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# Evaluation of Structural and Thermal Properties of Rubber and HDPE for Utilization as Binder Modifier

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Additional information is available at the end of the chapter

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## Abstract

Today, high-performance requirements for asphalt pavements demand enhanced properties for bitumen to withstand the environmental condition and traffic demand. On the other hand, the rapid growth in population and economy results in a continuously increased material consumption, and subsequently waste generation. Among various waste materials, rubber and plastic, including high-density polyethylene (HDPE), constitute some part of the non-biodegradable solid wastes worldwide. Because of the great difficulties in managing the non-biodegradable wastes and the required volume of bitumen, the idea of using plastic and rubber as bitumen modifier in new asphalt mixtures appears to be an effective and meaningful utilization of these materials. As binder plays an important role in the final performance of the asphalt mixture, an understanding of modified binder properties is essential in designing an asphalt mixture. To this point, since compatibility of asphalt mixture with polymer is the most important factor in the blend of polymers and asphalt, the properties of the waste polymers were evaluated in this ongoing research by means of advanced thermal analysis and scanning electron microscope (SEM). This chapter presents the results of this experimental study to evaluate the properties of polymers as potential modifier for virgin bitumen in asphalt mixture.

**Keywords:** bitumen, modified binder, plastic, rubber, HDPE, TGA, DSC, SEM

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## 1. Introduction

Aggregate and binder are two principal constituents of asphalt mixtures. Although the mechanical and chemical properties of aggregates can vary significantly depending on their

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source, the overall durability and other performance characteristics of asphalt mixtures are generally limited by the performance of the asphalt binder. Failure of asphalt pavement due to the asphalt binder can be attributed to three main sources including:

- rutting occurs at high temperatures as asphalt softens and the elasticity of the binder decreases,
- fatigue cracking due to the repeated loading and aging of the pavement, and
- thermal cracking at low temperatures as asphalt becomes brittle.

Failure of asphalt binders is obviously undesirable. Referring to the considerable research in recent years focused on improving the binders' functional properties, the use of polymers as additives greatly improves the performance of bitumen, including elasticity increase, cohesion improvement, and temperature susceptibility reduction, which all subsequently lead to the improvement of asphalt mixture performance in terms of flexibility, cohesion, and deformation resistance at high temperatures. However, the costly nature of polymer modifiers has stimulated research into cheaper and more cost-effective modifiers produced from recycled materials. For these reasons, and as a quite effective way of disposing of the increasing volume of non-biodegradable wastes, which each year are unavoidably generated in different sectors of human activity, polymer wastes like plastic and rubber can be a reasonable potential materials for consideration as binder modifier.

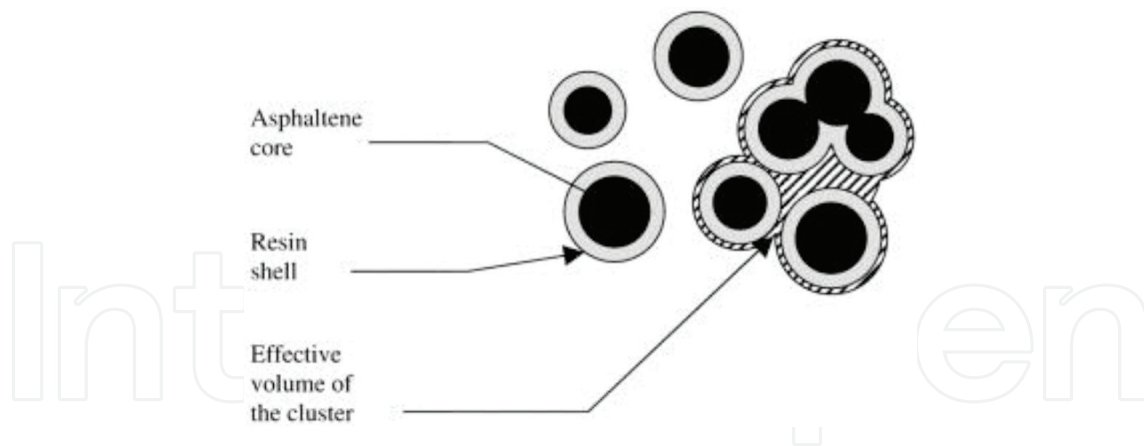
In light of this, the purpose of the present work is to study the characteristics of waste polymers as potential modifier of bitumen. In that sense, as discussed in the following sections, several samples of bitumen and waste polymers were prepared, and a further thermal and microstructural characterization was carried out on these materials.

## 2. Bitumen

Bitumen is a construction material obtained from crude oil through distillation processes in the petroleum refinery. Bitumen is useful in road construction due to some of its properties such as adhesion, being water proof and durable. The bitumen is principally used in the road construction as a binder where it is mixed with aggregates to produce asphalt mixture. The asphalt mixture must have adequate properties in order to withstand the permanent deformation, fatigue cracking, and thermal cracking, which are the main distress modes of flexible pavements. Therefore, it should have proper stiffness and bearing capacity and must be able to spread load evenly over the pavement layers.

A large number of procedures have described different fractions in bitumen. Based on the most common procedure, bitumen is divided into four generic groups of saturates, aromatics, resins, and asphaltenes, namely SARAs. The molecular weight of these fractions increases in the order  $S < A < R < A$  [1].

The structure of bitumen is mostly regarded as a colloidal system. In this system, the asphaltene particles are dispersed into the oily dispersion medium called the maltenes, which is composed of saturates, aromatics, and resins. As illustrated in **Figure 1**, a shell of resins has covered the asphaltene particles. The temperature and equilibrium between the covering part and dissolved part of resins affect the shell thickness [2–4].



**Figure 1.** A simplified view of the colloidal structure of bitumen [2].

In 1987, as part of the Superior Performing Asphalt Pavement Program (Superpave), an asphalt binder specification system was developed for evaluation of asphalt performance properties and classification of binders based on its maximum and minimum service temperature. In this specification, the physical properties of an asphalt binder was matched with a performance grade (PG) based on climatic and environmental condition.

In this PG system, two numbers are assigned to each asphalt grade. For example, for asphalt grade of PG 67-22, the first number shows the maximum temperature (in °C) at which the binder can still resist permanent deformation adequately. This number is an average seven-day maximum pavement service temperature. The second number is the minimum temperature at which the binder can perform properly to resist thermal cracking, and hence it is the minimum pavement service temperature. The binders with the maximum temperature ranging from 46 to 82°C and the minimum temperature ranging from -10°C to -46°C (both in increments of 6°) are commercially available, as shown in **Figure 2**. The diagonal line that connects the asphalt grades of PG 82-10 to PG 46-46 is the border between the asphalt grades, which can be produced at refineries and are those produced only by modification (shaded areas). Useful temperature range (UTR) is a measure of the difference between upper and

		Lower Specification Temperature, °C						
Upper Specification Temperature, °C	PG 82	-10	-16	-22	-28	-34		
	PG 76	-10	-16	-22	-28	-34		
	PG 70	-10	-16	-22	-28	-34	-40	
	PG 64	-10	-16	-22	-28	-34	-40	
	PG 58		-16	-22	-28	-34	-40	
	PG 52	-10	-16	-22	-28	-34	-40	-46
	PG 46					-34	-40	-46

**Figure 2.** Performance grades for commercially available binders (after Ref. [5]).

lower service temperatures. The binders produced at refineries without modification have a UTR of not more than 86°C, whereas the modified binder often have a UTR of more than 92°C. Therefore, UTR can be used as an indicator showing the degree of required modification and the cost needed for modification. As UTR increases, this cost increases accordingly [5].

### 3. Polymer modifiers

The binder characteristics strongly influence the mechanical properties of asphalt mixture. To this point, binder should have a certain mechanical and rheological requirements as follows in order to fulfill the pavement criteria:

- For homogeneous coating of aggregates, the bitumen should be fluid enough at mixing and construction temperatures of about 160°C.
- To resist permanent deformation, the bitumen should be stiff enough at high temperatures (about 60°C depending on the local climate)
- To resist the cracking, the bitumen should be soft enough at lower temperature that pavement experiences (approximately down to -20°C depending on the local climate).

