



Colloidal Stability and Dynamic Mechanical Properties of Asphalt Modified with Unsaturated Polyester Prepared from Waste Polyethylene Terephthalate



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THIS research aims to prepare unsaturated polyesters (UP) from polyethylene terephthalate waste (WPET) and studying their effects on the colloidal stability and dynamic mechanical properties of the prepared modified asphalt samples. To achieve this aim WPET is chemically recycled through glycolysis reaction using different glycols namely, diethylene glycol (DEG), triethylene glycol (TEG) and propylene glycol (PG) at molar ratios of PET wastes/glycol; 1:1.2 separately. The glycolized products were converted into unsaturated polyester (UP) via reaction with maleic anhydride. The prepared unsaturated polyesters (UPd, UPt and UPpg) were characterized using FTIR, GPC and TGA and then added to asphalt 60/70 in percentages ranging from 2wt% to 8wt% using wet process to prepare modified asphalt binder with desirable physical and engineering properties. The prepared modified asphalt samples were evaluated for thermal stability using TGA, physical and chemical properties using conventional tests, colloidal stability index while their rheological properties were investigated using Superpave binder tester, namely, dynamic shear rheometer (DSR) to determine the rutting and stiffness resistance of the prepared samples. The results showed an improvement in asphalt properties which became more thermally, colloidally stable and resistant to rutting and plastic deformation.

Keywords: Asphalt, Waste PET, Glycolysis, Rutting parameter, Wet process.

Asphalt is defined according to American Society for Testing and Materials (ASTM D8-13) as a dark brown to black cementations material in which the predominating constituent is bitumen [1]. Conventional asphalt tended to perform satisfactorily in most highway pavement applications. However, in recent years, the increase in traffic load causes axle load of road to increase and causes serious damage of paving so, enhancing the properties of existing asphalt material is needed. Asphalt modification by different additives offers an important solution to overcome the existence deficiencies of traditional asphalt and thereby improve the overall properties and performance of road paving [2]. Polyethylene Terephthalate

(PET), a thermoplastic polyester which constitutes 18% of the total polymer produced worldwide [3] and commonly used to make plastic bottles is used as a polymeric additive in this research. The large-scale use of PET for manufacturing of plastic material in various forms including bottles has made it a major cause for environmental pollution. The non-biodegradable nature of waste PET bottles has led to scientists looking into ways to recycle it. Currently, both chemical and physical methods have been employed to recycle different types of waste materials among which waste PET [4]. Glycolysis and methanolysis are the main depolymerization processes that have reached commercial maturity [5]. However, chemical recycling

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of waste PET is a useful route to produce several industrially products and eliminating the practice of disposal in landfills [6]. In previous studies, PET waste was generally added to the asphalt using wet process or used as aggregate (dry process) in the asphalt mixture in order to improve its resistance to permanent deformation, in addition to Marshall stability, stiffness and fatigue life of road pavement [7,8]. However, phase separation of the modified asphalt have been reported due to the inhomogeneous distribution of PET pellets in asphalt [9], therefore, an additive form of PET whose surface texture has been degraded using chemical treatment might be more suitable for pavement applications [10,11]. Also, recycling of waste PET plastics can make significant contribution to environment and economy aspects. The recycling helps to reduce the exploitation of natural resources to reduce the environmental pollution level, saving energy and money as well as modifying the physical and engineering properties of construction materials such as asphalt and building concrete [12]. During the wet process, the additive firstly mixed with bitumen with a proper mixer until achieving a homogenous blend, then the blended materials are added to aggregates. In dry method, according to additive's type and nature this material is mixed with aggregates before adding bitumen or added after mixing the bitumen and aggregates as a part of solid materials. Due to high melting point of waste PET, it is not easy to be mixed with bitumen in wet process and achieve a homogeneous blend [13].

Materials and Methods

Materials

- Virgin asphalt cement (AC) of penetration grade 60/70 type which was obtained from El-Nasr for petroleum processing company (NPC), Egypt.
- Waste polyethylene terephthalate (WPET) bottles used in this study were collected from some restaurants after proper identification. The bottles were stripped of all labels and cleaned with normal detergent solution followed by proper washing and drying to remove any potential contaminants. The bottles were then cut into small pieces about 5 mm and dried at a temperature of 80 °C temperature for 4 h for complete drying.
- Diethylene glycol (DEG), triethylene glycol (TEG) and 1,2-propylene glycol (PG) which purchased from Alfa Easer.

