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Preparation of Protective Coating Using Polymer Modified Asphalt

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Abstract

The present interests of scientists whom concerned with asphalt and bituminous materials focuses on asphalt modification for improvement the characteristics of asphalt as a binder of aggregates in paving. One of the recent trends is to take the different properties of the asphalt as adhesion and water repellence in the preparation of protective coatings. Asphalt/polymer binary blends were prepared using PET. Conventional physical tests include penetration, softening point and ductility, were performed to investigate the effect of polymer modification on the mechanical properties of asphalt. The good dispersion and homogeneity of PET with asphalt was examined using SEM. SEM proved that polymer content of 6% represented the most homogeneous polymer distribution in the asphalt as the continuous phase. Thermal Gravimetric analyses (TGA) showed that thermal stability of asphalt is improved by modification with PET. The ability of modified asphalt samples, to serve as protective coatings, was examined by preparation of coating formulations from the PMA samples and examining the physical characteristics as adhesion, bending and impact resistance also, examining the resistance of coatings to aggressive media; water, acid alkali and organic solvent. PMA coatings showed a good resistance to different media except the organic solvent that destroy the coating layer by dissolving the asphaltic material.

Keywords

Asphalt, Polymer Modified Asphalt, Protective Coatings, Anticorrosion

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1. Introduction

Asphalt is a Black to dark-brown solid or semi solid cementitious materials which gradually liquefied when heated, in which the predominating constituents is bitumen. Bitumen is a mixture of hydrocarbons of natural or pyrogeneous origin, or combination of both, frequently accompanied by their non-metallic derivatives, which may be gaseous, liquid, semisolid, or solid, which are completely soluble in carbon disulphide. Bitumen or asphalt all of which occur in the solid or semi-solid form in nature or are obtained by petroleum refining [1].

The earliest record of human use of asphalt to date, is as a hafting material 180,000 years ago in the El Kowm Basin in Syria, where itwas applied to stick flint implements to the handles of various tools in a way that persisted until Neolithic time [2]. At first, its adhesive and waterproofing properties were generally emphasized. Even the Bible cites examples such as the waterproofing of Noah's arch, of the Babel tower or of the cradle of Moses [2, 3].

Another well studied historical application was for the embalming of mummies by the Egyptians [3-5]. Asphalt isa viscoelastic material with suitable mechanical and rheological properties for waterproofing and protective

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coverings for roofs and roads, because of its good adhesion properties [6].

Modification of base asphalt is required to improve the material's performance (e.g. adhesion, temperature sensitivity, and durability) [7]. Three kinds of modifications are discussed. The first one is the modification of asphalt by an acid. This process has become of increasing importance in recent years, especially for the production of harder grades of asphalt. The effect of the acid can directly be understood in the light of the colloidal model. Then, the modification of asphalt by mineral fillers is addressed. asphalt and mineral filler blends are usually referred to as mastics. Mineral fillers are generally not commercial modifiers as such. Since they are always present as part of the mineral aggregates, a mastic is indeed formed in-situ when manufacturing a hot mix. Therefore, it is in this mastic form that the bitumen really acts within the final mix, hence its critical importance. Finally, the last modification presented is that by a polymer.

The modificationasphalt by blending with SBS was developed by Ouyang et al. [8, 9]. The main objective of this work is the use ofPET in modification of asphalt and take the advantages of asphalt as water repellent and of a good adhesion for preparation of a novel protective coatings.

2. Materials and Experimental Procedures

2.1. Materials Used

Asphalt: Local asphalt of penetration grade 25/85, produced by El-Nasser Petroleum Company Suez – Egypt was used in this study,and having characteristics as illustrated in Table 1.

Polymer: Polyethylene terephthalate (PET), used bottles of drinking water.

Carbon Steel specimen: The carbon steel of grade IS: 2026 composed of (Fe = 97.82, C% = 0.23, Mn% = 1.5, S% = 0.050, Si%= 0.40) and was obtained from Ezz Steel Company, Alexandria, Egypt.

Miscellaneous: Benzene and white-spirit were obtained from EL–Nasr Pharmaceutical Company, Egypt.

