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## Micro-Encapsulation of Asphalt Rejuvenators using Melamine-Formaldehyde

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# MICRO-ENCAPSULATION OF ASPHALT REJUVENATOR USING MELAMINE-FORMALDEHYDE

A Thesis

Submitted to the Graduate Faculty of the  
Louisiana State University and  
Agricultural and Mechanical College  
in partial fulfillment of the  
requirements for the degree of  
Master of Science in Construction Management  
in  
The Department of Construction Management

by  
Max Abelardo Aguirre Deras  
B.S., Louisiana State University, 2013  
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## **ABSTRACT**

Self-healing microencapsulation in asphalt concrete is an emerging technology that would allow this particular material to resist cracking damage caused by vehicular and environmental loading. The objectives of this study were to evaluate the effect of an asphalt rejuvenator on asphalt binder in reversing the aging process and to develop a synthesis procedure for the production of microencapsulation of asphalt rejuvenators. Production parameters such as agitation rate, heating temperature and EMA concentration were varied to determine the effect on microcapsules properties such as size, shell thickness and morphology. Based on the results of the experimental program, it was concluded that the use of PennzSuppress D as a rejuvenator was effective in partially reversing the aging of asphalt binder by positively influencing both the high temperature and low temperature grades of the binder 70-22. In contrast, the use of PennzSuppress D as a rejuvenator did only influence the low temperature grade of the binder 76-22 and the high temperature grade of the RAP. A synthesis procedure was developed for the preparation of microencapsulation of PennzSuppress D and to characterize microcapsule properties such as diameter, shell thickness and morphology of the prepared microcapsules.

## **CHAPTER 1–INTRODUCTION**

Asphalt pavements are the most common road types in the United States given their cost efficiency, noise reduction, improved safety and comfort, ease of maintenance, and recyclability. The durability of asphalt roads is affected by traffic loadings and natural elements such as rain, sunlight, and chemicals that may influence pavement performance. The exposure of asphalt to those natural elements produces cracking, which is the main issue affecting serviceability and quality (Wu Z. , Mohammad, Wang, & Mull, 2005). Cracking occurs when the binder ages and the capacity of relaxation is reduced (Yildirim, 2007). Different kinds of cracking can be presented into the asphalt such as fatigue or alligator cracking, longitudinal cracking, transverse cracking, block cracking, slippage cracking, reflective cracking, and edge cracking (U.S. Department of Transportation, 2003). Maintenance is the key to enhance pavement performance. According to the World Bank's Pavement Deterioration Model, the maintenance of a deteriorated asphalt pavement can be up to four times the cost of maintaining a pavement in good conditions (Sahin, 2005).

Asphalt rejuvenators have shown to be the only product that can partially restore the properties of the pavement while in-service (Karlsson & Isacsson, Material-related aspects of asphalt recycling—state of the art, 2006). Asphalt rejuvenators are engineered cationic emulsions containing maltenes (Brownridge). The purpose of an asphalt rejuvenator is to penetrate into the asphalt concrete and soften or rejuvenate the asphalt binder; it also helps to seal the pavement and minimize future oxidation (Brown, 1988). The effectiveness on restoring the properties of asphalt is related to the amount of penetration into the asphalt (Chiu & Lee, 2006). Previous

studies have shown that asphalt rejuvenators did not penetrate more than 2 cm, which is not sufficient to benefit from the product (Chiu & Lee, 2006). Therefore, innovative methods to incorporate the use of rejuvenators such as encapsulation methods have been studied (Garcia, Schlangen, van de Ven , & Sierra-Beltrán , 2010).

Self-healing solutions have been successful in applications in polymeric materials; hence, the interest in using self-healing microcapsules with rejuvenators in asphalt pavement have increased (Zhang & Rong, 2012). The idea to develop self-healing microcapsules containing rejuvenator is that micro-cracks produced into the asphalt break the microcapsules producing the release of the rejuvenators, which will seals the micro-cracks and rejuvenate the surrounding binder.

The performance of self-healing microcapsules in asphalt applications is influenced by the physical properties of the microcapsules such as size distribution, encapsulation ratios, and non-biodegradable characteristics (Zhang, Xing, Shi, & Du, 2011). Selection of materials, encapsulation method, and optimum amount of healing agent are also important aspects to investigate to enhance self-healing mechanisms in asphalt applications.

## **1.1 Problem Statement**

Through the years, asphalt binder's property degrades due environmental factors such as rain, sunlight, and chemicals. Asphalt rejuvenators help reconstitute the chemical composition of aged binder and recover the properties of aged binder (Shen, Amirkhanian, & Miller , 2007). Asphalt rejuvenators must be able to penetrate deep into the asphalt in order to have the desired effect; however, studies have shown that it does not penetrate more than 2 cm (Chiu & Lee, 2006). Self-healing microcapsules have emerged as an innovative idea to apply asphalt rejuvenators and to allow for greater penetration. However, the evaluation and application of this method has not been considered to date.

## 1.2 Objectives

To address the aforementioned problem statement, the objectives of this study are as follows:

- a) Evaluate the effects of asphalt rejuvenator on asphalt binder in order to test its effectiveness to restore the rheological properties of asphaltic materials;
- b) Develop a synthesis procedure for production of microencapsulation of asphalt rejuvenator;
- c) Identify the optimum production parameters that control microcapsule size and morphology; and
- d) Characterize microcapsule properties such as diameter and morphology and their change with production parameters.

## 1.3 Scope

This study will aim to evaluate the effect of PennzSuppress D, a commercial resin, to modify the binder rheological properties. Furthermore, this study will identify the factors that control the success of the encapsulation method such as microcapsules size and microcapsule shell thickness. Properties such as size, thermal stability, and mechanical strength of self-healing microcapsules for asphalt applications will influence the efficiency of the self-healing mechanism to restore the binding property of asphalt (Su, Schlangen, & Qiu, 2012). The synthesis method used to produce microcapsules containing rejuvenator was the in-situ polymerization as it has been described as the most cost-effective method (Samadzadeh, Hatami, Peikari, & Ashrafi).

The single-walled microencapsulation procedure for this study was adapted from Su and Schlangen that is an in-situ polymerization with a two-steps coacervation (Su & Schlangen, 2012). The optimization of the parameters in the new encapsulation method for a new core material is the key to obtain microcapsules with optimum size and strength. Variation of

parameters on the synthesis of the microcapsules such as speed, time, and heat temperature will determine the optimum parameters to encapsulate a new core material.

## **1.4 Research Approach**

Proposed research activities will be organized into two phases and six tasks as detailed in the following section.

### **Phase 1: Laboratory Testing of Asphalt Rejuvenator**

#### **Task 1: Asphalt Binder Blends Preparation**

In Task 1, asphalt binder blends will be prepared by mixing asphalt binder with the rejuvenator at a dosage rate of 30% by weight of the binder: a) PG 70-22 b) PG 76-22. Both binder blends will be prepared at a mixing temperature of 163°C.

#### **Task 2: Short-Term and Long-Term Aging Simulation**

Short-term aging will be simulated using the Rolling-Thin Film Oven (RTFO). On the other hand, long-term aging will be simulated using the Pressure Aging Vessel (PAV).

#### **Task 3: Characterization of Prepared Blends**

The characterization of the prepared blends will be accomplished by using rheological tests such as dynamic shear rheometer, rotational viscometer, and bending beam rheometer; and by comparing the Superpave Performance Grade (PG) of the modified blends to the unmodified binder. Blends will be characterized using the entire suite of PG grading system as per AASHTO M 320-09 (Standard Specification for Performance-Graded Asphalt Binder).

#### **Task 4: Evaluation of the Effect of Asphalt Rejuvenator**

The effect of the rejuvenator will be evaluated by blending them with aged binder

extracted from Recycled Asphalt Pavement (RAP), sampled from a local contractor.

Asphalt binder extraction will be performed in accordance AASHTO T 164, “Standard Method of Test for Quantitative Extraction of Asphalt Binder from Hot Mix Asphalt HMA – Method A.” Also, the recovered of asphalt binder will be conducted in accordance to AASHTO R 59, “Standard Practice for Recovery of Asphalt Binder from Solution by Abson Method.” Afterwards, the recovered asphalt binder will be blended with the rejuvenator at a 30% and 40% dosage.

## Phase 2: Microcapsule Synthesis and Characterization

### Task 5: Microcapsule Production

Microcapsules will be prepared at varying production parameters including heating temperature, agitation rate, and concentration of EMA used. The amounts of PennzSupppress D will be held constant at 8 grams during these experiments. The experimental test matrix developed for this study is presented in Table 1.1.

### Task 6: Microcapsule Characterization

Characterization of microcapsules will be conducted using Scanning Electron Microscopy (SEM) to analyze the effects of the production parameters on the size and morphology. Based on the results of this task, the ideal microcapsule production parameters will be determined for use in asphalt applications.

Table 1.1: Experimental test matrix for microcapsule production

Variables		
Agitation Rate (rpm)	Temperature (°C)	Concentration of EMA (%)
800	75	0.5
800	75	2
800	75	3
800	75	4
800	75	8
800	70	3
800	80	3
500	75	3
2000	75	3

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## **CHAPTER 2-LITERATURE REVIEW**

### **2.1 Introduction**

The United States has more than 2.6 million miles of paved roads and highways, of which 93 percent are surfaced with asphalt. Asphalt is a liquid or semi-solid substance derived from petroleum. The American Society of Testing Materials (ASTM) defines asphalt as a “dark brown to black cementitious material in which the predominant constituents are bitumens which occur in nature or are obtained in the petroleum processing” (Asphalt Institute, 1994).

Asphalt is most commonly used for paving roads. In addition, asphalt offers valuable properties to engineers such as good permeability and strong bonding with aggregates, making asphalt a very versatile material. Providing another useful property for engineers, asphalt presents different behaviors at certain temperatures. At high temperatures, the material may be used as a lubricant, yet on the other hand, the asphalt behaves on a viscoelastic state at low temperatures, enabling it to hold aggregates together. All these properties present the versatility of asphalt, thus allowing it to be used not only for paving roads, but also for recreational projects such as a) playgrounds, b) bicycle paths, c) running tracks, d) agriculture projects such as barn floors and greenhouse floors, and e) industrial sectors such as ports and landfill caps.

Asphalt is selected as the choice for roads, because asphalt is smooth, quiet, durable, safe, sustainable, and easy to construct. The smoothness of the asphalt improves a vehicle’s fuel economy, allowing less of an impact on a vehicle’s maintenance due to lower wear and tear on the vehicle. Durability on asphalt roads does not represent a concern if such roads are designed and constructed adequately. In addition, the maintenance of asphalt roads is fast and economic.

Another benefit of asphalt is that it is environmentally friendly, since it can be recycled and reusable. Lastly, asphalt requires no long curing time, which makes for a rapid construction.

Maintenance is the key toward enhancing the performance of asphalt, which serves to extend the life of asphalt pavement as well as to improve the quality of the ride. According to World Bank's Pavement Deterioration Model, if an asphalt pavement road is left to deteriorate, the cost of bringing back that road may be four times more expensive than the cost of maintenance to keep it in good condition (Sahin, 2005). Further, a Utah Department of Transportation (UDOT) study demonstrated that it cost less to maintain roads that were in good condition than those in poor condition (Zavitski). Another study conducted by the National Cooperative Highway Research Program revealed that every dollar spent on maintenance at the corrected time saves \$3 - \$4 in future costs (Geoffroy, 1996). Finally, Figure 2.1 presents the results from a study conducted by Galehouse, Moulthrop and Hicks, where the results show that the future rehabilitation cost savings were \$6 - \$10 for every \$1 spent on preventive maintenance (Galehouse, Moulthrop, & Hicks, 2003).

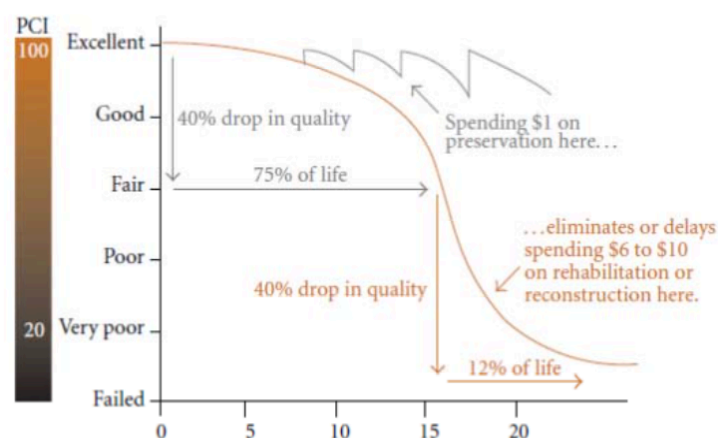


Figure 2.1. Effect of Preventive Maintenance at Life Cycle Cost of the Pavement (Galehouse, Moulthrop, & Hicks, 2003)

## 2.2 Asphalt Binder

Asphalt mixture is a mix between aggregates and binders. Asphalt binders can be divided into two different parts: asphaltenes and maltenes. Asphaltenes may be defined as the fraction of the asphalt that is insoluble in n-heptane and soluble in toluene (Mitchell & Speight, 1973).

Asphaltenes are the most refractory compounds present in crude oil and are generally distinguished by a fused aromatic core with polar heteroatom functionality (Yen, Erdman, & Pollack, 1961). The main function of asphaltenes is to serve as a binding agent. Maltenes constitutes the fraction of asphalt, which is soluble in n-alkane solvents such as pentane and heptane. Maltenes may be divided in four different bodies: polar compounds, first acidifins, second acidifins and saturated hydrocarbons. The polar compounds or nitrogen bases are highly reactive resins, which act as a peptizer for asphaltenes (Boyer, 2000). The first acidifins are components of resinous hydrocarbons, which function as a solvent for the peptized asphaltenes (Boyer, 2000). The second acidifins are unsaturated hydrocarbons that are used as the first acidifins (Boyer, 2000). Lastly, the saturated hydrocarbons or paraffins are used as a jelling agent (Boyer, 2000).

Oxidation is the principal cause of deterioration on asphalt pavement. It usually occurs on the binder part, where it suffers from premature hardening. A test conducted by Rostler and White (Rostler & White, 1970) revealed that the asphaltenes and the paraffins are the most stable components during the oxidation process, while the first acidifins, second acidifins, and nitrogen bases are the components most affected during the deterioration of asphalt. During the oxidation process, the aromatics component reacts with the oxygen to produce asphaltenes, which produces an increase in the asphaltenes material on the binder (Peterson, Davison, Glover,

& Bullin, 1994). As the saturates and asphaltenes are not soluble in one another, the insolubility between them leads to an incompatibility that results in a decrease of the ratio between maltenes to asphaltenes, which produces the drying and brittleness on asphalt pavement.

The aging of asphalt binder occurs in two stages: short-term and long-term. Short-term aging occurs when the oily components are absorbed or vaporized in the maltenes during mixing and construction (Tran, Taylor, & Willis, 2012). Long-term aging happens in the field and is due to changes in composition through the reaction between asphalt constituents and atmospheric oxygen, causing a chemical reaction between molecular components and formation of a structure within the asphalt binder (Roberts, Kandhal, Brown, Lee, & Kennedy, 1996). Figure 2.2 shows the changes in the chemical composition with aging of asphalt pavement.

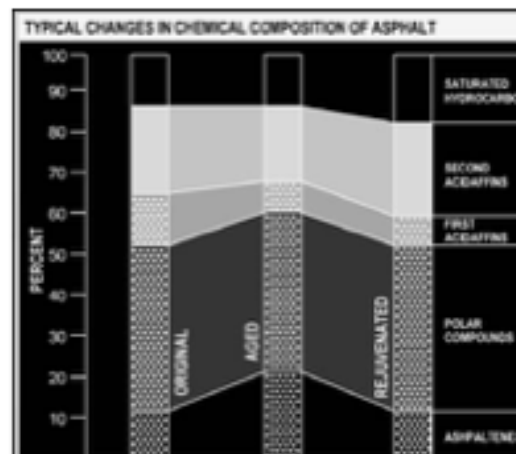


Figure 2.2. Changes in chemical composition of asphalt (Roberts, Kandhal, Brown, Lee, & Kennedy, 1996)

The study conducted by Baek, Underwood, and Kim examined the effects of oxidative aging on the dynamic modulus and fatigue performance of asphalt mixtures (Baek, Underwood, & Kim, 2011). For the study, an asphalt binder sample was aged four times and at each level of aging,

three different types of laboratory testing then were performed: the dynamic modulus test, the constant crosshead test, and the cyclic fatigue test. The results found that the stiffness of the asphalt binder sample increased with the aging time, causing a significant effect on the dynamic modulus. With respect to damage properties, aging clearly differentiates among the damage characteristic curves of the aged mixtures. Based on the results from the cyclic fatigue tests, the study found that the fatigue failure in the asphalt binder sample represented a function of temperature as well as of aging level.

### **2.3 Asphalt Pavement Distresses**

Through the years, the binder on asphalt tends to become more brittle, based on an increase in the stiffness and the reduction of the relaxation capacity (Yildirim, 2007). This aging process on the binder in turn produces defects and/or deteriorations on the asphalt, called distresses.

Identifying the type of distress and how to treat it is key to maintaining a road in good quality.

Critical distresses that occur on asphalt pavement include a) fatigue cracking, b) block cracking, c) edge cracks, d) longitudinal and transverse cracks, e) reflection cracks, f) slippage cracks, g) corrugation and shoving, h) rutting, i) settlement, j) swell, k) patch failure, l) pot hole, m) weathering, and n) streaking.

ASTM definitions for each type of distress that can be localized on asphalt pavement are:

- Alligator (fatigue) cracking: A type of crack that is interconnected or interlaced, forming a pattern resembling an alligator's hide. Some of the causes for this type of distress are excessive loadings, a weak surface or base, a thin surface or base, and poor drainage. It is recommended that a full-depth patch be applied to repair it.

