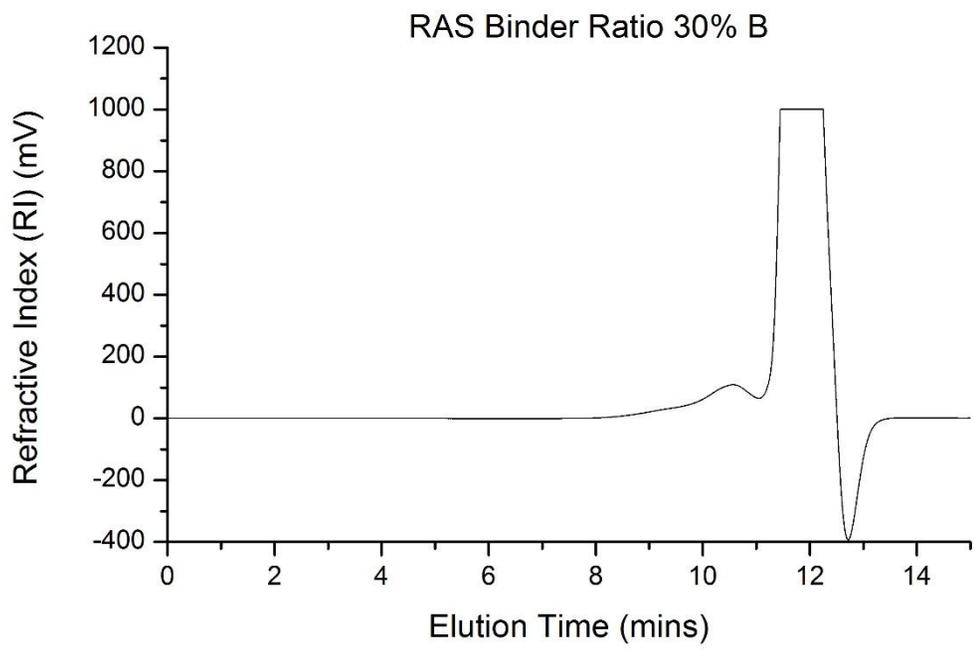
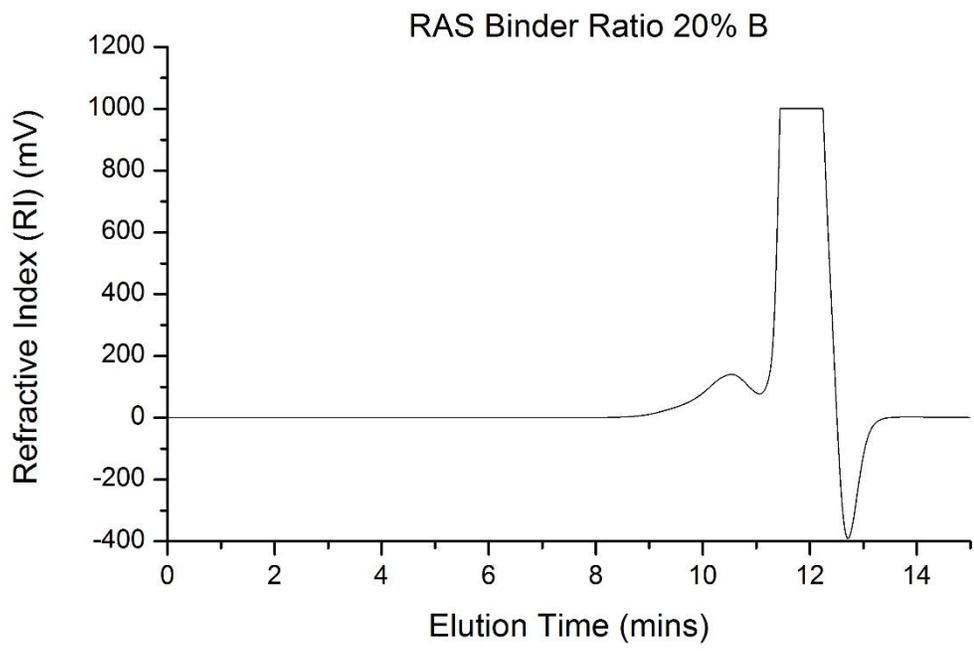


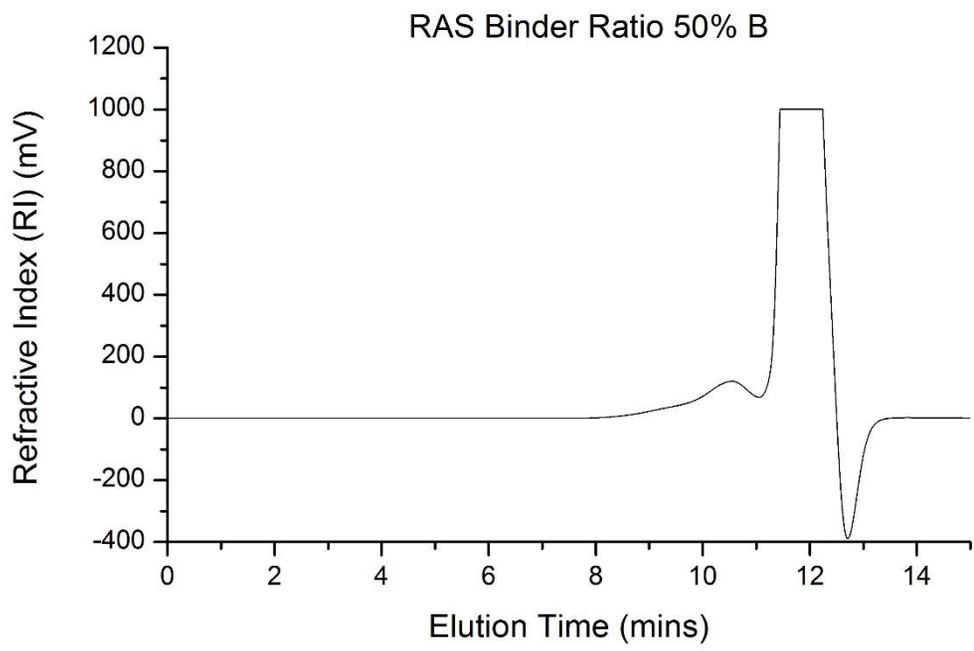
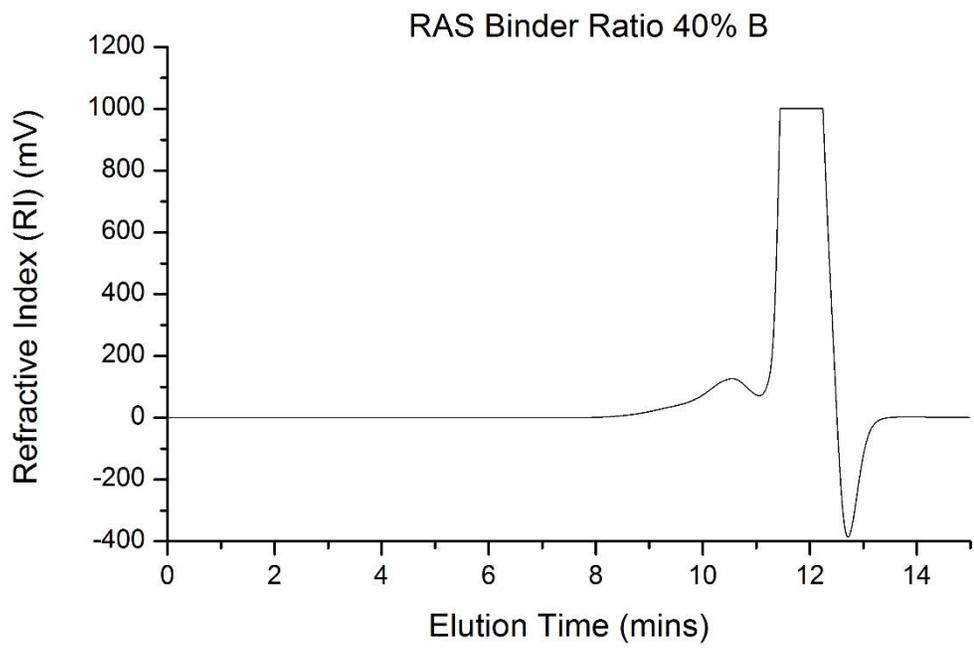


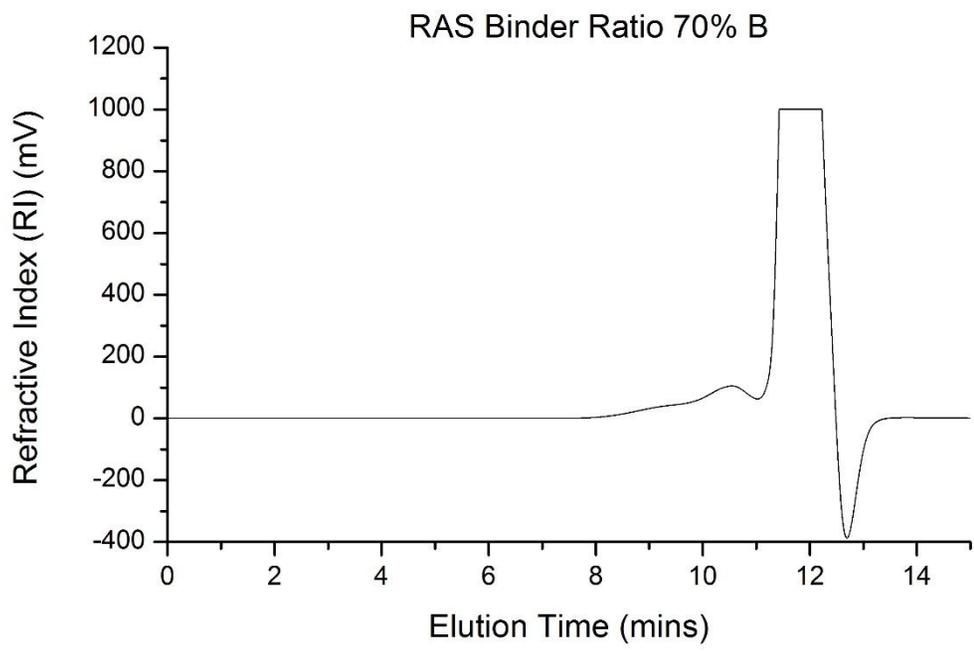
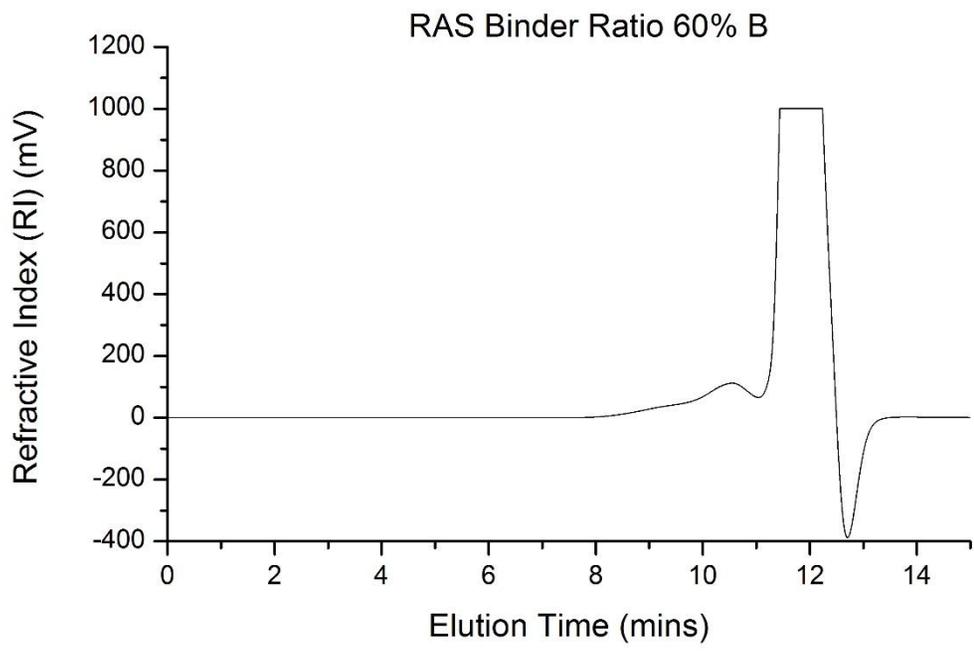


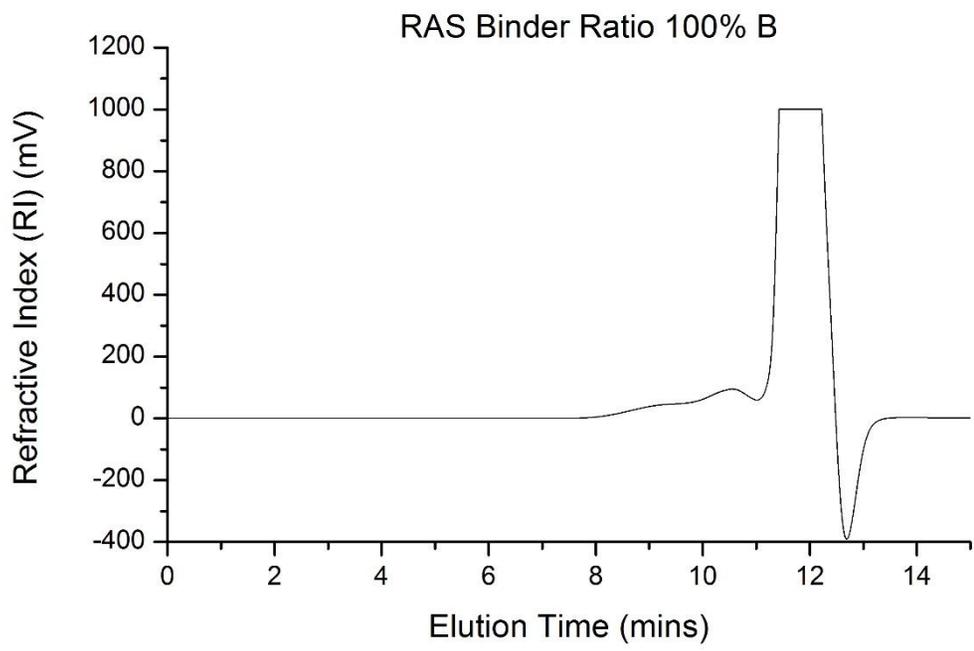
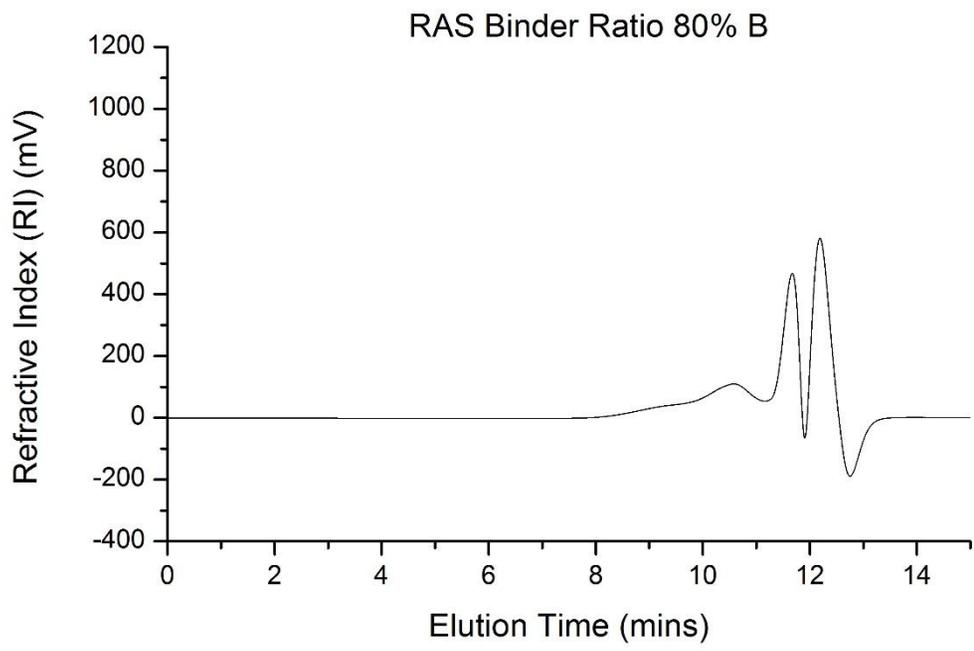




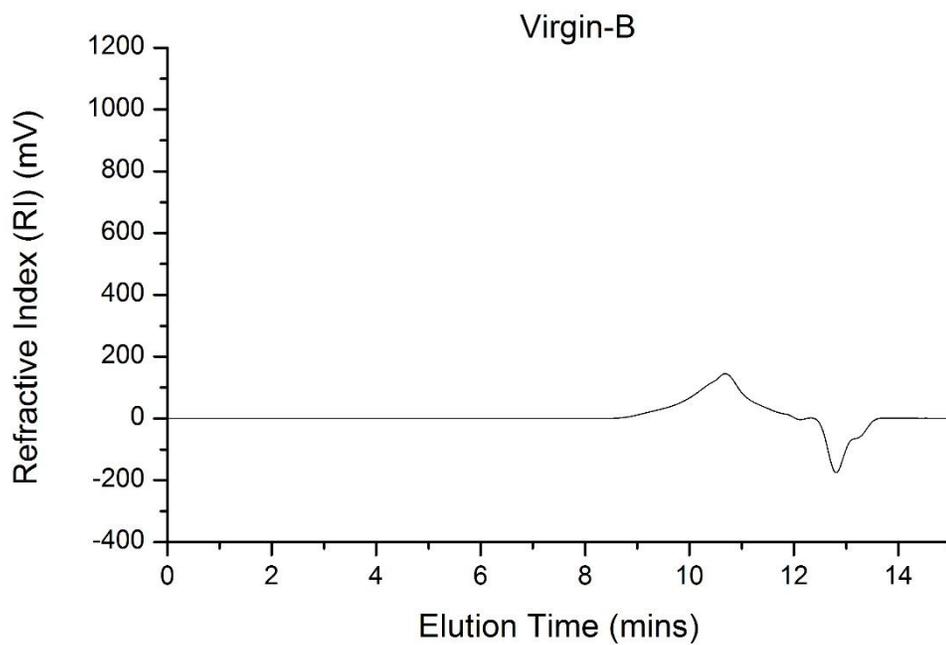
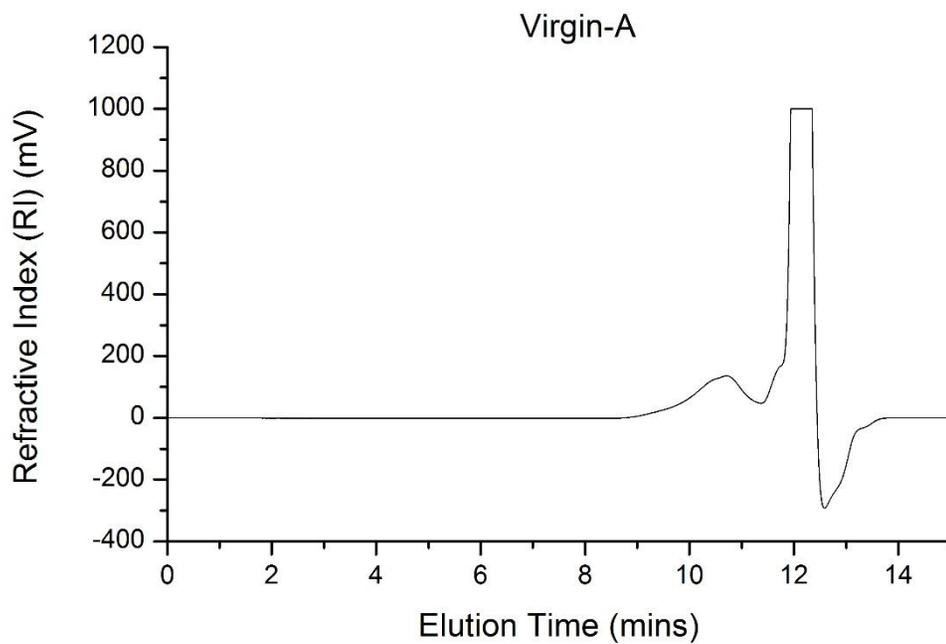


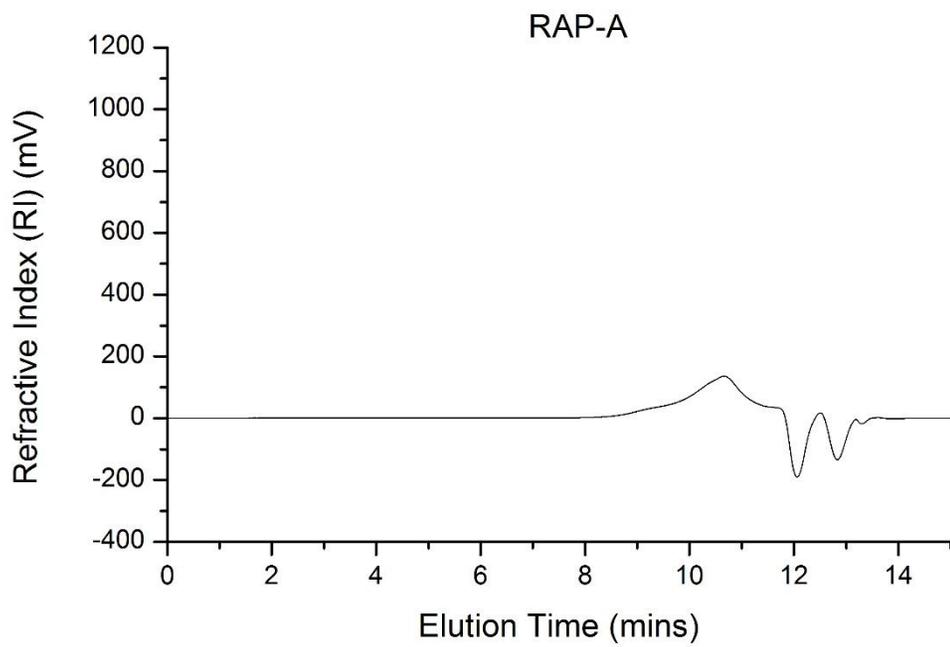
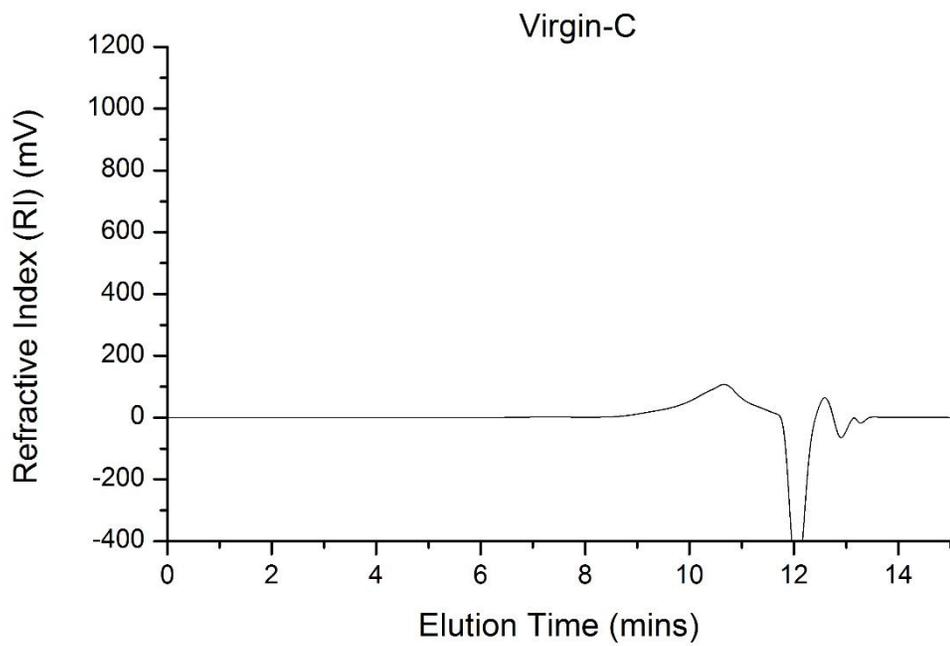


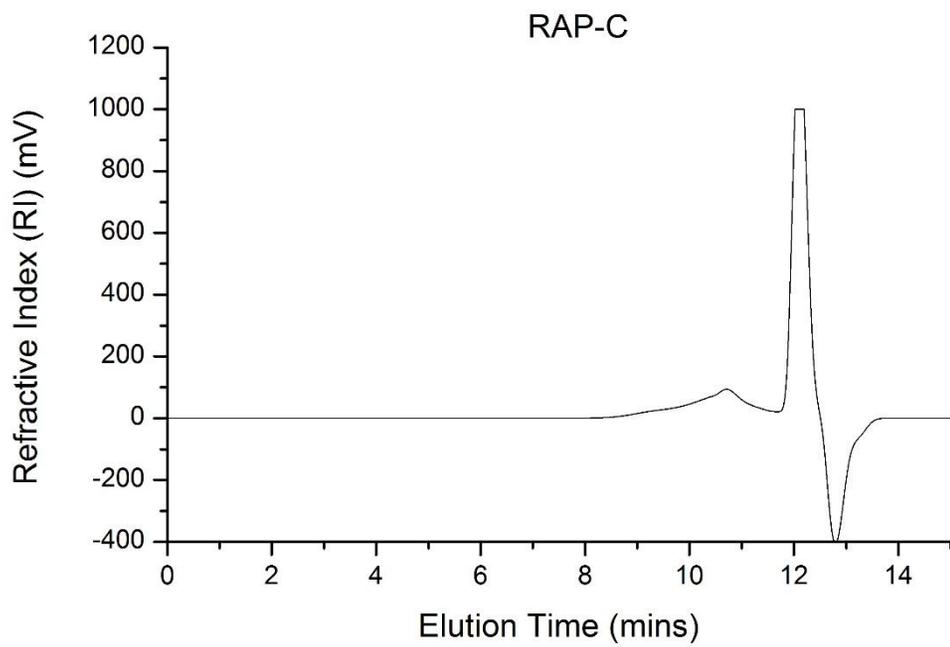
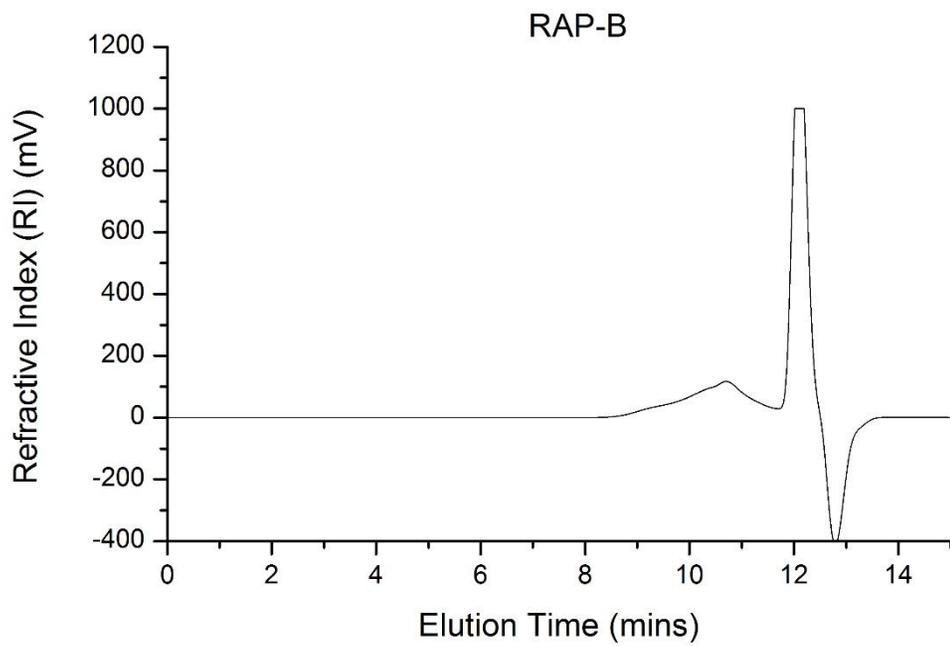