2.2. Experimental Procedures

2.2.1. Preparation of Modified Asphalt

A 85/25 asphalt derived from vacuum industrial distillation process was used as base asphalt and is referred to as A in the following text. Binary blends were then produced by modifying the base asphalt A with polymer. The binary blends, referred to as PMA, is a asphalt/polymer blend prepared by adding an PET to the base asphalt in different proportions.

Binary blends were prepared by the following procedure; the asphalt was heated in an iron can. When the asphalt temperature reached 170°C, a low-shear mixer was dipped into the can and set to 1200 rpm. The polymer was added gradually (about 0.5 g/min) while keeping the temperature within the range of ±5°C during the polymer addition. Polymer modifier was added in portions of 2, 4, 6, 8 and 10%, and the processing time was 0.5 hr. Finally, the obtained polymer modified asphalt (PMA) was split in appropriate amounts to prepare samples for characterization.

2.2.2. Testing Procedure

The principal test methods on the raw materials and the modified blends of the asphalt were:

(i) Characteristics of Asphaltic Materials

A- Conventional characteristics

Bothbase and modified asphalt samples were characterized by conventional asphalt test as penetration at 25°C (ASTM D5), softening point (ASTM D36), and ductility (ASTM D113).

B- Thermal gravimetric Analysis (TGA)

The thermal stability was assessed by the thermal gravimetric analysis (TGA) (SDT Q600 V20.5 Build 15) in the temperature range of 20–800°C (10°C /min) under a nitrogen atmosphere.

C-Scanning Electron Microscope (SEM)

Scanning electron microscopy has been used to investigate the microstructure of both base and modified asphalt by determining the state of dispersion of the polymer within the base bitumen as well as characterize the nature of the continuous and discontinuous phase. By far, scanning electron microscopy is the most valuable method for studying the phase morphology of polymer-modified asphalt [10], as it allows the observation of the homogeneity and the structure in the raw state [11].

The asphalt rich phase appears dark or black, whereas the polymer rich phase appears light. Samples were prepared (for imaging purposes) by placing a drop of heated asphaltic sample between microscope slides. Samples were then examined at room temperature under SEM model quanta FEG.

(ii) Preparation of Asphaltic Coatings

In order to prepare coatings from the prepared blends, certain amount (100 gm) of hot asphaltic material was dissolved in preheated solvent (Benzene/white-spirit) followed by proper mixing using a mechanical stirrer, with a speed of 800 rpm for about 30 min. After stirring, homogeneous coating was obtained. Carbon steel grade IS plates were grinded, polished using 320 1200 and 2000 grade emery papers and used as substrate coated with the developed coatings. All the carbon steel samples were pretreated acetone, ethanol and benzene solution to degrease prior to coating and surface of all samples were smooth and shiny after polishing. The liquid coatings were coated on the substrate by dipping and then were dried in the room temperature till complete curing.

(iii) Evaluation of the Prepared Blends as Protective Coatings

In this step, the prepared coating samples were evaluated as protective coatings using mechanical and chemical resistance tests. The mechanical tests include; drying time, dry film thickness, adhesion, bending and impact resistance. The chemical resistance of prepared coatings were evaluated in different media include; tap water, acid resistance (using 20% H_2SO_4), alkali resistance (using 5% solution of $NaCO_3$) and solvent resistance (benzene / mineral turpentine mixture). The evaluation of coatings were done according to ASTM standard methods.

3. Result and Discussion

3.1. Characteristics of Base Asphalt

Blown asphalt used in this study was tested for physical, Scan Electron Microscope (SEM) and Thermal Gravimetric Analysis (TGA). The results will be shown in the following subsections:-

3.1.1. Physical Characteristic

Physical characteristics of base asphalt is illustrated in table 1

Table 1. Characteristics of base blown asphalt.

Characteristics	Result	Egyptian specification limits
Penetration (100 g, 25°C, 5s), 0.1mm	23	20/30
Softening Point, °C	84	80/90
Ductility at 25°C (cm)	14	+3
Penetration Index (PI)	3	>2
Asphaltene Content(wt%)	30	NS*

(NS*): Not specified.

The results revealed that sample analysis result is complying with the standard specification limits.

3.1.2. Thermal Gravimetric Analysis (TGA)

TGA of virgin blown asphalt is shown in figure 1.