- Manganese acetate, maleic anhydride and p-toluene sulfonic acid, styrene solvents such as n-heptane, cyclohexane, benzene and methanol.

Methods:

Glycolysis of waste PET [14].

In this step, PET waste flakes were depolymerized with diethylene glycol (DEG), triethylene glycol (TEG) and propylene glycol (PG) separately in the presence of 0.5% (by weight) manganese acetate based on the weight of PET, in a 4-neck glass reactor, equipped with mechanical stirrer rotating at 1000 rpm, thermometer, reflux system and N₂ gas. The reaction was carried out for 4h for all kind of glycols separately. The reactor was immersed in an oil bath and heated for 4h at 200 -210 °C.

Preparation of unsaturated polyester (UP) [15].

The glycolized products of WPET and maleic anhydride (ratio of hydroxyl: carboxyl = 1.1:1 mol/mol) were mixed in a 500 mL four necked round bottom flask connected to a stirrer, a thermometer, a condenser, and a N₂ gas inlet. The reaction was carried out at 180 °C for 1.5 h then it was raised up to 200 °C for 4h under nitrogen atmosphere. The reaction temperature was then lowered gradually to 100 °C and left to cool to room temperature. The UP products were subjected to FTIR spectroscopic analysis to confirm inclusion of maleic anhydride in the chemical transformation process and the reaction product was diluted with styrene (30 % (w/w) of the resin) to obtain a clear mixture with some yellowish color.

Preparation of modified binders.

In this step; about 500g of virgin AC60/70 was heated to 165 °C until it became pourable. The mixing was performed in the laboratory with a mechanical stirrer at a frequency of 1000 rpm. After the mixing temperature was reached, the modifying agents namely; UPd, UPt and UPpg were added separately and slowly in order to avoid agglomeration of the material. The typical time used for the preparation of the blend was 1h. After the blend was prepared, it was allowed to settle for 1 h. The percentage of each modifier added varied from 2 to 8 (w/w %) of asphalt.

Physical evaluation of prepared modified asphalt samples:

In order to evaluate the physical properties of virgin asphalt and the prepared polymer

modified asphalt, conventional asphalt tests such as penetration, softening point and ductility were performed according to the ASTM D36, ASTM D5, and ASTM D113 standard methods respectively. In addition, results were used to calculate penetration index (PI), which is a measure of temperature susceptibility of asphalt binders. PI calculation has been performed in accordance with the following equation [16]:

PI =

However, asphalt with lower PI values have higher temperature sensitivities. When asphalt with higher PI are placed into asphalt mixtures, the mixtures become more resistant to permanent deformation at high temperature and low temperature cracking [17]. Also, colloidal stability was calculated and specific gravity test (ASTM D 70) was performed.

Determination of the average molecular weight of the glycolyzed PET using hydroxyl number method.

The number average molecular weight of the glycolyzed PET was determined according to the end group analysis by determining the acid numbers and hydroxyl number [15]. The content of free carboxylic end groups (N_a) was determined by the conventional acidimetric titration method by using aqueous KOH solution while the content of free hydroxyl end-groups (N_b) was determined by the acetic anhydride / pyridine back titration method [18,19].

Fourier Transform Infrared Spectroscopy (FTIR).

Infrared spectra of the Glycolyzed PET

samples using Diethylene Glycol, Triethylene Glycol and Propylene Glycol (Gd, Gt and Gpg), the prepared unsaturated polyesters (UPd, UPt and UP_(pg)) in addition to virgin and poly modified asphalt samples were recorded via FTIR spectrophotometer (Model 960 Moog, ATI Mattson Infinity Series, USA). The spectra of all studied samples were measured in the range of 4000 – 400 cm^{-1} by summing 32 scans at 4 cm^{-1} resolution and 32 background scans.

Gel Permeation Chromatography (GPC) [20].

GPC analyses of the prepared unsaturated polyesters (UPd, UPt and UP_(pg)) were performed by waters 515/2410 gel permeation chromatography (GPC waters, America) using THF as a solvent at 40 °C. For making measurements, 200 μL sample was injected at a flow rate 1 $\text{mL} \cdot \text{min}^{-1}$ using a Waters 515 pump. Styragel column calibrated with polystyrene standards and series 2410 refractive index detector.

Thermal Gravimetric analysis (TGA) [21].

