MICROSTRUCTURE AND PERFORMANCE ANALYSIS OF POLYETHYLENE-MODIFIED ASPHALT

A Thesis

by

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ABSTRACT

Asphalt is one of the most commonly used materials in the road construction industry. Asphalt binder is used to bind aggregate particles to form the asphalt mixture, which is the material used for the construction of pavement layers. The properties of asphalt binder influence the durability and strength of the mixture. Virgin asphalt does not have the properties to withstand the severe service conditions as it is prone to resistance distresses such as rutting and cracking. Rutting is a result of plastic deformation due to application of heavy loads at elevated temperatures. Low temperatures cause thermal cracking while repetitive loading causes fatigue cracking. All these factors contribute to adverse effects on pavement performance and road safety leading to premature failures and extensive maintenance. The addition of modifiers to asphalt is a common technique to enhance the mechanical properties of virgin asphalt and reduce maintenance cost. These modifiers aim to increase asphalt resistance to permanent deformation at high temperatures and/or increase its resistance to cracking at low and intermediate temperatures.

This study analyzed the effect of adding two different grades of low-density polyethylene (LDPE) (LDPE4 and LDEP70) and polyethylene wax to asphalt binder as modifiers to enhance performance. LDPE 70 had a much higher melt flow index and lower molecular weight than LDPE4. The analysis focused on the microstructure and rheological properties. Various tests including optical imaging, dynamic and steady shear rheological measurements, thermogravimetric analysis, and differential scanning calorimetry were conducted. The results indicate that LDPE 70 showed lower crystallinity than LDPE4 and performed better in terms of dispersion and uniform particle size distribution along with better performance grade of the binders. On the other hand, although, PE wax reduced the phase separation in LDPE4 blends, it caused agglomeration in LDPE70 blends. It is suggested that further research be done going forth with LDPE70 and other compatibilizers such as to reduce phase separation as PE wax is not a suitable one.

DEDICATION

To my beloved parents who gave me unconditional love and support.

To my siblings for being my source of inspiration and strength.

To my friends who were always by my side.

Last but not least, to my grandmother, Remi, without whom I would be nowhere in life.

This thesis is dedicated to you.

Thank you.

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NOMENCLATURE

PE	Polyethylene
LDPE	Low density polyethylene
HDPE	High density polyethylene
LLDPE	Linear low-density polyethylene
PE Wax	Polyethylene wax
LDPE4	LDPE of grade 4
LDPE70	LDPE of grade 70
1%LDPE4	1 wt% LDPE4
2% LDPE 4	2 wt% LDPE4
3% LDPE 4	3 wt% LDPE4
4% LDPE 4	4 wt% LDPE4
5% LDPE 4	5 wt% LDPE4
1%LDPE4_2%PEWax	1 wt% LDPE4 + 2 wt% PE Wax
2%LDPE4_1%PEWax	2 wt% LDPE4 + 1 wt% PE Wax
3%PEWax	3 wt% PE Wax
3%LDPE 70	3 wt% LDPE70
5%LDPE 70	5 wt% LDPE70
4%LDPE70_1%PEWax	4 wt% LDPE70 + 1 wt% PE Wax

RV	Rotational Viscometer
G*	Dynamic Modulus
δ	Phase Angle
MFI	Melt Flow Index
min	Minute

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1. INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction and Motivation

Road construction industry utilizes multiple materials amongst which asphalt is the most common. To construct pavement layers, asphalt binder is used to bind the aggregate particles to form a homogeneous asphalt mixture. The durability and strength of the mixture is directly correlated to the properties of the binder [1]. Virgin asphalt, under harsh climatic settings, is prone to resistance distresses such as rutting and cracking. Rutting is caused by the plastic deformation of the asphalt at high temperatures upon the application of heavy loads. Fatigue cracking is caused by repetitive loading while thermal cracking is caused by low temperatures. Each of these factors influence overall road safety and pavement performance which can lead to premature failures and extensive maintenance work. To enhance the durability and the mechanical properties of the virgin asphalt, modifiers are added and this in turn reduces the maintenance cost as well. The ultimate aim of the modifiers is to minimize the permanent deformation at elevated temperatures and/or increase the asphalts resistance to stress cracking at low to intermediate temperatures.

1.2 Literature Review

1.2.1 Polymer Modified Asphalt

One of the ways to modify asphalt binder is to use polymers in order to improve rheological properties resistance to aging and resistance to moisture. Asphalt modifiers can be categorized into three types; elastomers, plastomers, and crumb rubber. Elastomers work by improving the elastic properties of the material and plastomers work by increasing the stiffness of the material along with the resistance to deformation [2]. Styrene-butadiene-styrene (SBS) is one type of elastomer that improves the flexibility, flow and deformation resistance, strength, elasticity, and stiffness of the binder. However, some drawbacks of SBS include increased penetration, lower resistance to heat and oxidation, lower stability, and degradation when subjected to mechanical stress [3–5]. Crumb rubber includes natural and reclaimed rubber. Natural rubber has better rutting resistance, ductility, and elasticity. On the other hand, reclaimed rubber has the added advantage of being environmentally friendly and low cost [3–5]. Despite these advantages both natural and reclaimed rubber have some disadvantages. Natural rubber is susceptible to decomposition and oxygen absorption. It also poses compatibility issues due to its high molecular weight. Similarly, reclaimed rubber needs high temperature for mixing which increases the cost. High temperature is needed for even dispersion throughout the binder. Ethylene-vinyl-acetate (EVA), polypropylene (PP), polyvinyl chloride (PVC), and polyethylene (PE) are examples of plastomers. EVA and PP both show no significant increase in viscosity upon addition to the binder. Generally, plastomers provide no improvement in elastic recovery of the material. Furthermore, plastomers are more economically competitive compared to elastomers [3–5]. EVA shows good compatibility, thermal stability, dispersion in binder, and storage stability. PP exhibits good penetration resistance and resistance to deformation under loads however it has stability issues due to its non-polar nature. Furthermore, it has low resistance to thermal cracking. PVC is mainly used as filler for the mix. Lastly, PE has high temperature resistance, resistance to ageing, modulus, and it exhibits high resistance to deformation under traffic loads. Nevertheless, it has compatibility issues due to its non-polar nature and high polymer contents are needed to get the required properties of asphalt [3–5]. Due to differences in chemistry, each polymer has different solubility in the binder. At the microscopic scale, all polymer modified asphalt blends are heterogenous mixtures. The addition of polymer to the binder causes changes in the binder's morphology. As the polymer content increases, the blend goes from a continuous asphalt rich phase to a continuous polymer rich phase due to a phenomenon known as phase inversion. Interactions between asphalt and polymer result in swelling, which is the change in the polymer geometry. At low polymer concentrations, the degree of swelling is minimal and therefore the properties of the asphalt binder remain unchanged. Enough polymer swelling leads to phase inversion, which significantly affects the properties of the binder. The aim is to enhance solubility to reduce the phase separation while ensuring the polymer is not completely soluble in the binder in order to increase the mechanical properties. This is achieved at a swelling degree that ensures phase inversion but does not destroy the polymeric network. This keeps the polymeric network intact and enables the binder to have properties like that of the unswollen polymer [2]. Polacco et al. stated that at the phase inversion the blend is not stable enough for storage [2]. Further increasing the polymer content would decrease the mechanical properties until the mixture is completely soluble at which point the addition of the polymer would have had no effect on the properties of the binder. Figure 1, below, shows a graph of the stages of the various stages of polymer swelling and their effects on the mechanical properties of the asphalt binder. Polacco et al. noticed that for a short mixing time (low degree of swelling) the polymer rich phase (PRP) is dispersed in the asphaltene rich phase (ARP). At this stage the properties of the binder resemble that of the pure asphalt as the polymer has negligible significance on the properties. As the degree of swelling increases the phase inversion stage (PI) is reached where there is an abrupt but unstable change in binder properties. At this stage, the binder is not stable enough for storage. Further swelling (due to longer mixing time) after the phase inversion stage will lead to a slight decrease in performance. However, if the mixing time is increased too much then the phases will become completely soluble which will render the blend useless as the polymer will once again have negligible effect. The goal is to stop in the ideal zone [2]. The ideal zone is the zone at which the blend still retains its improved mechanical properties due to the polymer network while still being stable enough to be stored.

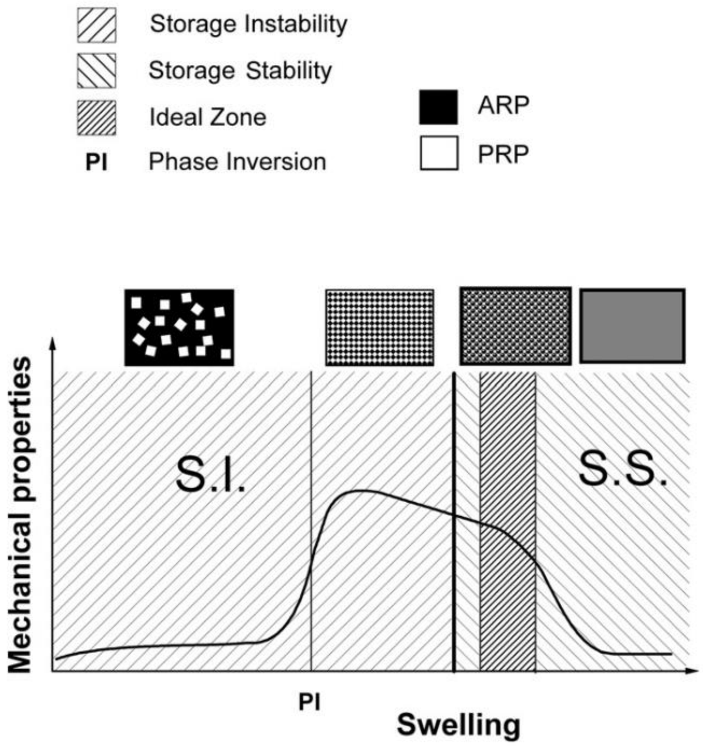


Figure 1: Effect of polymer swelling on the mechanical properties of the asphalt binder Reprinted with permission from [2]

Fuentes-Auden et al. state that at polyethylene modified asphalt undergoes phase inversion at high polymer concentrations of 5-15%. However, these high concentrations lead to storage stability issues [3].

Polyethylene Modified Asphalt

PE is the simplest polymer structure; each carbon atom is connected to two hydrogen atoms. PE is produced by the polymerization of ethylene and it is the most commonly used plastic. PE is categorized based on density into low density PE (LDPE), high density PE

(HDPE), and linear low-density PE (LLDPE) (Figure 2). The polymerization of LDPE is carried out at very high temperatures and pressures, while HDPE is produced at low pressure and temperatures [29]. However, HDPE is stronger and stiffer than LDPE. The differences in properties of three types of PE are shown in Table 1.

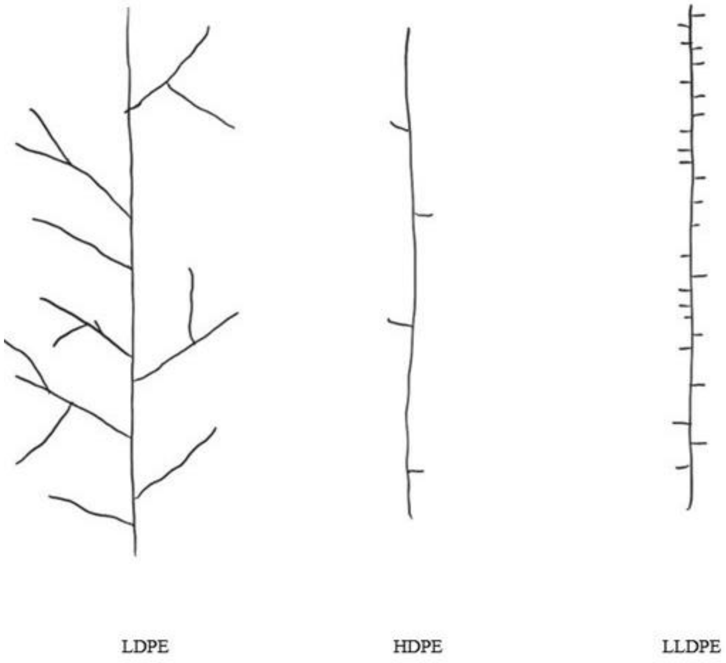


Figure 2: Structure of different types of PE

Table 1: Properties and mixing conditions of PE used for asphalt modification

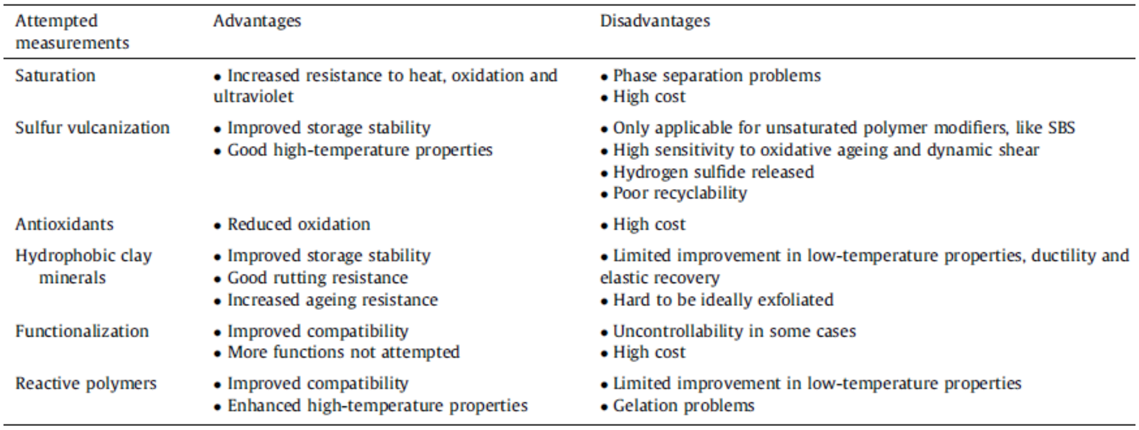
Property	LDPE	HDPE	LLDPE	PE wax	Reference
Density (g/cm^3)	≈0.914	≈0.954	≈0.924	≈0.880	[4–6]
Melting point (^{o}C)	108	131	124	103	[4,7]
Molecular weight distribution	3–12	7–18	3–7	1.33–1.71	[8–11]
Binder Blending Conditions	LDPE	HDPE	LLDPE	PE wax	Reference
Blending temperature (^{o}C)	160–185	180	180	160	[9,12,13]
Optimum PE content	3–4%	3–5%	5–6%	up to 4%	[6,8,9,14]
Blending speed (rpm)	1300–5000				[6,14,15]
Blending time (minutes)	30–60				[6,9,14]

These three types of PE are blended with the binder under different mixing conditions as shown in Table 1. In most of the literature, LDPE is used for asphalt modification and the mixing conditions affect the properties of binder [11,16–18]. The optimum mixing conditions depend on several parameters including the polymer type and molecular weight, the nature and grade of the asphalt binder, the type of mixing equipment, and the time-temperature profile during mixing. Polacco et al. (2015) reported that long and aggressive mixing changes the chemistry and molecular weight of the asphalt and having an increased influence on the swelling of the polymer.

1.2.2 Chemical Additives

These are several chemical additives that are used in polymer modified asphalt to enhance performance, reduce separation, and improve compatibility between asphalt and polymers. This section discusses some of these additives along with their advantages and disadvantages (see Table 2).

Table 2: Advantages and disadvantages of various modification techniques. Reprinted with permission from [19]



Attempted measurements	Advantages	Disadvantages
Saturation	• Increased resistance to heat, oxidation and ultraviolet	• Phase separation problems • High cost
Sulfur vulcanization	• Improved storage stability • Good high-temperature properties	• Only applicable for unsaturated polymer modifiers, like SBS • High sensitivity to oxidative ageing and dynamic shear • Hydrogen sulfide released • Poor recyclability
Antioxidants	• Reduced oxidation	• High cost
Hydrophobic clay minerals	• Improved storage stability • Good rutting resistance • Increased ageing resistance	• Limited improvement in low-temperature properties, ductility and elastic recovery • Hard to be ideally exfoliated
Functionalization	• Improved compatibility • More functions not attempted	• Uncontrollability in some cases • High cost
Reactive polymers	• Improved compatibility • Enhanced high-temperature properties	• Limited improvement in low-temperature properties • Gelation problems

Hydrophobic clay, such as montmorillonite, has been used to enhance various properties of the binder. This clay type can disperse into individual layers which consist of two tetrahedrally coordinated silicon atoms attached to the edge of an octahedral sheet of aluminium or magnesium hydroxide. The layers within the blend improve aging resistance as they inhibit the penetration of oxygen into the binder. The storage stability is also enhanced as the dispersion of the layers into the binder decreases the differences in density of the blend. The structure of the clay can be exfoliated which is better for polymer modified asphalt. Addition of hydrophobic clay into the polymer modified binder has been shown to increase viscosity, stiffness, rutting resistance as well. However, there is only very limited improvement in the low temperature properties of the binder [19].

The addition of certain functional groups to the polymer is known as *functionalisation*. The added functional groups interact with the binder by forming chemical bonds which improves compatibility. Polymers can be functionalised by adding amino and carboxylic groups or by grafting compounds such as maleic anhydride, methacrylic acid, and glycidyl methacrylate. However, this should be done with care as large amounts of these additives could lead to the demolition of biphasic nature of the blend. Functionalisation is not recommended for unsaturated polymers such as SBS. Studies have been carried out in which maleic anhydride and glycidyl methacrylate have been grafted onto polymers [19].

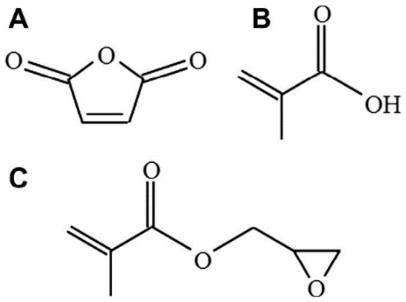


Figure 3: Structures of various additives used for functionalization (a) Maleic anhydride (b) Methacrylic acid (c) Glycidyl methacrylate. Reprinted with permission from [19].

