

# Asphalt – Polymer Blends: Leverage of Chlorine Gas on the Topography, Thermal Stability and Fuel Resistance

Shaymaa S.A. Al-Mutlaq<sup>1a</sup>, Faridah Sonsudin<sup>b</sup> Ehab S.A. Mahal<sup>a</sup>, Rosiyah Yahya<sup>a</sup>

**Abstract** -- This paper evaluates the fuel resistance and the morphology of the asphalt physio-chemically modified using waste polymer namely high density polyethylene and chlorine gas. Different percentages (2%, 4%, 6% and 8%) of the waste polymer were used in the preparation of the asphalt blends followed by chlorination. Modified standard procedure was used to examine the solubility of asphalt blends in leaded petroleum kerosene while the morphology of the asphalt blends was characterized using optical microscope and the topography of these blends was computed by the aid of software. The obtained results showed that chlorination significantly reduces the asphalt solubility in the kerosene. It was also found that the new topographic method applied to identify the asphaltic blends further and to determine the homogeneity were clearly effective. The thermal stability has been improved for all samples. The dynamic shear rheometer outlined significant improvement in the viscoelasticity as well as the stiffness of the modified samples in compare to the original binder. Observing absorption band at  $668\text{ cm}^{-1}$  in the Fourier Transform Infra-Red spectroscopy disclosed that the chlorine was introduced to asphalt binder matrix chemically meaning no phase separation may expect; in one word the modified samples tend to be more stable.

**Keywords:** Fuel resistant, solubility, kerosene, morphology, topography, thermal analysis

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<sup>1</sup> Corresponding author: phone: +60173085710, fax: +60379677185; shaymaasultan75@yahoo.com (Shaimaa Al-Mutlaq)

a) Department of Chemistry, Faculty of Science, University of Malaya, 50603, Kuala Lumpur, Malaysia

b) Chemistry Division, Centre for Foundation Studies in Science, University of Malaya, 50603, Kuala Lumpur, Malaysia

## 1. Introduction

Enormous volumes of plastic wastes are being generated from household and agricultural wastes, e.g., plastic bottles, containers and packaging, and it is feasible for some of this material to be incorporated into asphalt as an aggregate replacement. The type of plastics/polymers most suited for use in asphalt is olefins such as LDPE and HDPE. Although the infrastructure does not currently exist to provide these materials in bulk, changes in waste management regulation mean that these waste streams are likely to become more refined in future to enable applications in downstream markets such as asphalt to avoid landfill disposal costs [1].

Recycling waste materials serves a much-needed purpose of eliminating an expensive and environmentally unacceptable solid waste disposal problem for those products. At present, considering the risks associated with landfilling of waste materials and the disposal problem, researchers are finding ways of incorporating recycled materials into asphalt pavements that have brought about action throughout the world [2]. Though using virgin additives can improve asphalt characteristic mixtures, it will increase road construction cost. So, in recent years many investigations have been conducted on asphalt cement (AC) mixtures containing waste materials as additives. Using waste materials as secondary materials in road pavement would reduce road construction cost in one hand, and in other hand it would be a solution to decrease environmental pollution. Effects of adding different types of waste materials on AC mixtures have been investigated in asphalt pavement. Among these waste materials, waste plastics or/and polymers, had a noticeable usage in asphalt mixture as aggregate replacement, binder modifier or mixture reinforcement [3, 4].

HDPE has been shown to enhance the elastic properties of bitumen binder at high temperatures, in the region where permanent deformation can affect the pavement service and provides better adhesion between the asphalt and the aggregate [5, 6]. Waste HDPE-modified bituminous binders gave rise to better resistance against permanent deformations due to their high stability and high Marshall Quotient and it contributes to recirculation of plastic wastes as well as to protection of the environment [7]. Meanwhile, the dynamic elastic modulus remained approximately constant (degraded slowly) for most specimens up to the end of fatigue life [8, 9]. Significant differences in the rutting properties of asphalt binders and asphalt matrix at higher temperatures and frequency loading have been noticed, but elastic resilience found to show insignificant improvement [5, 6, 10-14].

Most past studies prefer to use reasonable amount of polymer (1-5%) as a customary optimum blend mix; the addition of recycled HDPE up to a 5% addition to bitumen has been found to enhance the conventional and morphological properties of the modified binder prepared in high shear laboratory mixer as well as the level of performance and the service life of the road [15-17].

This paper analyzes the effect of using chlorine on the compatibility and the fuel resistancy of the asphalt being modified simultaneously with waste high density polyethylene as a way to produce compatible and stable binders. The test conditions used to evaluate binder's performance were solubility, thermal stability by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), Fourier Infra-Red spectroscopy to prove the chemical addition of the chlorine to the asphalt binders, and the strain sweep using dynamic shear rheometer as a tool to determine the viscoelasticity and the stiffness of the asphalt binders in addition to the empirical asphalt tests (softening point, penetrability and ductility) and the optical microscopy. The topography of the optical micrographs was used for the first time to explore the morphology further.

