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Feasibility Study of Incorporation of Recycled High-Density Polyethylene in Asphalt

(Project Title: Use of Recycled Plastics in Asphalt Pavements)

Final Report

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Executive Summary

Waste plastics have been studied to improve the properties of asphalt binders. According to the US Environmental Protection Agency (EPA), in 2015, approximately 34.5 million tons of plastics were disposed. Of this total, 3.14 million tons were recycled, 5.35 million tons were incinerated, and the remaining 26.01 million tons of plastics were landfilled. The increasing cost, decreasing landfill space, and corresponding environmental pollution concerns have forced policymakers and researchers to look for alternative solutions for waste plastic disposal. Given the ubiquity of asphalt pavements nationwide, there exists an opportunity for significant reductions in landfilled plastics by incorporating these materials into asphalt mixtures.

A significant challenge of using the plastic-modified binder is its poor storage stability. This study evaluated the storage stability of high-density polyethylene (HDPE) powder-modified binders with different treatments and modifiers. For this purpose, flame treatment and acid treatment methods were developed. Particular attention was paid to the Fourier-transform infrared spectroscopy (FTIR) characterization of the flame and acid-treated HDPE powder and the description of sample preparation, lacking in other studies. Then, the optimum flame-treated HDPE powder, optimum sulfuric, and mixed acid-treated HDPE powder were selected. Kaolinite, bentonite clay, and rejuvenator were selected as other candidate modifiers. A control neat binder and nine modified binders (i.e., Plastic Pellet-modified Binder (PPLB), Plastic Powder-modified Binder (PPDB), Flame-treated Plastic-modified Binder (FPB), Flame-treated Plastic and Kaolinite-modified Binder (FPKB), Flame-treated Plastic and Bentonite-modified Binder (FPBB), Flame-treated Plastic and Rejuvenator-modified Binder (FPJB), Sulfuric Acid-treated Plastic-modified Binder (SAPB), Mixed Acid-treated Plastic-modified Binder (MAPB), and Mixed Acid-treated Plastic and Kaolinite-modified Binder (MAPKB)) were prepared. Softening point and FTIR were used to assess the different modified binders' storage stability and chemical compatibility. The softening point and FTIR results were consistent. They both showed that PPDB had better storage stability than PPLB, which means plastic with a smaller size can dissolve better in the binder. FPB, SAPB, and MAPB had better storage stability than PPDB, which indicates the flame and acid treatment improved the modified binders' storage stability. MAPKB had the best storage stability results among all binders.

The rheological behaviors of the plastic-modified binders were also evaluated in the study. The performance tests were conducted on the PPDB, MAPKB, and the control binder. MAPKB was the

optimum binder selected due to its best storage stability. PPDB was selected as a control-modified binder. The testing results show that the differences caused by storing time are insignificant for modified binders. In other words, the storing time does not affect binders' rheological performance. The results also show that all the modified binders had a much higher viscosity than the control binder, and PPDB showed slightly less viscosity than MAPKB. All modified binders also had much higher rutting resistance than the unmodified binder. However, all modified binders increased resistance to fatigue cracking than the unmodified binder. In terms of low-temperature performance, the incorporations of HDPEs powders, treated HDPEs and clay increased the tendency for low-temperature cracking of the base asphalts. Further investigations are also recommended to characterize the performance of asphalt mixtures using HDPE modified binder.

Chapter 1 Introduction

1.1 Problem Statement

According to the US Environmental Protection Agency (EPA), in 2015, approximately 34.5 million tons of plastics were disposed. Of this total, 3.14 million tons were recycled, 5.35 million tons were incinerated, and the remaining 26.01 million tons of plastics were landfilled. The increasing cost, decreasing landfill space, and corresponding environmental pollution concerns have forced policymakers and researchers to look for alternative solutions for waste plastic disposal. Additionally, according to the National Asphalt Pavement Association, approximately 350 million tons of asphalt pavement are produced in the US annually. The most common plastics in the municipal waste stream include polyethylene terephthalate (PET), high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polyvinyl chloride (PVC). Given the ubiquity of asphalt pavements nationwide, there exists an opportunity for significant reductions in landfilled plastics by incorporating these materials into asphalt mixtures. In that case, there will be environmental and potentially commercial benefits arising from:

1. Reduced landfill.
2. Reduced reliance on virgin non-renewable resources.
3. Improved road-building material options.
4. Improved sustainability.
5. Climate and infrastructure resilience benefits.

The development of the science of recycling waste plastics in asphalt is still at an early stage and needs much more research. Currently, there are considerable data gaps regarding quantifying the performances and impacts of asphalt binders/mixtures containing recycled plastics. It is critical to explore the viability of using recycled plastics in asphalt and to identify potential issues when incorporating recycled plastics into asphalt/mixture. In this study, the methods to incorporate recycled plastic into asphalt mixtures have been explored, and the effects of recycled plastic on the performance of bituminous materials have been evaluated. The wet methods in which plastic was blended with asphalt binder before mixing have been predominately investigated in this research. The wet method does not require contractors to have additional equipment or change the current procedure for mixing; thus, this method has been considered to be practical and cost-effective.

The research in this Phase I study focuses on improving the compactibility and storage stability of the plastic-modified asphalt binder. The performance of the material and the feasibility of the

methods have also been evaluated in the binder scale. In the follow-up Phase II study (Use of Recycled Plastics in Asphalt Pavement Year 2, 2021-MST-03), the performance and the durability of the plastic-modified asphalt will be assessed in the mastic, mixture, and structural scales.

1.2 Objectives

The goal of this project is to explore the feasibility of the incorporation of recycling waste plastic in asphalt in terms of storage stability and compatibility. The objectives of this project are to: (1) investigate the viability of using recycled plastics in asphalt, (2) investigate the effects of different recycled plastics on the properties/performances of asphalt binder, and (3) identify potential issues of recycled plastics in asphalt.

1.3 Organization of the Report

The report documents the details of the research efforts and summarizes the findings in the study. Chapter 1 presents the objective and the methodology of the study, followed by a comprehensive literature review presented in Chapter 2. Chapter 3 presents the development of the methodologies for improving the compatibility between recycled plastic and binder and the storage stability of the modified binder. Chapter 4 presents the evaluation of the storage stability of the binders with plastic treated with different methods using the Fourier Transform Infrared Spectroscopy (FTIR) analyses. After assessing the storage stability, the performance of the recycled plastic-incorporated binders is presented in Chapter 5. Chapter 6 summarizes the findings, conclusions, and the recommendation in this study.

Chapter 2 Literature Review

2.1 Introduction

Waste plastic is the accumulation of plastic objects in the Earth's environment that adversely affects wildlife, wildlife habitat, and humans (Hwang et al. 2019). It also refers to the significant amount of plastic that isn't recycled and ends up in landfills or, in the developing world, thrown into unregulated dump sites. According to an Australian plastics recycling survey (Chin and Damen 2019), the total plastics consumption in 2016 was 3.5 million tons while only 0.41 million tons were recycled. According to the US Environmental Protection Agency (EPA), in 2015, approximately 34.5 million tons of plastics were disposed each year. Of this total, 3.14 million tons were recycled, 5.35 million tons were incinerated, and the remaining 26.01 million tons of plastics were landfilled (EPA 2020). The increasing cost, decreasing landfill space and corresponding environmental pollution concerns have forced policymakers and researchers to look for alternative solutions for waste plastic disposal.

Civil engineers have been attempting to recycle the waste plastics into civil infrastructures, such as wood-plastic composites (Keskisaari and Karki 2018) and concrete blocks (Meng et al. 2018). Arulrajah et al. (2017) explored the possibility of using plastic granules with crushed brick and reclaimed asphalt pavement (RAP) waste as base materials. Additionally, according to the National Asphalt Pavement Association, approximately 350 million tons of asphalt pavement are produced in the US annually. Given the ubiquity of asphalt pavements nationwide, there exists an opportunity for significant reductions in landfilled plastics by incorporating these materials into asphalt mixtures. Suppose recycled plastic can be successfully incorporated into pavements. In that case, there will be environmental and potentially commercial benefits arising from: (1) reduced landfill, (2) reduced reliance on virgin non-renewable resources, (3) improved road-building material options, (4) improved sustainability, and (5) climate and infrastructure resilience benefits (Sabina et al. 2011, Poulikakos et al. 2017, Leng et al. 2018).

2.2 Plastic Types and Their Properties

Plastics are polymers, composed of repeated segments, called monomers, with carbon backbones. A polymer is a very large molecule consisting of many smaller units joined, generally end to end, to create a long chain. Plastics are generally classified into seven categories by the U.S. Society of the Plastics Industry in 1988.

- **Category #1:** Polyethylene terephthalate (PET), which is usually used in soft drinks, juice,

water, beer, mouthwash, peanut butter, salad dressing, detergent, and cleaner containers. It generally softens at around 85 °C and has a specific gravity (SG) of 1.38.

- **Category #2:** High-density polyethylene (HDPE), usually used in opaque milk, water, juice containers, bleach, detergent and shampoo bottles, garbage bags, yogurt and margarine tubs, and cereal box liners. It generally softens at around 135°C and has an SG of 0.96.
- **Category #3:** Polyvinyl chloride (PVC), which is usually used in toys, clear food and non-food packaging (e.g., cling wrap), some squeeze bottles, shampoo bottles, cooking oil and peanut butter jars, detergent and window cleaner bottles, shower curtains, medical tubing, and numerous construction products (e.g., pipes, siding). It generally softens at around 70-110°C and has a specific gravity (SG) of 1.40. PVC is one of the most hazardous consumer products ever created. Leaches di (2-ethylhexyl) phthalate (DEHP) or butyl benzyl phthalate (BBzP), depending on which is used as the plasticizer or softener (usually DEHP). DEHP and BBzP are endocrine disruptors mimicking the female hormone estrogen; have been strongly linked to asthma and allergic symptoms in children; may cause certain types of cancer; and are linked to negative effects on the liver and kidney spleen, bone formation, and body weight.
- **Category #4:** Low-density polyethylene (LDPE), usually used in the grocery store, dry cleaning, bread and frozen food bags, most plastic wraps, and squeezable bottles (honey, mustard). It is generally translucent and withstands solvents. It softens at around 115 °C and has an SG of 0.92.
- **Category #5:** Polypropylene (PP), usually used in ketchup bottles, yogurt and margarine tubs, medicine and syrup bottles, straws, and Rubbermaid and other opaque plastic containers, including baby bottles. It softens at around 165 °C and has an SG of 0.90.
- **Category #6:** Polystyrene (PS), used in Styrofoam containers, egg cartons, disposable cups and bowls, take-out food containers, plastic cutlery, and compact disc cases. It softens at around 90 °C and has an SG of 1.65.
- **Category #7:** Others. This is a catchall category that includes all other resins and multi materials (laminates) acrylonitrile butadiene styrene (ABS), acrylic, nylon, polyurethane (PU), polycarbonates (PC) and phenolics.

2.3 Methods of Incorporate Waste Plastics into Asphalt

There are generally two ways to incorporate waste plastics into asphalt: the dry and the wet processes. In the dry process, waste plastics are added to hot aggregate prior to the addition of binder, and then a

prolonged mixing process is followed to make a homogenous mixture; on the other hand, the modifier is mixed with the binder prior to addition to the aggregate in the wet process (Sharp et al. 2017).

2.3.1. Dry Process

There are two ways of using plastics in the dry process. One is to use plastic as aggregate replacements and another one is to use plastic to coat aggregates. In the first way of using plastic as aggregate replacements, the waste plastics are cleaned and shredded prior to mixing. Then the shredded plastics are added directly into the asphalt mixture to partially replace aggregates. This method is mainly applied to hard and rigid plastic types with high melting points, such as HDPE and PET. The hardness and rigidity of plastic particles contribute to the integrity of asphalt mixtures, playing a similar role as fine aggregates in the skeleton of asphalt mixtures. Hassani et al. (2005) investigated the possibility of using PET waste in asphalt mixes as aggregates replacement, also called Plastiphalt. This research could imply that PET has the potential to be used as an aggregate in mixes. Sarang et al. (2014) utilized the shredded waste plastic in stone matric asphalt (SMA) as a stabilizing additive to control drain down by stiffening the SMA mixture. Stiff plastics such as PET can be further processed into a finer dimension, and they can replace fine aggregates that pass a 4.75-mm sieve.

LDPE pellets (5.00-2.36 mm) were used in dense graded bituminous mixes to replace a portion of the mineral aggregates of equal size (Zoorob and Suparma 2000). The results indicated that at the same air-void content, the compacted Plastiphalt mix has a lower bulk density than the conventional control mix. A 30% (by volume) aggregate replacement with the LDPE has managed to reduce bulk compacted mix density by 16%, which can reduce the costs in haulage. LDPE partial aggregate replacement have also increased the Marshall stability (strength) by 150% and improved the Marshall quotient value (resistance to deformation) (Zoorob and Suparma 2000). Some other studies also indicated that the waste plastic modified mixtures from the dry process have showed better Marshall stability and indirect tensile strength than virgin mixtures (Ahmadinia et al. 2012, Modarres and Hamedi, 2014). However, a study also reported a concern that the adhesion between aggregates and binder may be compromised in case of the dry process as some portion of plastic might melt when added to the heated aggregates and coat them (Moghaddam et al. 2014).

When recycled plastic was used to coat aggregates in the dry process, the aggregate was first heated to 170°C, and then the waste plastics with the size of 2.5mm – 4.36mm were sprayed over the hot aggregate. The plastics soon softened and coated over the aggregate (Rajasekaran et al. 2013). The hot asphalt binder was then added at 160°C. The added binder spreads over the aggregate. Both the coated

plastics and bitumen were in the liquid state at this temperature, capable of easy diffusion at the interphase. This process was further improved by increasing the contact area (increased surface area). This method created a thin layer of plastic covering the aggregate (Lastra-González et al. 2016 Liang et al. 2017). The modified aggregates were called plastic coated aggregates (PCA). PCA had advantages, such as reducing the need for binder by around 10%, increasing the strength of the pavement, avoiding the use of anti-stripping agents, reducing the cost, and reducing the disposal of plastic waste (Vasudevan et al. 2012). PCA also increased the Marshall stability, stripping, and strength of the asphalt mixture (Rajasekaran et al. 2013). These results were explained by the following model in Figure 2.2 (Rajasekaran et al. 2013). As shown in Figure 2.1, when bitumen is mixed with plastic-coated aggregate, a portion of bitumen diffuses through the plastic layer and bound with aggregate. During this process, a three-dimensional internal cross-linked network structure between polymer molecules and bitumen constitute is formed, and the bonding between stone aggregate and bitumen is improved due to the presence of plastic polymers (Rajasekaran et al. 2013).

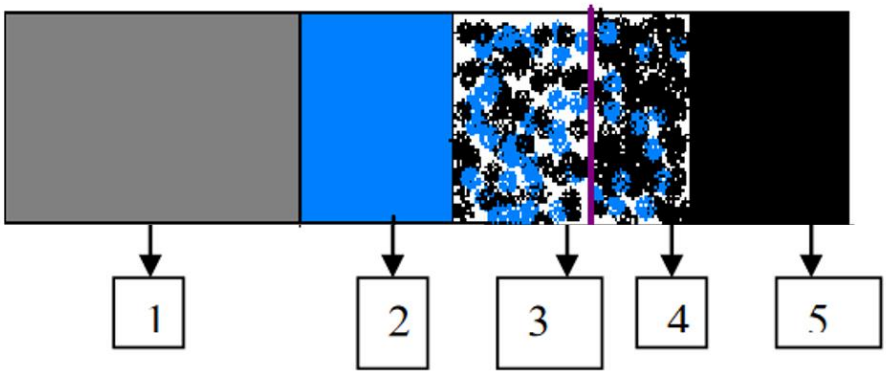


Figure 2.1 A plastic aggregate bitumen interaction model

Note: 1. Aggregates; 2. Area of plastics bonded with aggregate (polymer coating); 3. Area of bitumen-plastic blend (due to diffusion between molten plastics & hot bitumen); 4. Area of loosely bonded bitumen with dispersed plastics; 5. Area of plain bitumen layer

The size of waste plastics has a viral impact on the mixture's performance. India reportedly has over 15 years of experience with the dry process for low-volume roads. It suggested that the size of the shredded waste plastics should be within 2-3 mm for better melting the plastics and coating the aggregates (Sahu and Singh 2016). Dalhat et al. (2019) found that the dense-graded asphalt mixture containing finer sizes ranging from 2.38 mm (No. 8) to 2 mm (No. 10) exhibits a better performance than that containing plastic sizes ranging from 0.42 mm (No. 40) to 2.38 mm (No. 8) based on the

moisture sensitivity test. Choudhary et al. (2018) claimed that coarser size PET (2.36–1.18 mm) showed comparatively superior performance considering volumetrics, Marshall parameters, and resistance against moisture-induced damage than finer size PET (300–150 μm). Besides the size, the dosage of plastic is an essential factor affecting the performance of asphalt mixtures; 8% was recommended as the optimal percentage (Mishra and Gupta 2018).

2.3.2. Wet Process

In most studies, the researchers preferred using the wet method for polyethylene modification. This is attributed to having better control on the binder performance before implementing on site (Masad et al. 2020). In the wet process, the modifier is mixed with the binder prior to addition to the aggregate. The waste plastics also need to be cleaned and shredded before adding into the asphalt binder as a modifier in the asphalt plant in the wet process. In the laboratory, the high shear mixer is used to blend the plastic with high shearing speed and high temperature (Colbert and You, 2012). The mixing temperature and time depend on the plastic and asphalt binder type. For example, Naskar et al. (2010) investigated the effect of waste plastic as a modifier on thermal stability and degradation kinetics of bitumen. They mixed different waste plastics with a 60/70 penetration grade binder for 45 min at 180 °C. Garcia-Morales et al. (2005) used four types of waste plastics to mix with 60/70 penetration grade bitumen. Their samples were processed for 6 hours at 180 °C. Lu and Isacsson (1993) suggested that the mixing temperature should not exceed 185 °C. Otherwise, the binder would burn, and the mixing time should be adequate for homogeneous dispersion of the waste plastic within the binder matrix.