- **Block cracking:** A cracking pattern that divides the asphalt into small rectangular pieces. The possible causes are old and dried out mix, asphalt mix placed too dryly, and fine aggregates mixed with a low penetration asphalt and absorptive aggregates. This type of cracking may be fixed by collocating a thin asphalt layer over the affected area.
- **Bituminous bleeding:** This distress occurs where there is an excess of bitumen on the surface of the road. Bleeding occurs when the seal coating is not well constructed. In addition, it could happen when there is too much asphalt in the mix. Bleeding may be stopped by using seal coatings and collocating a thin asphalt layer over the seal coating.
- **Corrugation:** Defined as transverse undulations at regular intervals in the surface of the pavement, this distress consists of alternate valleys and crests not more than 3 feet apart. Possible causes are that the mix contains too much asphalt, low air voids in the mix, a too high fine aggregate content, and excessive moisture in the mix. For this distress, it is recommended to do a full-depth patch.
- **Edge cracking:** A type of crescent-shape cracking located near the edge of the pavement. This type of crack is usually caused by the lack of lateral support on the road. Other possible causes are settlement of material, shrinkage of dried out material, and heavy traffic volume. Edge cracking can be avoided by improving the drainage on the road and by removing vegetation close to the edge. After construction, filling the cracks with seal coats or emulsified asphalt could fix the problem.
- **Polished aggregate:** This distress occurs when aggregates are exposed to the surface, affecting the frictional characteristics of the roads. This occurs when soft aggregates are used for the mix.

- **Potholes:** These holes have a greater diameter than 4 inches with a depth of 1 inch. Holes on the asphalt surface are usually a consequence of a continued deterioration on the asphalt, made by another distress. Also, it may occur if there are weak spots in the road base. The solutions for this distress are to do a partial, full-depth, or injection patching.
- **Raveling:** This damage happens when the aggregates are dislodged and degradation of the binder occurs through the loss of pavement surface material. The recommended solution is to collocate a thin asphalt layer over the affected area.
- **Reflection cracking at joints:** This problem is a type of crack on the surface of the asphalt that occurs on the joints of the concrete pavement. It usually occurs by the movement on the asphalt and concrete layers. It can be repaired by using crack seals.

From all the different distresses discussed above, the different cracking types that could occur present the major distresses that affect the serviceability and quality on asphalt pavement roads (Wu, Mohammad, Wang, & Mull, 2005). The American Association of State Highway and Transportation Office (AASHTO) represent the organization responsible for providing methods to design pavement structures, where serviceability is a considered aspect during the design process. Thus, the serviceability on asphalt pavement is strongly dependent on both designing and maintenance processes.

## **2.4 Preservation of Asphalt Pavement**

Many methods are employed to preserve asphalt pavement, but the most common solutions for maintaining asphalt pavements include using seal coatings and rejuvenators. Other components used to prevent deterioration are softening agents, which not only offer minimal improvement, but also can exacerbate an extant instability within the binder material. The notion to use either



seal coating or rejuvenators is required to extend the life of asphalt beyond a major reconstruction, and thus decreases the annual maintenance cost.

#### 2.4.1 Rejuvenators

Rejuvenators are cationic emulsions containing maltenes, which purpose is to recover the properties of aged binders by softening the oxidized asphalt concrete pavement surface and its flux to extend the life of the pavement (Brownridge). In other words, rejuvenators will restore the asphaltenes/maltenes ratio. The oxidation on an asphalt surface indicates that the binder presents a lower concentration of reactive components (nitrogen base and first acidifins), together with a higher concentration on less reactive components (paraffins and second acidifins). As a result, a rejuvenator to restore the rheological properties on asphalt must have a minimum N/P ratio of 0.5 to avoid incompatibility problems between the rejuvenator and the asphalt (Shen, Miller, & Amirkhanian, 2007). Rejuvenators tend to be highly aromatic as they increase the peptizing power of the maltenes phase (Venable, Peterson, & Robertson, 1983). ASTM provides several requirements in order to use a rejuvenator to recover the properties of aged binders. Rejuvenators must satisfy requirements for viscosity, flash point, volatility, compatibility, chemical composition, and specific gravity (ASTM, 1980). In addition, hardening susceptibility and temperature susceptibility are other properties improved by the use of rejuvenators (Peterson, Davison, Glover, & Bullin, 1994).

For a rejuvenator to restore all the rheological properties of asphalt, the rejuvenator's formulation must have certain aspects: A proper base and the rejuvenator must be emulsion based (Brownridge). A naphthenic or wax free base is ideal to use as a base, since it offers more solvency or absorption and fluxing ability with the binder (Brownridge). In addition, it is recommended that the rejuvenators be manufactured as an emulsion in order to wet the asphalt

binder (Brownridge). A rejuvenator needs to be cationic, with an oil-in-water emulsion of selected maltene components to both facilitate and assure a desired incorporate of maltene fractions into the asphalt. A rejuvenator must be a cationic emulsion, thus leading the product to penetrate the pores of asphalt easily without displacing the asphalt films from the aggregate or destroying the existing structure of the asphalt-aggregate mix (Brownridge). Therefore, it is important to have a well-manufactured rejuvenator. Importantly, the blended maltene fractions deposited by the rejuvenators should not disturb the existing structure of asphalt-aggregate mix with respect to adhesion, cohesion, and stability (Brownridge). Other aspects considered in manufacturing rejuvenators is the stability of the emulsion, together with the handling and the simplicity of the application. Properties necessary for a manufactured rejuvenator are summarized in Table 2.1.

#### 2.4.2 Seal Coatings

Seal coating is a thin coat consisting of binder and aggregates, which are spread over the road in order to heal surface cracks and raveled surfaces (O'Brien, 1989); the result is a waterproofing of the underlying pavement layers (Brown, Preventive maintenance of asphalt concrete pavements, 1988). Therefore, seal coatings are expected to improve the asphalt condition in both ride quality and pavement deterioration. A positive impact on pavement deterioration should be expected, since seal coatings can reduce the level of oxidation on asphalt by simply preventing the access of oxygen to the binder. Another well-received impact on asphalt deterioration occurs when a seal coating impedes the penetration of water, thus preventing an eventual stripping to occur on the asphalt pavement.

Table 2.1. Specific Properties for a Rejuvenator

Tests	Test Method		Requirements	
	ASTM	AASHTO	Min.	Max.
Test on Emulsion				
Viscosity @25C, SFS	D-244	T-59	15	40
Residue, %w	D-244 (mod)	T-59 (mod)	60	65
Miscibility Test	D-244 (mod)	T-59 (mod)	No Coagulation	
Sieve Test, %w	D-244 (mod)	T-59 (mod)	-	0.1
Particle Charge Test	D-244	T-59	Positive	
Percent Light Transmittance	GB	GB	-	30
Cement Mixing	D-244	-	-	2.0
Test on Residue from Distillation				
Flash Point COC	D-92	T-48	196	-
Viscosity @60C, cST	D-445	-	100	200
Asphaltenes, %w	D-2006-70	-	0.4	0.75
Maltene Distribution Ratio	D-2006-70	-	0.3	0.6
PC/S Ratio	D-2006-70	-	0.5	-
Saturate Hydrocarbons, S	D-2006-70	-	21	28

## **2.5 Performance Grade**

The characterization of an asphalt binder for asphalt pavement applications was based on the penetration grading and viscosity grading of the asphalt binder. However, the characterization based solely on those two criteria was limited. Therefore, a new binder test and new specifications were established to provide a more accurate and more in-depth characterization of asphalt binders for HMA pavements applications. The new tests and specifications are focused on the performance parameters of HMA pavement, such as rutting, fatigue cracking, and thermal cracking.

The concept of Superpave performance grading (PG) is centered on the understanding that the properties of an asphalt binder are linked with the environmental conditions under which it will be employed. Climatic conditions are expected to have an effect on the asphalt binder's properties. The developed performance grading adapts the same fundamental tests, such as penetration and viscosity tests, and then it states that not all binders must satisfied these developed tests at the same temperature, because each particular asphalt binder is dependent on the environmental conditions of the region of application. Thus, the asphalt binder applied in a pavement road located at the Sonoran Desert of California would be different from the one used in the Alaskan tundra. Table 2.2 shows how the Superpave PG system addresses specific penetration, as well as AC and AR grading systems in general limitations.

The following asphalt binder tests are performed to determine the Superpave performance grade: Rolling thin film oven (RTFO), Pressure aging vessel (PAV), Rotational viscometer (RV), Dynamic shear rheometer (DSR), Bending beam rheometer (BBR), and Direct tension tester (DTT).


Table 2.2. Prior Limitations vs. Superpave Testing and Specification Features (Roberts F. , Kandhal, Brown, Lee, & Kennedy, 1996)


Limitations of Penetration, AC and AR Grading Systems	Superpave Binder Testing and Specification Features that Address Prior Limitations
Penetration and ductility tests are empirical and not directly related to HMA pavement performance.	The physical properties measured are directly related to field performance by engineering principles.
Tests are conducted at one standard temperature without regard to the climate in which the asphalt binder will be used.	Test criteria remain constant, however, the temperature at which the criteria must be met changes in consideration of the binder grade selected for the prevalent climatic conditions.
The range of pavement temperatures at any one site is not adequately covered. For example, there is no test method for asphalt binder stiffness at low temperatures to control thermal cracking.	The entire range of pavement temperatures experienced at a particular site is covered.
Test methods only consider short-term asphalt binder aging (thin film oven test) although long-term aging is a significant factor in fatigue cracking and low temperature cracking.	Three critical binder ages are simulated and tested: <ol style="list-style-type: none"> <li>1. Original asphalt binder prior to mixing with aggregate.</li> <li>2. Aged asphalt binder after HMA production and construction.</li> <li>3. Long-term aged binder.</li> </ol>
Asphalt binders can have significantly different characteristics within the same grading category.	Grading is more precise and there is less overlap between grades.
Modified asphalt binders are not suited for these grading systems.	Tests and specifications are intended for asphalt “binders” to include both modified and unmodified asphalt cements.

### 2.5.1 Performance Grade Nomenclature

Two numbers are used to inform the Superpave performance grade: The first number is the average seven-day maximum pavement design temperature ( $^{\circ}\text{C}$ ); and the second one is the minimum pavement design temperature ( $^{\circ}\text{C}$ ). An important observation is that the measured temperatures are from the pavement and not from the air. An algorithm, which can be contained in the LTPP Bind program, can be used to determine the pavement temperature from air. Figure 2.3 shows the different crude oils mixes for a specific performance grading.

		High Temperature, °C				
		52	58	64	70	76
Low Temperature, °C	-16	52-16	58-16	64-16	70-16	76-16
	-22	52-22	58-22	64-22	70-22	76-22
	-28	52-28	58-28	64-28	70-28	76-28
	-34	52-34	58-34	64-34	70-34	76-34
	-40	52-40	58-40	64-40	70-40	76-40

 = Crude Oil

 = High Quality Crude Oil


 = Modifier Required

Figure 2.3. Type of crude oil mixes for a specific performance grade (Pavement Interactive, 2008)

### 2.5.2 Rolling Thin-Film Oven Test

The short-term aging on asphalt pavement occurs when the oily components are absorbed or vaporized in the maltenes during mixing and construction (Tran, Taylor, & Willis, 2012).

ASTM D2872-12 is the rolling, thin-film, oven test. The purpose of this test is to measure the effect of heat and air on a moving film of semi-solid asphaltic materials. Furthermore, this test is used to determine changes in properties of asphalt during hot mixing at about  $150^{\circ}\text{C}$  as indicated by viscosity and other rheological measurements. In addition, it can be used to determine mass

change, which is a measure of asphalt volatility. Figure 2.4 shows a schematic picture from the instrument used to do the rolling thin-film oven test.

The ASTM D2872-12 test procedure is the following: The asphalt binder sample is heated in an oven not exceeding 150°C until the sample is liquid and able to be stirred manually. Then, pour 35g of the sample in each of the glass containers. Immediately after pouring the sample into a glass container, turn the container to a horizontal position. Rotate the container slowly for at least one full rotation. Place the container horizontally in a clean cooling rack for one hour. With the oven at operating temperature and the airflow set at 4000 mL/min, arrange the containers holding the asphalt in the carriage so that the carriage is balanced. Fill any unused spaces in the carriage with empty containers. Close the door and rotate the carriage assembly at a rate of 15 r/min. Maintain the samples in the oven with the air flowing and the carriage rotating for 85 min. The test temperature of 163°C shall be reached within the first 10 min; otherwise, discontinue the test. At the conclusion of the testing period, transfer its contents to a container.

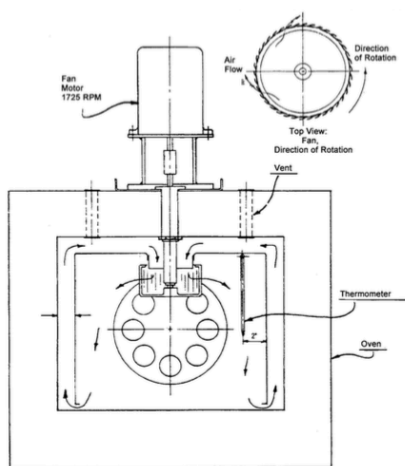


Figure 2.4. Schematic drawing of the instrument utilized on rolling thin-film oven test (ASTM D2872-12)

### 2.5.3 Pressurized Aging Vessel

ASTM D6521-13 is the standard practice for accelerated aging of asphalt binder using a pressurized aging vessel (PAV). The purpose of this standard is to simulate the rheology changes that occur in asphalt binders during in-service oxidative aging. This test is usually performed on the residue from ASTM D2872. The residue from the PAV is used to determine changes on the physical or chemical properties of asphalt binder after several years of aging. Figure 2.5 shows a schematic drawing from the instrument used to do the pressurized aging vessel test.

The ASTM D6521-13 test procedure is as follows: Set the temperature to 110°C in the pressure vessel. Place the pan holder inside the pressure vessel. Combine the hot residue from the ASTM D2872-12 bottles into a single container, stir to blend, and then transfer to PAV pans. Place each PAV pan on a balance and add 50g mass of asphalt binder to the pan. Place the filled pans in the pan holder. Pans containing asphalt binders from different sources and grades may be placed in the pressure vessel during a single conditioning run. Maintain the temperature and air pressure inside the pressure vessel for 20 h. At the end of the 20-h conditioning period, begin the slow reduction of the internal pressure of the PAV, using the air pressure bleed valve. Remove the pan holder and pans from the PAV and place the pans in an oven set to 168°C for 15 min. Preheat the vacuum degas oven to 170°C. Remove the pans from the oven and scrape the hot residue from all pans containing the same sample into a single container.

### 2.5.4 Rotational Viscosity

The viscosity is an important asphalt property that usually is used as an indication of aging on asphalt. The viscosity of the asphalt binder sample is measured before and after placing a rejuvenator to determine whether the rejuvenator had an effect on the viscosity. ASTM D2195 is



the standard test to measure the viscosity of non-newtonian material by rotational viscometer. The test determines the apparent viscosity of coatings and related materials by measuring the torque on a spindle rotating at a constant speed. Figure 2.6 shows a schematic drawing from the instrument used to do the rotational viscosity test.

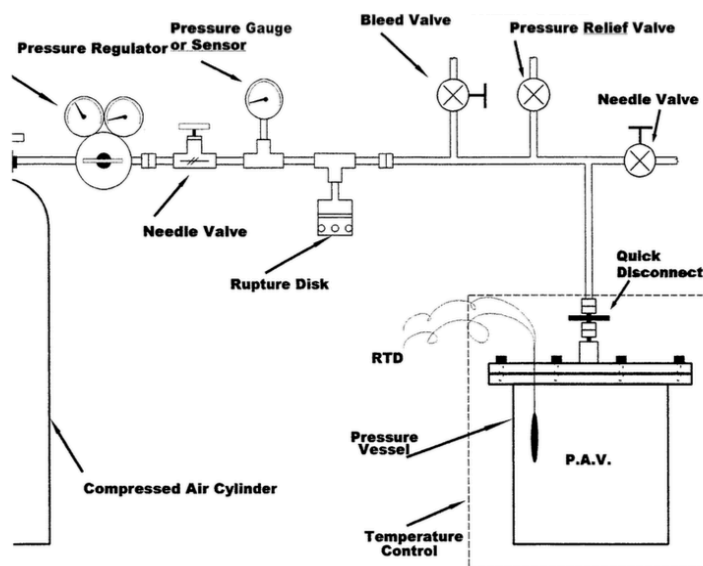


Figure 2.5. Schematic drawing of the instrument utilized on pressurized aging vessel test (ASTM D6521-13)

The ASTM D2195 test procedure is as follows: All measurements should be undertaken at a temperature of 25°C. Place the instrument on the adjustable stand. Lower the viscometer to a level that will immerse the spindle to the proper depth. Level the instrument. Attach the spindle to the instrument. Lower the viscometer until the immersion mark on the shaft just touches the specimen. Leave the specimen inside on the instrument with the immersed spindle for 30 min. Initiate the rotation of the spindle. After 10 min, read the viscosity torque. Repeat this for 1 min twice. Take out the specimen.

### 2.5.5 Dynamic Shear Rheometer

ASTM D7175 is used to determine the dynamic shear modulus and phase angle of asphalt binders. The evaluation of the complex shear modulus in an aged asphalt binder is important as an indicator of the stiffness or resistance of the binder to deformation under a load. Both the complex shear modulus and phase angle are used to define the resistance to the shear deformation of the asphalt binder in the linear visco-elastic region. A highly complex shear modulus is usually present on a stiff binder and aged binders, compared to less stiff binders and un-aged binders. Figure 2.7 shows a schematic drawing from the plate used in a dynamic shear rheometer.

The ASTM D7175 test procedure is as follows: Heat the asphalt binder sample in a container in an oven until the sample is sufficiently fluid to pour. Transfer the asphalt binder to one of the test plates. Immediately after transferring the sample into one of the test plates, trim the excess of the binder. Set the temperature controller to the temperature required to obtain the test temperature in the test specimen between the test plates. Initiate the testing within five to ten minutes after reaching a thermal equilibrium at each test temperature. Obtain a test measurement by averaging data for an additional 8 to 16 loading cycles, using the analytical technique and software provided by the manufacturer.

### 2.5.6 Bending Beam Rheometer

ASTM D6648 is purposed to determine the flexural-creep stiffness or compliance and m-value of asphalt binders by means of a bending beam rheometer. This test measures the mid-point deflection of a simply supported prismatic beam of asphalt binder, subjected to a constant load applied to its mid-point. The flexural-creep stiffness or compliance describes the low-

temperature stress-strain-time response of an asphalt binder at the test temperature within the range of linear visco-elastic responses. The creep stiffness and the m-value are indicators on the low-temperature thermal cracking performance on asphalt pavement. Figure 2.8 shows a schematic drawing from a dynamic shear rheometer.