Accordingly, it can be concluded that obtaining bitumen to work well under all aforementioned conditions can be difficult. To surmount this problem, many researchers have tried to develop the asphalt pavement performance by improving the asphalt binder behavior using different modifiers. There are a large varieties of materials, which are often used for modifying the binder, of which polymers are widely known to be easy to use and cost effective. Referring to available literature (for example, see [6–9]), polymer addition may result in both a more flexible binder at low in-service temperature and enhanced properties at high in-service temperature, which significantly prevent the pavement from being deformed. They also improve the adhesive bonding to aggregate particles [10]. Polymers can exist in two different morphologies while in a solid phase:

- Amorphous, in which molecules are randomly oriented within the polymer when the material is cooled in a relaxed state. The cooled state of amorphous materials is highly similar to their molten state. The only difference between these two states is the molecules' distance. These polymers can easily be altered in shape and generally exist in a rubbery state.
- Semicrystalline is an arrangement of ordered molecules with some amorphous regions. As the semicrystalline polymer cools, a portion of the molecular chains forms crystals by folding up into densely packed regions. The polymer is classified as semicrystalline, if more than 35% of the polymer chain forms these crystals. These polymers are stiff and exist in a glassy state.

The degree of crystallinity in a polymer is affected by different factors such as polymer type, additives, and cooling rate. The morphology and degree of crystallinity significantly influence the polymers' properties. Polymers with high degree of crystallinity have a higher glass transition temperature and higher modulus, toughness, stiffness, tensile strength, and hardness. In addition, they have more resistance to solvents but are less resistant to impact strength [11].

Today, there are a large varieties of polymers that are often used for modifying the binder. These polymers can be mainly classified into the following categories:

- Elastomers such as rubber can be stretched and then recover their shape when the stretching force is released. Elastomers contribute to the elastic component of binder. The addition of elastomers to the binder results in an increase in the binder stiffness at high temperatures and loading and subsequently will improve the resistance to permanent deformation. However, elastomers will not substantially improve the ability of asphalt mixtures in thermal resistance.
- Plastomers such as polyethylene can form tough, rigid, three-dimensional networks within the bitumen resulting in increase of the initial strength of the bitumen, and subsequently improving the ability of asphalt concrete to resist the heavy loads. Plastomers have less elasticity compared to elastomers as they do not provide an increase in the plastic component of binder while they increase the binder's stiffness at high temperature and loading [12]. Therefore, plastomers can improve the rutting resistance, but they lack the improvements in fatigue resistance, cracking resistance, and low-temperature performance [13] because of increased intermediate and low-temperature stiffness. This makes them inferior to elastomers.

Although modifying the binders will result in the enhancement of binder's properties, using virgin additives as modifier will increase the road construction cost. Therefore, in recent years, many investigations have been conducted on modifying binders using waste materials as additives. Among these waste materials, application of waste plastics and rubbers in certain amount as binder modifier can substantially enhance the stability, strength, fatigue life, and generally the asphalt performance in one hand [14], and on the other hand, it would be an ideal solution for reducing the environmental pollution associated with these non-biodegradable wastes. In light of this, according to the characteristics of elastomers and plastomers, this chapter analyses the characteristics of high-density polyethylene (HDPE) and crumb rubber as potential binder modifier. The tests used to evaluate the polymer properties were thermal analysis by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and microstructure analysis by scanning electron microscopy (SEM).

## 4. Materials

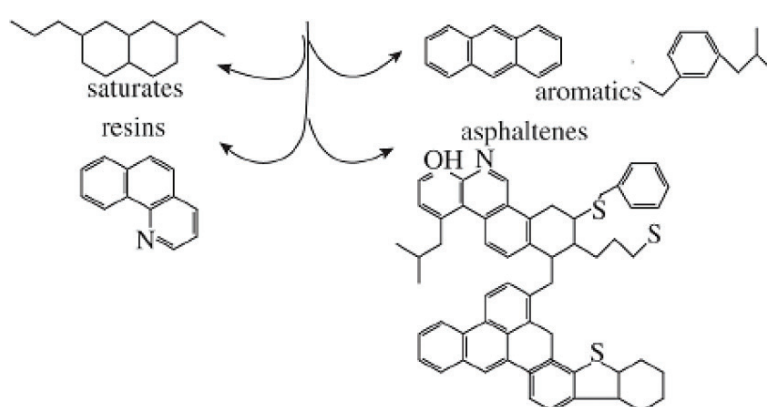
### 4.1. Bitumen

Bitumen of C320 was used as a base material for this research, which was kindly supplied by Boral Ltd. This bitumen corresponds to the most common bitumen used in Australia. C320 is classified and manufactured in accordance with AS 2008 (2013) and is suitable for medium to heavy asphalt applications as well as for heavy duty and hot climate seals. The typical characteristics of bitumen C320 are presented in **Table 1**.

As emphasized earlier and shown in **Figure 3**, the complex structure of bitumen is composed of unsaturated structures divided into two main groups of asphaltenes (which are insoluble in n-heptanes) and maltenes. The maltenes are further split into saturates, aromatics, and resins. The proportion of bitumen fractions and the molecular weight of each fraction is presented in **Table 2**.

Characteristics	Unit	Methods	Value
Softening point	°C	AS 2341.18	52
Penetration at 25°C	dmm	As 2341.12	Min 40
Flashpoint	°C	AS 2341.14	Min 250
Viscosity at 60°C	Pa·s	AS 2341.2	320
Viscosity at 135°C	Pa·s	As 2341.2	0.5
Specific Gravity	Kg/m <sup>3</sup>	AS 2341.7	1.03

**Table 1.** Characteristics of the original bitumen.



**Figure 3.** Main compounds in representative structures of the four bitumen fractions [15].

Fraction	Proportion of the overall bitumen	Molecular weight	Description
Asphaltenes	5–25%	600–3000	Substantial effect on bitumen rheological properties
Resins	15–25%	500–1300	Dispersing agent for asphaltenes; their proportion to asphaltenes determines the structural character of the bitumen
Aromatics	40–65%	300–800	Major dispersion medium for asphaltenes
Saturates	5–20%	300–600	Non-polar viscous oil

**Table 2.** Proportion and molecular weight of bitumen chemical fractions [3, 16–19].

The rheological properties of bitumen are highly affected by the asphaltene content due to its physical parameters such as glass transition and bitumen viscosity [20, 21]. An increase in the asphaltenes content will generally result in harder bitumen with a lower penetration, higher softening point, and higher viscosity [22].

## 4.2. HDPE

Among plastics, polyethylene (PE) forms the largest portion followed by polyethylene terephthalate (PET). To this point, this study focused on polyethylene and particularly on high-density polyethylene (HDPE). The HDPE used in this research were obtained from plastic recycling plant. As shown in **Figure 4(a)**, the HDPE is in the granular form with the particle size of 2.36 mm. HDPE like other plastics is a polymer consisting of very large molecules made up of smaller units called monomer, which are joined together in a chain by a process called polymerization. Polyethylene is semicrystalline material with a wide range of properties and appropriate resistance to chemicals and fatigue. A molecule of polyethylene has a very simple structure and is composed of a long chain of carbon atoms with two hydrogen atoms attached to them, as shown in **Figure 4(b)**. Sometimes other elements such as oxygen, nitrogen, chlorine, or fluorine are attached to these polymer molecules. These are lightweight molecules with low moisture absorption rates and good resistance to organic solvents.