Maleic anhydride is used as an asphalt modifier and is also known to improve the compatibility of the asphalt binder with the polymer [2]. Use of a chemical additive such as maleic anhydride would result in the formation of chemical bonds between polymers and asphalt instead of having the polymers only physically dispersed. Maleated asphalt binder has a maleic anhydride group attached to it. It is preferred over conventional asphalt binder as it has a higher storage stability. Enhanced storage stability is due to the chemical interactions between the maleic anhydride functional group on the asphalt binder and the hydroxyl group on the LDPE [20]. Singh et al. carried out a study in which maleated asphalt binder was prepared using various concentrations of maleic anhydride (1, 2, 3, 5, and 10wt %) and recycled LDPE (3, 5, 7, and 9wt %). These maleated asphalt binder-LDPE blends were then also compared to maleated asphalt binder-LDPE blends that were further modified with modifiers such as SBS (1, 2, 3, and 5wt%), natural rubber (2, 4, and 6wt%), and castor oil (5 and 10wt%). It was found that maleic anhydride reduced the penetration and increased the softening point and viscosity of base asphalt binder. The affects were more pronounced at higher maleic acid concentrations (~10wt %). Singh et al. also concluded that temperature susceptibility of the binder also decreased due to an increase in viscosity and stiffening effect. Maleated asphalt binder-LDPE blend had a higher softening point, elastic recovery and a lower penetration than the base asphalt binder-LDPE blend. Even though this temperature difference was greater than the 4℃ criteria, the maleated blend exhibited higher polymer dispersion throughout both top and bottom sections of the samples unlike the base binder which had a clear polymer rich section at the top and an asphaltene section at the bottom. Furthermore, Mancini (1993) found 2-12% maleic anhydride followed by polymer loading to be the optimum. Ciplijauskas et al. (1979) found maleic anhydride an inexpensive way of reducing the moisture sensitivity of the asphalt binder [21]. Vargas et al. also confirmed that the stability of blends containing grafted polyethylene had better stability than blends containing non-grafted polyethylene [22]. Fluorescence microscopy showed both asphalt/LDPE-g-MA (LDPE grafted with maleic anhydride) and HDPE-g-MA (HDPE grafted with maleic anhydride) had smaller spherical particles sizes which indicated better compatibility.

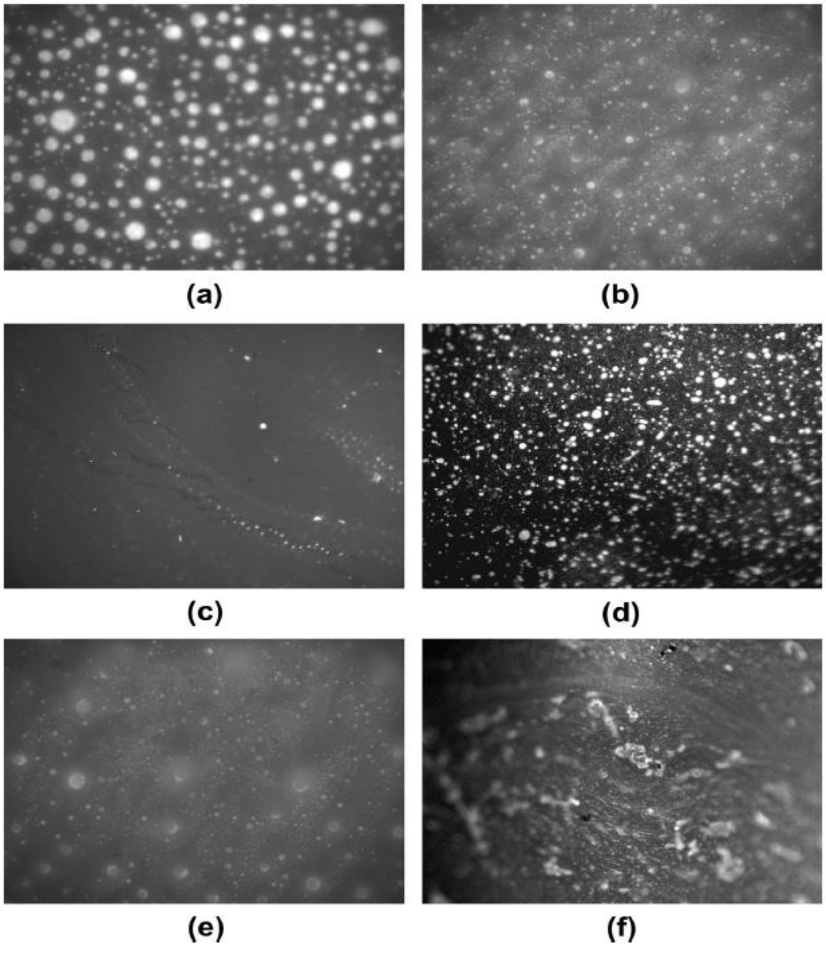


Figure 4: Fluorescence Photomicrographs (a) asphalt/LDPE, (b) asphalt/LDPE-g-MA, (c) asphalt/HDPE, (d) asphalt/HDPE-g-MA, (e) asphalt/BHDPE and (f) asphalt/BHDPE-g-MA. Reprinted with permission from [22]

Moreover, HDPE-g-MA had higher storage stability compared to all the other blends of asphalt binder (LDPE, HDPE, bimodal polyethylene (BHDPE), LDPE-g-MA, and BHDPE-g-MA). The softening point temperature difference between the top and bottom sections of the samples was only 6°C which was significantly less than to the other samples (46, 42, 24, 29, and 36°C respectively). No phase separation was seen in three days.

Reactive Ethylene Terpolymers (RET) are produced by grafting *glycidyl methacrylate (GMA)* and acrylic acid derived from GMA to LDPE to improve PE polarity by introducing ester linkage that can form chemical networks. This network formation can prevent or reduce phase separation [23] as these types of additives chemically react with the blend rather than physically mix in. In a study in which modified asphalt binder with different concentrations (3, 4, 5, and 6wt %) of LDPE and GMA-g-LDPE (GMA grafted LDPE) was created, the morphological analysis revealed enhanced dispersion of the PE in the blend and FTIR confirmed the reaction between GMA-g-LDPE and the binder unlike the case of LDPE where no chemical reaction with the binder was observed. Moreover, modification of the binder with GMA-g-LDPE improved the softening point, rutting resistance, low temperature cracking resistance, ductility, and the blends were as less temperature sensitive [23].

Sulphur addition to the PE/asphalt blend enhances the storage stability by forming cross linkages between the polymer molecules and between the polymer and bitumen through sulphide and/or polysulfide bonds [19]. These bonds create a strong stable network that reduces phase separation even at high temperatures and enhance the elasticity, deformation resistance, and rheological properties. However, incorporating sulphur into the blend requires strict monitoring of various factors and it has some draw backs. The mixing temperature should be kept above 140℃ to ensure the formation of C-S bonds. Temperatures below 140℃ could lead to formation of hydrogen sulphide via dehydrogenation reaction [24]. The formation of this hazardous gas, especially at high temperatures, is one of the main drawbacks of sulphur vulcanization. This was combatted by Shell Oil Company by using disulphide instead of free sulphur to avoid the release of sulphur at high temperature. However, this solution is not economically favorable. Moreover, it is crucial that the blend is homogenous before the addition of sulphur as the cross-linkages formed by sulphur interacting with the molecules will 'freeze' the blend as it is. As a result, the final blend would be unusable due to its heterogenous nature. It is recommended to avoid using sulphur as a sole modifier as sulphur vulcanization could lead to oxidative aging [24]. Along with that, sulphur can only be used for unsaturated polymers like SBS. Another drawback of sulphur vulcanization is the poor recyclability of the polymer modified asphalt after the procedure.

Polyphosphoric acid (PPA) is an oligomer of phosphoric acid (H_3PO_4) that can increase the asphalt range of service temperature. According to Jaroszek (2012), PPA improves viscosity, softening point, penetration, stiffness, resistance to rutting, and resistance to moisture. Furthermore, PPA has good compatibility with the binder and therefore shows no phase separation during long term storage [25]. It is claimed that polar interactions between asphaltene molecules are neutralized through esterification or protonation when PPA is used [24]. In a study carried out by [26], it was found that the optimum dosage of PPA for 4wt% HDPE was 0.8wt%. In the same study, it was seen that the addition of

0.8wt% of PPA to LDPE increase the softening point from 44℃ to 52℃ which the addition of the same PPA content to HDPE increase its softening point from 50.6℃ to 61.7℃. Addition of PPA also showed similar values in softening point, penetration value, and viscosity in the storage stability test for both top and bottom halves of the samples indicating minimal separation within the sample. This stabilization may be due to PPA changing the binder structure towards gel-type [27]. Furthermore, it was also determined that the modification of the binder was highly dependent on the grade of PPA used as well as the composition of the binder [27].

1.3. Research Objectives

The primary objective of this study is to develop polyethylene modified asphalt with enhanced stability and performance. This objective is achieved through the following goals:

1. Evaluate the impact of the polyethylene type and concentration on the blend stability and performance of modified asphalt.
2. Examine the effect of Polyethylene wax as a compatibilizer on the blend microstructure and stability of polyethylene modified asphalt.
3. Correlate the microstructure findings to the blend properties in order to recommend the optimum formulation.

2. METHODOLOGY

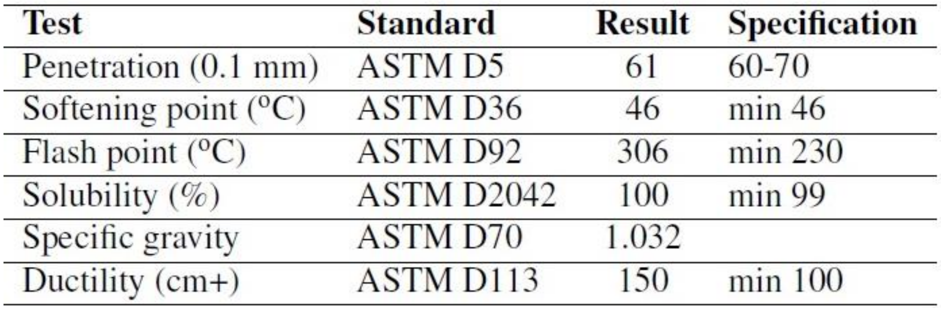
The aim of this section is to present the materials and the experimental techniques used. This section starts off by giving the basic properties of the materials in used and talks in detail about the sample preparation protocol, the various sample blends to be created, and the testing matrix. The experiments are divided into two categories; microstructural analysis, performance tests. This section details the testing procedure as well as the analysis of the tests. The tests that are covered are; optical microscopy, small angle X-ray scattering, transmission electron microscope, thermogravimetric analysis, differential scanning calorimetry, dynamic shear rheometer, and rotational viscometer.

2.1 Materials

The following materials were used as received from their suppliers. The asphalt binder is unmodified Pen 60/70 which corresponds to the performance grade of PG 64-22. Two grades of low-density polyethylene (LDPE 4 and LDPE 70) along with PE wax were supplied by Qatar Petrochemical Company (QAPCO). Table 3 and

Table 4 shows the basic properties of the binder and thee materials used respectively.

Table 3: Basic Properties of Pen 60/70 binder



Test	Standard	Result	Specification
Penetration (0.1 mm)	ASTM D5	61	60-70
Softening point (°C)	ASTM D36	46	min 46
Flash point (°C)	ASTM D92	306	min 230
Solubility (%)	ASTM D2042	100	min 99
Specific gravity	ASTM D70	1.032	
Ductility (cm+)	ASTM D113	150	min 100

Table 4: Properties of Materials

Material	Melting Point (℃)	Density at 23℃ ($g.cm^{-3}$) (ASTM D-1505)	Viscosity (cP at 121℃)	MFI (ASTM D-1238) (g/10min)
LDPE 4	108 (ASTM E-794)	0.923	-	4
LDPE 70	102	0.918	-	70
PE Wax	103 (ISO 3146)	0.88	150	-

2.2 Sample Preparation

The asphalt binder samples were prepared using a method described in previous studies. According to literature, the heating of the binder is done at temperatures in a range of 160-180℃. The optimum polyethylene weight content was reported to be within the range of 3-5% by weight [3,14,16,26,28–30]. Asphalt binder was heated to 180℃ for an hour. Once the binder is fully melted, a specific weight percentage of low-density polyethylene and additive was added into the binder and heated at 180℃ for 30 minutes. This heated mixture was then sheared for an hour at 2000rpm using a mechanical stirrer. This process was then be repeated for polyethylene contents of up to 5% by weight with additives/compatibilizers. Two different grades of LDPE were used; LDPE 4 and LDPE 70. The additive used to enhance stability is polyethylene wax. The materials are shown in

Table 4.

2.3 Experimental Measurements

Table 5 shows the testing matrix for this thesis. Microstructure analysis and performance analysis will be performed. The techniques to be used for testing are microscopy, temperature sweep using the rotational viscometer, TGA, SAXS, TEM, frequency sweep using DSR, DSC, shear sweep using rotational viscometer, and PG grading. The details of the tests are listed next section. The aim is to use these tests to accomplish the research objective and goals.

Table 5: Testing Matrix for the Project

Material	Microscopy	Rheology		Thermal Analysis		PG Grade
		Steady Shear	Dynamic	TGA	DSC	
Unmodified Asphalt (Pen 60/70)	✓	✓	✓	✓	✓	✓
1% LDPE 4	✓	✓	✓			
2% LDPE 4	✓	✓	✓			

Table 5 Continued

Material	Microscopy	Rheology		Thermal Analysis		PG Grade
		Steady Shear	Dynamic	TGA	DSC	
3% LDPE 4	✓	✓	✓	✓		✓
4% LDPE 4	✓	✓	✓			
5% LDPE 4	✓		✓		✓	✓
1%LDPE4_2%PEWax	✓		✓			
2LDPE4_1%PEWax	✓	✓	✓	✓	✓	✓
3%PEWax	✓	✓	✓	✓	✓	✓
3%LDPE 70	✓	✓	✓		✓	✓
5%LDPE 70	✓	✓	✓		✓	✓
4%LDPE70_1%PEWax	✓	✓	✓		✓	✓

2.3.1 Microstructural Analysis

Optical microscopy is carried out to study the dispersion of the particle and analyze the homogeneity of the modified binder. First, the samples were prepared by casting a very thin layer of polyethylene modified asphalt binder on a glass slide. The slides were then heated for approximately 3 minutes at 180℃. The sample was then cooled at room temperature and 5 images were taken at a magnification of 10x at 30, 60, 90, 120, 150 min and after 24 hours. The images were then compared to assess the dispersion of the polymer in the binder. The microscopy is carried out using Zeiss AxiVert 40 MAT fitted with ERc5s camera.

Figure 5: Glass slides prepared for optical microscopy

2.3.2 Thermal Analysis

Differential Scanning Calorimetry (DSC) tests were performed to analyze the homogeneity/phase separation of the blend. This test involves heating 10-20mg of the LDPE modified asphalt binder from room temperature to 200°C at the rate of 10°C/min. The melting point temperature (T_m) and the heat of fusion (ΔH_f) is determined from the collected thermogram. DSC was carried out using Perkin Elmer's Jade DSC machine.

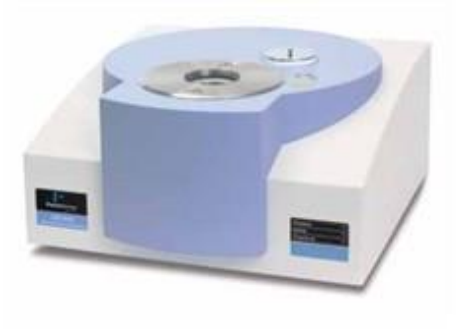


Figure 6: Perkin Elmer Jade DSC machine

Thermogravimetric Analysis (TGA) was used to determine the thermal stability of the sample. This test is carried out by heating a sample of approximately 15 mg from 30 to 550℃ at rate of 10℃/min. The percentage weight lost is then determined as function of temperature.

Figure 7: Perkin Elmer TGA machine

2.3.3 Performance Testing

Rotational Viscosity test is performed to determine the apparent viscosity of asphalt usually in temperatures within the range of 38 to 260 °C (100 to 500 °F). This test is done according to AASHTOT316/ASTM DD4402 standards. This test was carried out to determine the viscosity of the blends using the Brookfield rotational viscometer with a Thermosel temperature controller and SC 4-27 spindle.

Figure 8: Brookfield rotational viscometer

The protocol of the test is shown in Figure 9. The aim of the test is to analyze the phase separation of the binders using the difference in the viscosity of the binders during testing as the difference in temperatures may cause the phases to separate and result in varying viscosities. At high temperatures, the rotational viscometer is used to measure the apparent viscosity. The torque on the equipment gives the relative resistance to motion, which can then be used with the speed to calculate the viscosity. For this test 10.5g of the samples were poured into rotational viscometer containers. The speed of the spindle during the test was 20rpm. The blends were heated to 160℃ and the test was started. The testing protocol consisted of first reducing the temperature from 160℃ to 100℃ by 15℃ increments and then heating it back up to 160℃ by 15℃ increments. The samples were sheared at the testing temperatures for 15min out of which the first 5min were considered as preconditioning to ensure a homogenous temperature. The last 10min of the 15min were the actual testing time and during this an average of the 6th, 7th, and 8th minute data was used to calculate the viscosity.

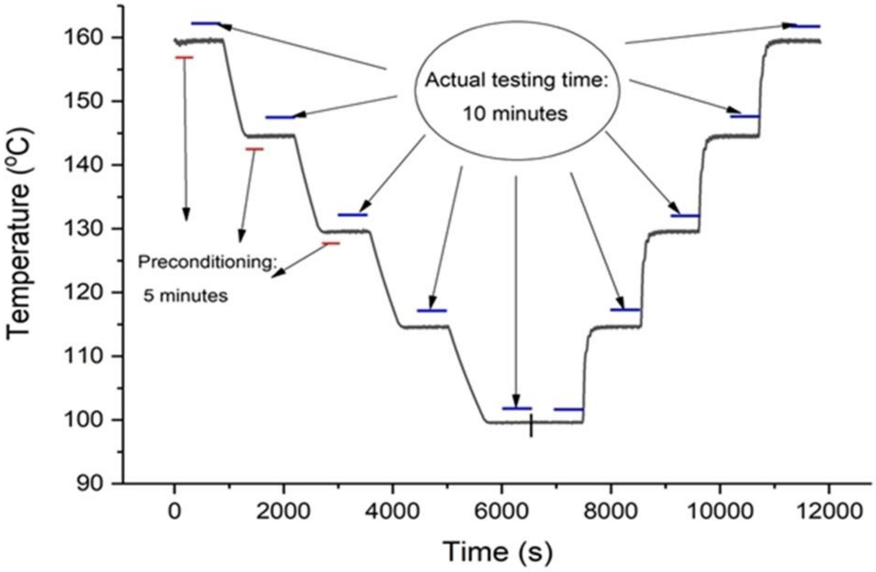


Figure 9: Testing protocol

Dynamic shear rheometer (DSR) measures the viscoelastic behavior of the material. This test is carried out to characterize the binder resistance to rutting (permanent deformation) and fatigue cracking. The DSR test is carried out using 25mm parallel plates for a temperature range of 40-80°C although the range may be altered slightly.

Figure 10: TA Instruments DSR machine

The absolute dynamic modulus (G^*), storage modulus, and loss modulus are given by the following equations:

$$G^* = \frac{\sigma_{max}}{\gamma_{max}} = \frac{Maximum\ Shear\ Stress}{Maximum\ Shear\ Strain} \tag{1}$$

$$G' = |G^*|cos\delta \tag{2}$$

$$G'' = |G^*|sin\delta \tag{3}$$

The dynamic modulus increases as the temperature decreases (the material becomes stiffer as the temperature decreases). The storage modulus (Eq. 2) is the elastic component of the dynamic modulus. It represents the amount of energy that is stored and released elastically.

The loss modulus (Eq. 3) is the viscous component of the dynamic modulus. |G*| is the dynamic modulus while δ represents the phase angle. A higher |G*| indicates an increase in stiffness while an increase in δ indicates an increase in the viscous behavior of the material.