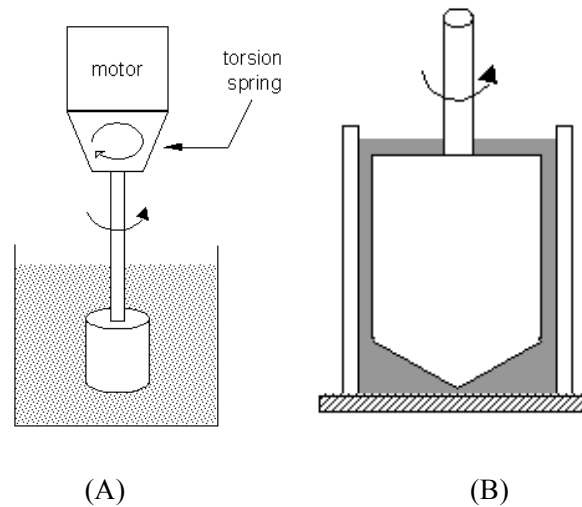


Figure 2.6. (A) Schematic drawing of a Brookfield-type viscometer; and (B) cone and plate configuration

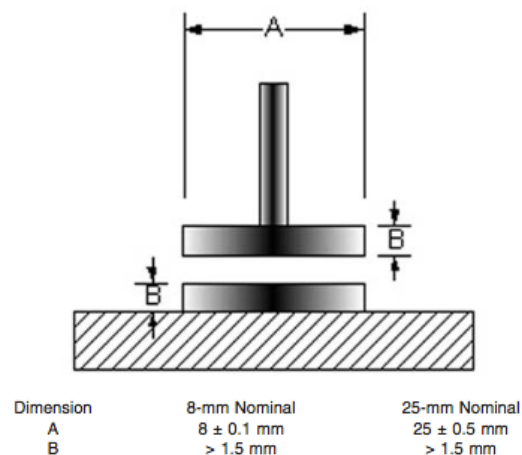


Figure 2.7. Schematic drawing of plate dimensions utilized in a dynamic shear rheometer (ASTM D7175)

The ASTM D6648 test procedure is as follows: Heat the asphalt binder in an oven set at 168°C until the asphalt binder is completely fluid and then pour, stirring the fluid gently. Prepare the metal molds. Begin by pouring the binder from one end of the mold, moving toward the other end. Select the appropriate test temperature. Check the thickness of the test specimen. Check the adjustment of the contact load and test load prior to testing. Enter the specimen identification information, and other information as appropriate. Place the test specimen on the test supports and gently position the backside of the test specimen against the alignment pins. Manually apply a 35 mN contact load for no longer than 10 s to the test specimen. Apply the contact load as follows: (1) adjust the two load regulators; (2) lift the loading shaft manually; (3) place the test beam on the supports; and (4) lower the shaft manually to make contact with the test beam. After applying the contact load, activate the automatic test system. Remove the specimen from the supports and proceed to the next test.

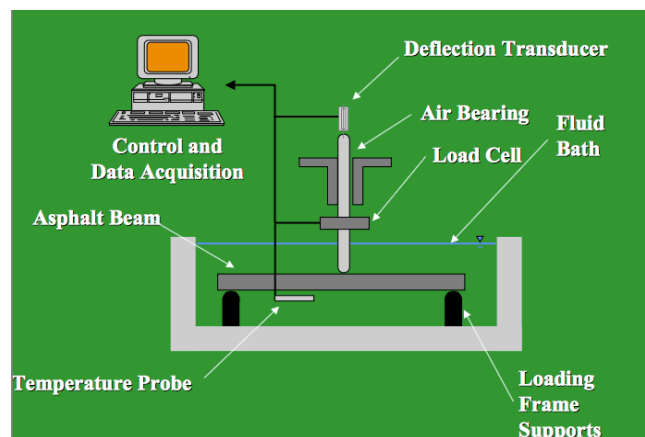


Figure 2.8. Schematic drawing of equipment utilized in a bending beam rheometer (Horan, 2003)

#### 2.5.7 Direct tension tester

ASTM D6723 determines the failure strain and failure stress of asphalt binders by means of a direct tension test. This test may be performed on an un-aged binder or an aged binder by rolling

a thin-film oven or pressure air vessel. This test is performed on asphalt binders at temperatures where the binders exhibit either brittle or brittle-ductile failure. A brittle or brittle-ductile failure will result in a fracture of the asphalt binder, as opposed to a ductile failure where the asphalt binder stretches without fracturing. A displacement transducer monitors the elongation of the test specimen as it is pulled in tension at a constant rate of 1.00 mm/min. The tensile strain and stress are reported as failure strain and failure stress when the specimen reaches the maximum load.

Figure 2.9 shows a schematic drawing from a test specimen on a direct tension tester.

The ASTM D6723 test procedure is as follows: Prepare a test specimen. Mount a specimen on the load frame by matching the holes on the end tabs at each end of the specimen to the loading pins on the load frame. Remove the slack between the specimen and the loading pins. Set the strain rate to 3 %/min. After the specimen fractures, or after the elongation of the specimen reaches 10 %, whichever comes first, stop the test and remove the specimen or pieces. The strain at failure is easily identified as the strain at peak load when the failure is by fracture. Record the failure load and elongation at failure.

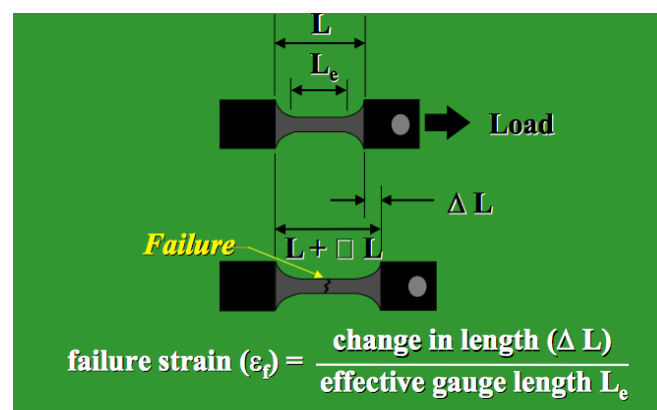


Figure 2.9. Schematic drawing from a test specimen on a direct tension tester (Horan, 2003)

## **2.6 Studies on Rejuvenators**

Studies on asphalt rejuvenators have shown that they are the most effective treatment to partially restore the asphalt properties (Karlsson & Isacson, 2006). However, in order for rejuvenators to restore the aged binder, they must be able to penetrate deep into the asphalt; other than that, rejuvenators could cause the surface to become slick, especially in wet weather (Brown E. , Preventive maintenance of asphalt concrete pavements, 1988).

### **2.6.1 Effectiveness of Seal Rejuvenators for Bituminous Pavement Surfaces**

In a study by Chiu and Lee (Chiu & Lee, 2006), three different rejuvenators, one cutback and two emulsions (one tar-based and the other asphalt-based), were tested on a 12-year old parking lot to assess the effectiveness of these applications. The study showed that any of the three rejuvenators were able to penetrate more than 2 cm deep into the asphalt, even though the air void content was 9.7%. However, it also revealed that rejuvenators produced a softening effect on the top 1 cm of the asphalt, thereby decreasing by 90% the viscosity of the binder at 60° C. More results showed not only a reduction on the pavement surface friction, but also in the pavement surface tension as well. Finally but not least, Chiu and Lee observed that because the area presented a dangerous environment for drivers after the application of these rejuvenators, the parking lot was closed.

### **2.6.2 Evaluation of Rejuvenators for Bituminous Pavements**

Another study by Brown and Johnson (Brown & Johnson, Evaluation of Rejuvenators for Bituminous Pavements, 1976) evaluated the performance of pavement treated with rejuvenators. For the study, five different rejuvenators were applied in three different locations in the U.S. One of the purposes of the study was to evaluate the ability of rejuvenators to penetrate into oxidized

pavement. Other purposes were to evaluate the ability to soften the binder, to reduce the amount of cracking, to reduce surface fines, and to minimize reduction in skid resistance. After the pavements were rejuvenated, pieces were taken to determine the penetration of rejuvenator. Three of the five rejuvenators show an average of 3/8 inch of penetration. The other two rejuvenators did not present any significant amount of penetration.

The next part of the study was to evaluate the performance of the five rejuvenators to restore the properties of the aged binders. Viscosity was one of the evaluated properties. Three of the five rejuvenators showed signs of rejuvenation, while the other two stiffened the binders. Also, every rejuvenator tested reduced the skid resistance for at least one year. The amount of cracking was evaluated three years after the rejuvenation of the pavements. The results on the amount of cracking indicated that both control and rejuvenated samples displayed the same amount of rejuvenation. Finally, all five rejuvenators showed a reduction in the loss of surface lines.

### 2.6.3 Reclamite as a Life Extender for Asphalt Concrete Pavements

A technical report conducted by the Naval Civil Engineering Laboratory (Navy Facilities Engineering Command, 1970) consisted of a study on a proprietary rejuvenator product called Reclamite. The study evaluated the claims on the performance by the manufacturer against actual field use by several agencies; among these agencies were federal users and the California State Division of Highways, together with city and county governments. The conclusion was that the manufacturer's claims for the performance of Reclamite were essentially correct. No further investigations were required to determine the effectiveness of the product.

#### 2.6.4 Report on Reclamite Usage, Naval Weapons Center, China Lake, California

The same proprietary rejuvenator product was evaluated in another study by the U.S. Navy (Navy Facilities Engineering Command, 1973). The study focused on the performance of the rejuvenator on three roads at the Naval Weapons Center, China Lake, California. The plan of study for the evaluation was to treat the three roads with the proprietary product, while retaining an untreated test section at each test site. Core samples used in taking asphalt penetration measurements, judgments, and photographs were taken periodically to assess the effectiveness of the rejuvenator. The evaluation of the rejuvenator was performed over a period of two years. The conclusion of this evaluation revealed that field tests and laboratory reports "show[ed] conclusively that Reclamite does prolong the life of asphalt concrete pavements."

#### 2.6.5 Evaluation of rejuvenators for Bituminous Pavements

A treating study on adjacent pavement areas at three Air Force bases with four proprietary rejuvenator products and an asphalt emulsion seal was conducted by the U.S. Army Corps of Engineers and sponsored by the Air Force Civil Engineering Center (Air Force Civil Engineering Center, 1963). The tests were conducted at a base in the dry, hot, southwestern part of the United States, a base in the humid, hot, southeastern part of the country, and a third base located in the cold, north central part of the country. The four rejuvenators used on the study were Koppers BPR, Reclamite, Petroset and Gilsabind; the SS-1 Asphalt emulsion seal was also evaluated. The study spanned a period of four years and reached the conclusion that Koppers BPR, Reclamite, and Petroset do rejuvenate the old asphalt binder, while Gilsabind and SS-1 Asphalt Emulsion have a hardening effect. Interestingly, at the end of a study the researchers concluded that an



indication of viscosity in a treated asphalt presents a better indicator of the performance of a rejuvenator's effect than the penetration test on the materials tested.

#### 2.6.6 High Temperature Properties of Rejuvenating Recovered Binder with Rejuvenator, Waste Cooking and Cotton Seed Oils

Chen, Xiao and Wu evaluated three sources of aged asphalts recovered from RAP materials, mixed with one type of virgin oil and with different percentages of rejuvenators, i.e., cottonseed oil and waste cooking oil (Chen, Xiao, & Wu, 2014). One result from the study was the conclusion that any of the three products mixed to the aged asphalt were effective in reducing the rutting resistance factor. However, the reduction on the rutting resistance factor of the sample with a rejuvenator was the greatest among all the samples in the experiment. Another result was that the phase angles of binders increased, due to the addition of rejuvenators, cottonseed oil, or waste cooking oil. The aged binder mixed with a rejuvenator was also the best one under the elastic recovery performance. However, the complex modulus of binders decreased due to the addition of any of these three products. In addition, the resistance to flow deformation of the asphalt containing rejuvenator proved to be better than that of the asphalt containing cottonseed oil or waste cooking oil. Another important detail from the study was that the failure temperature for all of the samples decreased with the addition of any of the three products. Finally, the addition of rejuvenators, cottonseed oil and waste cooking oil had a positive effect on the viscosity of the rejuvenated binders as they reduced the value. However, the rejuvenator was the one with the more significant reduction in viscosity.

### 2.6.7 Rejuvenators, Rejuvenators/Sealers, and Seal Coats for Airfield Pavements

The U.S. Air Force conducted a study to investigate the comparative field performances of different rejuvenators and seal coat materials on hot-mix asphalt airfield pavements (Shoenberger, 2003). The study was conducted over a period of more than one year to determine the field performance of the materials. All of the rejuvenators and seal coats used were proprietary products. The author stated “[T]he purpose of the study was not to determine the best or optimum rejuvenator, but was to provide information for the development or updating of guide specifications for the use of these types of materials.”

The two hot-mix asphalt airfields selected to place the materials were MacDill AFB, located in Tampa, FL, and McGuire AFB, located in south-central New Jersey. Also, another important aspect in the study was the comparison of the binder properties on the treated pavement as compared to untreated areas. The field performances of the rejuvenator and seal coat materials were evaluated by the effects of each one on skid resistance, texture, and changes in visual appearance. Another aspect to this study was that every manufacturer applied the material at different application rates and was allowed to apply each material by individual, selective methods.

The rejuvenator materials used in this study reduced the viscosity of the recovered asphalt cement binder in the treated pavement. Also, the application of rejuvenators showed a reduction of skid resistance on a short-term basis. In regard to skid resistance, the results indicated that the use of sand with rejuvenators will improve the skid resistance of the pavement. Finally, the author stated that the use of DSR testing to evaluate the effectiveness of rejuvenating material was not recommended. The author suggested that in order to better evaluate the performance of

rejuvenators and seal coats, these two bases should be periodically evaluated over the next few years. Moreover, the author recommended that how much of what component should be tested to determine what should be applied to the pavement to provide effective rejuvenation.

#### 2.6.8 An Evaluation of a Sealer-Rejuvenator Treatment

An experiment conducted by the State Materials Office (SMO) evaluated a sealer-rejuvenator product provided and applied by Asphalt Maintenance Co. of Orlando, FL (Sholar, Musselman, & Page, 2000). The purpose of the experiment was to determine or to verify whether the product could seal and rejuvenate the pavement as claimed by the manufacturer. Also, the effects on the frictional properties of the pavement were evaluated. The product applied was a coal tar-based proprietary product named SR-20. The test location was a 500 feet long shoulder section on southbound SR 9 (I-95) between mileposts 218 and 219. This shoulder had been resurfaced approximately 10 years prior. This shoulder was chosen because it exhibited some deterioration due to weathering and aging. The results on the friction number decreased with the application of the sealer-rejuvenator. However, the friction numbers after application were far too low for this product to be considered as a routine maintenance procedure. Also, authors stated that the use of this product could be dangerous in wet conditions, since the shoulder of the road is used in situations requiring a sudden stop. The conclusion of the experiment was that based solely on the friction number, the State Materials Office does not recommended the product's use for State Highway Applications.

#### 2.6.9 Evaluating the Performance of Hot Mix Asphalt with Reclaimed Asphalt Pavement and Heavy Vacuum Slops as Rejuvenator

The application of reclaimed asphalt pavement has increased in the last year due to the high price of crude oil. Therefore, the studies on the use of rejuvenator on hot mix asphalt with RAP have

become widely interesting to researchers. Yaghoubi, Ahadi, Sheshpoli and Pahlevanloo conducted a study to investigate the effects of adding a rejuvenator to hot mix asphalt with RAP (Yaghoubi, Ahadi, Sheshpoli, & Pahlevanloo, 2013). Five different samples were prepared to evaluate the effects of rejuvenators. However, in order to evaluate the properties of the asphalt samples, the study implemented the penetration, softening point, and saybolt viscosity tests. One conclusion of the study was that any of the samples with or without a rejuvenator presented a greater stability as the virgin sample. Nevertheless, the samples with rejuvenator met Iran's Highway Asphalt Paving Code. Also, the results showed that both the virgin sample and the sample with 10% of rejuvenator had almost the same resilient modulus determined by the indirect tensile test. The Dynamic Creep Test shows that the virgin sample had the greatest resistance to deformation, while the sample with 10% rejuvenator performed 5.1% lower than the virgin sample. Lastly, the aforementioned tests results show that the sample with 10% rejuvenator can perform properly as an alternative to a virgin hot-mix asphalt. As a result, the authors recommended applying 10% of the rejuvenator used as a cost-effective alternative to the virgin hot-mix asphalt.

#### 2.6.10 Effects of Rejuvenating Agents on Superpave Mixtures Containing Reclaimed Asphalt Pavement

A study conducted by Shen, Amirkhanian and Miller evaluated the performance of rejuvenators as a softening agent on reclaimed asphalt pavement (RAP) (Shen, Miller, & Amirkhanian, 2007). For the study, different Superpave mixtures containing RAP were prepared, using rejuvenators and softer binders. One objective of the study was to evaluate the properties of Superpave mixtures with RAP, by using a rejuvenator and comparing the results to Superpave mixtures that used a soft binder. Another objective was to investigate blending charts of aged binders with a

rejuvenator to determine the optimum amount of rejuvenator for the design of Superpave mixtures containing RAP. An asphalt pavement analyzer was used to determine the rutting resistance of the samples. Also, the susceptibility of the samples were evaluated by determining the indirect tensile strength and then calculating the tensile strength ratio. The conclusion of the study was that the properties of the Superpave mixtures containing RAP, when using rejuvenators, an asphalt pavement analyzer, and indirect tensile strength, were better than the samples containing soft binders.

#### 2.6.11 Effects of Rejuvenator Seal and Fog Seal on Performance of Open-Graded Friction Course Pavement

The use of rejuvenators and fog seal as preventive maintenance materials on an open-graded friction course (OGFC) was evaluated in a study research conducted by Qureshi, Tran, Watson and Jamil (Qureshi, Tran, Watson, & Jamil, 2013). The main purpose of the research was to optimize the fog and rejuvenator seal application rates by evaluating the performances in terms of surface friction and durability. Three types of seal material were evaluated: Pavegaard (PG) and Pavepreserve (PP) asphalt rejuvenators and cationic, slow-setting, asphalt emulsion (CSS-1H) as a fog seal. Each material was applied at three different application rates. The evaluation was conducted through both the fieldwork and laboratory testing. The location for the study was at the National Centre for Asphalt Technology (NCAT) pavement test track in Opelika, Alabama. The friction properties of the samples were evaluated using a dynamic friction tester and a circular texture meter. Also, a bulk specific gravity measurement test, Hamburg wheel-tracking device, and Cantabro abrasion test were performed.

The results of the study show that both rejuvenators and fog seals affect the micro and macro texture of the OGFC. However, the use of rejuvenator and fog seal reduced the surface friction

up to 24%, which can be dangerous for drivers. Another concern was that the use of rejuvenator and fog seal reduced the air voids, which could negatively affect the functionality of OGFC mix. Also, the Cantabro loss values were much higher than acceptable values for the OGFC mix design. A positive result was that the rejuvenator improved the abrasion factor.

