

Binder performance and testing

Deriving and Characterising Alternative Bitumen from Waste Plastics

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Abstract

This study presents a research on laboratory production and experimental characterisation of an alternative bitumen using municipal waste plastics. Six different waste plastics produced by local waste recycling manufacturers were selected and characterised to investigate their feasibility in modifying the bitumen binders. Thermal characteristics were firstly obtained using Differential Scanning Calorimetry (DSC) device and the chemical functional groups were obtained by Fourier Transform Infrared Spectroscopy (FT-IR) test, which was used to identify the plastic types existing in the recycled plastics. Then the rheological properties of the bitumen modified with two nominated plastic waste (LDPE and MR10) were examined using the Dynamic Shear Rheometer (DSR) device by conducting frequency sweep tests. Additionally, the engineering performance of the waste plastics-derived bitumen was also obtained and compared against the control bitumen, including fatigue, rutting and healing performance using Time Sweep (TS) test, Multiple Stress Creep and Recovery (MSCR) test and Healing test, respectively. Results show that the LDPE and MR10 were consisting of low-density polyethylene (LDPE) and polypropylene (PP), respectively. The recycled waste plastic MR6 (plant and batch) are mainly LDPE as well. Whereas, other recycled plastics (MR8-V1 and MR8-V2) consist of a variety of materials and impurities. Thus The LDPE and MR10 were selected in the current study to modify the bitumen binder. The LDPE-modified bitumen exhibited more elastic and less viscous behaviour compared to the control bitumen, showed by increased shear modulus and reduced phase angle. Whereas, the MR10 (mainly PP) reduced the shear modulus significantly for the control bitumen. Both LDPE and MR10-modified bitumen had a substantially improved resistance to rutting and fatigue cracking compared to the control bitumen. Meanwhile, the LDPE led to an increased healing potential to the bitumen while the MR10 did not show obvious improvement to the healing performance of the bitumen.

1. INTRODUCTION

Plastics are multi-purpose products that are used in all aspects of urban life from food containers, to construction materials and automobiles industries. Therefore, the plastics are produced in large quantities to cover these high demands. The largest groups in total nonfiber plastics production are polyethene (PE) (36%), polypropylene (PP) (21%), and polyvinyl chloride (PVC) (12%), followed by polyethene terephthalate (PET), polyurethane (PU), and polystyrene (PS) (<10% each). About 2.8 Mt of waste plastics is generated per annum in the UK alone, which makes 7.3% of the total demand for plastic in Europe. However, the end-of-use for these materials is a cause for environmental concerns. The plastic is a non-biodegradable product that leads to negative implications on the environment if not disposed properly, such as in waste land-fills. It was estimated that eight million tons of plastic waste is being dumped into the ocean annually around the globe. However, since the plastic is a very versatile material, it is not possible to cut the use of plastics completely. Therefore, the solution to end the plastic problem does not involve the reduced use of plastic alone but finding better ways to recycle waste plastics that exist in bulk quantities [1-6]. The recycling of waste plastics can delay their end of useful lifetime and discarding process. The use of plastics in construction applications have the longest useful lifespan of the plastics, in which the materials take decades before they need to be recycled/disposed again; this is generally due to the long lifespan of the construction products. Whereas, other products of high plastics demand, such as packaging, mostly have less than one year of product life; therefore, the plastic will need to be processed/discarded again in a short period, which causes an economic and environmental burden [5].

The use of plastics in the manufacturing of flexible pavements helps to consume large quantities of plastic wastes and reduces the demands for producing petroleum-based bitumen. Therefore, it solves an environmental problem and helps in saving natural resources. Several studies investigated the utilisation of plastic waste in flexible pavement mixtures. The incorporation of plastics in the asphalt mixtures was introduced in three forms: (1) the partial replacement of aggregate with recycled plastic shreds of similar particle size [7]; (2) partial replacement of bitumen binder by recycled plastic shreds [8]; (3) the plastic waste is introduced as a binder modifier in powdered form [9]. The percentage of plastics replacing the aggregate was found to reach up to 30% by weight of aggregate. However, some asphalt mixtures require increasing the binder content when replacing the traditional aggregate with plastics waste. Whereas, the percentage of plastic to replace the bitumen was found to reach up to 10% by the bitumen weight [6, 8]. Most of the studies reported that the use of recycled plastics indicates reduced permanent deformation in the form of rutting and reduced low-temperature cracking of the pavement surface [8]. The reported literature indicates the use of several types of plastics in the asphalt mixtures, including Low- and High-Density Polyethylene (LDPE and HDPE, PET [10, 11], PVC, and PP [8]. It was found that the LDPE and HDPE possess a relatively low softening point temperature of 130 °C and thermal degradation temperature more than 180 °C. Therefore, PE is compatible with the current mixing procedures and doesn't require any modification to existing asphalt production plant facilities and techniques if used to replace the aggregate in the asphalt mixture [4, 7]. Whereas, PET-aggregate modified mixtures exhibited higher fatigue lives compared to mixtures without PET [12]. Although, these studies examined the first-use of these materials in the pavement manufacturing applications, however, the use of the recycled waste of these plastics is still limited.

Nevertheless, the use of plastic products as bitumen modifiers or replacements has been hindered due to several uncertainties. These uncertainties include: (1) chemical and physical characteristics of plastics when mixed with the bitumen binders (for examples, the effect of plastics' particle size on the mixing time to achieve full dispersion and to avoid phase-separation); (2) the suitability of the current mixing procedures and equipment for the modified binder and asphalt mixture is unknown (for example, the mixing temperature and time required for full melting and dispersion of plastic into the bitumen binder, as well as, the laying out and compaction time in the field before the mixture hardens); (3) availability of recycled waste plastics in large bulk quantities while maintaining consistent properties for different patches and producers and; (4) apart from technical factors, concerns over the use of plastics in asphalt pavement also manifest from their potential of causing environmental problems, such as run-off pollutants and leaching [4]. Moreover, the focus of existing studies is on the physical characteristics of the mixture and mechanical performance upon the addition of waste plastics with few studies addressing the effects of plastics on the binder characteristics [13, 14]. Therefore, a fundamental study on the bitumen interaction with plastic wastes is needed, which is covered in the current study.

The current study aims to investigate the chemical and physical characteristics of the waste plastics produced by local waste recycling suppliers and their effect on the bitumen binder when mixed, in order to investigate the feasibility of modifying the bitumen with waste plastics. The physical properties, such as the thermal characteristics of waste plastics were obtained by using the Differential Scanning Calorimetry (DSC) device, whereas, the chemical functional groups were obtained by the Fourier Transform Infrared Spectroscopy (FT-IR) test, which was used to

identify the types of plastic which exist within the produced batches of recycled waste plastics. Following the physical and chemical characterisation of the plastic, the rheological properties of the bitumen modified with plastic waste were examined by using the Dynamic Shear Rheometer (DSR) device by conducting frequency sweep tests. Additionally, the engineering performance of the waste plastics-derived bitumen was obtained and compared with the performance of control bitumen. The engineering performance characterisation included fatigue and rutting performance and healing potential of the plastic-modified binders. Different schemes of DSR tests were utilised to obtain the engineering properties, including Time Sweep (TS) test; Multiple Stress Creep and Recovery (MSCR) test and Healing test.

The focus of this study is on the thermal and chemical characterisation of several locally-produced recycled waste plastics for the use in asphalt pavements. Additionally, the study compared the preliminary mechanical performance of two waste plastic-modified bitumen at the unaged condition. Therefore, further tests are required to examine the after-mixing and processing field performance, and the long-term performance in the field of the waste-plastic modified bitumen and asphalt mixtures.

2. MATERIALS

2.1 Recycled plastic

Six types of recycled plastics were evaluated in this study, namely A1-A6 (shown in Figure 1). Within the six plastic types, the A1 is a white or brown thin pellet, A2 is in a green and thick pellet shape, A3 is white or colourless flakes, and A4 is mixed-coloured particles of plastic shreds, while A5 and A6 are also mixed and coloured plastic particles, but the latter are finer than A4. All the plastics types are supplied from local recycled-plastic providers. The recycled-plastic samples were not produced for a specific use; therefore, they are not provided with technical data sheets to indicate their chemical composition, origin or physical properties.



Figure 1: Recycled plastic types as provided by the supplier

2.2 Bitumen binder

The prime asphalt binder used in this study is known as Bitumen X70 classified as a 40/100 according to BSEN14023:2010 for general asphalt applications and road constructions. It was used as a base (control) binder to examine the effect of adding the recycled plastics. Table 1 lists the engineering specifications of the control binder according to the supplier.

Table 1. Conventional properties of the control binder

Property	Value
Penetration @ 25 °C (0.1 mm)	45–80
Softening point (°C)	≥ 45
Flash point (°C)	> 250
Force Ductility @ 5 °C (J/cm ²)	> 3

2.3 Plastic waste-derived bitumen

In order to develop the plastic waste-derived bitumen, control bitumen X70 was mixed with the plastic waste by mass percentages. The mixing percentage of the plastic waste was optimised by examining different plastic percentages (5, 7, 10 and 12 % by w/w of X70 binder) and testing them by frequency sweep tests at various temperatures. It was found that adding 6 % of recycled plastic achieved higher complex shear modulus with considerably good phase angle. Therefore, X70 bitumen was mixed with 6 % plastic waste by using the mechanical high-shear mixer at high mixing temperature. Mixing of the binder with plastic waste at high-temperature conditions is vital to allow the binder compounds to be incorporated uniformly with the plastic and to sustain a homogenous mixture. There are several mixing schemes suggested by existing studies for plastic, bio-oil and polymer components [4, 7, 8, 15-20], therefore, to ensure a complete melting and mixing of plastic-waste with the bitumen, a temperature of 180 °C and mixing speed of 900 rpm were maintained for 60 minutes to avoid excessive ageing of the samples. Finally, before the DSC testing, the samples were placed in the oven at 180 °C for 5 hours to easily pour them into the DSC moulds of 8- and 25-mm diameters. After evaluating their thermal characteristics and chemical composition by the DSC and FT-IR, two plastic waste types were selected to be mixed with the control binder (which are, A1 and A2), to evaluate their engineering performance; further details are illustrated in the following sections.

3 EXPERIMENTAL METHODS

3.1 The thermal characterisation of waste plastics by the Differential Scanning Calorimetry (DSC)

The recycled plastic samples were tested by using the DSC device to observe their thermal stability and phase changes upon heating. Since the recycled plastics are obtained from a local waste plastic supplier, therefore, the exact components of these recycled materials are unknown. The DSC test will help to identify the types of plastics present in these samples by subjecting them to dynamic thermal conditions where the temperature increases at a constant rate, then the heat flow is recorded and attributed to the thermal phases of the tested sample. The DSC technique, when used under the dynamic thermal rate, can measure the melting temperature and crystallinity of polymers.

The DSC measurements were done using the METTLER TOLEDO gas control CG10 - heat-flux DSC, aluminium crucibles (without lid), and pure nitrogen as the purge gas at a flow of 10 °C/min. The device uses a reference (empty aluminium crucible) which sits on the sensors to monitor the differential heat flow between the reference crucible and the crucible carrying the sample.

In this study, the waste plastic samples were cooled from the room temperature (25 °C) to -50 °C, to start the test. Some samples were heated to a temperature of 190 °C then cooled down to -50 °C in order to consider the thermal history effects, wherein this case all the samples will have a similar thermal history, therefore, there will be no differences in behaviour resulting from the differences in the thermal history of these samples. Once the start temperature (-50 °C) was set, the samples were heated to a temperature of 300 °C to pass the melting point and possibly degrade. The samples masses were kept in the range of 5.1 to 5.8 mg.