The amount (or dosage) of waste plastic incorporated into asphalt binder through the wet process plays an important role in the performance of waste plastic modified asphalt binders. According to the research findings, there is an optimal waste plastic dosage for waste plastic modified asphalt binders (Brasileiro et al. 2019). Too much or too little may adversely affect the properties of the asphalt binder. According to Singh and Kumar (2019), modified asphalt binders with a high concentration of waste plastic were not storage stable. The plastic particles separated from asphalt binder at high temperatures while the properties of modified asphalt binders' low plastic concentration have the issue of underutilization of polymer modification. A review article summarized the dosages for different waste plastics from the past studies, as presented in Figure 2.3.

Based on previous study, 5% of waste HDPE is recommended as the best content to achieve better asphalt performance properties in terms of stiffness and rutting resistance (Suksiripattanapong et al. 2022). In terms of PET, 6 - 8% has been recommended as an ideal modifier that increases fatigue life

and, as such, improves the long-term performance and durability of the asphalt mixture (Mashaa et al. 2021). For the wet process, a significant limitation is the potential phase separation at high storage temperature due to the difference in densities and viscosity of waste plastics and asphalt binder coupled with the chemical incompatibility between these two components (Brasileiro et al. 2019, Wu and Montalvo 2020).

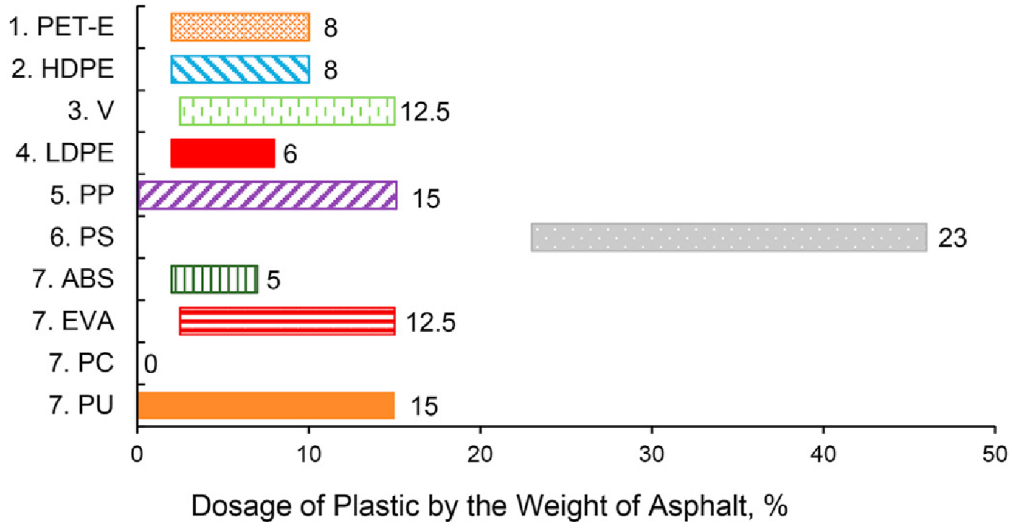


Figure 2.2 Dosages of waste plastic used for asphalt (wet process) (Wu and Montalvo 2020)

Regarding the type of the plastics, the wet process can be properly applied with plastics with melting points below 160°C such as LDPE, HDPE, and PP. For PET, which has melting point around 250°C, it is difficult to achieve a uniform blend segregating from asphalt binder when it is used in the wet process. (Casey et al. 2008).

Both the wet process and the dry process have their advantages and disadvantages. Angelone et al. (2016) conducted a comparative study of bituminous mixtures with recycled polyethylene using both dry and wet processes. The study found that the mixtures containing plastic added by the wet process have lower stabilities and more flowable than the control mixture; however, in the dry process, increasing the plastic content can increase stability and flow. For the ethylene-vinyl-acetate (EVA)-modified mixture, the wet method appeared to have a slightly more positive effect on the asphalt mixtures' rutting and fatigue cracking resistances (Ranieri et al. 2017). The wet method requires specific equipment for blending asphalt and waste polymer at high temperatures while the dry method requires no special equipment.

2.4 Properties of Waste Plastics-Modified Asphalt Binder

Numerous studies have investigated the effect of adding recycled plastics into bituminous materials. In

the last decade, many studies have focused on using polymers in asphalt. It has been reported that adding waste plastics into asphalt binder increased the softening point while decreasing the penetration of asphalt binder, and the effect was more significant with the increase of waste plastic content (Brasileiro et al. 2019; Wu and Montalvo 2020). The finding indicated that adding waste plastics stiffened the asphalt binder, which potentially improved the permanent deformation resistance at high temperatures. Studies also found that the addition of 3% (by weight of base asphalt) of PE could bring a reduction in penetration by 7% to 42% and an increment in softening point by 2% to 50% (Polacco et al. 2005, Ahmedzade et al. 2014, García-Travé et al. 2016, Brasileiro et al. 2019). Adding 3% of PP could reduce penetration by 18% to 30% and an increment in softening point by 4% to 30% (Casey et al. 2008, Habib et al. 2011, Ahmedzade et al. 2015, Brasileiro et al. 2019). The addition of 5% of EVA could bring a reduction in penetration by 33% to 51% and an increment in softening point by 21.6% to 53% (Luo and Chen 2011, González et al. 2016, Costa et al. 2017). The rates for penetration decrease or softening points increment mainly depended on the properties of the base asphalt binder used. Some studies investigated the effects of waste plastics on the ductility of asphalt binders at low temperatures. Al-Hadidy and Tan (2009) reported that adding 5% PE decreased the ductility of asphalt binder at 15°C by around 20%.

Another important property of waste plastic modified asphalt binder is viscosity, which is directly related to its workability. Previous studies reported that the addition of waste plastics into asphalt binder increased the rotational viscosity, regardless of the type of plastic, i.e., PE (Casey et al. 2008, Ahmedzade et al. 2014, Ma et al. 2016), PP (Yeh et al. 2005, Ahmedzade et al. 2015, Al-Abdul Wahhab et al. 2017), PVC (Behl et al. 2014; Köfteci et al. 2014), and EVA (Alataş and Yilmaz 2013; Yuliestyan et al. 2016; Liu et al. 2019). The increase in viscosity, to some extent, implies higher stiffness of asphalt binder at high temperatures, which indicates improved resistance to permanent deformation. However, it also means that the temperature required to mix and compact the mix with modified asphalt binder is increased. The Superpave asphalt binder specification specifies that the rotational viscosity of the asphalt binder should be lower than 3.0 Pa·s at 135°C to ensure good workability (ASTM D 6373). While some studies reported that rotational viscosity of the modified asphalt binder with 3% or 5% PE did not exceed this criterion (Ma et al. 2016, Wahhab et al. 2017), Casey et al. (2008) pointed out that in their study, the rotational viscosity modified asphalt binder with 3% PE was higher than 3.0 Pa*s at 135°C. Casey et al. (2008) also indicated that the modified asphalt binder with PP did not meet the specification requirement in terms of rotational viscosity. Researcher

also revealed that some special treatments on PP, such as maleic anhydride treatment, could help to decrease the rotational viscosity of PP modified asphalt binders (Yeh et al. 2005, Nien et al. 2008). Behl et al. (2014) and Köfteci et al. (2014) indicated that adding PVC could increase the viscosity of asphalt binder by almost 300%, but the values were still within the specification limit.

Laboratory studies have also reported that waste plastic can improve the performance of asphalt binder, indicated by lower temperature susceptibility (Angelone et al. 2016), higher rutting factor G*/sin δ (Amirkhanian 2018), and better high-temperature rheological properties (Costa et al. 2019) of asphalt binders. Ahmedzade et al. (2015) found that adding LDPE/PP increased the complex modulus (G*) and decreased the phase angle values at all frequencies. Köfteci et al. (2014) found that the PVC had similar effects on G* and phase angle. Amirkhanian (2018) evaluated the rheological properties of PE-modified asphalt binders with different PE contents (2%, 4% and 6% by weight of base binder). The results indicated that the PE modifier could effectively increase the failure temperature and the G*/sin δ value of the asphalt binder. The modified asphalt binders with higher PE content showed better high-temperature performance than those with lower PE content. Dalhat and Wahhab (2017) revealed that the modified asphalt binder's high-temperature performance grade (PG) could be bumped one grade for every 2% increase in the LDPE or HDPE content.

Based on the literature, the waste plastic modified asphalt binder showed better high-temperature properties than the unmodified asphalt binder. However, many conclusions were developed based on outdated research methods with limitations, such as penetration and softening point. The rheological analyses were mainly limited to G* and phase angle characterization. The rutting resistance of the waste plastic modified asphalt binders was mainly evaluated by using the Superpave parameter, G*/sin δ. However, the limitations of applying G*/sin δ in evaluating polymer-modified asphalt binders have been reported by many studies (Bouldin et al. 2001, Bahia et al. 2001, D'Angelo and Dongré 2002, D'Angelo et al. 2007). More fundamental tests, such as the Multiple Stress Creep and Recovery (MSCR) test, are needed to better understand waste plastics' effects on the rutting resistance of asphalt binder. In addition, it should be noted that stiffer asphalt binders generally are prone to cracking. Thus, cracking susceptibility or other related characteristics of waste plastic-modified asphalt binders may be the main aspects that need to be investigated. Besides, the long-term performance and aging resistance evaluations are needed to further understand the behaviors of waste plastic modified asphalt binders.

In terms of asphalt mixtures, existing studies indicated the addition of waste plastics could produce asphalt mixtures with higher modulus and better resistance to rutting and fatigue damage

(Casey et al. 2008, Alataş and Yilmaz 2013, Behl et al. 2014, Modarres and Hamedi 2014). Modarres and Hamedi (2014) indicated that the indirect tensile strength and resilient modulus of asphalt mixtures at 5°C and 20°C could be increased by adding 2% PET directly into the asphalt mixture by dry process. The authors also found the addition of the PET could improve the fatigue cracking resistance of the asphalt mixture. The fatigue life of asphalt mixture at a given stress level increased with the increase of PET content. Similar findings were also reported in Alataş and Yilmaz (2013), which indicated that the addition of EVA had a notable effect on the stiffness and fatigue life of the asphalt mixture, and the results were more profound at higher EVA content. Behl et al. (2014) reported that adding PVC improved the indirect tensile strength of asphalt mixture at intermediate temperatures. It should be noted that the study pointed out that PVC is a carcinogenic plastic, but they did not include any discussions about the hazard effect on human health in their study. In terms of the properties of stone mastic asphalt (SMA) containing waste plastics, Casey et al. (2008) reported that the SMA with 4% HDPE showed better performances in rutting and fatigue cracking resistance than the virgin SMA. However, the HDPE-modified SMA did not exhibit the equivalent level of performance to the SMA with a commercial SBS-modified asphalt binder. Ahmadinia et al. (2012) indicated that the addition of waste PET could improve the rutting resistance and the drain down properties of SMA.

The bond strength between asphalt and aggregate is critical, which determines the asphalt pavement moisture susceptibility. Gürü et al. (2014) indicated that adding waste plastics into asphalt using wet method could weaken the bond strength between asphalt and aggregate and pointed out that the asphalt mixtures containing PET didn't show ideal moisture damage resistance. Jafar (2016) attributed this bond strength weakening to the poor compatibility between asphalt and waste plastic and the inert nature of waste plastic. Jafar (2016) believed this issue could be overcome by activating the waste plastic with a dichromate/sulfuric acid solution. The reaction between the waste plastic and the solution could induce an active ionic functional group, forming a crosslinking network between asphalt binder and waste plastic to enhance the asphalt-aggregate bond strength. Although the chemical activation could solve the weak bond strength problem, Jafar (2016) stated that 'it is not economical to use these materials as alternative aggregates unless their use adds sufficient value to the bituminous product so that the cost of the materials can be justified.'

Table 2.1 presents a summary of the effect of recycled waste plastics on the performance of asphalt binder and asphalt mixtures regarding asphalt binders' stiffness and viscosity, and asphalt mixtures' air voids content, strength, rutting resistance, fatigue resistance, thermal cracking resistance,

and moisture resistance, based on the past studies. The addition of waste plastic will most likely increase the stiffness, viscosity, strength, rutting resistance, and fatigue resistance of the base asphalt binder and mixture. At the same time, some results show negative or offsetting results for other performance parameters.

Table 2.1 Summary of effect of recycled plastics on asphalt and asphalt mixtures' performances (Wu and Montalvo 2020)

Plastic Type	Parameters of interest (as compared to conventional asphalt binder/mixtures)						
	Binders' Stiffness	Binders' Viscosity	Mixtures' Strength	Mixtures' Rutting Resistance	Mixtures' Fatigue Resistance	Thermal Cracking Resistance	Mixtures' Moisture Resistance
PET	∧	NA	∧	∧	∧	∨	∨
HDPE	∧	∧	∧	∧∨	∧∨	NA	∧
PVC	∧	∧	∧	∧	∧	∧ ∨	∧
LDPE	∧	∨	∧	∧	∧	∧ ∨	∧
PP	∧∨	∧	∧∨	∧∨	∧	NA	∨
PS	∧	∧	∧	∧∨	NA	∨	∧
ABS	∧	∧	NA	∧	NA	∨	NA
EVA	∧	∧	∧	∧	∧	∧	∧
PU	∧	∧	∧	∧	∧	∧	NA

Note: ∧ denotes improve or increase; ∨ denotes worsen or decrease; ∧∨ denotes conflicts reported in past studies; and NA denotes not available.

2.5 Road Trials with Waste Plastics

Engineers have been trying to construct asphalt pavements with recycled waste plastic in the past 30 years. In the 1990s, a proprietary product known as "Novaphalt" was marketed as an asphalt pavement modified with polyethylene. The Novaphalt system used a proprietary high shear blender to keep the polyethylene/asphalt blend from separating. Due to material availability, mixer expense, and field performance issues, this product did not gain widespread use beyond limited demonstrations. Also, in the 1990s, a proprietary product named Polyphalt used polyethylene modified through a chemical process to enhance the material stability of polyethylene/asphalt blends. This product was not a commercial success due to unspecified "economic and performance" limitations (FHWA, 2020).

A patented process in India has been developed to use shredded mixed plastics as a coating for

aggregates used in hot-mix asphalt. The first plastic road in India was constructed in Chennai in 2002 from shredded waste plastic. This plastic road is reported to be durable and pothole-free (Vasudevan et al. 2012). Today, there is more than 33,000 km of road with waste plastic in India, among which are primarily rural roads and a small number of roads in cities such as Chennai and Mumbai (Subramanian 2016). In November 2015, the government made it mandatory for road developers to use waste plastic along with bituminous mixes for road construction in urban areas (Chin and Damen 2019). In 2013, the Indian Road Congress published a specific guideline for using waste plastic as a modifier for asphalt. The guideline specified that only HDPE, LDPE, PET and PU can be used in pavement construction, and the plastic size must pass the 2.36 mm sieve but be retained on the 600 μm sieve (Subramanian 2016). The waste plastic content for dense-graded and open-graded mixes has been set at 6 - 8% of the mass of the bitumen (Sharp et al. 2017).

Recently, proprietary products have gained much attention on social media. Road trails with MacRebur's plastic-based material have been built in the United Kingdom and Australia in 2017 and 2018, respectively. The laboratory results showed that MacRebur's plastic-based asphalt material performed better than the conventional asphalt material in terms of rutting resistance and fracture resistance (MacRebur. 2015). However, no field performance data have been reported so far. Field trail with Reconophalt product were built in the north of Melbourne in 2018. Reconophalt was a high-performance material even under heavy traffic compared with standard asphalt. The product was reported to be able to enhance the characteristics of the asphalt, last 65% longer than standard asphalt and exhibit high resistance to rutting. However, long-term performance has not been demonstrated to show how it is different from the traditional asphalt pavement (Chin and Damen 2019). Reconophalt costs 2-5% more than traditional asphalt due to the additive production and transport costs, but it is less expensive than the proprietary polymer-modified asphalt binders (Chin and Damen 2019).

Wu and Montalvo (2020) summarized the field projects incorporated with waste plastics. Table 2.2 presents the details concerning the projects' locations, construction year, and projects features. Wu and Montalvo (2020) also reported that the projects are relatively new and there is no field performance demonstrated so far.