## **2.7 Microcapsule Synthesis**

The effectiveness of rejuvenators on restoring the properties of asphalt is related to the amount of penetration into the asphalt (Chiu & Lee, 2006). Previous studies have shown that asphalt rejuvenators penetrate no more than 2 cm, which is insufficient for applying the benefits of the product (Chiu & Lee, 2006). Therefore, studies sought innovative methods to incorporate the use of rejuvenators such as encapsulation methods (Garcia, Schlangen, van de Ven, & Sierra-Beltrán, 2010).

Microencapsulation may be defined as the process to encapsulate a solid, liquid, or gas as a core material, surrounded by a coating layer or shell (Samadzadeh, Hatami, Peikari, & Ashrafi).

Microencapsulation has been evaluated in numerous construction materials including mortar, lime, cement, concrete, marble, sealant, and paints (Boh & Sumiga, 2008). Also, a microencapsulation process has been implemented in other industries such as food, chemical, textile, and pharmaceutical industries.

Microcapsules have a spherical or irregular shape. Microcapsules may be divided into two parts: core and shell. The core, the intrinsic part, contains the active ingredient. The shell, the extrinsic part, protects the core material from external factors of the atmosphere (Ghosh, 2006). A schematic picture from a microcapsule is shown in Figure 2.10.

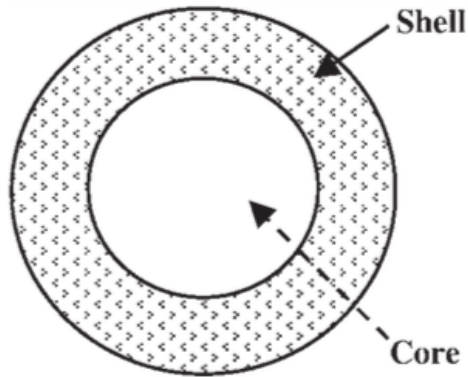


Figure 2.10. Schematic drawing of a microcapsule (Ghosh , 2006)

The idea of microencapsulation is to protect the core material from external elements such as environmental conditions, or it can control a release of the core material by controlling the permeability of the shell material. For asphalt applications, the use of self-healing microcapsules containing a rejuvenator is promising, as it will allow the material to resist the initiation and propagation of cracking caused by vehicular and environmental loading. When cracking occurs due to the aging process of the binder, the shell of microcapsules containing rejuvenator will rupture, and the rejuvenator will flow through the binder, which consequently results in reversing the aging process.

In general, the production of microcapsules can be categorized as chemical, physico-chemical, or physical methods. The type of core material and the physical properties of microcapsules will define the microencapsulation technique. Other factors that influence the selection of a microencapsulation technique are the shell wall, the yield rates, the morphology, and the particle size (Ghosh , 2006). Table 2.3 shows the typical particle sizes that result from each respective encapsulation technique.

Table 2.3. Particle size according to microencapsulation process (Ghosh , 2006)

Microencapsulation Process	Particle Size ( $\mu\text{m}$ )
Extrusion	250-2500
Spray-drying	5-5000
Fluid bed coating	20-1500
Rotating disk	5-1500
Coacervation	2-1200
Solvent evaporation	0.5-1000
Phase separation	0.5-1000
In-situ-Polymerization	0.5-1000
Interfacial polymerization	0.5-1000
Miniemulsion	0.1-0.5
Sol-gel encapsulation	2-20
Layer-by-layer assembly	0.02-20

The morphology of microcapsules depends on the type of core material encapsulated, and the microencapsulation process that is utilized. Microcapsules have regular or irregular shapes that can be classified as mononuclear, polynuclear, and matrix. Mononuclear microcapsules are those that contain a shell around a core material. Polynuclear microcapsules, differing from mononuclear microcapsules, have many cores enclosed within the shell. Matrices, the last type of microcapsules, distribute the core material homogenously within the shell. Figure 2.11 shows the different types of microcapsules based on this morphology.



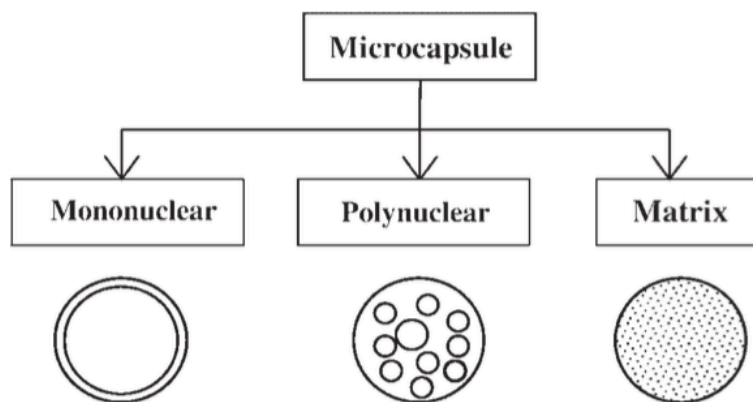


Figure 2.11. Types of microcapsules based on the morphology (Ghosh, 2006)

As mentioned before, the synthesis of microcapsules may be accomplished by different methods, such as interfacial polymerization, coacervation (Shulkin & H. D. H. Stover, 2002), in-situ polymerization (Brown, Kessler, Sottos, & White), extrusion, and sol-gel methods. From all these methods, the in-situ polymerization method is considered the easiest and the most cost-effective method for encapsulation, since it requires no high levels of technology (Samadzadeh, Hatami, Peikari, & Ashrafi, A review on self healing coatings based on micro/nanocapsules). A few microencapsulation techniques will be reviewed in the following sections.

### 2.7.1 Coacervation

Coacervation is a phase separation, where the homogenous polymer solution is partially dissolved into a polymer-rich phase (coacervate) and the poor polymer phase (coacervation medium) (Bungenberg de Jong, 1949). There are two types of coacervation processes: the simple process, where a desolvation agent is used in the phase separation, and the complex process, which implies complexation between two oppositely charged polymers. Figure 2.12 shows the schematic representation of the coacervation process.

2.7.1.1 Complex Coacervation. Accomplishing a complex coacervation requires three steps: preparation of emulsion; encapsulation of core material; and rigidization of the coating. The procedure starts by dispersing the core material into a polymer solution. Then the second polymer (water-soluble) solution is added to the prepared dispersion. The encapsulation of the core material occurs when the two polymers form a complex by changing the pH, the temperature, or by dilution of the medium. The shell thickness can be controlled by the rate in which the second polymer solution is added. Finally, the rigidization of the coating occurs by crosslinking (Ghosh, 2006). Crosslinking may be defined as the formation of chemical links between molecular chains to form a three-dimensional network of connected molecules (Jyothi, Prasanna, Prabha, Seetha Ramaiah, Srawan, & Sakarkar, 2008).

## 2.7.2 Interfacial Polymerization

In this particular type of microencapsulation method, the shell of microcapsules is formed at or on the surface of the droplet by polymerization of the reactive monomers. The most common monomers used on interfacial polymerization are multifunctional acid chlorides and multifunctional isocyanates; these can be used in combination or individually. The interfacial polymerization starts with the dissolving of the monomer in a liquid state core material, allowing the monomer to be dispersed in an aqueous phase containing a dispersing agent. After that, a co-reactant multifunctional amine is added which generates a fast polymerization in forming the capsule shell (Scher, 1983). The types of shell formed during this microencapsulation method depends on the material with which isocyanate reacts. A polyurea shell will be formed with the reaction between isocyanate and amine; a polyurethane shell will be formed when isocyanates react with a hydroxyl-containing monomer; and lastly, a polynylon or polyamine shell will be

formed when acid chloride reacts with amine (Saihi , Vroman, Giraud, & Bourbigot, 2006).

Figure 2.13 shows a schematic representation of interfacial polymerization.

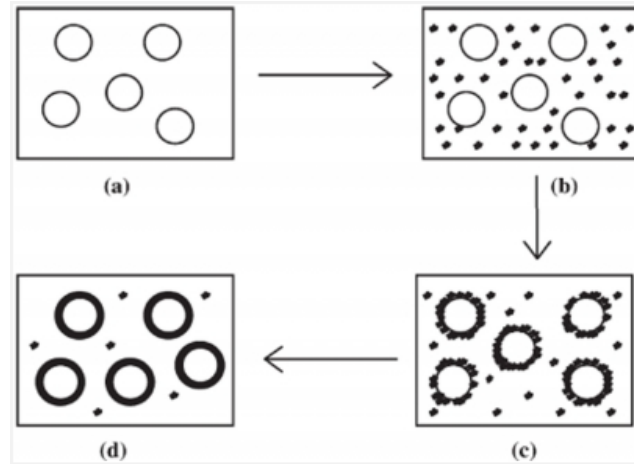


Figure 2.12. Schematic representation of coacervation process. (a) Core material dispersion in solution of shell polymer; (b) separation of coacervate from solution; (c) coating of core material by microplets of coacervate; and (d) coalescence of coacervate to form a continuous shell around core particles

The average size of commercial microcapsules synthesized with interfacial polymerization is in the 20-30  $\mu\text{m}$ . However, bigger microcapsules may be produced. A successful example of interfacial polymerization was the encapsulation of di-ammonium hydrogen phosphate (DAHP) by a polyurethane-urea membrane. The average size of DAHP microcapsules was 13.35  $\mu\text{m}$ , and 95% of the particles had a diameter less than 30.1  $\mu\text{m}$  (Saihi , Vroman, Giraud, & Bourbigot, 2006).

### 2.7.3 In-situ Polymerization

The in-situ polymerization involves a chemical reaction resulting in the formation of a reinforcing phase within a matrix. The polymerization of monomer, added to the encapsulation reactor, is responsible for the shell formation in this microencapsulation method. The entire

polymerization process occurs in the continuous phase and on the continuous phase side of the interface. This process is formed by the dispersed core material and the continuous phase. The deposits of the prepolymer on the surface of the disperse core material generate solid capsule shell (Jyothi, Prasanna, Prabha, Seetha Ramaiah, Srawan, & Sakarkar, 2008).

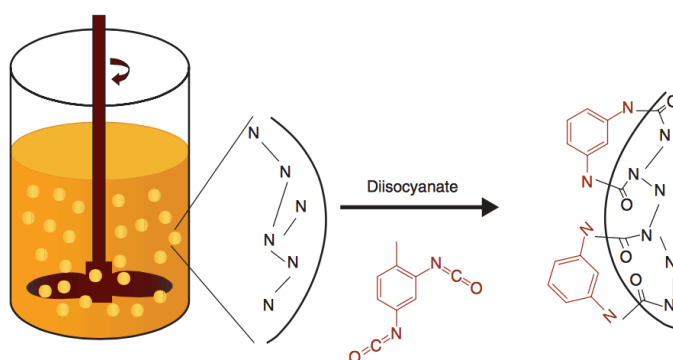


Figure 2.13. Schematic representation of microencapsulation via interfacial polymerization (Saihi , Vroman, Giraud, & Bourbigot, 2006)

Some examples of in-situ polymerization are urea-formaldehyde and melamine-formaldehyde capsules. In-situ polymerization is usually performed by oil-in-water emulsion and high shear mixes, yielding a stable emulsion. After obtaining a stable emulsion, a water-soluble melamine resin is added and dispersed. Then, reduction of the pH of the mix yields cross-linked resins, and initiates the polycondensation. The formation of microcapsules occurs during the hardening process of the wall material, and the aqueous dispersion of polymer-encapsulated oil droplets is produced (Gemma, Amaia, & Marta, 2011). Figure 2.14 shows a schematic representation of the melamine resin microencapsulation process.

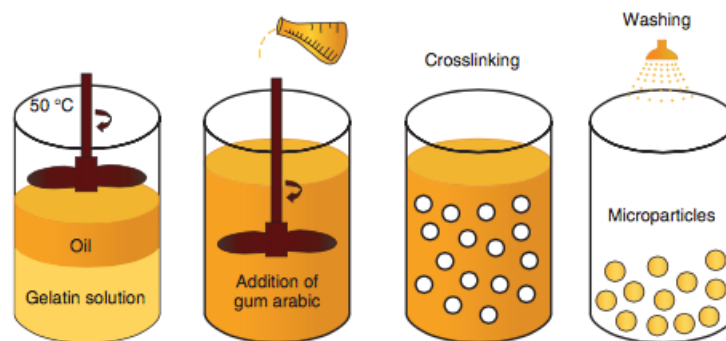


Figure 2.14. Schematic representation of the melamine resin microencapsulation process (Saihi , Vroman, Giraud, & Bourbigot, 2006)

#### 2.7.4 Optimization of microencapsulation process

The efficiency of an encapsulation procedure depends on several parameters as it shows on Figure 2.15.

2.7.4.1 Solubility of polymer in organic solvent. Mehta et al. (1994) conducted a study regarding the solubility of different PLGA polymers in methylene chloride. They compared the solubility of the different polymers by measuring the methanol cloud point (Cs). The results showed that a polymer was more soluble in methylene chloride when it had a high Cs values and therefore, it required a greater amount of methanol to precipitate from the polymer solution. Another observation was that a lower molecular weight polymer had a higher solubility in methylene chloride than a higher molecular weight polymer. The last observation on the study was that hydrophobic end-capped polymers were more soluble than non-end-capped polymers of the same molecular weight and component ratio.

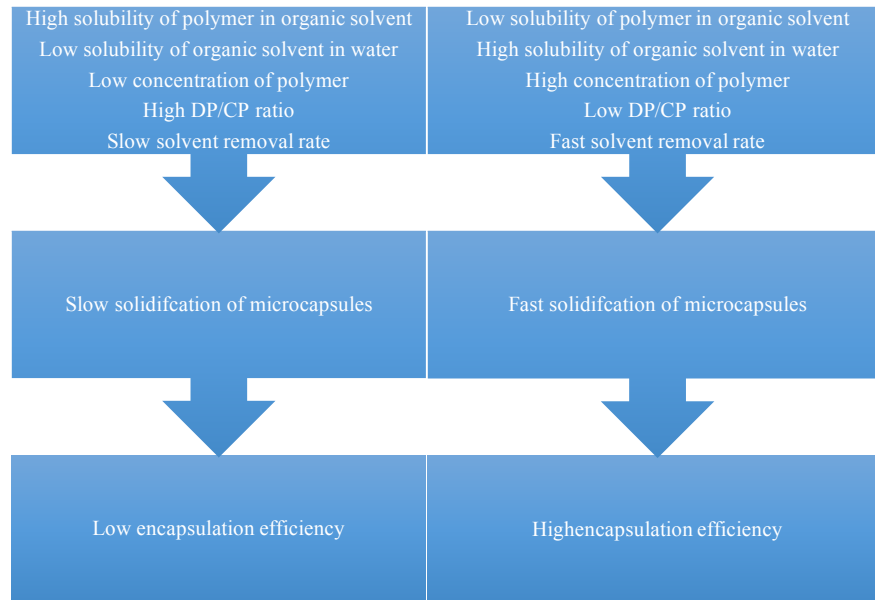


Figure 2.15. Factors influencing encapsulation efficiency (Yeo & Park, 2004)

Another study conducted by Johansen et al. (1998) concluded that using hydrophilic PLGA polymers resulted in a significantly higher encapsulation efficiency, compared to that of an end-capped polymer. The study noted that hydrophilic PLGA polymers are less soluble in methylene chloride, and precipitate faster than end-capped polymers. Finally, the authors concluded that a high efficiency on the encapsulation process might be due to a high solidification rate.

2.7.4.2 Solubility of organic solvent in water. A study of solubility of organic solvent in water, conducted by Bodmeir and McGinity (1988), concluded that using methylene chloride provides a higher encapsulation efficiency when compared to the use of chloroform or benzene. Advantages of using a highly soluble organic solution in water present an allowance for a fast, mass-transfer between the dispersed and continued phase that leads to a fast precipitation of the polymer. The increase of encapsulation efficiency was confirmed with studies using water-miscible-co-solvents, such as acetone, methanol, or ethyl acetate.

A study to determine the effect of high solubility on organic solvents in water was conducted by Park et al. (1998). The study was performed by preparing lysozyme-loaded PLGA micro-particles, using a single oil in a water emulsion technique. Some materials used on the experiment were dimethyl sulphoxide to solubilize the lysozyme and PLGA, while methylene chloride was used to generate emulsion drops and to solubilize the PLGA. The results showed that as the volume fraction of dimethyl sulphoxide in the co-solvent system increased, the encapsulation efficiency also increased, while the initial burst decreased. Also, another observation was that the increase on dimethyl sulphoxide resulted in an increase of particle sizes and a decrease in the density of the micro-particles. The authors concluded that the presence of dimethyl sulphoxide increased the hydrophilicity of the solvent system by allowing the fast extraction of the solvent into the continuous phase, which led to higher encapsulation efficiency and larger particle size.

2.7.4.3 Concentration of the polymer. Studies have shown that the encapsulation efficiency increases as the polymer concentration increases (Metha, Thanoo, & DeLuca, 1996). An example of this statement may be found in a study conducted by Mehta et al. (1996), where the encapsulation efficiency increased from 53.1% to 70.9%; the concentration of the polymer increased from 20.0 to 32.5%. Also, it has been observed that high viscosity and fast solidification of the dispersed phase can contribute to a reduced porosity of microcapsules (Schlicher, Postma, Zuidema, Talsma, & Hennick, 1997). The relationship between a higher polymer concentration and encapsulation efficiency may be interpreted in two ways: first, when the polymer is highly concentrated, the precipitation occurs faster on the surface of the dispersed phase, which prevents drug diffusion across the phase boundary (Rafati, Coombes, Adler, Holland, & David, 1997); and second, an increase of the polymer concentration will result in an

increase of the viscosity of the solution, which delays the drug diffusion within the polymer droplets (Bodmeir & McGinity, 1988).

2.7.4.4 Ratio of dispersed phase to continuous phase (DP/CP ratio). A study conducted by Mehta et al. (1996) concludes that the encapsulation efficiency and particle size increases as the volume of the continuous phases increases (Metha, Thanoo, & DeLuca, 1996). In this study, an increase in encapsulation efficiency is demonstrated as the ratio of the dispersed phase to continuous phases (DP/CP ratio), showing a decrease from 1/50 to 1/300 (Metha, Thanoo, & DeLuca, 1996). The presence of this large volume of continuous phases provides a high concentration of organic solvent to the solution across the phase boundary, which leads to a fast solidification of the microcapsules.