Waste plastic samples were tested by the DSC twice for obtaining the test repeatability. The replicates were identical in terms of thermal behaviour for each sample, which indicates that the results are reliable. The samples were named according to their visual appearances and colours. The properties and visual appearance for the samples tested by DSC are listed in Table 2. Since the materials A4, A5 and A6, appear to consist of a group of different components according to their visual appearance; therefore, random components were collected and tested separately. Additionally, representative samples that consist of a mixture of these components were also included in the DSC testing program.

Table 2. The visual description and masses of waste plastic samples tested by the DSC device

Sample	Description	Mass (mg)
A1-01-CLR	White/colourless A1 sample	5.3
A1-02-CLR	White/colourless A2 sample	5.3
A1-01-DRK	Dark/brown A1 sample	5.3
A1-02-DRK	Dark/brown A1 sample	5.3
A2-01	Green, A2 sample	5.2
A2-02	Green, A2 sample	5.3
A3-01	Colourless A3 sample in flakes	5.4
A3-02	Colourless A3 sample in flakes	5.3
A4-01	A random mixture of A4 samples (mixed colour)	5.8
A4-02	A random mixture of A4 samples (mixed colour)	5.6
A4-BK	Black, a sample chosen randomly from A4.	5.7
A4-CLR	Colourless, a sample chosen randomly from A4.	5.5
A4-Y	Yellow, a sample chosen randomly from A4.	5.5
A5	A random mixture of A5	5.7

A6-Y	Yellow, a sample chosen randomly from A6.	5.3
A6-W	White, a sample chosen randomly from A6.	5.4
A6-BK	Black, a sample chosen randomly from A6.	5.1

3.2 The chemical characterisation of waste plastics by the Fourier Transform Infrared Spectroscopy (FT-IR) test

FT-IR test was utilised to evaluate the chemical structure and functional groups which are present in the recycled waste plastics. The results from the FT-IR test will help in identifying the plastic-type used in their manufacturing by comparing the functional groups obtained with the signature (standard) functional groups of polymers in a fast, efficient, and non-destructive procedure [20]. The chemical structures of HDPE and LDPE are difficult to differentiate. However, recent researches were able to distinguish between the two polymers using FT-IR spectra [21].

The FT-IR measurements were done using the PerkinElmer FT-IR Spectrometer device. The device was set to scan in a range of $(400-4000) \text{ cm}^{-1}$, with a scanning frequency number of 16 and a resolution of 4 cm^{-1} . Background scanning was made before testing the samples. The names and description of visual appearance for the samples scanned under the FT-IR device are listed in Table 3.

Table 3. The identification and visual description of the waste plastics tested by the FT-IR device

Sample	Description
A1-CLR	White/colourless A1 sample
A1-DRK	Dark/brown A1 sample
A2	Green, A2 sample
A3	A sample is chosen randomly from A3
A4-B	Blue, a sample chosen randomly from A4.
A4-BK	Black, a sample chosen randomly from A4.
A4-CLR	Blue, a sample chosen randomly from A4.
A4-G	Colourless, a sample chosen randomly from A4.
A4-GY	Grey, a sample chosen randomly from A4.
A4-R	Red, a sample chosen randomly from A4.
A4-W	White, a sample chosen randomly from A4.
A4-Y	Yellow, a sample chosen randomly from A4.
A5-B	Blue, a sample chosen randomly from A5.
A5-CLR	Colourless, a sample chosen randomly from A5.
A5-G	Green, a sample chosen randomly from A5.
A5-R	Red, a sample chosen randomly from A5.
A5-Y	Yellow, a sample chosen randomly from A5.
A6-BK-01	Black, a sample chosen randomly from A6.
A6 -BK-02	Black, a sample chosen randomly from A6.
A6-B	Blue, a sample chosen randomly from A6.
A6-CLR	Colourless, a sample chosen randomly from A6.
A6-G-01	Green, a sample chosen randomly from A6.
A6-R	Red, a sample chosen randomly from A6.
A6-W	White, a sample chosen randomly from A6.

3.3 Rheological characterisation of waste plastics-derived bitumen: Frequency sweep test by the Dynamic Shear Rheometer (DSR)

The inclusion of waste plastics into the bitumen will affect the rheological properties of the bitumen, resulting in a different viscoelastic performance compared to the control binder. The frequency sweep test was used to characterise the rheological behaviour of the waste plastics-derived bitumen by examining the shear modulus and phase angle at undamaged conditions. The frequency tests were conducted at a temperature range of $10 - 70 \text{ }^{\circ}\text{C}$ with temperature intervals of $10 \text{ }^{\circ}\text{C}$. The selected temperature range was chosen to simulate the wide temperatures range in the field. Additionally, the strain level at temperatures between $10-30 \text{ }^{\circ}\text{C}$ was chosen to be 0.3% strain to induce a lower torque, because bitumen binders become stiffer at low temperatures, so a low strain is applied to prevent cracking. Whereas, for temperatures exceeding $30 \text{ }^{\circ}\text{C}$, 0.5% strain is applied as the bitumen binders are softer (less viscous), which implies a higher tolerance to strain, so the binders will not fail by cracking [22]. The frequencies were set to be $0.1 - 25 \text{ Hz}$. The undamaged shear moduli and phase angles were obtained from the temperatures master curves by using the time-temperature superposition principle (TTSP) [23, 24].

3.4 Engineering performance characterisation of waste plastics-derived bitumen

Three testing schemes were utilised to evaluate the engineering performance of waste plastics-derived bitumen by using the DSR device, including: (1) time sweep (TS) test to examine the fatigue cracking resistance of the modified bitumen binders under strain-controlled cyclic loading conditions; (2) multiple stress creep and recovery (MSCR) test

to determine the rutting resistance performance and; (3) healing test to determine the percent recovery and healing capability upon unloading.

The TS test was performed at a strain level of 5%, at an intermediate temperature of 20 °C and a frequency of 10 Hz, up to 24,000 loading cycles. The previous study by the authors conducted on the same source of bitumen indicates that the bitumen tends to experience fatigue cracking at the loading cycle of 24,000 [25]. Therefore, the same loading cycle ($N= 24,000$) has been selected as the TS loading limit in this testing scheme. The shear moduli and phase angles were recorded throughout the test. Additionally, the fatigue cracking was quantified by using the (DSR-C) growth model based on dissipated strain energy equilibrium principle and damage mechanics [25]. The study employed the DSR to determine the shear moduli and phase angles at both undamaged and damaged conditions. The fatigue damage was quantified directly by the predicted crack length (c_p), illustrated in Eq. (1).

$$c_p = \left[1 - \left(\frac{|G_N^*|/\sin(\delta_N)}{|G_o^*|/\sin(\delta_o)} \right)^{\frac{1}{4}} \right] r_o \quad (1)$$

where,

r_o = the original radius of the sample (4 mm)

$|G_N^*|$, $|G_o^*|$ = the shear moduli for the damaged and undamaged samples, respectively

δ_N , δ_o = the phase angles of the damaged and undamaged samples, respectively.

c_p = the predicted crack length at the Nth loading cycle of the time sweep fatigue test.

Binders modified with plastic can be prone to rutting at high temperature. Therefore, it becomes imperative to evaluate the extent of damage that can occur [26]. The MSCR test was utilised to characterise the rutting resistance performance of the modified binders effectively. The test is conducted according to the standard test method (ASTM standard D7405-15) [27]. MSCR test records two important parameters: Percentage recovery (%R) and non-recovery compliance (J_{nr}) of asphalt binders.

Healing tests have been conducted to examine how asphalt binders can recover their mechanical properties (i.e. stiffness and strength, etc.) under loading in a fatigue test [28, 29]. The ability to self-heal is controlled by many factors (i.e. viscosity level, temperature and rest duration) and has been associated with improving the longevity of a roads service life. Therefore, an investigation into this field is important to identify which binders can self-heal to reduce the need to carry out replacement or maintenance of roads. The self-healing capability of waste plastic-derived bitumen will be examined using DSR healing test. The test consists of two loading stages of stain-controlled time sweep tests separated by a rest period (unloading stage) where there is no torque/strain applied for 20 minutes. The time sweep stages are conducted with a frequency of 20 Hz and 5 % strain at an intermediate temperature of 20 °C. The healing was quantified by measuring the shear moduli before and after the healing stage. The

Healing Index (HI) (illustrated in Eq. 2).

$$HI = \frac{G_{after}^* - G_{before}^*}{G_{before}^*} * 100 \quad (2)$$

where G_{after}^* is the complex shear modulus of the self-healed binder in MPa, and G_{before}^* is the complex shear modulus before healing the binder in MPa.

4 THE THERMAL AND CHEMICAL CHARACTERISATION OF WASTE PLASTICS

The recycled waste plastics from municipal land-fills sources usually come from a variety of resources and contain several components, such as several plastic types and other impurities (wood, rocks, etc.). Therefore, to utilise these waste-plastics in the flexible pavement industry, these materials should be identified, and the chemical composition and physical properties should be characterized. The thermal behaviour (melting point, degradation point and thermal stability) of waste plastics was examined by using the DSC, whereas the chemical composition (represented by the chemical functional groups) was identified by conducting the FT-IR scanning. The results for each supplied plastic-type are illustrated in the following sub-sections.

4.1 DSC and FT-IR results for plastic-type (A1)

Figure 2 shows the DSC test results for two samples of A1. It can be observed that the peak is more distinguished for the dark/brown coloured samples (A1-01-DRK and A2-02-DRK), this suggests a slight difference in composition

compared with the clear/colourless samples. Therefore, the dark samples needed more heating time/energy to complete the melting process and reach the liquid state. The melting point of A1 was found to be 126 °C, which is matching with a reference low-density polyethylene LDPE sample (Resin code #4). Polyethylene is used in products such as containers, tapes, and stationary. A low-density polyethylene of density equals 0.934 g/cm³ has a melting point of 126 °C, melting heat of 141 J/g, and a degree of crystallisation of 49%. The samples started to experience thermal degradation at a temperature of 220 °C.

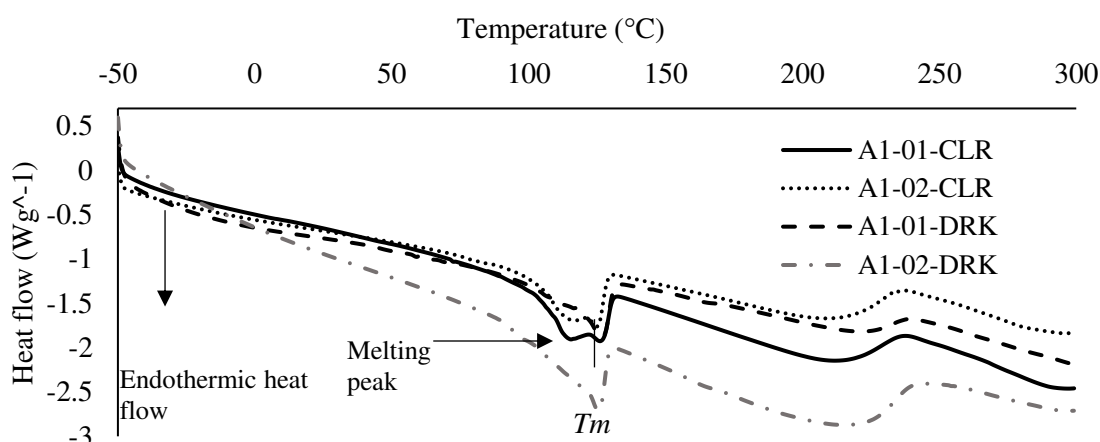


Figure 2: DSC test results for four samples of A1, each has a mass of 5.3 mg placed in open-lid crucibles, tested in nitrogen gas cell at a temperature range of (-50 – 300 °C), with a constant temperature rate of 10 °C/minute. The samples were classified according to their visual appearance, where (CLR) refers to the colourless samples and DRK refers to the brown to dark coloured samples.