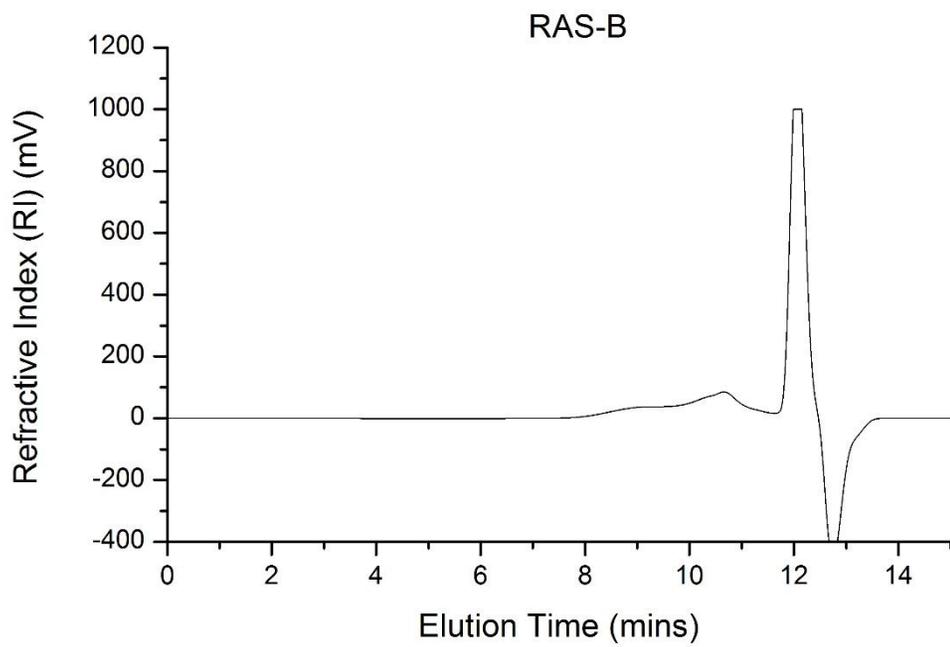
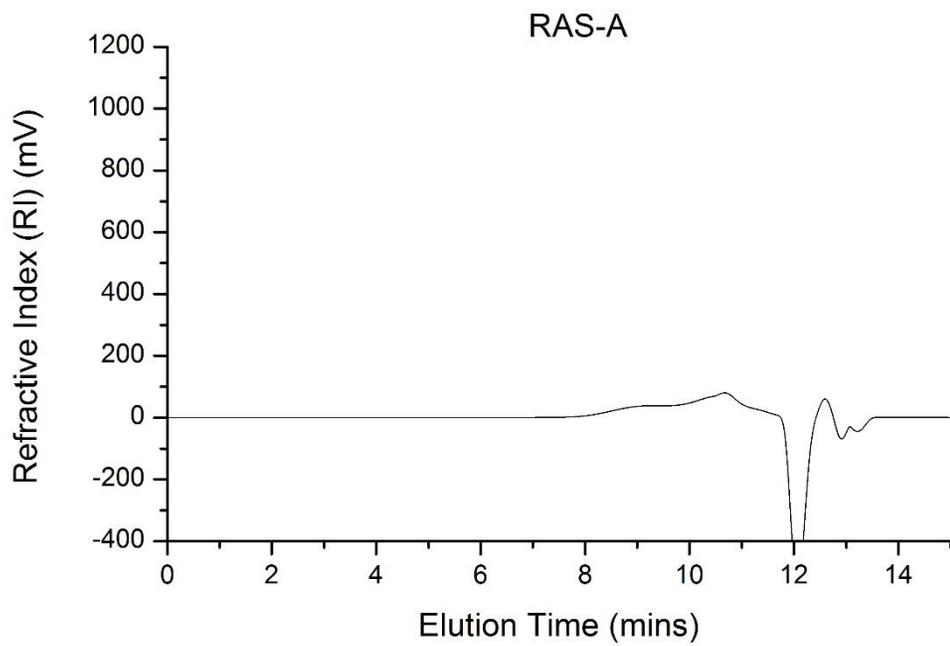


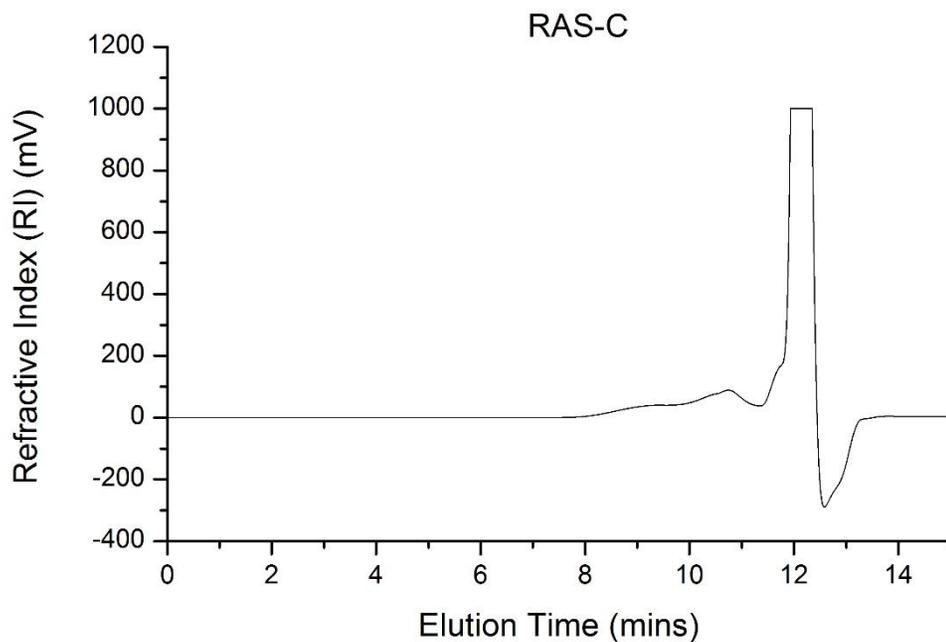
APPENDIX B: GPC Chromatograms of Test in Figure 3-4



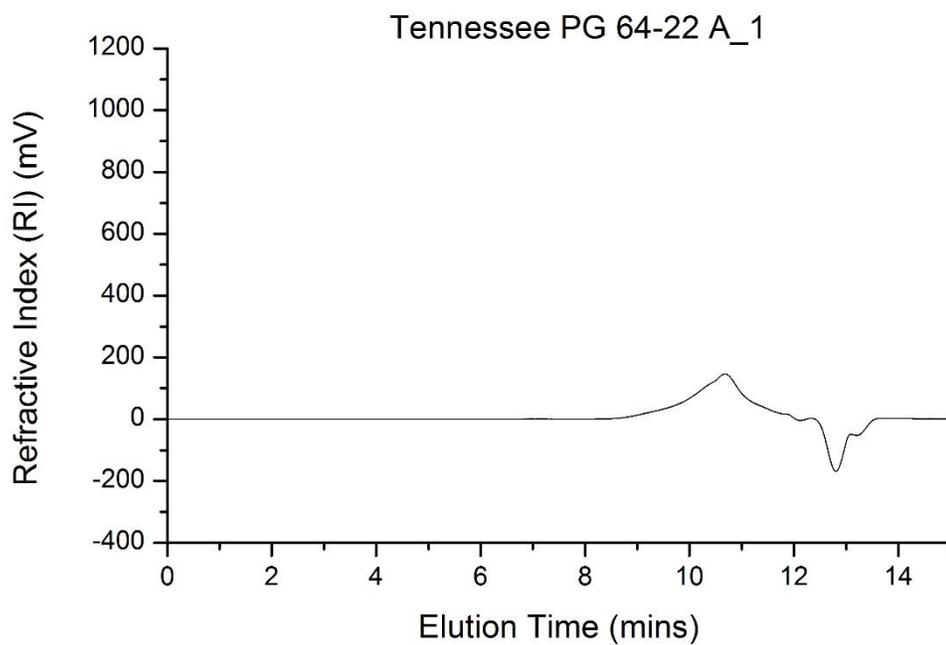


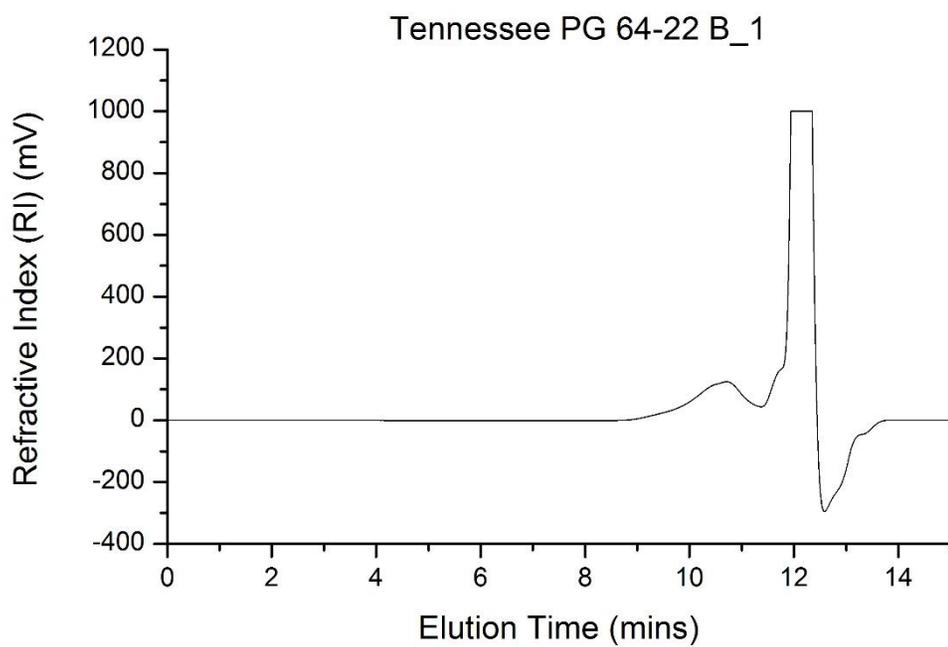
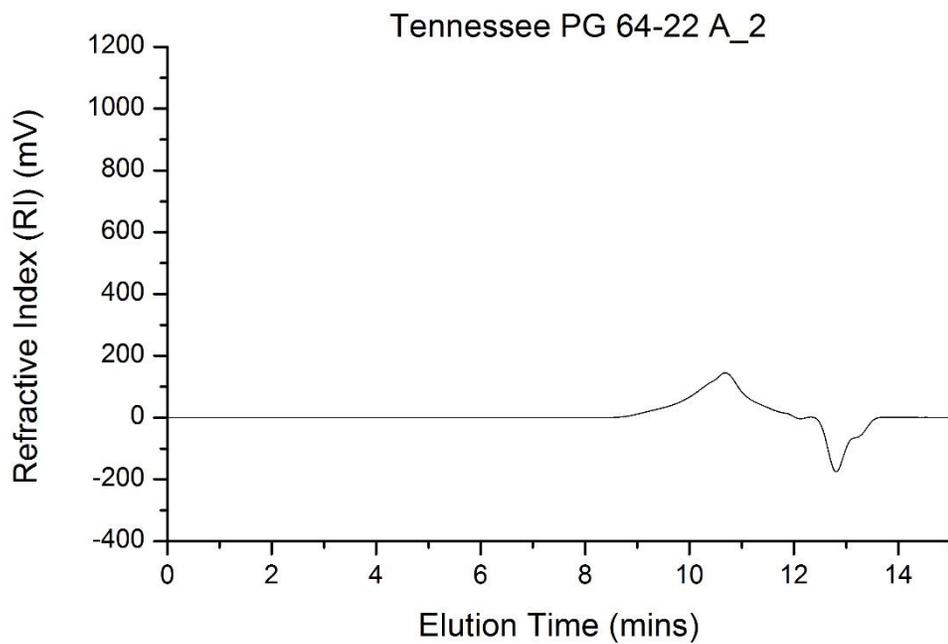


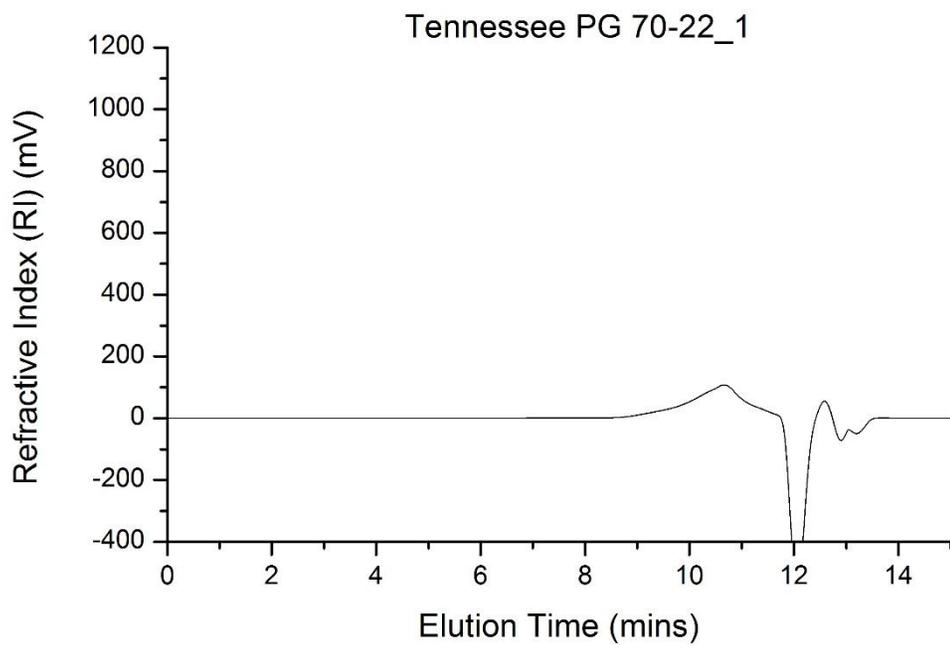
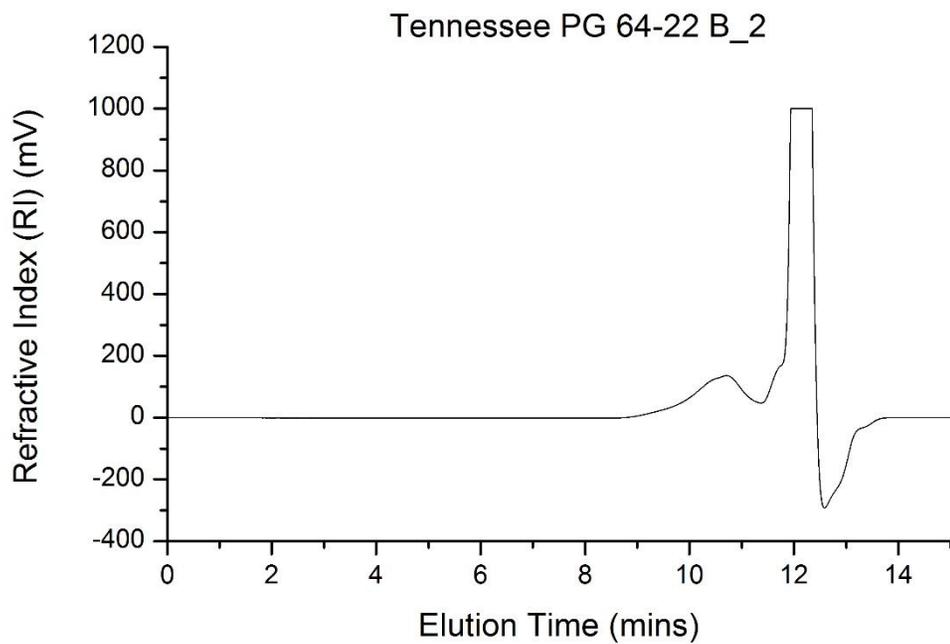


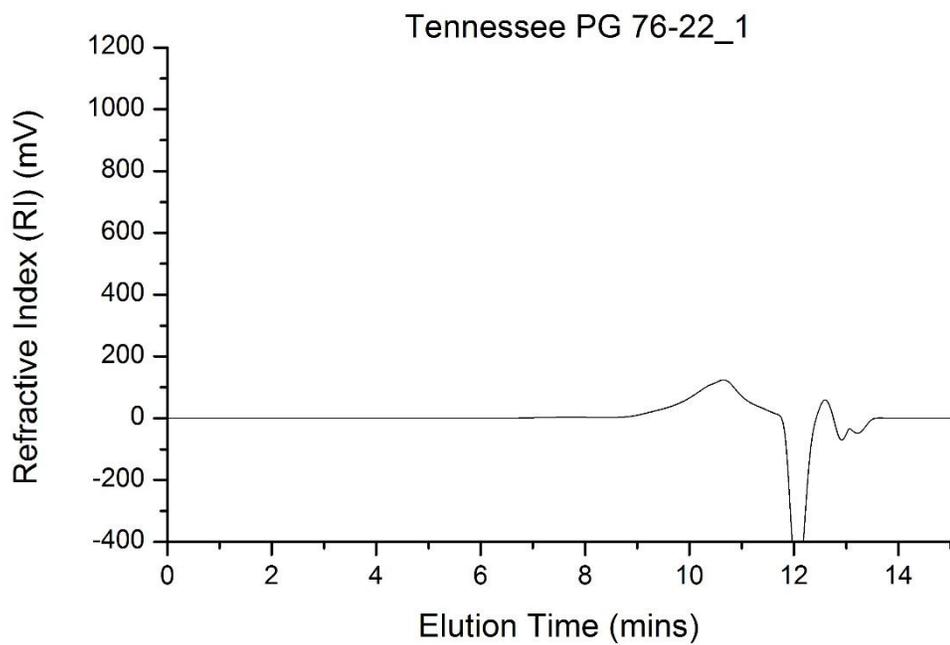
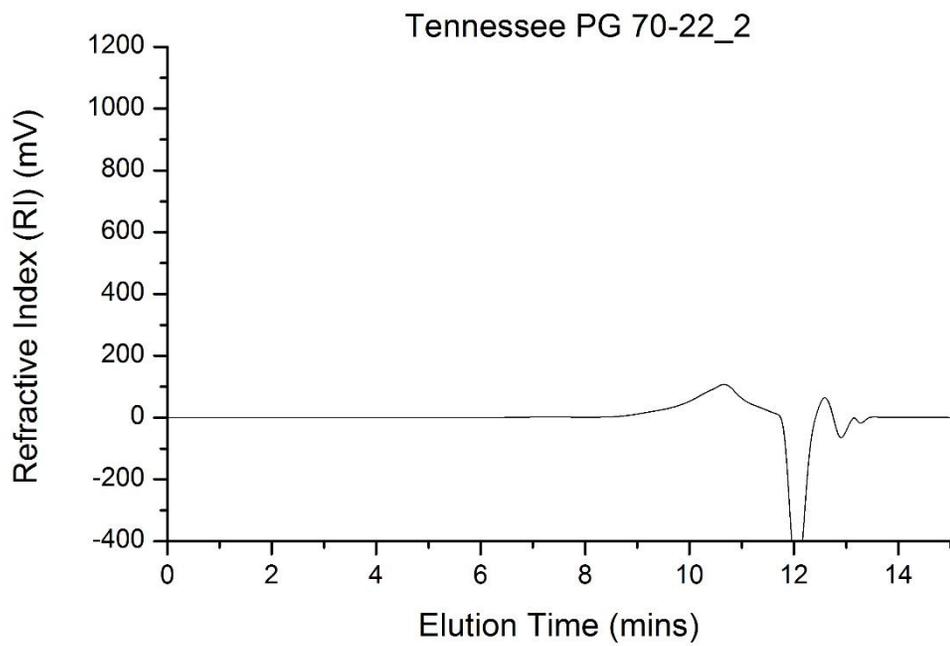


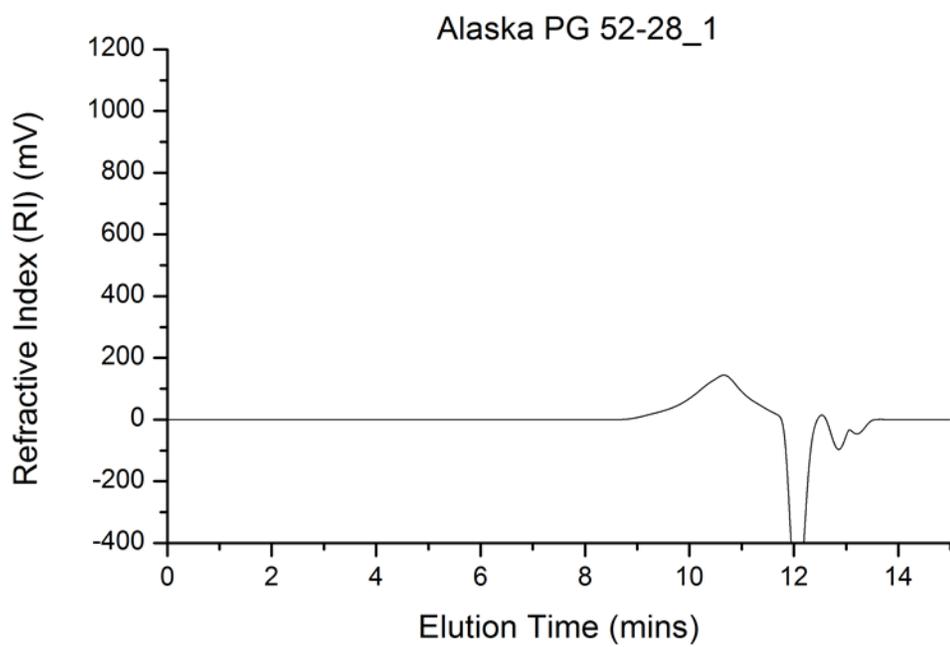
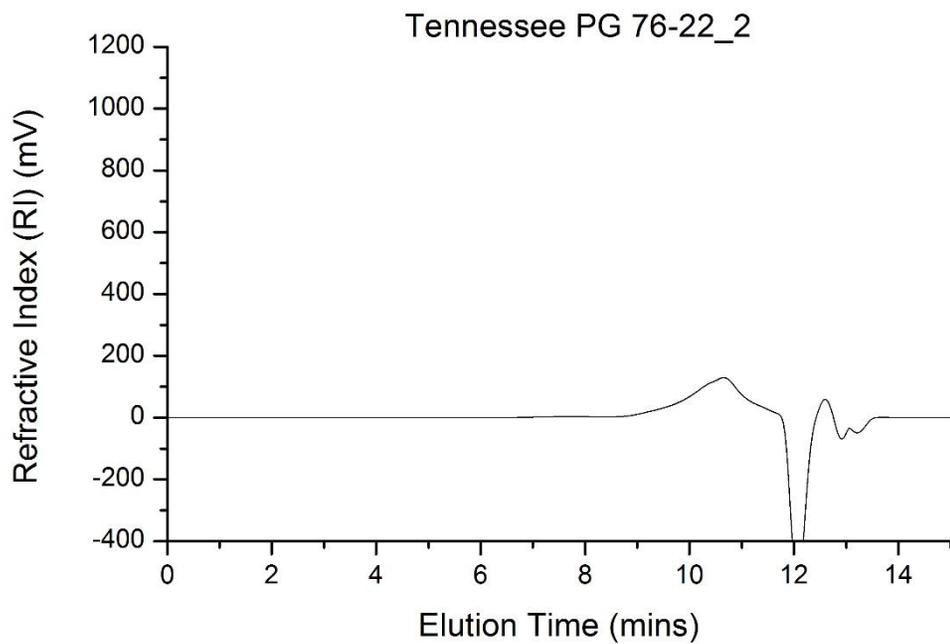
APPENDIX C: GPC Chromatograms of Test in Figure 3-5

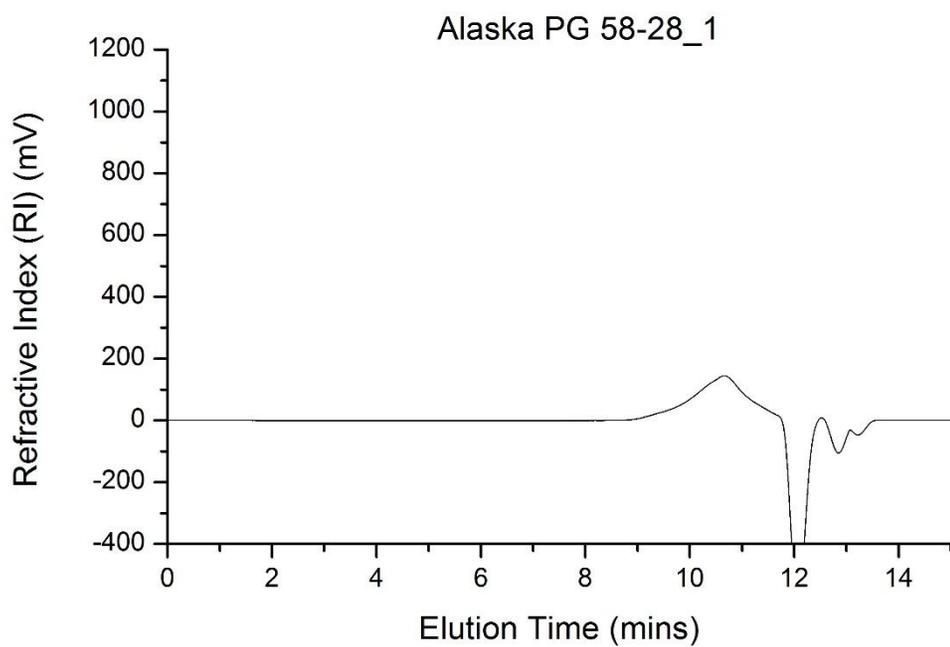
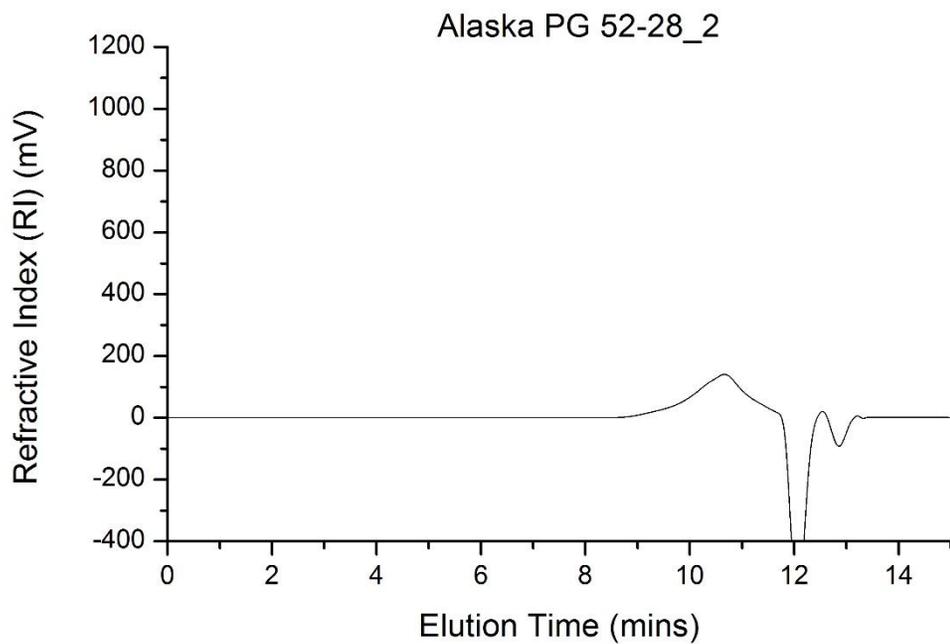