Sah performed a study to observe the effect of a continuous phase on microencapsulation efficiency by preparing micro-particles, using ethyl acetate as a solvent; the formation of the particles depended on the volume of the continuous phase (Sah, 1997). During the study, Sah observed that pouring 8mL of PLGA solution into 20 or 50mL of a water phase produced a well-disintegrated polymer solution in dispersed droplets. However, when he used 80 mL or more of continuous phase, the result was a fast-hardening and irregular formation of micro-particles. The author observed that using a large volume of continuous phase resulted in a sink condition for ethyl acetate and an instant extraction of the solvent. Thus, the particle size increased with an increase of the volume of continuous phase, due to the fast solidification of the polymer. The low bulk density of micro-particles generated from a low DP/CP ratio was an indicator of a higher porosity of the polymer matrix (Metha, Thanoo, & DeLuca, 1996). However, a study conducted by Jeyanthi et al. (1997) showed an increase in the porosity of micro-particles, as a higher DP/CP ratio was used (Jeyanthi, Mehta, Thanoo, & DeLuca, 1997). Mehta et al. (1996) explained that



this discrepancy reflects the fact that a low bulk density is not a true indicator of porosity, but it is an indicator of particle size (Metha, Thanoo, & DeLuca, 1996).

2.7.4.5 Rate of solvent removal. It has been shown that the method and rate of solvent removal influences the sollicitation rate of the dispersed phase, as well as the morphology of resulting micro-particles (Mehta, Jeyanthi, Calis, Thanoo, Burton, & DeLuca, 1994). Different ways to remove solvents may be utilized when using an emulsion-solvent evaporation/extraction method: The solvent can be removed by evaporation around its boiling point; or it can be extracted into the continuous phase. On the other hand, the removal of solvent also may be controlled by a temperature ramp and by a dilution medium in the latter.

In a study conducted by Mehta et al (1994), different micro-particles were prepared by the emulsification method, followed by different solvent removal methods. For the first removal method, a temperature-dependent process was used to remove methylene chloride by increasing the temperature from 15 to 40C at different rates. The result displayed micro-particles with a hollow core and a porous wall from this removal process. Also, it was observed that core sizes and wall thicknesses were dependent on the temperature ramp. A small core size was obtained by ramping the temperature in steps, from 15 to 25C and then to 40C; however, a thin wall and a hollow core were obtained from a rapid rise in the temperature. The authors explained that the appearance of hollow cores was due to the rapid expansion of methylene chloride entrapped within the solidified micro-particles. For the second removal method in extraction of solvent, the solvent was removed gradually and slowly by dilution of the continuous phase, which resulted in softer micro-particles for a longer period of time. For the extraction method, highly porous micro-particles without hollow cores were obtained. Another study conducted by Li et al. (1995) determined that the porosity of micro-particles was a function of the amount of water diffused

into the dispersed phase from the continuous phase (Li, Anderson, Metha, & DeLuca, 1995). The observation made by Li et al. explained that the high porosity of the micro-particles produced was due to the slow solidification of the micro-particles.

## **2.8 Synthesis of microcapsules containing rejuvenator**

The encapsulation of a rejuvenator serves to place a rejuvenator deep into asphalt in order to extend the service life of asphalt pavement. Two different studies about synthesis and the characterization of microcapsules containing a rejuvenator will be reviewed.

### **2.8.1 Synthesis and physicochemical properties of high compact microcapsules containing rejuvenator applied in asphalt**

The study, conducted by Su and Schlangen (2012), purposed to synthesize and characterize microcapsules containing a rejuvenator by in-situ polymerization of a methanol-melamine-formaldehyde prepolymer. The authors applied a two-step coacervation to enhance thermal stability; furthermore, the authors used styrene-maleic anhydride to enhance compactability of the microcapsules. Parameters such as particle size, shell thickness, shell density and encapsulation efficiency were optimized by adjusting the stirring rate and core/shell ratio. Figure 2.16 shows schematic drawings for the fabrication process of the microcapsules synthesized.

**2.8.1.1 Effect of stirring rate.** The study determined that stirring rates determine core particle size rather than microcapsule size, which at the same time is influenced by shell thickness as well. Figure 2.17 shows the average diameters of microcapsules with different stirring rates between  $1000\text{--}6000\text{ r}\cdot\text{min}^{-1}$  and different core/shell ratios. Results showed that with an increase of the stirring rate, the average diameter decreased from 23.5 to 5.9  $\mu\text{m}$ . The study concluded that the average size was influenced by the core material dispersal speed.

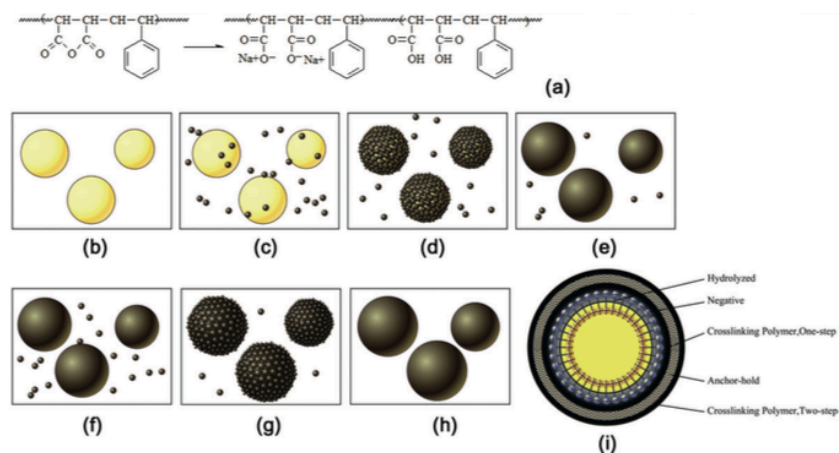


Figure 2.16. Fabrication process of microcapsules containing rejuvenator: (a) Chemical structure of SMA copolymer and hydrolysis copolymer, (b-e) first step coacervation, (f-h) second step coacervation; and (i) microstructure of microcapsules (Su & Schlagen, 2012)

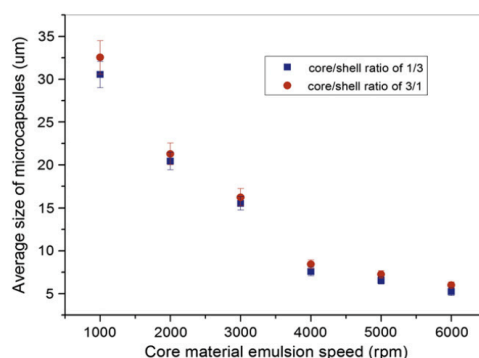


Figure 2.17. Average diameter of microcapsules (Su & Schlagen, 2012)

2.8.1.2 Thermal stability of microcapsules . Thermal stability of microcapsules was evaluated by determining the weight loss between 337°C and 469 °C. The study observed the evaporation of the core material under high temperature. Figure 2.18a shows the decrease in mass due the evaporation of the core material as the temperature increased. Also, the thermal stability study of the MMF prepolymer determined a degradation temperature of 192 °C. The final thermal

degradation of MMF prepolymer is observed at about 265 °C. Figure 2.18b shows the loss on mass on the microcapsules due the degradation of MMF prepolymer as the temperature increased.

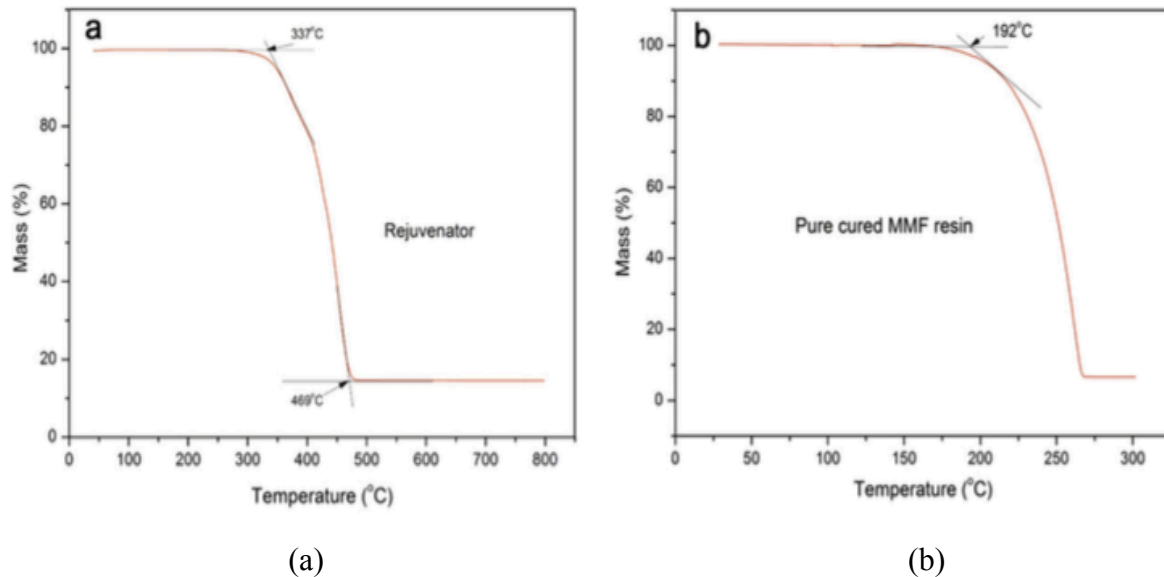


Figure 2.18. Thermal Stability of Microcapsules: (a) Mass loss due the oil evaporation and (b) Mass loss due the degradation of MMF prepolymer (Su & Schlangen, 2012)

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## **CHAPTER 3-SUPERPAVE PERFORMANCE GRADING AND MICROENCAPSULATION PROCESS**

### **3.1. INTRODUCTION**

Highways assume an important role in modern society by providing an excellent resource for the mobilization of people, goods and services. The United States has more than 2.6 million miles of paved roads and highways, and 93 percent of those are surfaced with asphalt. As a result, the large percentage of asphalt roads through the country makes the maintenance of asphalt an important aspect in regard to innovations.

The serviceability and the quality of asphalt are most affected by cracking (Wu Z. , Mohammad, Wang, & Mull, 2005). Cracking occurs when the binder on the asphalt becomes more brittle, based on an increase in the stiffness coupled with the reduction on the relaxation capacity (Yildirim, 2007). Some of the more common solutions for asphalt deterioration are the use of seal coatings and rejuvenators.

Asphalt rejuvenators are shown to be the only solution that partially restores the properties of the pavement (Karlsson & Isacson, Material-related aspects of asphalt recycling—state of the art , 2006). The purpose of the asphalt rejuvenator is to repair the binding property of asphalt, with the goal of bringing back the asphaltenes/maltenes ratio (Shen, Amirkhanian, & Miller, 2007).

However, the use of rejuvenators presents a disadvantage by causing a penetration into the asphalt, which is necessary to repair (Chiu & Lee, 2006). Therefore, encapsulation methods were studied as alternative methods in order to incorporate the use of rejuvenators into asphalt pavements (Garcia, Schlangen, van de Ven , & Sierra-Beltrán , 2010).

The encapsulation of a rejuvenator may be applied as a self-healing concept. The use of self-healing microencapsulation was investigated to enhance the efficiency of self-healing processes (Aissa, Therriault, Haddad, & Jamroz, 2012). Microcapsules containing a rejuvenator can be broken by micro-cracks; the released rejuvenator then seals the micro-cracks and permeates the surrounding bitumen. The restoration of the binder properties on the asphalt thus serves to extend the serviceability time of highways.

In any encapsulation process, certain properties of the microcapsules, such as size distribution, encapsulation ratios, and non-biodegradable property must be taken into account, due to their influence on the performance of the microcapsules (Zhang, Xing, Shi, & Du, 2011). Hence, the study of microcapsules properties becomes highly important if one chooses to achieve an enhanced, self-healing mechanism.

## **3.2 Methodology**

### **3.2.1 Rejuvenating Efficiency of the Core Material**

The core material to be evaluated for the synthesis of self-healing microcapsules is PennzSuppress D as a Heavy Resin. The alteration on the binder rheological properties, due to the effects of PennzSuppress D, was examined prior to preparation of the microcapsules. Asphalt binder blends mixed with the rejuvenator were prepared to assess the effects of this heavy resin on the binder aging mechanisms. Two binder types, classified as PG 70-22 and PG 76-22, were blended with the rejuvenator at a dosage rate of 30% by weight of the binder. The blends were prepared at a mixing temperature of 163°C. Two different aging mechanisms were simulated: short-term aging was simulated using the Rolling-Thin Film Oven (RTFO) and long-term aging was simulated using the Pressure Aging Vessel (PAV). The evaluation of rheological properties of prepared blends was conducted using fundamental rheological tests such as dynamic shear

rheometry, rotational viscosity, and bending beam rheometer; to form a comparison between the Superpave Performance Grades (PG) of the modified blends relative to the unmodified binder. The characterization of binders was conducted using the PG grading systems described in AASHTO M 320-09 (Standard Specification for Performance-Graded Asphalt Binder). Figure 3.1 show the schematic process followed to evaluate the effectiveness of PennzSuppress D on virgin binders.

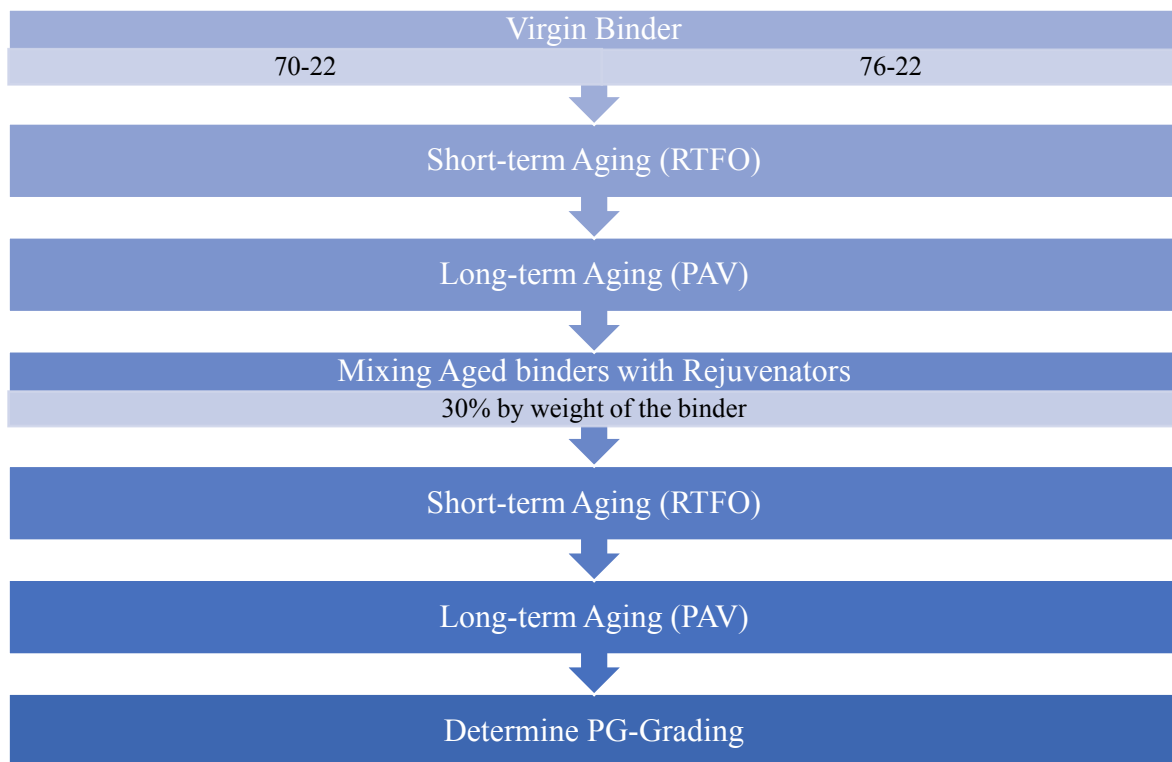


Figure 3.1 Methodologies to Assess the Effectiveness of Rejuvenator on Virgin Binders

An aged binder extracted from Recycled Asphalt Pavement (RAP) and sampled from a local contractor, was also blended with the rejuvenator to evaluate the effect of the heavy resin. The procedure to extract the reclaimed asphalt binder was performed in accordance AASHTO T 164, “Standard Method of Test for Quantitative Extraction of Asphalt Binder from Hot Mix Asphalt HMA – Method A.” Afterwards, the solution of solvent (trichloroethylene) and asphalt binder

obtained from AASHTO T 164 – Method A was then distilled to a point where most of the solvent was removed; finally, carbon dioxide gas was introduced to remove all traces of trichloroethylene. This procedure was conducted in accordance with AASHTO R 59, “Standard Practice for Recovery of Asphalt Binder from Solution by Abson Method.” The recovered asphalt binder was then blended with the rejuvenator at a 30% and 40% dosage rate. Figure 3.2 show the schematic process followed to evaluate the effectiveness of PennzSuppress D on Reclaimed Asphalt Pavement (RAP).