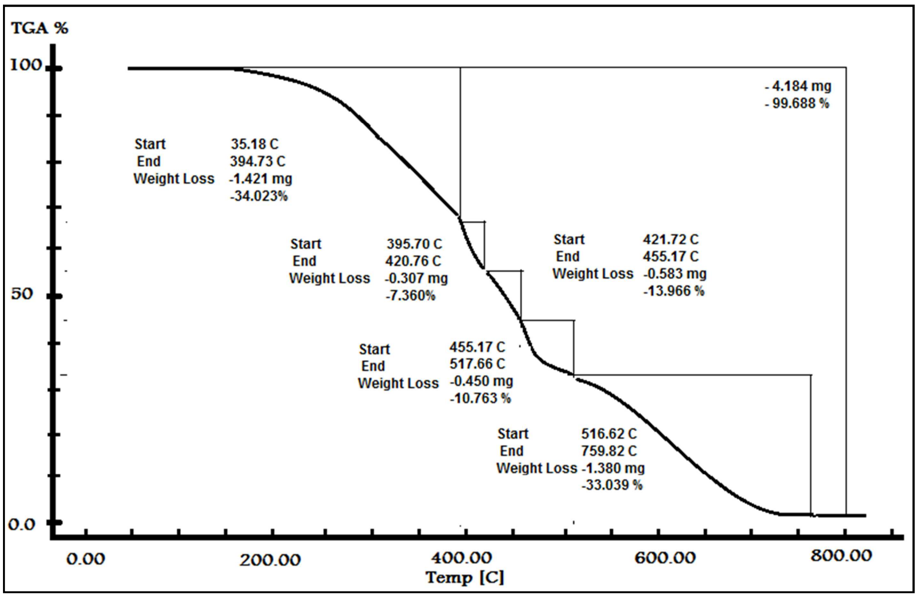


Fig. 1. TGA of virgin blown asphalt.

Thermal gravimetric analysis (TGA) of base asphalt as shown in fig.1 illustrates the material stability by measuring its weight changes as a function of temperature under controlled atmosphere. Figure shows five regions of weight loss corresponding to initial (IDT) and final (FDT) decomposition temperatures.

The first event presented a decomposition temperature of approximately 35.18°C, the other events took place at decomposition temperatures of 395.70, 421.72, 455.17 and 518.62°C respectively.

The sample has IDT equal to 35.18°C which is very low, while it has very high FDT equal to 759.82°C with weight loss = 98.37%. This result is due to the increase in asphaltene content which lowers its thermal stability but causes slowing of decomposition rate after its IDT, so five decomposition regions appear in the figure [12]. However, the mass loss of the sample was mainly due to volatilization of light components present in asphalt such as saturates and aromatics and also to decomposition of asphaltene [13]

3.2. Characteristics of Polymer Modified Asphalt

3.2.1. Conventional Tests

The effect of PET modification on the properties of the base asphalt can be seen in Table 2. Generally, the characteristics of all prepared PMA samples are completely different from the base asphalt as they have lower penetration & ductility and higher softening point values, so, PET is considered as strengthening agent for asphalt.

A decrease in penetration and ductility values and an increase in softening point temperatures with the increasing polymer contents can be remarked. The increase in softening point temperature, which is an indicator of the stiffening of PMA [14], is favourable since asphalt with higher softening point may be less susceptible to permanent deformation [15].

Table 2. Physical characteristics of PMA with PET in different proportions.