## 2. Materials and Methodology

### 2.1. Materials

#### 2.1.1. Asphalt

Petroleum asphalt (Petronas Berhad – Malaysia), has been used in this study and its physical properties are presented in Table 1.

**Table 1**  
**Characteristics of the original asphalt**

Characteristics	Original asphalt
Softening point, °C (ASTM D36-95)	50
Penetration, 0.1mm, 25°C (ASTM D5 – 97)	90
Ductility, cm, 25°C (ASTM D113 – 99)	100
Flash point, °C, (Min) (ASTM D92 – 02b)	276
Solubility in Kerosine, % (ASTM D 4 – 86)	100
Specific Gravity (ASTM, D70-03)	1027

#### 2.1.2. Waste HDPE

Hawker HDPE plastic bags sold in retails shops were collected from domestic waste, and used without any pretreatment except resizing by shredding of the waste plastic bags manually, to pieces with dimension of 2 x 2 cm.

#### 2.1.3. Chlorine

Chlorine gas 100% (CCM Chemicals Sdn. Bhd.) was used for the chlorination of the asphalt-HDPE blends.

### 2.1.4. Kerosene

Petroleum Kerosene (Petronas Bhd, Malaysia) was used as received.

## 2.2. Methodology

### 2.2.1. Preparation of modified asphalt blends

Asphalt-polymer blends were prepared in a closed system (to prevent any excess of the chlorine gas or the generated HCl gas to escape to the environment) provided with digital thermometer (UNITEST – Therm 100) and heavy duty mechanical stirrer (IKA-RW 20 digital) as well as an energy source. The heating was started from above the softening point until the melt was soft enough for the stirring to start by the stirrer with a steady speed of 350 rpm. The heating was continued until the temperature reached 170°C; once the temperature had reached 170°C, addition of 2% waste shredded HDPE and chlorine gas (flow rate of about 0.5 ml min<sup>-1</sup> from the regulator) was introduced to the asphalt melt simultaneously. The heating temperature was maintained in the range of (170±1)°C for 2 h. After that the gas flow was discontinued and the contents heated at same temperature for 15 min to expel out any un-reacted chlorine and HCl. Then the viscous mixture was poured out into a metal container and left to cool for the later characterizations. This procedure was repeated using 4%, 6% and 8% of shredded waste PE additions. These blends are referred as CPEA.

### 2.2.2. Testing of the asphaltic blends

The softening point of the neat and modified asphalts was performed according to ASTM D36 – 95 [18]. The penetration test was carried out at 25°C according to ASTM D5 – 97 [19] and finally the ductility test was performed according to the method of ASTM, D113 – 99 [20].

The solubility was tested in accordance to ASTM designation D4 using petroleum kerosene as a solvent [21]. For morphology characterization, micrographs using optical microscope (Olympus Binocular CX21 BIM) were taken using a photo camera (Kodak AF 3x Optical Aspheric Lens, 34 mm-102 mm, HD Stills, 8.2 MP).

The FTIR spectra for solid asphalt samples were recorded at 4 scans and 4 cm<sup>-1</sup> of resolution using a Perkin-Elmer Spectrum 400 FT-IR Spectrometer.

The rheology measurement was carried out using Anton Paar Physica MCR 301 Dynamic Shear Rheometer. A strain sweep was conducted to determine the flow behavior for the modified asphalt. Measurements were performed at temperatures of 46, 52, 58, 64, 70, 76 and 82°C with an amplitude gamma range from 0.01 to 100 % at 10 rad/s. The complex shear modulus G\* and the phase angle were determined and used to evaluate the viscoelasticity and the stiffness of the asphaltic blends.

Thermo-gravimetric (TGA) analysis was conducted to evaluate the thermal stability of the asphaltic blends. Measurements were recorded using Thermo-gravimetric Analyzer Perkin-Elmer TGA 4000 from room temperature up to 800°C with inlet flow of nitrogen gas at 20 cm<sup>3</sup> min<sup>-1</sup> and at a heating rate of 20°C min<sup>-1</sup>.

Differential Scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC 6 calibrated with indium for the temperature and enthalpy. A typical DSC measurement was conducted on about 10 mg sample sealed in an aluminum sample pan similar to that of the empty pan with cap as a reference. Each sample was heated from 30 to 250°C at 10°C/min.

## 3. Results and Discussion

### 3.1. Empirical tests results

Polyethylene modified asphalt chlorinated blends, CPEA, was obtained by physical mixing the asphalt in a closed system using 2%, 4%, 6% and 8% HDPE at 170°C for 2 h in the presence of high purity chlorine gas. The resulted blends have been physically tested through the empirical asphalt tests and the obtained data of the asphaltic blends are tabulated in Table 2.