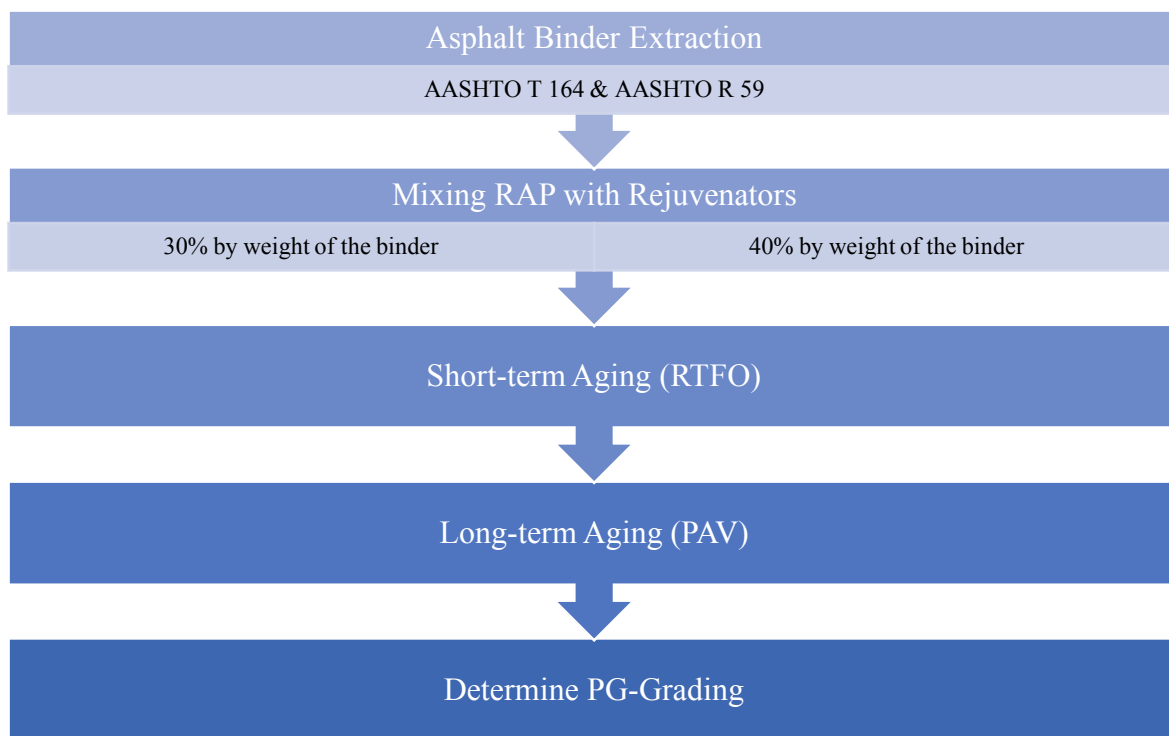


Figure 3.2 Procedures to Assess the Effectiveness of Rejuvenator on RAP

### 3.2.2 Microcapsules Preparation Procedure

Microcapsules were synthesized in this study via in-situ polymerization, using Methanol-Melamine-Formaldehyde, which resulted in single-walled microcapsules. The single-walled

microencapsulation was synthesized through a double polymerization process to enhance rigidity and toughness of shell (Su & Schlangen, 2012). The use of Methanol-Melamine-Formaldehyde as the shell material has been shown to increase the thermal stability and the mechanical properties of microcapsules (Sun & Zhang, 2002). A number of production parameters affect the encapsulation reaction: (1) temperature at which the emulsion is heated; (2) the choice of catalyst and the respective concentration; (3) the amount of time allocated for the reaction; (4) the agitation rate; and (5) the choice of the core material. As shown in Table 3.1, the experimental program evaluated the effects of the agitation rate (in revolutions per minute [rpm]), heating temperature (in degrees Celsius), and the EMA concentration. In the experimental program, each production parameter was varied while the others were kept constant at the reference levels. The reference values were selected at an agitation rate of 800 rpm, with heating at 75°C and an EMA concentration of 3%.

Table 3.1 Experimental Test Matrix for Microcapsules Preparation

Variables		
Agitation Rate (rpm)	Temperature (°C)	Concentration of EMA (%)
800	75	0.5
800	75	2
800	75	3
800	75	4
800	75	8
800	70	3
800	80	3
500	75	3
2000	75	3

### 3.2.3 Microcapsules Synthesis

The single-walled microencapsulation procedure was adapted from Su and Schlangen (Su & Schlangen, 2012). A mixture of 100 ml of de-ionized (DI) water and 3% concentration of EMA copolymer solution were combined in a 500 ml beaker. The solution was agitated by an overhead stirrer (IKA RW-20 and Caframo BDC6015 respectively), and was laid on top of a ceramic hot plate at 50°C. Under agitation at 800 rpm, 8g of the core material were dissolved. The pH was then adjusted drop-wise to 4-5 by using sodium hydroxide and/or hydrochloric acid solutions. In another beaker, where 20 ml of de-ionized (DI) water was used to dissolve 16g of Modified-Melamine-Formaldehyde (MMF). The pH of the MMF solution was adjusted to 4-5 by using sodium hydroxide and/or hydrochloric acid solutions. Once the pH was adjusted, it was added to the main solution slowly with a ratio of 1 mL/minute. After allowing 1 hour of mixing of the main solution at 50°C, the temperature was raised to 60°C by a rate of 1°C/min. Then, another MMF solution was prepared with the same characteristics described before. After adding the second MMF solution, the temperature was raised to 75°C by a rate of 1°C/min. Afterward, the main solution was mixed for 1.5 hour. Deionized water was added through the heating time to maintain the desired water level. Once the heating was complete, the solution was cooled down and vacuum-filtered. Figure 3.3 shows the schematic process for the single-walled microencapsulation process.

### 3.2.4 Scanning Electron Microscopy

A scanning electron microscope, a FEI Quanta 3D FEG Dual Beam SEM/FIB, was in this study to evaluate the size and morphology of the produced microcapsules. The microcapsules were sprinkled on top of a double-sided tape attached to a pin stub specimen mount. The samples

were then sputter-coated with platinum for four minutes before imaging them under a secondary electron mode at an accelerating voltage of 10 kV.

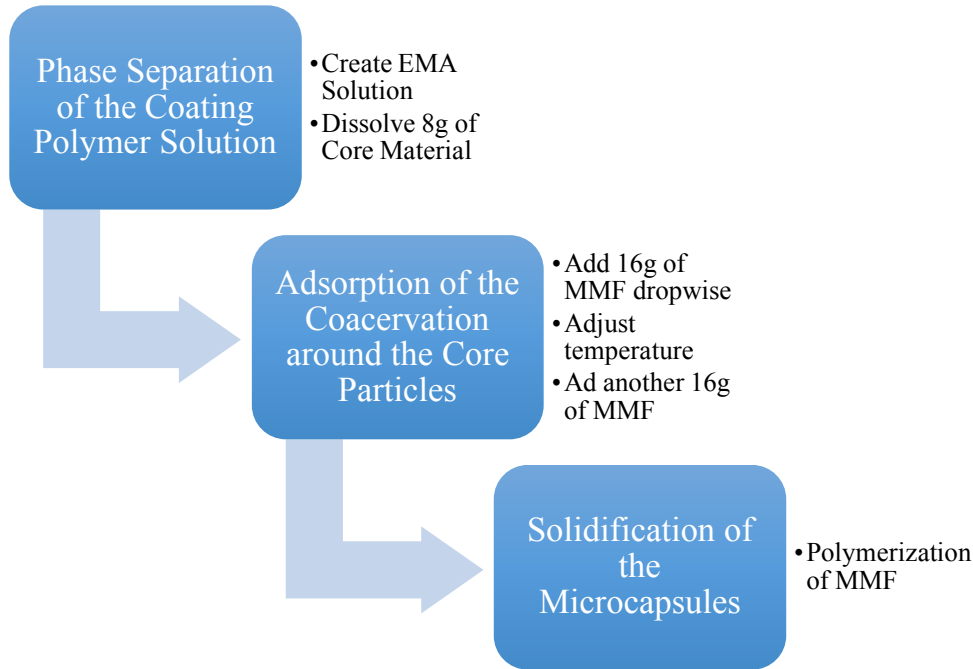


Figure 3.3 Schematic process for the single-walled microencapsulation process.

### 3.3 Results

#### 3.3.1 Effects of Rejuvenator on Rheological Properties

The evaluation of the effects of PennzSuppress D on the rheological properties of asphalt binder blends was performed by preparing six blends of asphalt binders to compare with the unmodified binder. Table 3.2 (a and b) presents the measured rheological properties of the binder blends, based on laboratory testing conducted by using a rotational viscometer, DSR, and BBR. Results are presented for six binder blends: Conventional PG 70-22, Aged PG 70-22, Aged PG 70-22 + 30% PennzSuppress D, PG 76-22, Aged PG 76-22, Aged PG 76-22 + 30% PennzSuppress D. The procedure followed to assess the effectiveness of the rejuvenator was showed on Figure 3.1.



The aged binder samples were prepared by processing the virgin binder in RTFO followed by PAV. The residue from PAV then was blended with the rejuvenator and tested according to AASHTO M 320-09.

The aging of virgin binders resulted in the stiffening at high temperature and the loss of one grade at low temperature; i.e., from PG 70-22 to PG 82-16 and from PG 76-22 to PG 94-16 as Table 3.2 (a and b) shows. Results shown that this heavy resin, PennzSuppress D, was more effective on the aged 70-22 by reducing its stiffness at high temperature and at low temperature; i.e. from PG 82-16 to PG 76-22. For the aged 76-22, PennzSuppress D was shown to have an effect only on the low temperature by a reduction of one grade, i.e., from PG 94-16 to PG 94-22. Similar trends were observed with the asphalt binder extracted from RAP. As shown in Table 3.3, the PennzSuppress was only effective in reducing the high temperature of the aged binder from PG 118-X to PG 112-X and from PG 118-X to PG 106-X. At low temperatures, there was an improvement on numbers, yet they were not sufficient to affect the PG of the reclaimed asphalt binder.

3.3.1.1 Gel Permeation Chromatography (GPC). The Gel Permeation Chromatography is used to determine the asphalt molecular weight distributions, i.e. the percentage of asphaltenes and maltenes that are present in an asphalt binder. Determining the percentage of asphaltenes and maltenes before and after blending the asphalt binders with the rejuvenator provides information about the efficiency of the rejuvenator to restore asphaltenes/maltenes ratio. In this study, the GPC was performed on the Recycle Asphalt Pavement (RAP) to assess the efficiency of PennzSuppress D to reestablish the asphaltenes/maltenes. The GPC results are shown in table 3.4. In table 3.4, it can be observed that the tested commercial product did not have any effect on the percentage of asphaltenes and maltenes presented in the asphalt binder blends.

Table 3.2 Rheological Test Results of (a) PG 70-22 Asphalt Binder Blends and (b) PG 76-22 Asphalt Binder Blends

(a)

Test	Specification	Temperature °C	70-22	RTFO+PAV (AGED)	AGED+ 0.3 PennzSuppress
Test on Original Binder					
RV at 20 rpm - AASHTO T316	<3.0 Pa.s	135 °C	0.935 Pa.s	1.23 Pa.s	1.17 Pa.s
DSR ( $G^*/\sin\delta$ ), 10 rad/s, AASHTO T315	>1.0 kPa	70 °C	1.63 kPa	6.06 kPa	3.24 kPa
DSR ( $G^*/\sin\delta$ ), 10 rad/s, AASHTO T315	>1.0 kPa	76 °C	0.85 kPa	2.48 kPa	1.585 kPa
Test on RTFO					
DSR ( $G^*/\sin\delta$ ), 10 rad/s, AASHTO T315	>2.2 kPa	70 °C	2.98 kPa	12.5 kPa	5.96 kPa
DSR ( $G^*/\sin\delta$ ), 10 rad/s, AASHTO T315	>2.2 kPa	76 °C	1.54 kPa	6.32 kPa	2.905 kPa
Test on RTFO+PAV					
DSR ( $G^* \cdot \sin\delta$ ), 10 rad/s, AASHTO T315	<5000 kPa	25 °C	4490 kPa	6827 kPa	887.5 kPa
DSR ( $G^* \cdot \sin\delta$ ), 10 rad/s, AASHTO T315	<5000 kPa	28,22 °C	6630 kPa (22 °C)	5170 kPa (28 °C)	1150 kPa (22 °C)
BBR-S- AASHTO T313	<300 MPa	-6 °C	-	108 MPa	-
BBR-S- AASHTO T313	<300 MPa	-12 °C	199 MPa	240 MPa	148.5 MPa
BBR-S- AASHTO T313	<300 MPa	-18 °C	284 MPa	-	246 MPa
BBR-m- AASHTO T313	>0.3	-6 °C	-	0.367	-
BBR-m- AASHTO T313	>0.3	-12 °C	0.301	0.284	0.3
BBR-m- AASHTO T313	>0.3	-18 °C	0.336	-	0.277
PG- Grading	-----	-----	70-22	82-16	76-22

(b)

Test	Specification	Temperature °C	76-22	RTFO+PAV (AGED)	AGED+ 0.3 PennzSuppress
Test on Original Binder					
RV at 20 rpm - AASHTO T316	<3.0 Pa.s	135 °C	0.895 Pa.s	2.14 Pa.s	4.022 Pa.s
DSR ( $G^*/\sin\delta$ ), 10 rad/s, AASHTO T315	>1.0 kPa	76 °C	1.71 kPa	7.27 kPa	6.49 kPa
DSR ( $G^*/\sin\delta$ ), 10 rad/s, AASHTO T315	>1.0 kPa	82 °C	0.995 kPa	4.26 kPa	3.61 kPa
Test on RTFO					
DSR ( $G^*/\sin\delta$ ), 10 rad/s, AASHTO T315	>2.2 kPa	76 °C	2.61 kPa	9.3 kPa	7.44 kPa
DSR ( $G^*/\sin\delta$ ), 10 rad/s, AASHTO T315	>2.2 kPa	82 °C	1.53 kPa	5.37 kPa	4.12 kPa
Test on RTFO+PAV					
DSR ( $G^* \cdot \sin\delta$ ), 10 rad/s, AASHTO T315	<5000 kPa	22, 25 °C	4450 kPa (22 °C)	4540 kPa (25 °C)	5930 kPa (25 °C)
DSR ( $G^* \cdot \sin\delta$ ), 10 rad/s, AASHTO T315	<5000 kPa	19, 28 °C	5040 kPa (19 °C)	6160 kPa (28 °C)	4390 kPa (28 °C)
BBR-S- AASHTO T313	<300 MPa	-6 °C	-	101 MPa	93.2 MPa
BBR-S- AASHTO T313	<300 MPa	-12 °C	151 MPa	198 MPa	204 MPa
BBR-S- AASHTO T313	<300 MPa	-18 °C	316 MPa	-	-
BBR-m- AASHTO T313	>0.3	-6 °C	-	0.350	0.355
BBR-m- AASHTO T313	>0.3	-12 °C	0.342	0.267	0.3
BBR-m- AASHTO T313	>0.3	-18 °C	0.282	-	-
PG- Grading	-----		76-22	94-16	94-22

Table 3.3 Rheological Test Results of Extracted Asphalt Binder Blends

Test	Specification	Temperature °C	RAP	RAP + 0.3 Pennzsuppress	RAP + 0.4 Pennzsuppress
Test on Original Binder					
RV at 20 rpm -AASHTO T316	<3.0 Pa.s	135 °C	10.59 Pa.s	9.76 Pa.s	9.21 Pa.s
DSR ( $G^*/\sin\delta$ ), 10 rad/s	>1.0 kPa	106 °C	2.43 kPa	1.715 kPa	1.59 kPa
DSR ( $G^*/\sin\delta$ ), 10 rad/s	>1.0 kPa	112 °C	1.39 kPa	0.65 kPa	0.779 kPa
DSR ( $G^*/\sin\delta$ ), 10 rad/s	>1.0 kPa	118°C	0.79 kPa	-	-
Test on RTFO					
DSR ( $G^*/\sin\delta$ ), 10 rad/s	>2.2 kPa	106 °C	10.047 kPa	4.31 kPa	6.90 kPa (88 °C)
DSR ( $G^*/\sin\delta$ ), 10 rad/s	>2.2 kPa	112 °C	5.301 kPa	2.255 kPa	3.325 kPa (94 °C)
DSR ( $G^*/\sin\delta$ ), 10 rad/s	>2.2 kPa	118 °C	3.083 kPa	1.3 kPa	1.645 kPa (100 °C)
Test on RFTO+PAV					
DSR ( $G^* \cdot \sin\delta$ ), 10 rad/s	<5000 kPa	31, 43 °C	6370 kPa (43 °C)	6350 kPa (31 °C)	7490 kPa (31 °C)
DSR ( $G^* \cdot \sin\delta$ ), 10 rad/s	<5000 kPa	34, 46 °C	5240 kPa (46 °C)	5590 kPa (34 °C)	6140 kPa (34 °C)
DSR ( $G^* \cdot \sin\delta$ ), 10 rad/s	<5000 kPa	37, 49 °C	4180 kPa (49 °C)	4920 kPa (37 °C)	4870 kPa (37 °C)
BBR-S- AASHTO T313	<300 MPa	-0 °C	182	222	166
BBR-S- AASHTO T313	<300 MPa	-6 °C	Sample Broke	442	249
BBR-m- AASHTO T313	>0.3	-0 °C	0.215	0.274	0.284
BBR-m- AASHTO T313	>0.3	-6 °C	Sample Broke	0.225	0.238
PG- Grading			118-X	112-X	106-X

Table 3.4 GPC Calculations for RAP

Sample name	High molecular weight %	Asphaltene%	Maltene %
	1000K-19K	19K-3K	< 3K
RAP	5.53	30.58	63.89
RAP+30% Rejuvenator	5.66	30.46	63.88
RAP+40% Rejuvenator	6.23	30.74	63.03

### 3.3.2 Microencapsulation of PennzSuppress D as a Rejuvenator

In this part of the study, the microencapsulation process was optimized by varying the production parameters and determining the effects of each parameter on the morphology and diameter of the microcapsules. The analyses of morphology, shell thickness and diameter were based on SEM images. Furthermore, the yield rate was calculated based on the following equation:

$$\% \text{Yield Rate} = \frac{\text{Weight of microcapsules}}{\text{Weight of ingredients}} \times 100 \quad (1)$$

Table 3.5 presents a summary of the diameter measurements and yield rates for the different preparation procedures. As shown in this table, the yield rates were lower than expected, indicating that the proposed preparation procedure must be modified to increase them. The effects of agitation rate, temperature, and EMA concentration on the prepared microcapsules are discussed in the following sections.

### 3.3.3 Morphology and Diameter of the Prepared Microcapsules

**3.3.3.1 Effect of Agitation Rate.** Figure 3.4 shows the effect of agitation rate on the mean diameter of microcapsules. An inverse relationship between the agitation rate and mean diameter have been stated in previous studies (Ovez, Citak, Oztemel, Balbas, Peker, & Cakir, 1997). In the referred study, a reduction in the diameter of the microcapsules was reported as the agitation rate

was increased. For the present experiment, this relationship was observed; however, the decrease on diameter from 800rpm to 2000rpm is not significant enough to determine whether the rpm has a direct effect on the size of microcapsules. Figure 3.5 shows SEM pictures with different agitation rates. Further, it was observed that the morphology of microcapsules decreases in quality for both 500rpm and 2000rpm. In Figure 3.5, it is possible to observe that microcapsules are not forming appropriately; as a result, the material becomes agglomerated.