Dynamic oscillatory measurements of the binders were conducted in the frequency range of 1-15 Hz and measurements were carried at different temperatures (25-75 °C). The Time-Temperature Superposition principle was used to generate master curves by shifting the moduli and δ data at different temperature to a reference temperature (35°C). The shifted frequency is called reduced frequency ($\omega_R = a_T \omega$). The dynamic modulus is the ratio of the maximum shear stress to maximum strain and a measure of the binder's total resistance to deformation. At higher frequencies and lower temperatures better fatigue resistance is desirable whereas at lower frequencies and higher temperatures a better rutting resistance (higher dynamic modulus value) is desirable.

2.3.4 Performance Grading

Performance grading is done to determine the temperature range at which the asphalt can be used at. In this system the first number represents the PG High temperature while the second number represents the PG low temperature. The aim to get the range as large as possible. However, unfortunately, often enhancing one leads to the deterioration of the other. The goal of asphalt modification is to get a stiffer binder at high temperature. Nevertheless, the stiffness should not be so high as to crack at low temperatures and affect low temperature properties. The letter provided after the PG high temperature represents the traffic loading. The symbols are as follow; S = Standard, H = Heavy, V = Very Heavy, E = Extra Heavy. Performance grading is carried out as per ASTM D 6373/AASHTO M332 standards.

For the binder to resist rutting and fatigue cracking, it needs to be stiff as well as elastic. Rutting at high temperature and fatigue cracking at intermediate temperature are tested using DSR. Finally, thermal cracking at low temperatures is tested using bending beam rheometer (BBR). In the BBR test a load is applied and the deflection is measured and used to calculate the creep stiffness of the asphalt. For the binder to able to be used for paving purposes, it has to have a G*/sinδ (called the rutting parameter ratio of dynamic modulus to phase angle) greater than or equal to 1kPa before aging and greater than or equal to 2.2kPa after aging using the rolling thin film oven. The minimum temperature at which these criteria are satisfied corresponds to the maximum pavement design temperature. The fatigue parameter (G* x sinδ) should be less than equal to 5000kPa.

The following two procedures were used to age the sample to certain long-term and short-term conditions for the tests:

Rolling Thin Film Oven is carried out to short term age the sample. It gives an indication of the change in properties at high temperature. It is used to prepare aged samples for DSR testing for rutting at high temperature. This is carried out according to AASHTO T240/ASTM D2872 standards. Samples are prepared by adding a specified amount of binder into the containers and immediately after rotating them horizontally so that the asphalt binder coats the internal area of the cylinder. Then, the samples are cooled for 1-3hours and added to a preheated oven with the fan on and start the carriage rotation. After

85 min, the rotation is stopped, and the containers are removed. The residue is stirred, and the excess is removed, and the mass change of the container is measured.

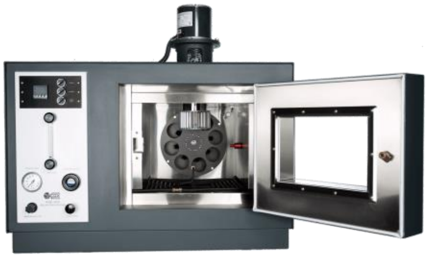


Figure 11: Rolling Thin Film Oven (RTFO)

Pressure Aging Vessel is carried out in accordance with AASHTO R28/ASTM D6521 standards. This is an accelerated way of calculating the long-term aging and the oxidation of the asphalt binder and is used to prepare the samples for to investigate thermal cracking and determine the PG low temperature. The oven is heated to a specified temperature, the sample is inserted, and 2.1MPa of pressure is applied. This pressure must be maintained for 20 hours. The pressure is then released from the oven in a linear manner to avoid air bubbles. The sample is then removed from the machine and put in the oven at 163℃ for 15min. Pour the heated binder into a container and immediately put in the vacuum oven at 170℃. Follow the procedure for the application of vacuum pressure.

Figure 12: Pressure Aging Vessel (PAV)

Along with these tests, basic tests of asphalt (such as softening point, separation tendency, penetration test, flash point, and solubility) were also done.

3. RESULTS AND DISCUSSION

The aim of this section is to analyze and discuss the data obtained from the experiments. This section starts off by highlighting the issues faced during sample preparation and the various methods used to combat them and obtain a homogeneous blend. It then analyzes the data with the help of graphs and tables in order to obtain a conclusion of which blend performs the best based on each experiment.

3.1 Microstructural Analysis

Effect of PE concentration on microstructure Figure 13 shows the optical images of the binder containing different concentrations of LDPE4 captured at 30, 60, 90, and 150 min at 10x magnification. As the concentration of LDPE in the binder increases, tendency of the polymer particles to agglomerate also increases. Furthermore, the higher the polymer concentration, the bigger the size of the particles became, which is an indication of phase separation.

To enhance the compatibility of the polymer with the asphalt binder, polyethylene wax was added. Figure 23 shows how the microstructure of the blend changes with varying the concentrations of LDPE and PE wax after 30 min. Analysis of the diameters of the particles at 30 and 150 min using Aviso and ImageJ software showed that the diameter of the particles increased with time as the concentration of the polymer in the binder increased as shown in Figures below.

Appendix B consists of Table 11-Table 20 detailing the polymer counts in each range and the percentage distribution of each blend obtained from the analysis.

The images in Figure 13, Figure 19, and Figure 23 are 460μm in width and 345μm in length. The scale bar on the images (red) reads 100 μm.

Figure 13: Microscopy images of LDPE4 modified asphalt binder at different times. The scale bar on the images (red) is 100 μm.

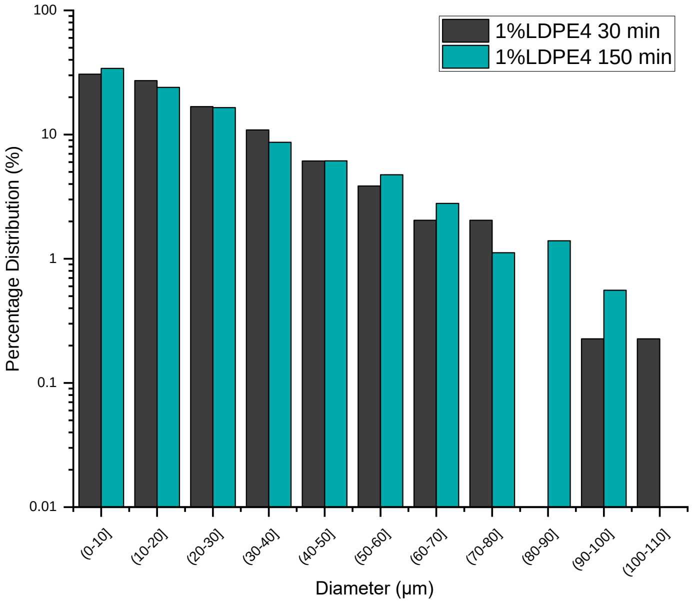


Figure 14: Particle size distribution of 1% LDPE4 modified asphalt binder at different times

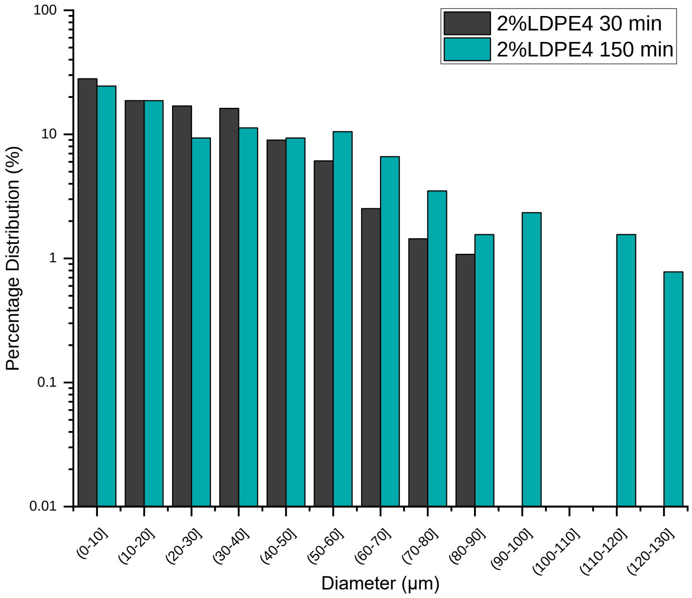


Figure 15: Particle size distribution of 2% LDPE4 modified asphalt binder at different time

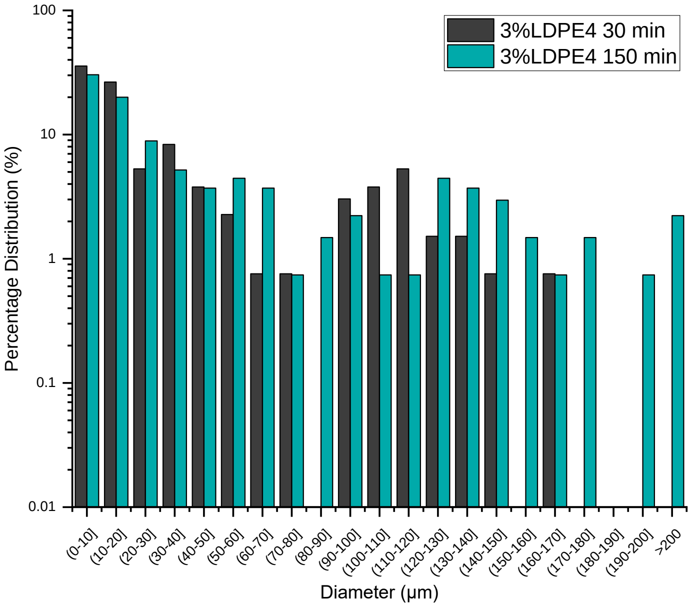


Figure 16: Particle size distribution of 3% LDPE4 modified asphalt binder at different times

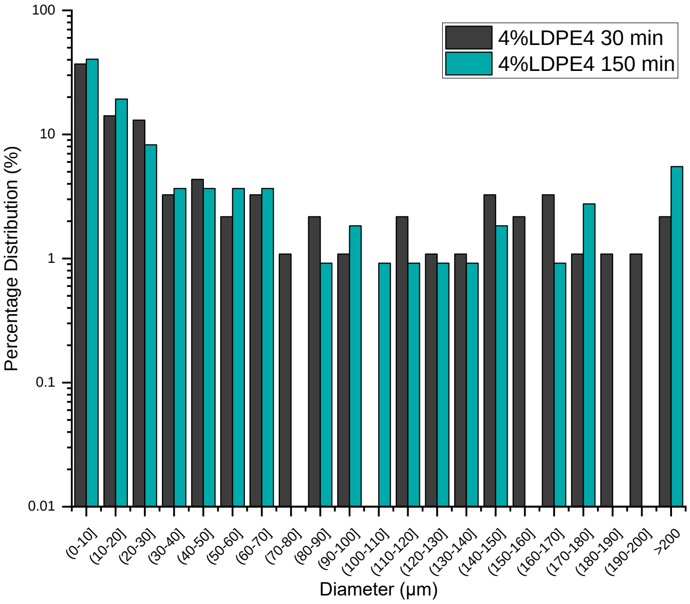


Figure 17: Particle size distribution of 4% LDPE4 modified asphalt binder at different times

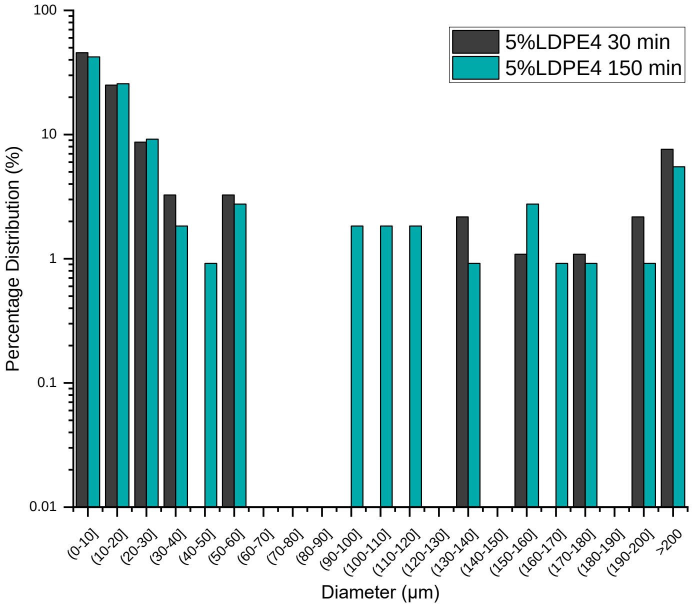
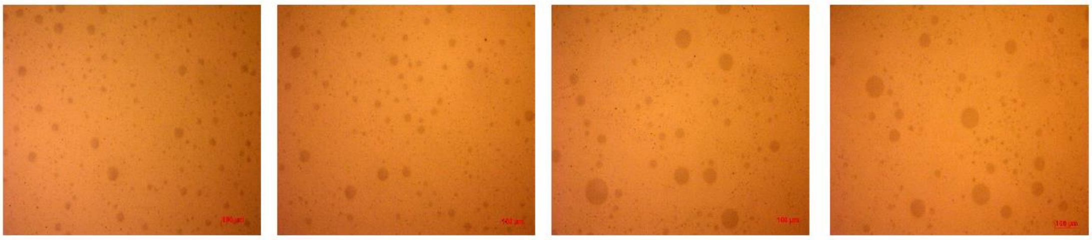


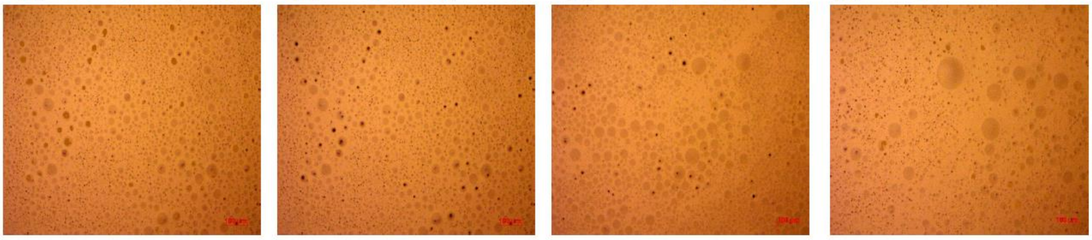
Figure 18: Particle size distribution of 5% LDPE4 modified asphalt binder at different times

Figure 14-Figure 18 show the particle distribution of LDPE4 modified asphalt binder at 30 and 150 min time stamps. The particle size increases as the concentration of LDPE4 and storage time increases. For example, the largest particle diameter for 1%LDPE4 was within the 100-110 µm range while the largest particle diameter for 5%LDPE5 was greater than 200 µm. Table 11-Table 15 show the exact percentage distribution of LDPE4 particles at 30 and 150min. Furthermore, for 2%LDPE4 at the 30min the largest particle diameter was within the range of 80-90 µm. On the other hand, for the same concentration of LDPE4, at 150min, the largest particle diameter was within 120-130 µm range. This increase in particle size, due to agglomeration caused by increasing LDPE concentration and increasing storage time, is an indication of phase separation.

Figure 19 shows the optical images of the LDPE70 blends after 30 and 150min time stamps at 10x magnification. Figure 19a and Figure 19d show 3%LDPE at 30 and 150min respectively. Figure 19e and Figure 19h show the 5%LDPE modified binder blends at 30 and 150 min. These Figures show LDPE70 particles surrounded by a pale PE wax film. For LDPE70, the particle size distribution was not significantly affected by the concentration of LDPE70, but it was affected by the storage time. This can be attributed to the high melt flow index of the polymer. The lower molecular weight of LDPE70 resulted in better particle size distribution. This is similar to the results found in literature [9]. At 30 min, both 3%LDPE70 and 5%LDPE70 have binders in the same ranges with the maximum particle diameter being at 50-60 µm (Figure 20 and Figure 21). On the other hand, at 150min, the largest particle diameter range for 3%LDPE70 is at 70-80 µm and at 5%LDPE70 the largest particle diameter is at 110-120 µm (Figure 20 and Figure 21).



(a) 3% LDPE70, 30 min (b) 3% LDPE70, 60 min (c) 3% LDPE70, 90 min (d) 3% LDPE70, 150 min



(e) 5% LDPE70, 30 min (f) 5% LDPE70, 60 min (g) 5% LDPE70, 90 min (h) 5% LDPE70, 150 min

Figure 19: Optical images of LDPE70 modified asphalt binder at different times

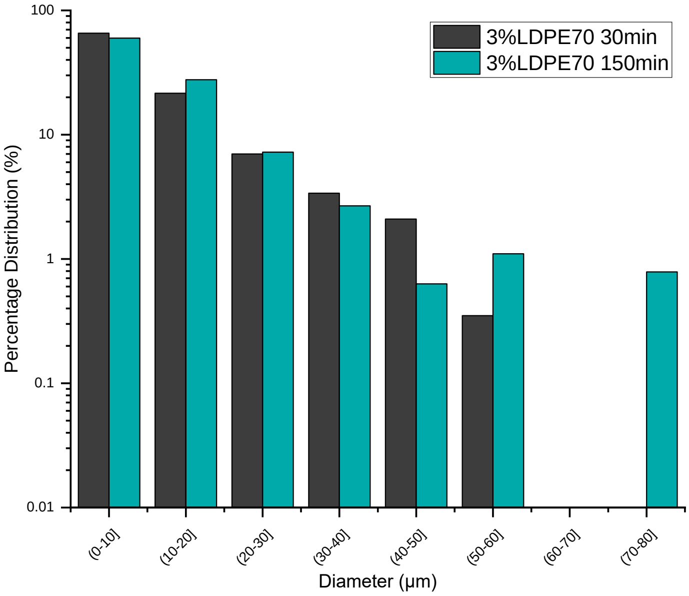


Figure 20: Particle size distribution of 3%LDPE70 at 30 and 150min

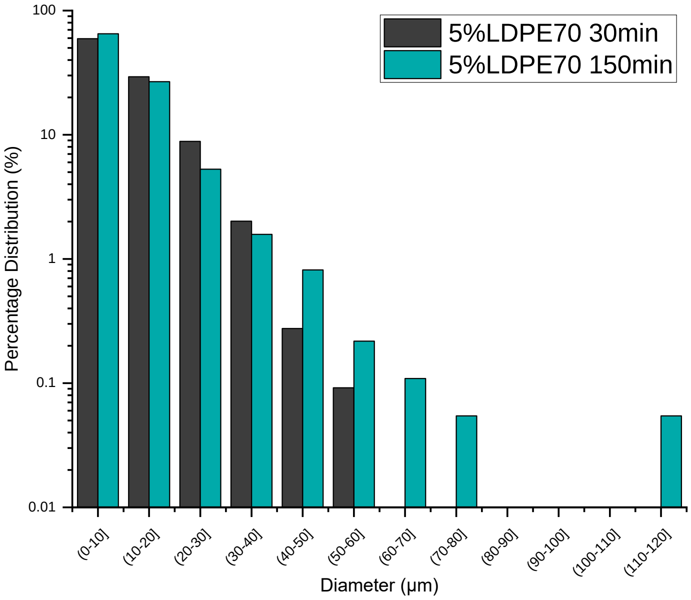


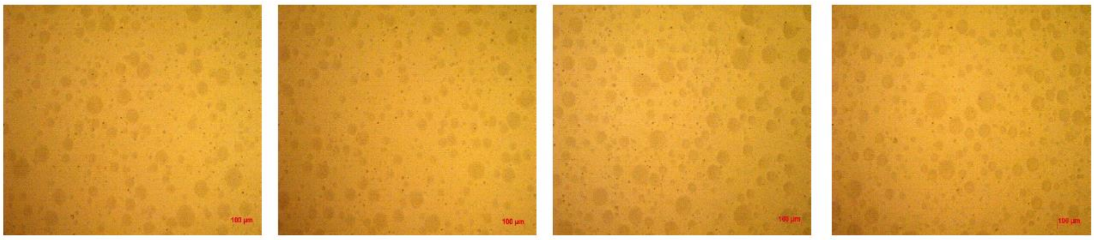
Figure 21: Particle size distribution of 5%LDPE70 at 30 and 150min

Effect of PE wax on microstructure

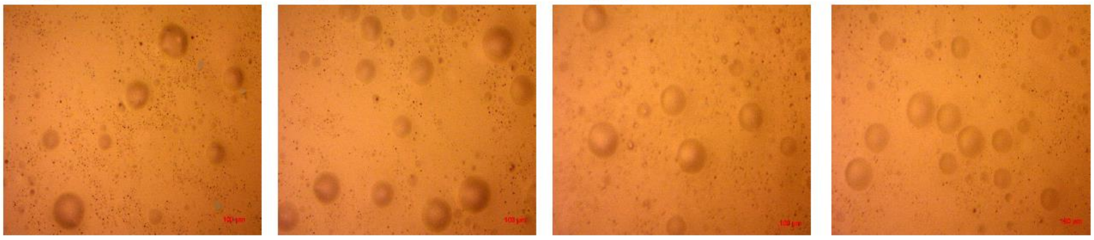
As shown in Figure 23, the addition of PE wax improved the distribution and the uniformity of the particle size of the polymer in the asphalt binder. Adding only PE wax to just the asphalt binder itself formed a thin waxy layer on top of the binder once the binder settled as seen in Figure 22 and Figure 23.