The FT-IR results of A1 are shown in Figure 3 for a colourless and dark/brown coloured sample. Generally, the absorption peaks of A1 are identical to the reference absorption peaks of a pure LDPE (2915, 2845, 1467, 1462, 1377, 730 and 717 cm⁻¹). It can be observed, however, that there are few extra small peaks for the dark/brown coloured sample, such as at 1741 cm⁻¹, 1578 cm⁻¹ and 1233 cm⁻¹, this can be attributed to the existence of impurities or fillers.

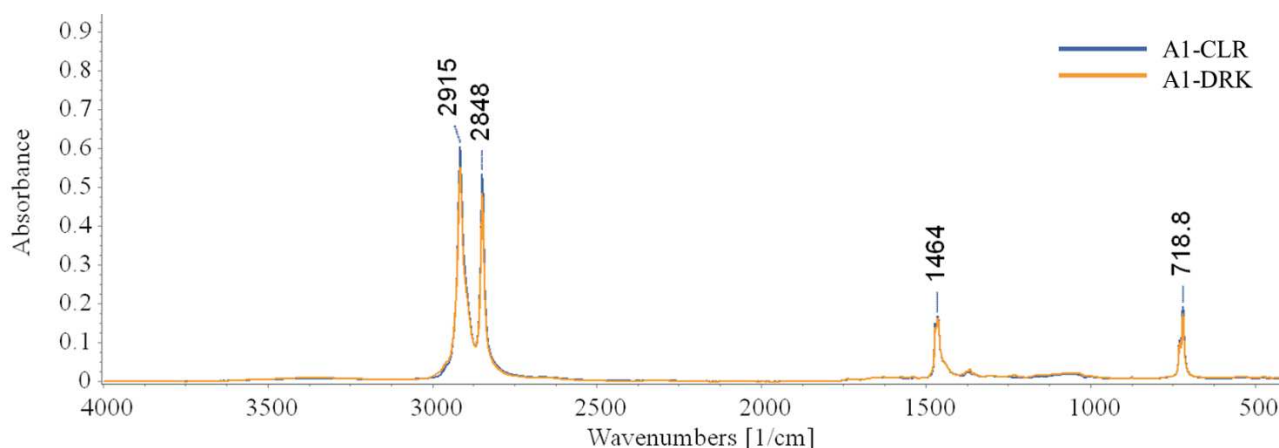


Figure 3: FT-IR test results for plastic-type A1 at a wave range of (4000-400) cm⁻¹ showing the absorbance peaks of the samples. A1-CLR indicates the FT-IR result of colourless sample, whereas, A1-DRK indicates the FT-IR result of a dark/brown sample

4.2 DSC and FT-IR results for plastic-type (A2)

Figure 4 shows the DSC test results for two samples of A2. It can be observed that the distinctive peaks for A2 samples are directed towards the endothermic heat flow direction, which indicates these peaks (at a temperature range of 165–170 °C) are the melting peaks. When the plastic is heated from its crystal state, the temperature increases at a constant rate, but when the temperature reaches the melting point (T_m), the temperature then holds steady until the plastic is completely melted. Once the plastic is melted, the temperature continues to increase again [30], this behaviour is matching with the DSC results for A2. There are no other noticeable trends in the DSC results for A2 samples. It indicates that the samples didn't experience thermal degradation at the tested heating temperature range (-50 – 300 °C).

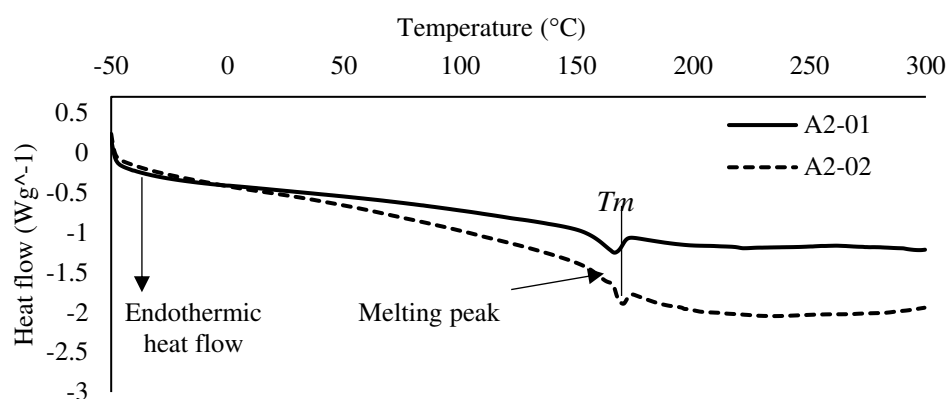


Figure 4: DSC test results for two samples of A2 with samples masses of 5.2-5.3 mg placed in open-lid crucibles, tested in nitrogen gas cell at temperatures range of (-50 – 300 °C), with a constant temperature rate of 10 °C/minute.

The FT-IR test result for sample A2 is shown in Figure 5. By comparing the results with the reference spectrum of the known plastic types, it was found that A2 sample has a similar wave pattern of that for the polypropylene (PP) (plastic with the Resin code no. 5). PP is a crystalline polymer that is available at low cost and has excellent formability, resistance to water and high strength. The absorption bands used for the identification of polypropylene are: 2950 cm^{-1} (C-H stretch), 2915 cm^{-1} (C-H stretch), 2838 cm^{-1} (C-H stretch), 1455 cm^{-1} (CH₂ bend), 1377 cm^{-1} (CH₃ bend), 1166 cm^{-1} (CH bend, CH₃ rock, C-C stretch), 997 cm^{-1} (CH₃ rock, CH₃ bend, CH bend), 972 cm^{-1} (CH₃ rock, C-C stretch, CH₂ rock, C-CH₃ stretch) and 808 cm^{-1} (CH₂ rock, C-C stretch, C-CH stretch). It can be observed that few other small peaks could have resulted from the additives and fillers during manufacturing. Furthermore, the melting point obtained by the DSC for A2 is similar to that of PP polymer (T_m range is 160 to 170 °C).

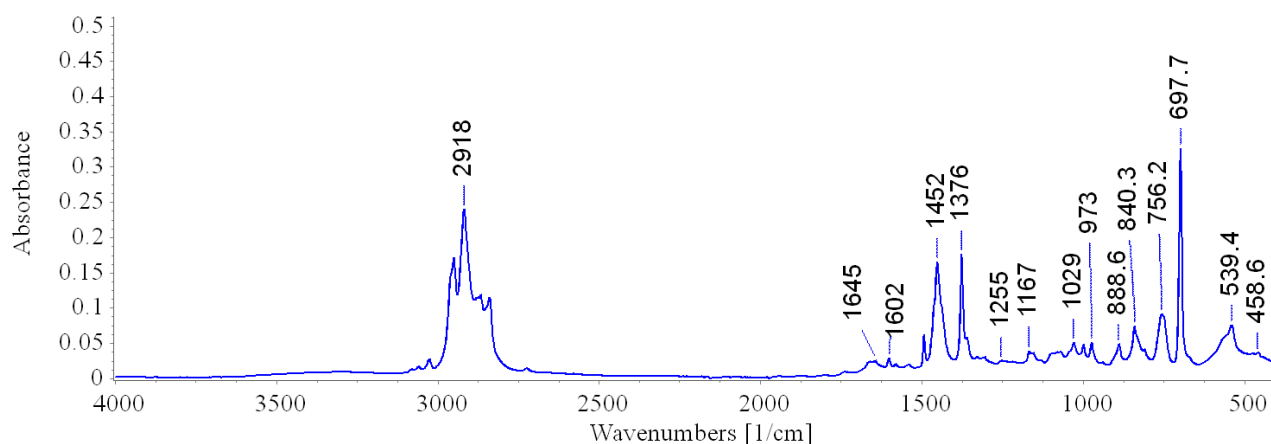


Figure 5: FT-IR test results for plastic-type A2 at a wave range of (4000-400) cm^{-1} showing the absorbance peaks of the sample.

4.3 DSC and FT-IR results for plastic-type (A3)

The DSC results for two samples of A3 are shown in Figure 6. It can be seen that there are no clear heat flow peaks for A3 at a heating rate of 10 °C/min for a temperature range of (-50 – 300 °C). Therefore, it is difficult to predict this material's composition by using DSC results alone. Since A3 samples didn't show a clear melting peak at this temperature range, this may suggest that the plastic could be amorphous polymer. Amorphous polymers are not arranged in crystalline form, but rather chains.

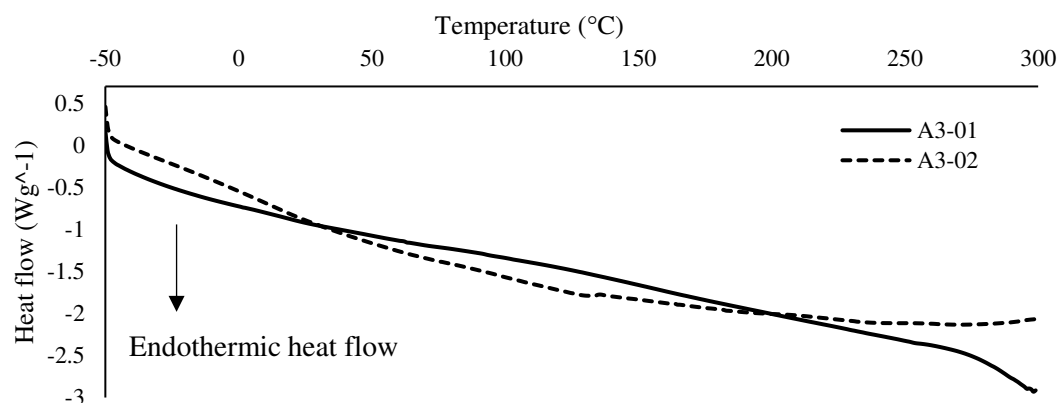


Figure 6: DSC test results for two samples of A3, having masses of 5.4 and 5.3 mg placed in open-lid crucibles, tested in nitrogen gas cell at temperatures range of (-50 – 300 °C), with a constant temperature rate of 10 °C/minute.

The FT-IR test result for A3 samples (shown in Figure 7) show absorption bands that correspond to the reference spectrum of poly(vinyl butyral) (PVB). PVB is a strong, transparent and flexible polymer. The absorption bands used for the identification of poly(vinyl butyral) are: 2957.6, 1323.4, 1054.6, 1434.5, 1239.5, 1001.1, 1379.4, 1136.5, 911.5 cm^{-1} . The melting point of the PVB is 90-120 °C. However, the DSC results didn't show a clear peak in this range. Therefore, more tests are required to identify the plastic-type used in this recycled material.