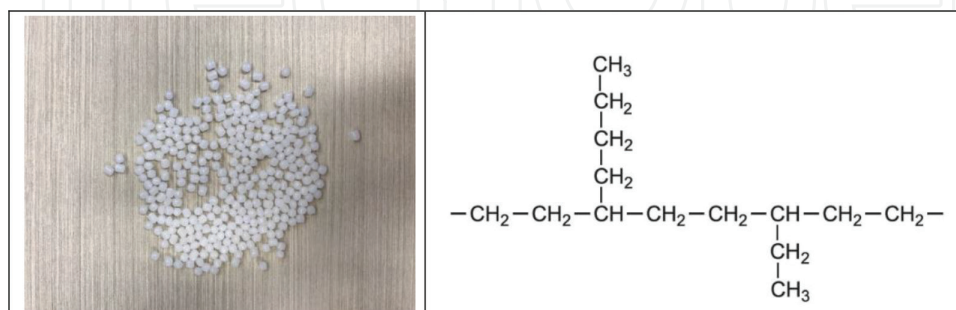
HDPE is one type of thermoplastics. As most of the thermoplastics can soften at temperature ranging from 130 to 140°C with no gas emission in the temperature range of 130–180°C, they can be a potential option for blending with bitumen in asphalt production because the heating temperature for bitumen ranges from 155 to 165°C in the whole processes for asphalt pavement construction [23]. **Table 3** presents the information regarding the thermal behavior of polyethylene, which emphasizes its suitability as a binder modifier.

In order to find the relevant properties of HDPE, some tests were conducted on this material and the result of these test are presented in **Table 4**.

## 4.3. Crumb rubber

Crumb rubber used in this research was obtained from tyre recycling plant that processes the car tyres into crumb rubber through the ambient grinding method. The crumb rubber was provided in granule form, as shown in **Figure 5(a)**.

The particle distribution test was performed on crumb rubber. The result of sieve analysis is presented in **Table 5**. The ground tyre rubber has a particle size averaged between 8 and 50 mesh (2.36 and 0.300 mm).



**Figure 4.** Analyzed material (a) HDPE and (b) chemical structure of HDPE.

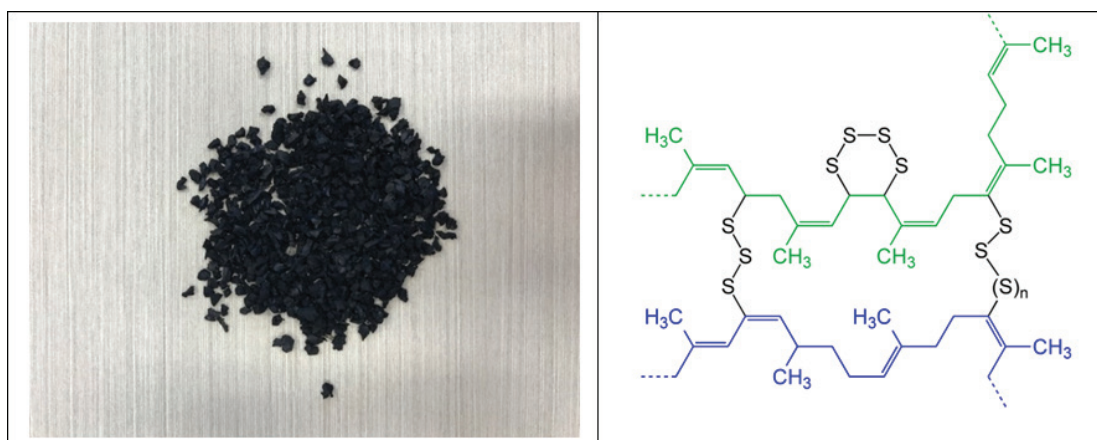


Characteristics	Unit	Methods	Reported products
Solubility in water	—	Nil	—
Softening temperature	°C	100–120	No gas
Decomposition temperature	°C	270–350	CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub>
Ignition temperature range	°C	> 700	CO, CO <sub>2</sub>

**Table 3.** Thermal characteristics of polyethylene [23].

Characteristics	Unit	Methods	Value
Density	g/cm <sup>3</sup>	AS 1141.5	0.963
Size	mm	AS 1141.11.1	2.36
Water absorption	%	AS 1141.5	0.0

**Table 4.** Characteristics of high-density polyethylene (HDPE).



**Figure 5.** Analyzed material (a) crumb rubber and (b) chemical structure of rubber.

Sieve no.	Sieve size (mm)	Mass retained (%)
4	4.75	0.0
8	2.36	25.7
16	1.18	67.7
30	0.600	6.2
50	0.300	0.4
100	0.150	0.0
200	0.075	0.0

**Table 5.** Particle size distribution of crumb rubber.

Characteristics	Unit	Methods	Value
Density	g/cm <sup>3</sup>	AS 1141.5	0.982
Size	mm	AS 1141.11.1	1.18–2.36
Water absorption	%	AS 1141.5	0.1

**Table 6.** Characteristics of crumb rubber.

The properties of crumb rubber are presented in **Table 6**, which are obtained from conducting relevant tests on crumb rubber. It should be noted that tyre rubber is typically a composition of three polymers including polyisoprene (natural rubber), polybutadiene, and polystyrene-butadiene [24]. The main compounds in rubber are shown in **Figure 5(b)**.

## 5. Methodology

In this research, different polymers (i.e., bitumen, HDPE, and crumb rubber) were analyzed based on their calorimetric curve, thermal transition, and their overall quality. The analysis of the materials was performed by means of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

### 5.1. Sample preparation

For performing analysis on polymers, the samples were prepared based on the requirements of equipment. In order to study the thermal behavior of individual polymers, in all cases, a small amount of material (5 to 10 mg) was placed in a measuring pan. To prevent pressure buildup during the test, it was advised to have a small opening in the small pan. After this preparation, the samples were placed in DSC or TGA equipment.

### 5.2. Analysis methodology

It is expected that the addition of polymers influences the microstructure of binder. In theory, the addition of polymers containing hard segments provides higher strength, whereas the soft segment polymers improve toughness and low-temperature cracking. Since the binder modification depends on the compatibility of bitumen and polymer as modifier, this chapter covers the study of the individual polymers to identify some of their physical and chemical properties, their thermal behavior, and their microstructure. The tests to characterize the analyzed materials were performed in the Advanced Materials Characterization Facility (AMCF) at Western Sydney University, Australia. These tests included thermal analysis, structural characterization, and microstructure analysis, and the main points of testing procedure are represented in the following sections.

#### 5.2.1. Thermal analysis

Thermal analysis corresponds to a group of techniques used to measure the physical and chemical properties of materials as a function of temperature. The measurements can be performed

in different atmospheres including inert atmosphere (nitrogen, argon, helium) or in an oxidative atmosphere (air, oxygen). The gas pressure can also selectively vary in thermal analysis. In this research, the thermal behavior of materials was investigated through DSC and TGA.

#### 5.2.1.1. Differential scanning calorimetry (DSC)

Parameters such as glass transition temperature ( $T_g$ ), melting point, and the degree of crystallization were monitored by DSC. It should be noted that the glass transition temperature is more important in polymer applications compared to the melting point, because it corresponds to the polymer behavior under ambient conditions.

In this research, DSC analysis was performed according to ASTM E473-85 in an NETZCH DSC 204 F1 to obtain the thermal critical points of materials. The test specimens weighing about 5 mg were heated up at different temperature ranges, depending on polymer type, in an aluminum crucible under an air flow (100 mL/min) at a rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$ .

For bitumen, DSC experiments were carried out on about 5 mg samples in aluminum crucibles with perforated covers. Before conducting DSC, the bitumen sample was homogenized at  $130^\circ\text{C}$  for about 1 hour and then placed in the DSC equipment. To conduct DSC, first, the samples were cooled from room temperature to  $-100^\circ\text{C}$  at a heating rate of  $-10^\circ\text{C}/\text{min}$ . The samples were maintained at the low temperature for about 15 minutes to ensure a stabilized initial reading. Then, they were heated up to  $200^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . The DSC thermograph recorded during this heating scan is considered as the first scan. On completing the first scan, the sample was maintained at  $200^\circ\text{C}$  for 5 min to remove thermal history and then quickly cooled from  $200^\circ\text{C}$  to its starting temperature ( $-100^\circ\text{C}$ ) at a cooling rate of  $-10^\circ\text{C}/\text{min}$  and again held for about 15 min before being reheated to  $200^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . The DSC thermograph recorded during this second heating scan is considered as the second scan. The same procedure was repeated to provide the third heating scan.