Thermogravimetric analysis (TGA) of the prepared polyesters (UP_d), (UP_t) and (UP_(pg)) in addition to polymer modified asphalt samples (AC + UP_d, AC+ UP_t and AC + UP_(pg)) was conducted using TA Instruments, model SDT Q600 V20.9 Build 20 system. The rate of heating was 10 °C/min up to 600°C under nitrogen atmosphere.

Dynamic Shear Rheometer (DSR) [22].

The dynamic shear rheometer (DSR) was used to characterize the elastic and viscous behavior of both virgin asphalt binder (1mm thickness) and the unsaturated polyester modified asphalt binders at different test temperatures as 58, 64, 70 and 76

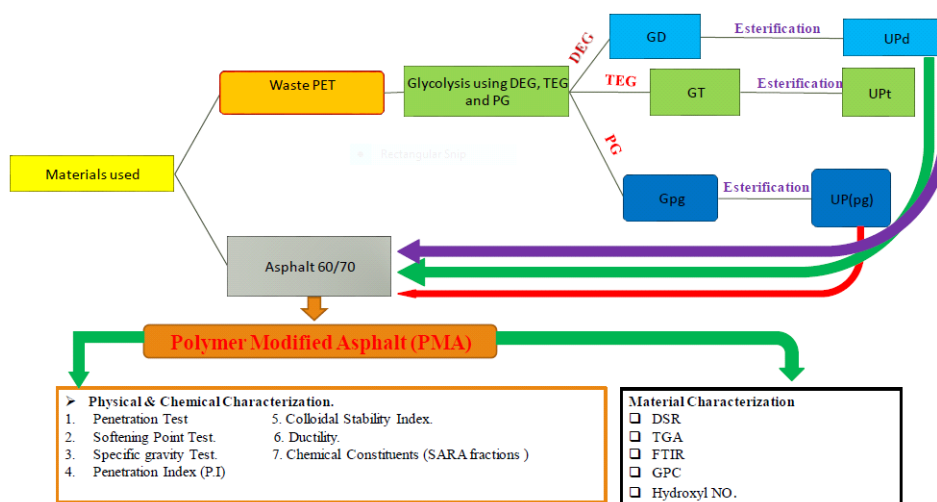


Fig. 1. Flow chart of the experimental program.

using a spindle of 25 mm in diameter and one loading frequency of 10 rad/sec (1.59 Hz) which has been related to traffic speed of 100 km/h. The DSR test was conducted using a stress-controlled testing mode in which a 12 percent dynamic shear strain (sinusoidal) was applied to the sample using the upper oscillating plate as described in the (AASHTO TP 5 test method) [23]. During the DSR test, the resulting shear stress (τ), the complex shear modulus value (G^*), and the phase angle (δ) were recorded using Anton Paar RheoCompass™ smart pave 102, V1.20.496-Release. The complex shear modulus (G^*) can be considered the sample total resistance to deformation when repeatedly sheared, while the phase angle (δ) is the lag between the applied shear stress and the resulting shear strain. The rutting parameter ($G^* / \sin \delta$) as well as stiffness parameter ($G^* \cdot \sin \delta$) were conducted. It is important that, the elastic portion of the complex shear modulus should be large and the minimum value for it is > 1.0 KPa for fresh asphaltic sample at the test temperature according to AASHTO T 315.

Results and Discussions

Glycolysis of WPET

The glycolysis consists of the transesterification of PET where destruction of its polymer chain takes place, resulting in the decrease of its molecular weight as shown in Fig. 2. Using glycols in the depolymerization of PET will result in forming oligomers ended with free -OH function as shown in Fig. 2. The choice of diethylene glycol (DEG) to carry out the glycolysis is usually determined by the necessity of having well flexural properties in the UPR, since the long chains of the glycol improves flexibility. In this work the glycolysis of PET was carried out using three glycols DEG, triethylene glycol (TEG) and propylene glycol (PG).

Mechanism of Glycolysis of PET.

The presence of free electron pair on the DEG oxygen initiates the reaction by attacking the carbonyl carbon of the ester group of the polyester as shown in Fig. 3. The hydroxyethyl group of diethylene glycol then forms a bond with the carbonyl carbon of the polyester breaking the long chain into short chain oligomers and finally bis-(2-hydroxydiethyl) terephthalate (BHDET). The metal forms a complex with the carbonyl group, facilitating the attack of DEG on PET leading to the formation of BHDET [24]. The glycolized product (kind of glycol in glycolysis reaction) was selected to impart flexibility and kind of glycols

used to the synthesized resins, increasing the spacing between the double bonds incorporated by maleic anhydride (MA) [25]. The propylene glycol (PG) was combined with glycolized product to increase the miscibility of the synthesized resins with styrene monomer and increase the activity of the anhydrides before starting the reaction. PG possesses good hydrolytic resistance and is of low cost, which imparts excellent physical and chemical properties to the product [15].