Table 2.2 Summary of field projects that incorporated waste plastics (Wu and Montalvo 2020)

Location, Year	**Plastic and Material type**	**Project Features**
India, 2002-2006	Plastic tar, PE, PP, and PS	More than 2500 km of plastic tar road were laid at different site. Plastic tar roads are showing better results and maintain good quality compared to the plain asphalt roads.
Scotland 2018	MacRebur's product that is plastic derived in C170 asphalt	A 400m long by 20m wide strip of road. This was equivalent of 500,000 plastic bottles and 800,000 one-time-use plastic bags. The product showed good torsional recovery and increased softening point based on laboratory results.
Craigieburn, Australia, 2018	200,000 plastic bags, 63,000 glass bottles, more than 4500 used printer cartridges and 50 tons of RAP	Reconophalt showed superior rutting and fatigue resistance in comparison to basic asphalt mix. The cost is a little higher than a base asphalt mix because of scarcity of producers, however, it is not as expensive polymer modified asphalt mix.
Jharkhand, India, 2017	Use of HDPE, LDPE, PET, and PU in 6-8% of the mass of asphalt	Showed improved moisture resistance, enhanced binding properties, higher softening points, the ability to withstand high temperatures and heavy load, lower penetration values, reduced construction costs and no toxic gas emissions
Vancouver, Canada, 2012	Converting 100% plastic into recycled plastic wax that is compatible with WMA with a high RAP content	Final mixing temperature was reduced from 160 to 120 °C, using 1 ton of wax per 400 tons of mix to produce WMA. Results showed good field compaction and meeting of conventional design criteria.
New Zealand, 2018	HDPE into appropriately classified asphalt binder	Paved fire station with Plastiphalt with 250 tons of asphalt using HDPE. The asphalt is made by shredding used plastic containers and then granulating the shreds into an ideal size for incorporating into asphalt.
KwaZulu-Natal, South Africa, 2020	HDPE to extend asphalt binder and incorporate into the asphalt mix	HDPE is turned into pellets and then melted at 190 °C until they are dissolved and then mixed with additives into the binder, at 6% of the binder content. Mix is reported to be more durable and water resistant than conventional asphalt, and able to withstand temperatures as high as 70 °C and as low as -22

		°C.
Freeport, Texas, 2019	Linear LDPE incorporated into PG 70e22 asphalt	These two private roads are open to traffic and used 1686 pounds of recycled LDPE. The roads cover 2600 feet and meet PG 70-22 grade requirements.
Mt. Pleasant, MI, 2019	Dow used K-Tech Specialty Coatings to blend the plastic into a PG 64-28 binder	This is the first public road using plastic waste in the asphalt mix in the United States. The parking lot consisted of a 12-mm mix while the roads consisted of a 4.75-mm "ultrathin" sand mix. The workability was a lower than a conventional mix, but the density requirement was still met.

2.6 Methods to Improve Compatibility of Plastic and Asphalt

Adequate thermal storage stability is essential for a modified asphalt binder to ensure that the composite offers integrity and homogeneous properties during its storage, handling, and transportation in the field (Kumar et al. 2021). Poor storage stability leads to inconsistent composition and rheology of binders between the top and bottom portions of a storage facility; thus, leading to poor performance against principal pavement distresses such as rutting (at high-service temperatures), fatigue cracking (at intermediate-service temperatures), and thermal cracking (at low-service temperatures) (Zani et al. 2017, Zou et al. 2017, Ren et al. 2020).

One of major challenges of incorporating waste plastic into asphalt using the wet process is the poor storage stability of waste plastic asphalt binders, which adversely affect the properties of the asphalt binder (Pérez-Lepe et al. 2006, Leng et al. 2018, Padhan and Gupta 2018). Polacco et al. (2005) studied the morphology of the PE-modified binder. They indicated that a fluorescent, polymer-based phase dispersed in a dark asphaltic phase in the form of almost spherical particles. The dispersed phase was spherical, and no linkages were visible between particles, indicating that the asphalt and PE particles were strongly immiscible. Very low interfacial adhesion presented between the two phases. Liang et al. (2017) pointed out that the poor storage stability at high temperatures concerns EVA-modified binders. The study indicated that the storage stability of EVA-modified binders is closely related to the vinyl acetate (EA) content of the EVA used. They pointed out that the EVA modified binder with higher EA content generally showed better storage stability.

Liang et al. (2019) studied the storage stability of polyethylene-modified asphalt through the cigar tube test (ASTM D7173) and fluorescence microscopy. Figure 2.4 presents FM images. In the morphology analyses of waste plastic-modified binders, the top sample exhibited large spots of

polymeric phase while the bottom sample showed a sparse polymeric phase (a phase separation). The HDPE-modified asphalt had a large amount of closely distributed polymer droplets, which indicated that the polymeric phase likely behaved as the rigid filler. Based on the tube test, Linear low-density polyethylene modified (LLDPT) asphalt showed the best stability, followed by medium-density polyethylene (MDPE), MDPE, HDPE and LDPE modified asphalt (Liang et al. 2019). Casey et al. (2008) accessed the compatibility of different plastics with the base binder. MDPE, PVC, PET and ABS were found not to have good compatibility. The PP was successfully blended but was subsequently found to offer excessive variation in basic binder characterization tests.

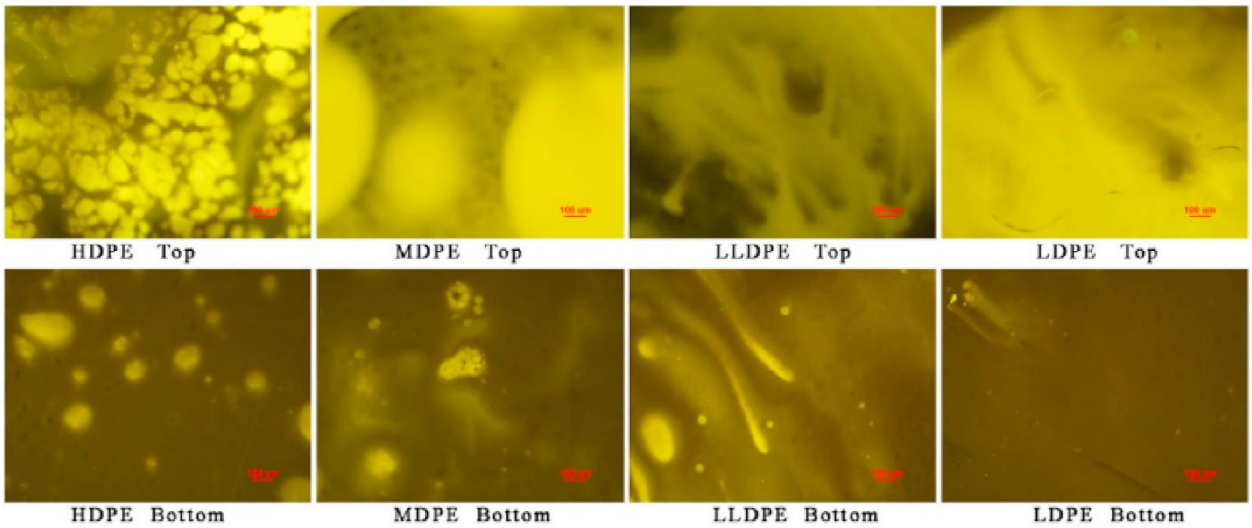


Figure 2.3 Fluorescence microscopy of PE modified asphalts from top and bottom parts of tube after storing for 120 min (Liang et al. 2019).

The poor storage stability of some plastic-modified binders is usually resulted from the poor compatibility between polymer modifiers and bitumen which is controlled by polymers and bitumen's different properties such as density, molecular weight, polarity, and solubility (Wang et al. 2010). The chemical structure and reactivity of polymers, however, are also supposed to affect their compatibility with bitumen, which may have a direct relationship with the resulting plastic-modified binders' properties (Chang et al. 2000).

In order to conquer the poor storage stability challenge, researchers have tried different categories of solutions, such as using of crosslinking agents, hydrophobic clay minerals, functionalization, and application of reactive polymers (Galooyak et al. 2010, Zhu et al. 2014). Coupling agents or crosslinking agents are commonly used additives to improve to compatibility between plastics and binders. Coupling agents are essentially bifunctional molecules, where one functionality is able to

react with the inclusion surface and the other with the polymer, thus coupling the two together (DeArmitt and Rothon, 2011). Coupling agents such as lignin and sulfur are commonly used in plastic-modified asphalt to improve the storage stability (Wen et al. 2001, Wen et al. 2002, Chen and Huang 2007, Zhu et al. 2014, Yuanita et al. 2017). Lignin is an amorphous biopolymer and has bipolar characteristics due to its distinct chemical function, which has carbonyl, carboxyl, hydroxyl and phenol chemical functions. Yuanita et al. (2017) did an experiment mixing lignin, polypropylene (PP), and asphalt binder. The Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscope (FESEM) results showed a new chemical structure due to the addition of lignin. The addition of lignin makes plastic-modified binders get better mixing and increases mechanical properties. In addition to lignin, the sulfur can also serve as a crosslinking agent in the plastic modified binders, chemically coupling the asphalt binder and polymer molecules and reducing the phase separation susceptibility (Chough and Chang 1996). As previously mentioned, waste plastics are also polymers. The sulfur can also be used to improve the storage stability of waste plastics modified asphalt binders. However, although the sulfur is capable of enhancing the storage stability and rutting resistance of polymer-modified asphalt binder (Wen et al. 2001, Zhu et al. 2014), some studies have indicated that the addition of sulfur may accelerate the oxidation aging of polymer-modified asphalt binder (Zhang et al. 2010, Zhang et al. 2011). In addition, during the process of sulfur vulcanization, a hazardous gas named hydrogen sulfide is generated, which may harm the body's health and environment (Zhu et al. 2016).

Hydrophobic clay minerals have also been reported to be used to improve storage stability. It enhances the storage stability of plastic-modified binders by decreasing the density difference between polymer modifiers and binders (Galooyak et al. 2010). Hydrophobic clay minerals' proper content (25% of the polymer by mass) improves the plastic-modified binders' storage stability and rutting resistance and increases viscosity and stiffness (Yu et al. 2007, Golestani et al. 2012).

Organic-modified montmorillonite (OMMT) is a commonly used clay mineral. Fang et al. (2014) indicated that adding a small amount of OMMT improved the storage stability of PVC-modified asphalt binder. The exfoliated structure of OMMT introduces numerous polar branches on PVC molecular chains inserted among the OMMT lamella, which is caused by the polarity of free radical chains and the large surface energy of OMMT. Therefore, the activity of PVC molecular chains increases, leading to the movement of the chain. Eventually, the PVC is dispersed into the asphalt matrix, forming the branched network structures and enhancing the surface combination of PVC and asphalt. The OMMT has also been found to improve the storage stability of PE-modified asphalt binder (Yu et al. 2015).

Functionalization is another method to improve the compatibility of polymer and binder. Functionalization means the chemical addition of specific functional groups to the plastics for obtaining specific functions of plastic modified binders, such as good storage stability, excellent aging resistance, strong adhesion with aggregates, high stiffness at high temperatures and good cracking resistance at low temperatures. By functionalization, various new functions of currently available plastic-modified binders can be obtained, and some new-type polymer modifiers (other than the currently used ones) can be developed, for instance, reactive polymers. Although not typical, saturation can also be considered a functionalization, adding hydrogen to saturate the polymer. Some chemical treatments of plastics are also functionalization, such as the steric method (Hesp et al. 1996), aminolysis reaction (Leng et al. 2018, Padhan and Gupta 2018) and glycolysis reaction (Gürü et al. 2014). These treatments have been reported to improve the compatibility between recycled plastic and asphalt. However, using chemicals to treat plastic surfaces requires storage and disposal of harmful or toxic materials and poses a health risk to employees. Moreover, additional procedures such as rinsing, washing, and drying are required before further processing plastics, which inevitably increase the amount of hazardous waste generated during a single surface treatment operation. Commercial compatibilizers were also added cooperatively with recycled plastics into asphalt binders (Yin and Moraes 2018), but the results showed that further improvements were needed.

Reactive polymer is another modifier that can be used to improve storage stability. Reactive polymers used in asphalt modification are those polymer modifiers that chemically react with some components of binder (Shivokhin et al. 2012). Isocyanate-based polymer is a type of reactive polymer. It was found to be able to increase the viscosity and improve the storage stability and rutting resistance of binder at high temperatures (Navarro et al. 2007).

2.7 Summary

Many plastics are disposed of yearly, so many researchers are attempting to recycle waste plastic into civil infrastructures such as asphalt pavement. The current practice of recycled waste plastics includes seven major types: PET, HDPE, PVC, LDPE, PP, PS and others such as ABS, EVA, PC, and PU. There are generally two ways to incorporate waste plastics into asphalt: the dry and wet processes. In the dry process, waste plastics are added to hot aggregate before adding a binder. Then a prolonged mixing process is followed to make a homogenous mixture; on the other hand, the modifier is mixed with the binder before addition to the aggregate in the wet process. The optimum dosage of waste plastics has been identified in literature based on appropriate engineering performance parameters such as viscosity

of asphalt, rutting, fatigue cracking, thermal cracking, and moisture resistance of asphalt mixtures. In lab tests and road trials, incorporating plastic wastes into asphalt mixes generally showed improvements in performance parameters such as stiffness, rutting and fatigue resistance. However, HDPE, PVC, LDPE, PP, and PS yielded conflicting performance measures. The major challenge of recycling plastics into asphalt binders is poor storage stability or compatibility. The poor compatibility of asphalt and polymers is a severe issue when using the wet method. It tends to split during heated static storage or transportation to pavement sites. The poor compatibility between polymer modifiers and binders is mainly controlled by polymers and binders' different properties such as density, molecular weight, polarity, and solubility. Numerous researchers have concentrated on this topic. There are multiple approaches to this problem, which is the focus of this review.

The approaches to improve storage stability include using crosslinking agents, hydrophobic clay minerals, functionalization, and application of reactive polymers. Coupling agents are essentially bifunctional molecules, where one functionality can react with the inclusion surface and the other with the polymer, thus coupling the two together. Hydrophobic clay minerals such as OMMT can introduce numerous polar branches on the plastic molecular chain caused by the polarity of free radical chains and the large surface energy of OMMT. Plastic can disperse into the asphalt matrix, forming the branched network structures and enhancing the surface combination of plastic and asphalt. Functionalization is another method to improve the compatibility of polymer and binder. Various new functions of currently available plastic-modified binders can be obtained by functionalization. Functionalization includes the steric method (Hesp et al. 1996), aminolysis reaction (Leng et al. 2018, Padhan and Gupta 2018) and glycolysis reaction (Gürü et al. 2014). These treatments have been reported to improve the compatibility between recycled plastic and asphalt. However, using chemicals to treat plastic surfaces requires storage and disposal of harmful or toxic materials and poses a health risk to employees.

Chapter 3 Development of HDPE Treatment Methods to Improve Storage Stability

Dry and wet methods are the two common methods to incorporate plastics into the binder. The wet method does not require contractors to have additional equipment or change the current procedure for mixing; thus, this method is practical and cost-effective. However, the storage stability is the major challenge of the application of the wet method. This study aims to improve the storage stability of HDPE-modified binders. Previous studies conducted by different researchers have been primarily focusing on LDPE. Because of the linear molecular structure with weaker intermolecular force, LDPE is more compatible with asphalt binder than HDPE. This study focuses on HDPE plastic; the goal is to explore the feasibility of incorporating pretreated HDPE in asphalt binders.

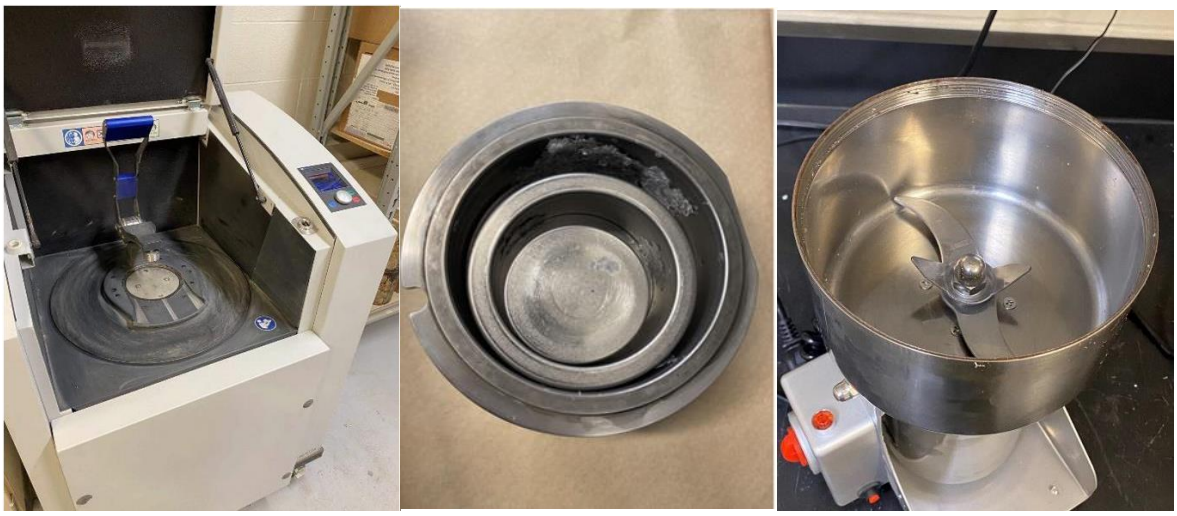
Pretreatment procedures are classified into two categories: physical methods and chemical methods. The physical methods aim to break HDPE into smaller particles, and the chemical methods intend to modify HDPE to be more chemically reactive. This chapter focuses on the chemical treatment, i.e., the flame treatment and the acid treatment. The effectiveness of the treatments is evaluated using Fourier transform infrared spectroscopy (FTIR). The treatment method to optimize the compatibility of HDPE with asphalt binder is determined based on the analysis results.

3.1 Materials

3.1.1 Physically Treated HDPE

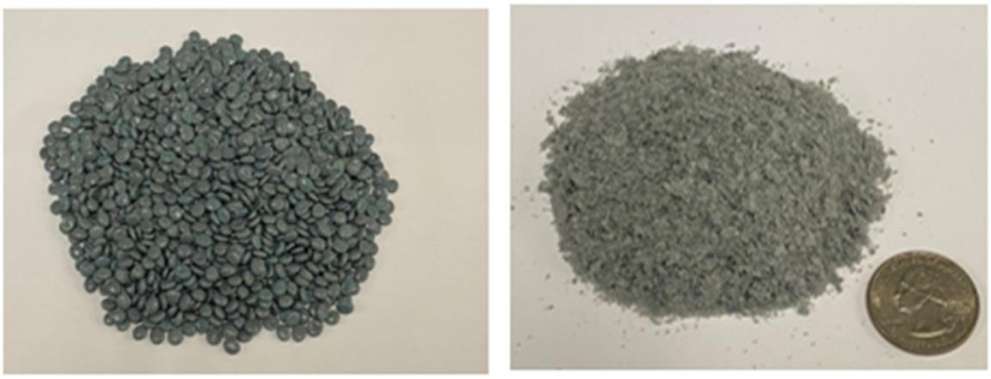
Perez-Lepe et al. (2005) reported that small polymer particles reduced the phase separation and stabilized the blend. Breaking recycled plastic into smaller particles is the most common physical method to improve the compatibility between plastics and asphalt binders. The physical treatment methods include grinding, shredding, pulverization, and extrusion. For instance, Costa et al. (2019) used liquid nitrogen to freeze HDPE, and then pulverized it into powders. Plastic with smaller particle sizes disperses and dissolves more easily into the binder due to enhanced swelling of polymer particles with large surface areas (Dalhat and Wahhab, 2017).