For rubber, similar to bitumen, three cycles of cooling and heating were considered as the method of the experiment with the same heating rate of  $10^\circ\text{C}/\text{min}$ , cooling rate of  $-50^\circ\text{C}/\text{min}$ , and temperature range of  $-100$ – $200^\circ\text{C}$ . For HDPE, the DSC procedure was the same as bitumen and rubber with an exception of the temperature range, which was considered from  $-160$  to  $200^\circ\text{C}$ .

Glass transition and melting point were measured from DSC curves. The percentage of crystallized fraction (CF) was determined from the following equation through dividing the observed melting enthalpy ( $\Delta H_{obs}$ ) by the melting enthalpy of 100% crystalline material ( $\Delta H_o$ ).

$$CF = \frac{(\Delta H_{obs} \times 100)}{\Delta H_o} \quad (1)$$

The values of  $\Delta H_o$  depend on the material type and can be found in literature. For example, a value of 200 J/g was used by Lesueur et al. [4] and Claudy et al. [25]. Values of 180 and 121 J/g were used by Michon et al. [26] and Lu and Redelius [27], respectively.

#### 5.2.1.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed to study the kinetics and to investigate the degradation process of materials at a higher temperature. In this study, the thermal

decomposition was verified in 5 mg samples in an aluminum crucible under air flow (100 mL/min) heated from 30 to 600°C at a heating rate of 10°C·min<sup>-1</sup>. The TGA curves and its differential (DTG) were carried out in an NETZSCH STA-449C thermogravimetric analyzer. The onset temperature of the mass loss effect ( $T_o$ ) and temperature of peak rate of mass loss ( $T_p$ ) were determined from TGA thermographs.

### 5.2.1.3. Microstructure characterization

The microstructure of the materials was investigated under scanning electron microscope (SEM). Scanning electron microscopic analysis was done in 6510LV SEM employing between 10 and 20 kW. The specimens in this study were examined with magnifications of 100–1000, and the results of this study with best magnification are presented in the following sections.

## 6. Results and discussion

### 6.1. Thermal analysis by DSC

Heating the polymers results in a number of phase changes such as the glass transition ( $T_g$ ), crystallization transition ( $T_c$ ), and melting point ( $T_m$ ). DSC analysis is a useful technique to identify the location of these thermal parameters. In the DSC curves, the sharp peaks are related to the polymer melting and the areas under these peaks provide the heat of fusion ( $\Delta H$ ). Furthermore, the smaller inconsistencies at the lower temperature are most likely related to the glass transition.

In this research, DSC technique is used to investigate the transition temperatures and the crystallization degree of different polymers. Accordingly, the DSC curves were examined to evaluate the physical characteristics of individual materials. It should be noted that for DSC runs, the complete set of heating-cooling process were repeated three times for each polymer, where the first run is usually carried out to remove any impurities and moisture from the sample. In addition, in order to evaluate the transitions accurately, a temperature scan over a wide range temperature is considered for DSC analysis.

In DSC analysis, the thermal parameters for bitumen depend on the refined petroleum source as well as the petroleum refining process. **Figure 6** shows the DSC thermograph of neat bitumen and its corresponding first-derivative curve. The effects detected in the thermograph, as assigned previously (for example, see [28–30]), are described below.

An increase in the heat capacity for neat bitumen can be observed in the DSC curve by an abrupt change in the slope of the curve placed in the low-temperature region (around -30°C) corresponding to the glass transition temperature ( $T_g$ ) of the bitumen. The glass transition temperature ( $T_g$ ) is a material's temperature at which all molecular transitional motion is frozen; therefore, the material becomes rigid and brittle at or below this temperature. The glass transition temperature of polymers is one of the most important parameters as it is related to the average molecular weight of polymers and hence provides information about their composition. Moreover, it demonstrates the viscoelastic behavior of polymers at low temperatures [31]. Therefore, the glass transition temperature of neat bitumen is believed to be closely related to the low-temperature performance of asphalts. As shown in **Figure 6**, the middle point of the temperature range where the transition occurs is considered as the

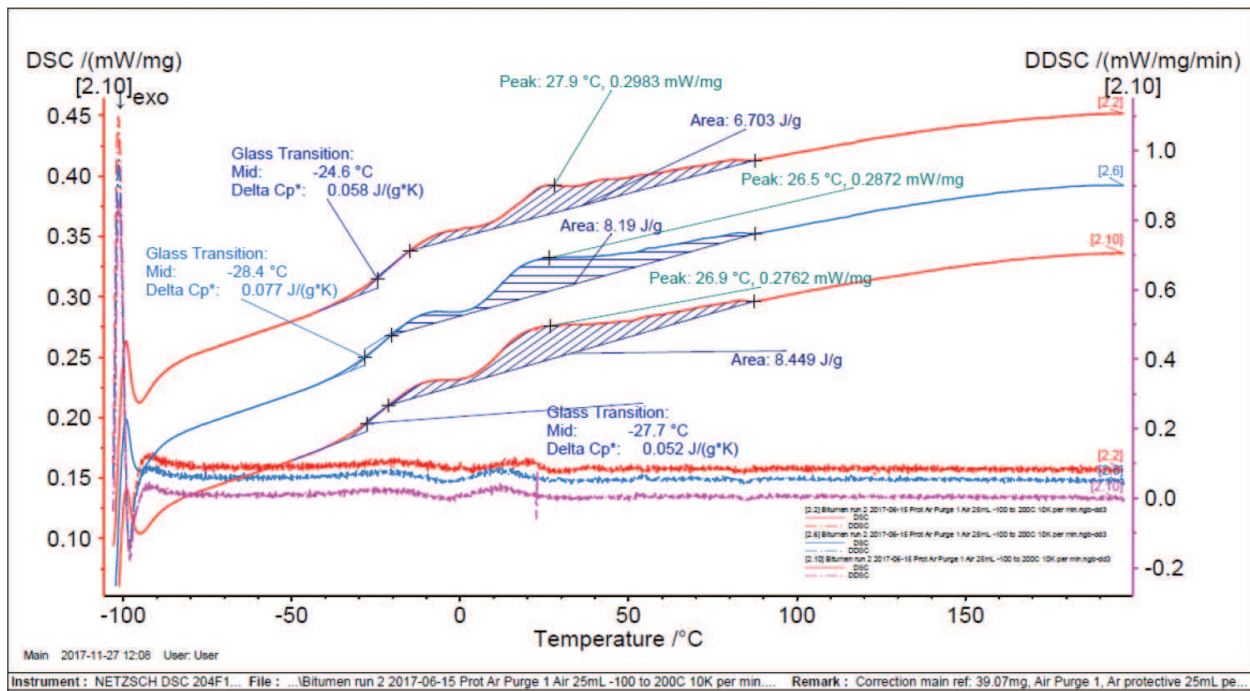


Figure 6. DSC and DDSC thermograms of bitumen.

glass transition temperature. In addition, as shown in Figure 6,  $T_{g\text{onset}}$  of bitumen is at about  $-40^{\circ}\text{C}$ . Referring to [32], the  $T_{g\text{onset}}$  temperature is more closely related to the glass transition temperature of the saturate fraction that has the lowest  $T_g$ . The main  $T_g$  reflects the characteristics of the glass transition temperature of the majority of components.

At temperature above  $T_g$ , an exothermic peak and a broad endothermic peak from about  $-20$  to  $85^{\circ}\text{C}$  is observed. The big exothermic peak next to the glass transition is most likely the result of crystallization of small paraffin molecules, and melting of the crystallites formed during heating or cooling is known as the main reason to produce endothermic peaks in this region [32].