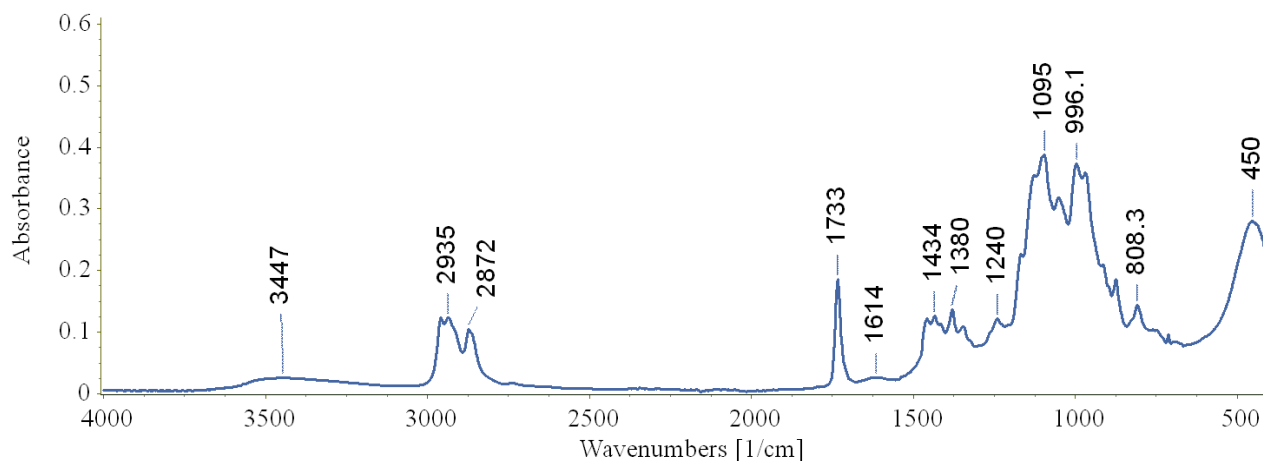


Figure 7: FT-IR test results for plastic-type A3 at a wave range of (4000-400) cm^{-1} showing the absorbance peaks of the sample.

4.4 DSC and FT-IR results for plastic-type (A4)

The recycled polymer A4 appears to consist of a variety of materials (see Figure 1). The composition and the first use of these materials are unrecognisable. Therefore, to study the thermal properties of A4 polymers by the DSC, mixed components, as well as separate components, were tested. The DSC results are shown in Figures 8a and 8b. Since the material appears to consist of a variety of components, therefore to unify the thermal history of the samples, the samples were first heated to a temperature of 190 °C then cooled down to -50 °C and heated again up to 300 °C, using a heating/cooling rate of 10 °C/min.

It can be noticed from Figure 8a that the mixed components have yielded several melting points; this is reasonable as they consist of different components, so each component will melt when it reaches a certain heating temperature. The range at which the melting process occurred for all the components is (110 -140 °C), indicating the main components of the A4 are LDPE. Additionally, the samples experienced signs of degradation at a temperature of 240 °C. Whereas, Figure 8b which shows the DSC for separate colour-coded samples selected from sample A4, it can be seen that some samples didn't experience a recognisable change in heat flow. Therefore, it is not possible to identify these components by using DSC in the current testing scheme.

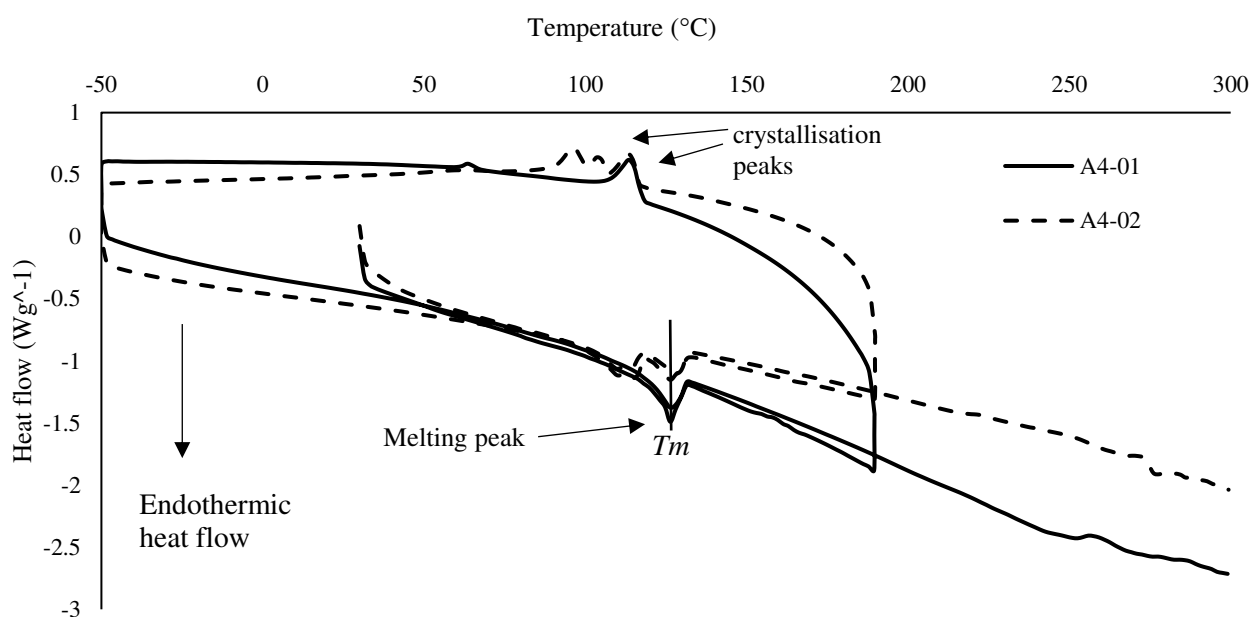


Figure 8a

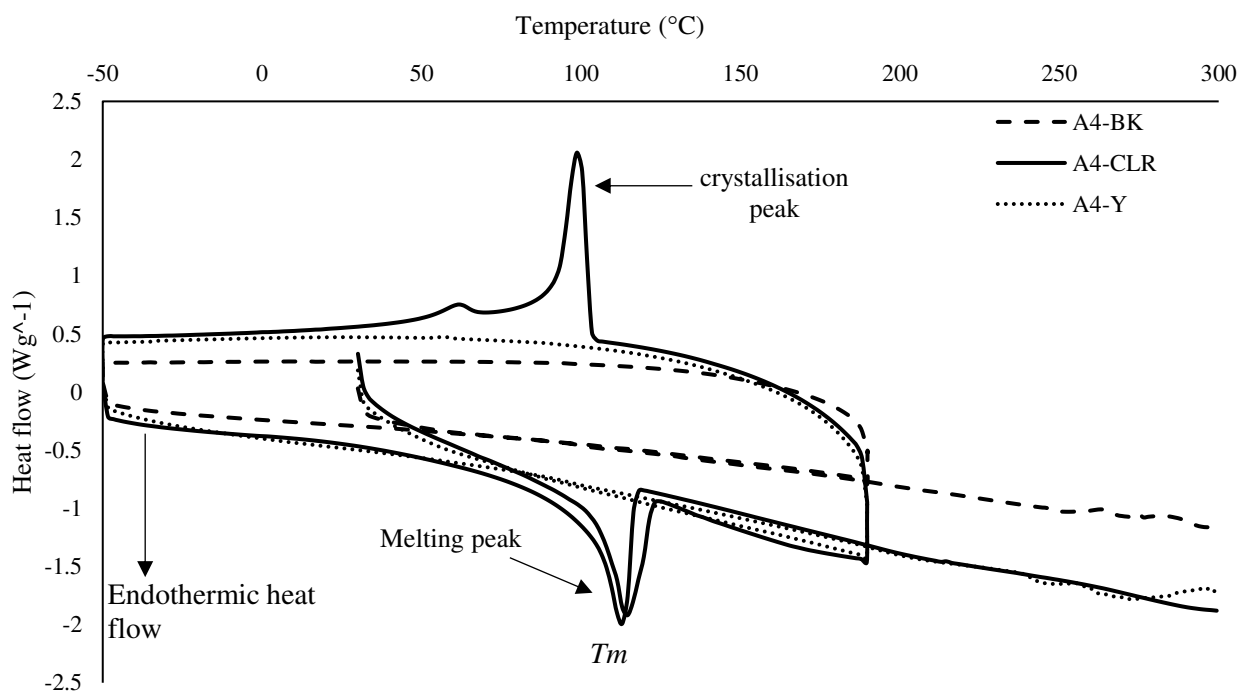


Figure 8b

Figure 8: DSC test result for the recycled polymer A4, having masses of (5.3-5.8 mg) placed in open-lid crucibles, tested in nitrogen gas cell at temperatures range of (-50 – 300 °C), with a constant temperature rate of 10 °C/minute. The DSC test was conducted for: (a) mixture of sample's components, (b) individual samples selected randomly from the plant.

Results of the FT-IR for samples obtained from A4 plant are shown in Figures 9-12. The FT-IR results are divided according to their similarity in the absorption bands. Therefore, the results have been divided into four groups:

1- The samples A4-B, A4-BK, A4-W, and A4-Y (details for each sample are listed in Table 3) are recognised as LDPE plastics (Resin code #4) (shown in Figure 9a).

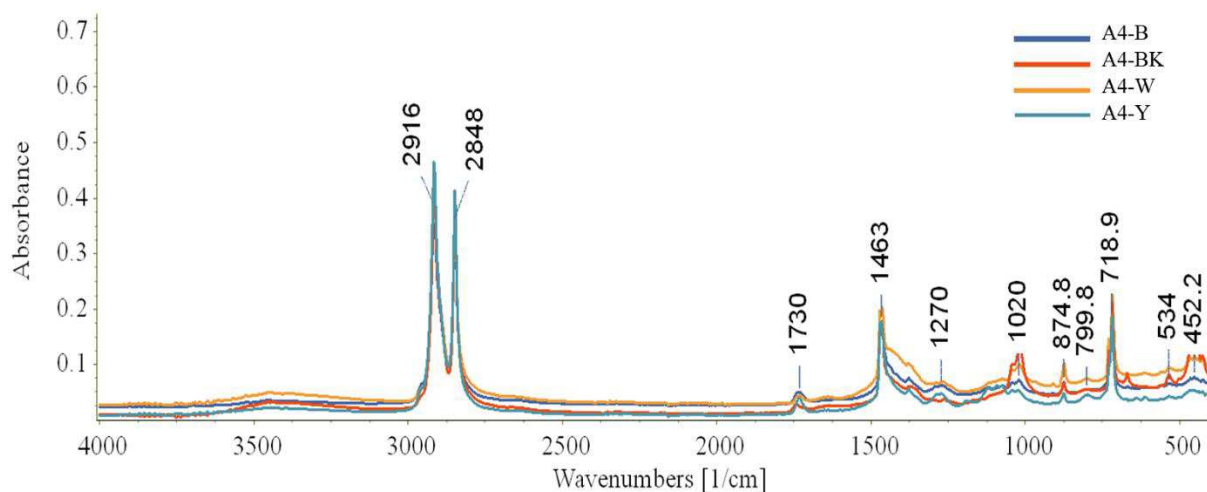


Figure 9: FT-IR test results for plastic-type A4 at a wave range of (4000-400) cm^{-1} showing the absorbance peaks of the samples A4-B, A4-BK, A4-W, and A4-Y

2- The sample A4-CLR (sample details are listed in Table 3) is recognised as polyethene terephthalate (PETE) (resin code #1). The absorption bands used for the identification of PETE are 1713, 1241, 1094, 720 cm^{-1} . The PETE has a high melting point of 260 °C. However, the visual inspection of the batch suggests that it is not a major component in the sample and can be considered as an impurity (shown in Figure 10).