The softening point results are shown to increase to a higher value of 126°C when the addition of the HDPE was 8%. The increase in the softening point was reported previously but not to this

**Table 2**  
**Physical properties of Chlorinated CPEA blends**

PE %	Softening point °C	Penetration 25°C, 0.1mm	Ductility cm	Solubility in kerosene (w/w) %	PI
0	50	90	100	95.05	0.3626
2	92	22	3.5	25.9	3.8888
4	94	26	3	60.2	4.4578
6	96.5	20	2	59.3	4.1509
8	126	15	2	27.95	6.1290

temperature [15]; this could be due to the changing in the maltenes and asphaltenes contents in the asphalt. When the maltene oil content of the bitumen is high, the molecules of the bitumen components move freely and consequently the system is fluid-like. As for the effect of heat in the presence of chlorine, the added chlorine reacts with certain amount of maltene molecules, which leads the system of maltene oils to coagulate and condense. It can be concluded that the chlorination has additionally enhanced the softening temperature of asphalt, thus improving its high temperature stability [15, 22].

Generally, small molecular components in asphalt will be reduced as a result of the effect of physical absorption when bulk materials like polymers are added, thus the asphalt hardens and its penetration decreases. The decrease in the penetration means that the consistency of asphalt increases as a result of the interactions between the chlorine, HDPE and the components of the asphalt. Further explanation can be due to the increase of paraffinic contents of asphalt and thus the viscosity of the blends increased. It is known that the chlorinated paraffins are typically viscous oils with low vapor pressure [23] and because of the increase of light constituent due to PE addition, the chlorination takes effect and thus increase the chlorinated paraffinic constituents leading to the blends becoming more viscous and making the mixtures harder. At this point, the chlorinated blends are viscous (sol-like) asphalt [22-25].

The temperature susceptibility which is normally referred to by using the penetration index, PI, is characteristic of bitumen [26], and is defined as:

$$PI = [(20\ 500A) / (1+50A)] \dots\dots\dots (1)$$

Where

$$A = [(\log Pen @ T - \log 800) / (T - T_{R\&B})] \dots\dots\dots (2)$$

The PI data of the asphalt blends calculated using equation (1) are shown in Table 2. The PI has improved in all the samples which mean that the asphalt susceptibility to changes in the temperature has increased. This is more preferable in the construction of road pavement as it reflects a good resistance to the loading and deformation [11]. On the other hand, Table 2 shows that the ductility in the chlorinated blends has decreased severely and then remained constant from the lesser content of the HDPE, to the higher contents. This is more understandable because chlorination gives more solid or more brittle products. Our explanation is that the addition of the HDPE increases the molecular weight of the samples and thus the viscosity also follows the same trend. This resulted in less diluted medium of the asphaltene-maltene, thus producing solid samples.

### 3.2. Solubility in Kerosene

Table 2 shows that the solubility of the CPEA blends has been increasingly improved with an exception of CPEA-4% which shows a slight decrease in the solvent (kerosene) resistance. Almost similar results were obtained for the asphalt modified with polymer using crumb rubber [27]. The results in the latter showed improvement in the solubility of the asphalt blends but not accompanied by similar improvements in the other properties which differs

certainly from our results which show a respected improvements in most of the physical and thermal properties revealing the benefit of our treatment. The reduction in solubility is probably a consequence of the absorption of the lighter, and essentially kerosene soluble, bitumen fractions into the HDPE molecules [27, 28]. It is worth to mention that the decrease in the ability of chlorinated modified asphalt opens a potential application for such samples to be used in the fuel stations, chemical store and the like.

### 3.3. Morphology

#### 3.3.1. Optical micrograph results

It is well established that the bitumen/polyolefin blends exhibit a multiphase morphology where polymer-rich phases and bitumen-rich phases can be clearly distinguished [29-32].

Microscopic observations of the original asphalt as well as the chlorinated bitumens modified with 2%, 4%, 6%, and 8% waste HDPE are displayed in the figures, Fig. 1-5.

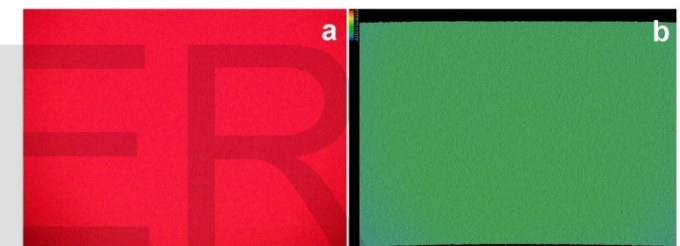


Fig. 1. (i) Microscopic observations of original asphalt; (ii) animation of the original asphalt optical micrograph.