Referring to [31], the exothermic effect just above the  $T_g$  in DSC thermographs is negligible, as it has been associated in previous studies (for example, see [28, 30]) with the crystallization of certain molecules, which are not crystallized during cooling.

In addition, referring to the literature (for example, see [25, 28–30, 33]), the dissolution of the crystallized fractions (CF) is the main reason of the enthalpy changes and can be calculated from the area under the peak to a reference enthalpy of dissolution. As shown in Figure 6, in order to calculate this parameter, a straight baseline between the end of the glass transition and the end of the endothermic effects is drawn. In this research, the reference enthalpy value of 180 J/g is used for the estimation of the amount of crystallized fraction of bitumen based on previous investigations [1, 4, 15, 25, 26, 33]. The calculation of the crystallizable fraction content shows a value of about 4%, which is considered small. The presence of wax content in bitumen is commonly responsible for the extent of crystallizable fractions, which is the main reason for the problem of pavement exudation and inappropriate thermal susceptibility [15].

To achieve DSC curve for rubber, similar to bitumen, three cycles of cooling and heating were considered as the method of the experiment with the same heating rate of 10°C/min, cooling rate of -10°C/min, and temperature range of -100–200°C.

The DSC thermograph of rubber (**Figure 7**) presented a glass transition temperature ( $T_g$ ) at -55° C. However, due to amorphous nature of rubber, DSC curve does not present a well-defined melting temperature.

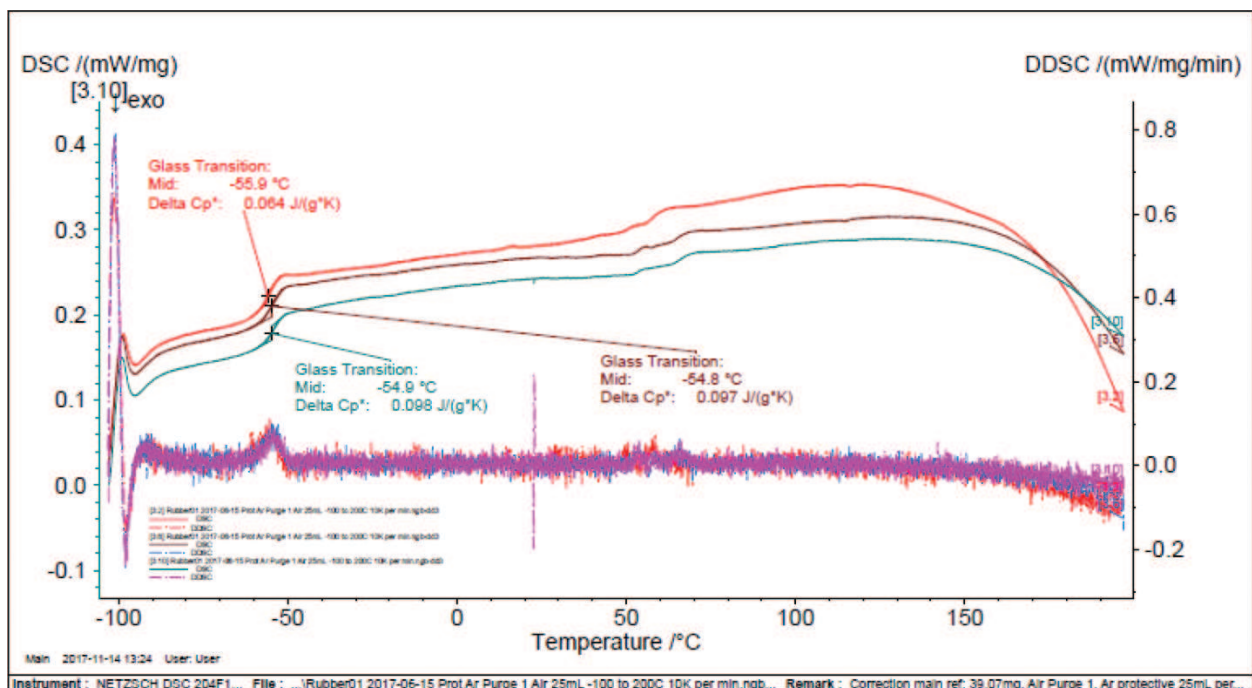
For HDPE DSC analysis, as shown in **Figure 8**, it can be observed that HDPE started to lose its solid form at around -100°C corresponding to the glass transition temperature ( $T_g$ ) of HDPE. As the temperature increases, a strong endothermic peak average value at 134°C can be observed, which is most likely related to the melting of crystalline domains of HDPE.

The DSC curve of HDPE in second heating cycle is illustrated in **Figure 9**. As can be observed, the energy consumption for melting of crystalline domain of HDPE was 221.1 J/g that occurred between the beginning and end of melting point.

The cooling cycle involves the rate of cooling temperature of 10°C/min. As shown in **Figure 10**, the peak point for HDPE becomes totally solid at around 115°C, which means that the crystallization temperature ( $T_c$ ) of HDPE, an exothermic peak, is 115°C.

To estimate the amount of crystallized fraction of HDPE, the values of  $\Delta H_f$  of 287.3 J/g has been found from literature for HDPE (for example, see [34, 35]). The calculation of the crystallizable fraction content for HDPE shows a value of about 76%.

It should be noted that fully crystalline polymers do not exhibit glass transition temperature, and their structure will not change until the melting point. However, according to DSC thermographs, HDPE is considered as semicrystalline polymer.



**Figure 7.** DSC and DDSC thermograms of rubber.

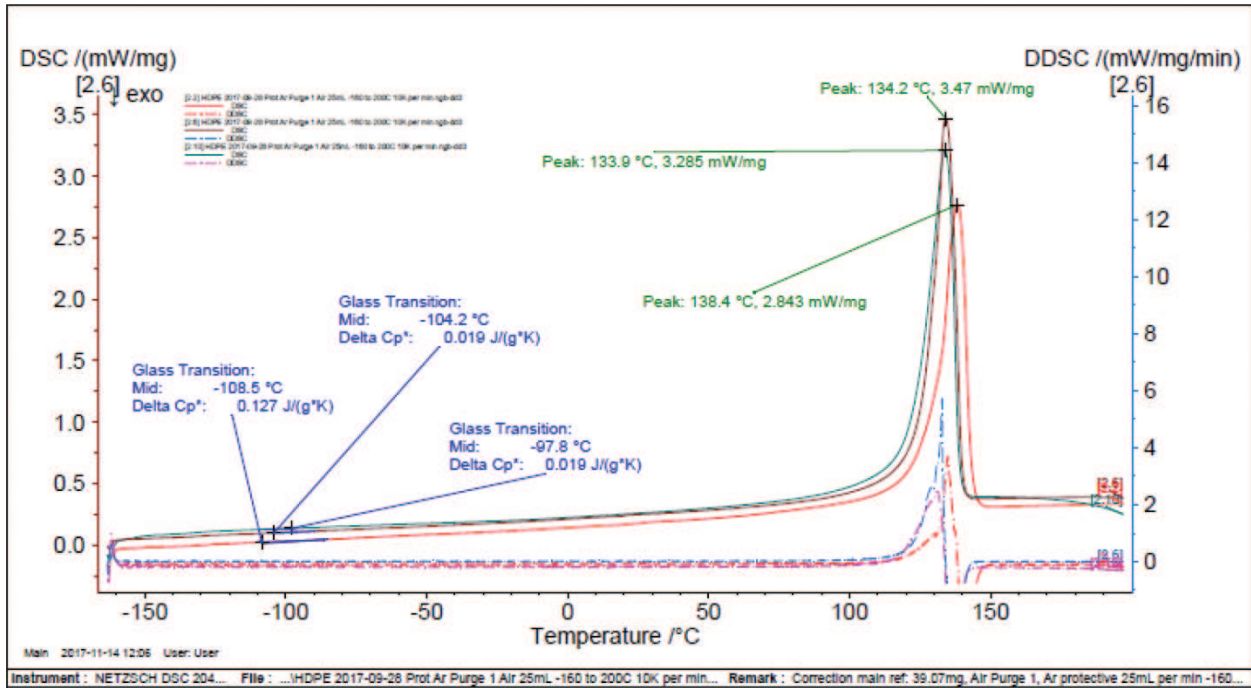


Figure 8. DSC and DDSC thermograms of HDPE for heating cycles.