Figure 22: White PE wax film on the modified asphalt binder.

Figure 23 shows 3%LDPE4 modified binder with polymer particles of varying sizes. Whereas, for the case of 2%LDPE4_1%PEWax (Figure 23a-d) modified binder the particle size is more uniform (Figure 24). The particles are also more evenly dispersed. Replacing 1%LDPE4 in 3%LDPE4 to form 2%LDPE4_1%PEWax reduces the maximum particle diameter at both 30 and 150 min. For the 30 min time stamp, the particle diameter decreased from 160-170 µm to 100-110 µm. For the 150 min time stamp, the particle diameter decreased from greater than 200 µm to 90-100 µm. However, the addition of PE wax to LDPE70 caused the agglomeration of the polymer as can be seen from Figure 23e-h and Figure 25. Replacing 1%LDPE70 in 5%LDPE70 to form 4%LDPE70_1%PEWax increases the maximum particle diameter at both 30 and 150 min. For the 30 min time stamp, the particle diameter increased from 50-60 µm to 130-140 µm. For the 150 min time stamp, the particle diameter increased from 110-120 µm to 150-160 µm.



(a) 2% LDPE4+ 1% PE wax, 30 min (b) 2% LDPE4+ 1% PE wax, 60 min (c) 2% LDPE4+ 1% PE wax, 90 min (d) 2% LDPE4+ 1% PE wax, 150 min



(e) 4% LDPE70+ 1% PE wax, 30 min (f) 4% LDPE70+ 1% PE wax, 60 min (g) 4% LDPE70+ 1% PE wax, 90 min (h) 4% LDPE70+ 1% PE wax, 150 min

Figure 23: Optical images of PE wax modified asphalt binder at different times

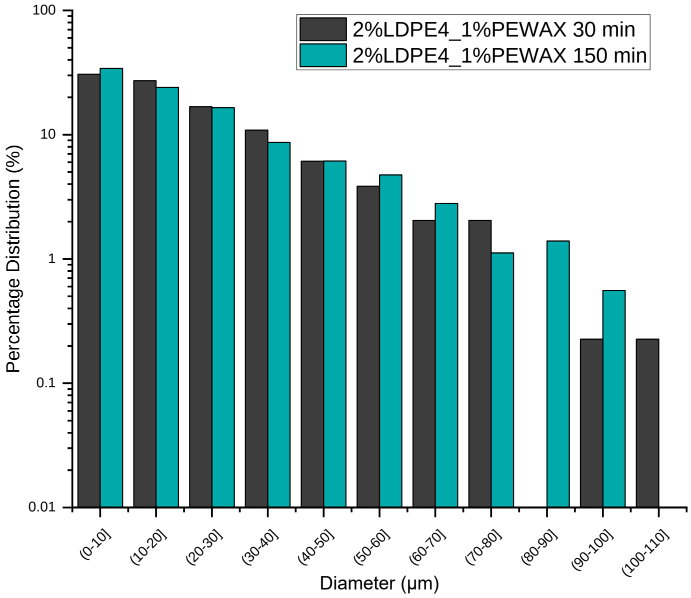


Figure 24: Particle size distribution of 2% LDPE4_1%PEWax at 30 and 150min

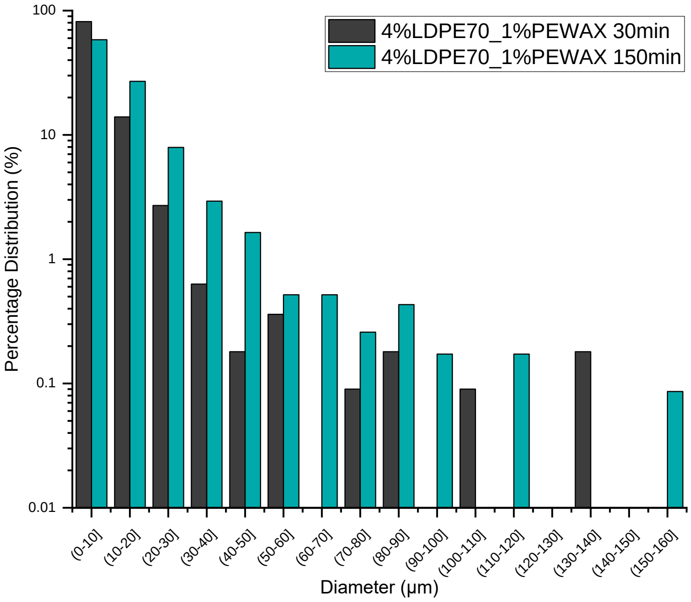


Figure 25: Particle size distribution of 4%LDPE70_1%PEWAX at 30 and 150min

The main outcome of this analysis is that the LDPE4 concentration should be kept below 3% and LDPE70 concentration should be kept below 5% (including PE wax) as until this loading there is not much agglomeration in the binders. Furthermore, PE wax can be used as a compatibilizer for LDPE4 to reduce phase separation. However, it is not affective in the case of LDPE70 as it caused agglomeration.

3.2 Thermogravimetric Analysis (TGA)

TGA curves provide an indication of the thermal stability of the binders. In this analysis the samples with a mass of approximately 15mg were heated from 30.00°C to 550.00°C at 10.00°C/min. Figure 26 shows the TGA graph of the various blends. As evident, the graphs show almost identical behavior for all the blends. All of the graphs show single stage degradation complete with very clear initial and starting points similar to those found in the literature [28]. Below 200℃, there is no mass loss and the onset of mass loss occurs after 200℃. Table 6 summarizes $T_{0.05}$ and $T_{0.5}$ of the blends. These temperatures are temperatures at which 5% and 50% of the polymer has decomposed (i.e. 95% and 50% of the polymer's original weight is remaining). It is seen that the degradation temperature increases for increasing concentration of polymer however the increases are very minute. These graphs are in line with the literature and indicate that all the blends undergo decomposition within the temperature range of 350-500℃. The trend for $T_{0.05}$ of the binder is as follows: Pen 60/70 < 3% PEWAX < 3%LDPE4 < 2%LDPE4_1%PEWAX. For $T_{0.5}$, the trend is as follows: Pen 60/70 < 3%LDPE4 < 2%LDPE4_1%PEWAX < 3%PEWAX. Modifying the binder increases the temperature at which the onset of decomposition occurs. There is a 18.6℃ difference in the $T_{0.05}$ of Pen 60/70 and the highest $T_{0.05}$ which was that of 2%LDPE4_1%PEWAX. On the other hand, the difference between $T_{0.5}$ of Pen 60/70 and the highest $T_{0.5}$ (3%PEWAX) is only 8.1°C. 3%PEWAX blend decomposed with least followed by 3%LDPE4 blend, and Pen 60/70. 2%LDPE4_1%PEWAX blend decomposed the most. This thermal decomposition and mass loss is the result of the decomposition of polymers and larger asphalt molecules along with the volatilization of saturates and aromatics (lighter asphalt components) [31,32]. Modification of the binder enhances the final stability of the blend however the difference is small and therefore the experiment was not carried on testing the stability of LDPE70 modified binder. Furthermore, the temperatures at which the binder decomposes is substantially higher than that of its use temperature. Consequently, this test does not provide much practical information.

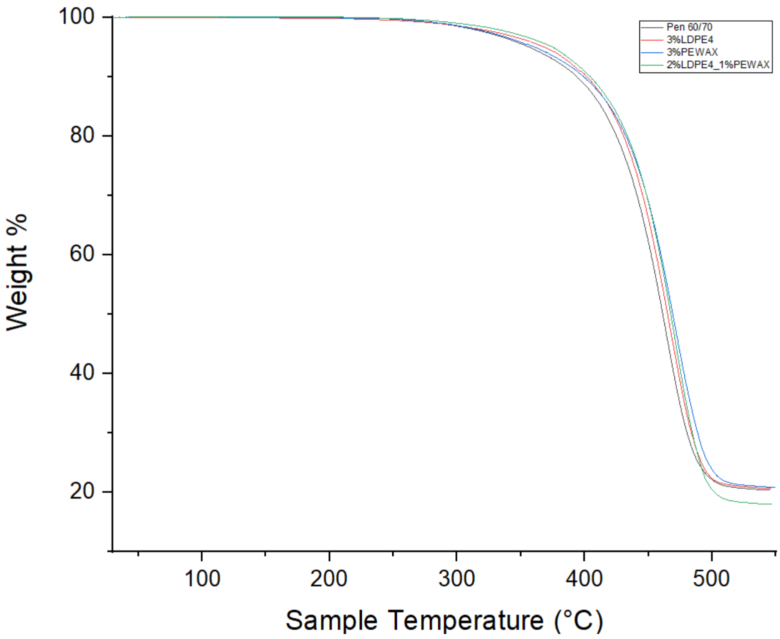


Figure 26: TGA plot of various blends

Table 6: Decomposition temperatures of various blends

Blend	Decomposition Temperature (°C)	
	$T_{0.05}$	$T_{0.5}$
Pen 60/70	356.7	461.1
3%LDPE4	368.6	465.1
3%PEWAX	360.1	469.2
2%LDPE4_1%PEWAX	375.3	467.7

3.3 Polymer Crystallization and Percentage Crystallinity

DSc can be used to quantify the interaction between the binder and the polymer as well as show the thermo-mechanical behavior of the blend. Samples with a mass of approximately 20mg were heated from 30°C to 200°C at 10°C/min. Area under the largest peaks can be used to calculate ΔH_f. The areas and the peak heights are given in the Table 7 below. At higher temperatures, the peak center points are indicators of the melting temperatures of the blends. As the range tested was from 30-200°C, it was not possible to obtain the glass transition temperatures due to unavailability if cryogenic equipment. It can be seen from Table 7 that the blends containing LDPE4 have higher melting points than those containing LDPE70. According to literature, the transition from 40-60°C is indicative of the crystallization of the paraffin wax in the blend [33]. Furthermore, it is stated that not all transformations are detected in a normal DSC scan with a rate of 10°C/min as at low temperatures the molecules have low kinetic energy and therefore lower velocity and may take several hours to reach equilibrium [33]. The theoretical value of 100% crystalline PE is stated as 293 J/g in literature [34].

Percentage crystallinity of the component was calculated using the following formula:

$$\chi_c = \frac{\Delta H_f}{(1-w) \times \Delta H_f^0} \times 100$$

Where:

χ_c : Degree of crystallinity (%)

ΔH_f : Heat of fusion of the blend

w : Mass fraction of LDPE

ΔH_f° : Heat of fusion of 100 % crystalline PE

Table 7: Melting point, melting heat flow and crystallinity of pure binder and polymers and their blends

Blend	Melting Point (°C)		ΔH_f	Crystallinity
	Onset	Peak	J/g	%
Pen 60/70				
LDPE4	106.4	119.3	65.3	22.6
5%LDPE4	93.9	103.8	5.3	36.7
LDPE70	100.3	111.8	44.8	15.5
3%LDPE70	82.7	94.1	2.5	28.8
5%LDPE	84.5	94.4	4.0	27.7
4%LDPE70_1%PEWAX	85.3	94.1	4.2	36.3
2%LDPE4_1%PEWAX	91.1	100.1	1.8	31.1
PEWAX	95.5	102.1	1.4	0.47
3%PEWAX	94.0	98.7	0.3	0.10

Table 7 shows the melting point onset temperature as well as the melting point itself along with the heat of fusion and the percentage crystallinity of the blends. The DSC plots of the various blends are shown below.

Some points of interest to consider from Table 7 and Figure 27-Figure 32:

- The grade of LDPE influences the heat of fusion and the melting temperature of the blend. 5%LDPE4 modified binder has a melting point that is 9.4℃ higher than that of 5%LDPE70 modified binder. Moreover, it also has higher heat of fusion and therefore higher percentage crystallinity than 5%LDPE70 modified binder. The heat of fusion and percentage crystallinity of 5%LDPE4 modified binder is 5.30J/g and 36.7% while for 5%LDPE70 they are 4.00J/g and 27.7% respectively.
- Addition of LDPE reduces the melting temperature and increases the heat of fusion.
- The percentage of LDPE70 does not affect the melting temperature but does affect the heat of fusion. Increasing the LDPE70 percentage from 3% to 5% increased the heat of fusion 1.5J/g.
- In 5%LDPE70, replacing 1%LDPE70 with 1%PEWax in order to create a blend of 4%LDPE70_1%PEWax has negligible effect on melting temperature and heat of fusion values but significantly increases the percentage crystallinity from 27.7% to 36.3%.
- Blends containing LDPE4 tend to have higher melting points and percentage crystallinity.

The lower percentage crystallinity and heat of fusion values are attributed to incomplete crystallization. Reduced crystal size is reported to be caused by the migration of paraffinic and aromatic compounds in the binder to the polymer rich phase where they break the crystals [28,35–37]. As such, the trends shown indicate the presence of interactions between the polymer and the binder, similar to what is seen in the literature [28]. Another reason for lower crystallinity and heat of fusion could be disruption of the crystalline structure caused by the swelling of the polymer [28,37]. As a result, smaller crystallites lead to lower melting point temperature which reduces high temperature performance of the binder.

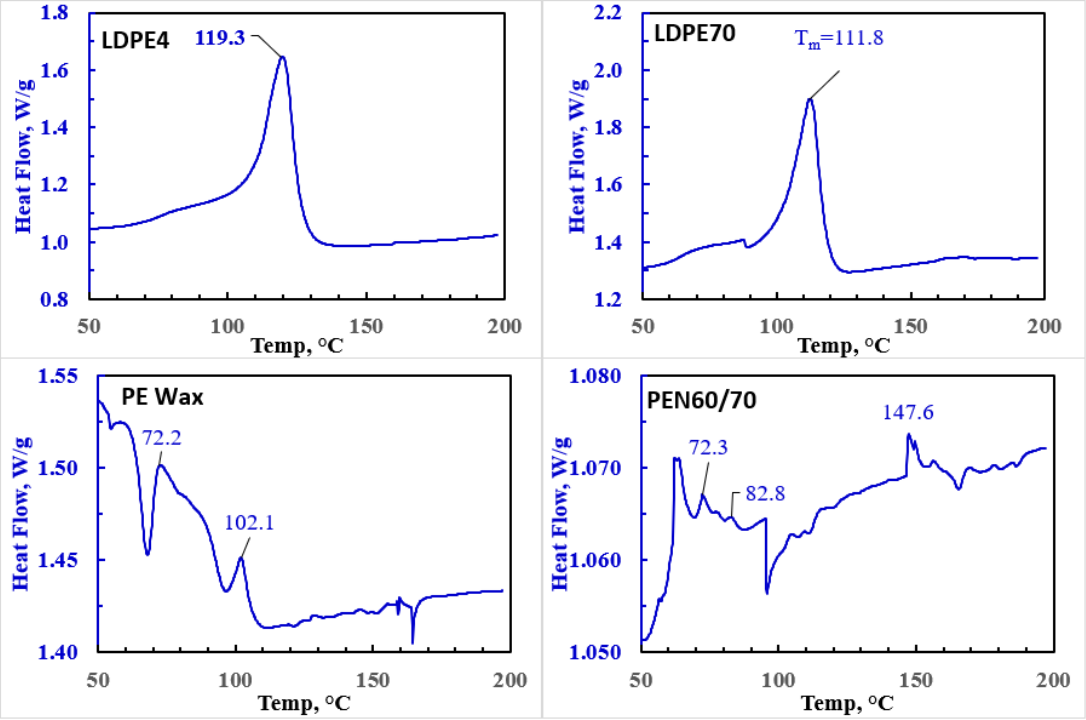


Figure 27: Heat flow vs temperature of pure LDPE4, LDPE70, PE wax and pure Pen 60/70 binder.