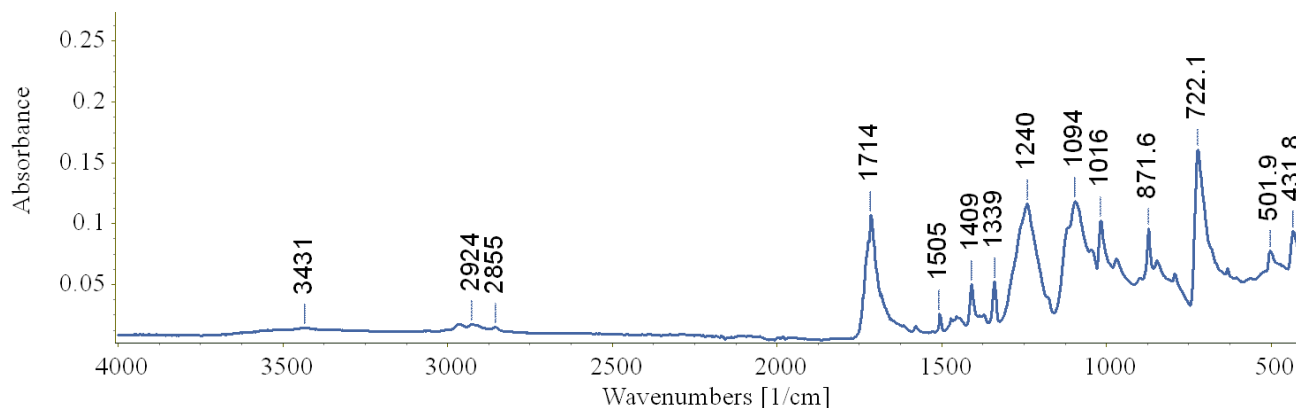


Figure 10: FT-IR test results for plastic-type A4 at a wave range of (4000-400) cm^{-1} showing the absorbance peaks of the sample A4-CLR

3- The sample A4-G (details for each sample are listed in Table 3) is recognised as a combination of polypropylene (PP) (resin code #5) and polyethene (PE). The wavenumbers 2845, 717, 2915 and 1377 cm^{-1} are used to identify the PE polymer, whereas, the wavenumbers 2950, 2915, 1455, 1377 cm^{-1} are used to identify the PP polymer (shown in Figure 11).

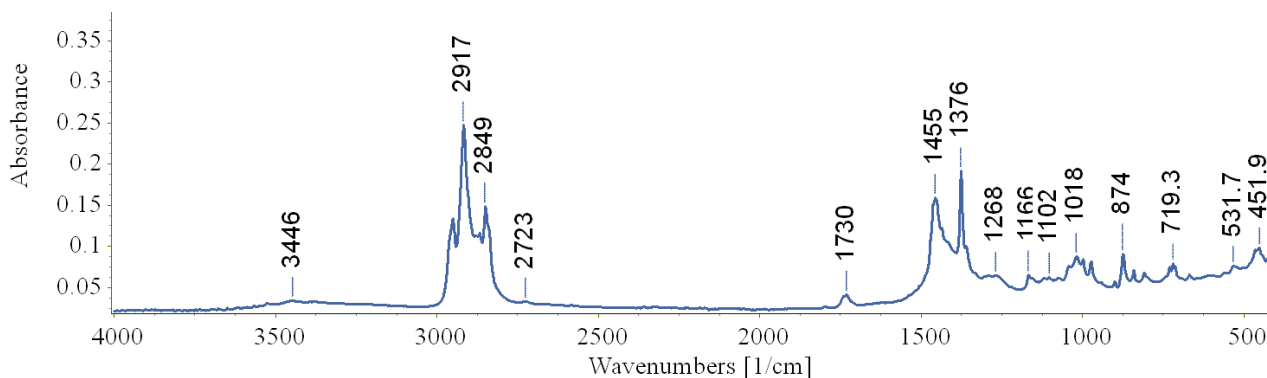


Figure 11: FT-IR test results for plastic-type A4 at a wave range of (4000-400) cm^{-1} showing the absorbance peaks of the sample A4-G

4- The FT-IR tests results for the samples A4-GY and A4-R (details for each sample are listed in Table 3), shown in Figure 12, show a strong peak at 1724 cm^{-1} which is related to the ketone group $\text{C}=\text{O}$, particularly, the unconjugated

ketone. Besides, the cluster peaks at 2920 are all related to C-H stretching, the peaks at 1424 and 1256 are CH₃ and CH₂, respectively. This functional structure suggests the material belongs to the polyketone group PK. Polyketones are thermoplastic polymers with high resistance to solvents and excellent mechanical properties. The melting point of polyketone is in the temperature range of 220-255 °C.

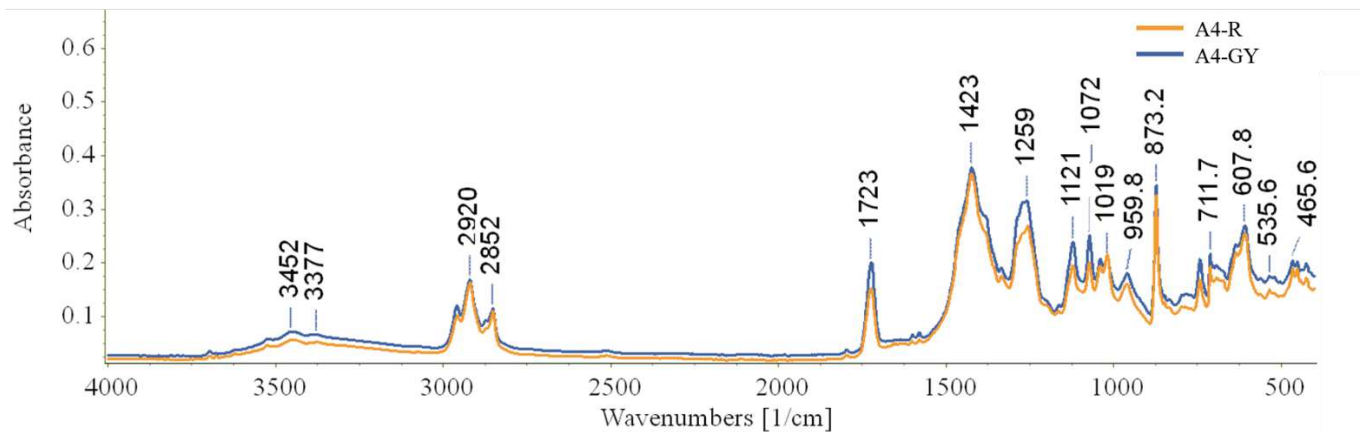


Figure 12: FT-IR test results for plastic-type A4 at a wave range of (4000-400) cm⁻¹ showing the absorbance peaks of the samples A4-R and A4-GY

4.5 DSC and FT-IR results for plastic-types (A5) and (A6).

Similar to sample A4, the recycled polymers A5 and A6 appear to consist of a variety of materials (see Figure 1). Therefore, to study the thermal properties of these polymers by the DSC, mixed components, as well as separate components, were tested. The DSC results are shown in Figures 13. In order to unify the thermal history of these components in the sample, the sample was first heated to a temperature of 190 °C then cooled down to -50 °C and heated again up to 300 °C, using a heating/cooling rate of 10 °C/min.

The DSC results (shown in Figure 13) show a melting point T_m at 130 °C, a crystallisation peak at 120 °C and a start of degradation at 250 °C. The thermal behaviour was observed to be identical for all the tested A5 and A6 samples. Additionally, the visual appearance of the samples suggests they are manufactured by using the same polymer type with different colours, and the components formed one molten mass after heating at 300 °C.

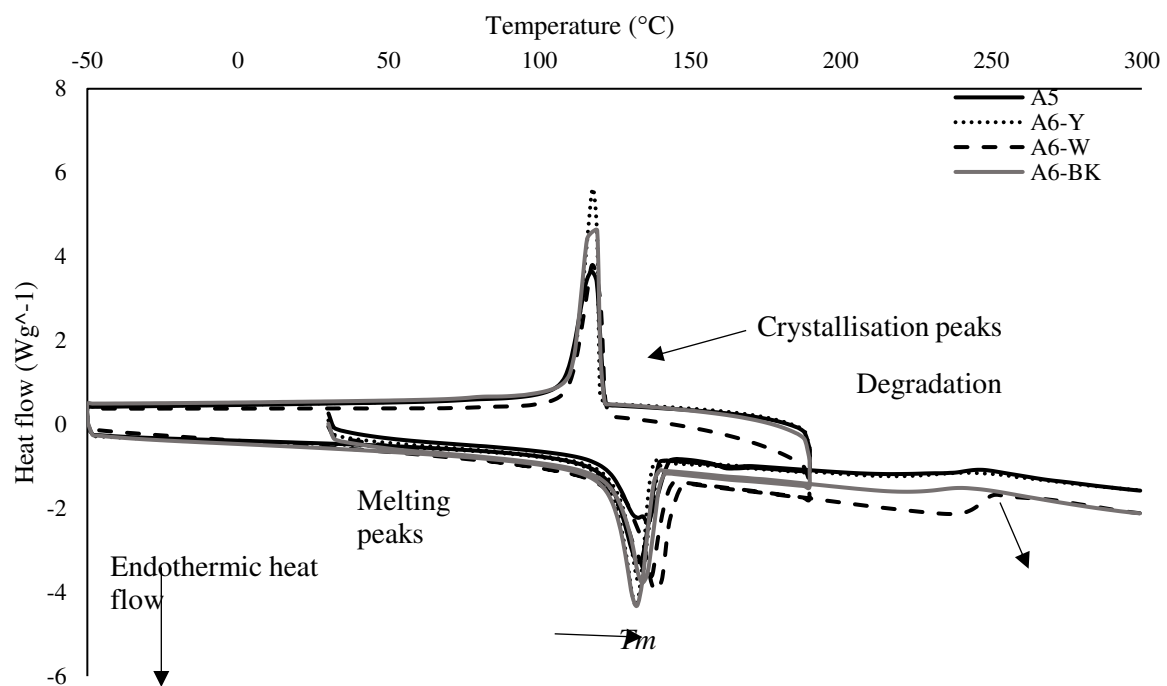


Figure 13: DSC test result for the recycled polymers A5 and A6, having masses of 5.1 to 5.7 placed in open-lid crucibles, tested in nitrogen gas cell at temperatures range of (-50 – 300 °C), with a constant temperature rate of 10 °C/minute.

The FT-IR results for the recycled polymer A5 and A6 samples (listed in Table 3) were all identical (shown in Figure 14); this indicates these materials were manufactured from one type of polymer. By comparing the absorption peaks with the reference polymer absorption peaks, it was concluded that A5 and A6 are made of LDPE polymer. The DSC results displayed earlier further confirm that A5 and A6 plastics consist of LDPE polymer.

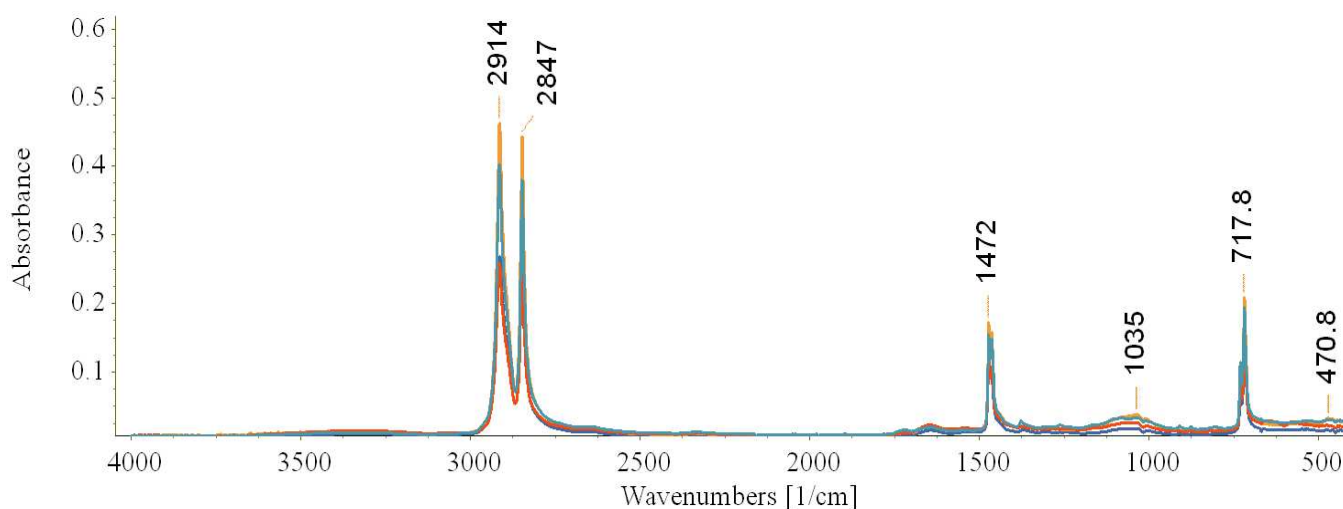


Figure 14: FT-IR test results for multiple samples from plastic-types A5 and A6 at a wave range of (4000-400) cm^{-1} showing the absorbance peaks.