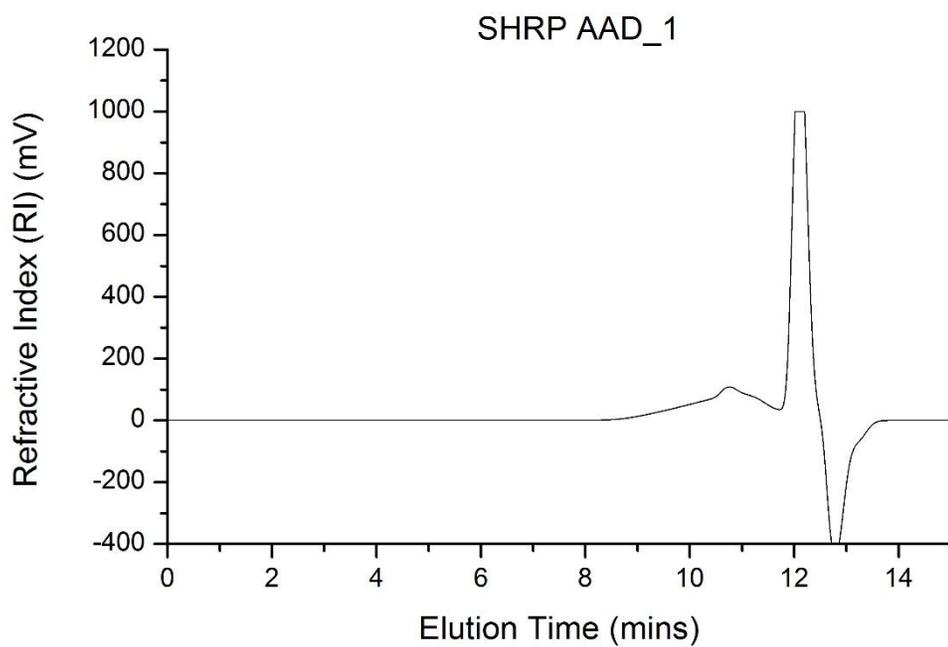
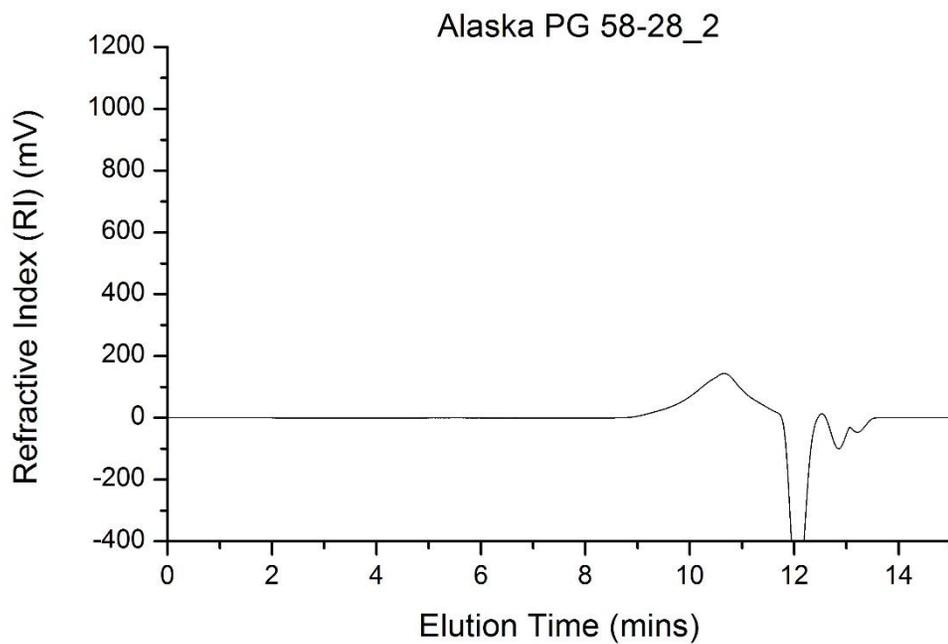


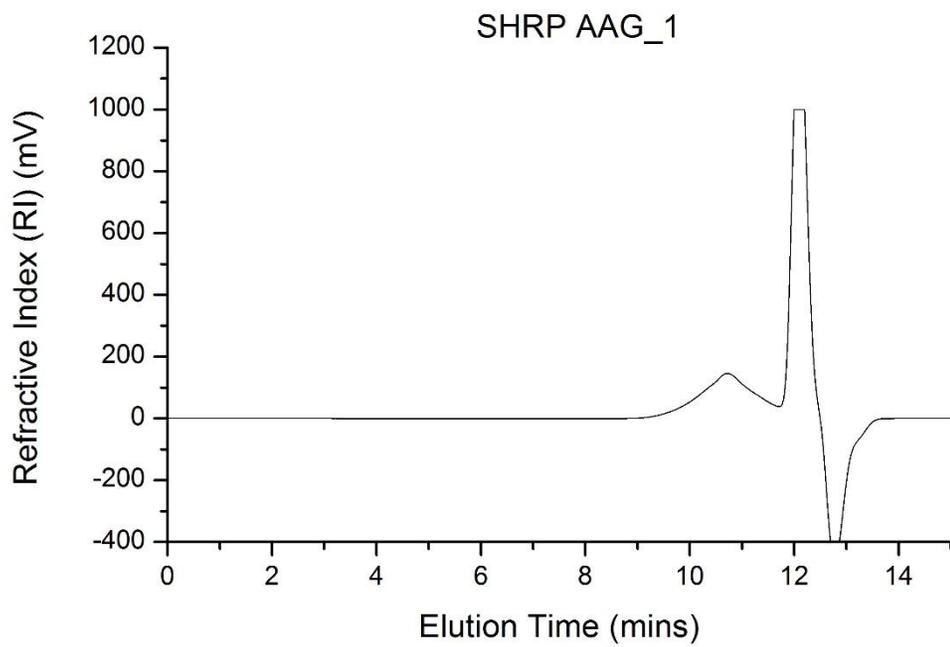
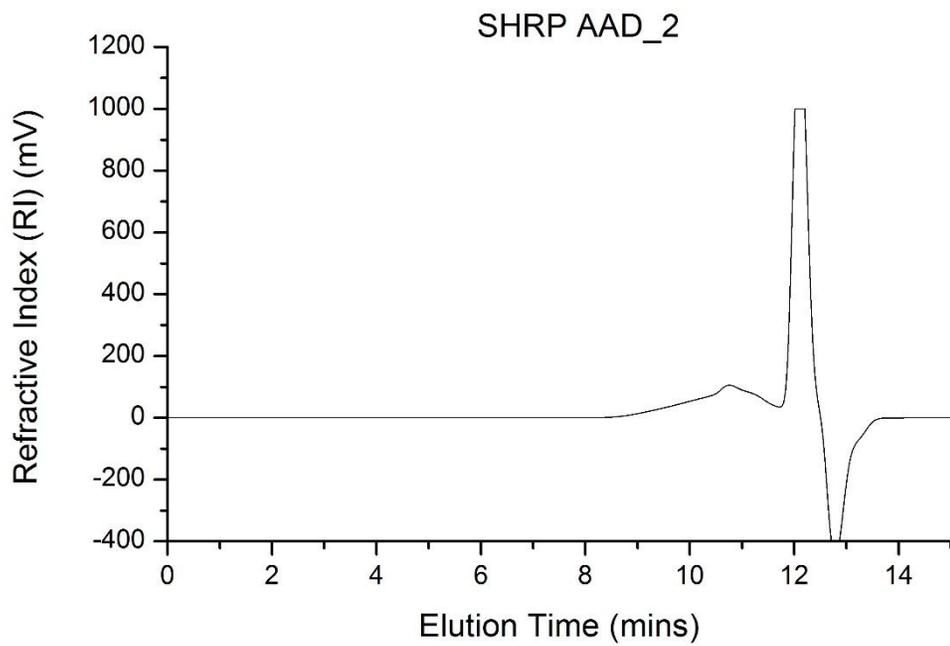


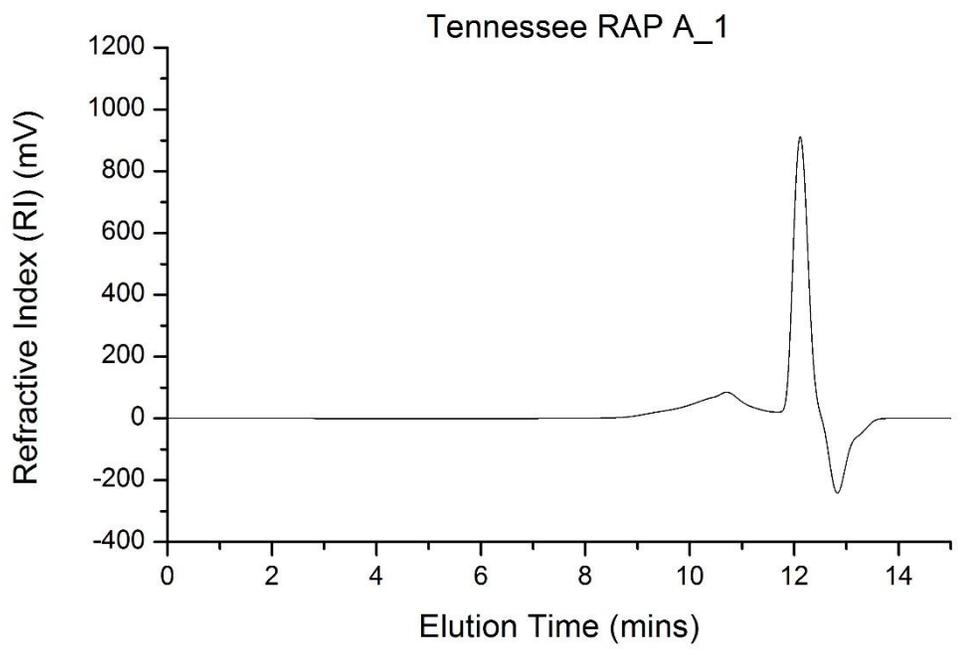
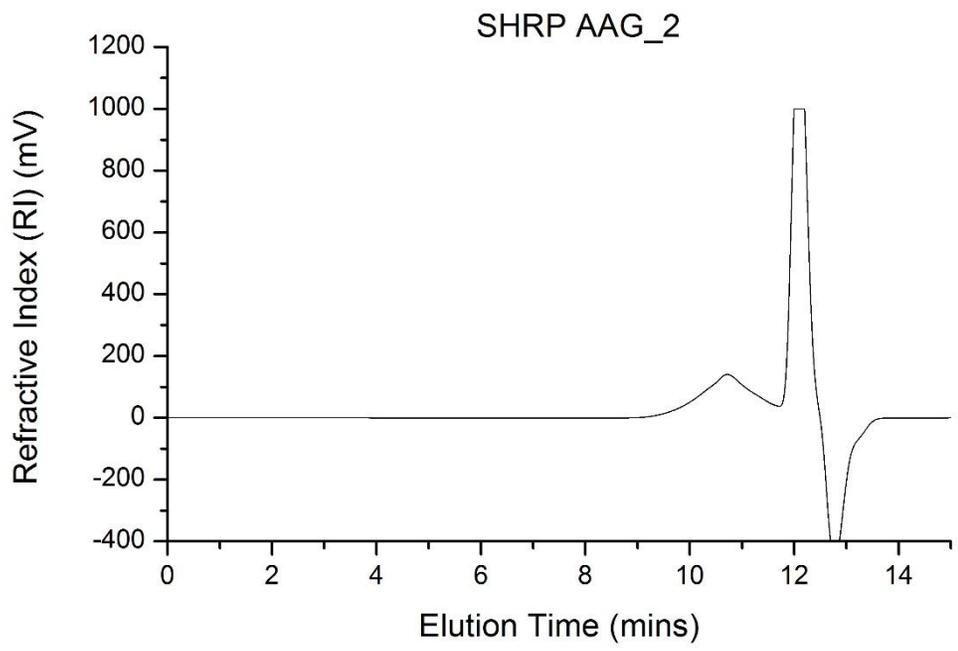


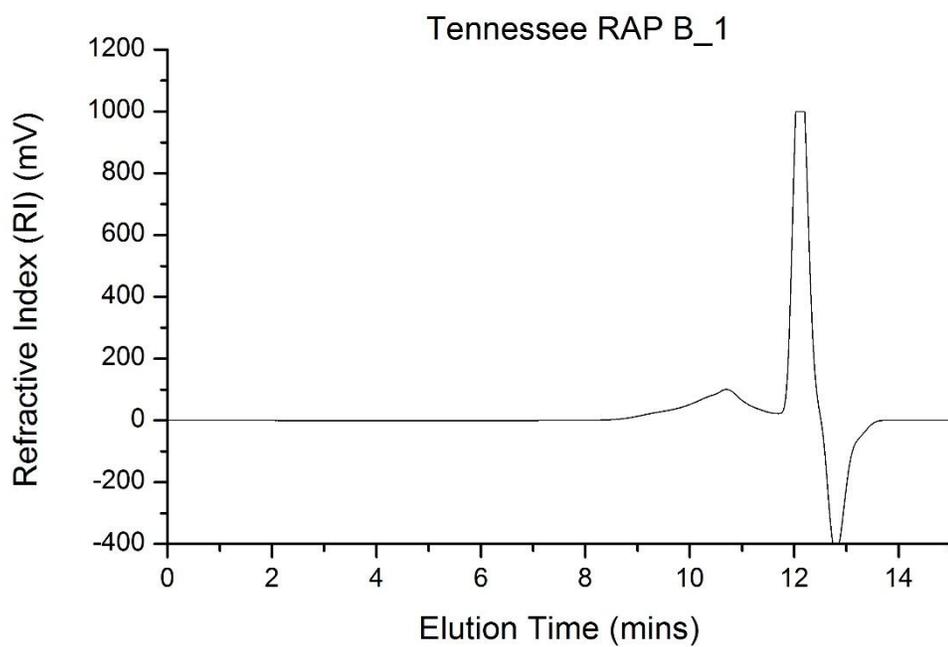
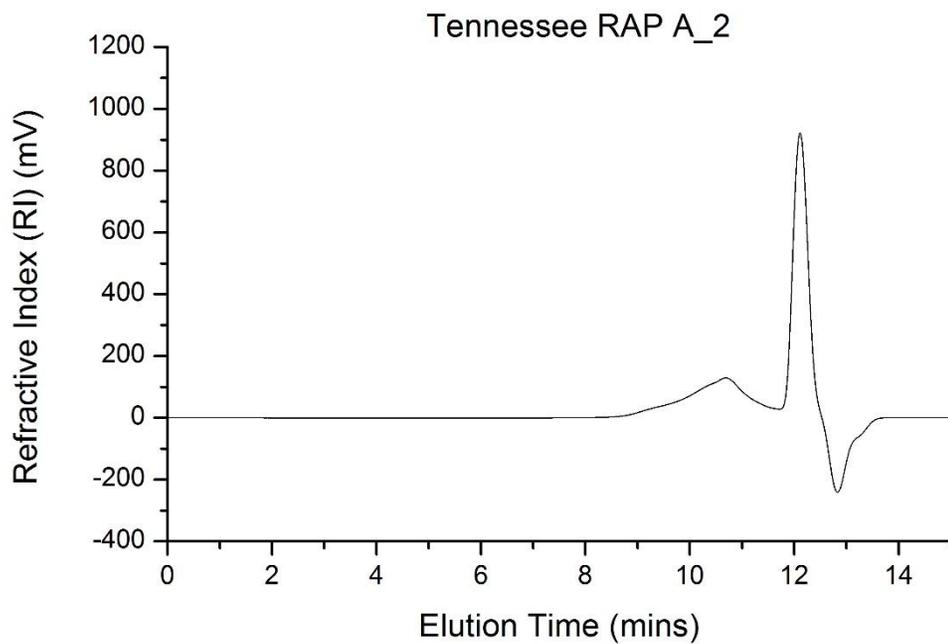


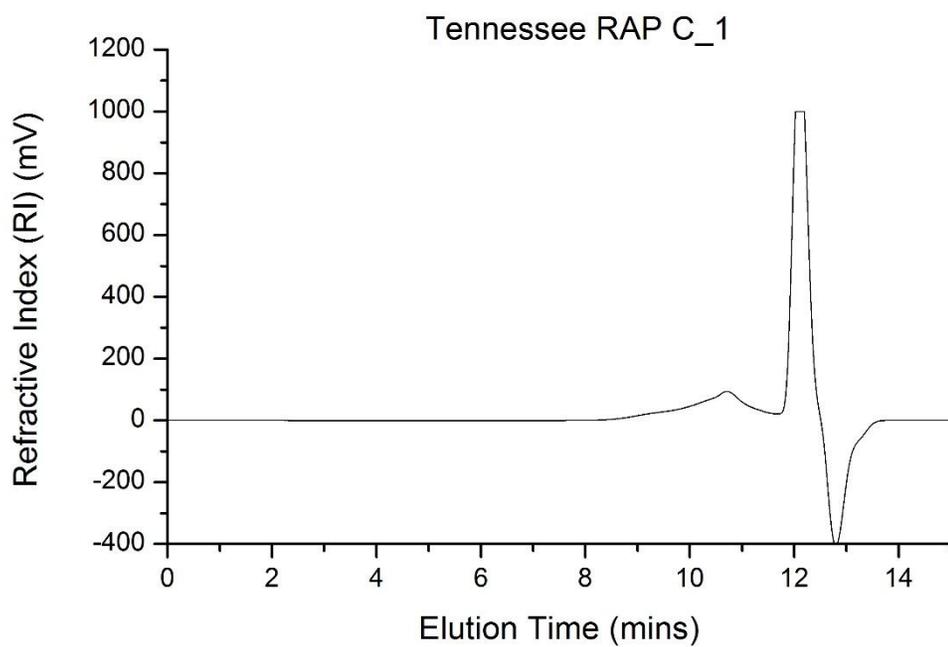
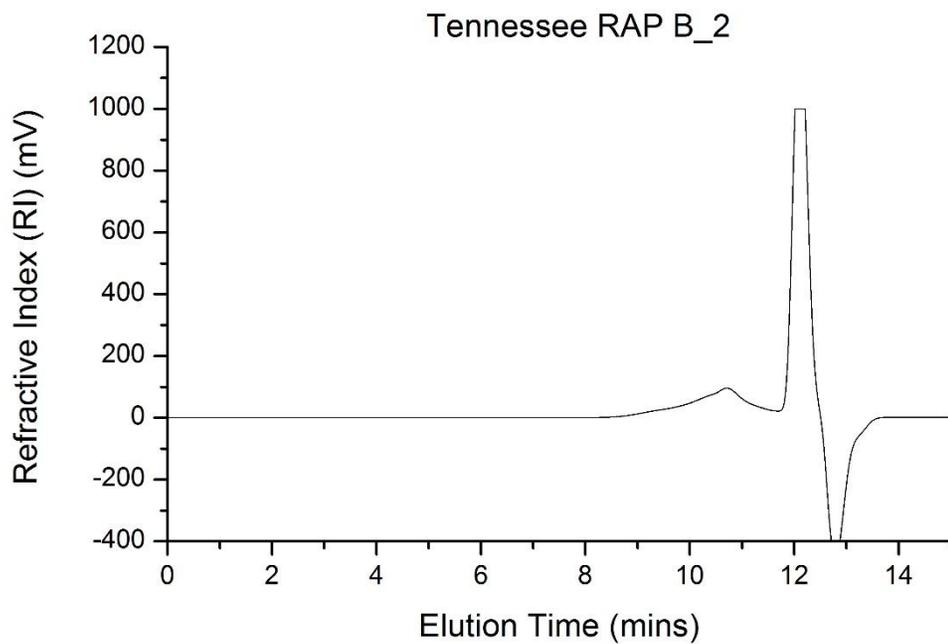


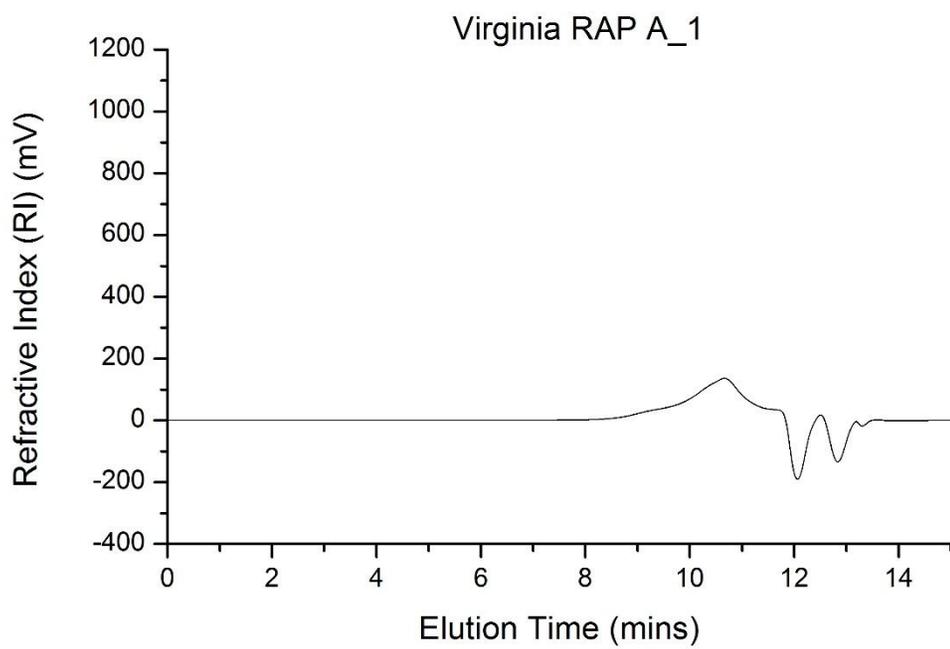
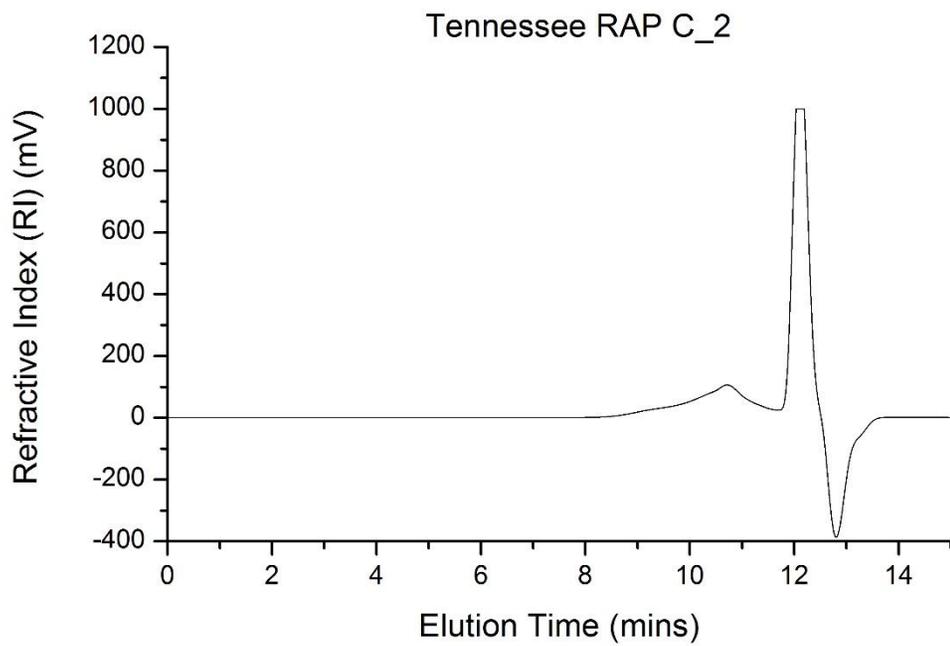


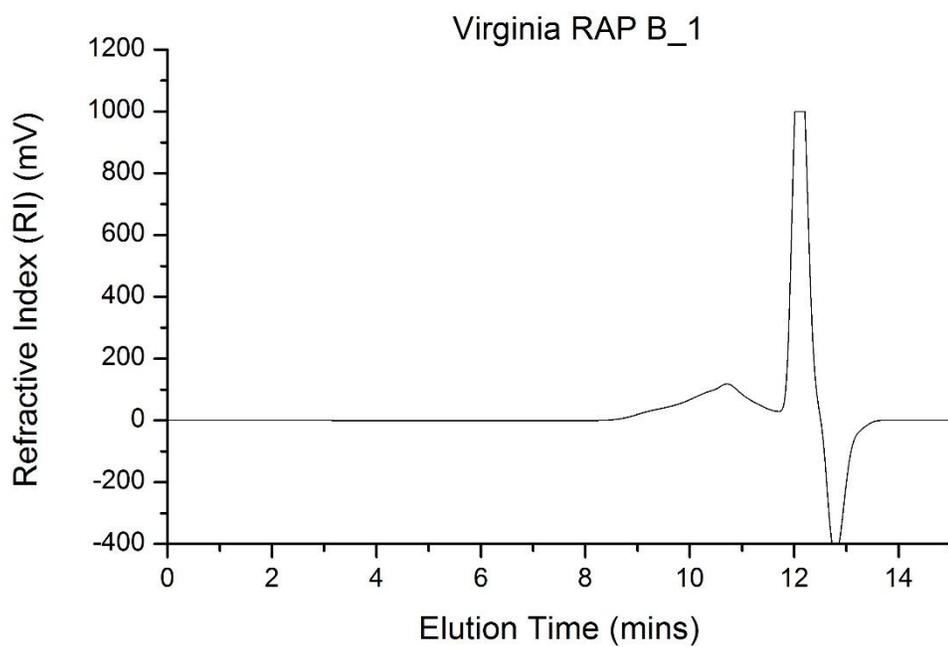
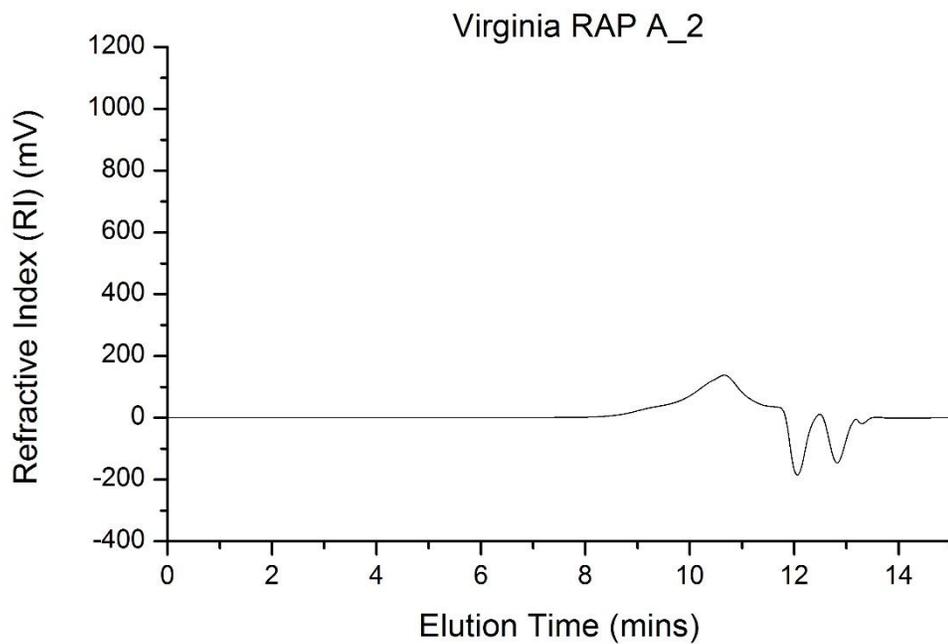


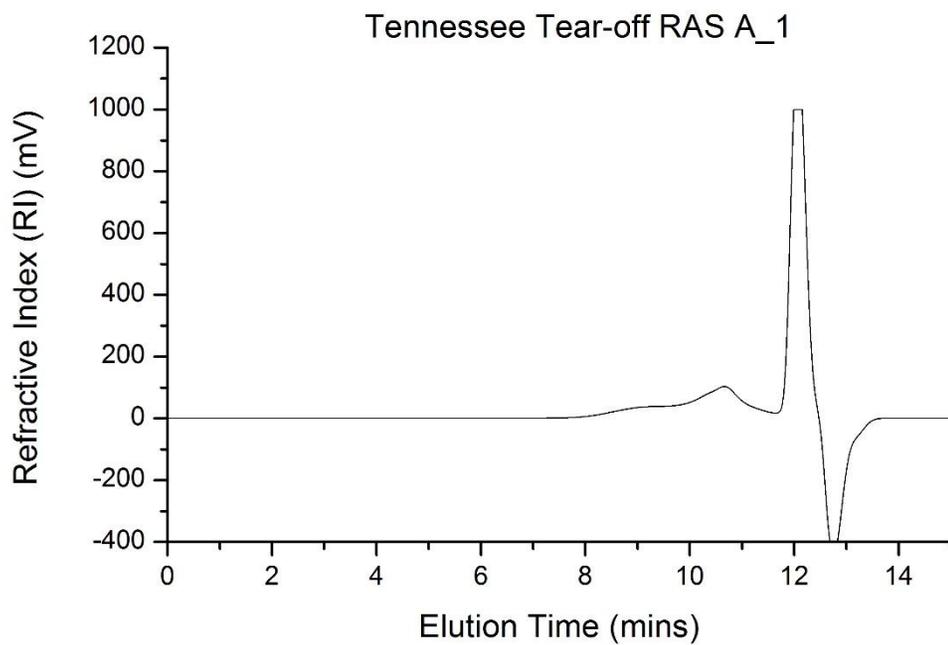
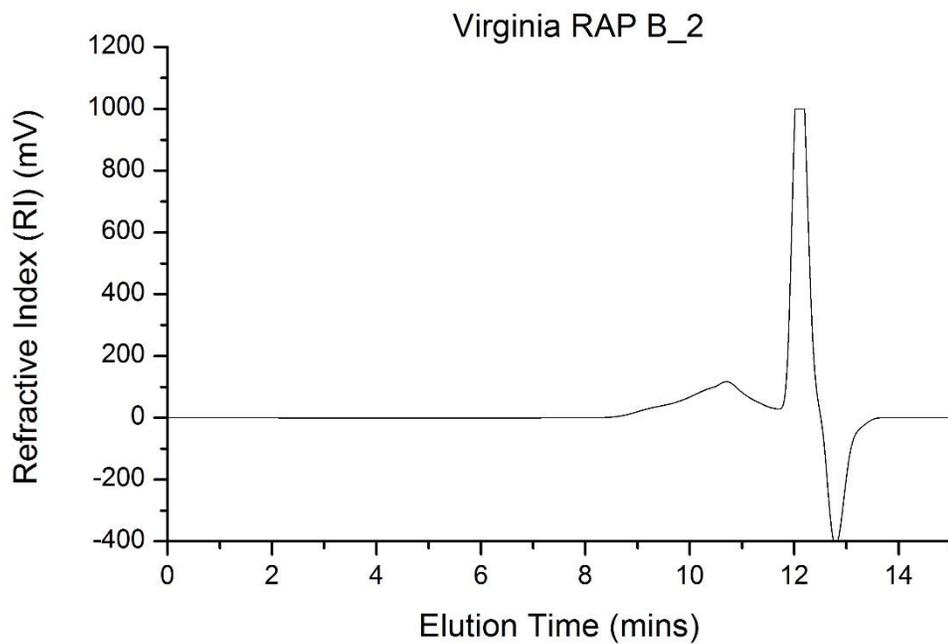