In this study, the physical treatment was applied on the recycled HDPE plastic. The ground HDPE was obtained from crushing HDPE pellets. First, about 10 grams of HDPE flakes were frozen using liquid nitrogen for two hours. Then, the frozen HDPE pellets were milled using the Vibratory Disc Mill (Figure 3.1a) for 3 minutes at 1500 rpm. Then, the milled HDPE pellets were frozen again using liquid nitrogen for 30 minutes. After that, these frozen HDPE flakes were grounded using the grinder (Figure 3.1b). The HDPE pellets and powder are shown in Figure 3.2.



(a) (b) (c)

Figure 3.1 a) Vibratory Disc Mill; b) grinding ring and disc; and c) grinder



(a) (b)

Figure 3.2 a) HDPE pellets and b) HDPE powder

3.1.2 Chemically Treated HDPE

Flame treatment has been widely used to introduce oxygen-containing functional groups (including hydroxyls, carbonyls, carboxyls, and amide) to make the plastic surface more reactive (Pascoe and O'Connell, 2003). Gas flame contains excited fragments and species such as atomic oxygen (O), NO, OH, and others that can abstract hydrogen from the surface of the polymer and replace it with oxygenated functional groups (mostly -C=O and -OH). These functional groups can be created from the surface to a depth of 4 to 6 nm and produces chain scissions and some cross-linking (Ebnesajjad 2015). In other words, the flame treatment increases the wettability of the plastic surface. Therefore, the flame-treated HDPE can be reactive, which will increase the compatibility with asphalt binder particles. It is important to control the optimum level of flame treatment.

In this study, the flame treatment parameters (i.e., the distance between flame and HDPE and treating time) were used to control the quality and level of treatment. The HDPE powder was placed on an aluminum plate, and propane flame torch with jet injection was installed in an actuator, as shown in Figure 3.3. The height of the flame torch was able to be adjusted, and the flame torch could move at a controlled speed on the actuator so that the treatment time was controlled. The distances between the flame and HDPE were set between 5 cm to 15 cm. Researchers have found that undertreatment without sufficient heating time can leave contaminants on the surface while excessive flame treatment damages or over oxidizes the surface of plastic (Walsh 2017). By controlling the actuator speed, the treating time was set between 0.13s and 0.33s (Sabreen 2013). Experiments with combinations of various treating distance and time were then designed and conducted to determine the optimum treating conditions.

Figure 3.3 Flame treatment set up

Besides flame treatment, acid treatment was also utilized in this study. Acid treatment introduces functional groups, such as S=O, to the plastic surface. HDPE powder was treated using sulfuric acid with different durations, and then the FTIR was used to determine the optimum treating time. After the optimum treating time was determined, sulfuric acid and nitric acid were mixed at various ratios to treat HDPE powder. Then, the FTIR test was used again to determine the optimum ratio of these two acids. After obtaining the optimum time and optimum ratio, optimum mixed acid-treated

HDPE powder was mixed with asphalt binder. The acid treated HDPE powder is presented in Figure 3.4.

Figure 3.4 Acid treated HDPE powder

3.2 Characterization Methods

FTIR has been increasingly used for the investigation of asphalt binders in recent years (Weigel and Stephan, 2017). The infrared spectrometer in the attenuated total reflectance (ATR) mode was used in this study. Researchers have found that FTIR in ATR mode is an efficient and reliable method to investigate and monitor the chemical arrangement and structure of asphalt samples (Lopes et al. 2016; Yut & Zofka, 2011; Kazarian and Martirosyan, 2002). The Nicolet iS50 FT-IR spectrometer (Figure 3.5) was used to perform the analyses. A resolution of 4 cm^{-1} for wavenumbers ranging from 400 to 2000 cm^{-1} was used for all FTIR spectra. FTIR tests were conducted to monitor the effectiveness of flame treatment and acid treatment on the chemical structure of HDPE powder by identifying the existence of functional groups based on the appearance of absorbance peaks at specific wavenumbers.

Figure 3.5 Nicolet iS50 FT-IR

Carbonyl is one of the most common oxidative functional groups. It is a new functional group appeared after flame treatment. Carbonyl group is chemically active, and the HDPE powder with high carbonyl index will also be active. When blending with asphalt binder, HDPE powder with higher carbonyl index should have better interaction with asphalt binder with improved the storage stability of modified binder. Therefore, the carbonyl index (CI) was used as an effective indicator of HDPE powder oxidation level after flame treatment. Sulfoxide is another major oxidative functional group, sulfoxide group appeared on HDPE powder after acid treatment. Sulfoxide index (SI) was selected to evaluate the effectiveness of acid treatment. The HDPE powder with higher sulfoxide index is expected to be more active.

The CI and SI were derived from the analysis and used to intuitively quantify the flame treated and acid treated HDPE powder oxidation degree, respectively. The calculations of these indices are shown in Eqs. (3-1) and (3-2):

$$CI = A_{1720cm^{-1}} / A_{1462cm^{-1}} \quad \text{Eq. (3-1)}$$

$$SI = A_{1031cm^{-1}} / A_{1462cm^{-1}} \quad \text{Eq. (3-2)}$$

where, CI refers to carbonyl index, $A_{1720cm^{-1}}$ is the infrared peak area of carbonyl at wavenumber of 1720 cm^{-1}. $A_{1462cm^{-1}}$ is the peak area of ethylene group (CH_2). It serves the purpose of reference peak in infrared quantitative analysis. SI refers to sulfoxide index, $A_{1031cm^{-1}}$is the peak area of sulfoxide group (O=S=O and S=O). All the areas are calculated using two-point method (Marsac 2014).

3.2 Testing Results

3.2.1 Flame Treatment

The optimum flame treatment was determined using FTIR. Figure 3.6 presents an example of spectra of flame-treated HDPE powder, and the circled functional groups are carbonyl group (C=O stretch) and the ethylene group. The spectral band (carbonyl group) at around 1700 cm^{-1} was the only new functional group generated after flame treatment. The intensity of ethylene group was used as a reference since it did not change with the flame treating condition. CI was defined and used to evaluate the effectiveness of flame treatment in this study.

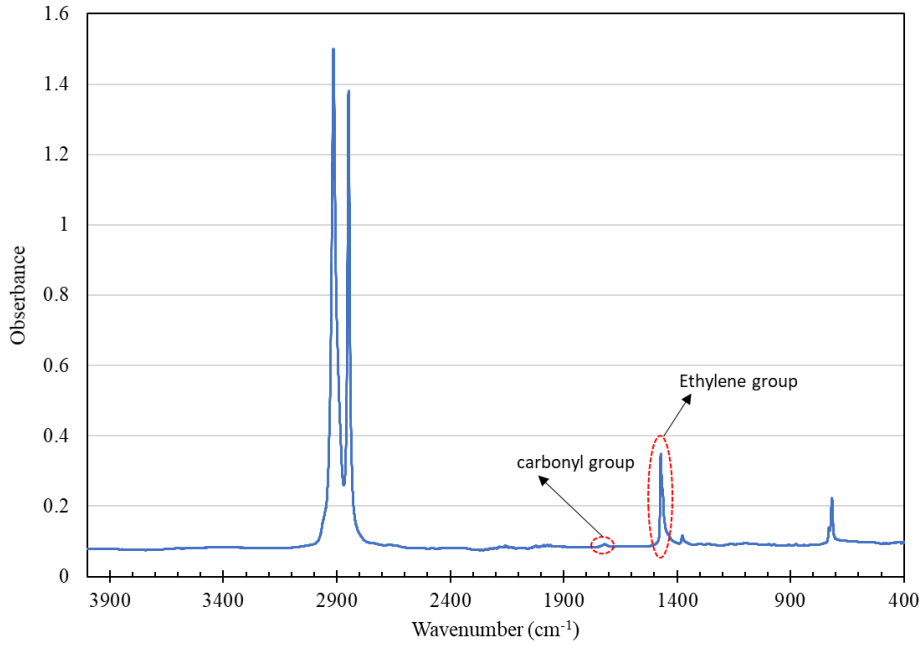


Figure 3.6 An example of spectra of flame treated HDPE powder

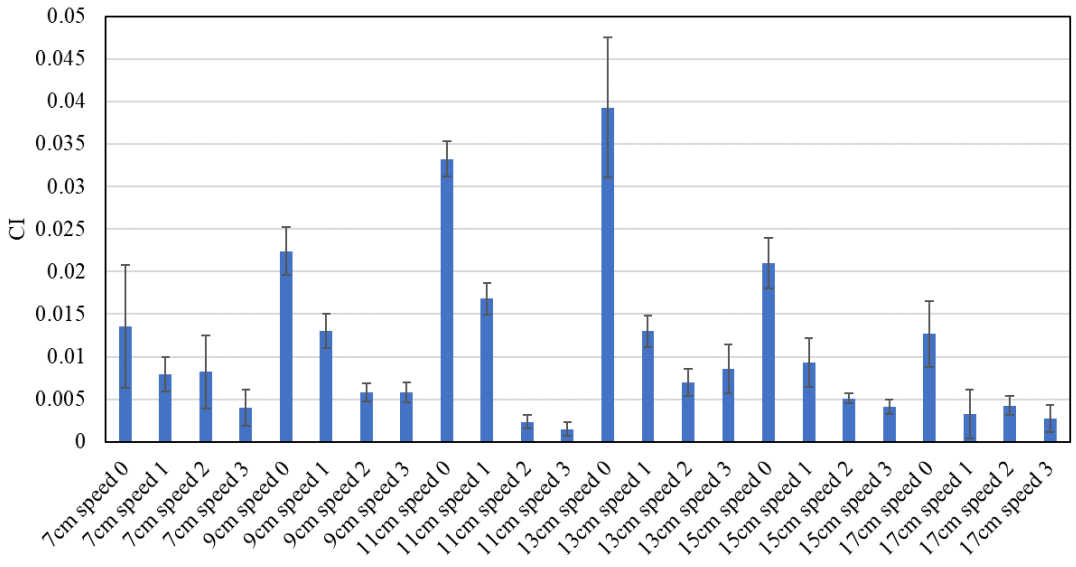


Figure 3.7 CI of flame-treated HDPE powder

Note: speed 0 = 3cm/s (0.33s); speed 1 = 4cm/s (0.25s); speed 2 = 6cm/s (0.17s); speed 3 = 8cm/s (0.13s).

The CI of each treating condition was calculated, as presented in Figure 3.7. When the flame distance was lower than 13 cm or higher than 13 cm, CI decreased. Therefore, the optimum distance of flame treating was 13cm. In terms of the treating time, treatment with 0.33s (speed 0) exhibited the highest CI. As speed increased, the treatment became less effective. 0.33s was the lowest speed that could be achieved in the lab. Overall, 13cm, 0.33s was selected as the optimum treatment condition as it could generate the most carbonyl group on the HDPE powder surface.

3.2.2 Acid Treatment

Figure 3.8 presents the FTIR spectra of sulfuric acid treated HDPE powder at different durations. The spectra curve of each treatment other than the control sample was raised by a certain offset value for illustration purposes. The difference between the peak values at corresponding wave numbers and the lowest point of the curve represented the intensity of the corresponding functional groups. After sulfuric acid treatment, there were a few new functional groups generated. The sulfoxide group was the most detectable new functional group. Since the intensity of ethylene group did not change with the change of duration, it was used as a reference. The SI was defined to assess the effectiveness of the acid treatment in this study. Higher SI indicated greater effectiveness of the acid treatment method. According to Figure 3.8 and Table 3.1, with longer treatment durations, SI increased. The SI increased dramatically from 1-day treatment to 7-day treatment, but there was not much change after 7 days. Given the SI

values and the practicality of the treatment time, 7-day treatment was selected as the proper treating time.

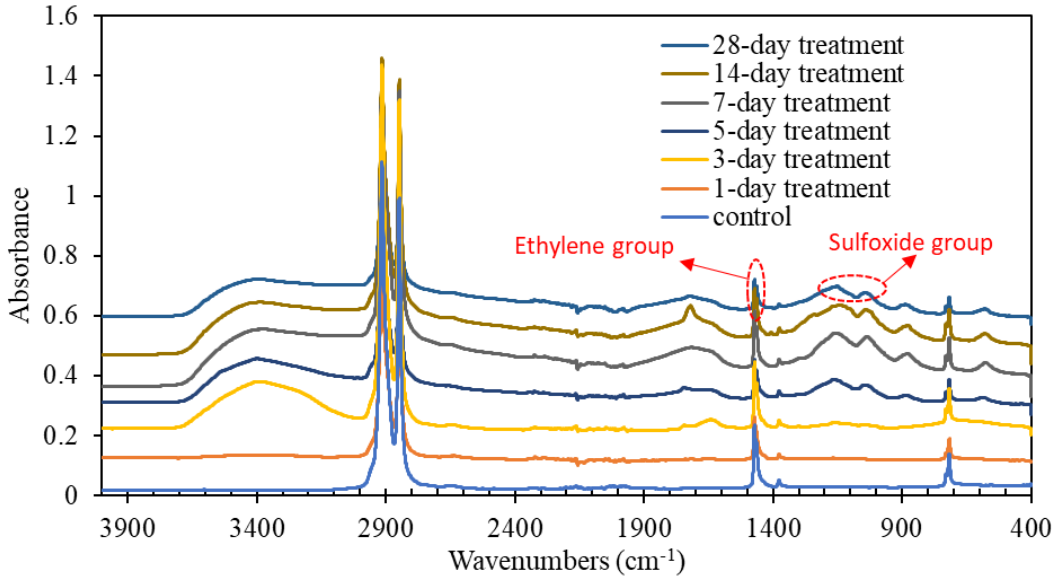


Figure 3.8 FTIR spectra of the acid treated HDPE powder at different durations

Table 3.1 Sulfoxide index of the acid treated HDPE powder at different days

	control	1-day	3-day	5-day	7-day	14-day	28-day
SI	0	0	0.3	1.0	1.7	1.8	1.8

To improve the treatment results, a new method using both sulfuric acid and nitric acid were adopted to achieve higher SI. The blending ratio was also determined using the FTIR spectra. Figure 3.9 and Table 3.2 present how the blending ratios affected the SI results. According to the testing results, ratio of sulfuric: nitric acid = 2:1 yielded the highest sulfoxide index values and therefore, was selected as the optimum blending ratio.

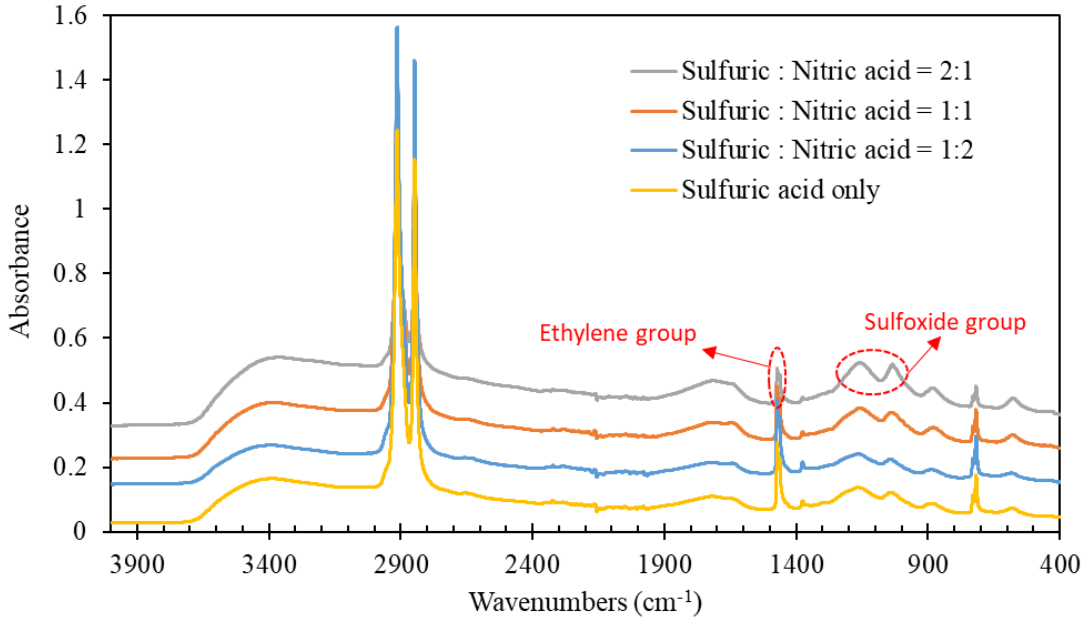


Figure 3.9 FTIR spectra of the acid treated HDPE powder at different ratios

Table 3.2 Sulfoxide index of the acid treated HDPE powder at different ratios (the ratios are mole ratios)

	Sulfuric: Nitric acid = 2:1	Sulfuric: Nitric acid = 1:1	Sulfuric: Nitric acid = 1:2	Sulfuric acid only
Sulfoxide index	4.1	3.4	1.8	1.7

3.3 Summary

One way to improve the storage stability of plastic-modified binders is the functionalization of plastic. Functionalization adds specific functional groups to the plastic so that the plastic are more chemically active with the asphalt binder. In this chapter, flame treatment and acid treatment methods were applied as the functionalization methods. For flame treatment, two parameters (i.e., the distance between flame and HDPE and treating time) were controlled as factors that may affect the effectiveness of flame treatment. For the acid treatment, treating durations and ratios between sulfuric acid and nitric acid were controlled as two factors affecting the effectiveness of acid treatment. The effectiveness of the flame and acid treatment were evaluated using FTIR. CI was used as an indicator of HDPE powder oxidation level for flame treatment. A high CI value indicated high activeness in the treated HDPE powder. SI was used to evaluate the effectiveness of the acid treatment because the sulfoxide group was the major oxidative functional group that appeared on HDPE powder after acid treatment.