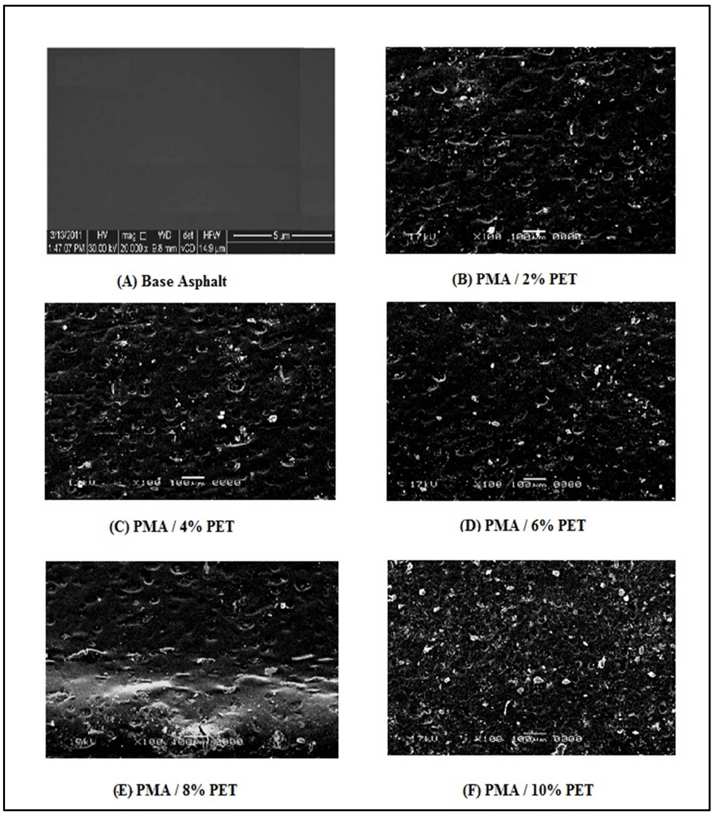
Test	Base Asphalt	PET%				
		2	4	6	8	10
Penetration (mm)	23	10	9	8	7	6
Softening point(°C)	84	133	135	137	140	143
Ductility (cm)	14	7.0	6.3	6.0	5.0	4.3
Penetration index (PI)	3	5.95	5.91	5.85	5.83	5.79

SP: Softening Point.
$PI = (1952-500\times LogP_{25°C}-20\times SP)/(50\times LogP_{25°C}-SP-120)$

Polymer modification reduces temperature susceptibility (as determined by the penetration index—PI) of the bitumen. Lower values of PI indicate higher temperature susceptibility [10]. Asphalt mixtures containing bitumen with higher PI are highly resistant to low temperature cracking as well as permanent deformation at high temperature [16]. As can be seen in Table 2, all PMA samples exhibited higher temperature susceptibility compared to base bitumen with the increase in the polymer content.

3.2.2. Scanning Electron Microscope

The microstructure of PMA samples has been investigated, using a scan electron microscope, by characterizing the nature of the continuous phase, fineness of the dispersion of the discontinuous phase as well as the description of the phases and shapes. A distinction can be made between the PMA samples whose continuous phase of a bitumen matrix and homogenous dispersed polymer particles. Scan electron microscopy images of PMA/PET with different ratio were shown with base asphalt in Fig. 2. In this figure, the dispersed polymer phase appears light while the asphalt phase appears dark. A clear distinction, regarding the homogeneity of the phases, is observed between the different modified samples as can be seen. PMA, with the polymer content (6%), may reveal the finest homogenous dispersion of polymers and it may be deduced that increasing the polymer content could reduce the homogeneity of the PMA/PET. This sample would be tested for TGA to observe the effect of PET on the thermal characteristics of asphalt.



(A) Base Asphalt

(B) PMA / 2% PET

(C) PMA / 4% PET

(D) PMA / 6% PET

(E) PMA / 8% PET

(F) PMA / 10% PET

Fig. 2. SEM of PMA with different percents of PET.

3.2.3. Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis of PMA with 6% PET compared to base asphalt is shown in figure 3. The figure shows three regions of weight loss (marked by the red colour) as compared to five decomposition regions for base asphalt (marked by black colour). As shown in figure 3, we can notice that; the IDT was shifted to higher temperature (from 35.18°C in case of base asphalt to 41.42°C in case of PMA) with decreasing in the amount of weight lost, (from 34.023 to 31.916%), this result may be attributed to decreasing of the asphaltene content by addition of polymer.