It is shown from the photomicrograph that the CPEA shows an obvious improvement in the morphology and good distribution of the waste HDPE in the asphalt medium which definitely can be attributed to the effect of the chlorination. Consequently, the CPEA (Fig 2.i) exhibits a noticeable heterogeneity which appears as light spots spread (waste HDPE) in the dark medium (asphalt).

The micrographs of the CPEA blends with the waste HDPE addition of 4% shows a very good increase in the homogeneity which obviously can be observed from the well distributed waste

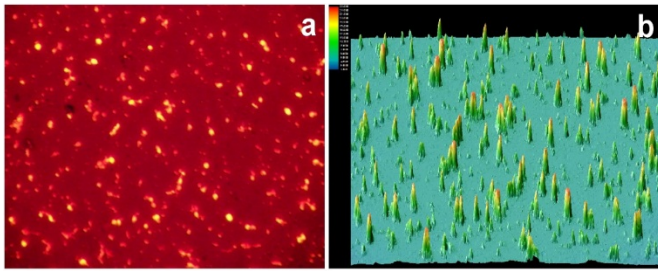


Fig. 2. (i) Microscopic observations of CPEA-2% blend; (ii) animation of the CPEA-2% optical micrograph.

HDPE within the asphalt as can apparently be seen from the changes in the light portions of the asphalt blends (Fig 3.i); same trends are observed in the last two additions of waste HDPE as shown in Fig 4.i and Fig 5.i.

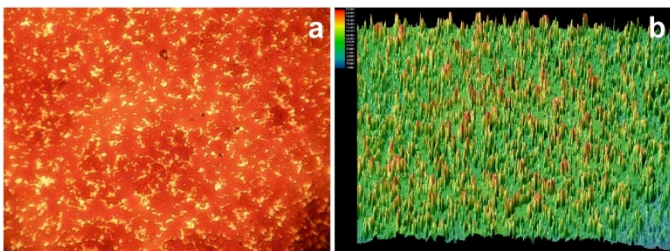


Fig. 3. (i) Microscopic observations of CPEA-4% blend; (ii) animation of the CPEA-4% optical micrograph.

It is worth to mention here that the micrographs of the additions of 6% and 2% waste HDPE for the CPEA blends are quite similar while the micrographs of the additions of 4% and 8% tend to have the same trend.

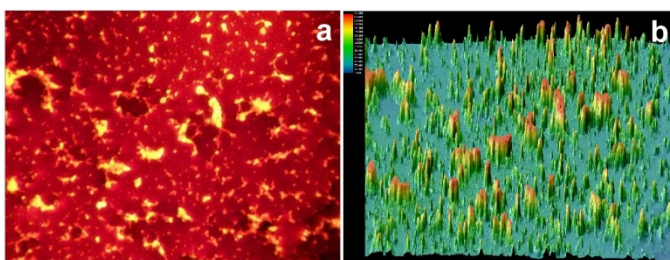


Fig. 4. (i) Microscopic observations of CPEA-6% blend; (ii) animation of the CPEA-6% optical micrograph.

As for the distribution of the polymer, the addition of 8% is the best among all samples but from an industrial point of view (with regards to the physical properties) CPEA samples of additions of 4% and 6% are preferred compared to others.

The change in the morphology from lower distribution to high or higher distribution (Fig. 3.i and 5.i) generally showed a narrow dispersion of bitumen droplets in a polymer-rich continuous phase. This feature is known as phase inversion, and it means that the compatibility of the polymer towards asphalt has increased and thus from

practical point of view, is significant for the roofing membrane where a continuous polymer-rich phase is routinely sought after [29, 31, 33].

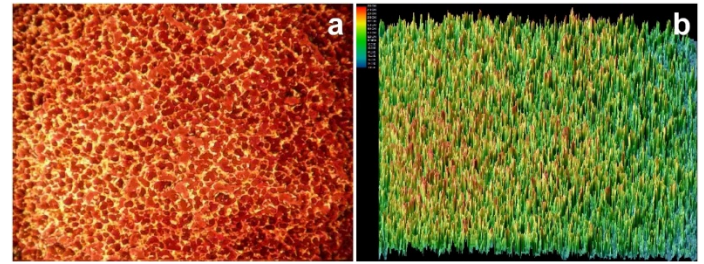


Fig. 5. (i) Microscopic observations of CPEA-8% blend; (ii) animation of the CPEA-8% optical micrograph.

The increase in the compatibility makes the polymer swelled by some of the lighter maltenic compounds and, therefore, the bituminous continuous phase is artificially enriched in asphaltenes by the so called "physical distillation process", leading to changes in the chemical composition of the matrix [29, 34].

The absorption of some bitumen compounds by the polymer can be confirmed by means of image analyses, which are shown in the Table 3. Therefore, the surface fraction occupied by the polymer phase increased beyond the proportion of polymer added for the bitumen modification. Taking into account that polymer and bitumen densities are quite similar, polymer swelling by maltenic compounds may be clearly deduced [5, 15, 29, 31, 33, 34].