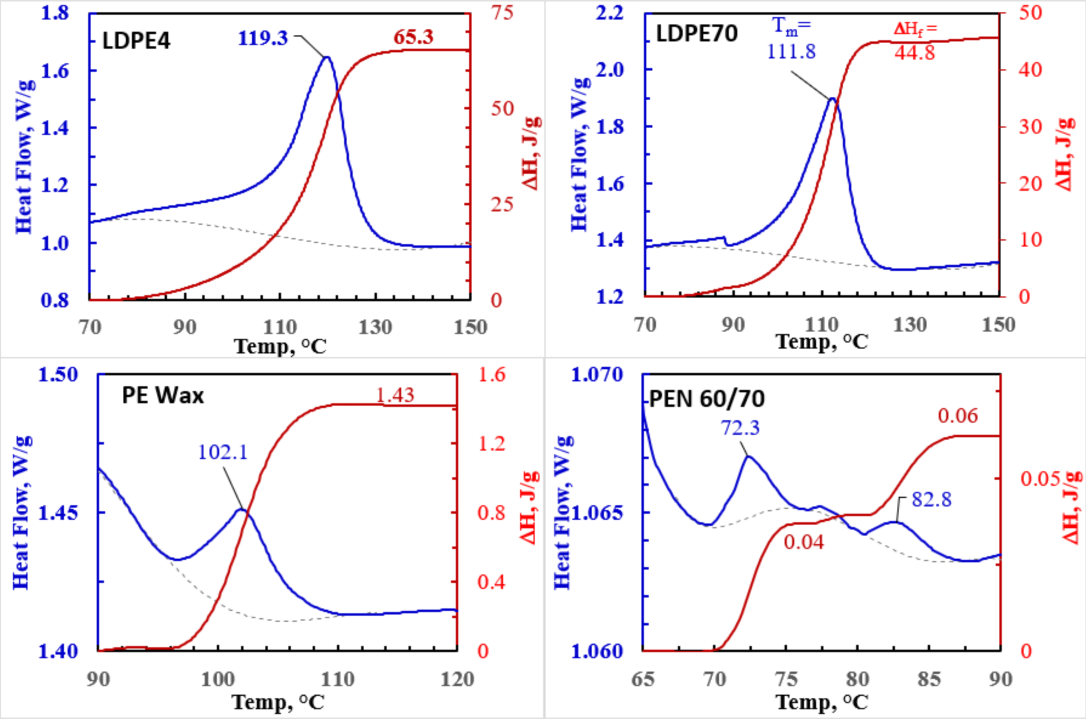


Figure 28: Heat flow and heat of fusion vs temperature for LDPE 4, LDPE70, PE Wax and Pen 60/70 binder.

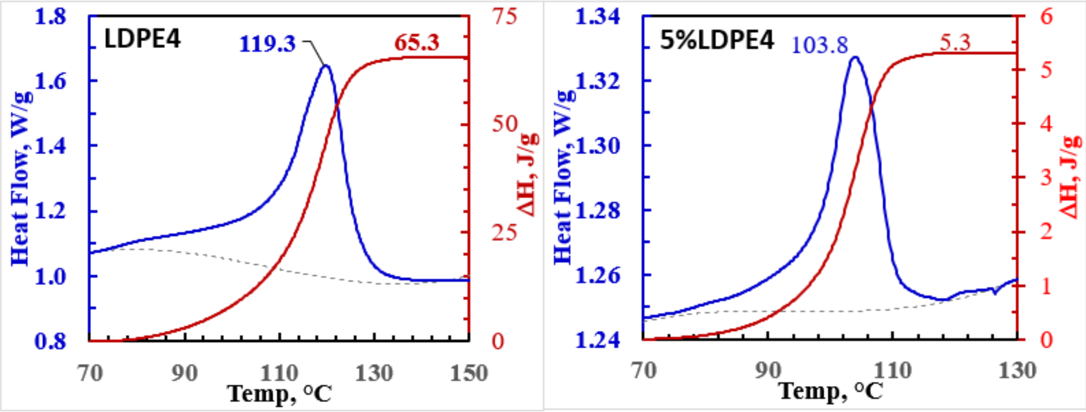


Figure 29: Heat flow and heat of fusion vs temperature for LDPE4 and 5%LDPE4 modified binder.

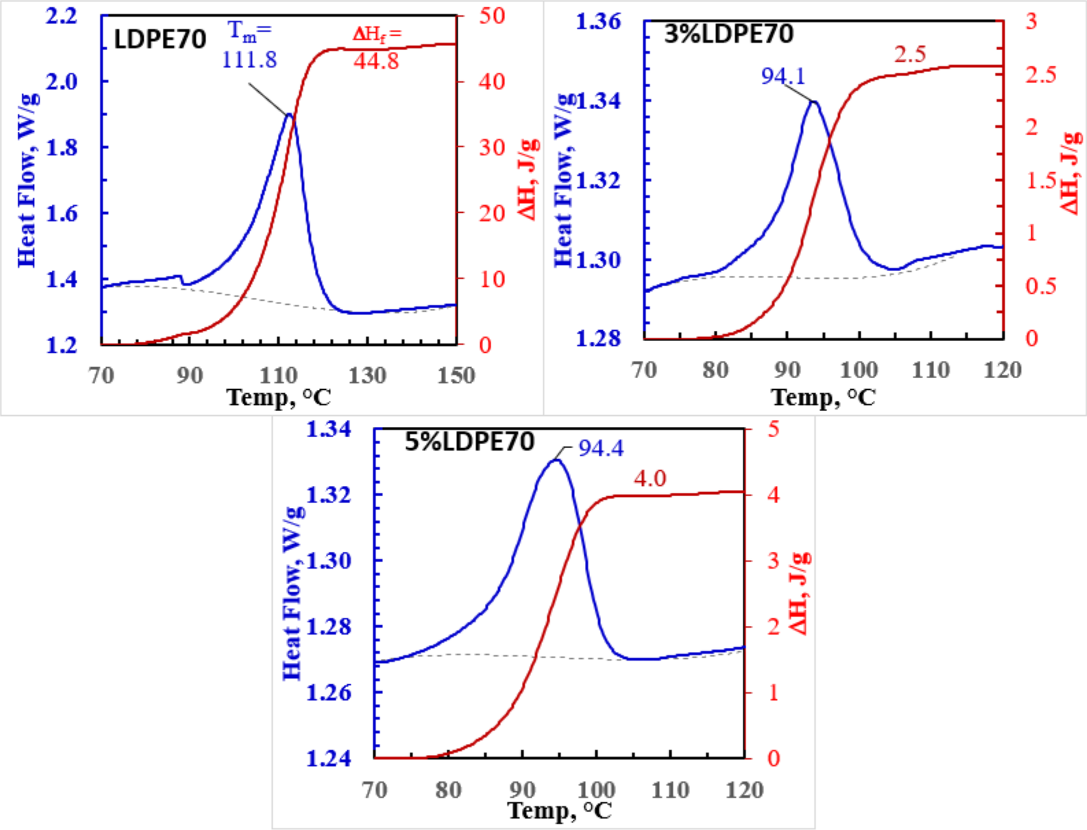


Figure 30:Heat flow and heat of fusion vs temperature for LDPE70, 3%LDPE70 modified binder, and 5%LDPE70 modified binder.

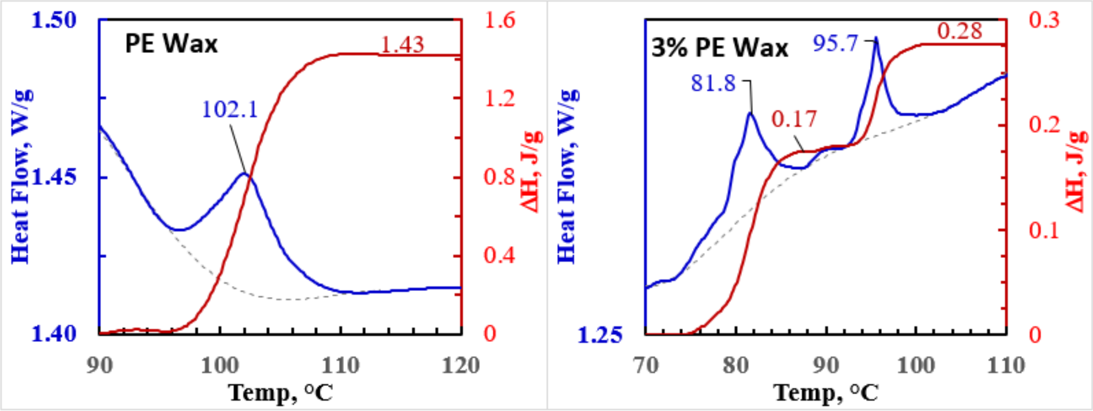


Figure 31:Heat flow and heat of fusion vs temperature for PE Wax and 3%PEWax modified binder.

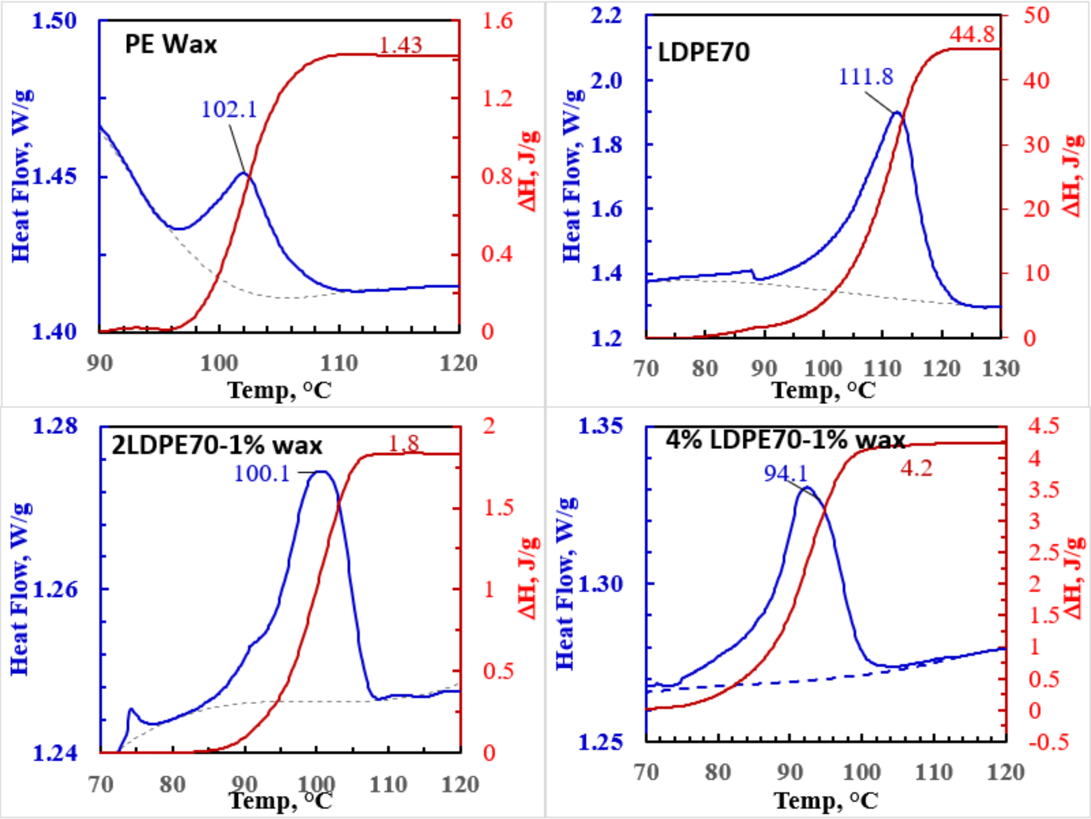


Figure 32:Heat flow and heat of fusion vs temperature for PE Wax, LDPE70, 2%LDPE70_1%PEWaX modified binder, and 4%LDPE70_1%PEWax modified binder.

3.4 Rheological Properties

The Figure 33-Figure 38: Phase angle as a function of reduced frequency at 35°C for PE wax blends below show the frequency sweep data at the reference temperature. These data can be used to determine various rheological parameters such as the dynamic, storage, and loss moduli along with the phase angle. The general trends shown in the master curves are similar. The dynamic modulus of both modified and unmodified binder (Pen 60/70) increase with an increase in frequency. The Figures clearly indicate a strong relationship between the addition of modifiers and the dynamic modulus which is in line with literature that states that the addition of polymers affects the stiffness of the asphalt binder [18,38]. The dynamic modulus increases with an increase in frequency and a decrease in temperature. Increasing dynamic modulus is an indication of increasing stiffness. Looking at the common temperature of roads in Qatar (35°C), the grade of the LDPE has a major effect on the rheological properties of the binder. The addition of LDPE 4 increased the dynamic modulus greater than the addition of LDPE 70 did. From amongst the various concentrations of LDPE 4 in the binder, it was found that 3%LDPE4, 4%LDPE4, and 5%LDPE4 show similar results (Figure 33). As a result, it can be concluded that above 3% concentration of LDPE4 there is not much difference between the results.

This data also analyzed the effect of adding PE Wax into the LDPE modified binder's rheological properties (Figure 35). The figure shows that all three samples show similar results but 1%PEWax_2%LDPE had the highest G* values. For LDPE70, it was found that the 5%LDPE70 and 4%LDPE70_1%PEWax show similar G* results (*Figure 34*). The shift factors for all the curves are shown in Table 21 in the appendix.

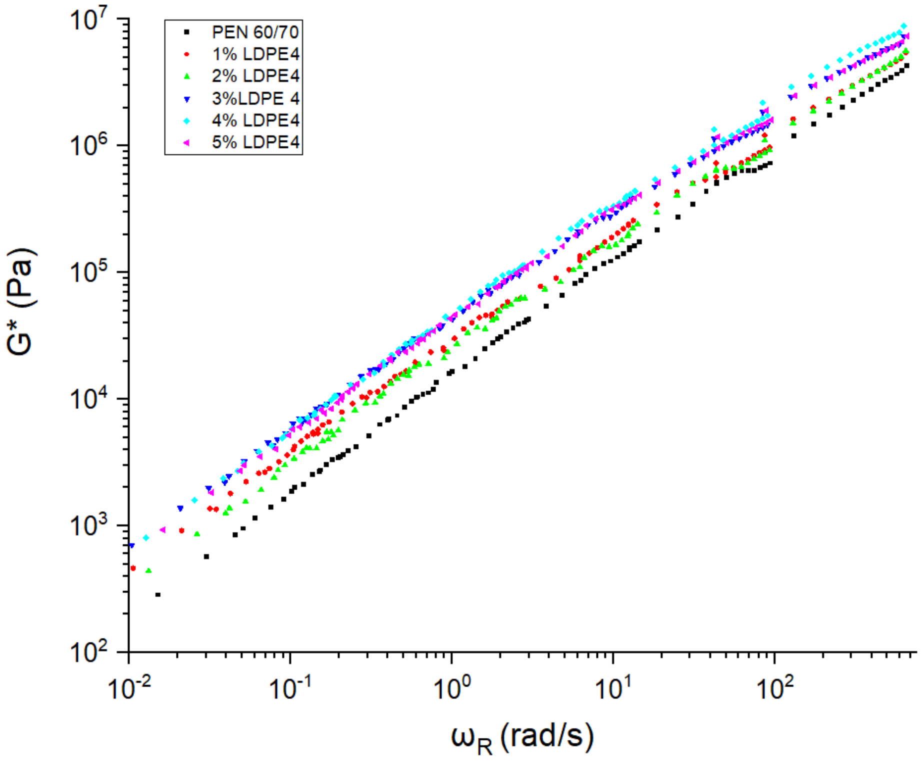


Figure 33: Master curve of dynamic modulus at 35℃ for LDPE4 blends

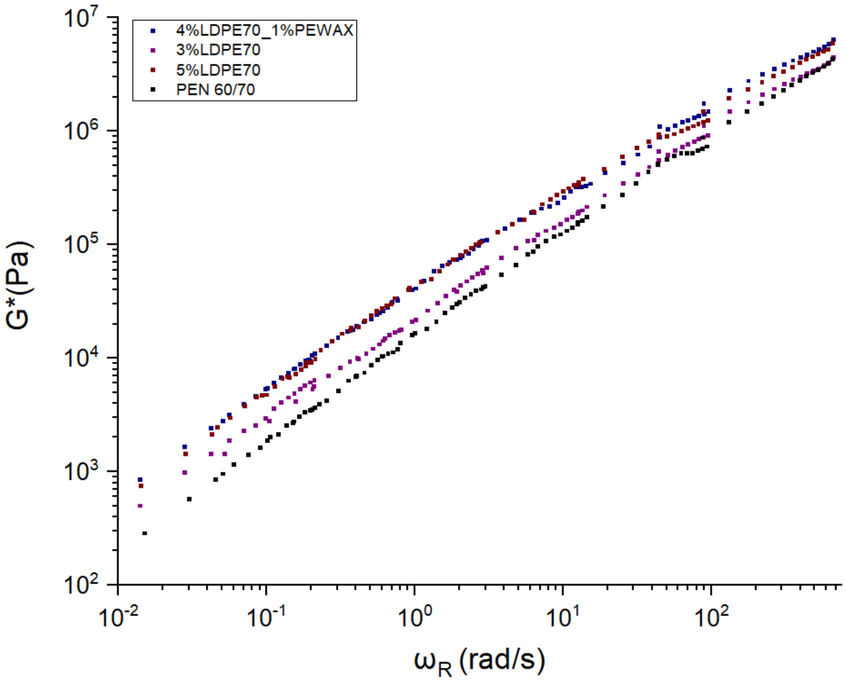


Figure 34: Master curve of dynamic modulus at 35℃ for LDPE70 blends

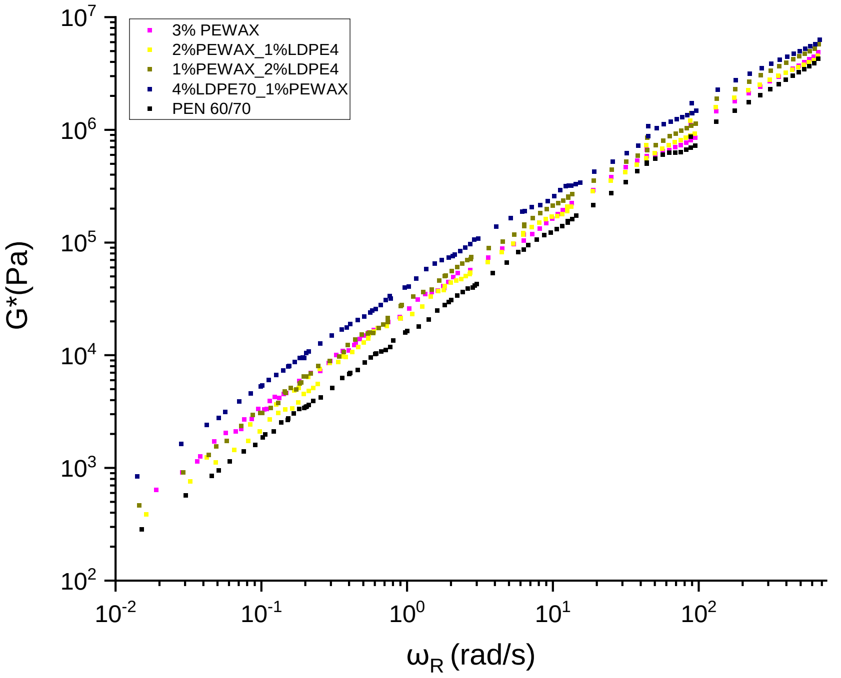


Figure 35: Master curve of dynamic modulus at 35℃ for PE wax blends

The phase angle variable is more sensitive to the physical structure of the blend compared to the dynamic modulus and therefore can be used to prove the existence of polymer elastic networks and entanglements [38]. This is indicated by a plateau in the phase angle master curve. The lower the phase angle the higher the elastic response of the material [39]. As the frequency increases so does the elastic response of the blends due to the reduction in the phase angle. The results indicated that the addition of modifiers reduces the phase angle corresponding to a higher elastic response. According to Figure 36, it was found that 3%LDPE4, 4%LDPE4, and 5%LDPE4 show similar results for phase angle. As a result, it can be concluded that above 3% concentration of LDPE4 there is not much difference between the elastic response of the binders. LDPE70 blends generally tend to have lower phase angles. For LDPE70, 5%LDPE70 and 4%LDPE70_1%PEWAX show similar phase angle results (Figure 37) indicating that the addition of PE wax did not affect the elastic response of the binders. Furthermore, according to Figure 38, all three samples show similar but 1%PEW_2%LDPE4 had the lowest phase angle, although the difference is small.