For flame treatment, the results showed that CI decreased when the flame distance was lower than 13 cm or higher than 13 cm. The treated HDPE powder at 0.33 s exhibited the highest CI. Therefore, 13 cm (5.12 inch), 0.33 s was selected as the optimum flame treatment method.

For the acid treatment, SI increased as the treatment duration increased. Also, SI increased dramatically from 1-day to 7-day treatment, but there was not much change after 7 days. Considering the SI values and the practicality of the treatment time, 7 days was selected as the proper treating time. The results also showed that the ratio of sulfuric: nitric acid at 2:1 yielded the highest SI values, and therefore, it was selected as the optimum blending ratio.

Chapter 4 Evaluate the Compatibility Between Different Treated HDPE with Asphalt Binder

To evaluate the compatibility between different treated HDPE with asphalt binder, the optimum flame treated HDPE powder, optimum acid treated HDPE powder, untreated HDPE powder, and untreated HDPE pellets were added into asphalt binder. Kaolinite nanoclay, bentonite nanoclay, and rejuvenator were also used as modifiers.

Nanoclay is a commonly used modifier to improve the storage stability of polymer-modified asphalt. When nanoclay is blended with asphalt and polymer, the separation of clay leads to a nanoclay with a large active surface area (up to 700-800 m2/g) (Yang and Tighe, 2013). Increasing the surface area can accelerate the formation of micro and macro composites. Thus, clay can decrease the density difference between polymer and binder as the driving force of separation (Golestani et al. 2015). Kaolinite clay and bentonite have been widely used to improve storage stability in polymer modified asphalt due to their micrometric scale (Golestani et al. 2015, Iskender 2016).

In addition to nanoclay, rejuvenators have also been used to improve the storage stability. I have been found that using rejuvenator can effectively increase the colloidal index (Ic) (also called the Gaestel Index) (Gaestel et al. 1971).

$$I_c = \frac{Asphaltenes + Saturates}{Aromatics + Resins} \quad \text{Eq. (4-1)}$$

The instability colloidal index implies that as the polymer absorbs maltenes, there is a reduction in the peptizing molecules still available to cover the asphaltenic micelles. The parameter indicates the phase segregation under the influence of a gravitational field. If the base asphalt has a high aromatic content, then after polymer swelling, the resin may still be able to peptize the asphaltenes, thereby reducing their tendency to separate (Polacco et al. 2015). Since rejuvenator usually has a high maltene content (Xie et al. 2019), it is used in this study to increase the storage stability of the plastic incorporated asphalt binder.

After preparing these modified binders, the storage stability tests (cigar tube test) and the softening point tests were conducted to evaluate the homogeneity of each modified binder. To investigate the working mechanism of different modifiers (i.e., rejuvenator, nanoclay, flame treated HDPE powder, and acid treated HDPE powder) in modified binder, FTIR tests were also conducted to monitor the functional group change before and after mixing, which can be used to quantify the interaction between plastic and binder.

4.1 Materials

4.1.1. Preparation of Binder and Plastic

The asphalt binder used in this study was PG 64-22 from Missouri. The HDPE plastic pellets were KWR102 (post-consumer mixed color copolymer high-density polyethylene resin) from KW plastics. HDPE plastic waste had a specific gravity of 0.95 g/ml and a melt flow of 0.5g/10 minutes.

4.1.2. Blending Process

For each modified binder, the modifier was added at the dosage of 5.0% by the weight of the asphalt binder (Suksiripattanapong et al. 2022). To prepare modified binders, the neat asphalt binder was preheated in an oven for 30 minutes at 180°C to fluid. The HDPEs were first added to the binder and blended for one hour at 180°C (Costa et al. 2013) using a high shear mixer at the speed of 3500 rpm (Kakar et al. 2021). Figure 4.1 presents the setup of a high shear mixer.

Figure 4.1 High shear mixer

In this study, nine types of modified binders are prepared. Table 4.1 presents the details of modifiers, their dosages of each modified binder prepared, and their designations in the research.

Table 4.1 Modifiers and their dosages of each modified binder

Type of binder	Designation	Modifiers and dosages (wt./wt. of binder)
Plastic Pellet-modified Binder	PPLB	HDPE pellet: 5%
Plastic Powder-modified Binder	PPDB	HDPE powder: 5%
Flame-treated Plastic-modified Binder	FPB	Optimum flame treated HDPE powder: 5%
Flame-treated Plastic and Kaolinite-modified Binder	FPKB	Optimum flame treated HDPE powder: 5% Kaolinite clay: 2%
Flame-treated Plastic and Bentonite-modified Binder	FPBB	Optimum flame treated HDPE powder: 5% Bentonite clay: 2%
Flame-treated Plastic and Rejuvenator-modified Binder	FPJB	Optimum flame treated HDPE powder: 5% Rejuvenator: 5%
Sulfuric Acid-treated Plastic-modified Binder	SAPB	Optimum sulfuric acid treated HDPE powder: 5%
Mixed Acid-treated Plastic-modified Binder	MAPB	Optimum mixed acid treated HDPE powder
Mixed Acid-treated Plastic and Kaolinite-modified Binder	MAPKB	Optimum mixed acid treated HDPE powder Kaolinite clay: 2%

4.2 Characterization Methods

The storage stability tests were conducted on asphalt binders containing recycled HDPE in this study. Storage stability refers to the tendency of HDPE to separate from asphalt binders and indicates the degree of chemical compatibility between the two individual components. Storage stability is important to ensure the integrity of modified binders during storage and handling in the field. Figure 4.2 presents the setup of a storage stability test. The ASTM D7131, *Standard Practice for Determining the Separation Tendency of Polymer from Polymer-modified Asphalt*, was used to determine the storage stability of modified binders. Fifty grams of modified binder was sealed in an aluminum tube and conditioned in a vertical position for 48 hours at 163°C. After the static heat conditioning, the sample was frozen at -10°C for four hours. The top and bottom portions of the sample were then separated and subjected to further testing to determine the degree of separation.

Figure 4.2 Storage stability test

After the binder testing specimens were prepared, softening point tests were conducted. The softening point test used a ring-and ball apparatus (ASTM 2012b) to evaluate the flow resistance at high temperatures and to determine the temperature at which the phase change occurred in the asphalt binder. The softening point was the temperature at which the asphalt binder cannot support the weight of a steel ball and begins flowing. After the thermal storage, the softening points of the top and bottom sections of the samples were tested, and the absolute value of the difference between the softening points of the top and bottom sections, ΔSP, was adopted as the storage stability index, as presented in Eq. (4-2).

$$\Delta SP = |SP_t - SP_B| \quad \text{Eq. (4-2)}$$

where:

SP_t = softening point of top section of sample (°C);

SP_B = softening point of bottom section of sample (°C);

ΔSP = difference in absolute value of the softening point of top and bottom sections (°C).

Difference in softening points, ΔSP, is one of the most used parameters for storage stability evaluation (Fernandes et al. 2008, Galooyak et al. 2010, Polacco et al. 2015, Sun and Lu 2003). ASTM D5892 (2000) specifies that if the ΔSP is less than 2.5°C, the sample is considered to have good high-temperature storage stability. The binders with higher softening point difference exhibit poor storage stability. The FTIR test was also conducted to evaluate the interaction between modifiers and asphalt. The detail of this method has been described in Chapter 3. Same as the tests in Chapter 3, FTIR in the ATR mode was used in this study. The total peak index (TI) is used to assess the level of the interaction between the modifiers and asphalt. High TI indicates a high interaction intensity. Four peaks of the spectra (i.e., C-O stretching, O=S=O stretching, S=O stretching, and C-H bending) were used as factors

reflecting the intensity of the interaction between modifiers and asphalt binder. The calculation of TI is shown in Eq. (4-3):

$$TI = \sum A_{multiple\ peaks} / A_{1462cm^{-1}} \quad \text{Eq. (4-3)}$$

where, TI refers to total peaks index; A refers to the characteristic peak area; $\sum A_{multiple\ peaks}$ refers to the total peak area. The multiple peak areas including peaks at around 1250 cm^{-1}, 1100 cm^{-1}, 1020 cm^{-1} and 800 cm^{-1} were chosen. The calculation of $\sum A_{multiple\ peaks}$ is shown in Eq. (4-4):

$$\sum A_{multiple\ peaks} = A_{1250cm^{-1}} + A_{1100\,cm^{-1}} + A_{1020\,cm^{-1}} + A_{800cm^{-1}} \quad \text{Eq. (4-4)}$$

The area of ethylene group is used as denominator since the area of ethylene group is consistent in all binders. The higher the TI is, the more functional groups have been generated, meaning the interaction between binder and modifiers is considered higher.

4.3 Testing results

4.3.1 Softening Point Results

The difference in softening points between the top and the bottom sections of the tube was measured and presented in Figure 4.3.

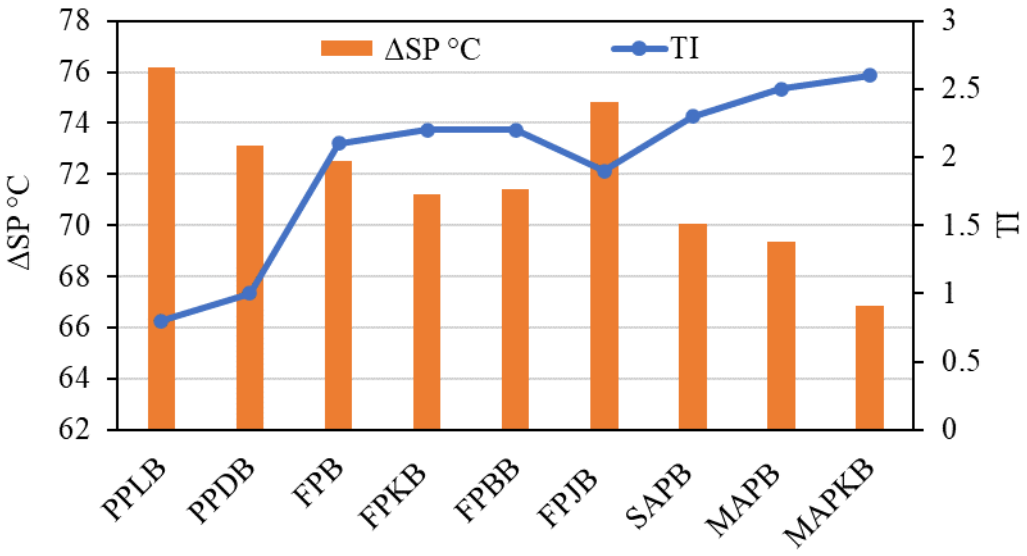


Figure 4.3 ΔSP and TI of various modified binders

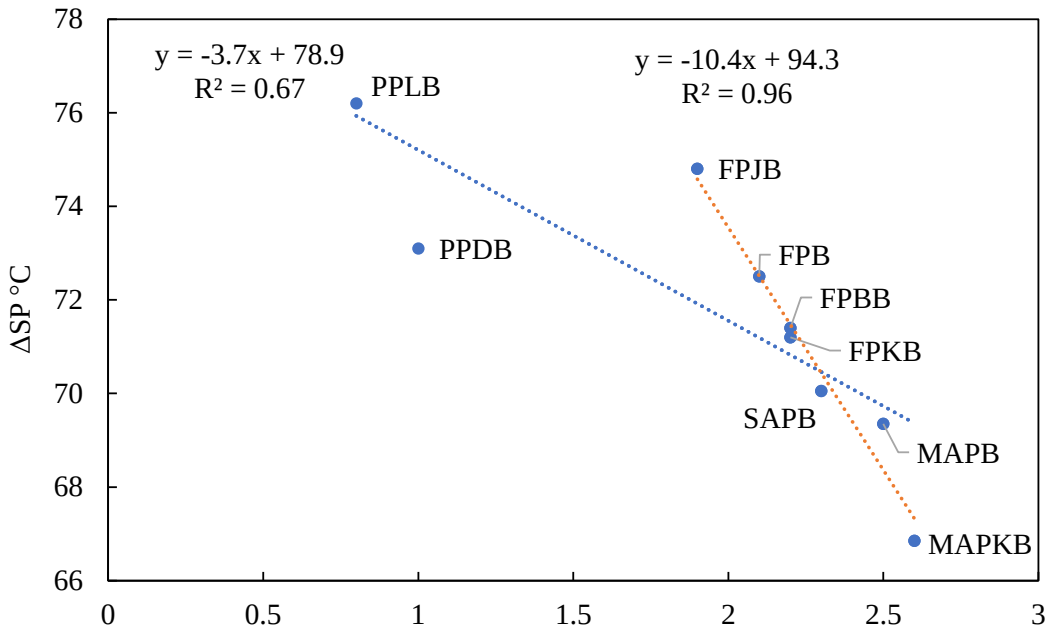


Figure 4.4 Correlation between ΔSP and TI of various modified binders.

The top sections exhibited much higher softening points than the bottom sections. The differences indicated segregation occurred between asphalt binder and HDPE during thermal storage. As HDPE had a lower density than asphalt binder, with poor storage stability, the top sections had more concentrated HDPE and higher softening points than the lower sections of the samples. According to the results presented in Figure 4.3, PPLB has the lowest storage stability, with a ΔSP of 76.2°C. Figure 4.3 also indicates that the size of plastic had a positive impact on storage stability. PPDB had a ΔSP of 73.1°C, which was 3.1°C less than PPLB. Flame treatment also improved the compatibility between HDPE powder and asphalt, as the ΔSP of FPB decreased by 0.6 °C compared to PPDB. The ΔSP was slightly reduced with the addition of kaolinite and bentonite clay. Kaolinite clay has a slightly better effect than bentonite clay. Adding a rejuvenator did not improve the compatibility between HDPE powder and asphalt.

The correlation relationship between the FTIR index and the softening points is presented in Figure 4.4. The regression analysis results showed that the FTIR TI index had a linear relationship with the measured differences in softening points. If only the binders with treated plastic were considered, the R-square of the regression was 0.96, which indicates a high correlation between the two parameters. The analyses results indicated that the FTIR TI index can well-reflect the storage stability of plastic-modified asphalt binder.

ASTM D5892 (2000) specifies that if the ΔSP is lower than 2.5°C, the sample is considered to have good high-temperature storage stability. According to the results presented in Figure 4.3, none of the treated plastic met the criteria. Yet, MAPKB was selected as the optimum modified binder in terms of best homogeneity. Acid treatment had a better effect than flame treatment in terms of storage stability.

4.3.2. FTIR Results

FTIR spectroscopy was employed to identify the presence of chemical functional groups in modified binders. The intensity of the newly generated functional groups was used to evaluate the interaction degree between modifiers and asphalt. In order to understand the impact of modifiers on the chemistry of bitumen, the FTIR characterization of the neat binder and the nine modified binders were conducted in the wave number range from 4000 to 400 cm^{-1}. Figure 4.5 presents the results from FTIR spectra. A strong spectral band around 1250 cm^{-1} represents the C-O stretching. The spectral bands between 1000 to 1100 cm^{-1} presented the O=S=O and S=O stretching, and they belonged to the sulfoxide functional groups. The band around 800 cm^{-1} was dominated by the C-H bending. These labelled peaks of the spectra (i.e., C-O stretching, O=S=O stretching, S=O stretching, and C-H bending) were the important peaks contributing to the storage stability. The absorbance of these peaks scatters clearly showed the different modified binder samples. The parameter, TI, was used to assess the interaction degree between modifiers and asphalt.