### 3.3.2. Image Analysis - Surface Topography

Many researches have been published on surface topography [35] but according to our available knowledge none of them use our method to identify the asphaltic blends further and to determine the homogeneity clearly [35-37]. The data obtained from the surface topography are found to be interesting and can be developed in the future to become one of the effective characterization methods. However due to lack of references, we have to depend on the principles of this field of science.

The 3D-graph of the original asphalt (Fig. 1.ii), looks like a football stadium with soft surface. It is obvious that the surface is almost flat with perfect pores distribution on its surface, which in turn, reflects the low roughness of the surface or more specific its high homogeneity.

In comparison to the CPEA binder, the polymer phase forms an inter-connected three-dimensional (3-D) sponge-like structure, yielding a gel-type morphology, which would remain stable with temperature, until the melting temperature of the polymer-rich phase is attained [5].

Surface topography was obtained from the analysis of the optical micrograph of the asphalt blend and the results are recorded in the Table 3. The properties of surface topography are assessed in accordance with the parameter values and visual images of the surface [38, 39].

Looking at the result in Table 3, the negative data of the surface skewness, Ssk, reveal the asymmetric distribution of surface heights and indicate a predominance of valleys while the positive skewness is seen on surfaces with peaks. Further description can be given as the sample, least dominated by surface summits (peaks), seems to give the best optical transmittance.

**Table 3**

Surface measurements of the CPEA blends and the original asphalt from the analysis of the optical micrographs.

Morphological parameter	Original	CPEA 2%	CPEA 4%	CPEA 6%	CPEA 8%	Unit
Roughness averages, Sa	1.43	7.13	14.83	17.33	22.73	nm
Root mean square, Sq	1.80	15.12	19.76	26.54	28.28	nm
Surface skewness, Ssk	-0.18	4.88	1.56	2.31	0.51	nm
Surface kurtosis, Sku	3.07	32.18	5.61	9.25	2.98	nm
Root mean square, Sdq	0.28	22.47	50.61	58.52	78.78	-
Max valley depth, Sv	8.71	163.9	105.43	161.54	128.23	nm
Max peak height, Sp	7.40	-2.75E-08	-1.25E-07	-6.34E-08	2.94E-07	nm
Mean height, S <sub>mean</sub>	-6.64E-09	1.75	2.55	2.75	4.13	nm
Surface area	8.37E+06	4.00E+06	6.46E+06	6.98E+06	1.34E+07	nm <sup>2</sup>

Surface kurtosis (Sku) is a measure of the “peakedness” of the height distribution histogram, or the distribution of spikes above and below the mean line [38-40]. The sample has a Gaussian-like distribution; surface with a Gaussian height distribution has a kurtosis value of three [40]. Unlike Ssk, Sku detects not only whether the spikes that are evenly distributed, but also provides a measure of the spikiness of the area. A spiky surface will have a high kurtosis value (Sku > 3) while a bumpy surface will have a low kurtosis

value (Sku < 3) and perfectly random surfaces have kurtosis of 3.

In the present study, the Sku value for the original asphalt is very near to 3 which means that there is a little distortion on the surface. The animation of the original asphalt (Fig. 1.ii), neither shows spikes nor bumps on the surface further supporting this finding.

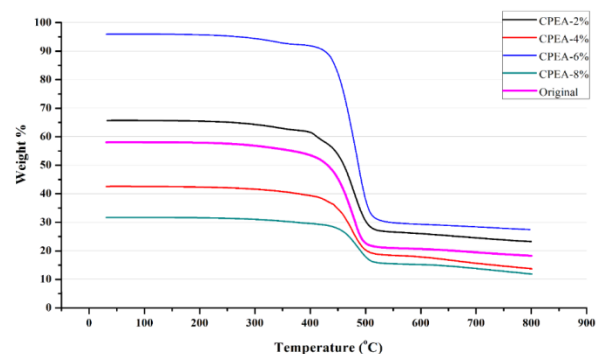
There were irregularities in obtained data for the case of CPEA-2% with data Sku > 30 and less severity in sample CPEA-6% with Sku > 9. This result means that the CPEA samples spikiness is of the order 2% > 6% > 4% > 8% which means that the CPEA-2% spikiness is high due to the low contents of the polymer and this polymer tends to be more crystalline after the chlorination and therefore it looks like spindles attached to a clay artifact with low distribution. As the polymer contents increased the spindles increased and thus the spikiness increased with more distribution giving less intensity of the spindles and this appeared very clear in the CPEA-4% and 8%. The irregularities in the CPEA-6% may be due to the agglomeration of the polymer in the asphalt medium which leads to forming a broad type of spindles and thus the intensity of the spindles increased leading to less distribution and therefore the Sku value increased. In general the CPEA samples follow the term of the Sku > 3 which means the surface is spiky as noticed in Table 3.