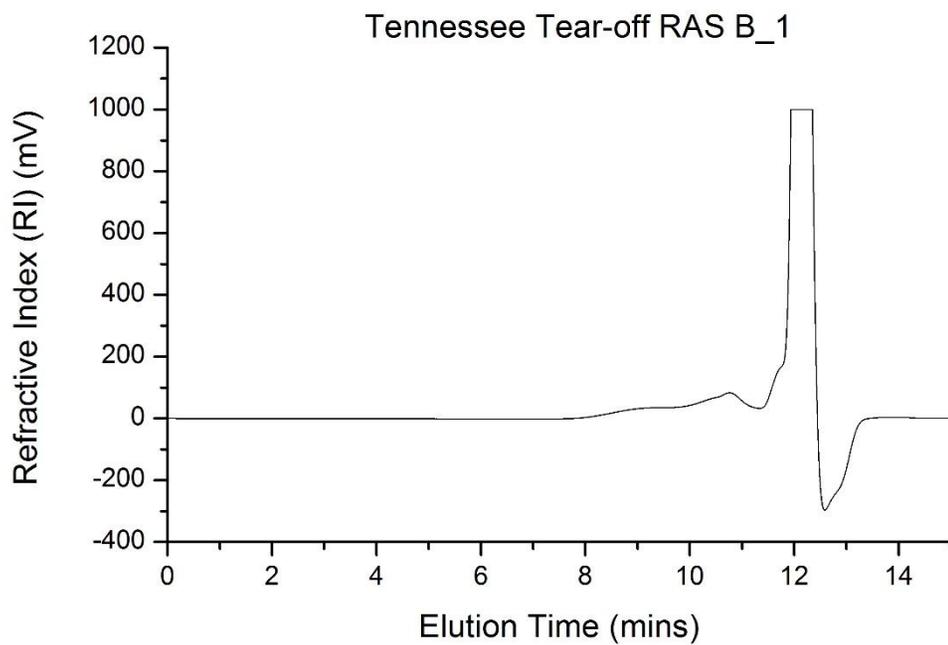
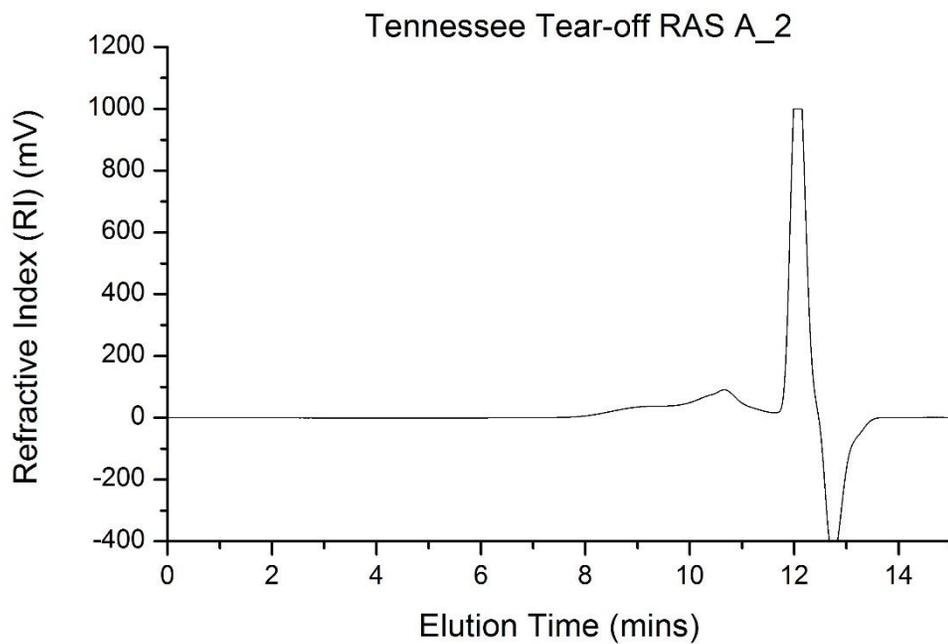


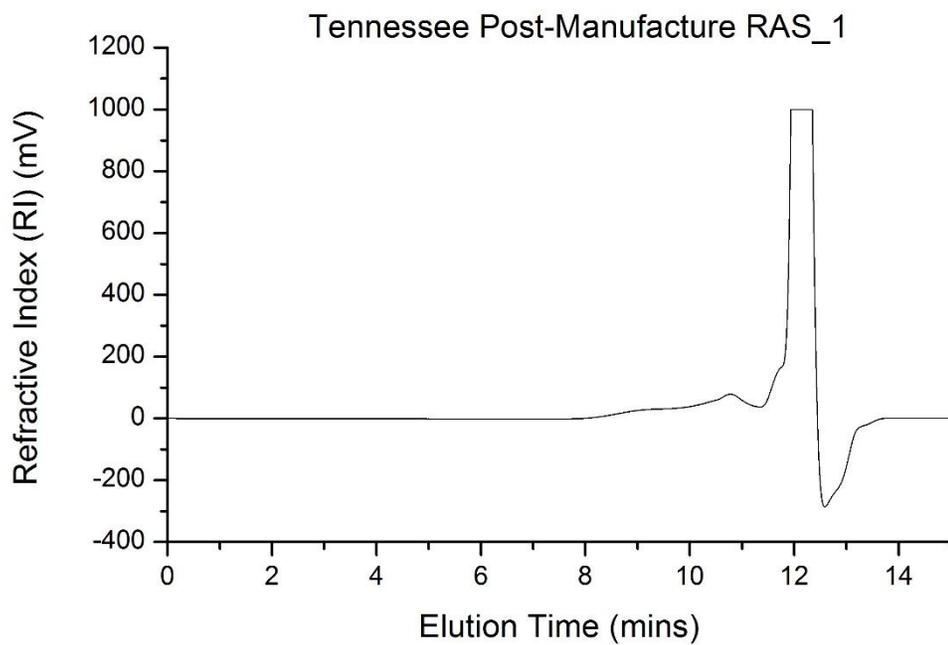
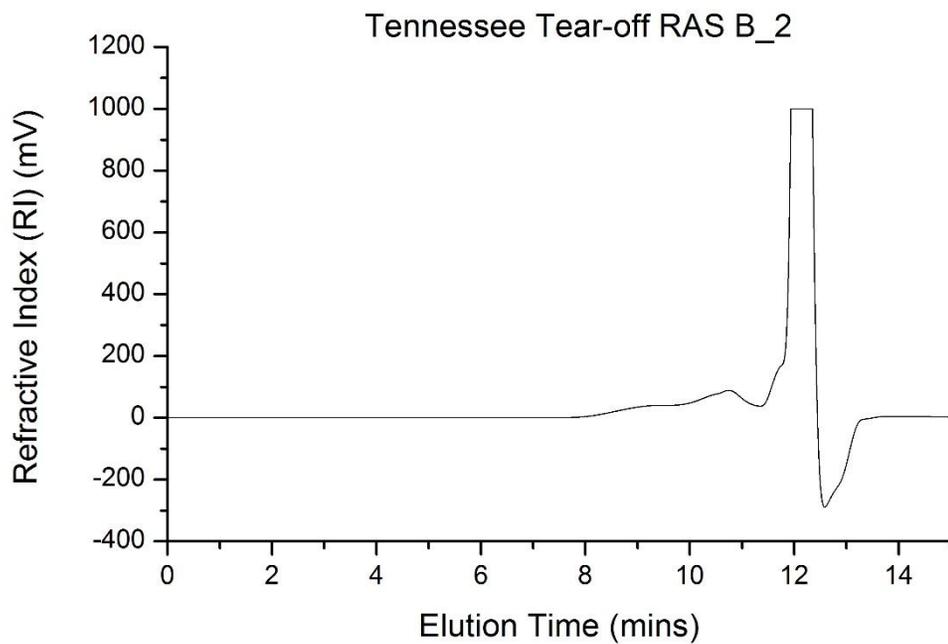


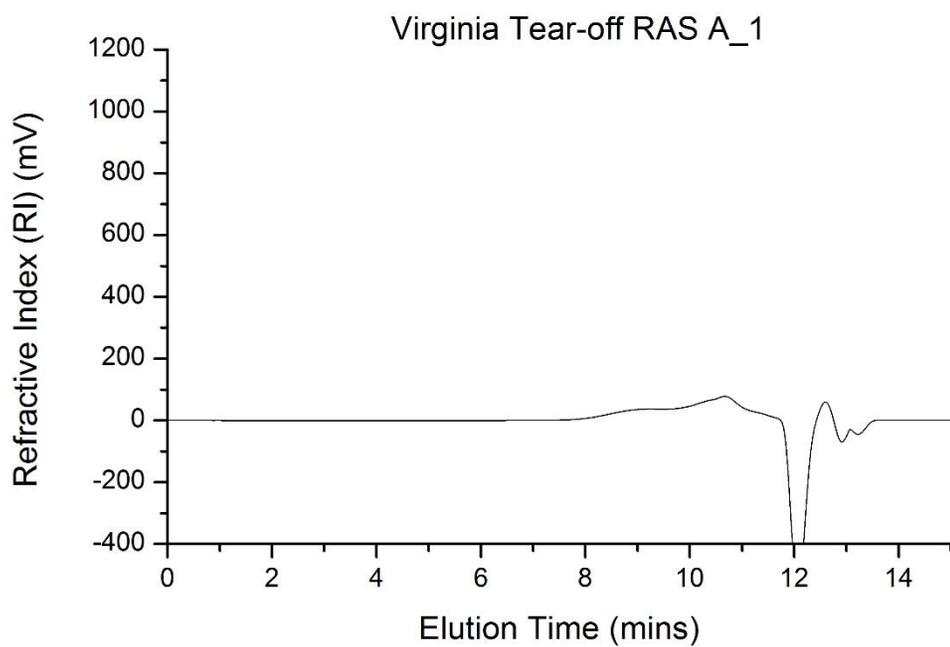
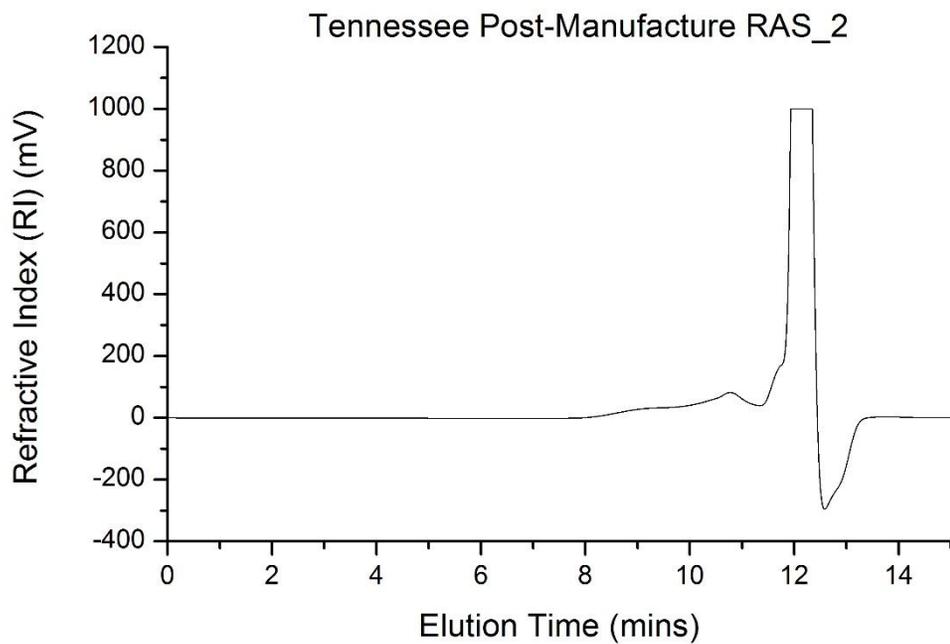


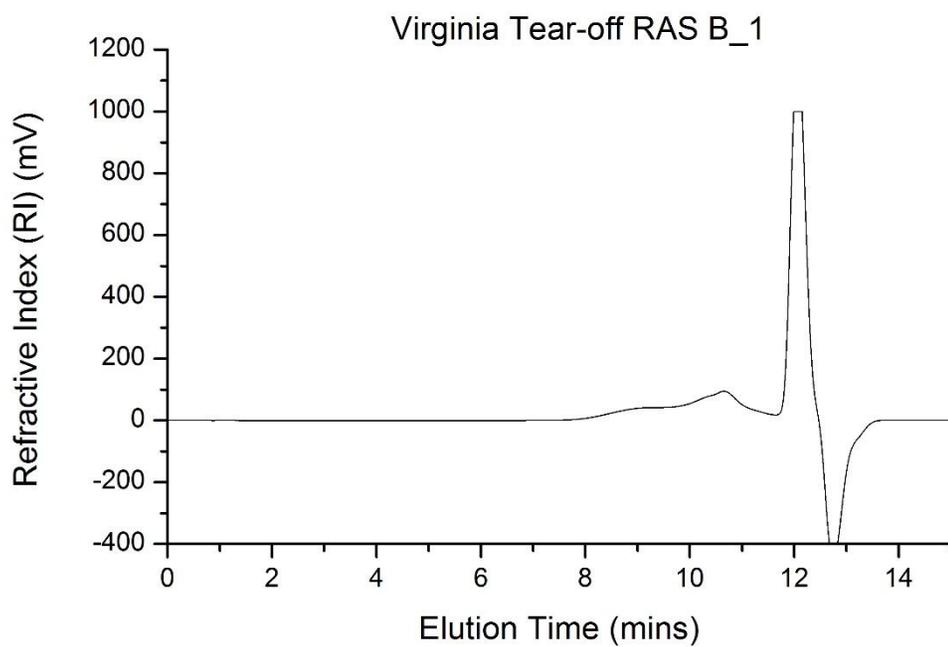
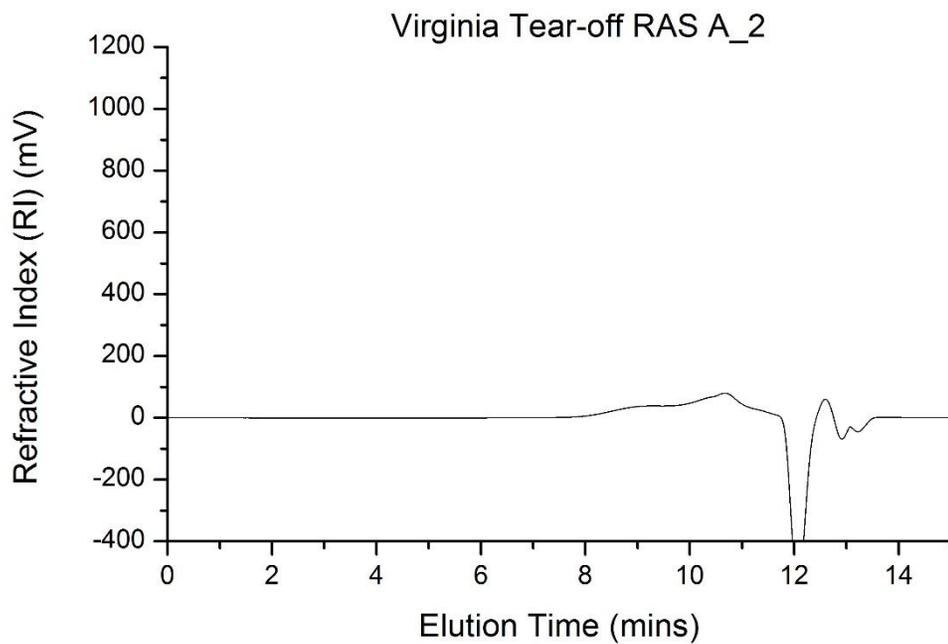


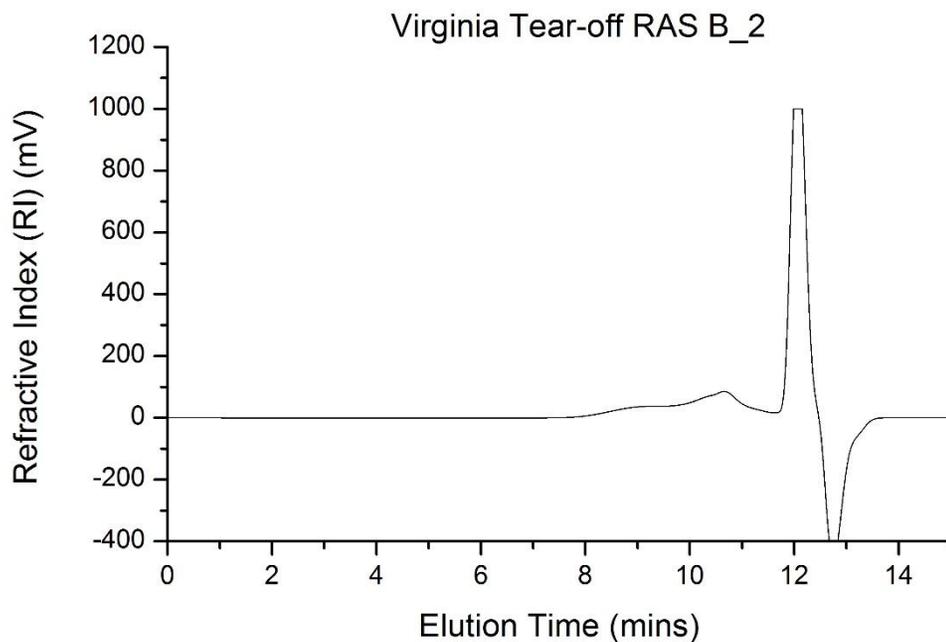




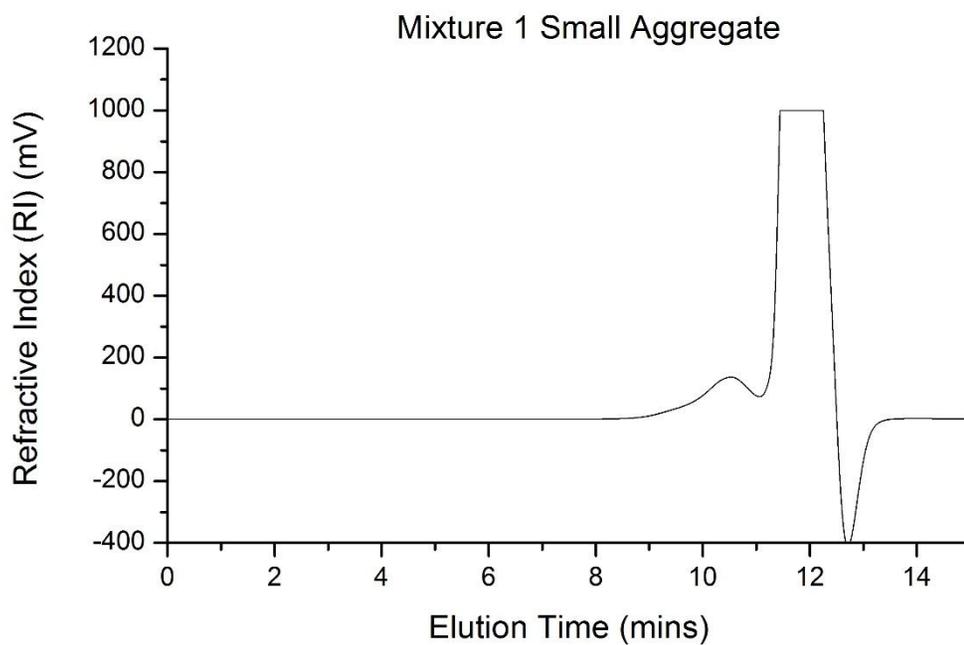


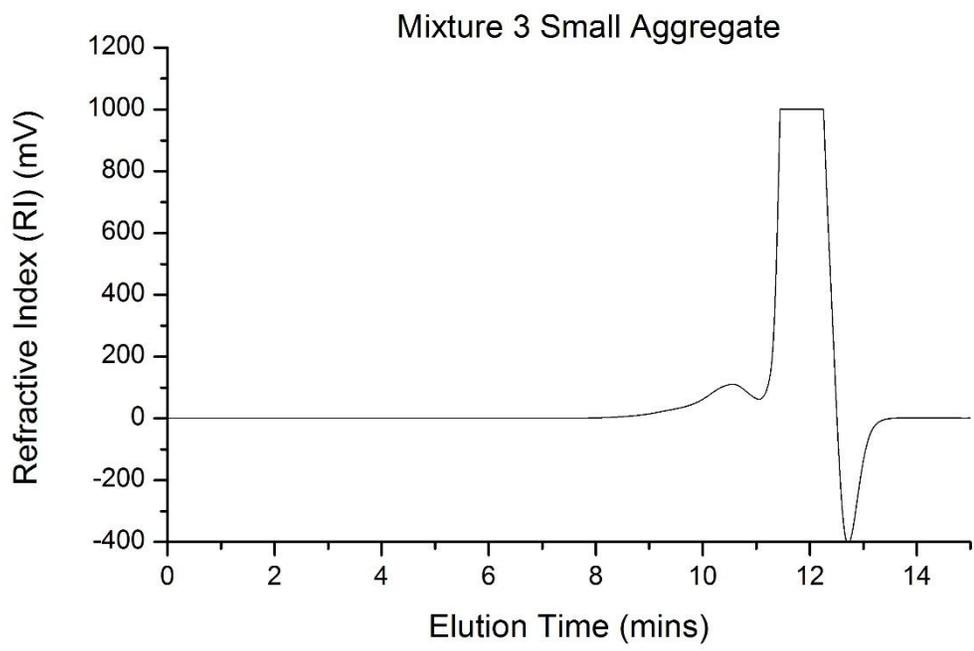
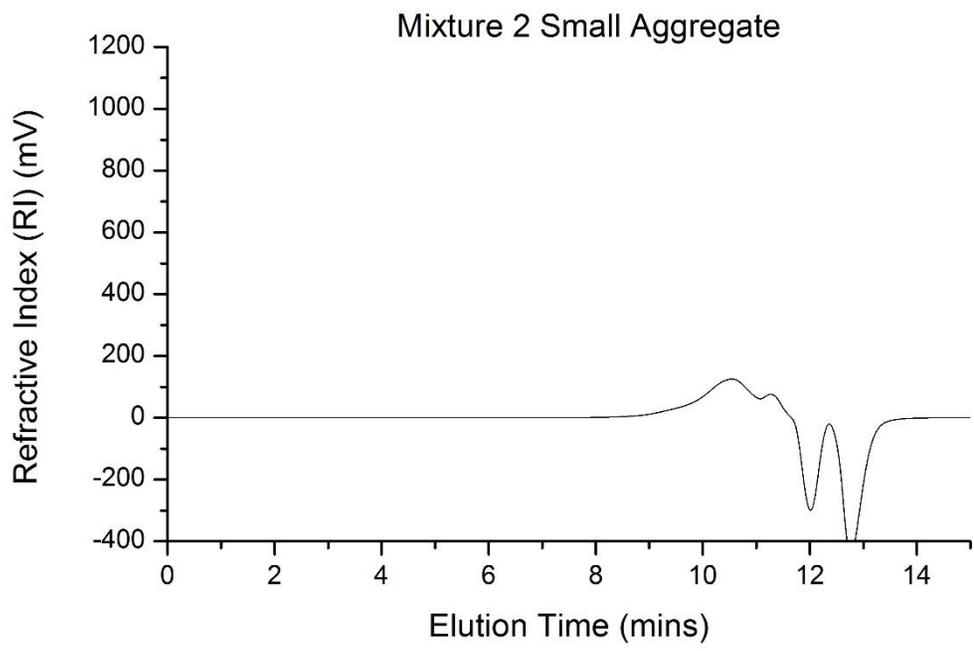


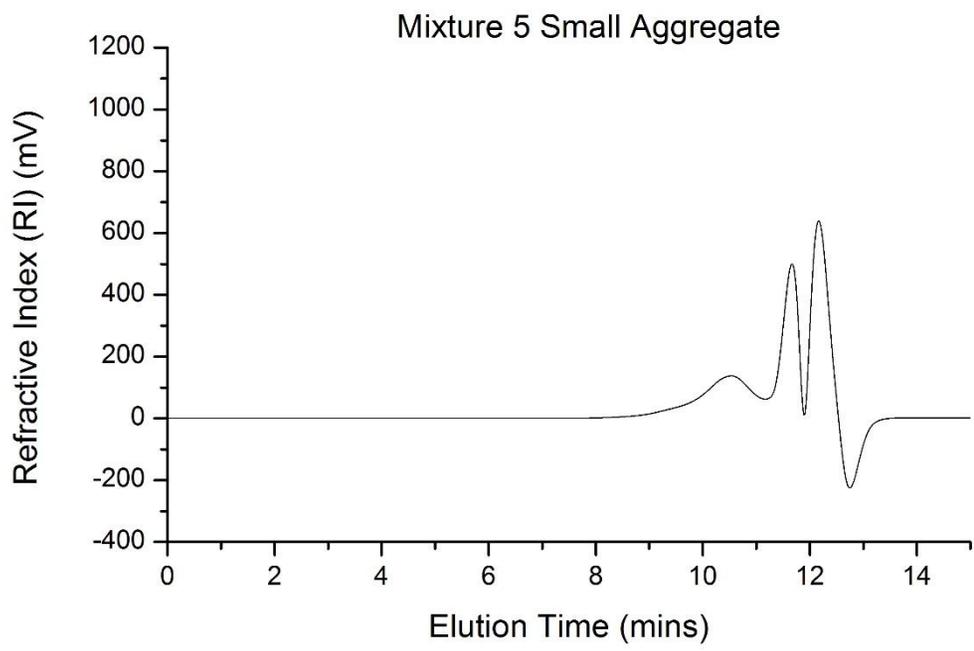
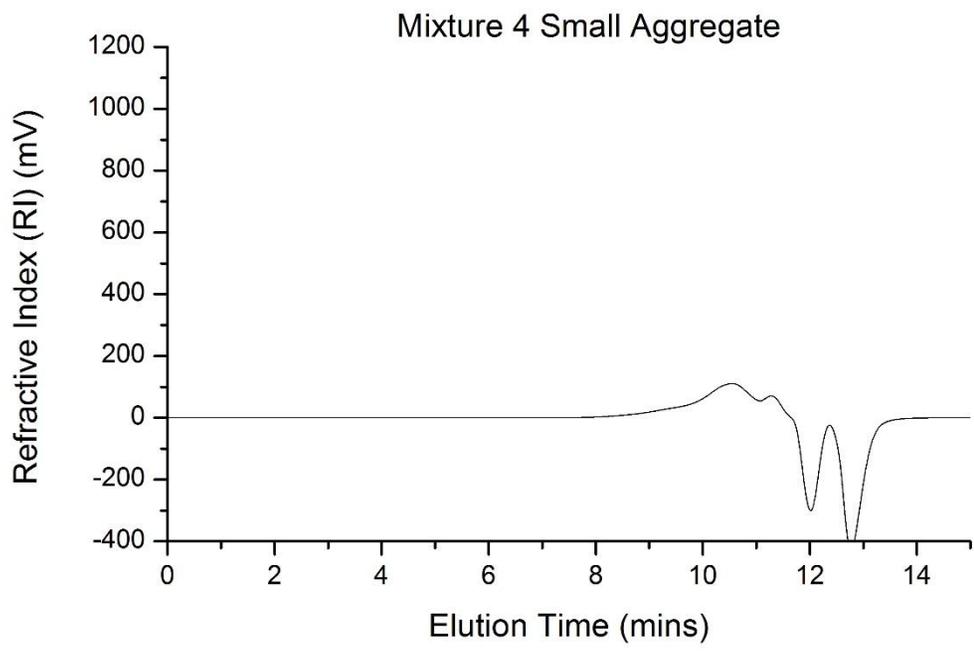