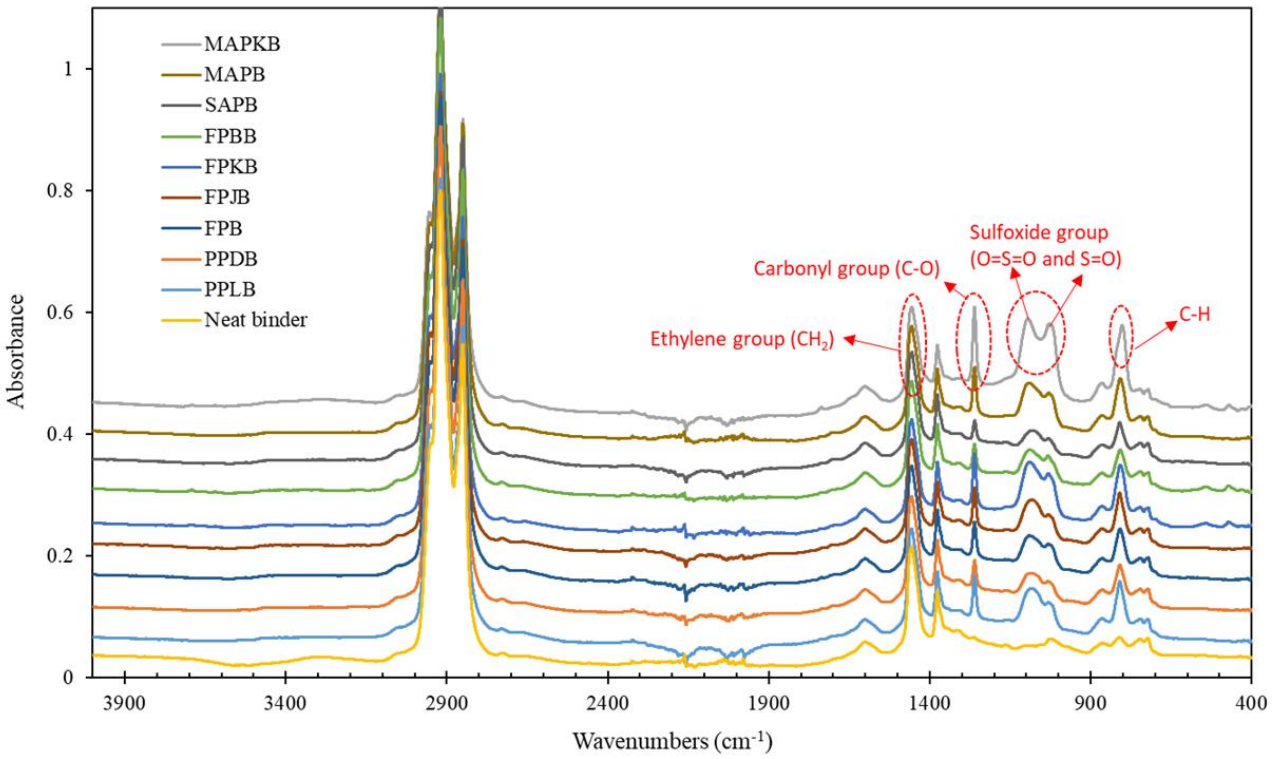


Figure 4.5 FTIR spectra of various modified binders

Figure 4.5 presents the FTIR spectra of all binders. By applying Eq. (4-3) to all the modified binders, TI were calculated, and the results are presented in Figure 4.3. PPLB had the lowest TI, followed by PPDB. This result was consistent with the softening point test because HDPE powder had larger surface area to interact with binder. FPB contained nearly doubled TI compared to PPDB, which meant the flame treatment further activated the HDPE powder. However, the impact of Kaolinite, bentonite, and rejuvenator on the storage stability was not significant. SAPB, MAPB, and MAPKB showed better results than FPB, which meant acid treated HDPE powder had more interaction with binder. Among all the modified binders, MAPKB has the highest peak intensity ratio, which indicated it had the highest interaction with asphalt binder.

4.4 Summary

After evaluating the effectiveness of each treatment, the flame-treated HDPE powder with the highest CI and the acid-treated HDPE powder with the highest SI was selected as optimum treated HDPE powder. Then, nine different modified binders (i.e., PPLB, PPDB, FPB, FPKB, FPBB, FPJB, SAPB, MAPB, and MAPKB) were prepared. Storage stability test (cigar tube test) and softening point test were conducted to evaluate the homogeneity of each modified binder. To investigate the working mechanism of different modifiers (i.e., rejuvenator, nanoclay, flame treated HDPE powder, and acid treated HDPE powder) in

modified binder, FTIR tests were conducted to monitor the functional group change after mixing and before mixing, which can be used to quantify the interaction between plastic and binder.

For the softening point tests, ΔSP, the difference in softening points between top and bottom sections, was adopted as the storage stability index. It indicated the level of segregation between asphalt binder and HDPE during thermal storage. The results showed that PPLB had the lowest storage performance, with a ΔSP of 76.2°C. However, PPDB had a ΔSP of 73.1°C, which is 3.1°C lower than PPLB. The result indicated that the size of plastic had a positive impact on storage stability. The results also show that adding a rejuvenator did not improve the compatibility between HDPE powder and asphalt. Kaolinite clay has a slightly better effect than bentonite clay. Flame treatment improved the storage stability. It has a better effect than using nanoclay. Acid treatment had an even better impact than flame treatment in terms of storage stability. MAPKB was selected as the optimum modified binder in terms of best homogeneity among these modified binders.

For the FTIR test, TI was used to estimate the interaction degree between modifiers and asphalt. The higher TI indicated a higher level of interaction. Four peaks of the spectra (i.e., C-O stretching, O=S=O stretching, S=O stretching, and C-H bending) were used to contribute to the better interaction between modifiers and asphalt binder. The results showed that FPB had about doubled TI as PPDB, which meant the flame treatment improved the interaction between HDPE powder and binder. Kaolinite, bentonite, and rejuvenator didn't show much improvement in the interaction. SAPB, MAPB, and MAPKB showed better results than FPB, which meant acid-treated HDPE powder had a higher interaction level with binder than flame-treated HDPE powder. MAPKB was selected as the optimum modified binder due to its highest TI. The TI results had a strong correlation with softening points difference results. The binder with higher ΔSP tended to have a lower TI value. High ΔSP and low TI values reflected poor modifier and binder compatibility.

Chapter 5 Rheology Performance Tests and Results

The Superpave binder tests (i.e., RV, DSR, and BBR) were conducted to 1) investigate the effect of storing time on the properties of modified binders 2) assess the workability of the optimum modified binders selected from chapter 4, and 3) investigates the effects of HDPE powder on the properties of asphalt binders. Five binders were tested including PPDB-0 (PPDB right after mixing), PPDB-14 (PPDB two weeks after mixing), MAPKB-0 (MAPKB right after mixing), MAPKB-14 (MAPKB two weeks after mixing), and control binder. The control binder is an aged neat binder. The neat binder was also preheated at 180°C for half an hour, followed by the mixing using a high shear mixer running at 3500 rpm for 60 min at 180°C because all the other modified binders had gone through the same process. MAPKB was the optimum binder selected from chapter 4 due to its best storage stability. PPDB was selected as a control-modified binder. The rheological effect of treatment can be evaluated by comparing PPDB with MAPKB.

5.1 Testing methods

The Superpave binder tests (i.e., RV, DSR, and BBR) were conducted for PPDB-0, PPDB-14, MAPKB-0, MAPKB-14, and control binder. Table 5.1 lists the modified asphalt rheology testing matrix.

Table 5.1 Modified asphalt rheology testing matrix

Test	Properties	Parameters of outputs	Binder status	Test temperatures (°C)	Standard
RV	Viscoelastic behavior	Viscosity	Original	120, 135, 150, 165,180	AASHTO T 316
DSR	Rutting and Fatigue properties	Rutting parameter (G*/δ)	Original RTFO	64 and up for rutting; 40 and below for fatigue.	AASHTO T 315
BBR	Thermal cracking	S; m-value[a]	RTFO+20h PAV	0,6,12,18	AASHTO T 313

[a]m-value is defined as the rate of change of stiffness with time.

5.1.1 Artificial Aging Process

The rolling thin film oven (RTFO) test was conducted to evaluate the effect of short-term aging during mixing and construction. According to AASHTO T 240-08, the RTFO (Figure 5.1) exposes fresh thin films of binder to heat (163°C) and air for 85 minutes by rotating coated bottles (15 revolutions/minute) and blowing air into the bottles (4000 ml/minute).

Figure 5.1 Rolling Thin-Film Oven (RTFO) equipment.

To simulate the long-term aging in the field, some of the RTFO residue was aged again in a Pressure Aging Vessel (PAV) (Figure 5.2). The binder was subjected to high temperature (100°C) and pressure of 2070 kPa for 20 hours according to AASHTO R 28. The sample pans are then placed in the degassing oven maintained at 163°C for 30 minutes to remove entrapped air from the samples.

Figure 5.2 Pressure Aging Vessel (PAV) equipment.

5.1.2 RV Test

The rotational viscosity characterized the asphalt binder for workability during pumping and mixing. The RV test utilized a Brookfield viscometer (including a temperature controller, a digital data controller and a rotational viscometer (Figure 5.3) to ensure constructability at the plant. The testing condition was attained by specifying a maximum viscosity of 3 Pa·s at 135°C. In addition, the RV tests were performed for all binders at temperatures from 120° C to 165°C to determine mixing and

compaction temperatures at which the viscosities of binders range between 0.15 and 0.2 Pa.s, and between 0.25 and 0.3 Pa.s, respectively.

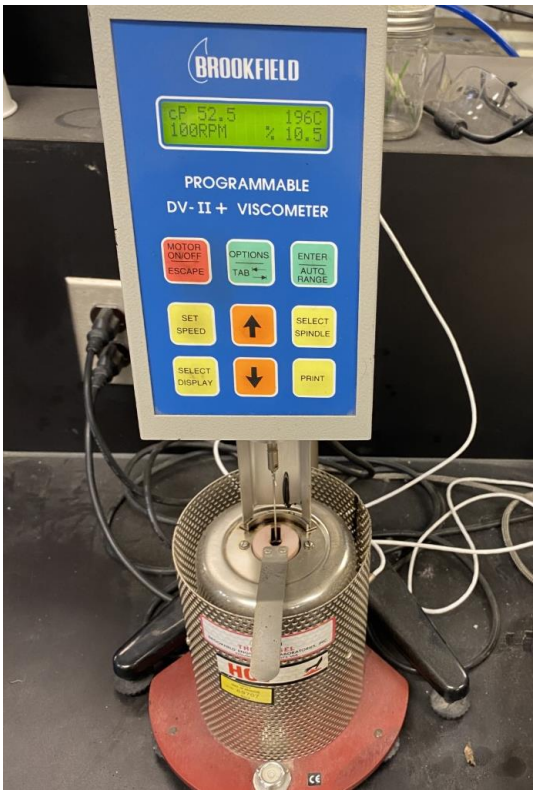


Figure 5.3 Rotational viscometer (RV) equipment

5.1.3 Dynamic Shear Rheometer Test

The rheological tests are conducted on both the original and aged binders with a dynamic shear rheometer (DSR) (Figure 5.4). The viscoelastic mechanical responses at different temperatures of the binders are measured under a controlled-strain shear loading mode. The DSR applies a torque to a thin film of binder specimen placed between two plates at a frequency of 10 radians per second. The applied torque and resulting shear strain are used in the computation of complex modulus (G*) and phase angle (δ). For original binder, the specification requires determining the temperature that corresponds to a minimum value of 1.0 kPa for G*/sinδ. For RTFO residue, the limit on G*/sinδ is 2.2 kPa for a loading rate of 10 radians/second. DSR tests on the original and RTFO aged binders are supposed to evaluate the binder's resistance to rutting. The PAV residue is also tested using the DSR to evaluate the fatigue resistance of the binder. The specification in this case requires determining the temperature associated with a maximum G*sinδ of 5000 kPa for a loading rate of 10 radians/second.

Figure 5.4 Dynamic Shear Rheometer (DSR) equipment

5.1.4 Bending Beam Rheometer (BBR) Test

The BBR test (Figure 5.5) is used to evaluate the stiffness of the PAV aged binder at low temperatures. The BBR subjects a small beam of binder to a constant creep load and measures the resulting deflection at a temperature related to the anticipated lowest pavement service temperature. By using simple beam theory, the creep stiffness (S) and the creep rate (m-value) which is defined as the rate of change of stiffness with time are calculated. The S at 60 seconds must be less than 300 MPa, and the m-value at this time of loading must be at least 0.30 in order to meet the binder specification (AASHTO M 320).

Figure 5.5 Bending Beam Rheometer (BBR) equipment

5.2 Testing Results

5.2.1 Effects of plastic on workability performance of Binders

Figure 5.6 illustrates the viscosity of plastic-modified binders at temperatures ranging from 120° C to 180°C. All binders exhibited decrease in viscosity with the increase of temperature. In addition, PPDB-0, PPDB-14, MAPKB-0, and MAPKB-14 all had much higher viscosity than control binder at each test temperature. The mixing and compaction temperatures of binders were determined based on Figure 5.6, with corresponding viscosities between 0.15 and 0.2 Pa.s, and between 0.25 and 0.3 Pa.s, respectively. The mixing temperature of the control binder was between 150-165°C, and compaction temperature of control binder was between 135-150 °C. However, the mixing temperature and compaction temperature of PPDB-0, PPDB-14, MAPKB-0, and MAPKB-14 were all above 165°C. PPDB-0 and PPDB-14 showed slightly less viscosity than MAPKB-0 and MAPKB-14 at each temperature (i.e., 120, 135, 150, 165 and 180°C).

From Figure 5.7 and the T-test results showing in Table 5.2, it can be concluded that the differences caused by storing time are not significant for binder PPDB and MAPKB. In other words, the storing time does not affect binders' viscosities.

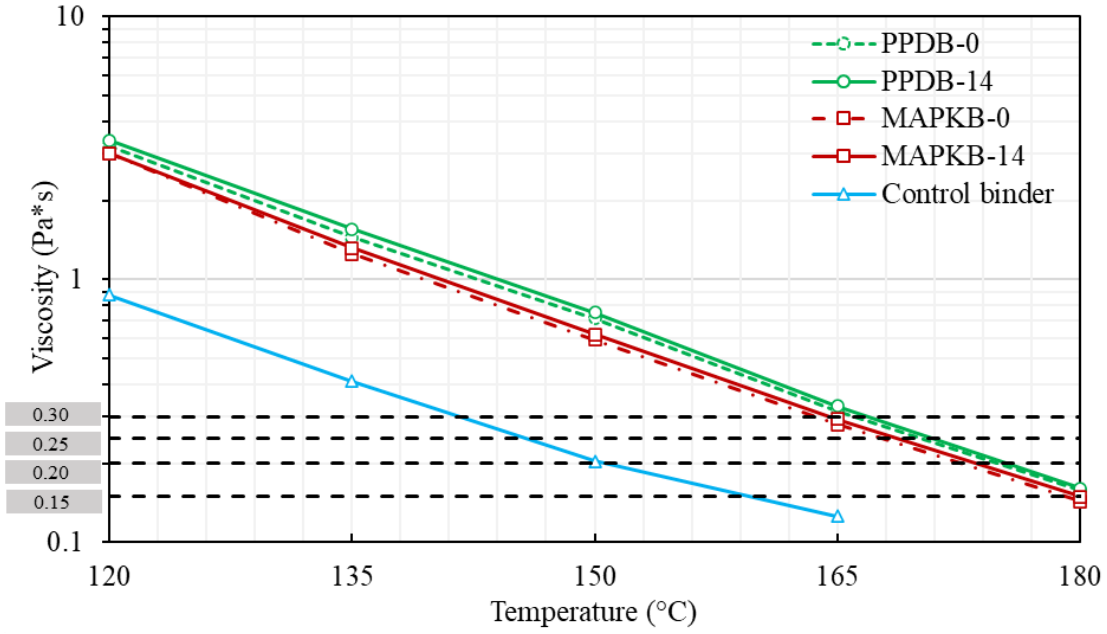


Figure 5.6 Binder viscosity vs. temperature

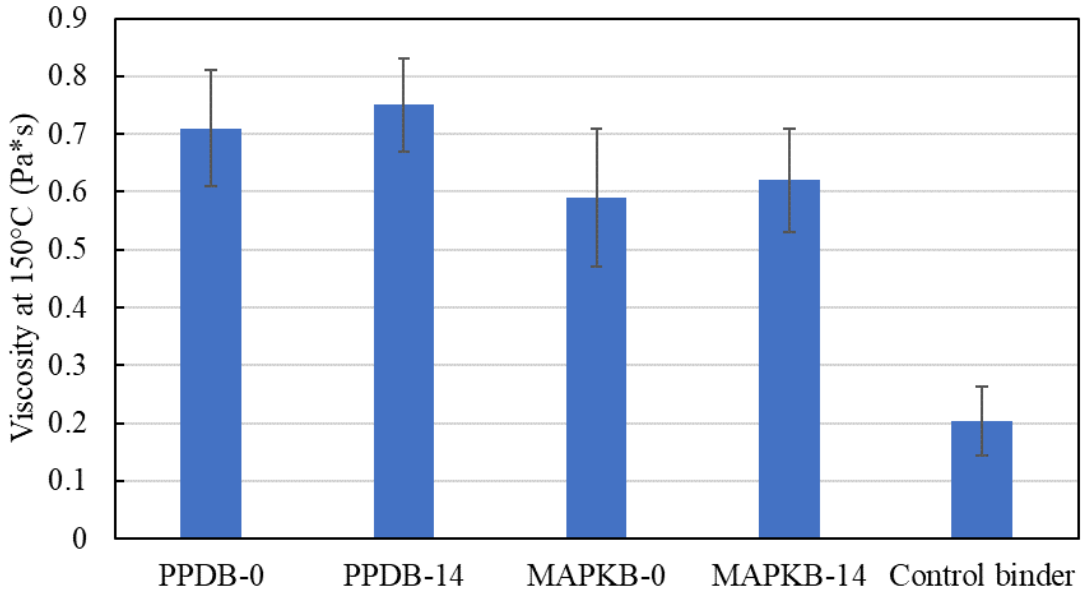


Figure 5.7 Viscosity at 150°C of unaged binders

Table 5.2 Viscosity T-test results of different binders

	PPDB-0	PPDB -14	" PPDB -0 and PPDB -14" P value	MAPKB-0	MAPKB-14	"MAPKB-0 and MAPKB-14" P value
Viscosity at 150°C (Pa*s)	0.71	0.74	0.36	0.59	0.61	0.36

5.2.2 Effects of HDPE on rutting resistance

The Superpave binder specification uses a rutting factor, G*/sinδ, as a measure of asphalt binder's stiffness or rutting resistance at high pavement service temperature. The testing results of G*/sinδ for both original and RTFO aged binders are illustrated in Figures 5.8 and 5.10, respectively. For both conditions, the rutting factor increased with the HDPE added. The high temperature of PG is determined based on that the G*/sinδ must be at least 1.00 kPa for the original asphalt binder and a minimum of 2.20 kPa for the RTFO aged asphalt binder when tested by DSR. As it shown in Figure 5.8, the control binder failed at 70 ºC. PPDB-0, PPDB-14, MAPKB-0, and MAPKB-14 all failed at 82 ºC. Therefore, all modified binders had much higher rutting resistance compared to unmodified binder. PPDB-0 and PPDB-14 had slightly better rutting resistance than MAPKB-0 and MAPKB-14. For RTFO aged binders, all modified binders had similar rutting resistance, regardless of treatment of HDPE powder or storing time. Table 5.3 also indicates that the storing time does not affect rutting resistance.