5 THE RHEOLOGICAL AND MECHANICAL CHARACTERISATION OF WASTE PLASTICS-DERIVED BITUMEN

The FT-IR and DSC tests results for the selected recycled waste plastics were utilised to identify the plastics types and the thermal properties of the tested materials. It was found that the materials named A1 and A2 were consisting of low-density polyethylene (LDPE) and polypropylene (PP), respectively. Whereas, other recycled plastics (A3 and A4) were consisting of a variety of materials and impurities. Therefore, since A1 and A2 were completely characterised and were found to possess a melting point lower than 170 °C which can be reached in the pavement mixing plants without significant alteration to the standard practices, A1 and A2 were selected in the current study to modify the bitumen binder. Since the recycled waste plastics (A5 and A6) also consist of low-density polyethylene, then they were not considered in the study to avoid duplication of the materials.

The control bitumen X70 was mixed with 6 % of A1 and A2, and the mixture was characterised by using DSR testing schemes to measure the rheological properties and the engineering performance of the waste plastic-derived bitumen. The results are illustrated in the following sub-sections.

5.1 Viscoelastic properties of the waste plastic-modified bitumen

The frequency sweep test helps to determine the degree of viscosity and elasticity in the modified bitumen binders at undamaged loading conditions. The selected temperature variation for all the tested samples is between 10-70 °C and loading frequency in the range 0.1-25 Hz respectively. Figures 15 (a, b and c) shows the phase angle versus loading frequency for the control binder X70, the A1- and A2-waste plastic modified binders, respectively. It can be observed that the addition of 6% A1 and A2 types waste plastic is causing the phase angle to decrease when compared to the control sample. Therefore, the waste-plastic is acting more towards the elastic material. This trend of the waste plastic-modified bitumen to have more elastic behaviour is somehow expected when tested at a temperature lower than the melting point for these plastic compounds.

Figure 16 shows the TTSP generated master curves for the complex shear moduli of the control bitumen X70, A1- and A2-waste plastic-modified samples. It can be observed that the shear modulus of A1-modified bitumen experienced less sensitivity to frequency and a higher shear modulus at low frequencies compared with the control sample X70. Since the shear modulus experience slight increase for A1-modified bitumen, while, the phase angle experienced a small drop, therefore it is expected that A1-modified bitumen will have higher rutting resistance ($G^*/\sin \delta$) and stiffer behaviour compared to the control binder. Whereas, the A2-modified bitumen sustained a similar shear modulus-frequency relationship to that for the X70 control sample but with overall slightly lower stiffness represented by a general decline in the shear moduli. The reason for the slight drop in the shear modulus of A2-modified bitumen while maintaining a lower phase angle compared to the control binder is not clear. Subsequently, the effect of this change on the fatigue, rutting and healing of bitumen is not clear and will need further testing. Nonetheless, it can

indicate a lower resistance to fatigue (by considering the fatigue parameter $G^* \sin \delta$). Previous studies [14] proposed the inclusion of PP plastic to bitumen will work as an elastomeric additive, expecting to achieve increased recovery capacity, but less resistance to deformation. Therefore, the following sections will further investigate the performance properties.

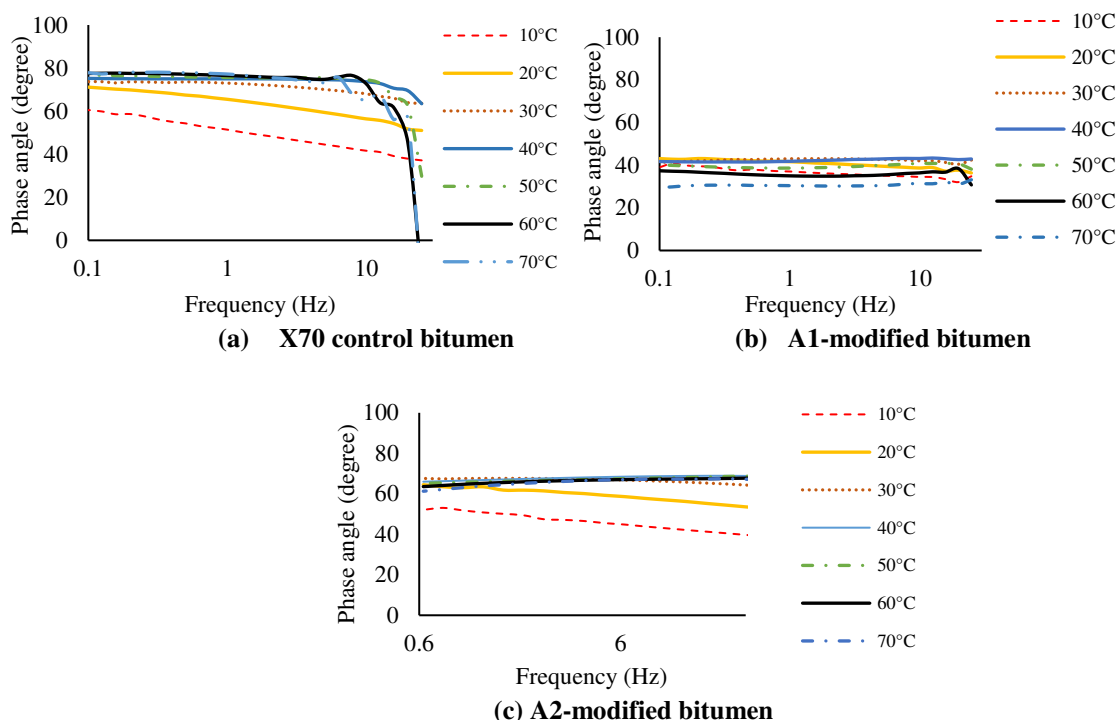


Figure 15: Frequency sweep test results for (a) X70 control bitumen; (b) A1-modified bitumen and; (c) A2-modified bitumen. The test is conducted at 10 to 70 °C with a loading frequency of 0.1-25 Hz.

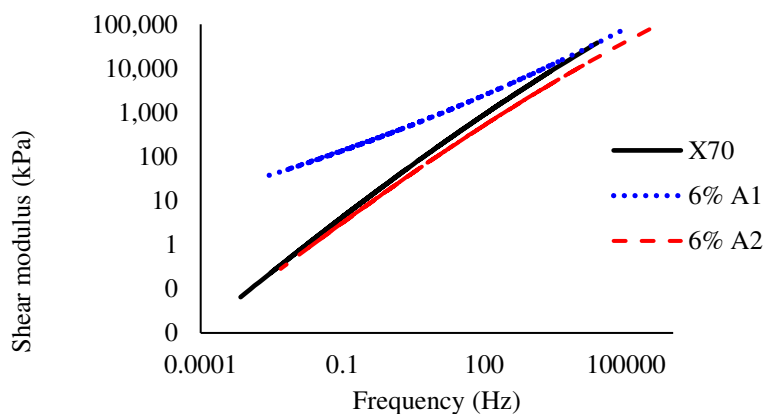


Figure 16: Shear modulus master curves calculated by using the time-temperature superposition principle for the frequency sweep test for the X70 control bitumen sample, A1- and A2-modified bitumen samples.

5.2 Fatigue-resistance performance

In order to evaluate the fatigue performance effectively, DSR records the viscoelastic parameters (i.e. shear modulus and phase angle) with the progression of time in the TS testing scheme. By selecting the appropriate conditions for the DSR parameters, the fatigue performance can be examined. e.g. strain level of 5%, frequency of 10 Hz and an intermediate temperature of 20 °C. Figure 17 shows the TS results for A2-modified bitumen. The shear modulus shows a sharp initial decrease until it stabilises with a slow rate of decrease following the initial stage, this behaviour can be attributed to the fatigue cracking stages that the sample experience when subjected to fatigue load. Where the initial stage is caused by the ‘edge flow’ occurring in the sample [31, 32].

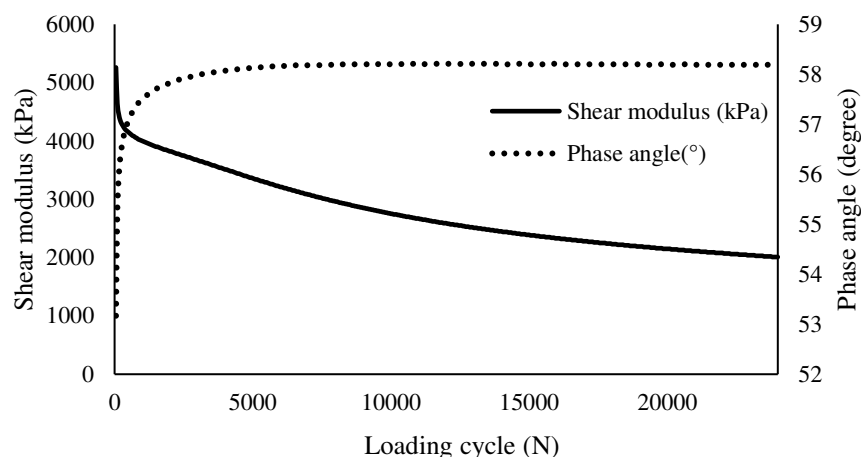


Figure 17: Time sweep (TS) test results for A2-modified bitumen (bitumen with 6% A2). The test is conducted at 20 °C temperature, 10 Hz loading frequency, 5% strain level, and up to 24,000 loading cycles.

Figure 18 illustrates the shear modulus results of the bitumen samples X70, A1- and A2-modified bitumen obtained from tests. It can be seen that A2-modified sample and control bitumen sample have similar initial shear modulus, so this enables cross-comparison. However, the reduction in shear modulus as the loading cycle increase is more prominent with the control bitumen X70. More specifically, X70 Bitumen showed a faster decrease in shear modulus, while A2 shows a gradual regression. This behaviour suggests the addition of A2 to bitumen is useful to improve the fatigue cracking resistance because it results in a lower energy dissipation through crack formation, so a lower percentage of damage accumulates. Whereas, the inclusion of A1 exerts the steepest decline in comparison to the control and A2-modified bitumen. It can be observed that there is a large reduction in the initial shear modulus and then a gradual decline. However, it becomes difficult to determine the true difference between the shear modulus of A1-modified sample and control bitumen because a large variation exists in the initial shear modulus.