Finally, Table 3 shows low value of Sa and Sq indicating short and sharp arranged hay on the surface of the sample. This means that the surface of the of the asphalt blends in CPEA samples is rather smooth. As a result, we can say that CPEA-8% is the best among all samples based on morphology analysis data.

### 3.4. Thermal Analysis

#### 3.4.1 Thermal Gravimetric Analysis

A graph of the TGA curve versus the temperature of the original asphalt and all modified asphalt blends is shown in Figure 6.



**Fig. 6.** TGA of original asphalt and CPEA blends.

From Fig. 6 the samples can be divided into three groups. The first group comprises of CPEA-6% where it appears to have low sensitivity to the temperature with a very low decrease in the mass (~ 2% weight) up to 445°C. After that there is a drastic decrease in the mass weight.

The second group consists of CPEA-2% and the original asphalt where the latter has the highest sensitivity to the temperature; the sensitivity to the change in the temperature is in the order of original asphalt > CPEA-2%, up to 408 and 419°C respectively with a low change in the mass loss (3-5%).

The last group comprises of CPEA-4% and CPEA-8%, where the latter is the best among them and in fact all blends as well. This last group has lowest mass change of ~ 1.5% up to 425-438°C and also overall mass change of ~18-25% while the second group and the first group have overall mass change of ~40% and of ~65% respectively. The differences shown by the curves in the temperature range above 500°C represent the coke residue.

It is obvious that the chlorination had improved the thermal stability of the asphaltic blends. This is clearly observed from the changes in mass as is reflected in the decrease in the volatile constituent of asphalt-polymer blends since the highest loss in the mass means the highest the volatile components evolved [41]. This finding is contrary to the literature [42, 43] where they concluded that addition of polymer does not affect the degradation of the asphalt. Three out of four samples were improved by chlorination whereby the presence of chlorine atom will generally increase the viscosity of the hydrocarbons, thus increase the rigidity of the compound. This leads to increase in the solid against the fluid components. Therefore the resistivity to the temperature is increased because the ability to lose light components decreased since their existence has decreased [25]. This explanation supports the fact that most of the fire resistant polymers are chlorinated polymers or have an additive containing chlorine [44, 45].

### 3.4.2 Differential Scanning Calorimetry

The results obtained from the DSC analysis are tabulated in Table 4 and plotted in the Fig. 7.

**Table 4**

DSC data of original asphalt and CPEA blends.

Sample	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	ΔH (J/g)	ΔH <sub>f</sub> (kJ/mol)
Original Asphalt	60.07	-	-75.441	-0.0754
CPEA-2%	88.41	122.5	-185.18	-0.1852
CPEA-4%	86.9	123.01	-238.03	-0.238
CPEA-6%	87.33	124.8	-141.3	-0.1413
CPEA-8%	77.81	125	-66.458	-0.0665

From Table 4, the chlorinated asphalt- polymer blends show significant change in the T<sub>g</sub>, due to the presence of chlorine atoms which increases the interaction of the polymer and the light component of asphalt leading to increase in the softening and decrease penetration, and consequently increase the viscosity of the asphaltic blends (representing by softening point). This has been previously reported [46]. The higher the T<sub>g</sub>, the more brittle the binder at low temperatures, which reflects that the chlorinated blends are suitable for the hot weather areas. The main melting for CPEA samples is observed between 112.5-125°C. Despite the endothermic fusion peaks of the asphaltic blends appearing at approximately the same temperature (122°C), it is noticeable that a steady increase with increasing the contents of the polymer in the presence of the chlorine is shown by the CPEA blends. This increase in melting temperature as the percentage of polymer concentration increases in polymer asphalt blends has been previously reported in the literature [11, 33, 47].

The slight increase in the T<sub>m</sub> suggests that the crystallization does occur and it is contributed by the chlorine atoms which increases the strength of the blends as shown by the softening, penetration and ductility results of the CPEA blends discussed earlier. The enthalpy and the heat of fusion (ΔH<sub>f</sub>) of the low polymer contents of the chlorinated blends show a sensible change revealing the interaction between the HDPE and the asphalt has improved due to the existence of chlorine. This further supports the results of the topographic analysis discussed earlier.

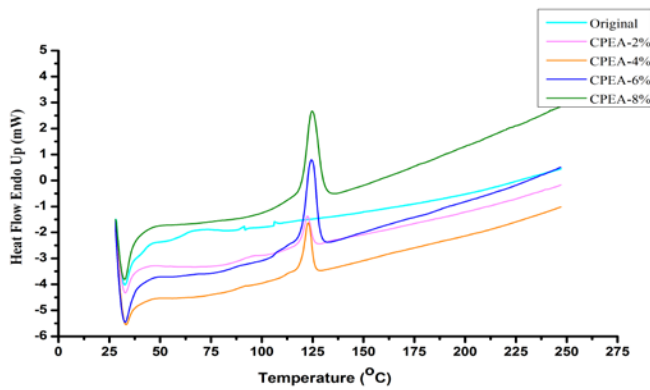


Fig. 7. DSC thermo-grams of original asphalt, and CPEA blends.