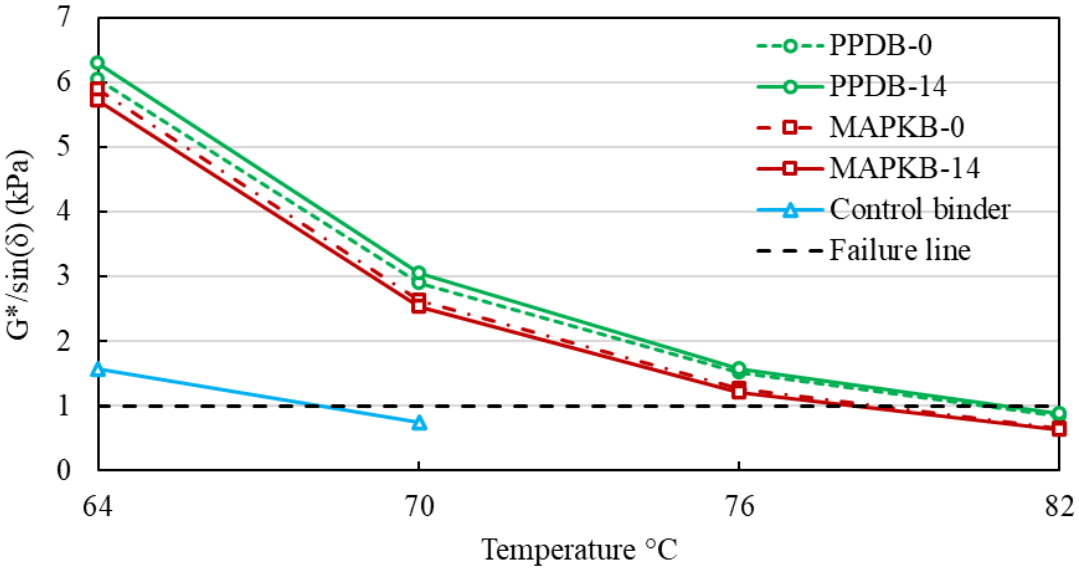


Figure 5.8 Rutting factor of unaged binders

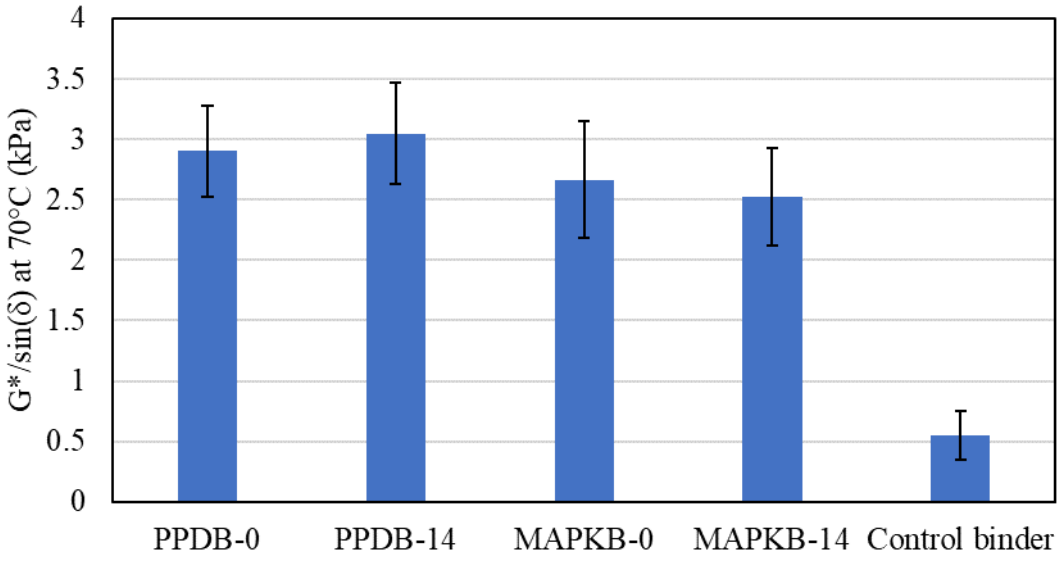


Figure 5.9 G*/sin(δ) at 70 °C of unaged binders

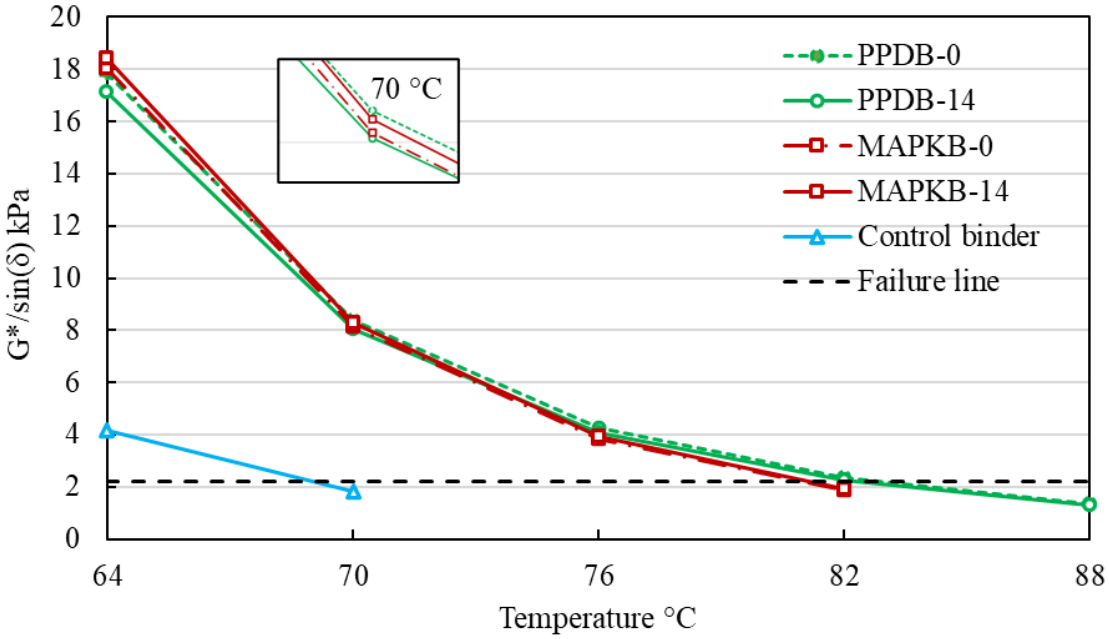


Figure 5.10 Rutting factor of RTFO aged binders

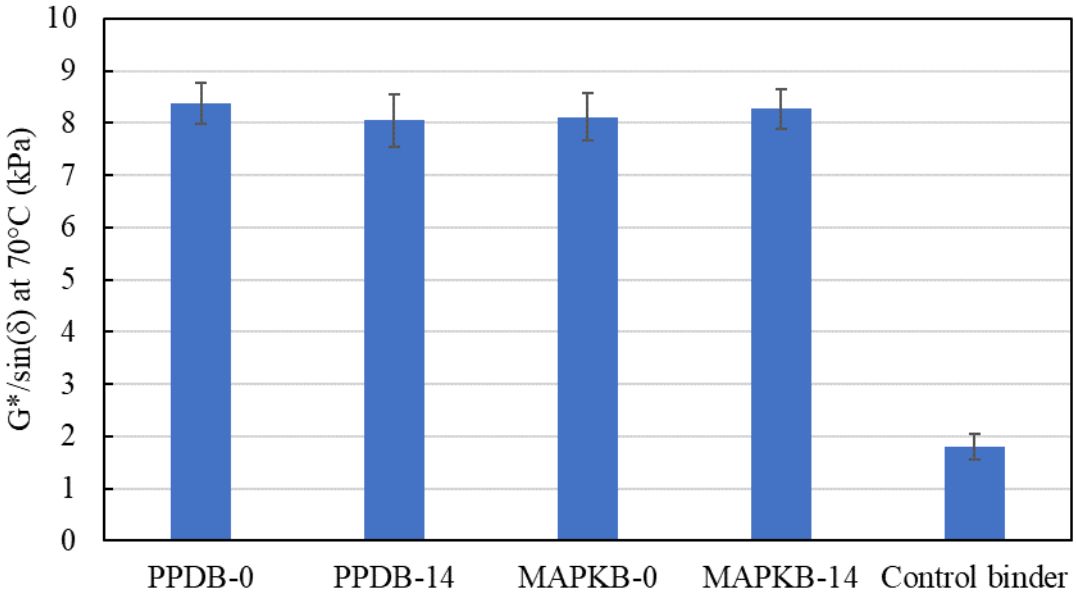


Figure 5.11 G*/sin(δ) at 70 °C of RTFO aged binders

Table 5.3 Rutting factor T-test results of different binders

	PPDB-0	PPDB-14	"PPDB-0 and PPDB-14" P-value	MAPKB-0	MAPKB-14	"MAPKB-0 and MAPKB-14" P value
Unaged binder G*/sin(δ) at 70°C (kPa)	2.67	2.52	0.36	2.90	3.05	0.34
RFTO aged binder G*/sin(δ) at 70°C (kPa)	8.38	8.05	0.21	8.11	8.28	0.33

5.2.3 Effect of HDPE on Fatigue Resistance

The effects of the HDPEs and treated HDPEs on the fatigue parameter (G*sinδ) of the binders were studied. Figure 5.12 illustrates the results of G*sinδ as a function of temperature for PAV aged binders. The G*sinδ value of all binders decreased as the test temperature increased. As shown in Figure 5.13, at 25°C, unmodified binder had the lowest G*, PPDB-0 and PPDB-14 had lower G* sinδ than MAPKB-0 and MAPKB-14. The results implied that all modified binders had lower fatigue factor than unmodified binder at same intermediate temperature and associated increased resistance to fatigue cracking. Table 5.4 also indicates that the storing time does not affect the fatigue resistance.

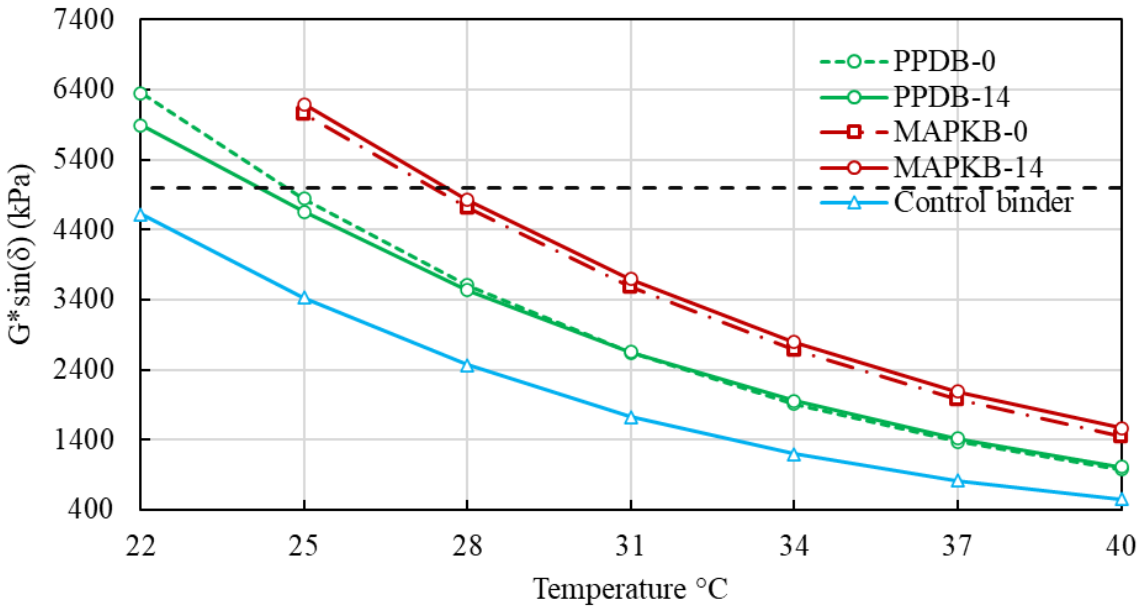


Figure 5.12 Fatigue factor of PAV aged binders

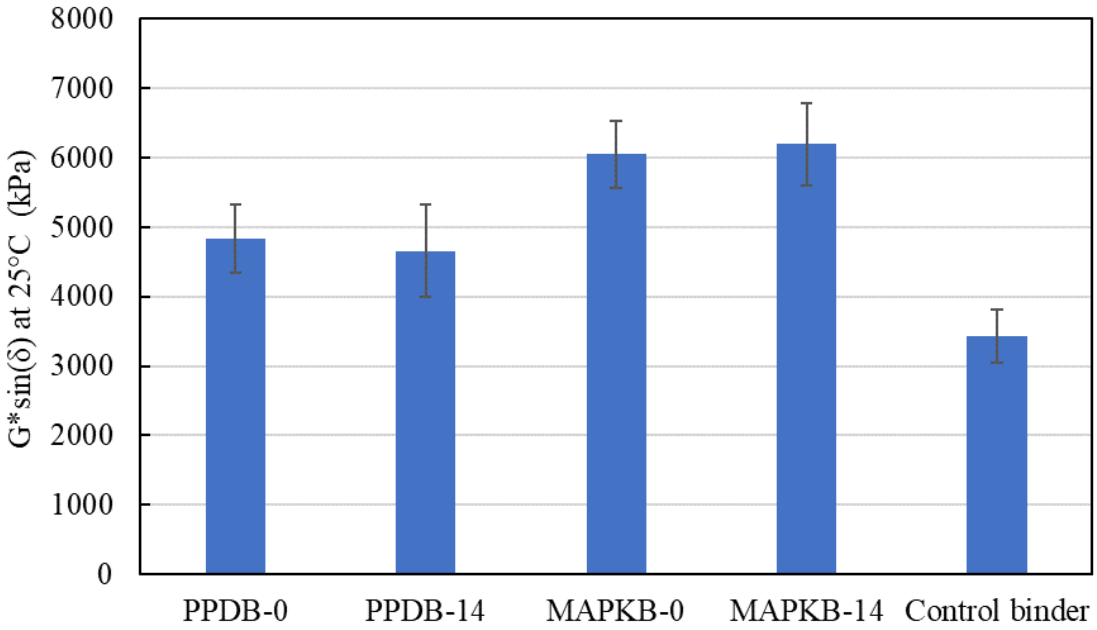


Figure 5.13 G*sin(δ) at 25 °C of PAV aged binders

Table 5.4 Fatigue T-test results of different binders

	PPDB-0	PPDB-14	"PPDB-0 and PPDB-14" P value	MAPKB-0	MAPKB-14	"MAPKB-0 and MAPKB-14" P value
PAV aged binder G*sin(δ) at 25°C (kPa)	4837.03	4659.31	0.36	6053.00	6195.00	0.38

5.2.4 Effect of HDPE on Low Temperature Performance of Binders

The BBR tests were conducted to evaluate the low-temperature performances of the modified binders. Figures 5.14 and 5.16 illustrates the m-value and the creep stiffness of the studied binders, respectively. As shown, the m-value increased while the stiffness decreased with the increase of temperature. A higher m-value and a lower creep stiffness of binder at a low temperature usually indicate a better resistance to low temperature cracking of pavement materials. As shown in Figures 5.15 and 5.17, MAPKB-0 and MAPKB-14 had slightly lower m-value than PPDB-0 and PPDB-14. In the meantime, MAPKB-0 and MAPKB-14 had slightly higher creep stiffness than PPDB-0 and PPDB-14. These two results are consistent, they both indicate that PPDB-0 and PPDB-14 had better low temperature resistance than MAPKB-0 and MAPKB-14. However, all modified binder had lower m-values and

much higher stiffness than unmodified binder at a given temperature. This indicates that the incorporations of HDPEs powders, treated HDPEs and clay increased the tendency for low temperature cracking of the base asphalts.