Table 3.5 Diameter Measurements and Yield Rates for Single Walled Microcapsules

Production Parameters <sup>1</sup>	DIAMETER STATS (μm)				
	Mean	Std. Deviation	Max	Min	Yield Rate (%)
800, 75, 0.5	2.690	0.454	4.488	1.934	52.5%
800, 75, 2	3.455	0.829	5.707	1.821	63.9%
800, 75, 3	2.854	0.816	5.316	1.339	63.1%
800, 75, 4	2.640	0.498	4.16	1.726	56.5%
800, 75, 8	2.756	0.580	4.354	1.517	64.8%
800, 70, 3	3.046	0.503	4.486	1.767	64.1%
800, 80, 3	2.243	0.331	3.087	1.49	65.7%
500, 75, 3	3.500	0.918	5.762	1.765	64.7%
2000, 75, 3	2.814	1.183	5.825	1.318	49.6%

<sup>1</sup> Agitation (rpm), Temperature (°C), and EMA Concentration (%)

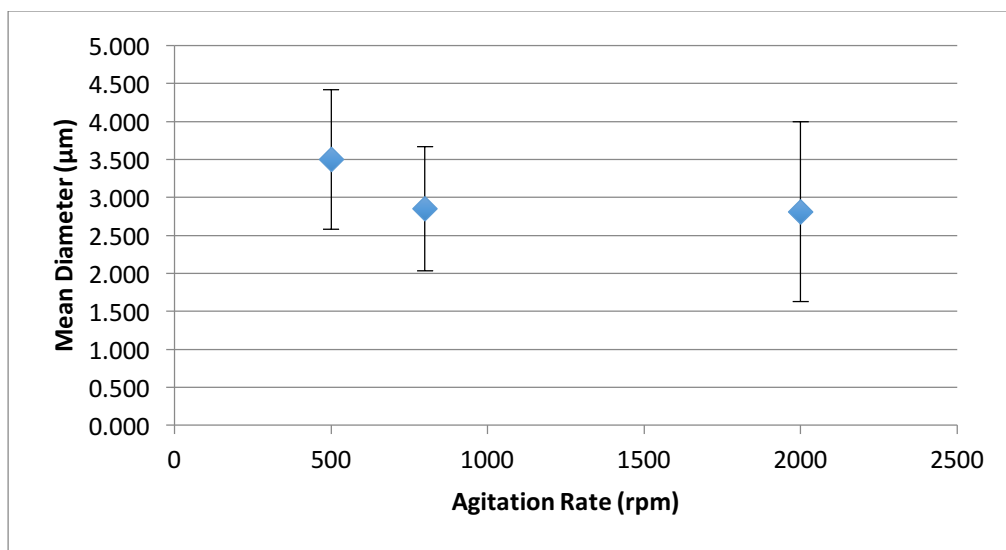


Figure 3.4. Effects of Agitation Rate on the Diameter of s Single-walled Microcapsules

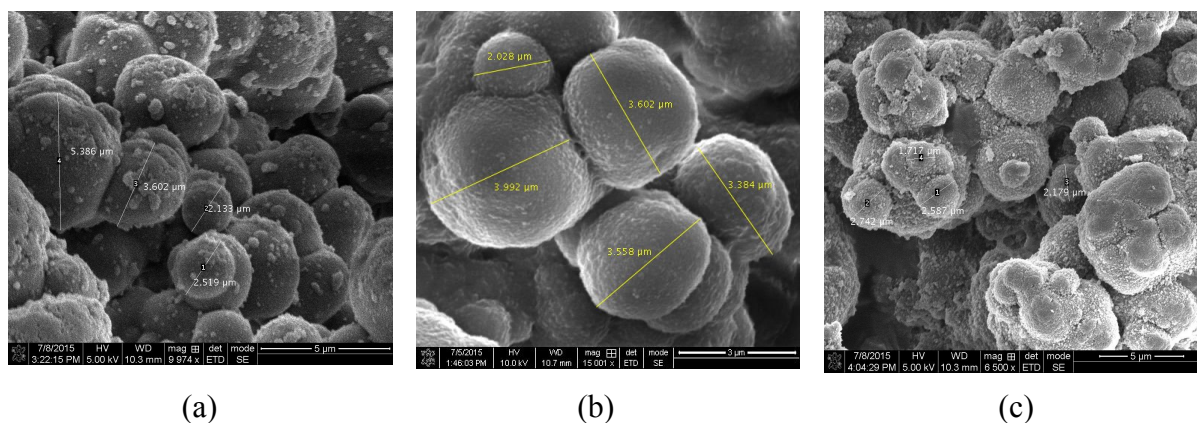


Figure 3.5. Effects of Agitation Rate on the Diameter of Microcapsules (a) 500 rpm, (b) 800 rpm, and (c) 2,000 rpm

3.3.3.2 Effects of Temperature. Figure 3.6 displays the effect of temperature on the mean diameter of microcapsules. Based on the results, it may be implied that the temperatures affect the size of diameter. As the temperature increases, the microcapsule size decreases. Figure 3.7 shows SEM pictures with different heating temperatures during the microencapsulation process. Also, it is interesting to notice that when the temperature dropped to 70 °C, it was possible to

observe many broken microcapsules. The broken microcapsules may happen due to the fact that the Modified-Melamine-Formaldehyde (MMF) requires high temperatures to polymerize.

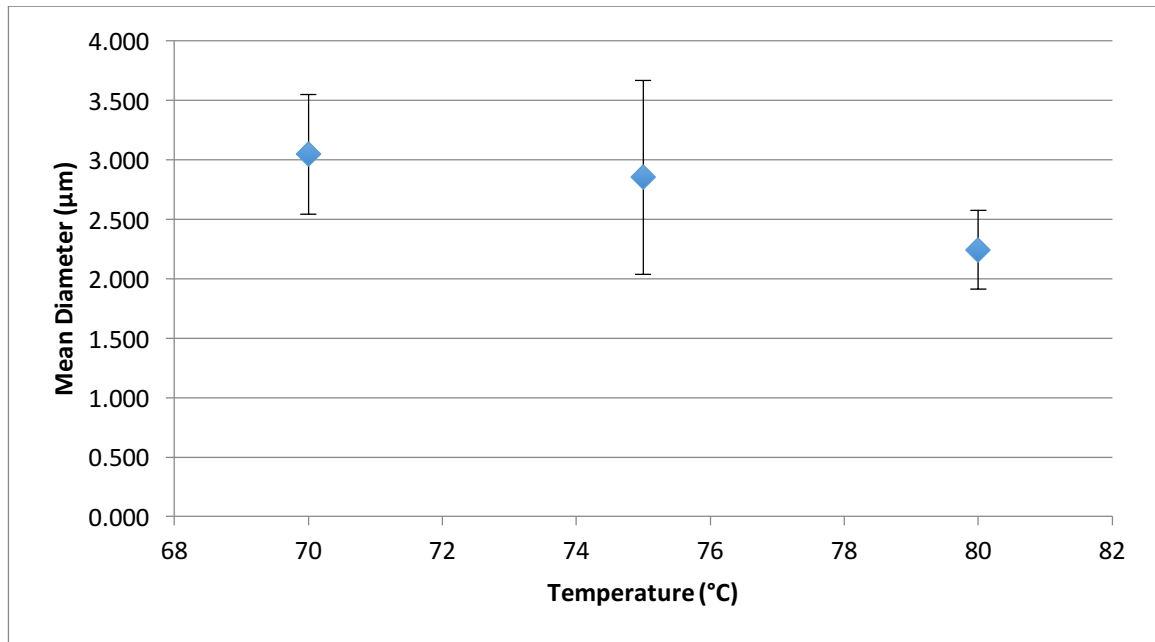


Figure 3.6. Effects of Temperature on the Diameter of s Single-walled Microcapsules

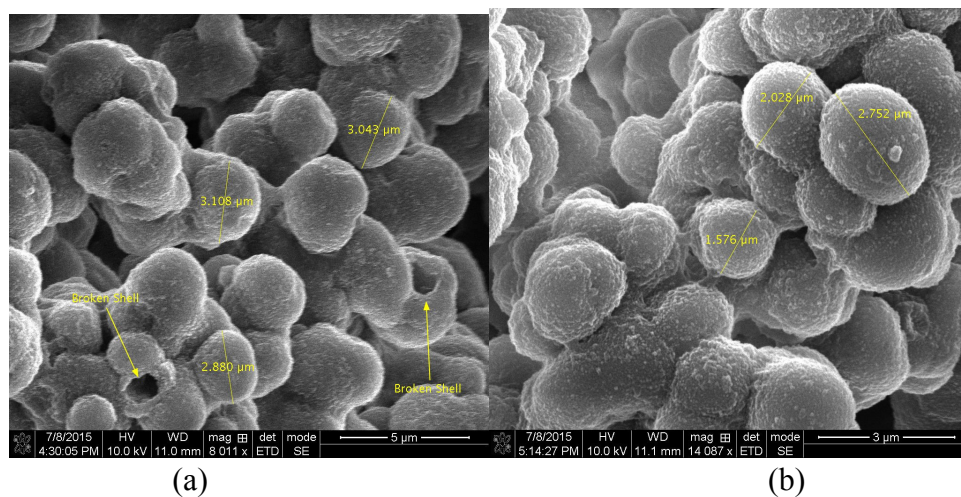


Figure 3.7. Effects of Temperature on the Diameter of Microcapsules (a) 70 °C and (b) 80 °C



3.3.3.3 Effects of EMA Concentration. Figure 3.8 shows the effect of EMA concentration on the mean diameter of microcapsules. Based on these results, the EMA concentration has no direct effect on the size of microcapsules. However, in the shell thickness measurements, one expects to see an increased shell thickness as the EMA concentration increases. Figure 3.9 shows SEM pictures with different EMA concentrations.

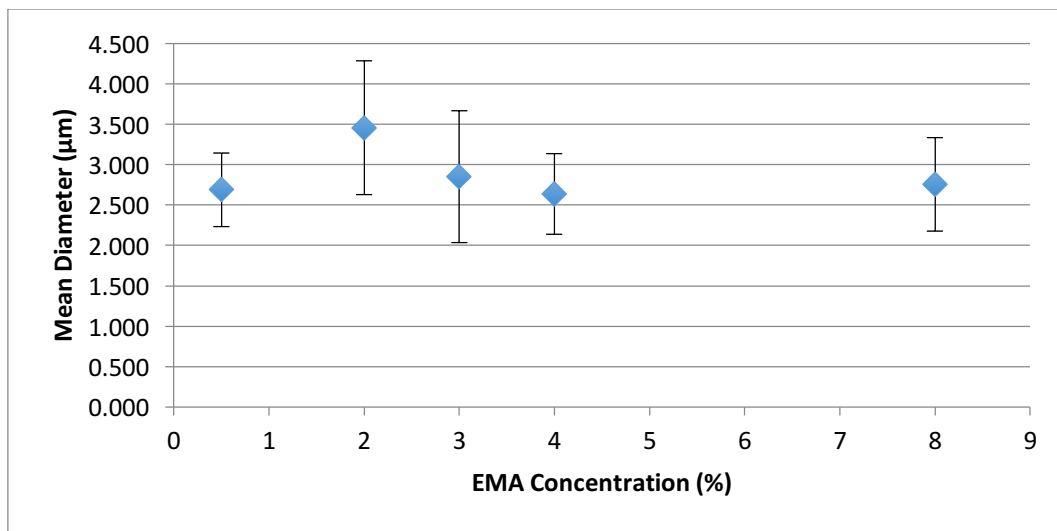
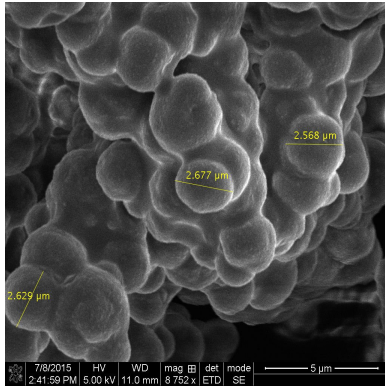


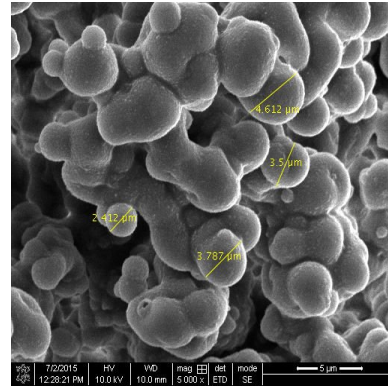
Figure 3.8. Effects of EMA Concentration on the Diameter of s Single-walled Microcapsules

### 3.3.4 Shell Thickness of the Prepared Microcapsules

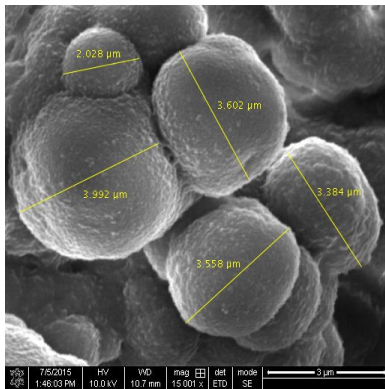
3.3.4.1 Effects of Agitation Rate. Figure 3.10 shows the effect of agitation rates on the measured microcapsule's shell thickness. Based on Figure 3.10, it may be determined that the shell thickness will increase by increasing the agitation rate, as shown between 800rpm and 2000rpm. However, the large standard deviation found in the variation of 2000 rpm may be the reason why there is a decrease in shell thickness between 500rpm and 800rpm. SEM pictures for this variation may be found on Figure 3.11.



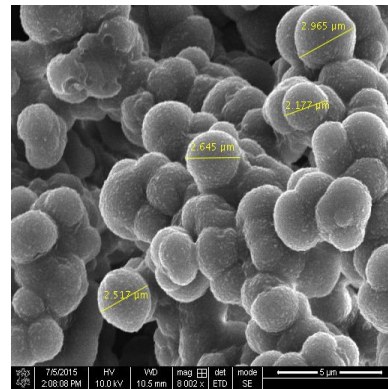
(a)



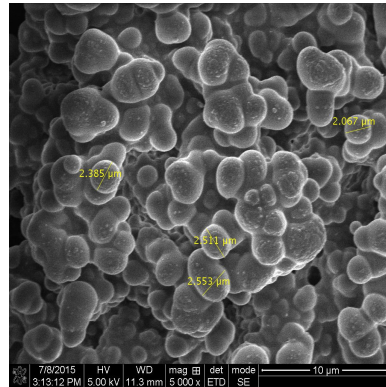
(b)



(c)



(d)



(e)

Figure 3.9. Effects of EMA Concentration on the Diameter of Microcapsules (a) 0.5%, (b) 2%, (c) 3%, (d) 4%and (e) 8%

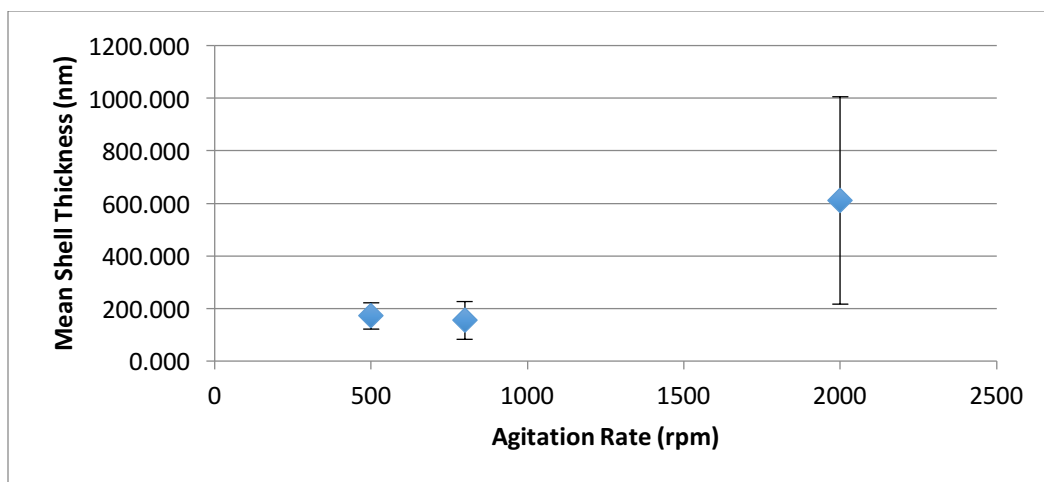
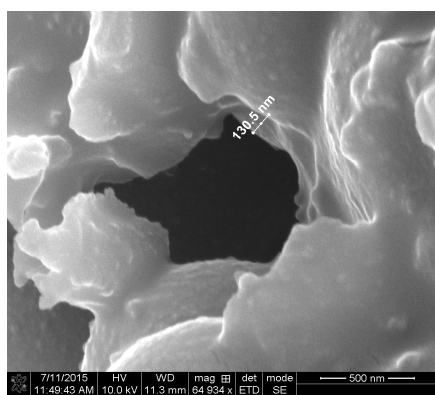
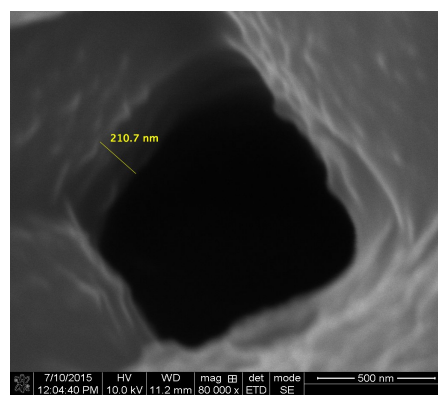


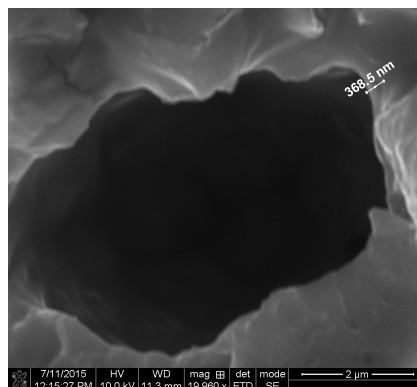
Figure 3.10. Effects of Agitation Rate on Single-walled Microcapsules Shell Thickness



(a)



(b)



(c)

Figure 3.11. Effects of Agitation Rate on the Shell Thickness of Microcapsules (a) 500 rpm, (b) 800 rpm, and (c) 2,000 rpm

3.3.4.2 Effects of Temperature. Figure 3.12 shows the effect of temperature on the shell thickness of the microcapsules. Based on the results, the shell thickness becomes thinner as the heating temperature increases. Figure 3.13 shows SEM pictures with different heating temperatures during the microencapsulation process.