At higher polymer contents, the enthalpy data show an increase for CPEA-6% while the CPEA-8% gives a sharp decrease nearly to the range of the original asphalt; the increase in the enthalpy implies that the phase severely separates and induces aggregation of HDPE chains to crystallize in the asphalt matrix. At this point we can expect a better swelling, and this can explain the sharp peaks in the CPEA blends. The enthalpies of the CPEA at higher polymer contents have dropped though they are still higher than those in the lower polymer contents. This could be due to the increase in the rigidity of the blends due to the increase in the viscosity of the asphaltic blends as a result of the polymer additions. The drop in the enthalpies could be attributed to the improvement in the phase crystallinity due to the increase of the interaction between the polymer and the asphalt components which is caused by the existence of chlorine. From the environmental point of view, these results are attractive because by increasing the usage of the larger amount of polymer can help reduce the bulk pressure on the environment (most works prefer the lower contents of the polymer below 5% due to the severe phase separation) and also improve the properties of the asphalt blends since the distribution and the stability are increased. [5,11, 12, 48-51].

### 3.5. FT-IR

Fig. 8 represents the FTIR spectra of CPEA binders with appearance of strong bands at 2919  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$  corresponding to the stretching absorption bands of the alkyl (C-H) of asphalt binder.

The C-H asymmetric deforming in  $\text{CH}_2$  and  $\text{CH}_3$ , and CAH symmetric deforming in  $\text{CH}_3$  vibrations are observed at about 1456 and 1376  $\text{cm}^{-1}$ . The characteristic absorption band around 1599  $\text{cm}^{-1}$  is attributed to C=C stretching vibrations in aromatics hydrocarbons [52].

In addition, there is an obvious appearance of new absorption band at about 668  $\text{cm}^{-1}$ , compared to the original

asphalt. This peak is associated with C-Cl bond stretching which provides clear evidence that chlorine has been introduced into the asphalt binder [53]. It is also noticed that the intensity of the C-Cl peak decreases with increase of the HDPE addition. This is due to the bulkiness of the aliphatic group, bonded to the chlorine atom affecting the appearance of the latter [54].

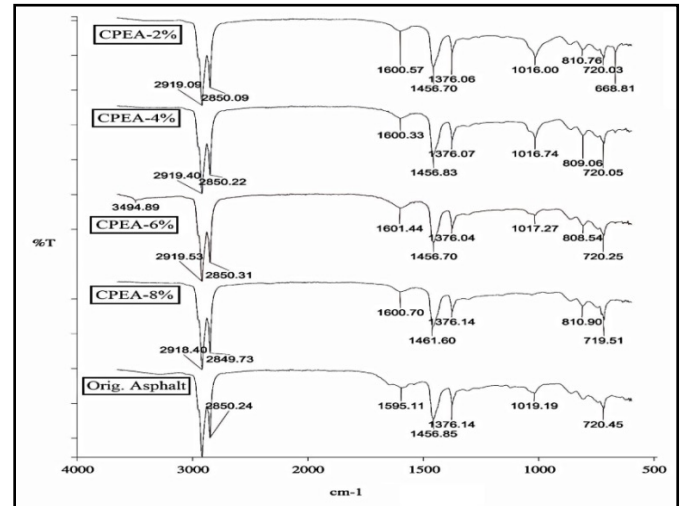


Fig. 8. FTIR spectra of CPEA binder compared to original asphalt.

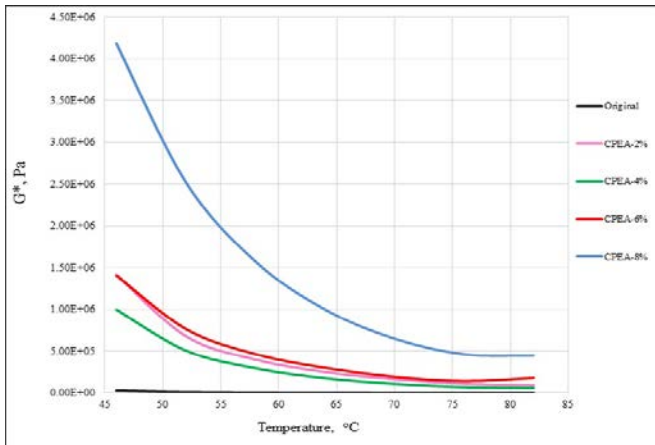
### 3.6. Rheology

The amplitude sweeps were performed to determine the complex modulus and phase angle values in terms of the strain responses at certain temperatures (46, 52, 58, 64, 70, 76, 82°C). The effects of the temperature on complex modulus and phase angle values of the original asphalt and the modified binders are presented in the figures 9 and 10. As shown in Fig. 9, the increase of the temperature did not obviously result in a decrease of complex modulus for the original asphalt. However,  $G^*$  and the phase angle of the binders reduced and increased respectively when the binders were tested at higher temperatures.