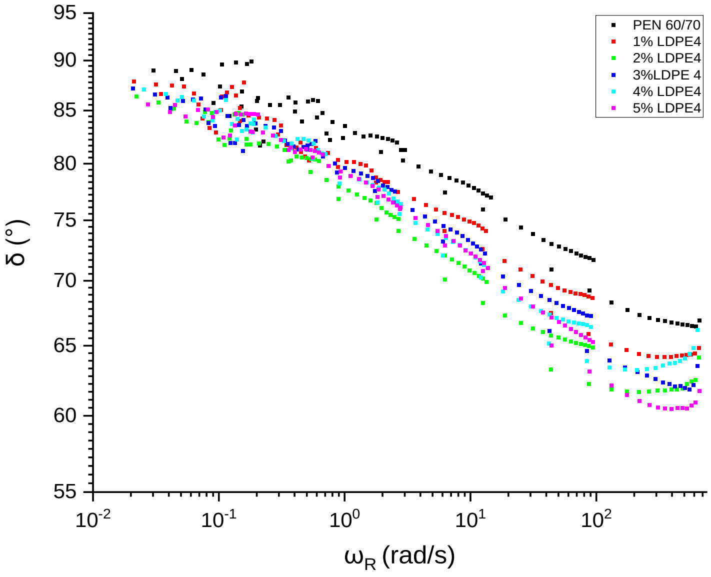


Figure 36: Phase angle as a function of reduced frequency at 35°C for LDPE4 blends

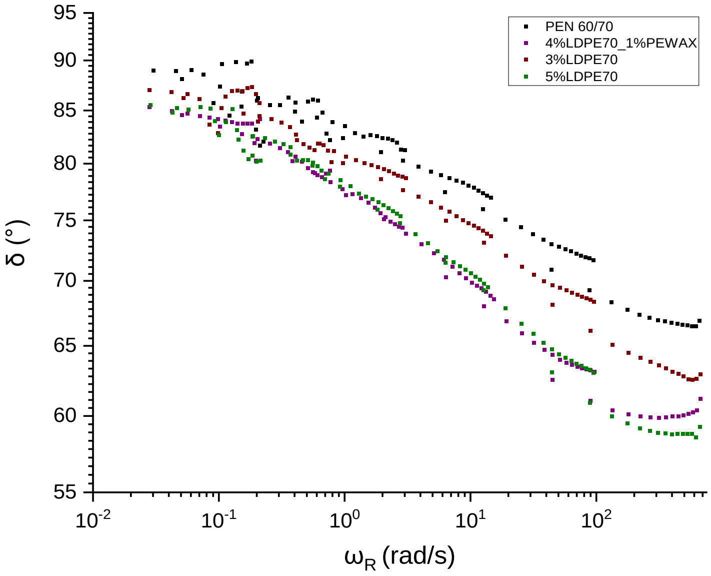


Figure 37: Phase angle as a function of reduced frequency at 35℃ for LDPE 70 blends

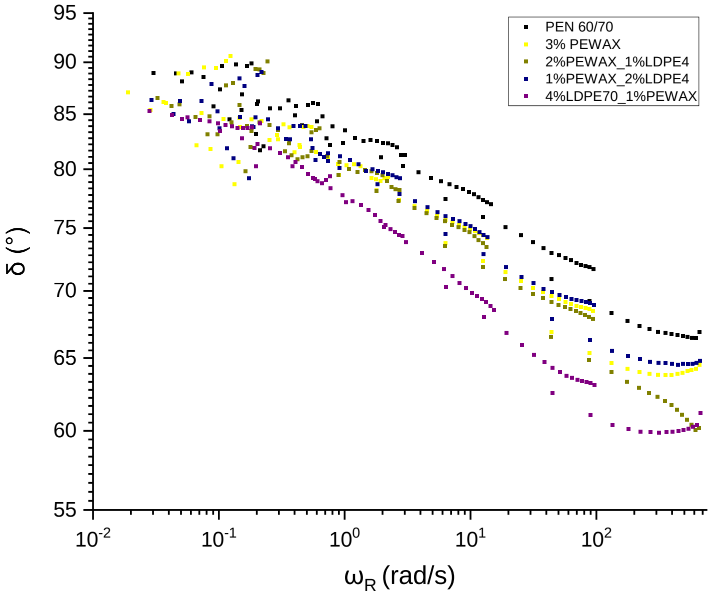


Figure 38: Phase angle as a function of reduced frequency at 35℃ for PE wax blends

3.5 Performance Grading

Table 9 and Table 10 show the data from PG high, intermediate, and low tests. They indicate the data obtained at various temperatures and the temperature at which the binder failed to achieve the specifications of the tests along with the actual grade temperature of the binder. Table 8 shows the overall PG grade obtained from the data of the aforementioned tables. If a binder fails to meet the criteria of at a certain temperature, then its grade temperature automatically becomes the one below that. For example, in the 64 to 70℃ range, 3% PE wax modified asphalt binder did not meet the criteria of G* ≥ 1.0 kPa. As a result, PG high of 3% PE wax modified asphalt binder was 64℃. Data from Table 8 indicates that all modified blends, except 3%PE wax modified binder, increase the PG high temperature from 64℃ to 70℃. However, modification of the binders increases the PG low temperature of all blends except that of 3%LDPE70. From this data, it is evident the that blend with the largest range and therefore best overall performance is 3%LDPE70 with the PG grade of 70S-22. 5%LDPE70, 4%LDPE70_1%PEWax, 2%LPDE4_1%PEWax, 3%LDPE4 and 5%LDPE4 all have the same PG grade of 70S-16.

Some interesting points to consider from Table 8:

- Addition of LDPE4 improved PG high temperature from 64 to 70℃ but negatively affected PG low temperature.
- Addition of LDPE70 improved PG high temperature from 64 to 70℃ but negatively affected PG low temperature for 5%LDPE70 and 4%LDPE7_1%PEWAX blends.

- Addition of LDPE4 and LDPE70 improved PG high temperature from 64 to 70℃ but negatively affected PG low temperature.
- 3%PEWAX did not improve PG high PG low temperature.

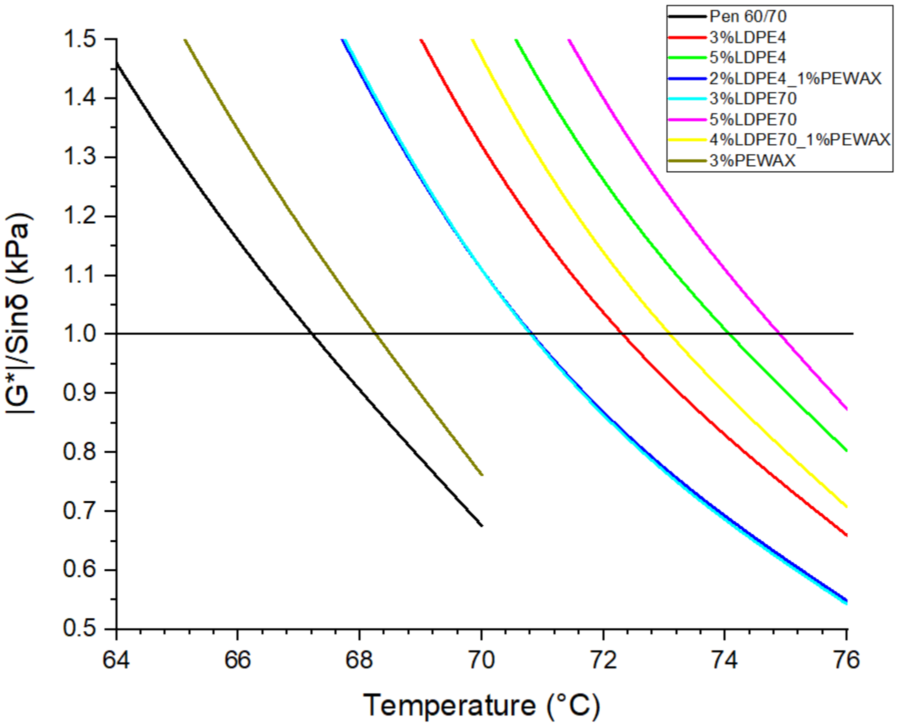


Figure 39: |G|/sinδ vs Temperature for various polymer modified asphalt binders*

Table 8: PG Grading of various blends

Material	PG grade
Pen 60/70	64S-22
3%LDPE4	70S-16
5% LDPE4	70S-16
3% LDPE70	70S-22
5% LDPE70	70S-16
3% PE Wax	64S-16
2%LDPE4_1%PEWax	70S-16
4% LDPE70_1%PEWax	70S-16

Table 9: PG High Temperature of Samples

PG High - Unaged

Temperature (℃)	Pen 60/70	3% LDPE4	5% LDPE4	3% LDPE70	5% LDPE70	3% PE Wax	2%LDPE4_ 1%PEWax	4%LDPE70_ 1%PEWax
52	8.11	15.40	19.20	12.60	22.40	10.20	13.10	18.60
58	3.36	6.39	7.88	5.24	9.06	4.14	5.45	7.53
64	1.46	2.81	3.45	2.38	3.91	1.72	2.39	3.23
70	0.68	1.32	1.61	1.11	1.80	0.76	1.11	1.47
76		0.66	0.80	0.54	0.87		0.55	0.71
Failing Temperature	67	72.4	74.1	70.9	74.9	68	70.9	73.2
Grade Temperature	64	70	70	70	70	64	70	70

PG High – RTFO Aged

Temperature (℃)	Pen 60/70	3% LDPE4	5% LDPE4	3% LDPE70	5% LDPE70	3% PE Wax	2%LDPE4_ 1%PEWax	4%LDPE70_ 1%PEWax
52	18.40	40.90	59.30	34.10	44.10	24.90	32.20	42.50
58	7.46	16.50	23.70	13.90	17.60	10.10	13.30	16.90
64	3.18	7.03	9.99	5.96	7.34	4.20	5.70	6.97
70	1.42	3.17	4.44	2.70	3.25	1.81	2.53	3.02
76		1.55	2.08	1.28	1.51		1.18	1.38
Failing Temperature	66.7	73.6	75.6	71.6	73.1	68.6	71.1	72.4
Grade Temperature	64	70	70	70	70	64	70	70

Table 10: PG Intermediate and PG Low Temperature

PG Intermediate

Temperature (°C)	Pen 60/70	3% LDPE4	5% LDPE4	3% LDPE70	5% LDPE70	3% PE Wax	2%LDPE4_ 1%PEWax	4%LDPE70 _ 1%PEWax
34	1890	2290	3150	2290	3170	1640	2270	3020
31	1820	3280	4450	3330	4520	2440	3280	4330
28	2810	4660	6380	4740	6320	3560	4680	6090
25	4310	6540		6700		5160	6570	
22	6540							
Failing Temperature	23.9	27.4	30	27.5	30.1	25.2	27.4	29.7
Grade Temperature	25	28	31	28	31	28	28	31

PG Low - BBR

Temperature (°C)	Pen 60/70	3% LDPE4	5% LDPE4	3% LDPE70	5% LDPE70	3% PE Wax	2%LDPE4_ 1%PEWax	4%LDPE70 _1%Wax
Stiffness at 0C	26.40	38.54	62.10	55.80	67.00	41.90	42.10	66.80
Slope at 0C	0.54	0.45	0.39	0.41	0.38	0.40	0.39	0.38
Stiffness at -6C	101.26	119	76.00	76.40	77.80	129.32	140.80	79.80
Slope at -6C	0.60	0.32	0.35	0.37	0.35	0.40	0.41	0.35
Stiffness at -12C	264.91	324.40	206.00	168.00	192.00	296.21	338.23	169.00
Slope at -12C	0.30	0.29	0.28	0.32	0.29	0.27	0.32	0.29
Failing Temperature	-12.00	-6	-6.00	-12.00	-6.00	-6.00	-6.00	-6.00
Grade Temperature	-22.00	-16	-16.00	-22.00	-16.00	-16.00	-16.00	-16.00

3.6 Rotational Viscometer

Figure 41 shows the viscosity plots of various blends. It should be noted that the test could not be performed properly for 5%LDPE4 modified samples as the torque exceeded 90% at 100°C at 20rpm and resulted in the machine stopping the test. Figure 40 shows the time, temperature, and viscosity data for 3% LDPE modified binder. The bottom line of the curve for each blend is the data obtained during cooling from 160°C to 100°C and the top line is obtained during heating from 100°C to 160°C. Figure 42 reports the area between each curve for the blends. As evident, the area between the curves increases as the LDPE concentration increases. 4%LDPE4 modified binder has an area that is 3.4 times greater than that of Pen 60/70 whereas the wax modified blends have areas that are 1.2-1.6 times greater than that of Pen 60/70. Therefore, it can be concluded that increasing the LDPE concentration increases instability within the blend. However, this instability can be reduced with the addition of PE Wax to the blend. The higher melt flow index value of LDPE70 allowed it to perform better than LDPE4 in this test. 3%LDPE70 had an area that was approximately 2.2 times smaller than that of 3%LDPE4. Similarly, compared to 4%LDPE4, 5%LDPE70 had an area that was approximately 2.3 times smaller. These results showed that grade of the LDPE significantly affects the stability of the blend. The area of 3%LDPE70 was similar to that of Pen 60/70 while the area of 5%LDPE70 showed slight variation indicating that the percentage of LDPE70 did not influence the stability of the binder. Furthermore, although the addition of PE wax decreased the area of the curve and improved the stability of the binder, the affect it had on LDPE70 was negligible compared to that of LDPE4. Therefore, it can be concluded that PE wax is a better compatibilizer for LDPE4 blends than for LDPE70.