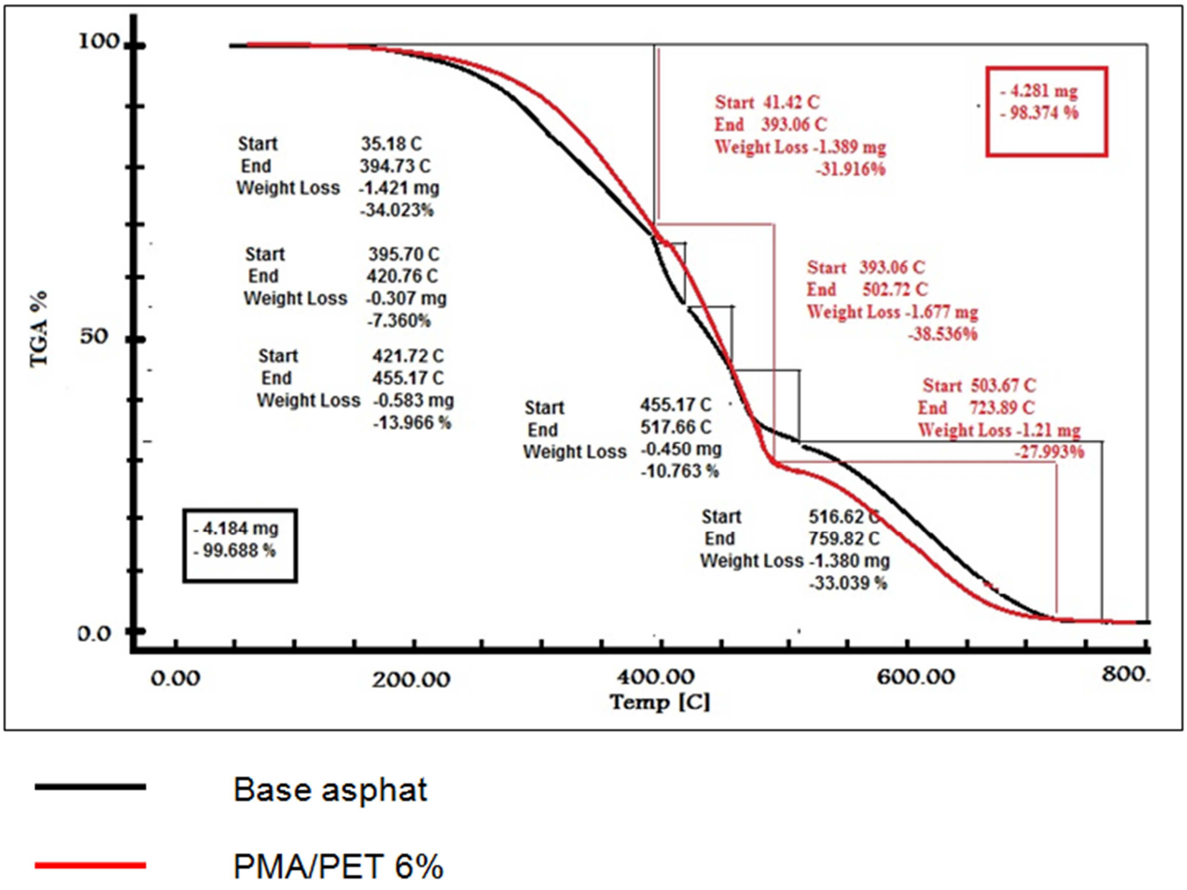


Fig. 3. TGA of PMA/PET6% as compared to BA.

Also, we can notice that the three decomposition regions in base asphalt may be merged in one region by modification with Polymer, this may be attributed to interaction of ester group of PET with the component of asphalt that may volatilize in this range of temperature. Finally, modification of asphalt with PET could enhanced the thermal stability of asphalt, this is seemed so obvious to reduce the overall percent of decomposition from 99.688% for base asphalt to 98.374% for PMA with PET.

3.3. Evaluation of Prepared PMA Samples as Protective Coatings

3.3.1. Curing Time

Table 3 shows the three curing stages of prepared coatings, and the following results were observed.

For virgin asphalt, the final curing time is very long and recorded more than 3 days. So, it is not suitable for industrial applications. This may due to the chemical constituents of asphalt itself as it contains high quantity of light hydrocarbons and low quantity of asphaltene (30%).

Table 3. Curing properties of modified asphalt coatings based on PET.

Sample ID	Curing time		
	1st Stage	2nd Stage	3rd Stage
	(Tacky)	(Finger Print)	(Cured)
Base	12 h	24 days	>3 days
PMA/PET 2%	10 h	20 h	66 h
PMA/PET 4%	8 h	18 h	60 h
PMA/PET6%	6 h	16 h	54 h
PMA/PET 8%	7 h	20 h	60 h
PMA/PET 10%	10 h	24 h	66 h