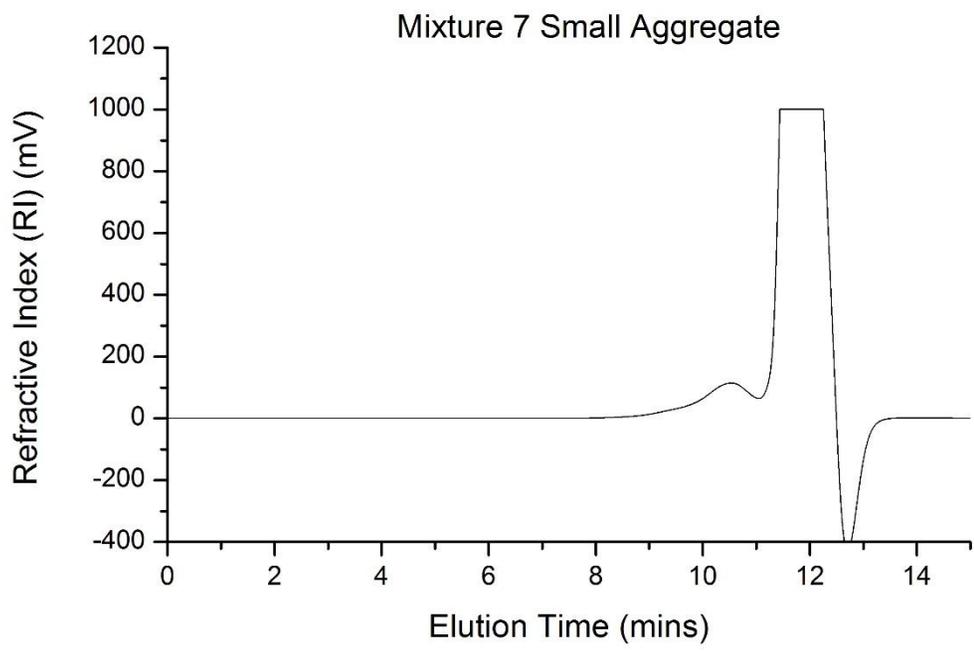
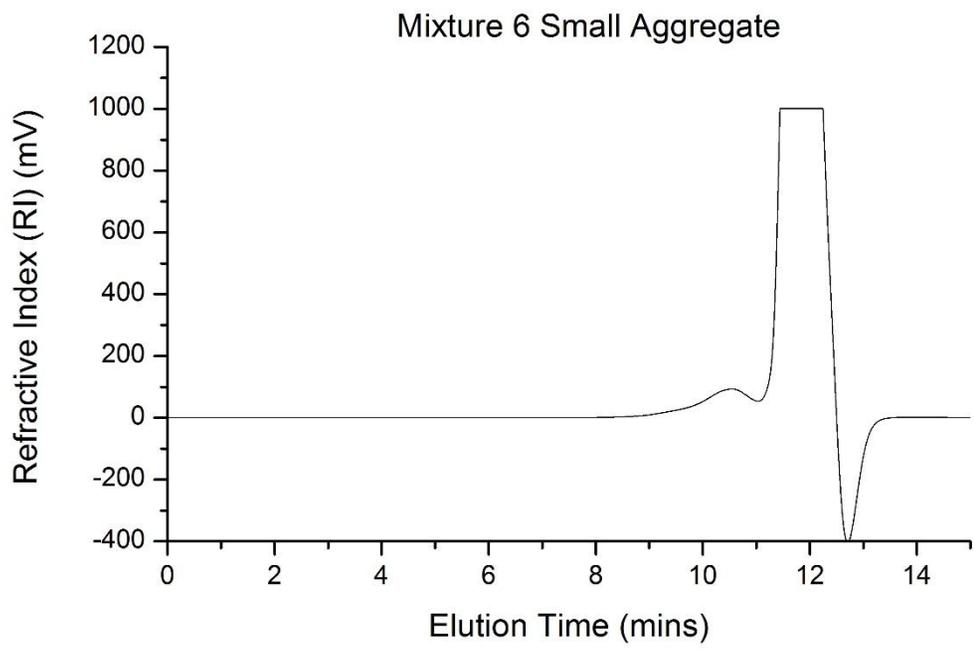


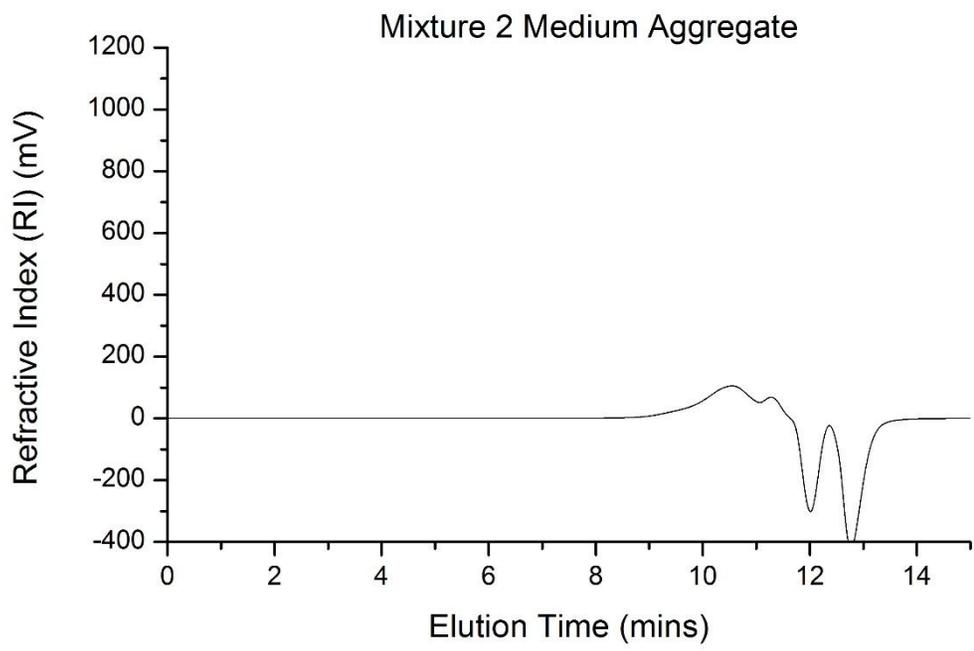
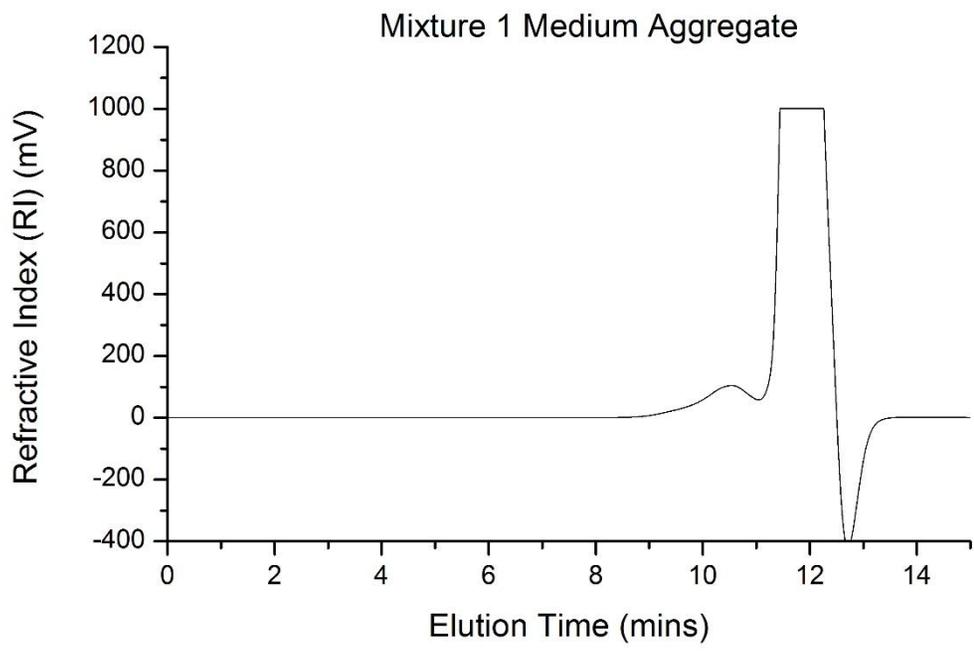
APPENDIX D: GPC Chromatograms of Test in Table 3-5

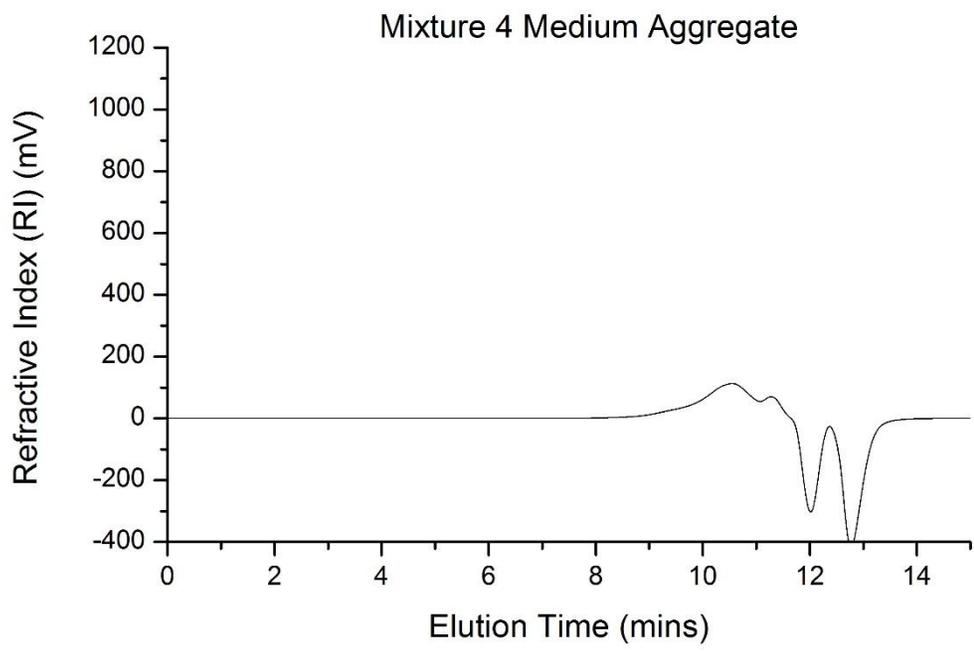
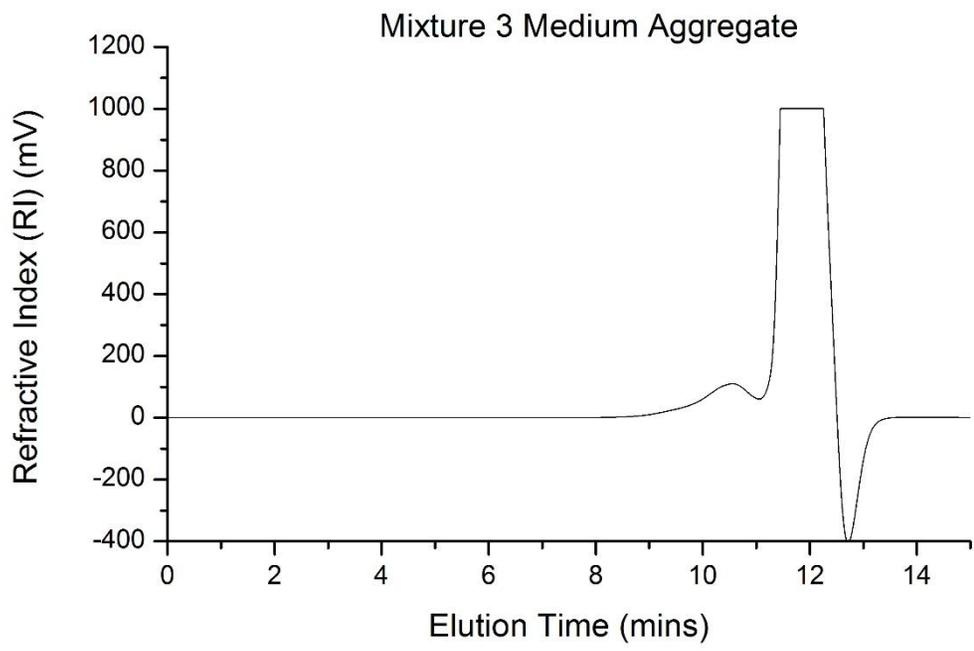


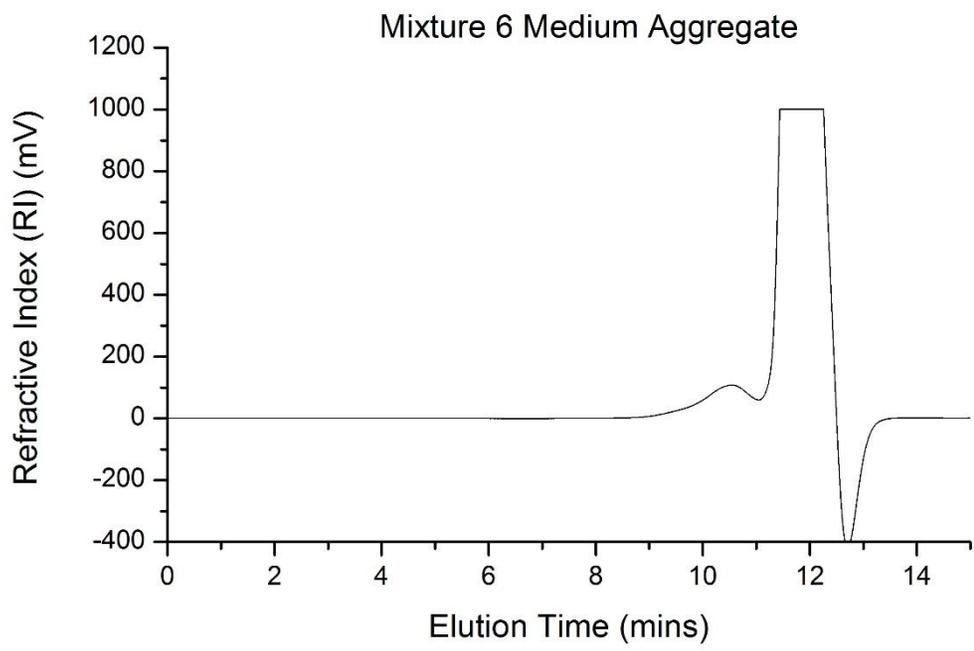
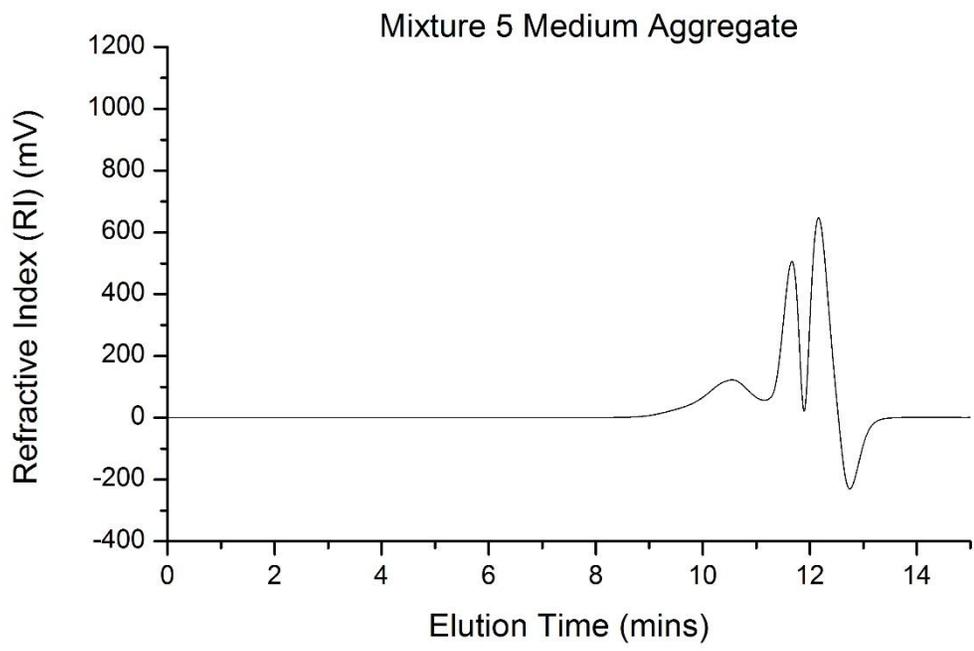


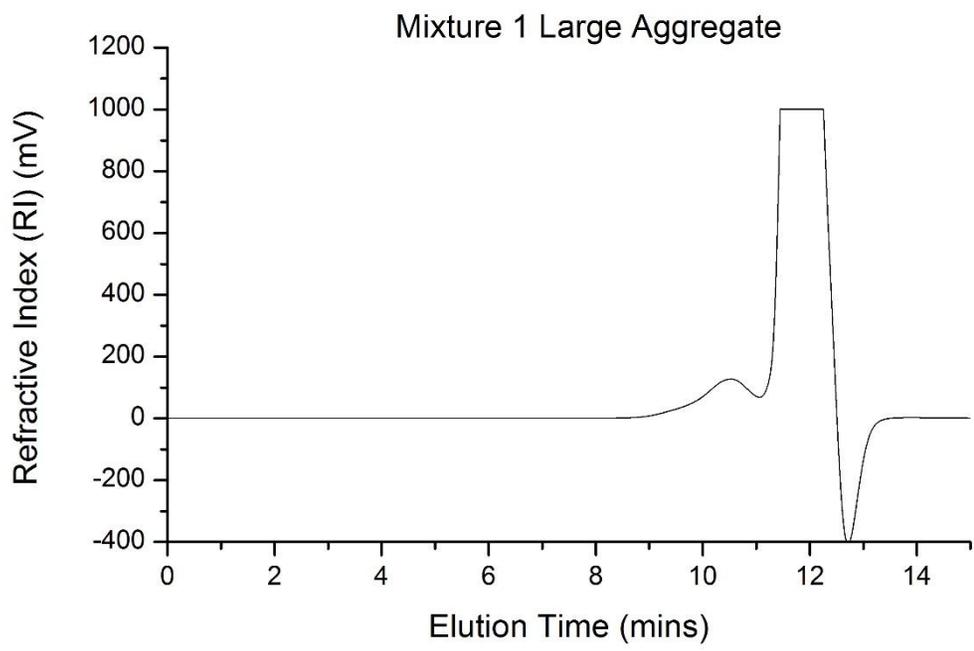
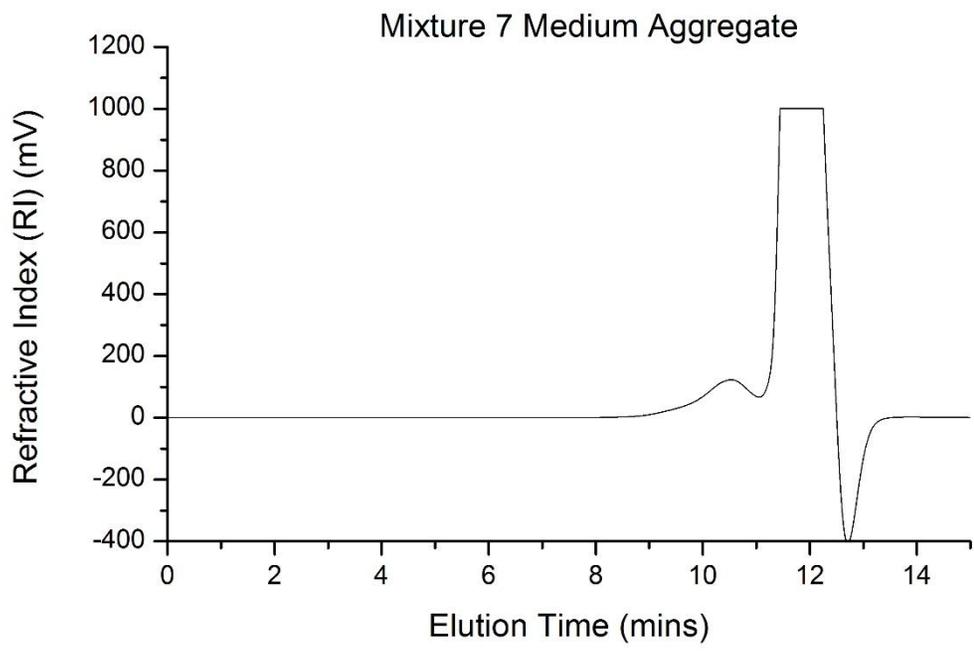


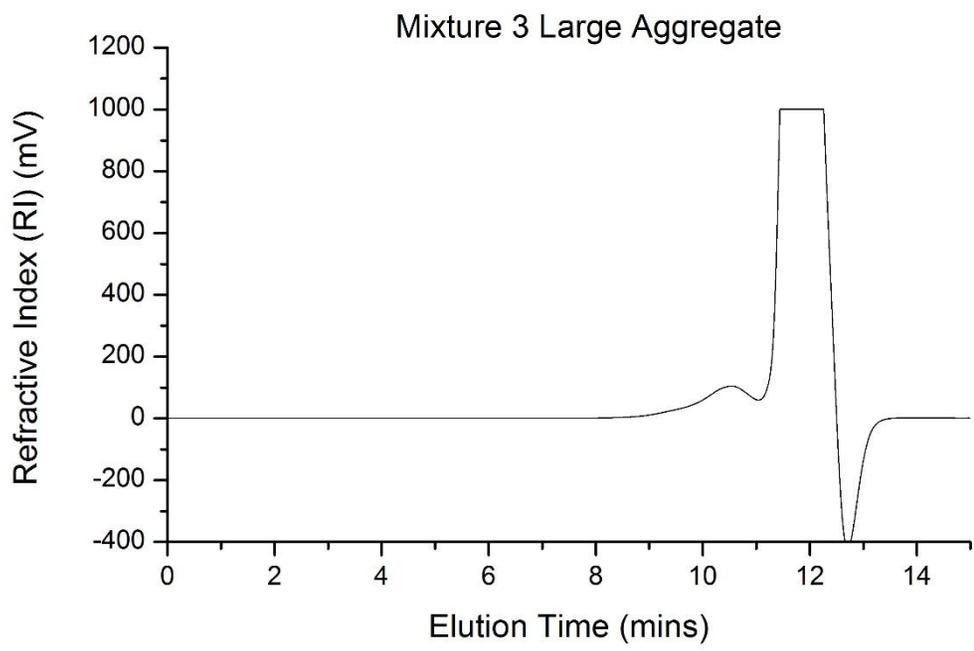
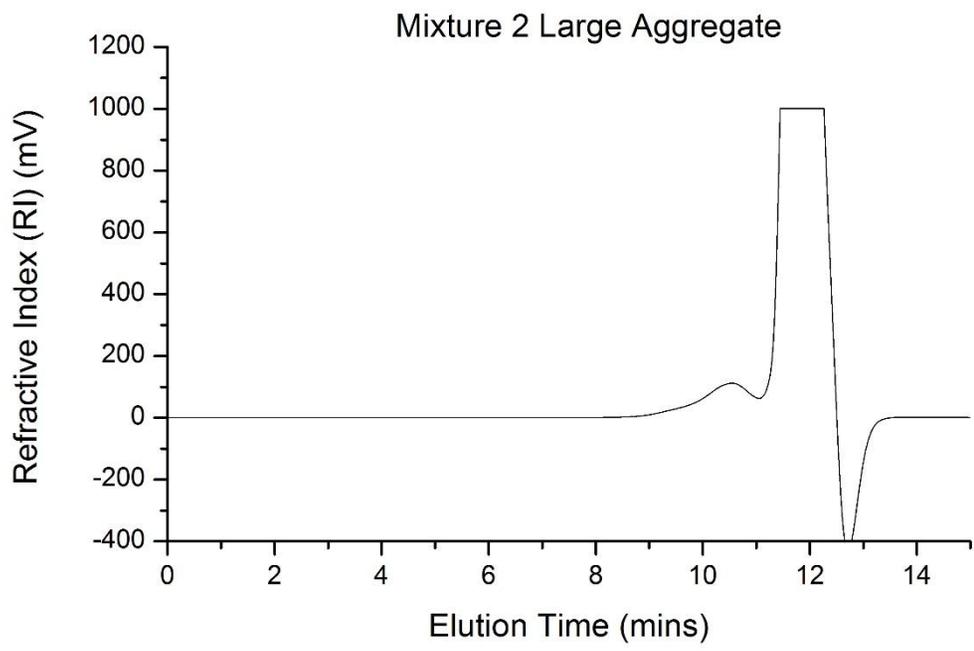


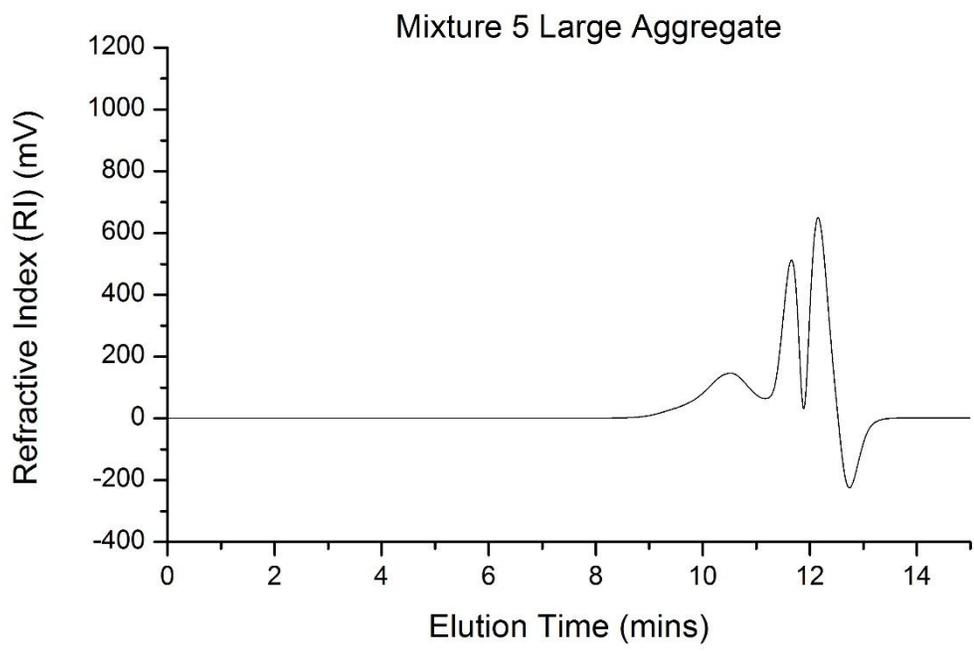
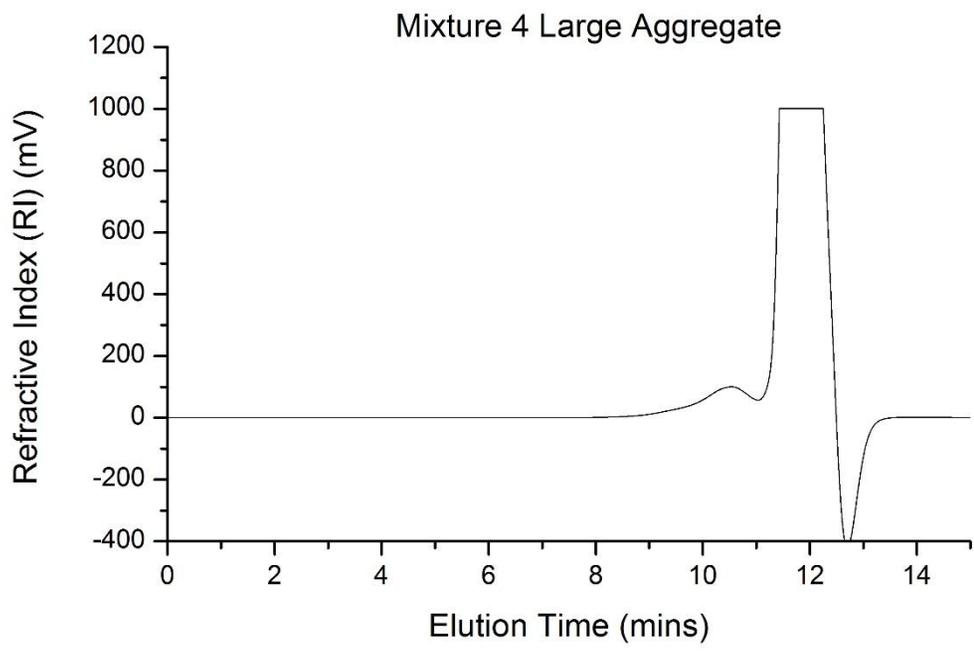