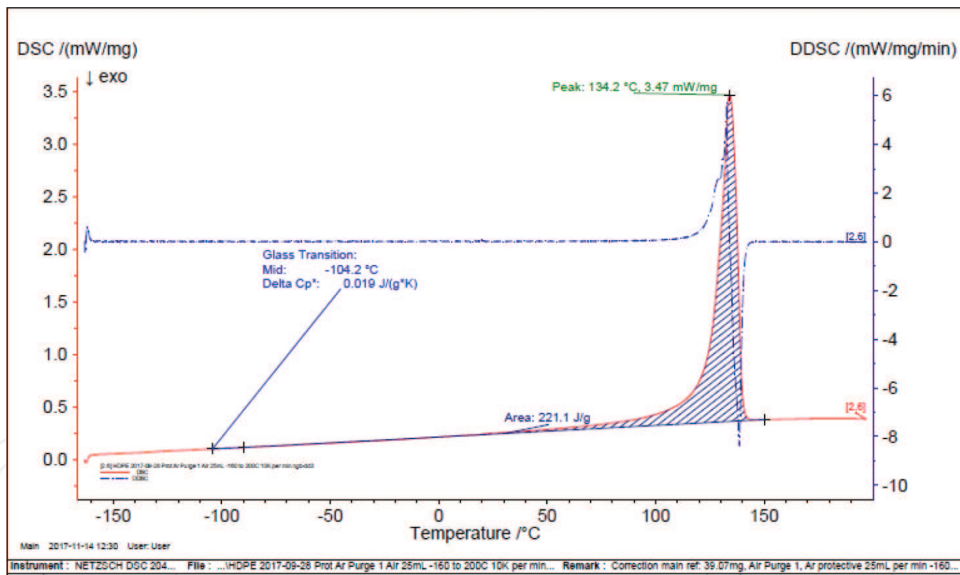


Figure 9. DSC and DDSC thermograms of HDPE for second heating cycle.

In addition, as HDPE has higher molecular weight than bitumen, the melting and crystallization temperature of HDPE is higher to provide more energy for reaching to these points. In addition, the melting and crystallization temperature of HDPE are close to each other, which can be confirmed from literature survey [36].

### 6.2. Thermal analysis by TGA

The thermal stability of polymers is an important property to be considered for fitting their performance to the proper final application. Thermogravimetric analysis is a good technique

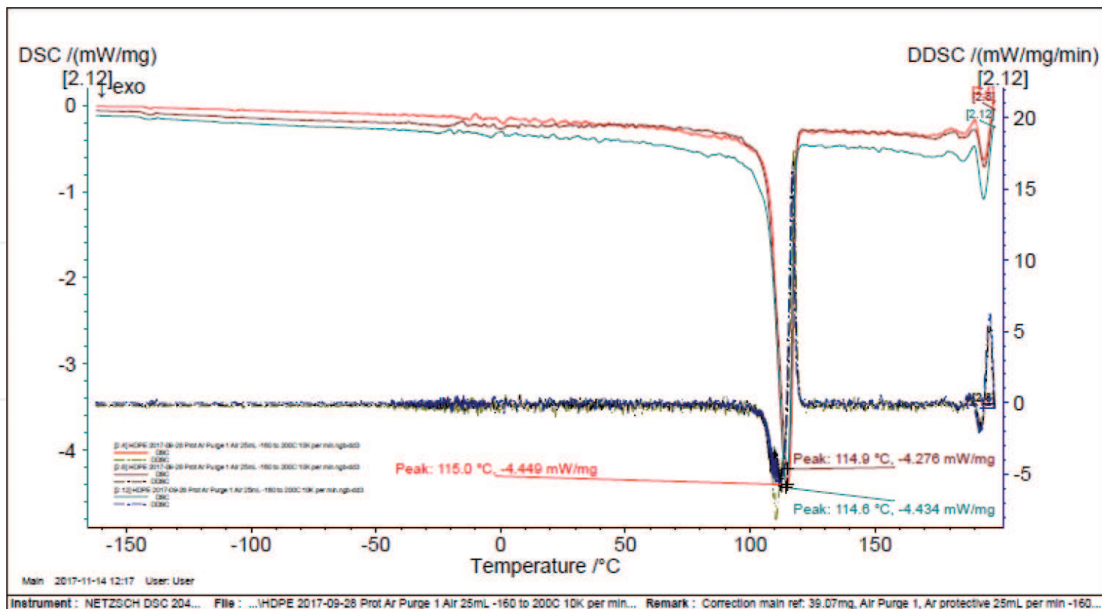


Figure 10. DSC and DDSC thermograms of HDPE for cooling cycles.

to evaluate the thermal stability of materials. Hence, in this research, the thermal stability of three polymers was studied by TGA in air and the main features of the curves including the onset temperatures of the mass loss effects ( $T_o$ ) and the peak temperatures ( $T_p$ ) were calculated from the TGA and DTG curves.

For bitumen, the thermogravimetric experiment results for 5 mg samples under air atmosphere over the temperature range of 30–590°C using a total purge gas flow of 100 mL/min and a heating rate of 10°C·min<sup>-1</sup> show that the onset temperature of the main mass loss effect ( $T_o$ ) is 370°C, as shown in Figure 11.

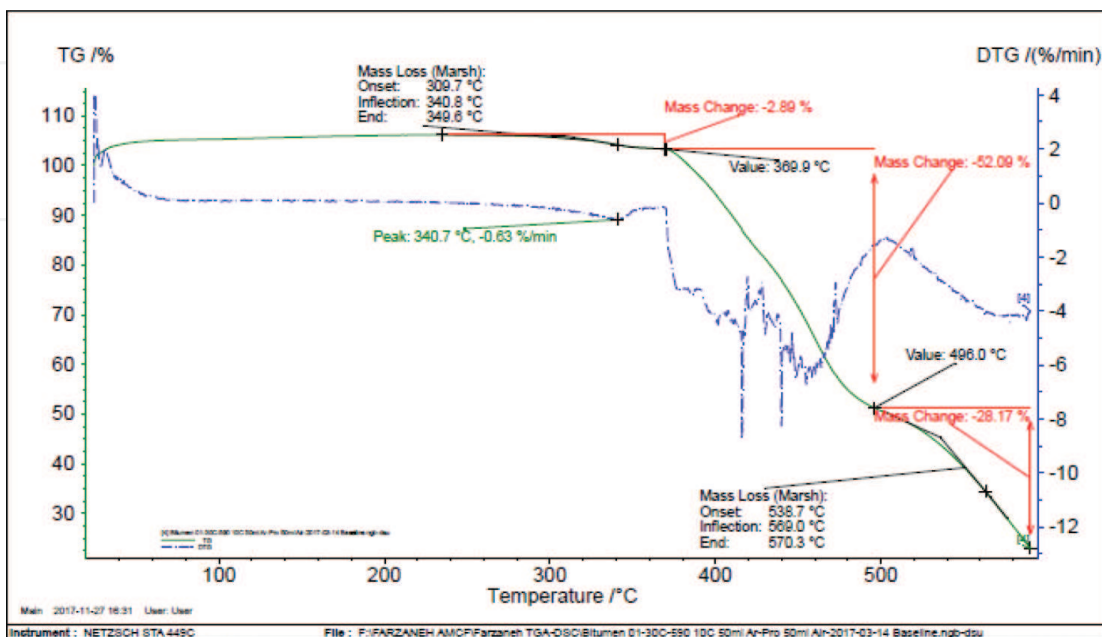


Figure 11. TGA, DTG, and D2TG thermograms of neat bitumen.