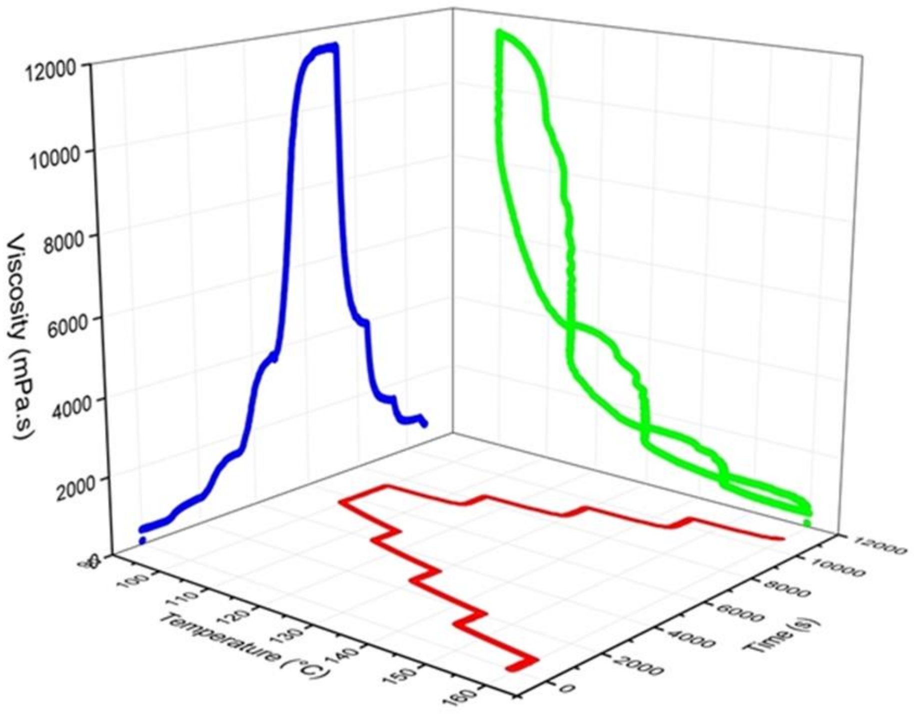


Figure 40: Time, temperature, and viscosity plot of 3%LDPE4 modified binder

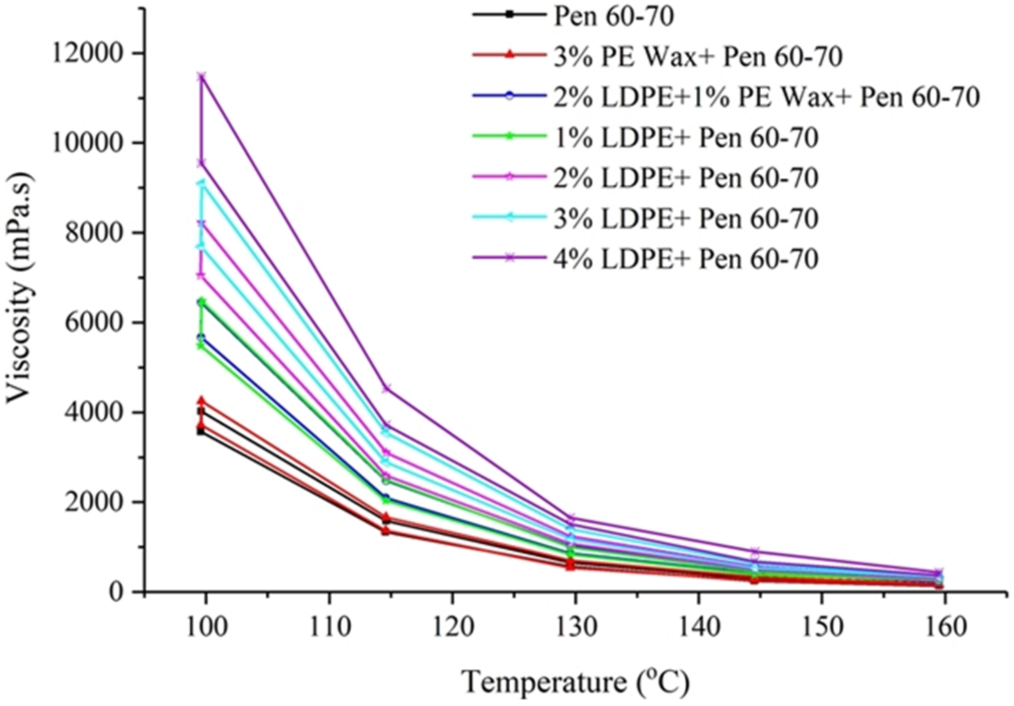


Figure 41: Viscosity plot of various blends of LDPE4

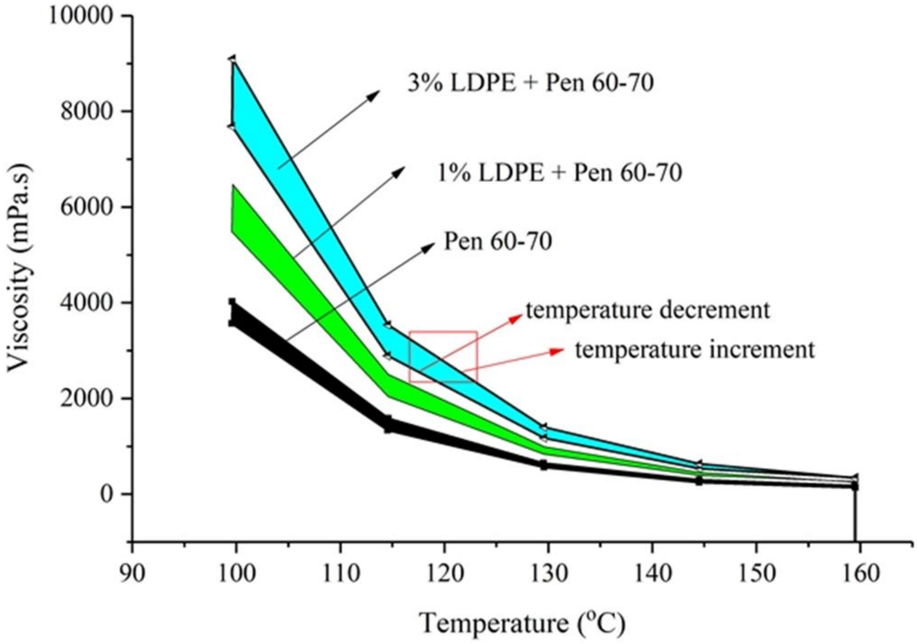


Figure 42: Area calculation for various blends

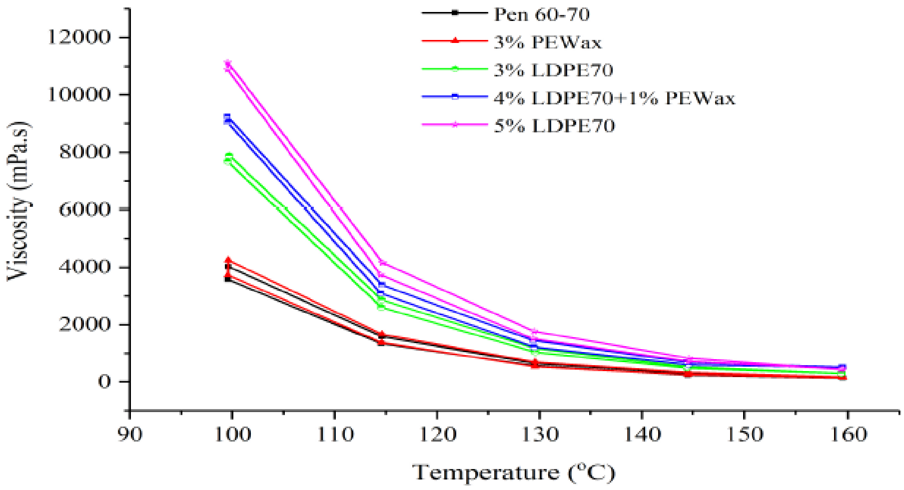


Figure 43: Viscosity plot of various blends of LDPE70

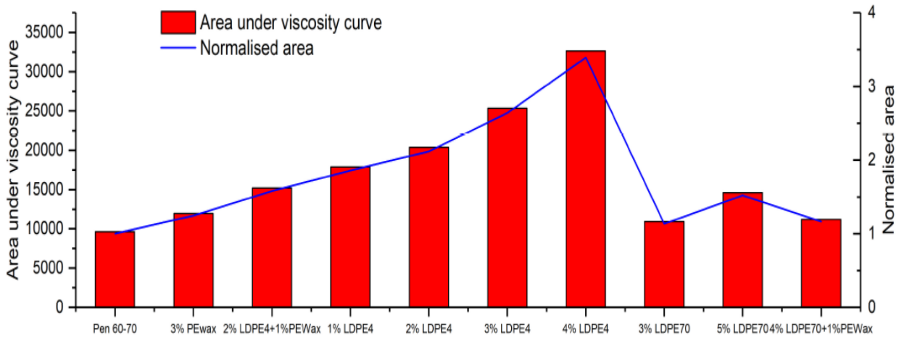


Figure 44: Area under the viscosity curves for various blends

4. CONCLUSION

In conclusion, modification of asphalt with polymers enhances numerous properties and using recycled polymers for asphalt modification have the added benefits of being both economically and environmentally friendly. Furthermore, recycled polyethylene performs on par with virgin polyethylene as an asphalt binder modifier. However, one of the main problems faced with polymer modified asphalt is phase separation during storage. Analysis of the literature suggests using low polyethylene contents (3-5wt%) in order to reduce phase separation. Additionally, compatibility of the asphalt binder with the polyethylene can be improved by using polymers of low molecular weight, high molecular distribution, low crystallinity, high MFI, and greater branching. It should be noted that the compatibility of the polymer should be high enough to reduce phase separation but not too high in order to avoid a dense network formation that would result in a gel-like binder rendering it inapplicable. Incorporation of functionalizing additives, reactive polymers, hydrophobic clay can be used to enhance the interaction of the polymer with the binder. Usage of chemical additives depends on the polymer being used as some additives perform better on unsaturated polymers while others work better on saturated polymers.

This research carried out morphological analysis and performance tests on polyethylene modified asphalt binder with various concentrations of polyethylene wax as an additive. It was found that LDPE70 performed better than LDPE4 as it had better PG grade and showed better polymer particle diameter distribution compared to LDPE4. Furthermore, LDPE70 had lower crystallinity than LDPE4 showing more interaction with the binder and as a result lower phase separation. LDPE70 also had the lowest phase angle in the DSR indicating the highest elastic response. Additionally, it was found that the addition of PE wax to LDPE70 increased agglomeration. It can be concluded that the PE wax is not a good compatibilizer between LDPE70 and asphalt binder.

Unfortunately, SAXS and TEM could be used to analyze the phase separation within the binder due to the current COVID-19 situation. It is recommended that this be carried out in future works to better understand the phase separation of the blends. Furthermore, it is recommended that future work be carried out with LDPE70, but with a different compatibilizer as PE wax is not suitable.

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APPENDIX A

Issues Faced During Sample Preparation

The sample preparation methodology stated in chapter II was achieved through some fine tuning done using trial and error. Initially, after the literature review was conducted the chosen method was to heat the binder at 160°C and then add in the specified mass of the polymer. The sample was then heated on the hot plate at 160 for an hour at very low speeds. There were several issues faced with this method and the major one was that the polymer and the binder were not forming a homogeneous blend. Firstly, heating the binder and polymer mixture straight on the hotplate caused the pellets to stick to the spindle of the mixer in clumps when they started heating up. This would render the sample useless as the wasted polymer would cause the composition of the blend to change. Furthermore, when the polymer clumper were removed from the spindle and put back into the binder to reheat, the process was not successful as they would remain as clumps and not melt. Secondly, the polymer, in its solid pellet form, would rise to the top while the binder remained at the bottom when the sample stored for short amounts of time. The higher the concentration of the binder the more the palettes separated from the mixture.

Figure 45: Solid LDPE 4 pellets phase separating from the binder

Several methods were discussed to overcome this issue:

1. Heating the polymer first and then incorporating it with the binder.
2. Heating the mixture to a higher temperature.
3. Increasing the shear rate of blending.
4. Increasing the time of blending.
5. Extrusion

During the trial of method 1, a specified weight of LDPE 4 polymer was taken and heated in the oven at 160℃. After some time, it was seen that the solid opaque white pellets of the polymer started to become translucent and started to melt. However, when left to further liquefy the polymer started to burn at the bottom of the container after melting rather than becoming less viscous and flowing as hoped. As a result, neither pouring binder on top nor pouring the polymer on top of the binder and blending would not have been possible as it was not of pouring consistency.

Figure 46: White opaque pellets of LDPE 4, as received, and the translucent pellets after a short period of heating.

During the implementation of method 2, the temperature at which the binder was heated at was increased to 175°C. Even though it did melt the polymer pellets to a higher degree than 160°C, the mixture formed was still not homogeneous. Methods 3 and 4 were applied both separately and combined however the result yielded was not that different.

Figure 47: LDPE 4 and binder pellets sticking onto the extruder inlet.

To carry out the extrusion the binder was formed into 1g pellets and then put in the fridge to cool overnight. The cooling was done to stop the binder from sticking to the inside of the extruder. However, as seen in Figure 47, the procedure was not successful as majority of the binder stuck onto the hopper and the piston of the extruder and was not able to pass the material through. Furthermore, LDPE 4 pellets in their solid form were found stuck onto the screws of the extruder when cleaning.

APPENDIX B

Table 11: 1%LDPE4 particle count and percentage distribution at 30 and 150 min

	PERCENTAGE	
	30MIN	150MIN
(0-10]	30.61	34.08
(10-20]	27.21	24.02
(20-30]	16.78	16.48
(30-40]	10.88	8.66
(40-50]	6.12	6.15
(50-60]	3.85	4.75
(60-70]	2.04	2.79
(70-80]	2.04	1.12
(80-90]	0.00	1.40
(90-100]	0.23	0.56
(100-110]	0.23	0.00

Table 12: 2%LDPE4 particle count and percentage distribution at 30 and 150 min

	PERCENTAGE	
	30MIN	150MIN
(0-10]	28.06	24.51
(10-20]	18.71	18.68
(20-30]	16.91	9.34
(30-40]	16.19	11.28
(40-50]	8.99	9.34
(50-60]	6.12	10.51
(60-70]	2.52	6.61
(70-80]	1.44	3.50
(80-90]	1.08	1.56
(90-100]	0.00	2.33
(100-110]	0.00	0.00
(110-120]	0.00	1.56
(120-130]	0.00	0.78

Table 13: 3%LDPE4 particle count and percentage distribution at 30 and 150 min

	PERCENTAGE	
	30MIN	150MIN
(0-10]	35.61	30.37
(10-20]	26.52	20.00
(20-30]	5.30	8.89
(30-40]	8.33	5.19
(40-50]	3.79	3.70
(50-60]	2.27	4.44
(60-70]	0.76	3.70
(70-80]	0.76	0.74
(80-90]	0.00	1.48
(90-100]	3.03	2.22
(100-110]	3.79	0.74
(110-120]	5.30	0.74
(120-130]	1.52	4.44
(130-140]	1.52	3.70
(140-150]	0.76	2.96
(150-160]	0.00	1.48
(160-170]	0.76	0.74
(170-180]	0.00	1.48
(180-190]	0.00	0.00
(190-200]	0.00	0.74
>200	0.00	2.22

Table 14: 4%LDPE4 particle count and percentage distribution at 30 and 150 min

	PERCENTAGE	
	30MIN	150MIN
(0-10]	36.96	40.37
(10-20]	14.13	19.27
(20-30]	13.04	8.26
(30-40]	3.26	3.67
(40-50]	4.35	3.67
(50-60]	2.17	3.67
(60-70]	3.26	3.67
(70-80]	1.09	0.00
(80-90]	2.17	0.92
(90-100]	1.09	1.83
(100-110]	0.00	0.92
(110-120]	2.17	0.92
(120-130]	1.09	0.92
(130-140]	1.09	0.92
(140-150]	3.26	1.83
(150-160]	2.17	0.00
(160-170]	3.26	0.92
(170-180]	1.09	2.75
(180-190]	1.09	0.00
(190-200]	1.09	0.00
>200	2.17	5.50

Table 15: 5%LDPE4 particle count and percentage distribution at 30 and 150 min

	PERCENTAGE	
	30MIN	150MIN
(0-10]	45.65	42.20
(10-20]	25.00	25.69
(20-30]	8.70	9.17
(30-40]	3.26	1.83
(40-50]	0.00	0.92
(50-60]	3.26	2.75
(60-70]	0.00	0.00
(70-80]	0.00	0.00
(80-90]	0.00	0.00
(90-100]	0.00	1.83
(100-110]	0.00	1.83
(110-120]	0.00	1.83
(120-130]	0.00	0.00
(130-140]	2.17	0.92
(140-150]	0.00	0.00
(150-160]	1.09	2.75
(160-170]	0.00	0.92
(170-180]	1.09	0.92
(180-190]	0.00	0.00
(190-200]	2.17	0.92
>200	7.61	5.50

Table 16: 3%LDPE70 particle count and percentage distribution at 30 and 150 min

	PERCENTAGE	
	30MIN	150MIN
(0-10]	65.62	59.84
(10-20]	21.56	27.72
(20-30]	6.99	7.24
(30-40]	3.38	2.68
(40-50]	2.10	0.63
(50-60]	0.35	1.10
(60-70]	0.00	0.00
(70-80]	0.00	0.79

Table 17: 5%LDPE70 particle count and percentage distribution at 30 and 150 min

	PERCENTAGE	
	30MIN	150MIN
(0-10]	59.42	65.11
(10-20]	29.34	26.78
(20-30]	8.85	5.28
(30-40]	2.02	1.58
(40-50]	0.28	0.82
(50-60]	0.09	0.22
(60-70]	0.00	0.11
(70-80]	0.00	0.05
(80-90]	0.00	0.00
(90-100]	0.00	0.00
(100-110]	0.00	0.00
(110-120]	0.00	0.05

Table 18: 2%LDPE4_1%PEWAX particle count and percentage distribution at 30 and 150 min

	PERCENTAGE	
	30MIN	150MIN
(0-10]	30.61	34.08
(10-20]	27.21	24.02
(20-30]	16.78	16.48
(30-40]	10.88	8.66
(40-50]	6.12	6.15
(50-60]	3.85	4.75
(60-70]	2.04	2.79
(70-80]	2.04	1.12
(80-90]	0.00	1.40
(90-100]	0.23	0.56
(100-110]	0.23	0.00

Table 19: 4%LDPE70_1%PEWAX particle count and percentage distribution at 30 and 150 min

	PERCENTAGE	
	30MIN	150MIN
(0-10]	81.62	58.33
(10-20]	13.96	27.01
(20-30]	2.70	7.94
(30-40]	0.63	2.93
(40-50]	0.18	1.64
(50-60]	0.36	0.52
(60-70]	0.00	0.52
(70-80]	0.09	0.26
(80-90]	0.18	0.43
(90-100]	0.00	0.17
(100-110]	0.09	0.00
(110-120]	0.00	0.17
(120-130]	0.00	0.00
(130-140]	0.18	0.00
(140-150]	0.00	0.00
(150-160]	0.00	0.09

Table 20: 1%LDPE4_2%PEWAX particle count and percentage distribution at 30 and 150 min

	PERCENTAGE	
	30MIN	150MIN
(0-10]	74.66	73.55
(10-20]	12.95	14.66
(20-30]	6.18	4.66
(30-40]	2.20	2.56
(40-50]	2.01	1.96
(50-60]	0.91	1.10
(60-70]	0.46	0.46
(70-80]	0.46	0.41
(80-90]	0.09	0.18
(90-100]	0.00	0.14
(100-110]	0.09	0.18
(110-120]	0.00	0.00
(120-130]	0.00	0.05
(130-140]	0.00	0.05
(140-150]	0.00	0.05