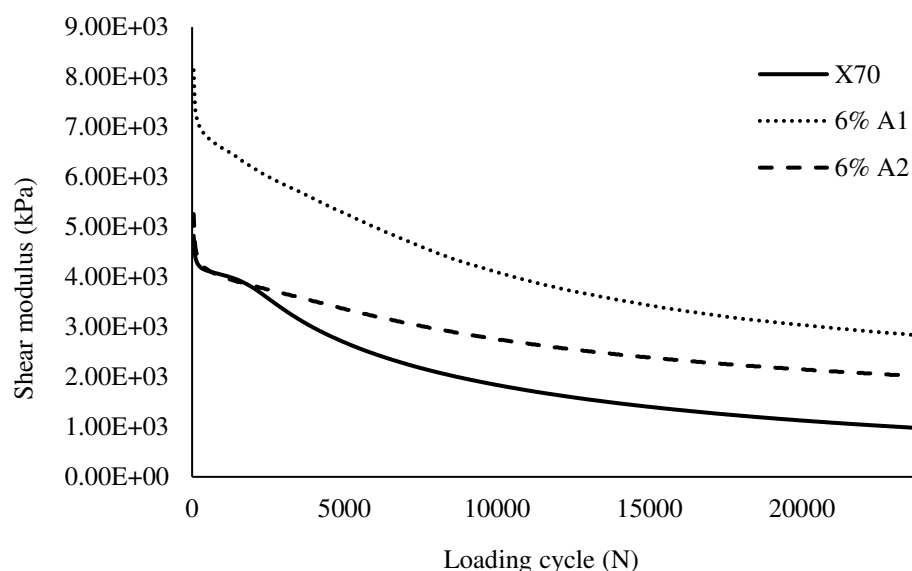


Figure 18: Time sweep test results showing the shear modulus vs loading cycle for bitumen X70, A1- and A2-modified bitumen

Figure 19 represents the phase angle obtained from the TS test for X70 bitumen, A1- and A2-modified bitumen samples. The A2-modified sample has a lower phase angle across the loading cycles and therefore, a greater ability to resist fatigue damage in comparison to the control sample X70. However, with A1-modified sample, it becomes difficult to compare as the phase angle during the initial loading cycle is significantly different. The initial phase angle value for A1-modified sample is 43.24 °, but for X70 bitumen it is 58.19 °. Nevertheless, a low initial phase angle value implies a better fatigue performance. Generally, there is an improvement in the fatigue resistance with the addition of plastic binders.

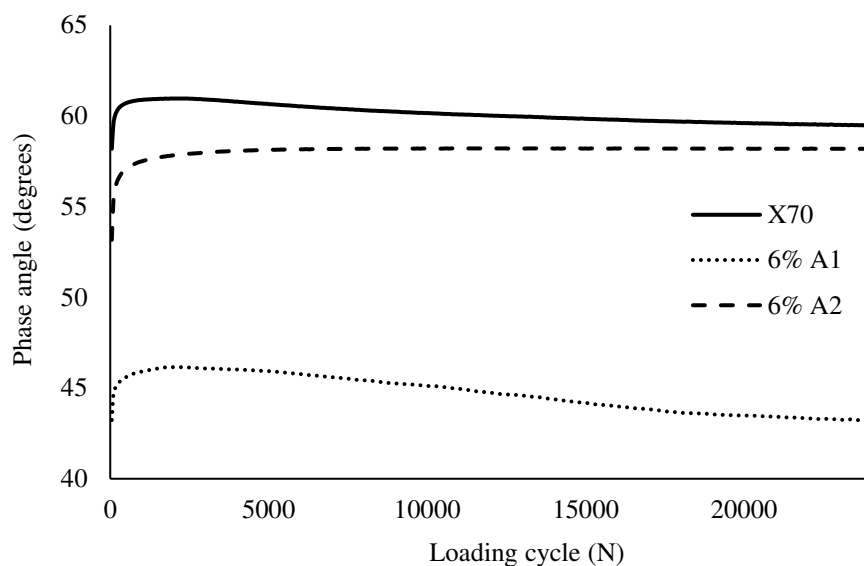


Figure 19: Time sweep test results showing the phase angle versus loading cycle for bitumen X70, A1- and A2-modified bitumen

To allow effective comparison of the results, the time sweep data were utilised to obtain the DSR-Crack Growth (DSR-C) graph which demonstrates how asphalt binders crack under the rotational shear test using shear modulus and phase angle (computed by the DSR-C method in Eq. 1). The undamaged and damaged conditions provide the measurement of the crack growth and the extent of fatigue damage undertaken by the TS test for all three asphalt binder samples. Figure 20 shows the crack length development with the loading cycles for all the tested samples. Generally, there is a major difference in the crack length for X70 bitumen and plastic modified samples.

Moreover, the cracking length for A1- and A2-modified samples are very similar, suggesting they acquire similar fatigue resistance properties. The cracking lengths for the waste-plastic modified samples are also much lower compared to the conventional control sample, representing they have a low susceptibility to cracking, therefore, help to prolong the fatigue life of the pavement. Additionally, it can be seen that at lower number of loading cycles ($n < 3000$ loading cycles) the initial crack length is higher for A1- and A2-modified samples. This initial cracking behaviour, if considered alone (i.e., by examining the results of undamaged TS test or frequency sweep test) can be misleading. Therefore, a fatigue test was employed to examine the fatigue behaviour accurately.

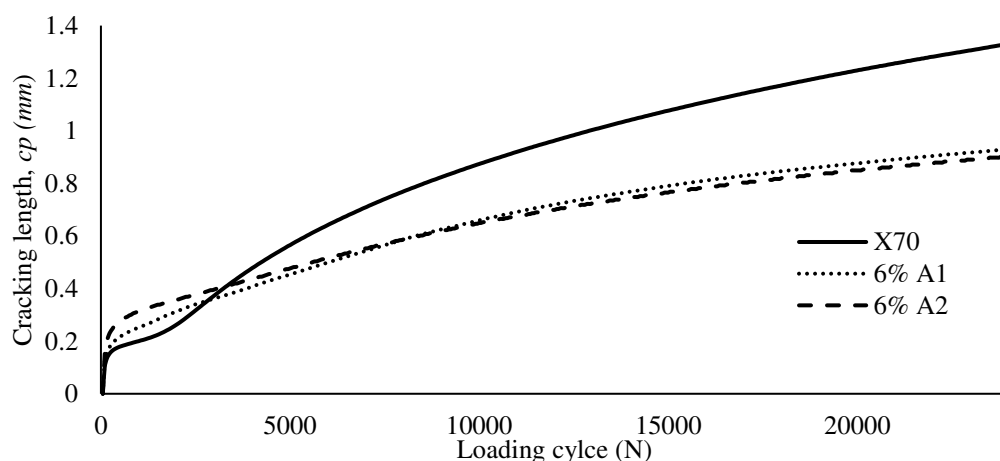


Figure 20: The crack length propagation under time sweep (TS) test conditions for bitumen X70, A1- and A2-modified bitumen. The crack lengths are calculated using DSR-C method.

5.3 Self-healing performance

Figure 21 demonstrates the healing results of all the tested samples, in which the samples are subjected to two constitutive time sweep tests separated by a rest (recovery) period. This DSR-testing scheme characterises self-healing of bitumen as the recovery of the stiffness when the binder is inclined to damage created by cyclic fatigue

loading. It can be observed from Figure 21 that the samples experienced a partial recovery in the second run of TS tests, and the second run of results have a less defined steepness curve in comparison to the first run.

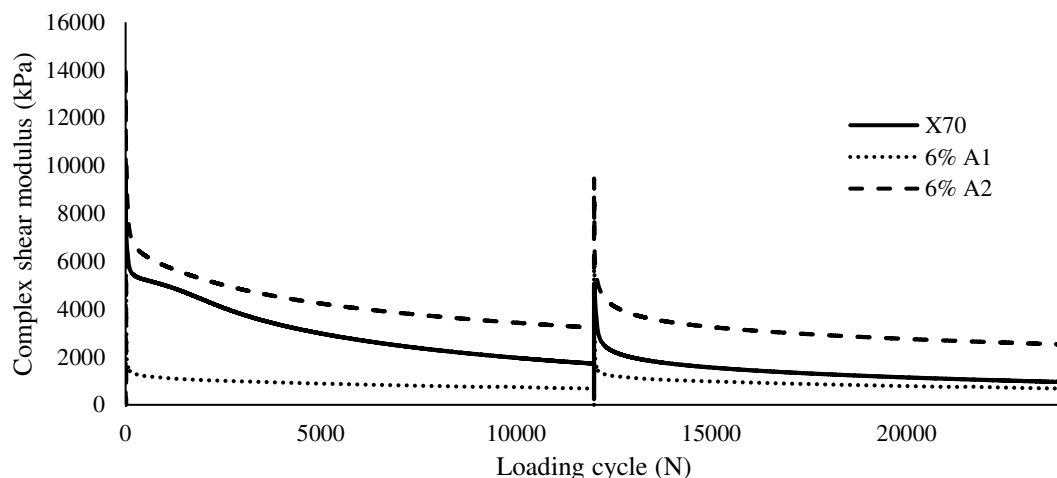


Figure 21: Healing test results showing the shear modulus versus loading cycles for the control bitumen sample X70, A1- and A2-modified bitumen samples

In order to quantify healing to a greater extent, the differences of the shear modulus before and after healing can be considered for the tested asphalt binders. The healing potential of the control bitumen X70, A1- and A2-modified bitumen was evaluated using the Healing Index (HI), illustrated earlier in Eq. 2. A better healing potential will have a higher HI value. It was found that the healing indices for all three samples are 65.80, 65.86 and 88.61 for A2-modified bitumen, X70 control samples and A1-modified bitumen, respectively. This finding highlights that some recycled waste plastics have greater healing potential (i.e., LPDE) while some do not (i.e., PP), in comparison to the base binder.

This indicates the LDPE-recycled plastic has a better built-in capability to recover microcracks; therefore, it can improve the durability of the bitumen binders. Additionally, PP-modified bitumen had almost an identical healing potential to that of the original binder X70. Therefore, using the recycled waste plastic A2 into X70 bitumen does not enhance the fatigue-healing efficiency.

5.4 Rutting-resistance performance

MSCR tests were conducted on the control bitumen sample X70, A1- and A2-modified binders at a temperature of 60 °C. The non-recoverable compliance (J_{nr}) and percentage recovery were plotted against all tested samples for comparison in Figures 22 and 23, respectively.

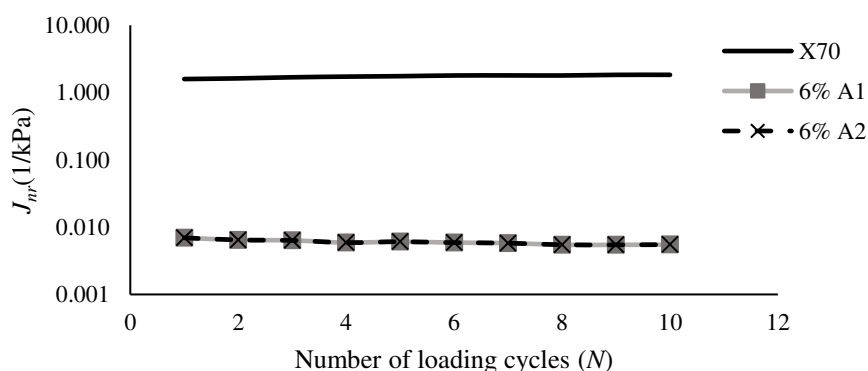


Figure 22: J_{nr} results for bitumen sample X70, A1- and A2-modified bitumen samples

It can be observed from Figure 22 that A1- and A2-modified bitumen acquire very similar J_{nr} values, so there is a similar expectation for their rutting performance. The J_{nr} values for both recycled waste plastics suggests that the plastic-modified binders can lead to a significant improvement in the high-temperature rutting performance in comparison to X70 bitumen as the J_{nr} values are comparably lower.