Generally, the curing time of modified asphaltic coatings is obviously lower than the virgin asphalt samples. This may due to the formation of PET network in asphalt sample. So, the hardness of prepared samples increased and the curing time in each stage decreased. However, the curing time in each stage decreased with increasing PET ratio. This may be explained by increasing PET will cause the amount of cross linking formation to increase and accordingly the curing time decreased, but this behaviour may changed after the mixing ratio of 6% as the drying times may deviate from the fall taken by first to come back on the rise again, bringing to 60 and 66 hours in the final stage of the percents 8 and 10%, respectively. This deviation may be explained by the obvious results of the SEM, where the percent of 6% was observed to the favorable mixing ratio that the uniformity and the homogeneity of the dispersion of PET was observed and after 6% the polymer was observed to agglomerated and separation of two phases (polymer rich phase & asphalt rich phase) was taken. Thus, the coating prepared from modified asphalt with 6% PET may has the most preferable curing time.

3.3.2. Mechanical Properties

Mechanical properties of prepared coating samples based on both base and modified asphalt is illustrated in table 4, this mechanical properties include; dry film thickness (DFT), Impact resistance, adhesion and bending tests.

Table 4. Mechanical properties of modified asphalt coatings.

SampleNo.	DFT(µm)	Adhesion test	Impact test	Bending test
Base	108	Pass	Fail	Fail
PMA/PET 2%	109	Pass	Pass	Pass
PMA/PET 4%	108	Pass	Pass	Pass
PMA/PET6%	110	Pass	Pass	Pass
PMA/PET 8%	109	Pass	Pass	Pass
PMA/PET 10%	111	Pass	Pass	Pass

Generally, the coatings prepared from modified asphalt have mechanical properties different from that recorded to the base asphalt. This is attributed to the enhancement of properties of asphalt by modification with PET.

All of the formed coatings are adhesive materials as a result of adhesive characteristics of both asphalt and formed PET. Impact resistance and bending (flexibility) of coatings were failed in case of base asphalt and enhancement was observed by modification with PET. This is attributed to the effect of the PET. Fig.4 illustrates the photographic pictures taken for coating sample in bending test.