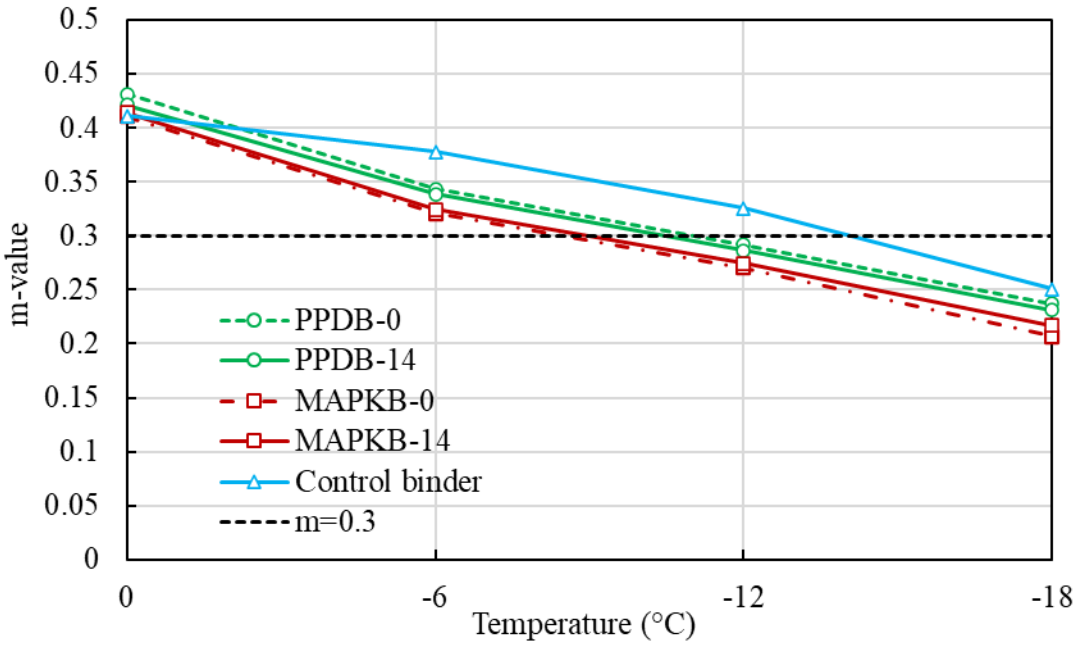


Figure 5.14 Binder m-value vs. temperature

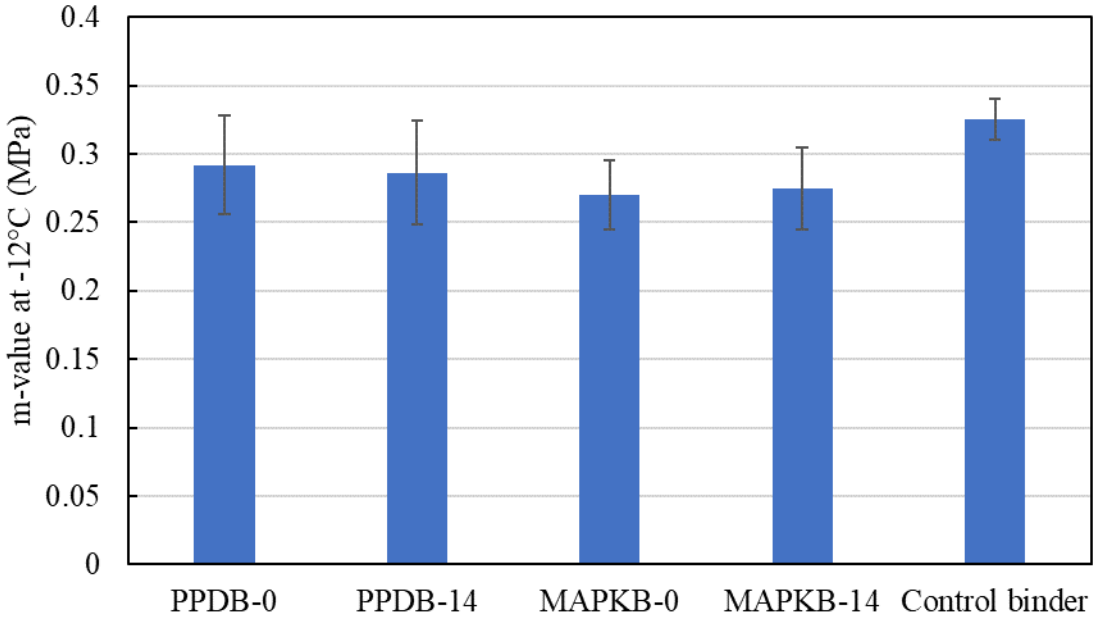


Figure 5.15 m-value at -12°C of PAV aged binders

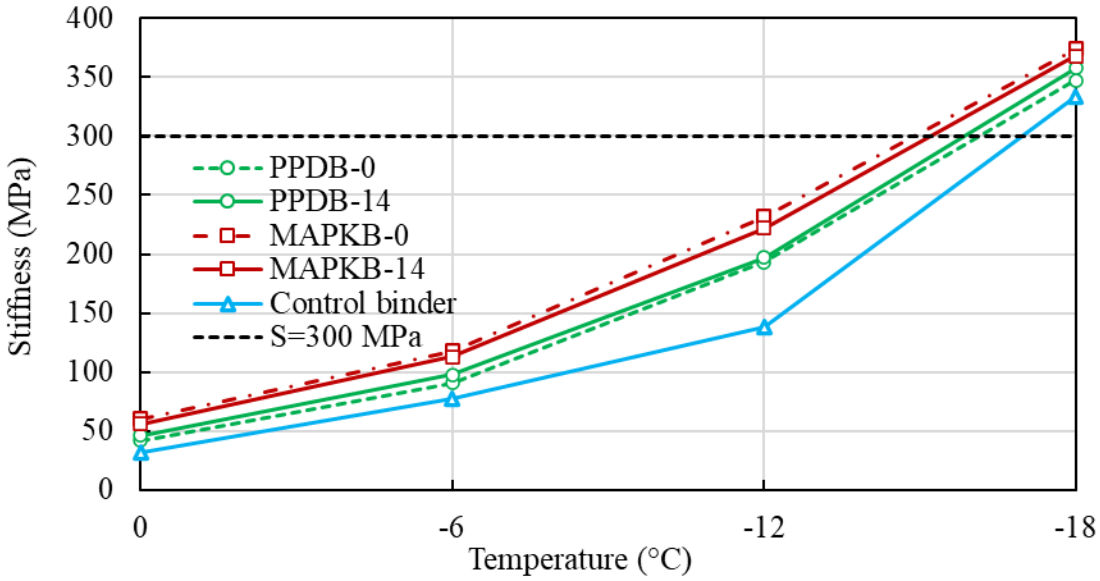


Figure 5.16 Binder stiffness vs. temperature

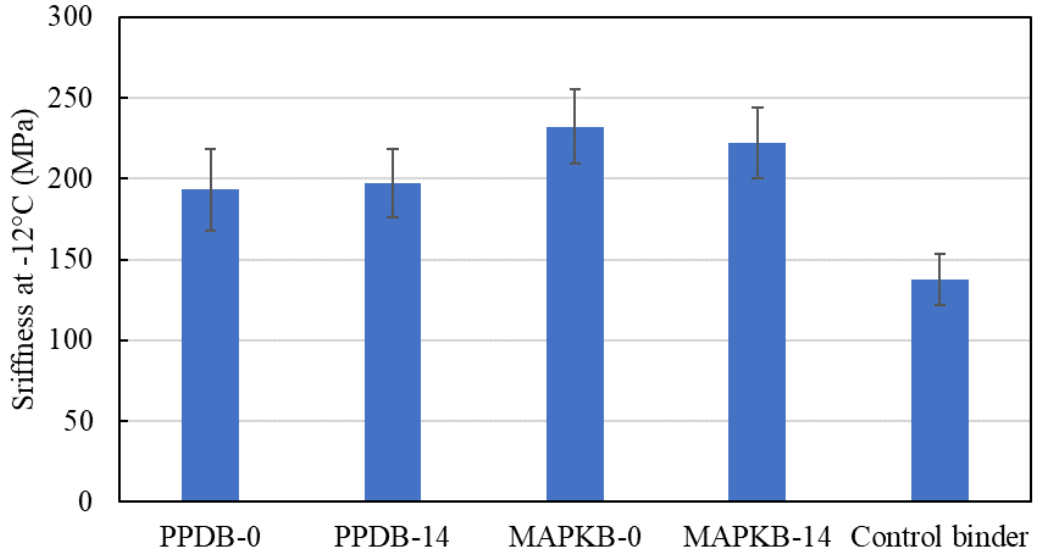


Figure 5.17 Stiffness at -12°C of PAV aged binders

Table 5.5 Low temperature PGs of different binders

Binders	Stiffness controlled cracking temperature	m-value controlled cracking temperature	Low temperature PG
Control binder	-17.24	-14.05	-22
PPDB-0	-16.1	-10.7	-16
PPDB-14	-15.9	-10.6	-16
MAPKB-0	-14.6	-8.5	-16
MAPKB-14	-14.8	-8.6	-16

Table 5.6 m-value and stiffness T-test results of different binders

	PPDB-0	PPDB-14	"PPDB-0 and PPDB-14" P value	MAPKB-0	MAPKB-14	"MAPKB-0 and MAPKB-14" P value
m-value at -12°C (MPa)	0.29	0.29	0.43	0.27	0.27	0.42
Stiffness at -12°C (MPa)	193.13	197.17	0.42	232.23	222.48	0.31

The temperatures at the intersections of the parallel dashed threshold line of each parameter (stiffness (300 MPa) and m-value (0.3) at 60 seconds) and the dotted lines generated by connecting tested values at different temperatures were used to determine the critical temperatures (Figures 5.14 and 5.16). Table 5.5 presents the critical temperature of each binder by limiting binder stiffness (300 kPa) at 60 seconds and m-value (0.3). The control binder had higher critical temperature than all the modified binders. All the modified binders (i.e., PPDB-0, PPDB-14, MAPKB-0, and MAPKB-14) same low temperature PG grade which is -16. PPDB-0 and PPDB-14 had slightly higher controlled cracking temperatures by both stiffness and m-value control. The two criteria (i.e., stiffness and m-value control) give similar results for unmodified binder. However, for modified binders, the critical temperature limiting by m-value is much higher than the one limiting by stiffness.

The T-tests in Table 5.6 show that in terms of low temperature performance, there's no difference between different storing time. The T-test results from all rheology tests indicate that fresh prepared modified asphalt binder can be used in pavement immediately or can be store at room temperature for long time and then melted again for further uses.

5.3 Summary

The RV, DSR, and BBR tests were conducted PPDB-0, PPDB-14, MAPKB-0, MAPKB-14, and control binder. The T-test results show that the differences caused by storing time are insignificant for modified binders (i.e., PPDB-0 and PPDB-14; MAPKB-0 and MAPKB-14). In other words, the storing time does not affect binders' rheological performance. The results also show that all the modified binders (i.e., PPDB-0, PPDB-14, MAPKB-0, and MAPKB-14) had a much higher viscosity than the control binder. PPDB showed slightly less viscosity than MAPKB. All modified binders also had much higher rutting resistance than the unmodified binder. However, all modified binders increased resistance to fatigue cracking than the unmodified binder. MAPKB had even worse fatigue cracking resistance than PPDB. In terms of low-temperature performance, the incorporations of HDPEs powders, treated HDPEs and clay increased the tendency for low-temperature cracking of the base asphalts.

Chapter 6 Conclusions

A great amount of plastic is disposed each year. One way to recycle waste plastics is to incorporate them into asphalt binders. This project aims to explore the feasibility of recycling waste HDPE plastics into asphalt binders. The objectives of this project are to: (1) investigate the viability of using recycled HDPE plastics in asphalt, (2) investigate the effects of different treated plastics on the properties of asphalt binder, and (3) identify potential issues of recycled plastics in asphalt.

Literature review was first conducted on plastic types, methods of incorporating waste plastics into asphalt, properties of the waste plastic-modified binder, road trials with waste plastics, and methods to improve the compatibility of plastics and asphalt. The current practice of recycled waste plastics includes seven major types: PET, HDPE, PVC, LDPE, PP, PS and others such as ABS, EVA, PC, and PU. There are generally two ways to incorporate waste plastics into asphalt: the dry and wet processes. In the dry process, waste plastics are added to hot aggregate before adding a binder; on the other hand, the modifier is mixed with the binder before adding to the aggregate in the wet process. In lab tests and road trials, incorporating plastic wastes into asphalt mixes generally showed improvements in performance parameters such as stiffness, rutting and fatigue resistance. However, HDPE, PVC, LDPE, PP, and PS yielded conflicting performance measures. The major challenge of recycling plastics into asphalt binders is poor storage stability or compatibility. The poor compatibility of asphalt and polymers is a severe issue when using the wet method. It tends to split during heated static storage or transportation to pavement sites. The poor compatibility between polymer modifiers and binders is mainly controlled by polymers and binders' different properties, such as density, molecular weight, polarity, and solubility.

Numerous researchers have studied this topic. There are multiple approaches to this problem, which is the focus of this literature review. The approaches include crosslinking agents, hydrophobic clay minerals, functionalization, and application of reactive polymers. Coupling agents are essentially bifunctional molecules, where one functionality can react with the inclusion surface and the other with the polymer, thus coupling the two together. Hydrophobic clay minerals such as OMMT can introduce numerous polar branches on the plastic molecular chain caused by the polarity of free radical chains and the large surface energy of OMMT. Plastic can disperse into the asphalt matrix, forming the branched network structures and enhancing the surface combination of plastic and asphalt. Functionalization is another method to improve the compatibility of polymer and binder. By functionalization, various new functions of currently available plastic-modified binders can be obtained. Functionalization includes the

steric method, aminolysis reaction and glycolysis reactio. These treatments have been reported to improve the compatibility between recycled plastic and asphalt. However, using chemicals to treat plastic surfaces requires storage and disposal of harmful or toxic materials and poses a health risk to employees.

This study aims to investigate the feasibility of incorporating HDPE into asphalt binder by wet method and improve the storage stability of HDPE modified binder. Two pretreatment methods for waste plastic were conducted before the plastic was blended with asphalt to improve the storage stability of HDPE-modified asphalt. This study focused on chemical treatment, including flame and acid treatment. For flame treatment, two parameters (i.e., the distance between flame and HDPE and treating time) were selected as factors that may affect the effectiveness of flame treatment. For acid treatment, treating durations and ratios between sulfuric acid and nitric acid were chosen as two factors affecting the effectiveness of acid treatment. The flame and acid treatment effectiveness were evaluated using FTIR. CI was used as an indicator of HDPE powder oxidation level for flame treatment. The Carbonyl group is chemically active, and the treated HDPE powder with high CI should be chemically active. SI was selected to evaluate the effectiveness of acid treatment because the sulfoxide group was the major oxidative functional group that appeared on HDPE powder after acid treatment. For flame treatment, the results show that CI decreased when the flame distance was lower than 13cm or higher than 13cm. The treated HDPE powder at 0.33s exhibited the highest CI. Therefore, 13cm, 0.33s was selected as the optimum flame treatment method. For acid treatment, SI increased as the treatment duration increased. Also, SI increased dramatically from 1-day treatment to 7-day treatment, but there was not much change after 7 days. Considering SI values and the practicality of the treatment time, 7 days was selected as the proper treating time. The results also show that the ratio of sulfuric: nitric acid at 2:1 yielded the highest SI values, and therefore, it was selected as the optimum blending ratio.

After evaluating the effectiveness of each treatment, the flame-treated HDPE powder with the highest CI and the acid-treated HDPE powder with the highest SI was selected as optimum treated HDPE powder. Then, nine different modified binders (i.e., PPLB, PPDB, FPB, FPKB, FPBB, FPJB, SAPB, MAPB, and MAPKB) were prepared. Storage stability test (cigar tube test) and softening point test were conducted to evaluate the homogeneity of each modified binder. To investigate the working mechanism of different modifiers (i.e., rejuvenator, nanoclay, flame-treated HDPE powder, and acid-treated HDPE powder) in a modified binder, FTIR tests were conducted to monitor the functional group change after mixing and before mixing, which can be used to quantify the interaction between plastic

and binder. For the softening point test, ΔSP, the difference in softening points between top and bottom sections, was adopted as the storage stability index. It indicates the segregation between asphalt binder and HDPE during thermal storage. The results show that PPLB has the worst storage performance, with a ΔSP of 76.2°C. However, PPDB had a ΔSP of 73.1°C, which is 3.1°C less than PPLB. This indicates that the size of plastic had a positive impact on storage stability. The results also show that adding a rejuvenator did not improve the compatibility between HDPE powder and asphalt. Kaolinite clay has a slightly better effect than bentonite clay. Flame treatment improved the storage stability. It has a better outcome than using nanoclay. Acid treatment had an even better effect than flame treatment in terms of storage stability. Among these modified binders, MAPKB was selected as the optimum modified binder in terms of best homogeneity. For FTIR test, TI was used to estimate the interaction degree between modifiers and asphalt. The higher the TI is, the better interaction is. Four peaks of the spectra (i.e., C-O stretching, O=S=O stretching, S=O stretching, and C-H bending) were used to contribute to the better interaction between modifiers and asphalt binder. The results show that FPB has about doubled TI as PPDB, which means the flame treatment improved the interaction between HDPE powder and binder. Kaolinite, bentonite, and rejuvenator didn't show much improvement in the interaction. SAPB, MAPB, and MAPKB showed better results than FPB, which means acid-treated HDPE powder has a higher interaction level with binder than flame-treated HDPE powder. MAPKB was selected as the optimum modified binder due to its highest TI. The TI results have a strong correlation with softening points difference results. The binder with higher ΔSP tends to have a lower TI value. High ΔSP and low TI values reflect poor modifier and binder compatibility.

The rheology tests (i.e., RV, DSR, and BBR) were then conducted on PPDB-0, PPDB-14, MAPKB-0, MAPKB-14, and the control binder. MAPKB was the optimum binder selected due to its best storage stability. PPDB was selected as a control-modified binder. The rheological effect of treatment on HDPE powder can be evaluated by comparing PPDB with MAPKB. The purposes of the rheology tests are 1) to investigate the effect of storing time on the properties of modified binders, 2) to assess the workability of the optimum modified binder, and 3) to investigate the effects of HDPE powder on the properties of asphalt binders. The T-test results show that the differences caused by storing time are insignificant for modified binders (i.e., PPDB-0 and PPDB-14; MAPKB-0 and MAPKB-14). In other words, the storing time does not affect binders' rheological performance. The results also show that all the modified binders (i.e., PPDB-0, PPDB-14, MAPKB-0, and MAPKB-14) had a much higher viscosity than the control binder. PPDB showed slightly less viscosity than MAPKB.

All modified binders also had much higher rutting resistance than the unmodified binder. However, all modified binders increased resistance to fatigue cracking than the unmodified binder. MAPKB had even worse fatigue cracking resistance than PPDB. In terms of low-temperature performance, the incorporations of HDPEs powders, treated HDPEs and clay increased the tendency for low-temperature cracking of the base asphalts.

More detailed chemical characterization and evaluation of the rheology of HDPE powder with different modifiers such as polyphosphoric acid and sulfur is recommended for future scope of the work. Further investigations are also recommended to characterize the performance of asphalt mixtures using HDPE modified binder.

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