The addition of the HDPE in the presence of chlorine showed an obvious increase in the  $G^*$  and decrease in the phase angle by increasing the HDPE addition especially at higher additions (In fact the lowest value of  $G^*$  for CPEA-8% at the higher temperature (82°C) is higher than the maximum value for the original binder).

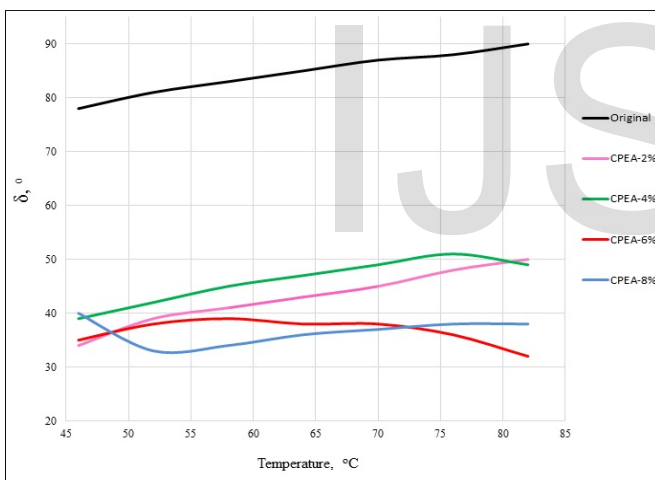
In another word, the chlorinated binders show increase in the  $G^*$  at low temperature which means that the stiffness increases compared to the neat asphalt, and are less temperature susceptibility than the neat asphalt.





**Fig. 9.** Complex modulus of the original asphalt and CPEA binders.

The resistance to the permanent deformation increases as observed in the Fig. 9 from the relationship between the complex modulus and the temperature. Moreover, the results may express that chlorine modification can improve the viscoelastic behaviors of asphalt having incorporation of linear polymers



**Fig. 10.** Phase angle of original asphalt and CPEA binders.

The viscoelastic behavior of the binders as represented by the relationship of the phase angle versus temperature (Fig. 10) is more complex than the uniform transition from elastic response (low phase angle) to viscous response (high phase angle) with increasing temperature for the conventional asphalt. Generally for the binders, the rutting resistance improved compared to the original asphalt.

The phase angle of the original sample increased with the temperature increase becoming viscous at higher temperature; same trends were observed for the 2% and 4% of HDPE additions. In the latter blends, the phase angle has increased reaching the middle viscoelastic region and the blends remained almost constant to the temperature

change. The additions 6% and 8% of HDPE tend to show a little bit decrease in the phase angle revealing that the viscoelastic properties of the chlorinated binders changes from a dominant viscous, liquid-like to a dominant elastic solid-like behavior implying the improvements in temperature susceptibility of the binders as we have mentioned before. The amplitude sweep tests indicate that the chlorination does significantly change the complex and phase angle trends of these binders as mentioned before [55-59].

#### 4. Conclusion

This paper describes a study of the effect of chlorine on the morphology and stability of the HDPE modified asphalt as a key to the compatibility and fuel resistancy and a future application in the fire retardancy of the modified asphalt in addition to the common physical properties. The following conclusions can be derived from this study:

- The chlorination of asphalt/polymer binder offered a good method to improve the homogeneity of the asphaltic blend with good to high polymer distribution within the asphalt leading to higher stability as confirmed by the thermal properties results.
- The chlorination of the asphalt significantly showed stability of the asphaltic systems with higher polymer contents (CPEA-8%) unlike most worldwide literature which may efficiently help to reduce the accumulation of the waste polymers and providing an environmentally friendly way to dispose these materials
- The topographic method to analyze the optical images was effective and gave further evidences about the dispersion which determines clearly the structure (i.e., morphology) of the final binder and hence its properties.
- Solubility in the petroleum solvents (kerosene) of the chlorinated asphalt/polymer binder increased in comparison to the neat asphalt adding another advantage to the chlorination of asphalt, which potentially may lead in the future to produce high fuel resistant materials.
- The physical properties generally improved in the chlorinated binders especially the thermal stability which may give potential in the fire retardancy or anti-aging applications.
- Further research is needed to prove the technical and the economy of the process especially in the roofing application which may need to the study of aging of the chlorinated asphalt as the chlorine atoms increase the resistant towards the oxidation and or the oxidizing materials.

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