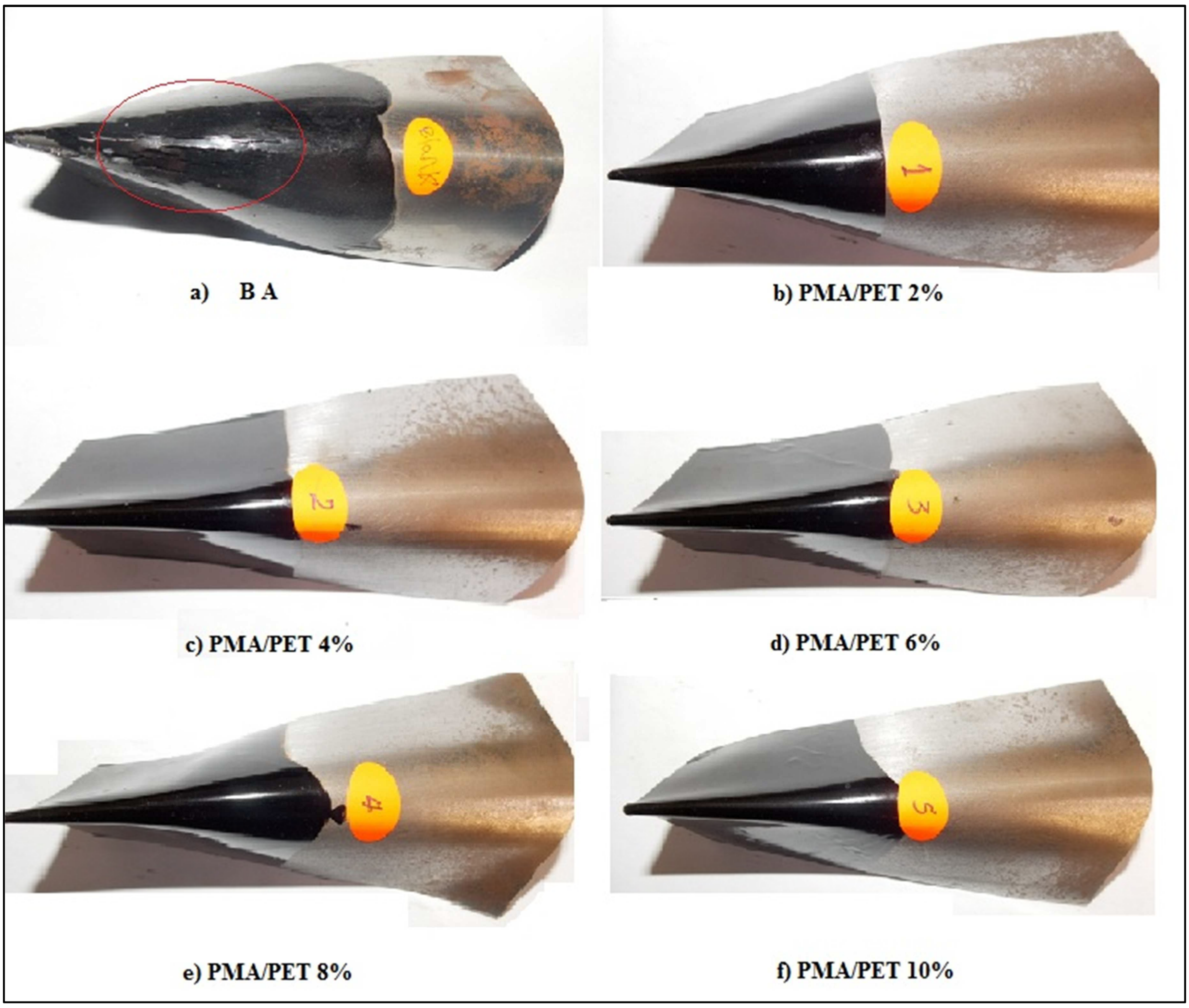


Fig. 4. Photographic picture of bending test for coating samples.

3.3.3. Chemical Resistance

Table 5 illustrates the chemical resistance of coatings based on modified asphalt using PET.

Table 5. Chemical resistance of coatings based on PMA/PET.

Media Sample	Water Resistance	Acid Resistance	Alkali Resistance	Solvent Resistance
BA	Exc.	F	Exc.	P
PMA/PET 2%	Exc.	G	Exc.	P
PMA/PET 4%	Exc.	Exc.	Exc.	P
PMA/PET 6%	Exc.	Exc.	Exc.	P
PMA/PET 8%	Exc.	G	Exc.	P
PMA/PET 10%	Exc.	F	Exc.	P

Exc.: Excellent, G: Good, F: Fair (partially attacked), P: Poor

From the tables, the following results are detected:-

- The chemical resistance of base asphalt in all chemical reagents improvedwithusingPETas a modifier. This is due to the presence of ester group which is highly resistance acid and alkali.
- Chemical resistance of coating in water and alkali media increased as the percent of PET increased but in acidic media this enhancement was stopped at the percent 6% PET after which the chemical resistance was back down. This may be attributed to the disturbance occurred in the homogeneity of both polymer and asphalt phase after the percent 6%.
- All prepared samples was observed to be failed in the test of solvent resistance, of course this is a normal result, that asphaltic materials are dissolved in benzene causing a destruction of the coating layer.

4. Conclusions

Bitumen/polymer binary blends were prepared using PET mixed with a base bitumen of grade 85/25. Thermal gravimetric analyses (TGA) and morphological analyses (SEM) as well as conventional characteristics (Penetration, Softening point andDuctility) were performed. Several effects were associated to the presence of PET in binary bituminous blends. The overall data confirm that PET has not a simple filler-like effect, but its presence has quite important effects on all characteristics of bitumen as follows:

- Gives a higher softening temperature (increase 49&59°C) than base asphalt by addition of 2&10% of PET.
- Decreases the penetration value by 56 & 74% by addition of 2&10% of PET as compared to base asphalt.
- Modification of asphalt with PET could enhanced the thermal stability of asphalt as decreased the rate and the ratio of decomposition.
- Modification of asphalt by PET in ratio of 6% give a homogeneous blend with asphalt, and increasing the ratio will causes agglomeration of polymer phase and separation from asphalt.
- The chemical resistance of base asphalt was improvedbyusingPETas a modifier.
- PMA/PET 6% was the most effective blend, it could hold out against various media with the exception of organic solvents that destroy the coating layer by dissolving the asphalt.
- Based on the overall findings it can be finally stated that polymer modification of asphalt using PET represents a step towards the introduction of a new generation of protective coatings characterized by improved stability and enhanced mechanical performances.

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