Figure 23 outlines the results for the percent recovery of the control bitumen sample X70, A1- and, A2-modified bitumen samples. The percent recovery indicates the delayed elastic response of an asphalt binder; therefore, it is desirable to obtain a higher percent recovery to reduce the rutting failure potentials. From the examination of the results, it was observed that the recovery of X70 bitumen is relatively poor. Whereas, the plastic-modified binders have a substantially improved rutting resistance as there is an enhancement of the % recovery. Concerning both A1- and A2-modified binders results, the recovery has improved by 8% and 24% respectively across the loading cycles 1 to 10 N, thus supporting the above trend.

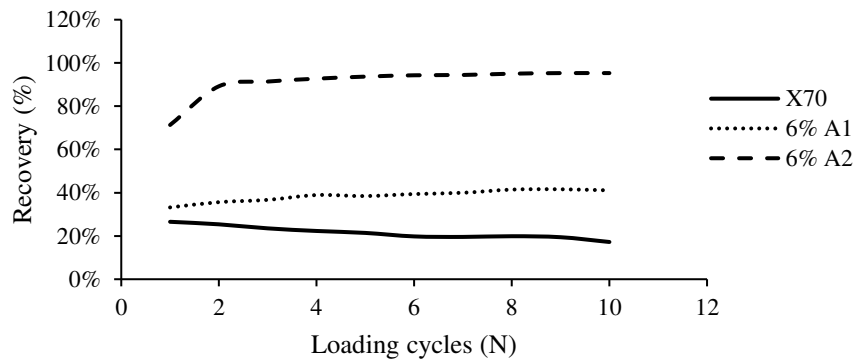


Figure 23: Percentage recovery results for bitumen sample X70, A1- and A2-modified bitumen samples

6 Conclusions

The use of plastics in the manufacturing of flexible pavements helps to consume large quantities of plastic wastes and reduces the demands for producing petroleum-based bitumen. Therefore, the current study aims to investigate the chemical and physical characteristics of the plastics wastes produced by local waste recycling manufacturers and their effect on the bitumen binder when mixed, in order to investigate their feasibility in modifying the bitumen binders. Six waste-plastic types which are being produced in great quantities by a local waste plastic-recycling supplier were tested. Then, two types were nominated for bitumen modification. A series of rheological and mechanical tests were conducted on the waste-plastic modified bitumen. The conclusions are summarised as follows:

- 1- The materials named A1 and A2 were consisting of low-density polyethylene (LDPE) and polypropylene (PP), respectively. Whereas, other recycled plastics (A3 and A4) were consisting of a variety of materials and impurities. The A1 and A2 were selected in the current study to modify the bitumen binder, as they have a melting point lower than 170 °C which can be reached in the pavement mixing plants without significant alteration to the standard practices. Since A5 and A6 also consist of low-density polyethylene, then they were not considered in the study to avoid duplication of the materials, although it can also be utilised for the modification of bitumen binders.
- 2- The plastic-modified samples examined in this study have significantly altered the viscoelastic behaviours of the bitumen binders. The A1-modified bitumen (mainly consists of LDPE) exhibited more elastic and less viscous performance compared to the control bitumen, showed by increased shear modulus and reduced phase angle. Whereas, the A2 (mainly consists of PP) reduced the shear modulus significantly for the control bitumen.
- 3- The plastic-modified binders (A1 or A2-modified bitumen) both have a substantially improved rutting resistance as there is an enhancement of the % recovery and a reduction in the non-recoverable strain compliance J_{nr} . In comparison, the A1 led to an increased healing potential to the bitumen while the A2 did not show obvious improvement to the healing performance of the bitumen.
- 4- The addition of plastic modified bitumen has improved fatigue performance. The cracking lengths for the waste-plastic (A1- and A2-modified) bitumen are much lower compared to the control bitumen, representing they have a low susceptibility to cracking, therefore, help to prolong the fatigue life of the pavement. The cracking length for the two-waste plastic modified bitumen is very similar, suggesting they acquire a similar fatigue resistance property.

The focus of this study was on the thermal and chemical characterisation of several locally-produced recycled waste plastics for the use in asphalt pavements. Additionally, the study compared the preliminary mechanical performance of two waste plastic-modified bitumen at the unaged condition. Therefore, further tests are being conducted to examine the after-mixing and processing field performance, and the long-term performance in the field of the waste-plastic modified bitumen and asphalt mixtures. Generally, the use of recycled PP and PE materials in the pavement industry is promising, particularly since the production of PP and PE make more than 50% of the nonfiber plastic production.

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REFERENCES

- [1] Bale, A.S., 2011. Potential reuse of plastic waste in road construction: a review. *International Journal of Advances in Engineering & Technology (IJAET)*, 2, pp.233-236.
- [2] Sen, T. and Mishra, U., 2010. Usage of Industrial Waste Products in Village Road Construction. *International Journal of Environmental Science and Development*, 1(2), p.122.
- [3] Gawande, A., Zamare, G., Renge, V.C., Tayde, S. and Bharsakale, G., 2012. An overview on waste plastic utilization in asphaltting of roads. *Journal of Engineering Research and Studies*, 3(2), pp.01-05.
- [4] Huang, Y., Bird, R.N. and Heidrich, O., 2007. A review of the use of recycled solid waste materials in asphalt pavements. *Resources, conservation and recycling*, 52(1), pp.58-73.
- [5] Geyer, R., Jambeck, J.R. and Law, K.L., 2017. Production, use, and fate of all plastics ever made. *Science advances*, 3(7), p.e1700782.
- [6] PlasticsEurope (2018). An analysis of European plastics production, demand and waste data. Plastics - the Facts 2018. PlasticsEurope.
- [7] Zoorob, S.E. and Suparma, L.B., 2000. Laboratory design and investigation of the properties of continuously graded Asphaltic concrete containing recycled plastics aggregate replacement (Plastiphalt). *Cement and Concrete Composites*, 22(4), pp.233-242.
- [8] Gawande, A., Zamre, G.S., Renge, V.C., Bharsakale, G.R. and Tayde, S., 2012. Utilization of waste plastic in asphaltting of roads. *Scientific Reviews & Chemical Communications*, 2, pp.147-157.
- [9] Hınıslıoğlu, S. and Açar, E., 2004. Use of waste high density polyethylene as bitumen modifier in asphalt concrete mix. *Materials letters*, 58(3-4), pp.267-271.
- [10] Ahmadinia, E., Zargar, M., Karim, M.R., Abdelaziz, M. and Shafigh, P., 2011. Using waste plastic bottles as additive for stone mastic asphalt. *Materials & Design*, 32(10), pp.4844-4849.
- [11] Chavan, M.A.J., 2013. Use of plastic waste in flexible pavements. *International Journal of Application or Innovation in Engineering and Management*, 2(4), pp.540-552.
- [12] Moghaddam, T.B., Karim, M.R. and Syammaun, T., 2012. Dynamic properties of stone mastic asphalt mixtures containing waste plastic bottles. *Construction and Building Materials*, 34, pp.236-242.
- [13] Costa, L.M., Hugo, M.R., Silva, D., Oliveira, J.R. and Fernandes, S.R., 2013. Incorporation of waste plastic in asphalt binders to improve their performance in the pavement. *International journal of pavement research and technology*, 6(4), pp.457-464.
- [14] White, G. and Reid, G., 2019, June. Recycled waste plastic modification of bituminous binder. In *Bituminous Mixtures and Pavements VII: Proceedings of the 7th International Conference 'Bituminous Mixtures and Pavements' (7ICONFBMP), June 12-14, 2019, Thessaloniki, Greece* (p. 3). CRC Press.

- [15] Fini, E.H., Kalberer, E.W., Shahbazi, A., Basti, M., You, Z., Ozer, H. and Aurangzeb, Q., 2011. Chemical characterization of bio-binder from swine manure: Sustainable modifier for asphalt binder. *Journal of Materials in Civil Engineering*, 23(11), pp.1506-1513.
- [16] Mashaan, N.S., Ali, A.H., Karim, M.R. and Abdelaziz, M., 2011. Effect of crumb rubber concentration on the physical and rheological properties of rubberised bitumen binders. *International journal of the physical sciences*, 6(4), pp.684-690.
- [17] Seidel, J.C. and Haddock, J.E., 2014. Rheological characterization of asphalt binders modified with soybean fatty acids. *Construction and Building Materials*, 53, pp.324-332.
- [18] Sun, Z., Yi, J., Huang, Y., Feng, D. and Guo, C., 2016. Properties of asphalt binder modified by bio-oil derived from waste cooking oil. *Construction and Building Materials*, 102, pp.496-504.
- [19] Yang, X. and You, Z., 2015. High temperature performance evaluation of bio-oil modified asphalt binders using the DSR and MSCR tests. *Construction and Building Materials*, 76, pp.380-387.
- [20] Fernandes, S., Peralta, J., Oliveira, J., Williams, R. and Silva, H., 2017. Improving asphalt mixture performance by partially replacing bitumen with waste motor oil and elastomer modifiers. *Applied Sciences*, 7(8), p.794.
- [21] Jung, M.R., Horgen, F.D., Orski, S.V., Rodriguez, V., Beers, K.L., Balazs, G.H., Jones, T.T., Work, T.M., Brignac, K.C., Royer, S.J. and Hyrenbach, K.D., 2018. Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms. *Marine pollution bulletin*, 127, pp.704-716.
- [22] Kim, Y.R., Little, D.N. and Lytton, R.L., 2003. Fatigue and healing characterization of asphalt mixtures. *Journal of Materials in Civil Engineering*, 15(1), pp.75-83.
- [23] Hintz, C., Velasquez, R., Johnson, C. and Bahia, H., 2011. Modification and validation of linear amplitude sweep test for binder fatigue specification. *Transportation Research Record*, 2207(1), pp.99-106.
- [24] Marasteanu, M.O., Clyne, T., McGraw, J., Li, X. and Velasquez, R., 2005. High-temperature rheological properties of asphalt binders. *Transportation Research Record*, 1901(1), pp.52-59.
- [25] Zhang, Y. and Gao, Y., 2019. Predicting crack growth in viscoelastic bitumen under a rotational shear fatigue load. *Road Materials and Pavement Design*, pp.1-20.
- [26] D'Angelo, J., Kluttz, R., Dongre, R.N., Stephens, K. and Zanzotto, L., 2007. Revision of the superpave high temperature binder specification: the multiple stress creep recovery test (with discussion). *Journal of the Association of Asphalt Paving Technologists*, 76.
- [27] ASTM D7405-15, Standard Test Method for Multiple Stress Creep and Recovery (MSCR) of Asphalt Binder Using a Dynamic Shear Rheometer, ASTM International, West Conshohocken, PA, 2015, www.astm.org
- [28] Bhasin, A., Little, D.N., Bommavaram, R. and Vasconcelos, K., 2008. A framework to quantify the effect of healing in bituminous materials using material properties. *Road Materials and Pavement Design*, 9(sup1), pp.219-242.
- [29] Shen, S., Chiu, H.M. and Huang, H., 2010. Characterization of fatigue and healing in asphalt binders. *Journal of Materials in Civil Engineering*, 22(9), pp.846-852.
- [30] Mutlur, S., 2004. Thermal analysis of composites using DSC. *Adv. Top. Charact. Compos*, pp.11-33.
- [31] Anderson, D.A., Le Hir, Y.M., Marasteanu, M.O., Planche, J.P., Martin, D. and Gauthier, G., 2001. Evaluation of fatigue criteria for asphalt binders. *Transportation Research Record*, 1766(1), pp.48-56.

- [32] Keentok, M. and Xue, S.C., 1999. Edge fracture in cone-plate and parallel plate flows. *Rheologica acta*, 38(4), pp.321-348.