Characterization of Glycolized WPET products.

Average molecular weight of the glycolized PET.

The results of the hydroxyl no. (OH.no) and average molecular weights of the glycolized products are presented in Table 1. The results include the number average molecular weight (M_n) of the oligomers produced using the hydroxyl number.

The Results of using PG for depolymerization of PET, indicates that a longer chain glycolized product is produced. Thus GD ($M_n=459.295$ g/mol), GT ($M_n=623.257$ g/mol) and Gpg ($M_n=1453.77$ g/mol) are suitable choices for preparation of unsaturated polyester resins with long chain and accordingly a high flexibility.

Fourier Transform Infrared Spectroscopy (FTIR) of glycolized products.

Figure 4 illustrates the FT-IR spectrum of the glycolized products. The figure shows that both of GD, GT and Gpg show absorption peak at $3200-3550$ cm^{-1} due to the -OH, $2840-3000$ cm^{-1} for the C-H stretching, $1715-1725$ cm^{-1} for the carbonyl group (C=O), near 1100 cm^{-1} for C-O-C and $670-900$ cm^{-1} for the aromatic ring. The FTIR spectrum revealed the similarity of molecular structure of all samples

Characterization of Unsaturated Polyester.

Fourier Transform Infrared Spectroscopy (FTIR) of Unsaturated polyester resins.

FTIR spectrum as in Fig. 5 shows the presence of an absorption band at 2976 cm^{-1} due to carboxylic acid of the saturated anhydride. This confirms the inclusion of maleic anhydride in the copolymer. The FTIR spectrum of the prepared resins shows that the absorption at 981 cm^{-1} for the C-H out of plane bending in CHR=CHR (in polyester), 1640 cm^{-1} for the C=C in polyester, $3200 - 3550$ cm^{-1} due to the -OH, $2840-3000$ cm^{-1} for the C-H stretching, $1715-1725$ cm^{-1} for the carbonyl group (C=O), near 1100 cm^{-1} for C-O-C and $670-900$ cm^{-1} for the aromatic ring.

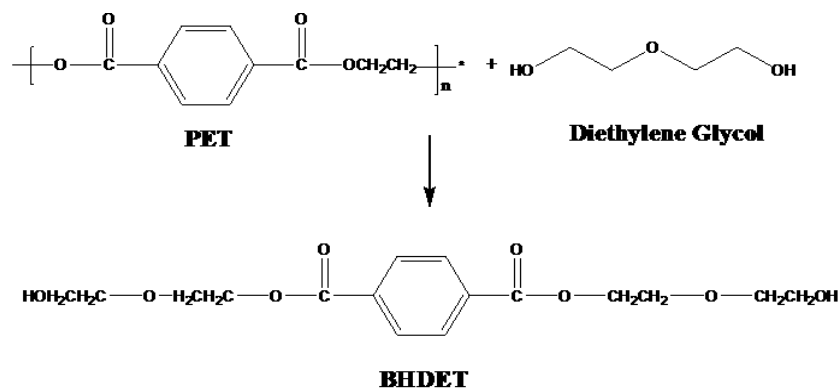


Fig. 2. Glycolysis of WPET using DEG.