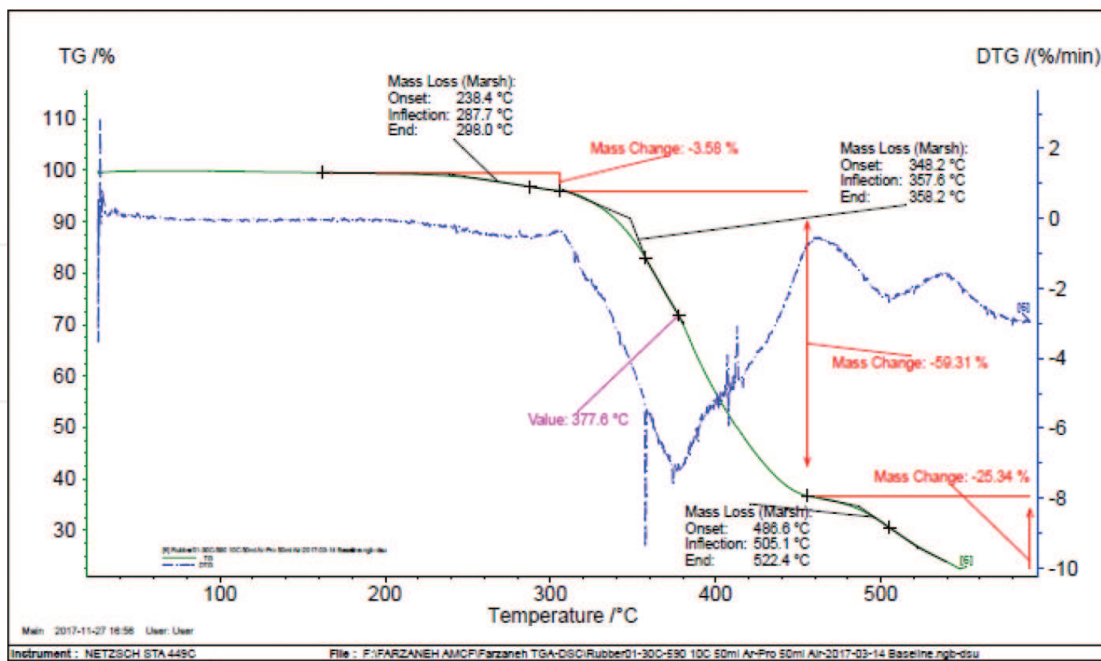


Figure 12. TGA, DTG, and D2TG thermograms of rubber.

Referring to [31], the decomposition of bitumen occurs in at least three steps, considering three temperature ranges, as shown in **Figure 11**. In the temperature range of  $T < 350^{\circ}\text{C}$ , the decomposition of saturates and aromatics results in mass loss of bitumen. Over the temperature range of  $350 < T < 500^{\circ}\text{C}$ , resins and aromatics as well as asphaltenes are the main decomposed fractions, and at high temperatures of  $T > 500^{\circ}\text{C}$ , the substantial mass change in bitumen occurs as a result of decomposition of asphaltenes. However, resins and aromatics are still decomposed in this range of temperature.

When selecting materials for modifying the binder, it is important that the modifier begins to degrade at a temperature above the bitumen modification temperature or the asphalt production temperature. Otherwise, it will lose its initial properties by the time the modification process is finished. In this research, TGA is used for determination of the degradation temperature of the waste materials, which are used for modifying the binder (i.e., rubber and HDPE). **Figure 12** shows the result of TGA on rubber.

As can be seen, the onset temperature of degradation for rubber is  $238^{\circ}\text{C}$  and the peak temperature of mass loss is  $378^{\circ}\text{C}$ , which can be observed as a peak in the first-derivative curve.

Similar to other polymers, TGA of the HDPE samples was done on approximately 5 mg samples over the range of room temperature to  $590^{\circ}\text{C}$  under air with 100 mL/min flow rate at a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$ .

The onset degradation temperature and peak temperature are determined from the derivative TGA curves for HDPE, as shown in **Figure 13**. In this figure, it can be observed that HDPE remains thermally stable up to a temperature of  $430^{\circ}\text{C}$ . After this temperature, HDPE starts to degrade dramatically followed by a substantial step with maximum mass loss rates placing at

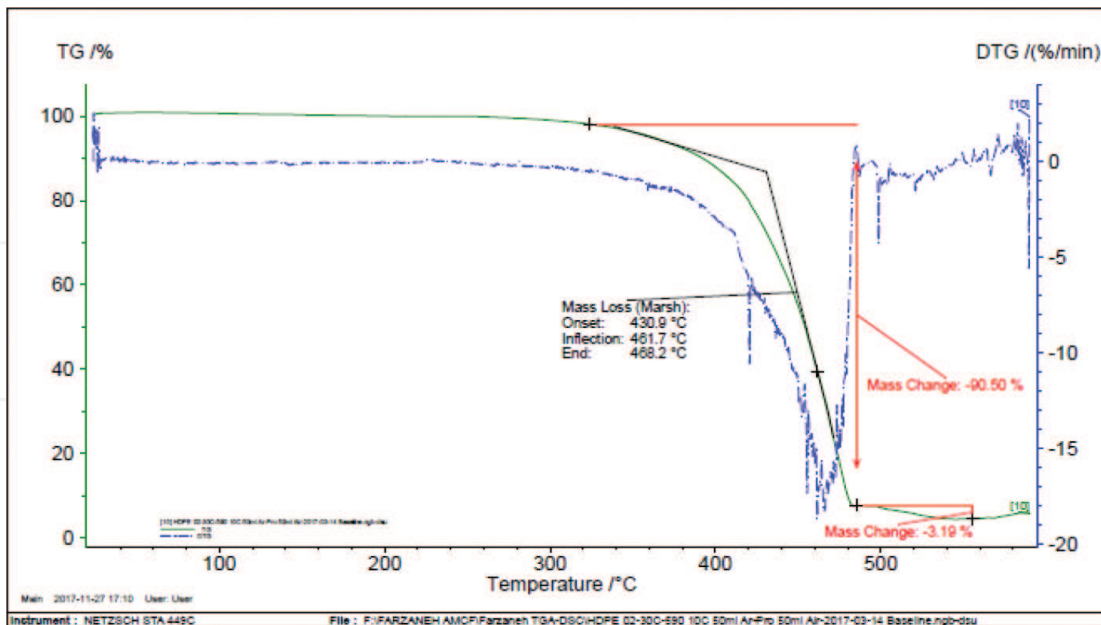


Figure 13. TGA, DTG, and D2TG thermograms of HDPE.

462°C in the DTG curve. This degradation involves a mass loss of about 91% in HDPE due to the thermal cracking of hydrocarbon chains and the production of oxygenated hydrocarbons including CO, CO<sub>2</sub>, and H<sub>2</sub>O [37]. The degradation ends approximately around 490°C.

### 6.3. Microstructure analysis by SEM

The analysis of the microstructure of polymers was performed using scanning electron microscope (SEM). The results of the microscopy of as well as the energy dispersive spectroscopy (EDS) analysis on the individual polymers are given in Figures 14–16.

As can be observed in Figure 14, the surface of bitumen appears as networks of highly entangled strings.