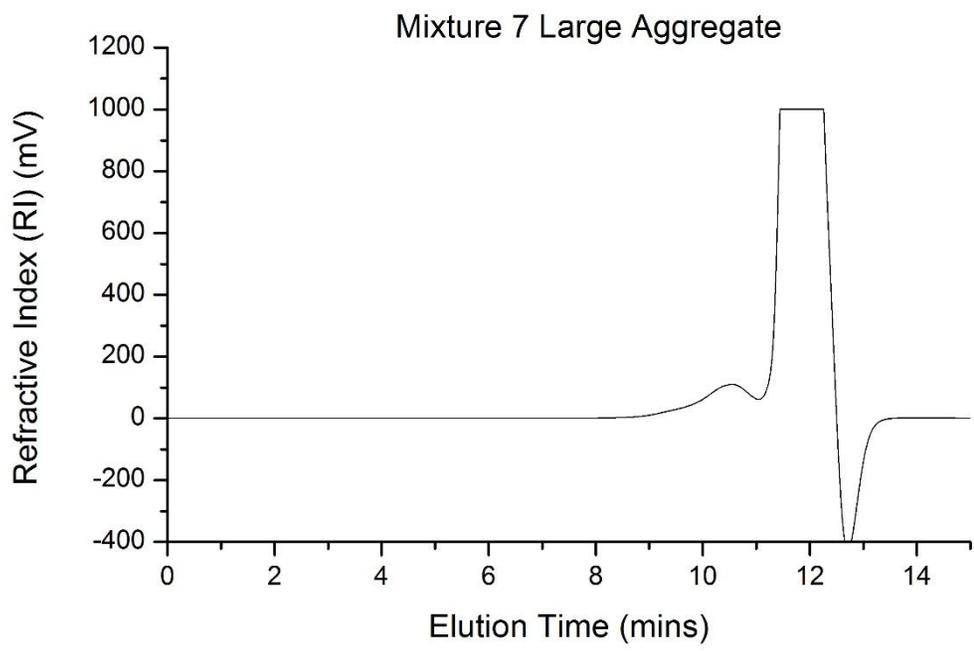
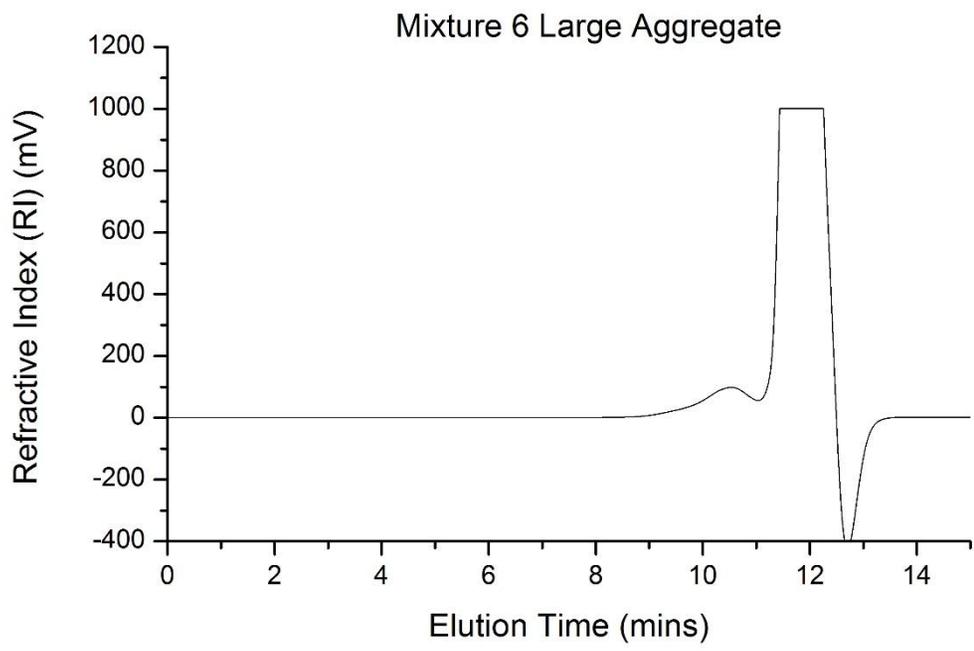




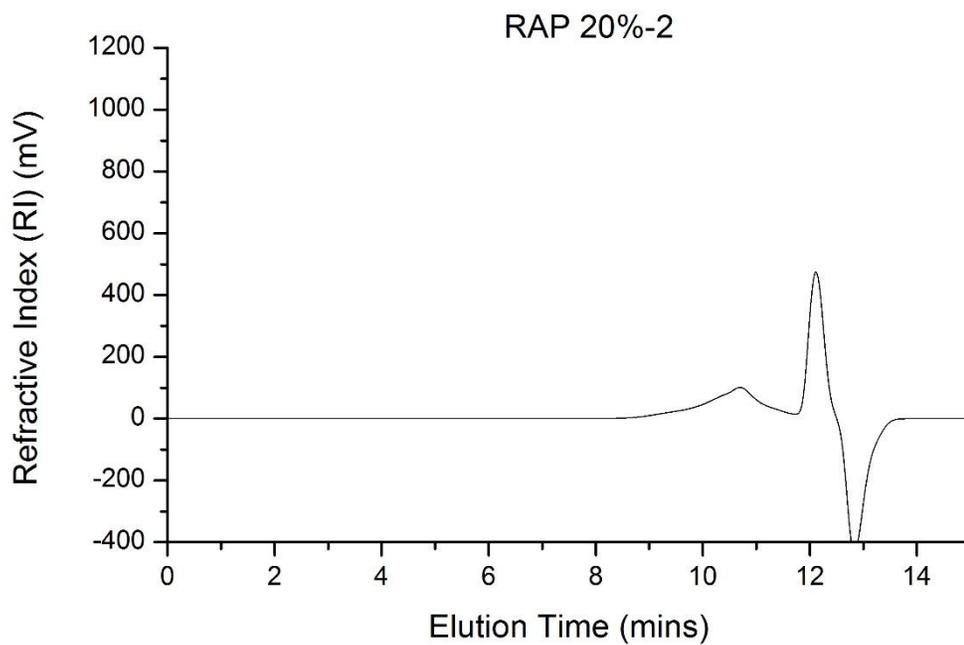
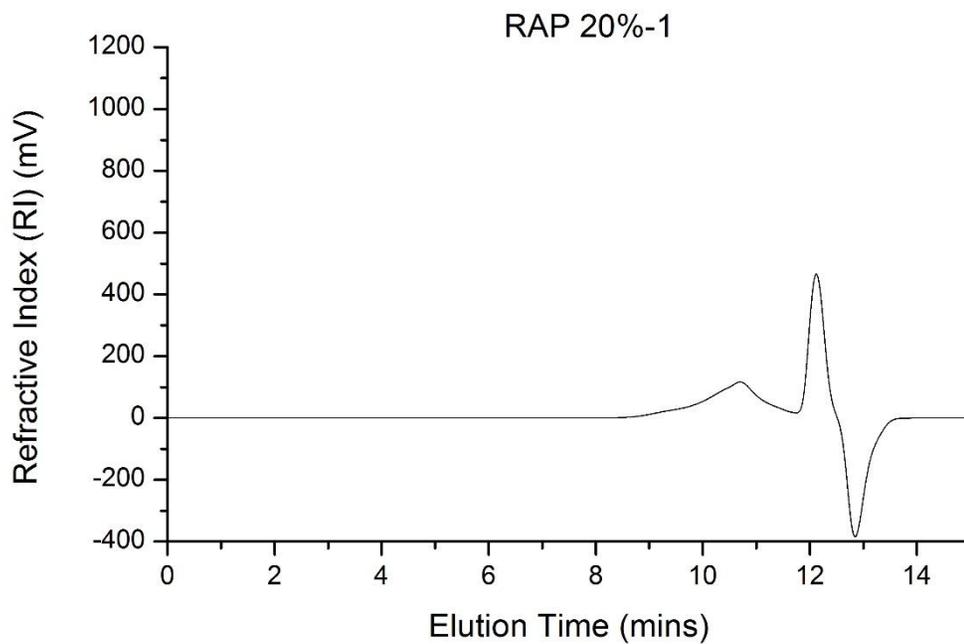


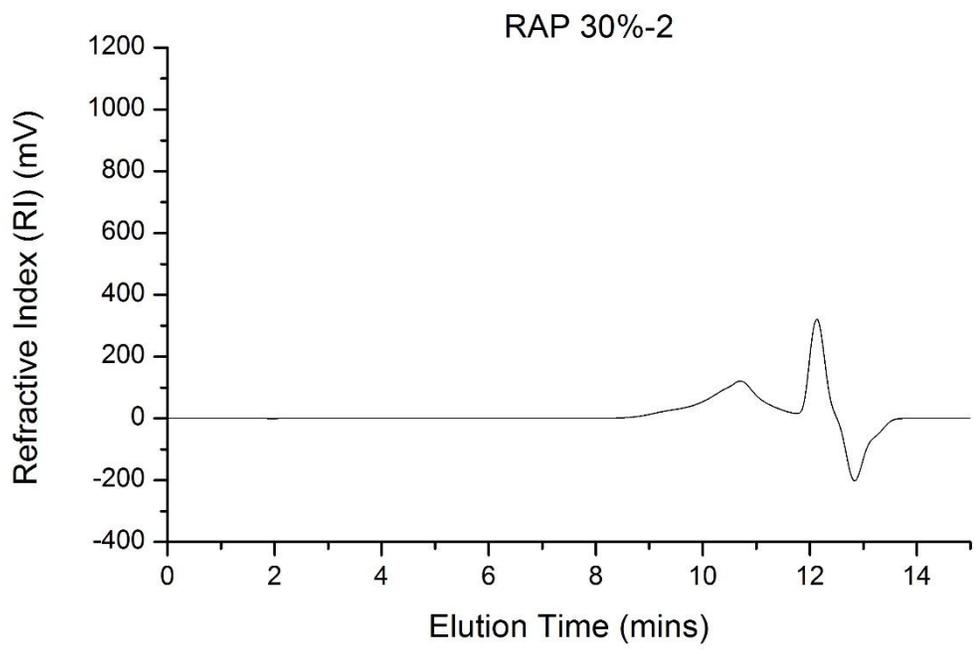
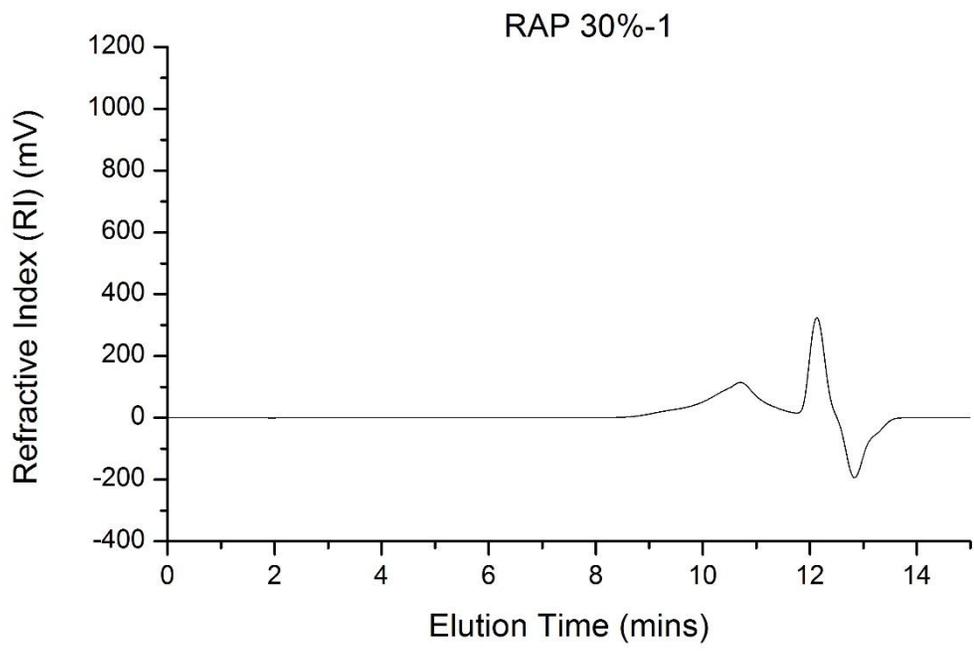


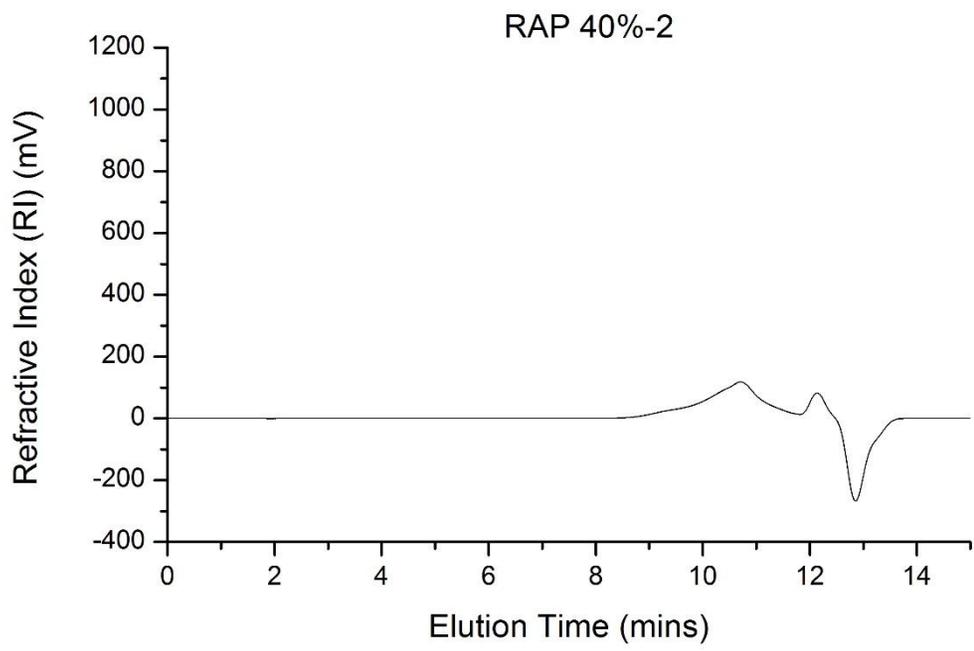
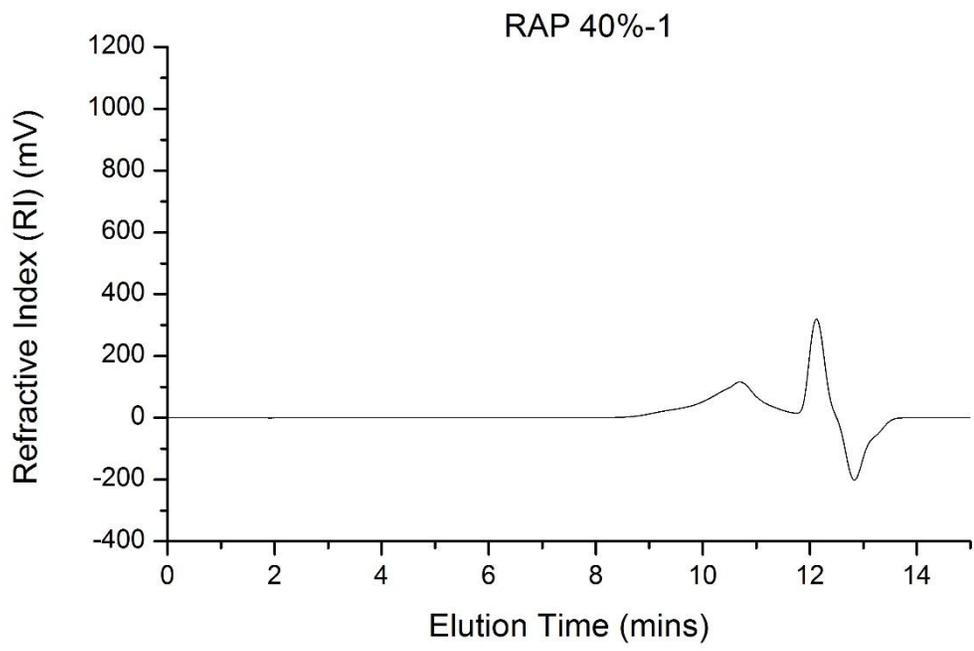


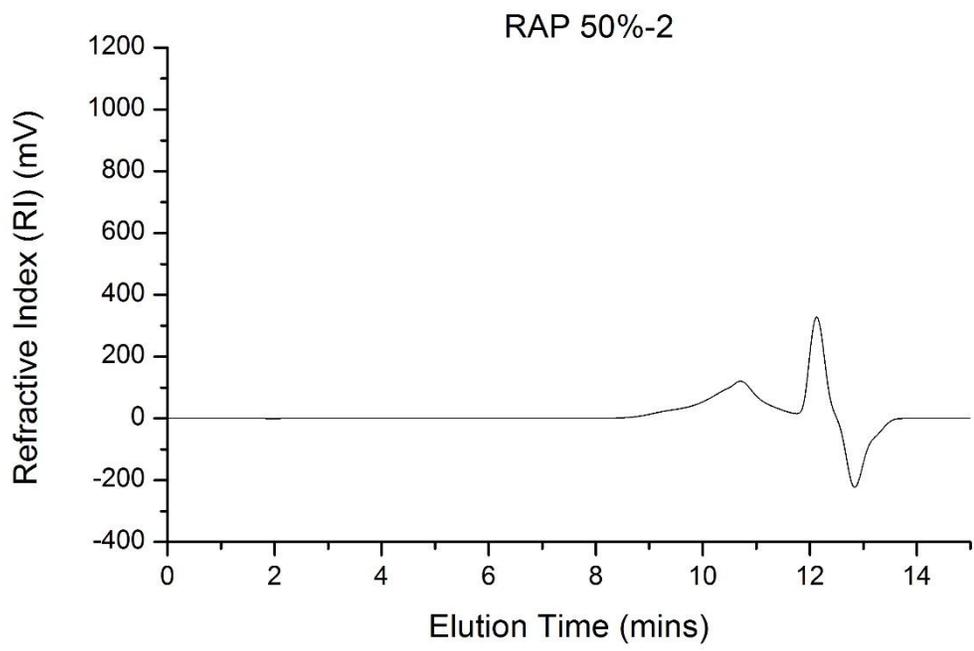
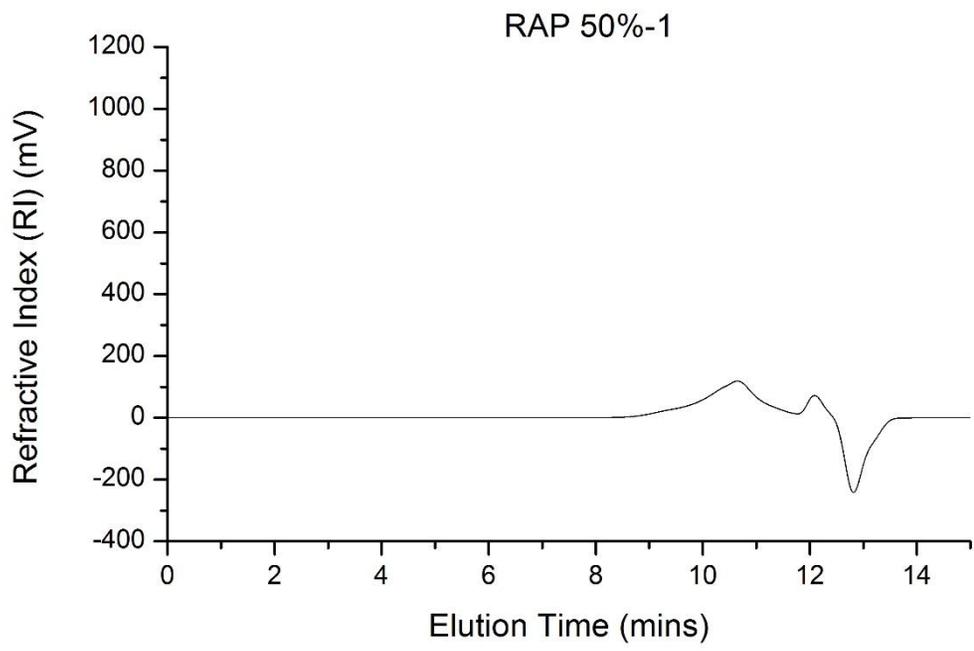


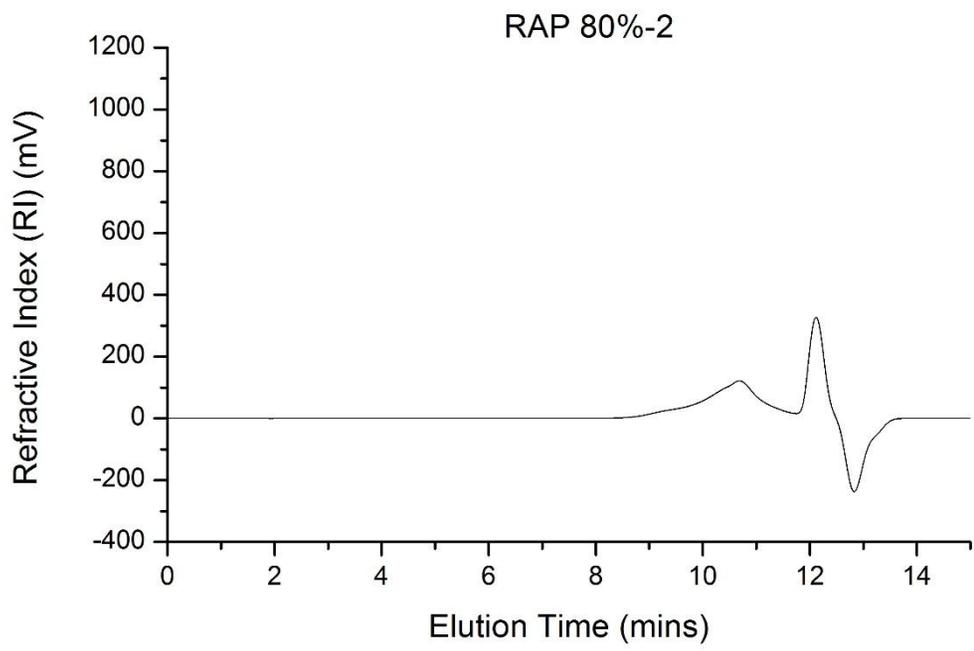
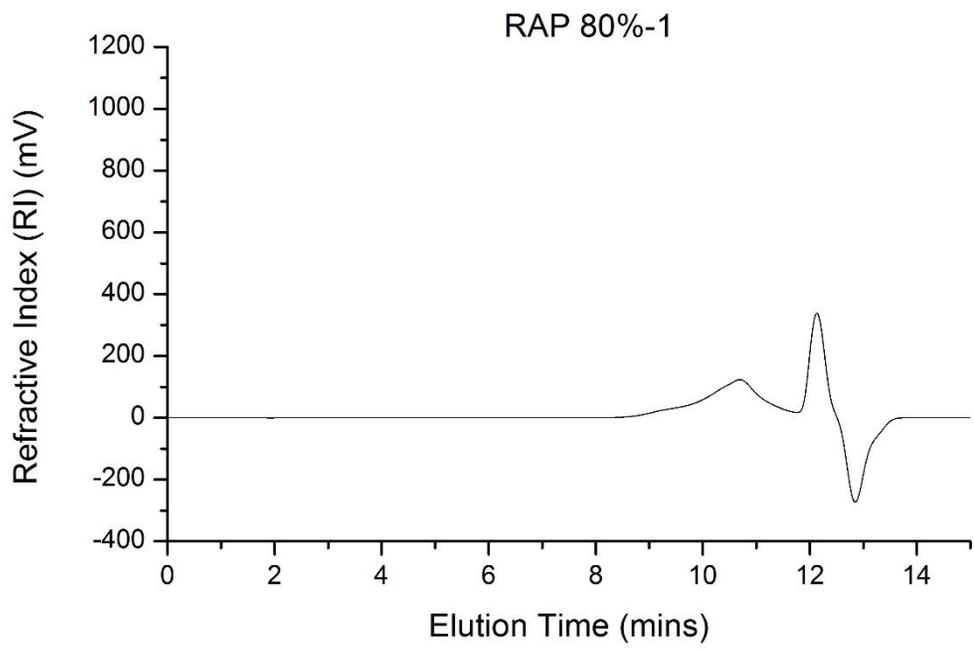
APPENDIX E: GPC Chromatograms of Test in Table 3-8

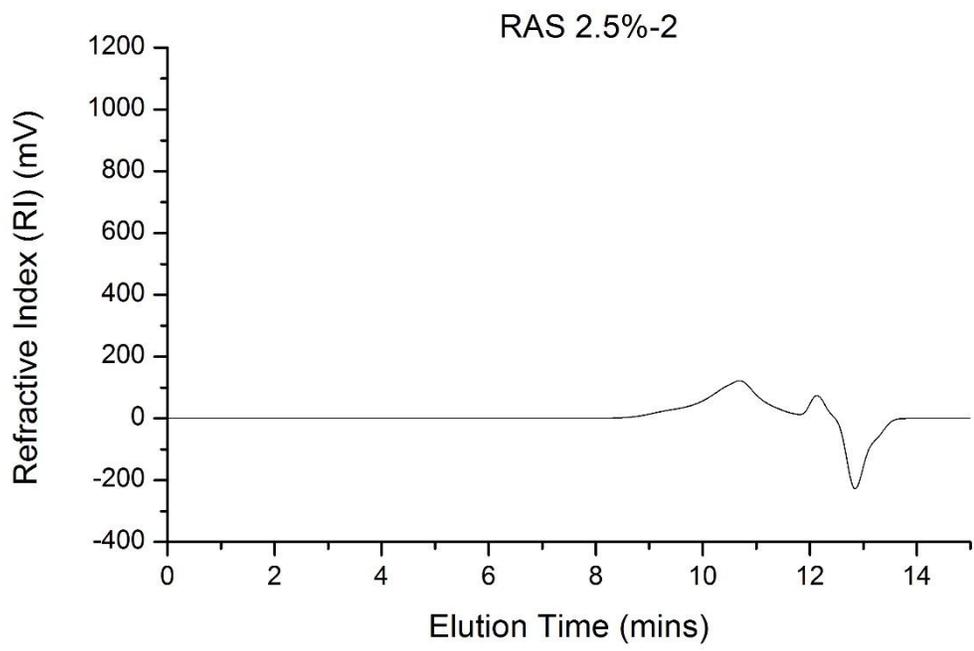
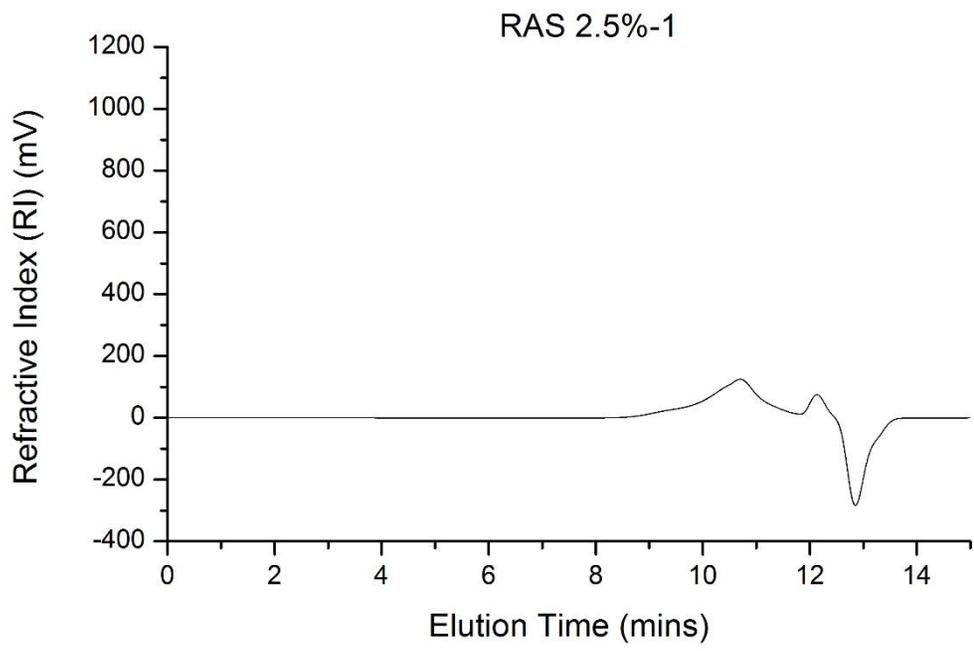