APPENDIX C

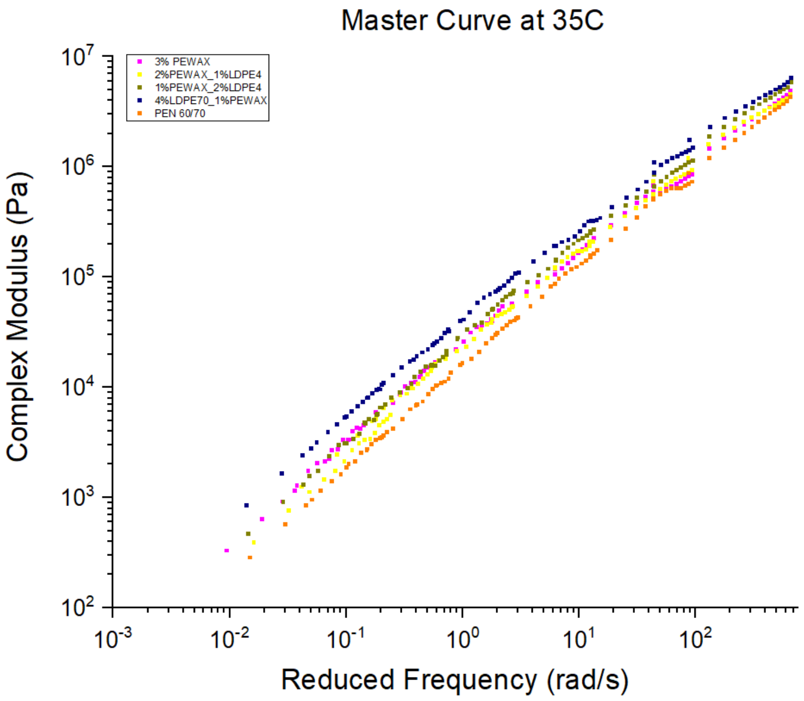

Figure 48: Master curve at 35C of PEWAX blends

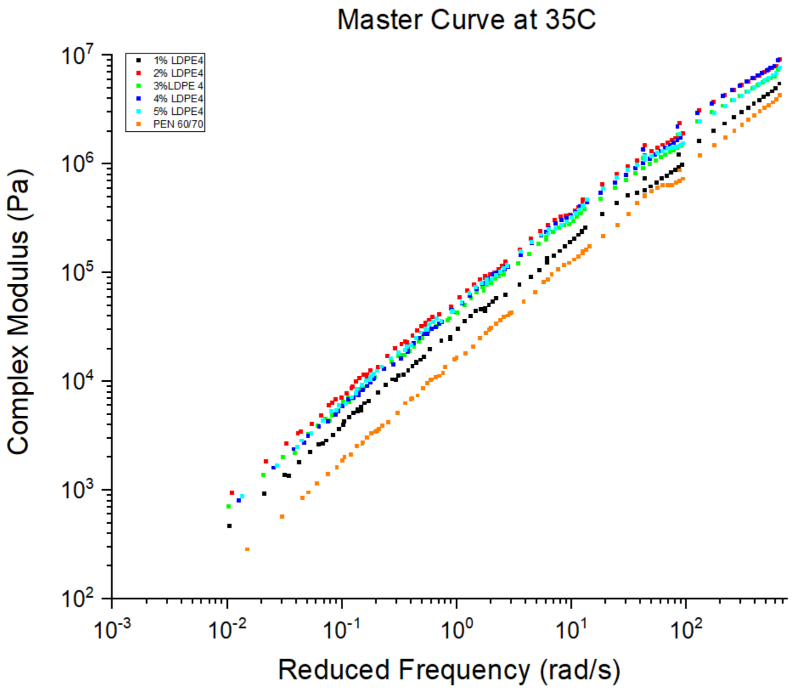

Figure 49: Master curve at 35C of LDPE4 blends

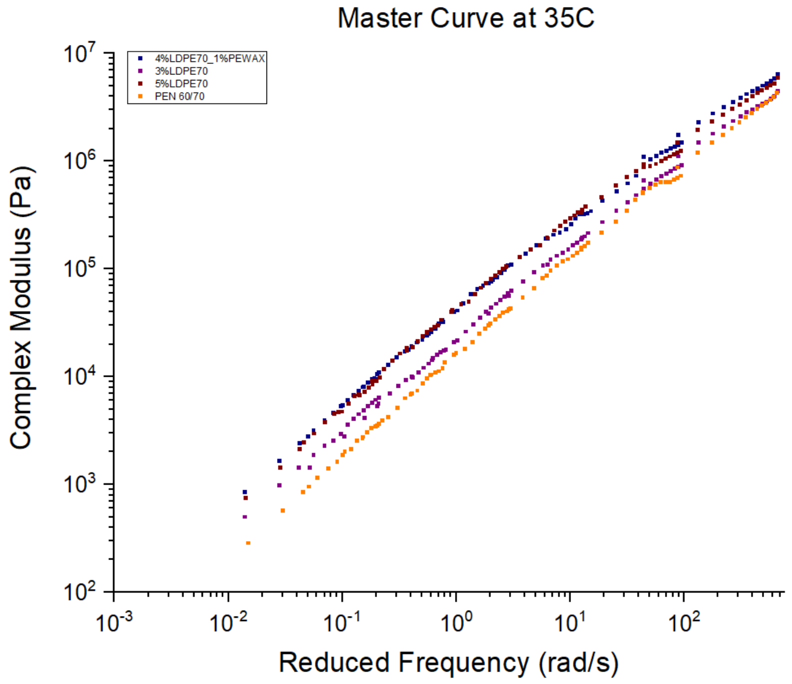

Figure 50: Master curve at 35C of LDPE70 blends

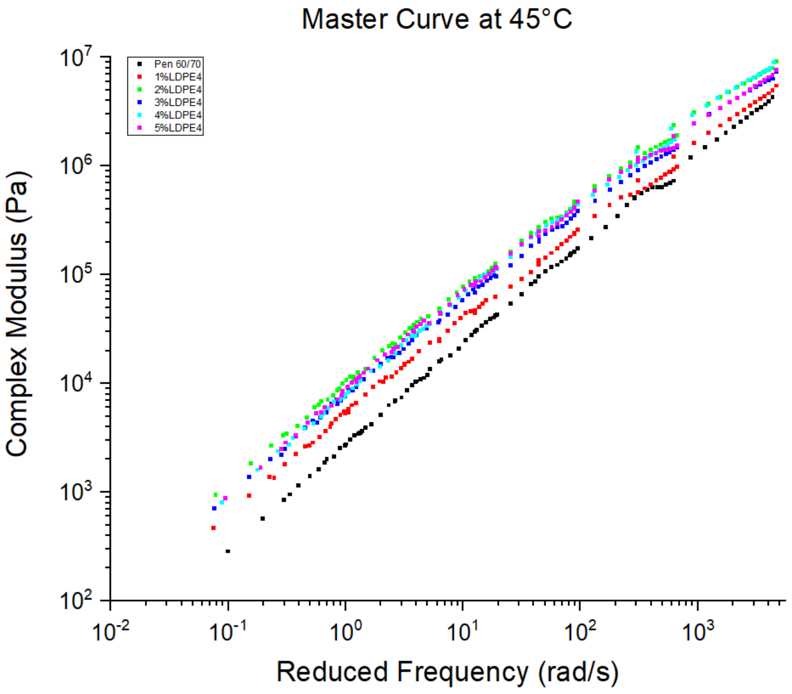

Figure 51: Master curve at 45C of LDPE4 blends

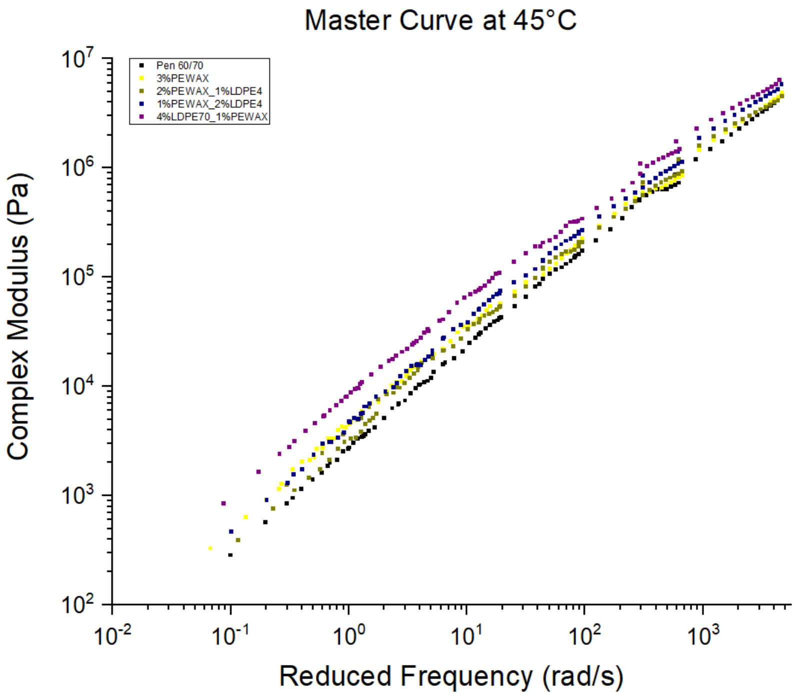

Figure 52: Master curve at 45C of PEWAX blends

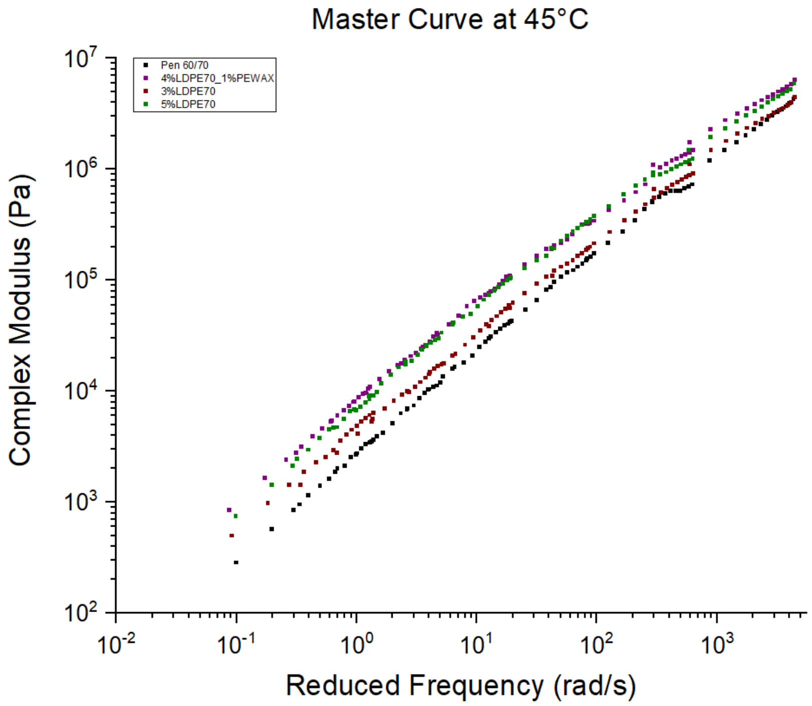

Figure 53: Master curve at 45C of LDPE70 blends

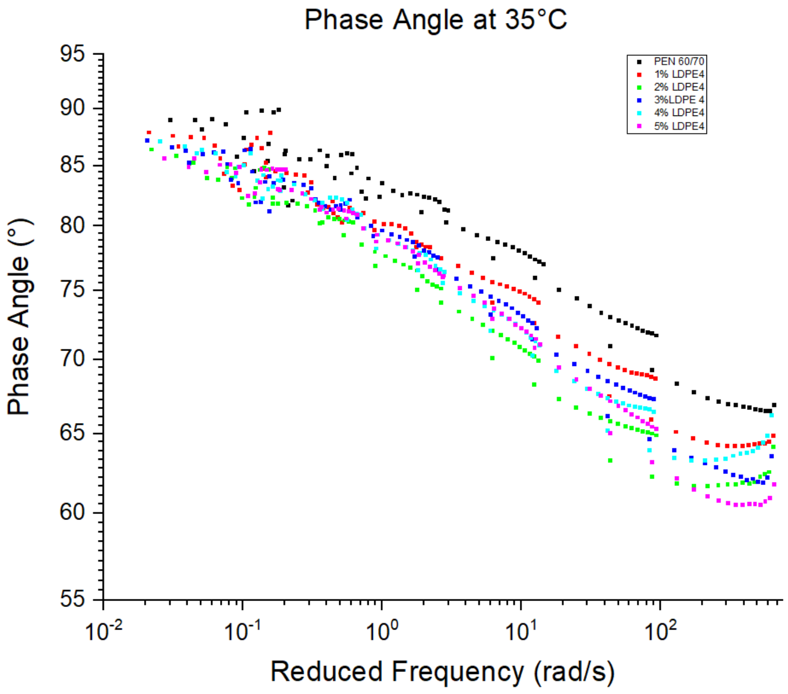

Figure 54: Phase angle at 35C for LDPE4 blends

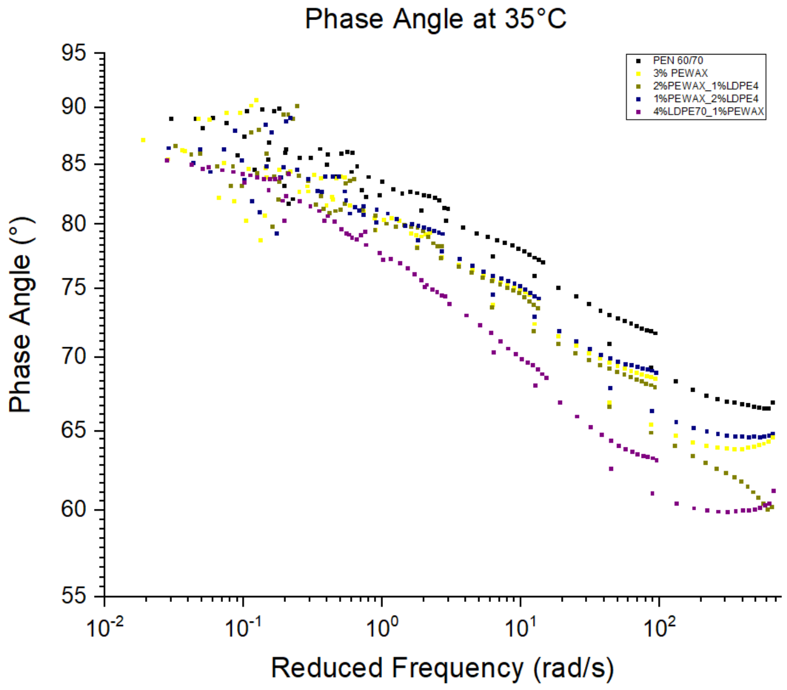

Figure 55: Phase angle at 35C for PE WAX blends

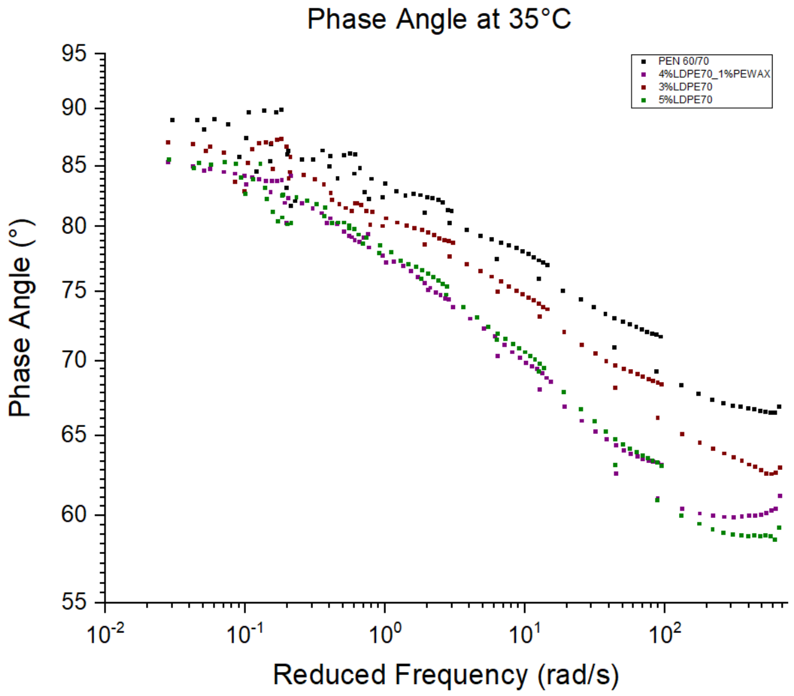

Figure 56: Phase angle at 35C for LDPE70 blends

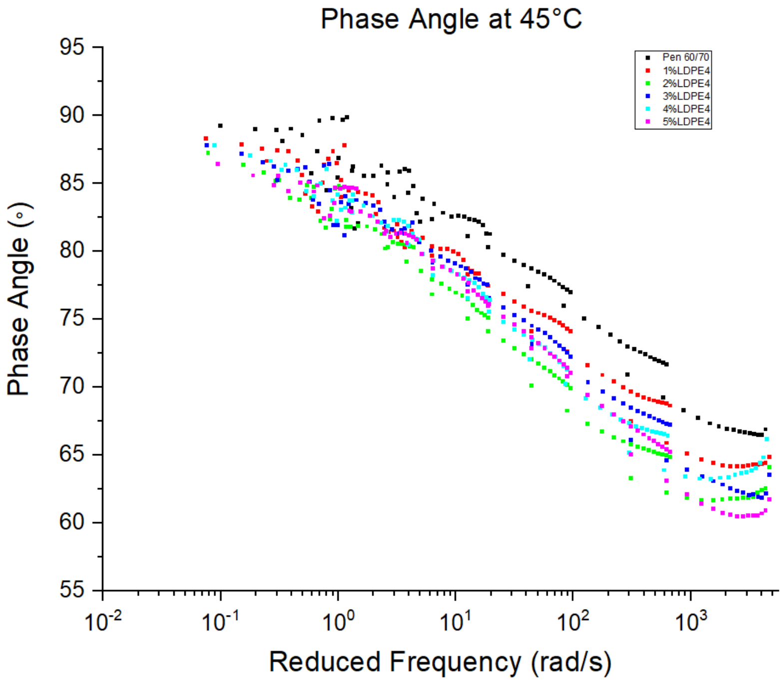

Figure 57: Phase angle at 45C for LDPE4 blends

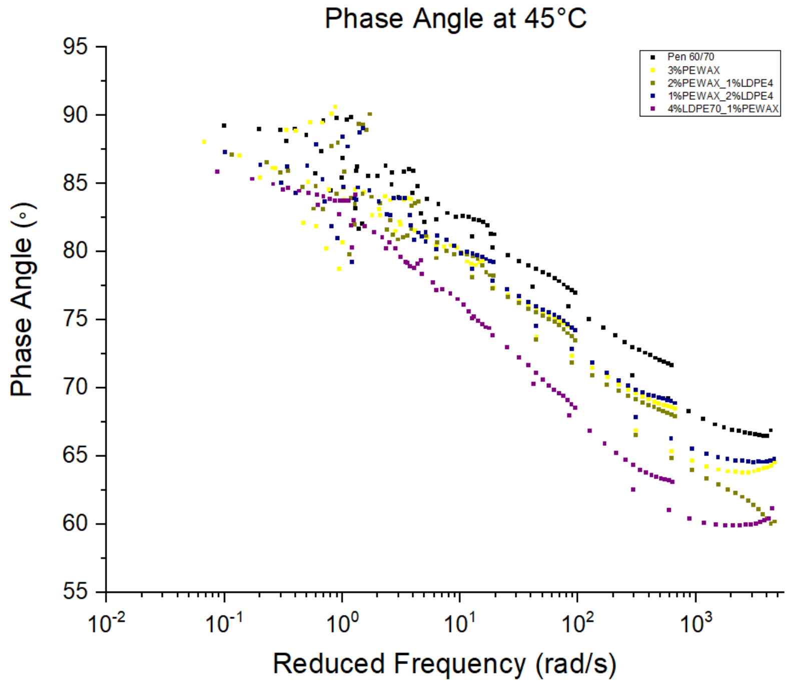

Figure 58: Phase angle at 45C for PEWAX blends

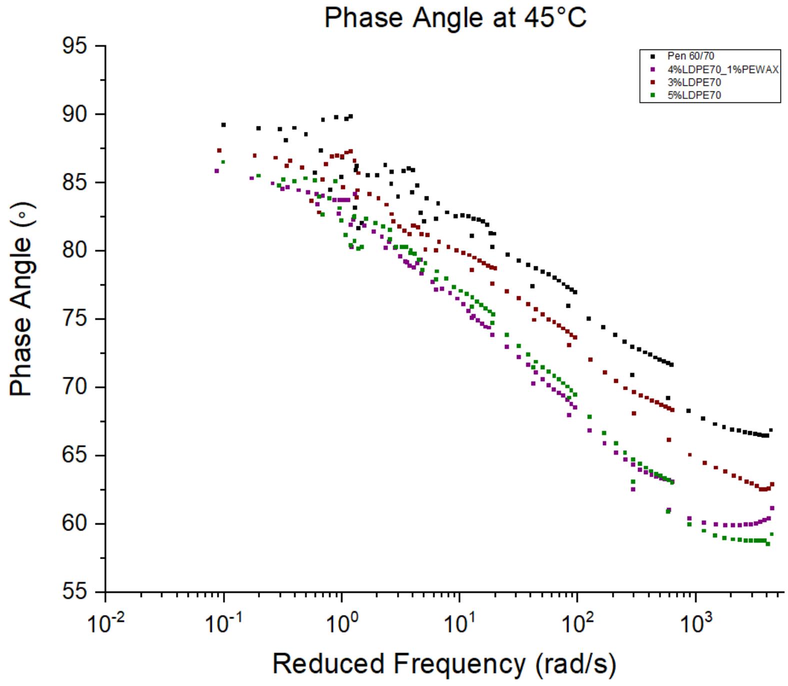

Figure 59: Phase angle at 45C for LDPE70 blends

Table 21: Shift factors for master curve at 35C

a_T	Pen 60/70	1% LDPE 4	2% LDPE 4	3% LDPE 4	4% LDPE 4	5% LDPE 4	3% PE Wax	2%LDPE4_ 1%PEWAX	1%LDPE4_ 2%PEWAX	4%LDPE70_1% PEWAX	3% LDPE 70	5% LDPE 70
25℃	6.997	6.997	6.997	6.997	6.997	6.997	6.997	6.997	6.997	6.997	6.997	6.997
35℃	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
45℃	0.154	0.143	0.152	0.144	0.151	0.153	0.143	0.143	0.143	0.160	0.151	0.144
55℃	0.032	0.024	0.029	0.028	0.031	0.033	0.023	0.029	0.029	0.030	0.032	0.029
65℃	0.008	0.006	0.007	0.006	0.008	0.008	0.006	0.007	0.008	0.008	0.008	0.007
75℃	0.002	0.002	0.002	0.002	0.002	0.003	0.002	0.003	0.002	0.002	0.002	0.002