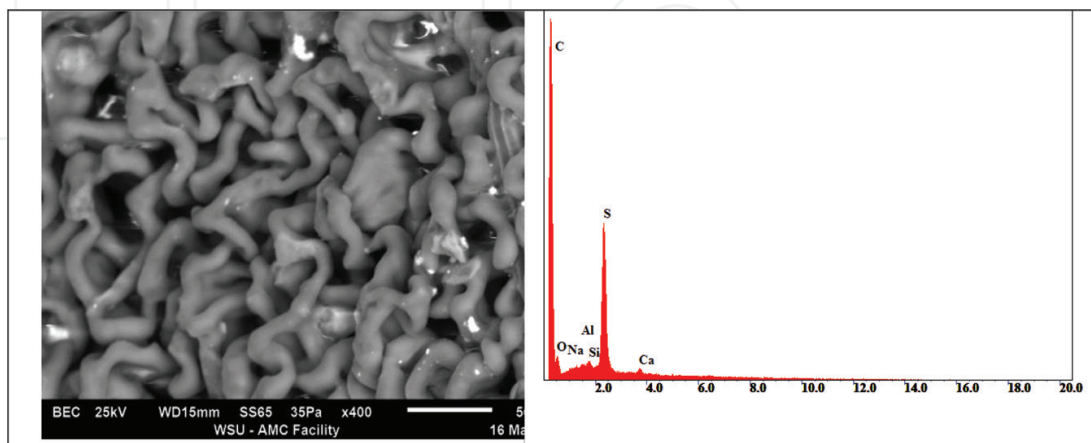


Figure 14. EDS analysis and SEM image of bitumen at 400 magnification.

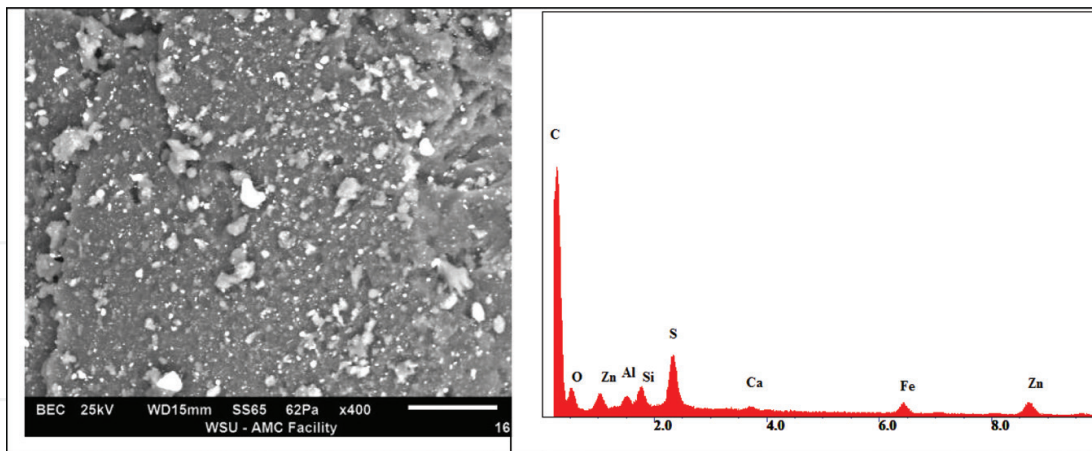


Figure 15. EDS analysis and SEM image of rubber at 400 magnification.

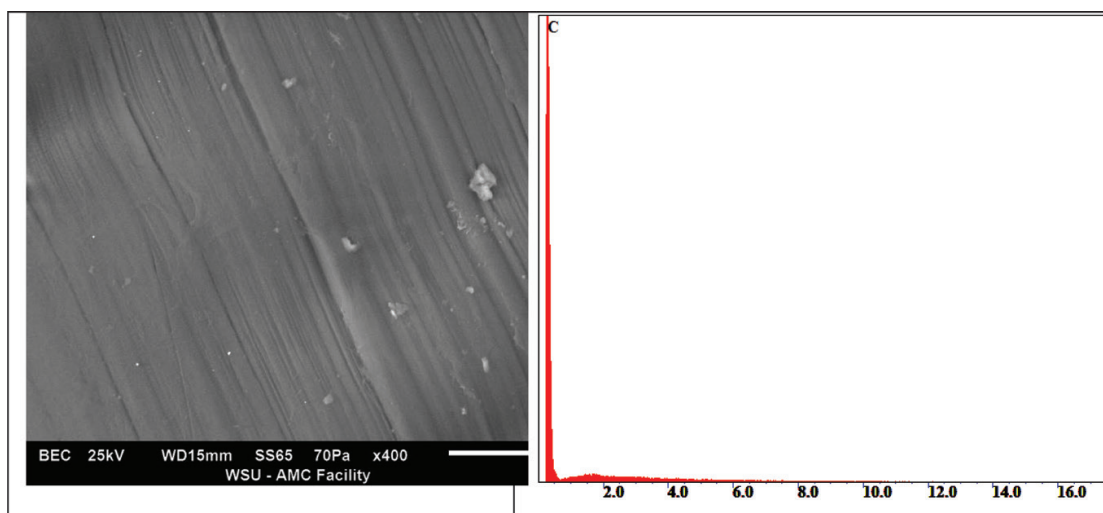


Figure 16. EDS analysis and SEM image of HDPE at 400 magnification.

Figure 15 shows the coarse texture of rubber. The irregular shape and rough texture of rubber can be attributed to its processing method, which is the ambient procedure.

Furthermore, the microstructure of HDPE is shown in Figure 16. It should be noted that HDPE has a higher viscosity compared to bitumen. The materials with high viscosity do not separate easily, and therefore, they present in the form of dispersed phase, as can be clearly observed in Figure 16.

## 7. Summary and conclusion

Today, pure bitumen no longer provides suitable performance for pavements due to the current traffic. Therefore, attempts have been made to maximize the effectiveness of asphalt binders selected for construction projects based on a standard asphalt binder classification system. Binder modification technique is used as an alternative to minimize the pavement failures

due to poor performance of asphalt binders, as well as to increase the PG grade of the asphalt binder [38]. Based on these research studies, the utilization of polymers as modifier improves some of the bitumen's properties such as elasticity, cohesion, and temperature susceptibility, which they all subsequently lead to the improvement of asphalt mixture performance.

For these reasons, and as a quite effective way of disposing of the increasing volume of non-biodegradable wastes, which are increasingly generated in societies, plastic wastes and rubbers can be a reasonable potential materials for consideration as binder modifier.

In modification of bitumen with additives, having knowledge about the effects of modifiers on thermal stability is of high importance resulting in manufacturing more thermally stable binders. Accordingly, in this research, the thermal behavior of modifiers and bitumen was studied using TGA, DSC, and SEM facilities. The thermal parameters of  $T_g$  and  $T_m$ , enthalpy of fusion,  $\Delta H_m$ , and the percentage of crystallinity, CF (%) of samples can be easily determined from the DSC curves. This information can be useful in understanding the characteristics and the composition of polymers. In addition, many researchers have proposed different equations for estimation of the glass transition temperature of mixture based on the composition and the glass transition of the components of the mixture. All these equations are basically representing the relation between the glass transition temperature of a mixture and those of its components using a basic mathematical form but with minor variations. The glass transition calculated using these equations for the blend of bitumen with 2% HDPE and 8% rubber is  $-28.8^\circ\text{C}$ . The calculated  $T_g$  value for blend is lower than those obtained for neat bitumen, which could be attributed to several effects including certain level of miscibility between the additives (i.e., HDPE and rubber) and bitumen. Thus, using these equations, it may be possible to achieve the formulation of the desired modified binder considering the composition of components and the results of DSC analysis on each component.

Furthermore, in this research, TGA is used in determining the degradation temperature of the waste materials. A modifier that begins to degrade at a temperature below the bitumen modification temperature or the asphalt production temperature is not adequate since it will have lost its initial properties by the time the modification process is finished. In the case of analyzed waste materials, all degrade at temperatures above  $200^\circ\text{C}$  and therefore should be adequate for bitumen modification. The main features of TGA curves for individual polymers were discussed in previous sections. From these results, it was observed clearly that HDPE followed by bitumen have higher thermal stability than crumb rubber.

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## Conflict of interest

The authors declare no conflict of interest.

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