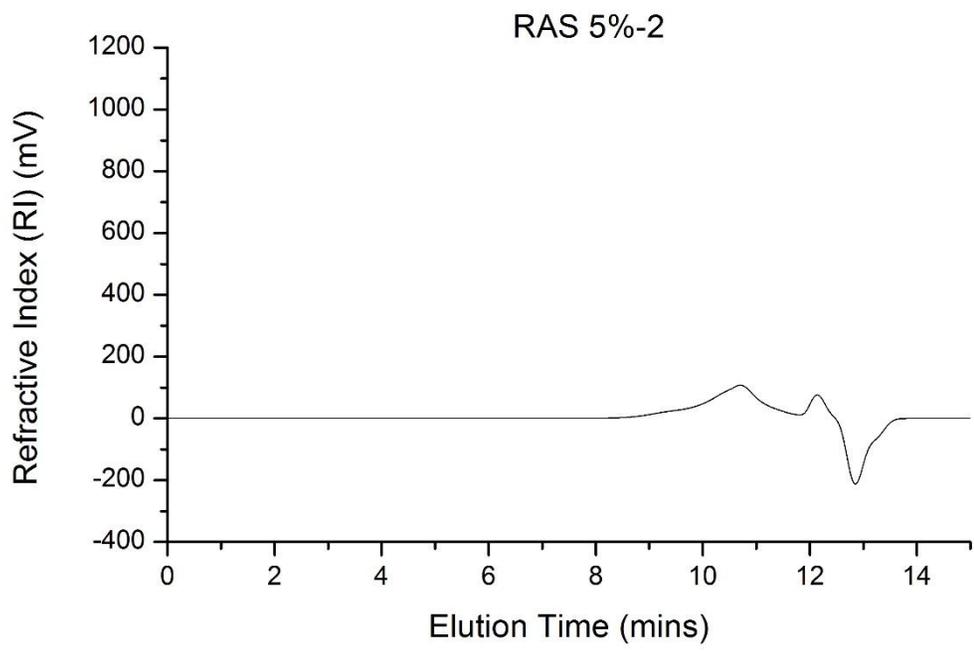
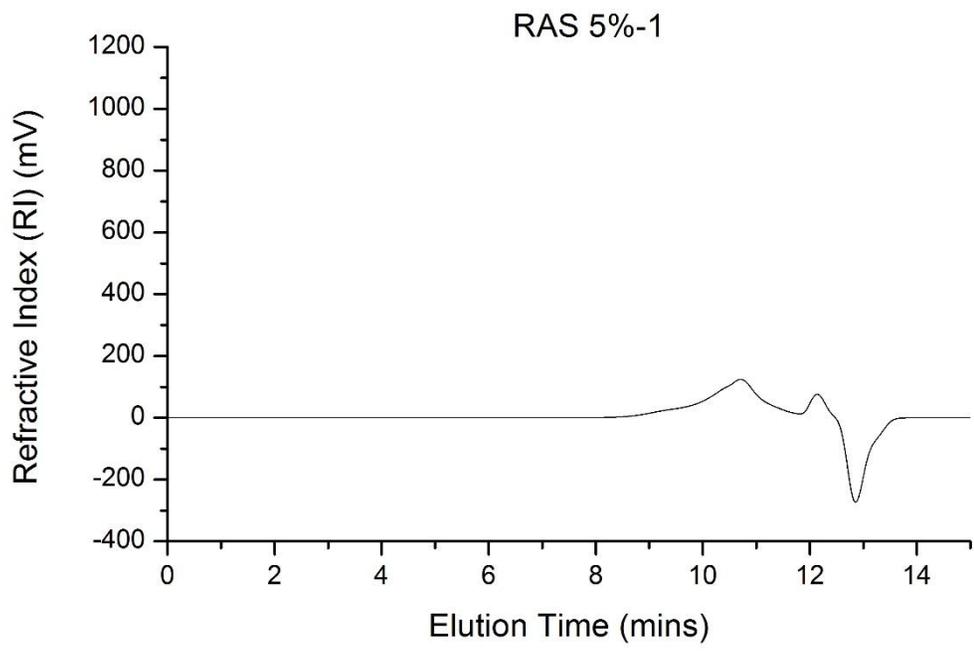


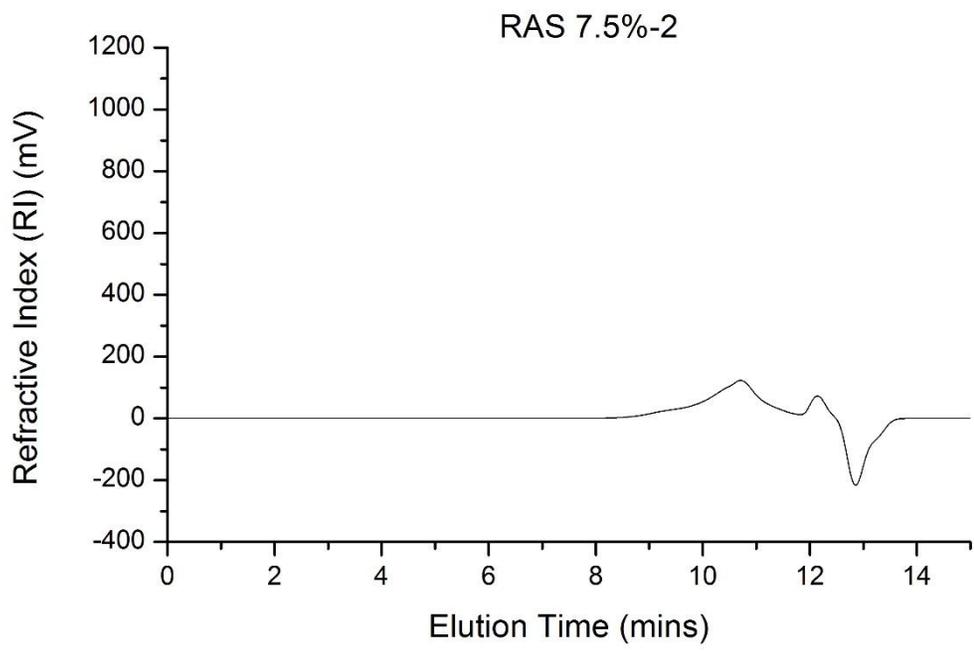
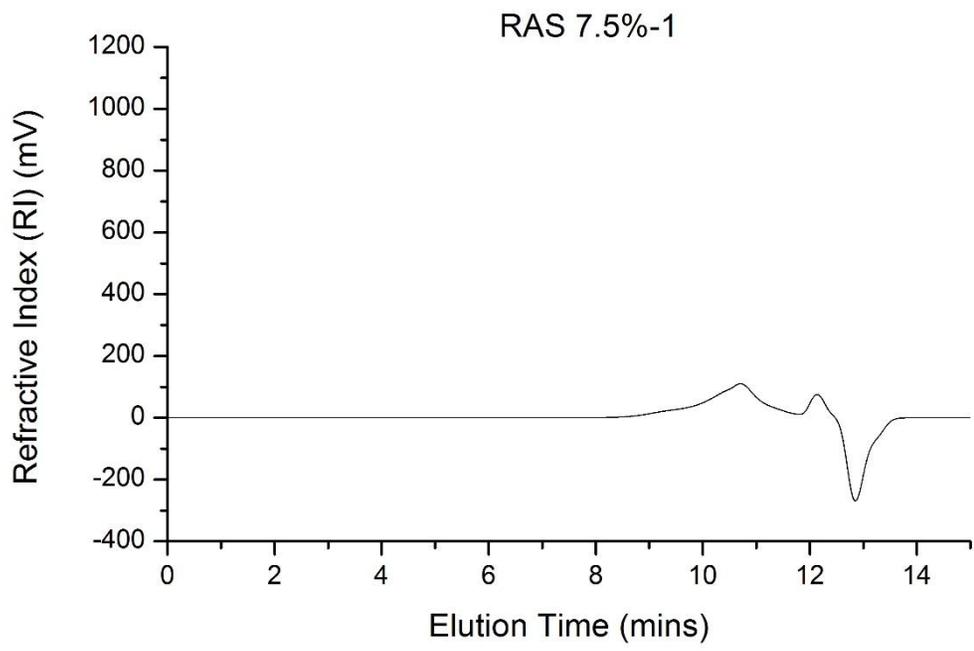


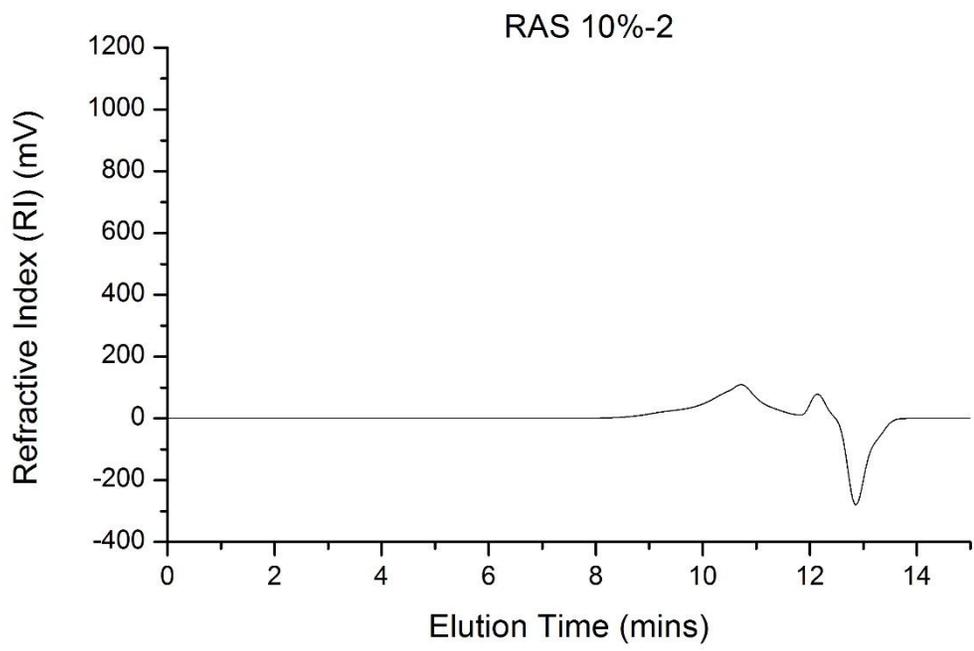
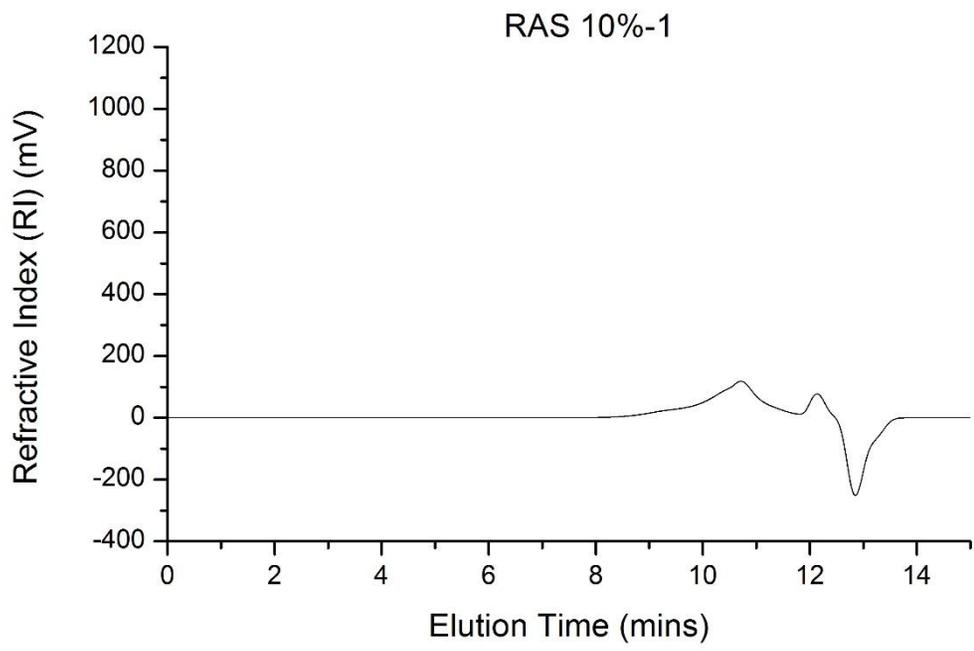




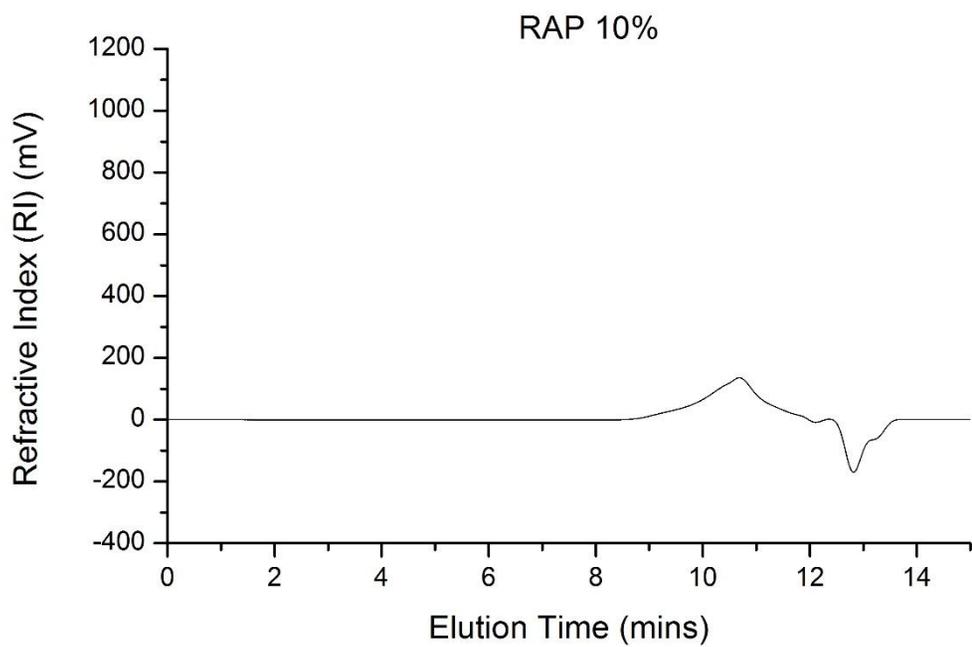
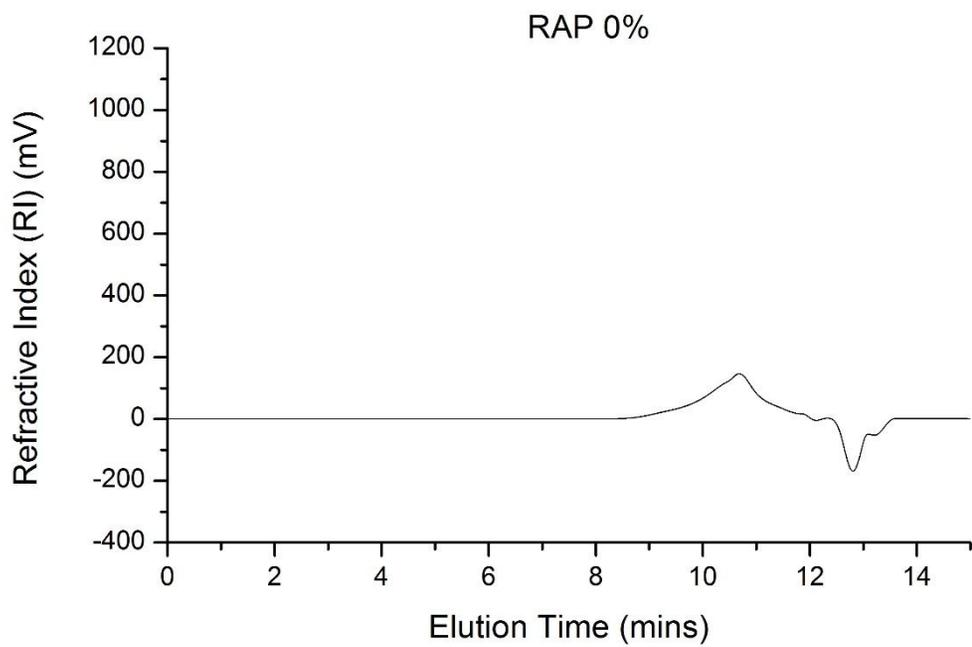


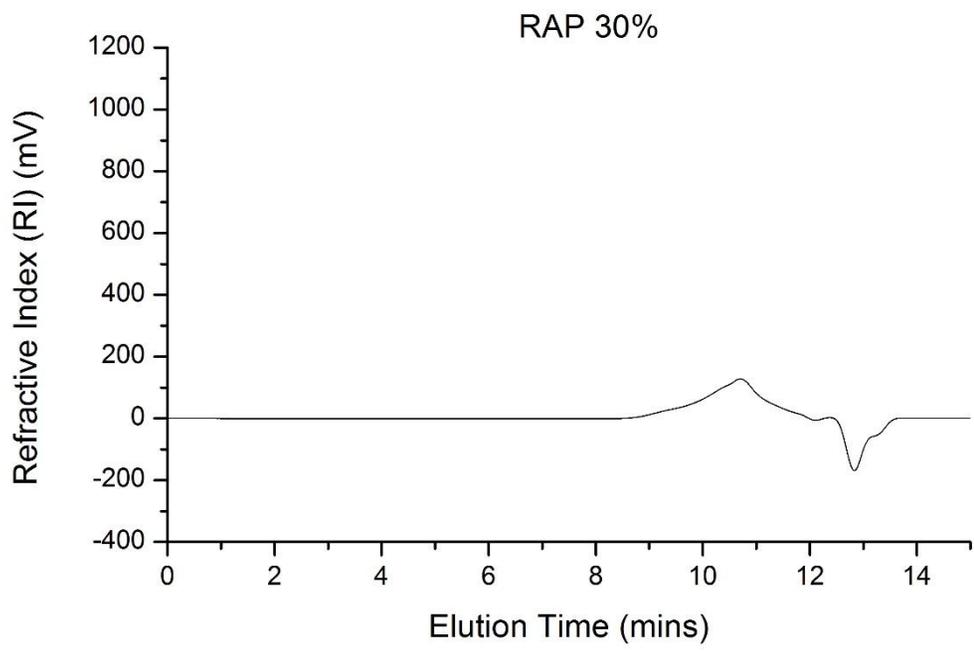
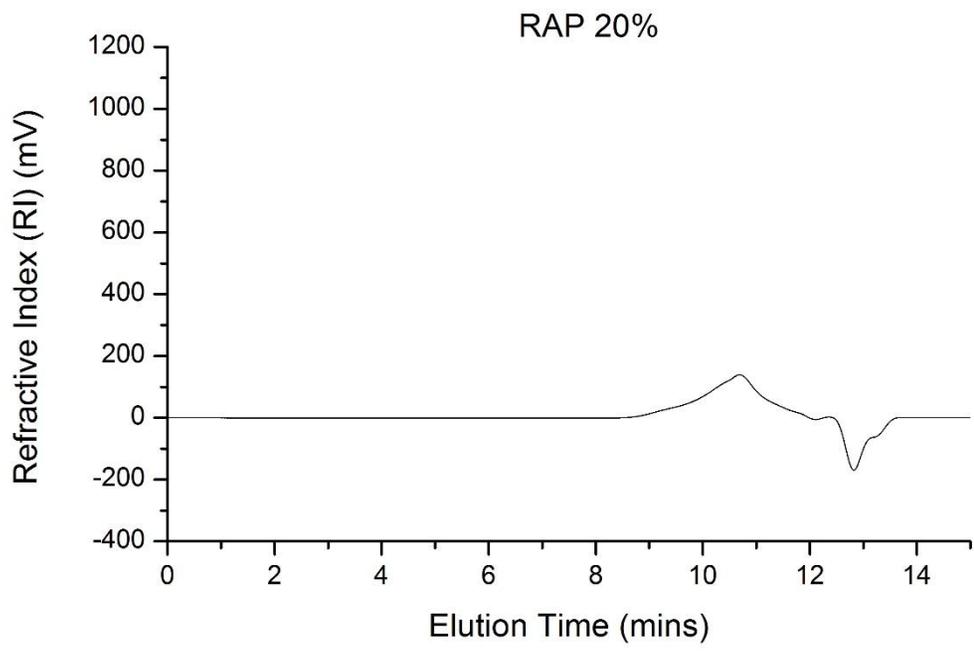


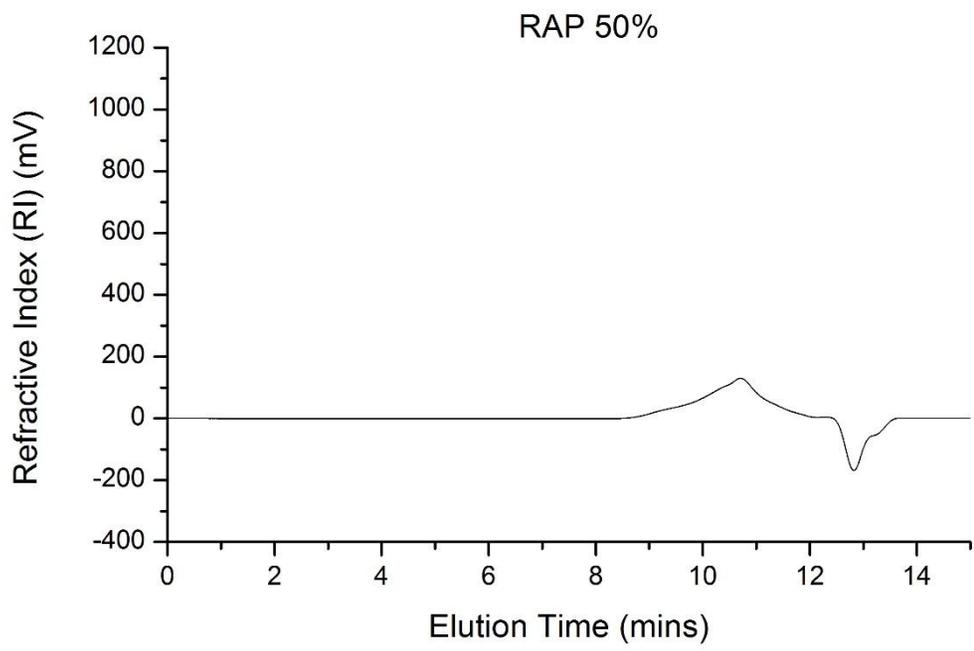
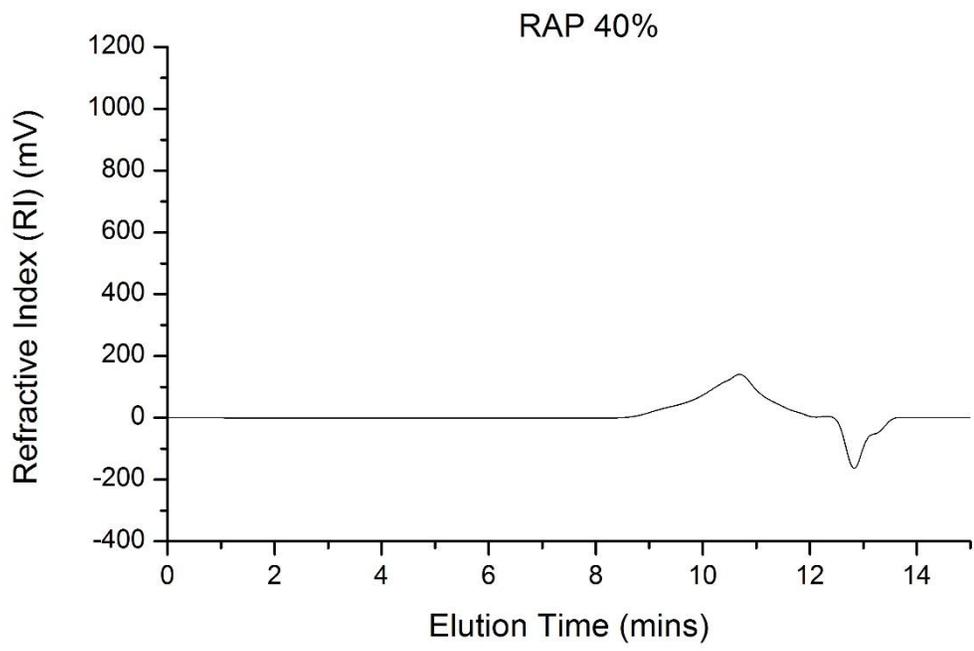


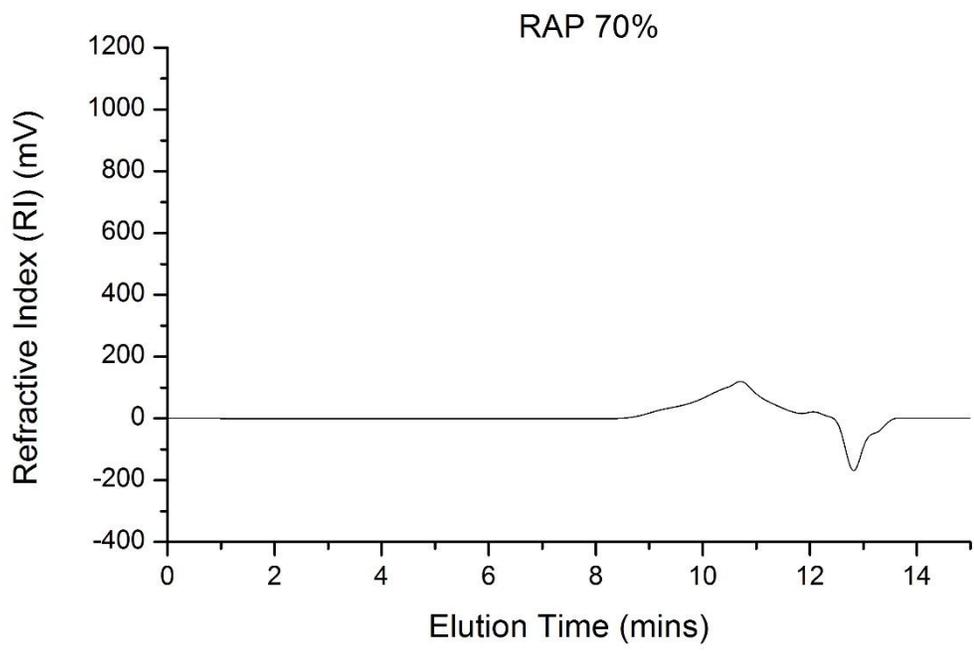
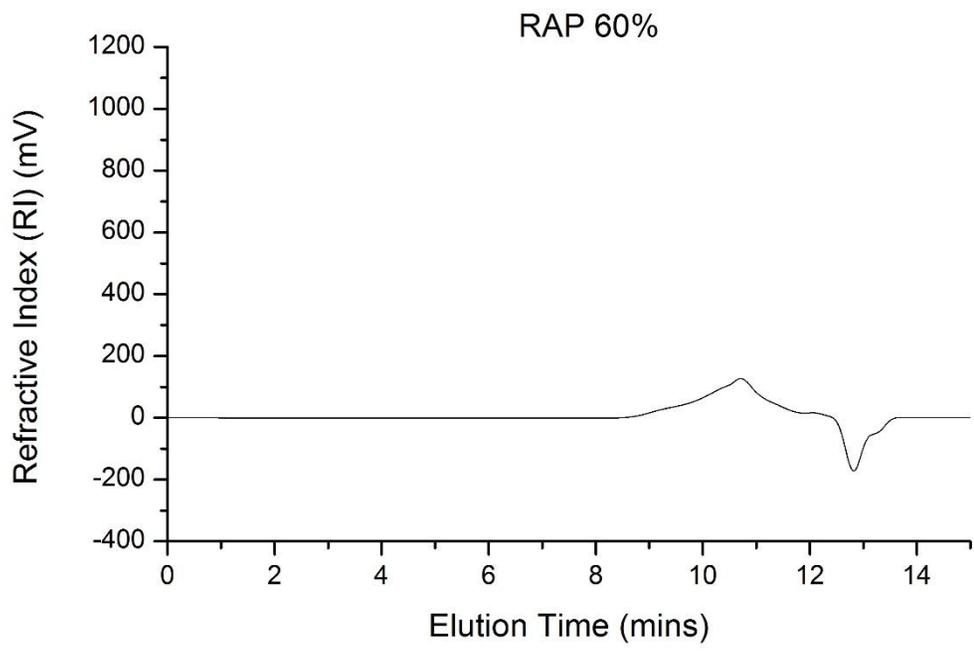