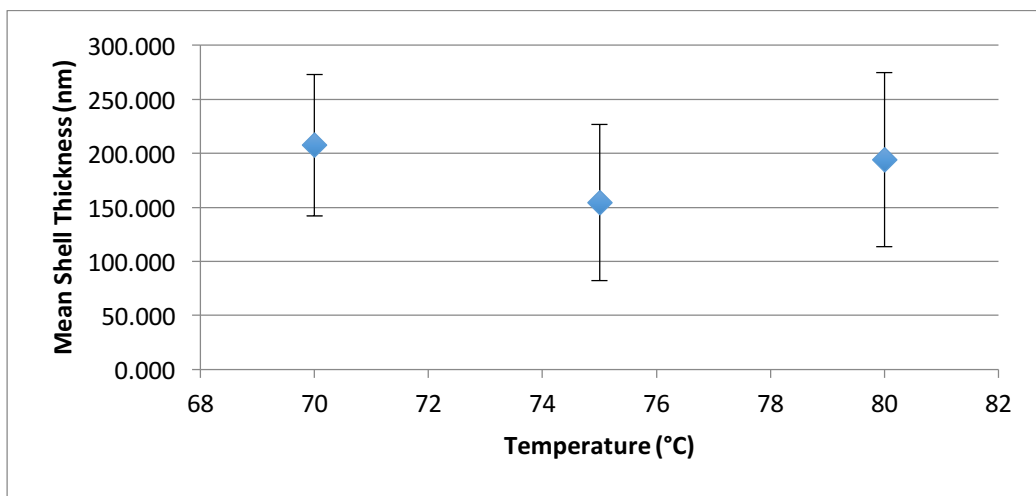


Figure 3.12. Effects of Temperature on Single-walled Microcapsules Shell Thickness

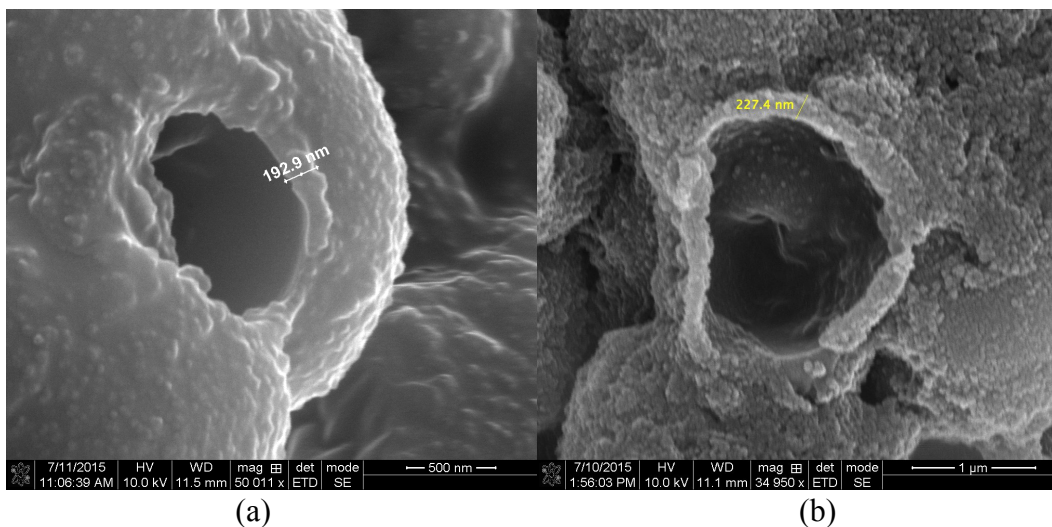


Figure 3.13. Effects of Temperature on the Shell Thickness of Microcapsules (a) 70 °C and (b) 80 °C

3.3.4.3 Effects of EMA Concentration. Figure 3.14 shows the effect of EMA concentration on the shell thickness of microcapsules. It was expected to see an increase in shell thickness as the EMA concentration increased. However, as may be observed, the thickest shell can be found at EMA=8%; there is a decrease in shell thickness between EMA=4% and EMA3%. Figure 3.15 shows SEM pictures with different EMA concentrations.

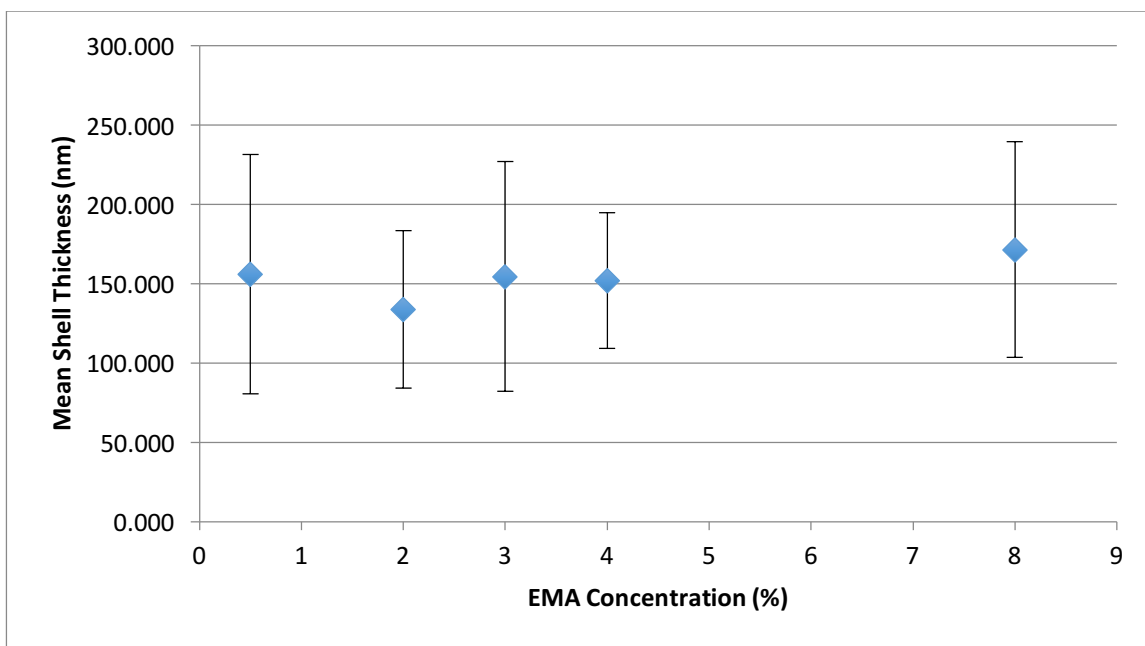


Figure 3.14. Effects of EMA Concentration on Single-walled Microcapsules Shell Thickness

### 3.3.5 Optimum Preparation Procedure for PennzSuppress D Microcapsules

Parameters such as agitation rate, heating temperature, and EMA concentrations were varied on the synthesis of self-healing microcapsules to determine optimum preparation procedure. For the evaluated microencapsulation process, an agitation rate of 800 rpm, a heating temperature of 75°C, and an EMA concentration of 3% were selected as the optimum conditions for the microencapsulation procedure. Those parameters were selected based on the size, uniformity,

and quality of the produced microcapsules. The selected procedure did not have the highest yield rate efficiency, but the difference was minimal between the highest yield rate results.

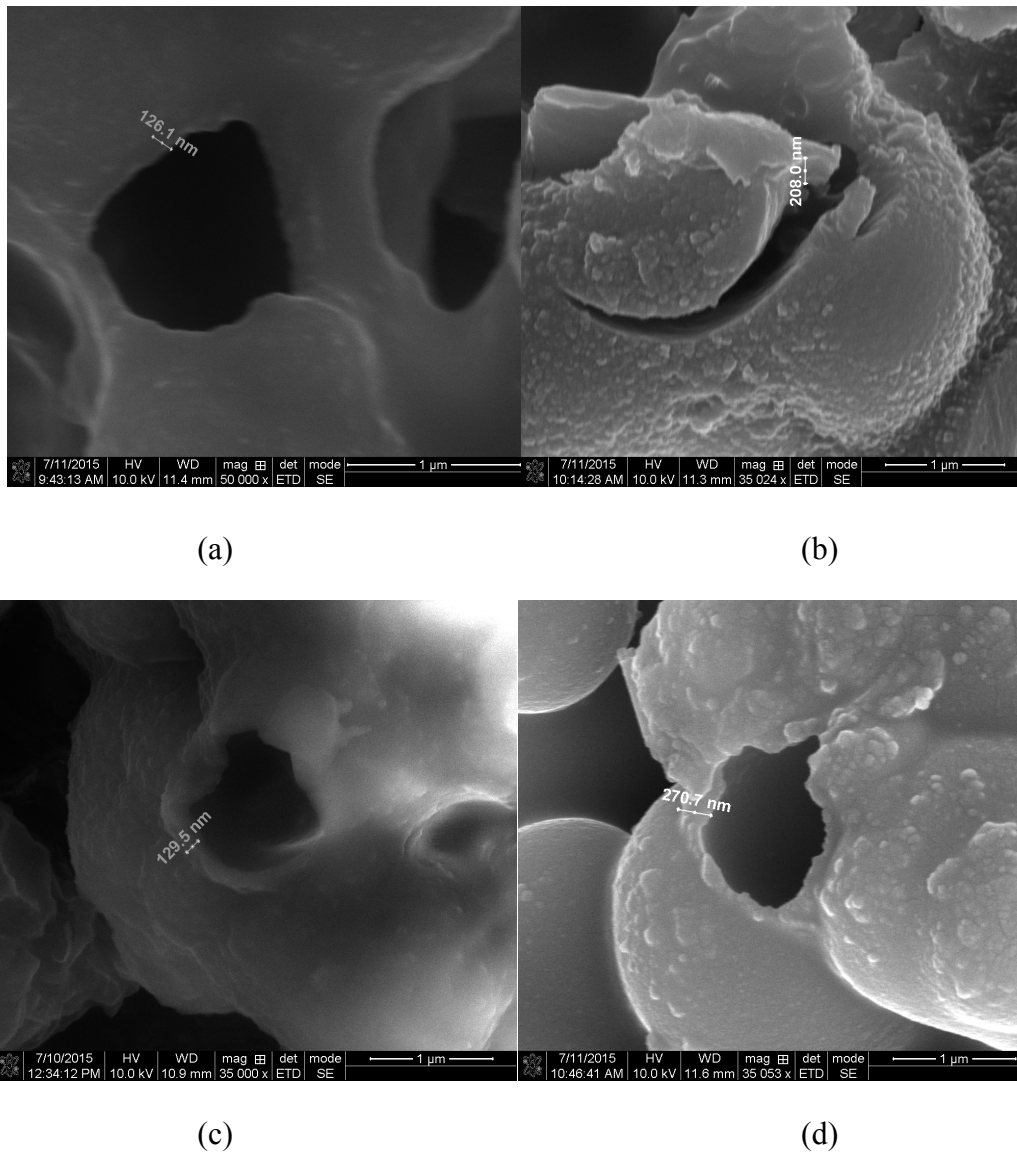


Figure 3.15. Effects of EMA Concentration on the Shell Thickness of Microcapsules (a) 0.5%, (b) 2%, (c) 4% and (d) 8%

### 3.4 Conclusions

The study evaluates the efficiency of PennzSuppress D to reverse the aging process on asphalt binders in order to determine the eligibility of the product to be a healing agent for asphaltic

materials and to develop the synthesis procedure for the production of microencapsulation of asphalt rejuvenators. SEM was utilized to characterize the produced microcapsules to evaluate the effects of preparation parameters on the size, morphology, and shell thickness of the microcapsules. Based on the results of the experimental program, the following conclusions may be drawn:

- The use of PennzSuppress D as a rejuvenator was effective in partially reversing the aging of asphalt binder 70-22, by wielding an influence on both the high temperature and low temperature grades of the binder.
- The use of PennzSuppress D as a rejuvenator was not effective in reversing the aging of asphalt binder 76-22, since its use only influenced the lower temperatures grades of the binder.
- The use of PennzSuppress D as a rejuvenator was not effective in reversing the aging of extracted binder, due to an influence only on the high temperatures grades of the binder.
- Microencapsulation of PennzSuppress D was synthesized and a characterization of microcapsules properties such as diameter, shell thickness, and morphology was conducted.

Evaluation of other rejuvenators is recommended to accomplish a better reversing of the aging process on aged binders. Enhancement of the proposed synthesis method is recommended. In addition, the performance of developed microcapsules in asphalt mix processes must be evaluated in future studies.

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## **CHAPTER 4–SUMMARY AND CONCLUSIONS**

Self-healing microencapsulation is an innovative emerging technique to enhance the serviceability and quality of asphalt pavements that are cracking damaged caused by vehicular and environmental loading. Microcapsules containing rejuvenators have the potential to impact road's infrastructure, but the efficiency of the encapsulated material and microcapsules must be evaluated. This study evaluated the effectiveness of an asphalt rejuvenator, PennzSuppress D as a heavy resin, on the rheological properties of aged asphalt binders to reverse aging process; and developed a synthesis procedure for the production of self-healing microcapsules. To achieve this, the project was split into two phases. The first phase of the project was to characterize virgin binders and aged asphalt binders blended with PennzSuppress D to assess the effectiveness on reversing the aging process. The second phase was to develop a microencapsulation process to synthesis self-healing microcapsules containing PennzSuppress D and to characterize the developed microcapsules.

In the first phase of the project, six different asphalt binder blends were compared to assess the effects of the rejuvenator on the binder aging mechanisms. Binders classified as PG 70-22 and PG 76-22 were blended with the rejuvenator at a dosage rate of 30% by weight of the binder. The aging process of virgin binders was simulated using the Rolling-Thin Film Oven (short-term aging) and Pressure Aging Vessel (long-term aging). The characterization of the prepared asphalt binder blends was conducted using the PG grading system as per AASHTO M 320-09 (Standard Specification for Performance-Graded Asphalt Binder). Rheological tests such as dynamic shear rheometry, rotational viscosity, and bending beam rheometer; and comparison between modified and unmodified asphalt binder blends were performed in the characterization process. Also, the effects of the rejuvenator were evaluated in an aged binder extracted from Recycled Asphalt

Pavement (RAP). Asphalt binder extraction was performed in accordance AASHTO T 164, “Standard Method of Test for Quantitative Extraction of Asphalt Binder from Hot Mix Asphalt HMA – Method A.” Asphalt binders blends of the RAP with the rejuvenator were prepared at a dosage rate of 30% and 40% by weight of the binder.

The use of PennzSuppress D as a rejuvenator was effective in partially reversed the aging of asphalt binder 70-22 by influence both the high temperature and low temperature grades of the binder. Also, this commercial product was effective to reduce the viscosity of the aged binder from 1.23 Pa.s to 1.17 Pa.s. The high temperature and low temperature were improved by one grade, i.e. from PG 82-16 to PG 76-22. However, this heavy resin was not effective to fully reverse the aging process on the 70-22 binder. On the other hand, the use of PennzSuppress D as a rejuvenator was not effective in reversing the aging of asphalt binder 76-22 and extracted binder. The increase on viscosity due the rejuvenator on the aged 76-22 was the first indicator of the ineffectiveness of the heavy resin. PennzSuppress D was only effective to improve the grade by one in the low temperature, i.e. from PG 94-16 to PG 94-22. However, the rheological test's results showed improvements in the numbers for the high temperature but they were not good enough to affect the PG grading result. In a similar way, in the Reclaimed Asphalt Pavement (RAP), the PennzSuppress D was only effective on improving the high temperature of the asphalt binder, i.e. from PG 118-X to PG 112-X and from PG 118-X to PG 106-X. The results from the rheological tests on the lower temperature were improving as the dosage rate increased but they were not good enough to affect the PG grading result.

The second phase was to develop a microencapsulation process to synthesis self-healing microcapsules containing PennzSuppress D and to characterize the developed microcapsules. Microcapsules were synthesized via in-situ polymerization using Methanol-Melamine-

Formaldehyde, which resulted in single-walled microcapsules. The effects of the variation of production parameters such as agitation rate (in revolutions per minute [rpm]), heating temperature (in degrees Celsius), and the EMA concentration were evaluated by comparing the characteristics of nine different samples. The characterization of microcapsules was performed using a scanning electron microscope, a FEI Quanta 3D FEG Dual Beam SEM/FIB, to determine the size and morphology of the produced microcapsules.

The developed microencapsulation process showed small yield rate percentages in all nine different samples. The highest yield rate was 65.7% (800rpm, 80°C, 3% EMA) and the lowest one was 49.6% (2000rpm, 75°C, 3% EMA). The variation of agitation rate, from 500rpm to 200rpm showed a decrease in the diameter size of the developed microcapsules as it was expected, i.e. from 3.5µm to 2.814µm. However, the increase in agitation rate resulted an increase in the shell thickness, i.e. 171.629 nm to 611.3 nm. In a similar way, the increase of the heating temperature from 70°C to 80°C decreased the diameter size of the microcapsules, i.e. from 3.046µm to 2.243µm. The variation on the heating temperature did not demonstrate any effect on the shell thickness of the microcapsules. The effects on changing the EMA concentration were also evaluated. In the microcapsules size, it was not possible to identify a pattern, therefore, it can be concluded that the amount of EMA does not have a direct effect on the diameter size of the microcapsules. The EMA concentration was expecting to have an effect on the shell thickness. Based on the results, there is an increased on the shell thickness but the results of the samples with EMA=0.5% and EMA=4% provided some unusual results.

In conclusion, PennzSuppress D is not recommended to be use as a rejuvenator in order to reverse the aging process of asphalt. PennzSuppress D showed improvements on the rheological test's results but it did not improve enough the rheological properties to affect the PG grading

results. Furthermore, a microencapsulation synthesis was effectively developed for PennzSuppress D. Enhancement on the microencapsulation process is recommended to increase yield rates. Finally, the effects of incorporation of microcapsules on the laboratory performance of asphalt concrete need to be evaluated in future studies.

#### **4.1 Future Work**

Although PennzSuppress D showed improvements on the rheological properties on aged asphalt binders and a microencapsulation process for this particular rejuvenator product was synthesized, the following investigations are recommended:

- Different rejuvenator products must be tested to determine the effect of each one on the rheological properties of aged binders.
- Test different dosage rates to define an optimum ratio between weight of rejuvenator and weight of a binder.
- Develop a microencapsulation process for an asphalt rejuvenator with better efficiency on reversing the aging process.
- Enhance the developed microencapsulation process to increase yield rates.
- Test the compressive strength of the developed microcapsules.
- Test the thermal stability of the developed microcapsules.
- Evaluate the performance of the developed microcapsules during an asphalt mixture process.
- Determine if the developed microcapsules are cost-effective technique to use to increase the serviceability of asphalt pavement roads.
- Test the developed self-healing microcapsules to determine their efficiency on reversing the aging process of asphalt.

## **VITA**

Max Aguirre was born in 1992 in San Salvador, El Salvador. In 2013, he finished her Bachelor of Science in Civil Engineering from Louisiana State University. He continued with his studies at Louisiana State University to pursue a Master of Science in Construction Management degree.