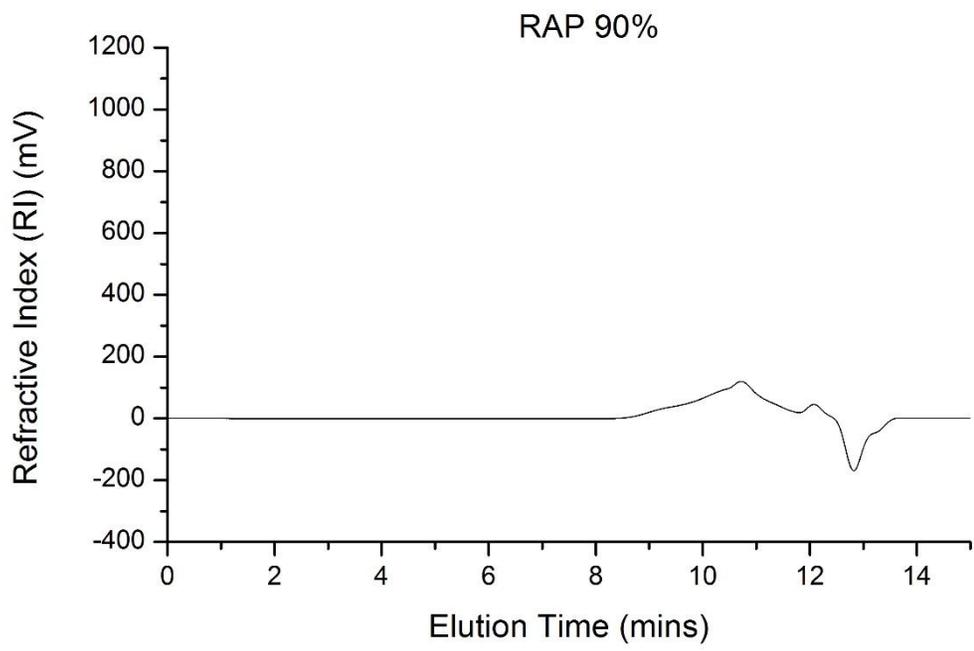
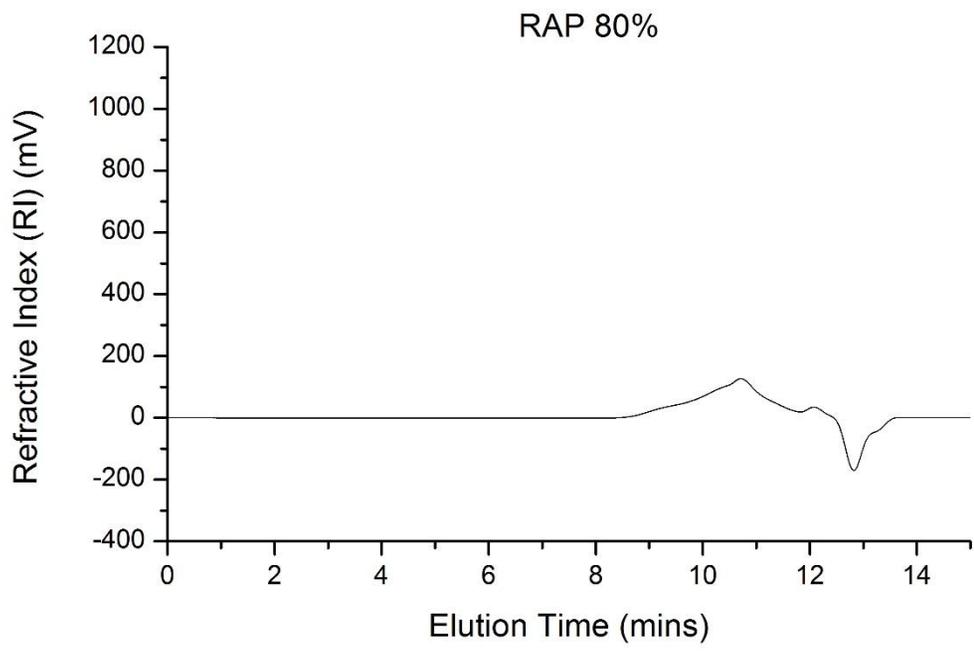
APPENDIX F: GPC Chromatograms of Test in Figure 4-1

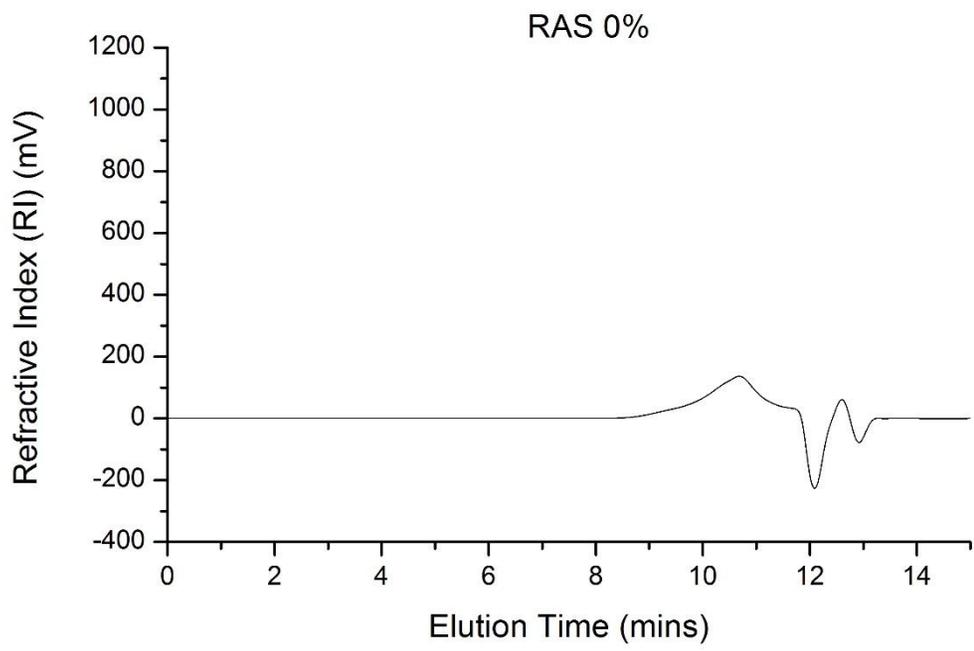
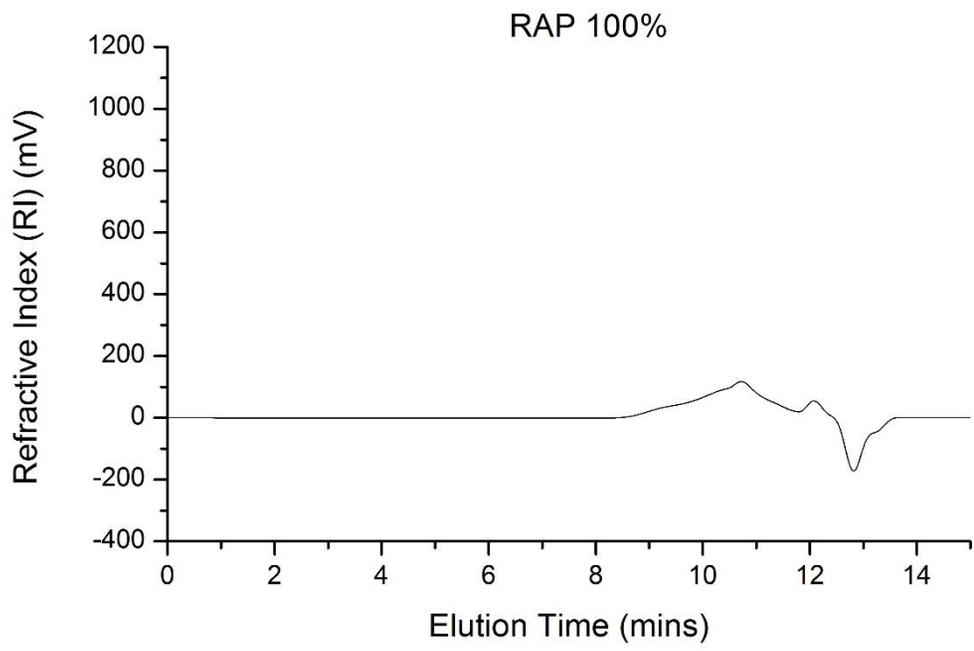


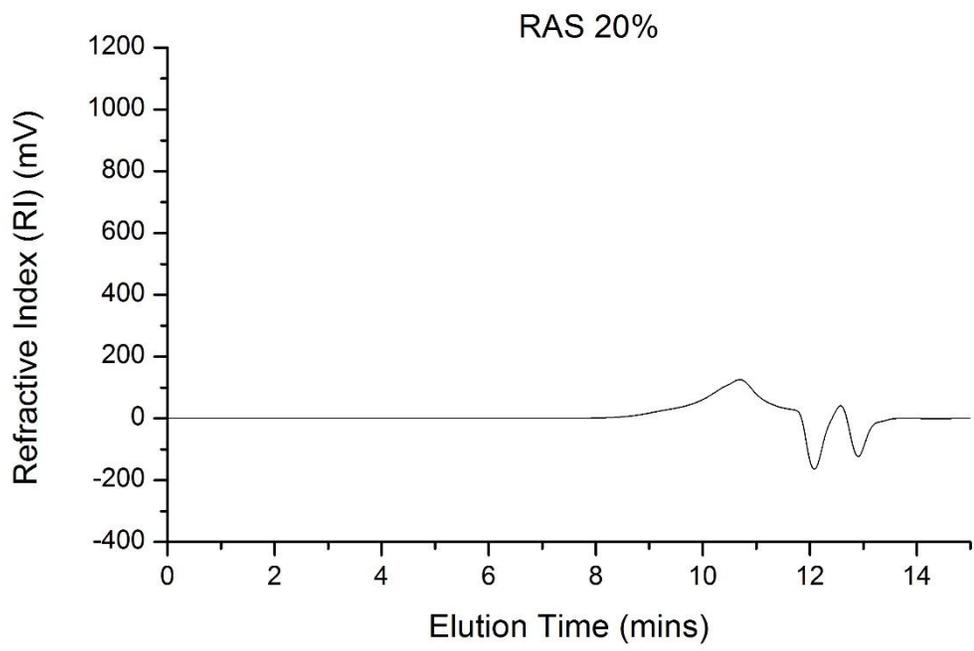
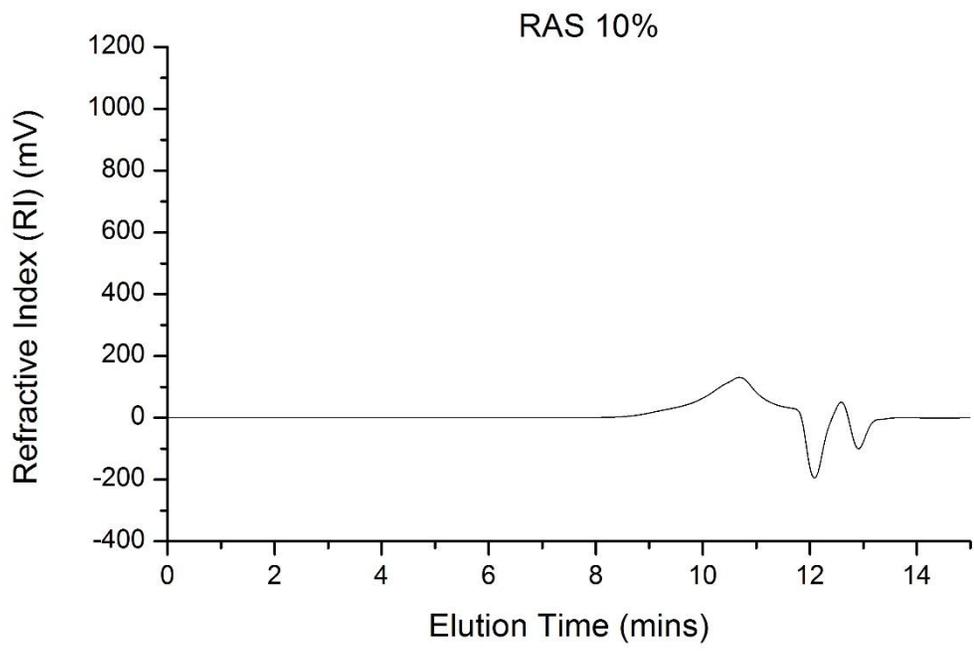


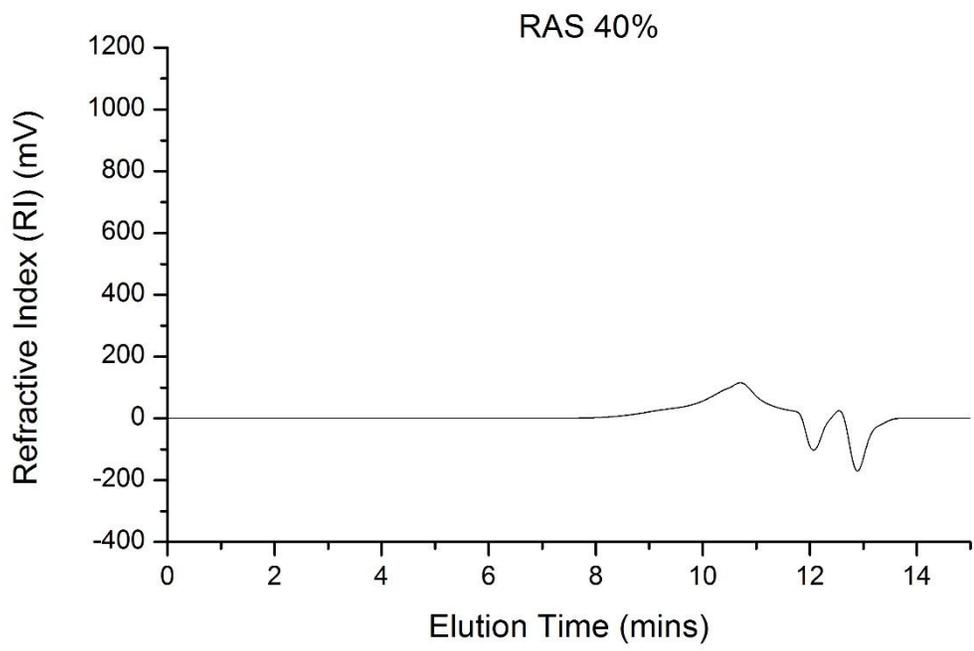
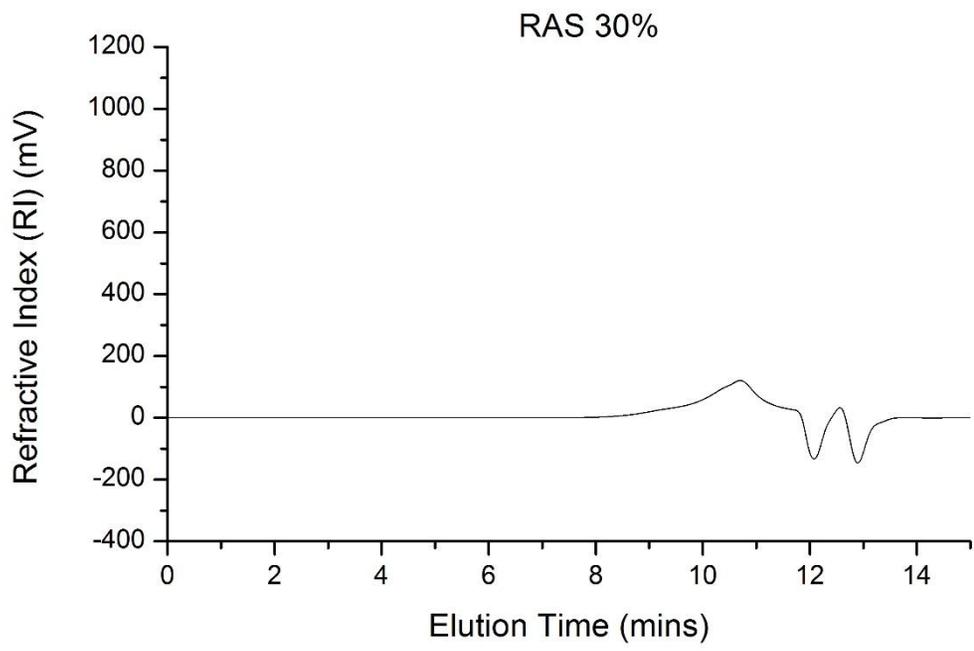


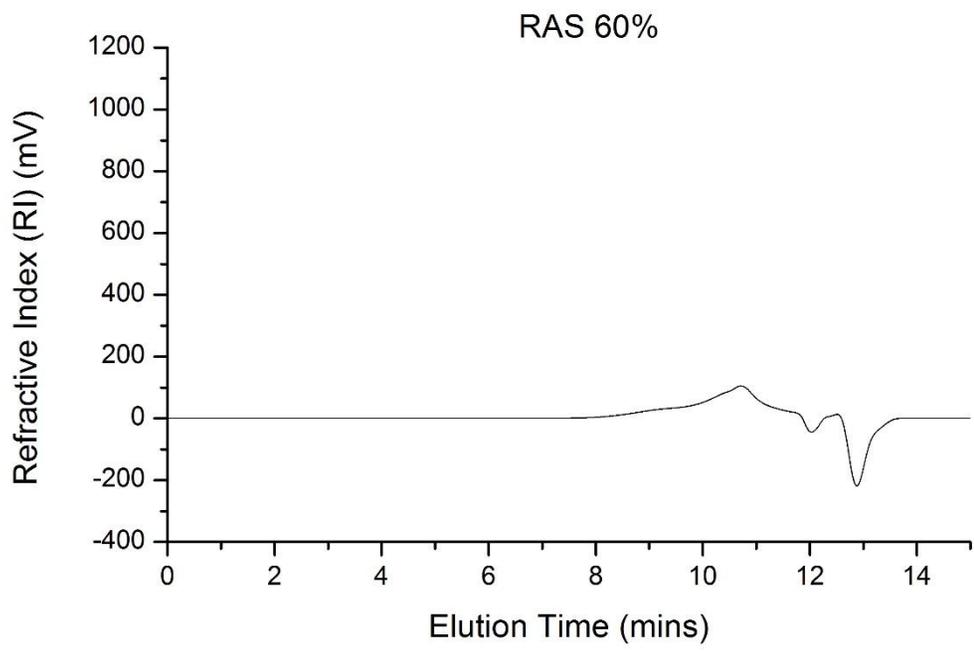
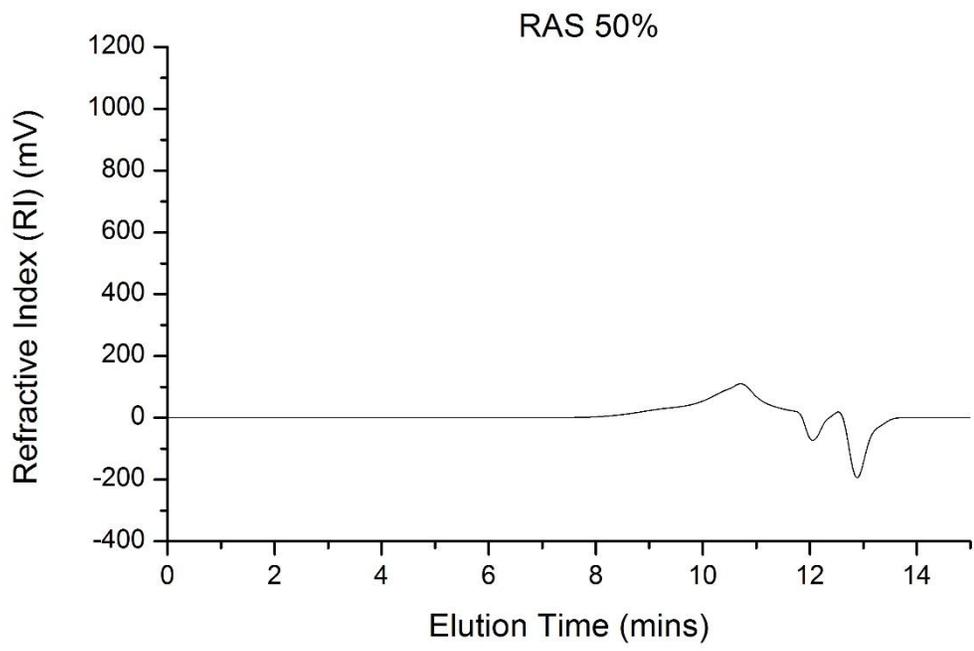


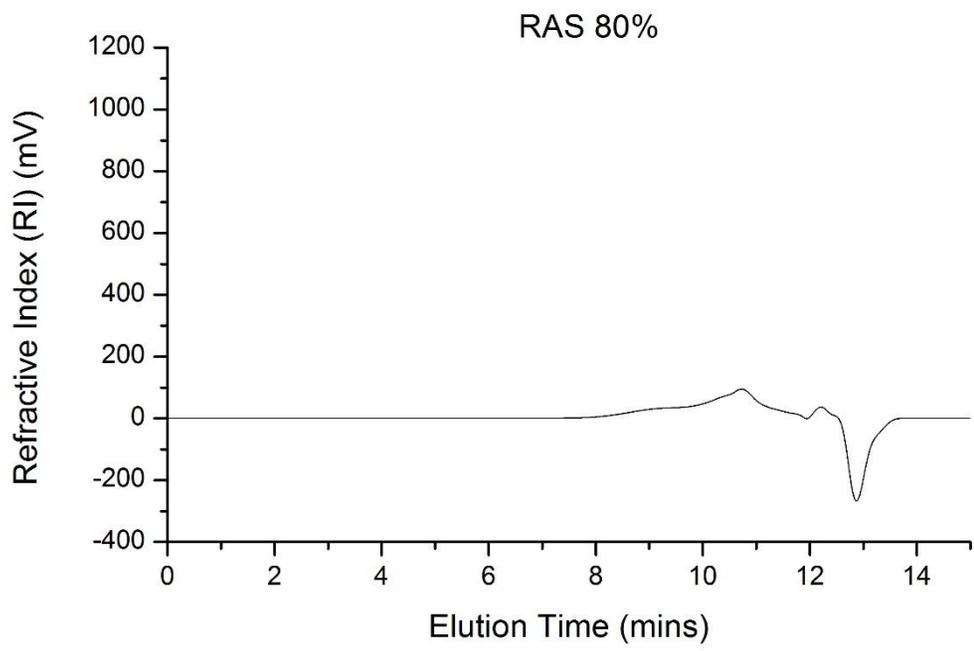
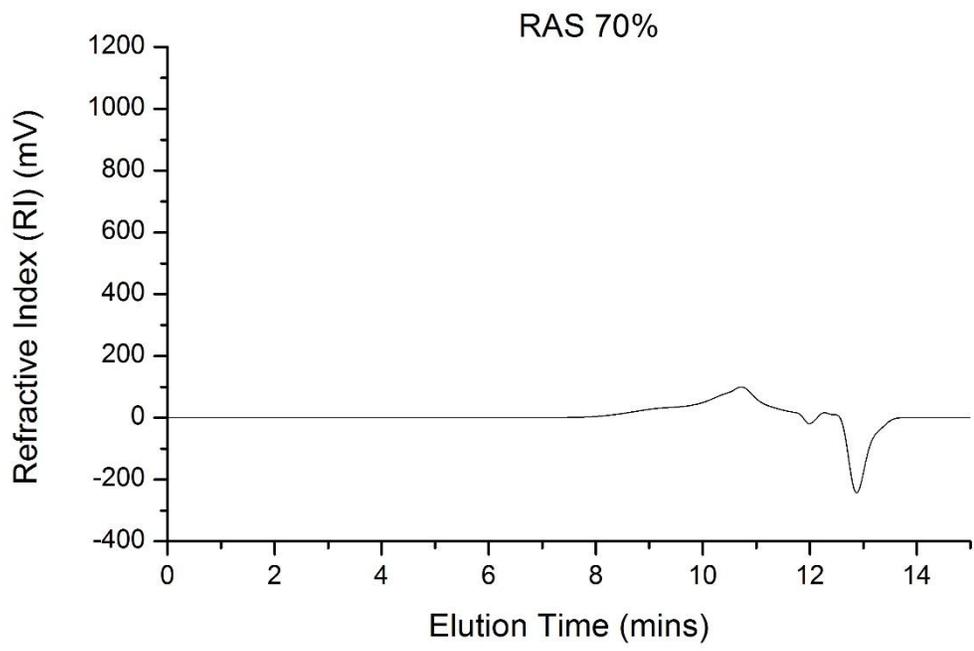


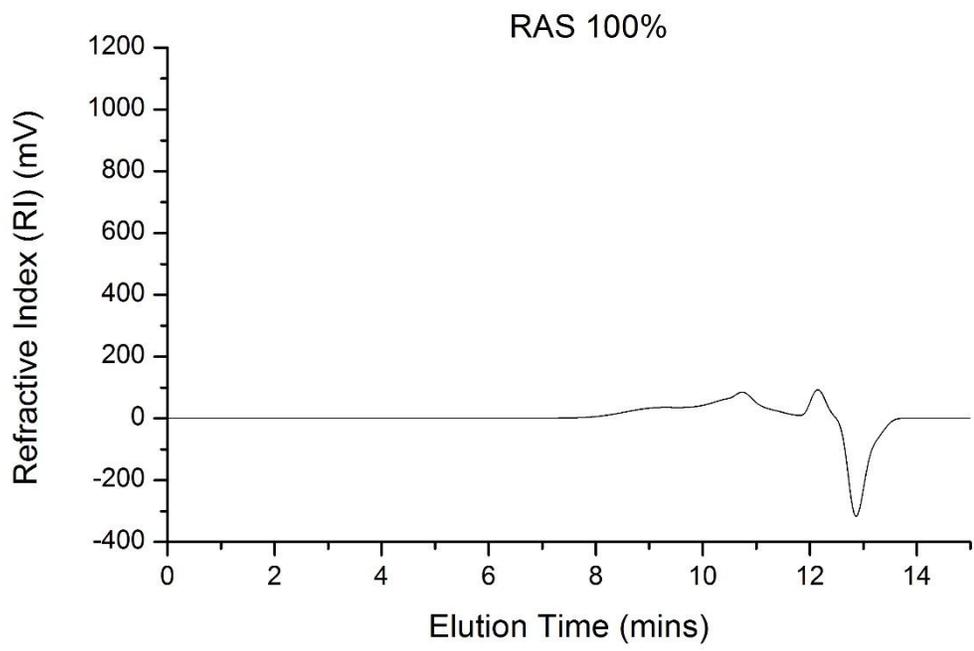
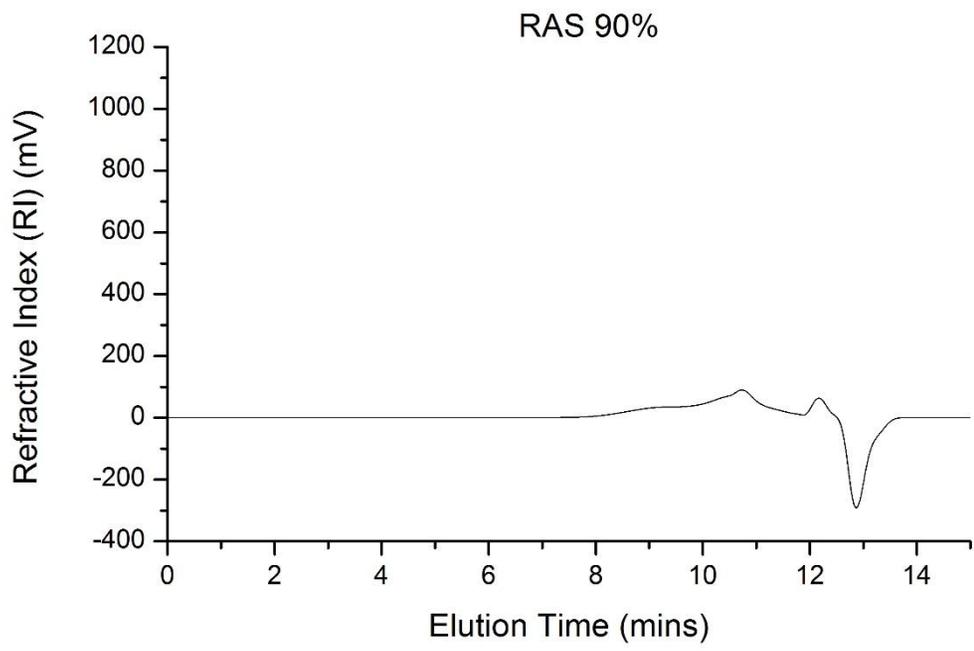












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