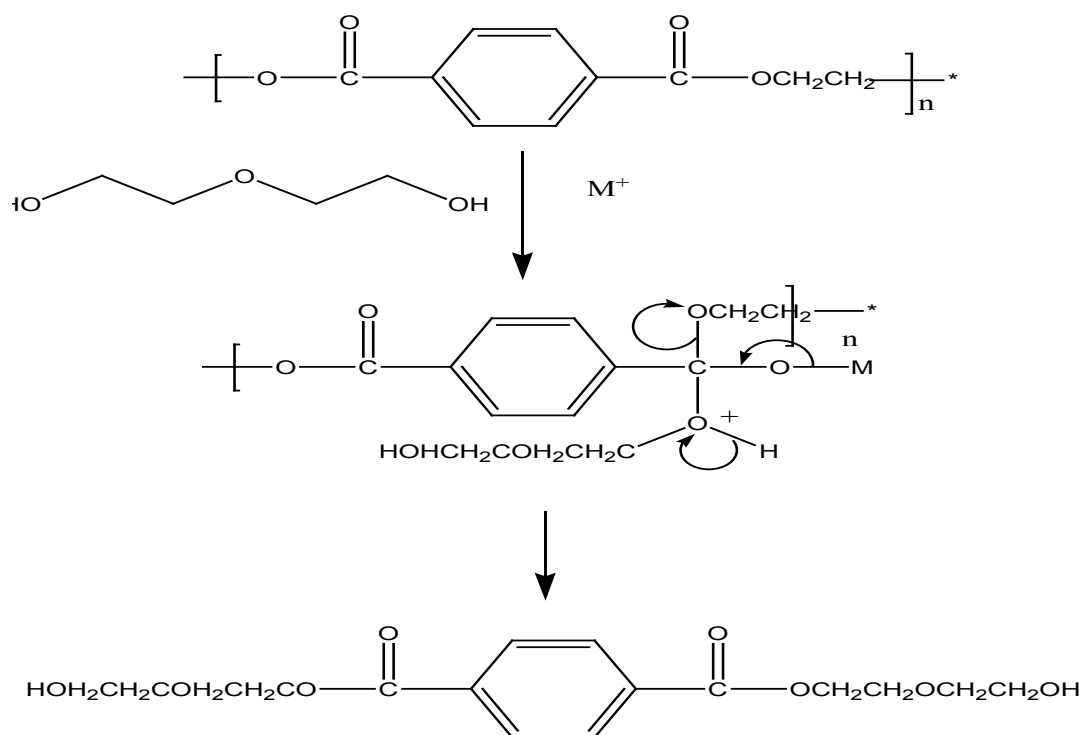


Fig. 3. Mechanism of Glycolysis of WPET.

TABLE 1. Average molecular weights of Glycolyzed PET waste by DEG, TEG and PG.

Glycolyzed Products.	Hydoxyl value, (mg KOH/g)	Number Average molecular Weight (Mn)
GD	244.287	459.295
GT	180.022	623.257
Gpg	77.046	1453.677

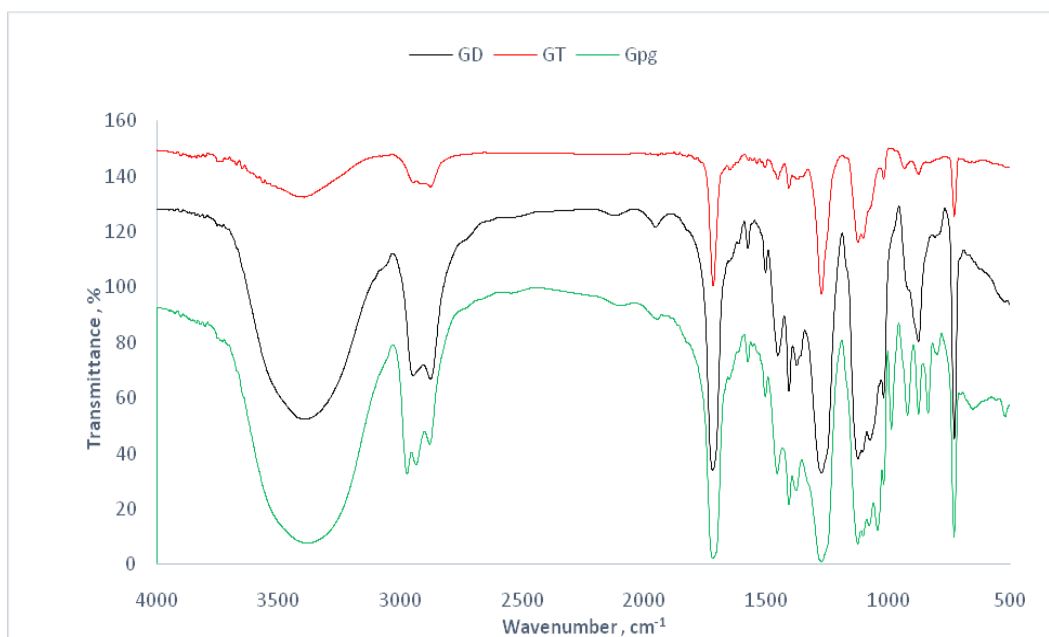


Fig. 4. FTIR Spectra of GD, GT and Gpg.

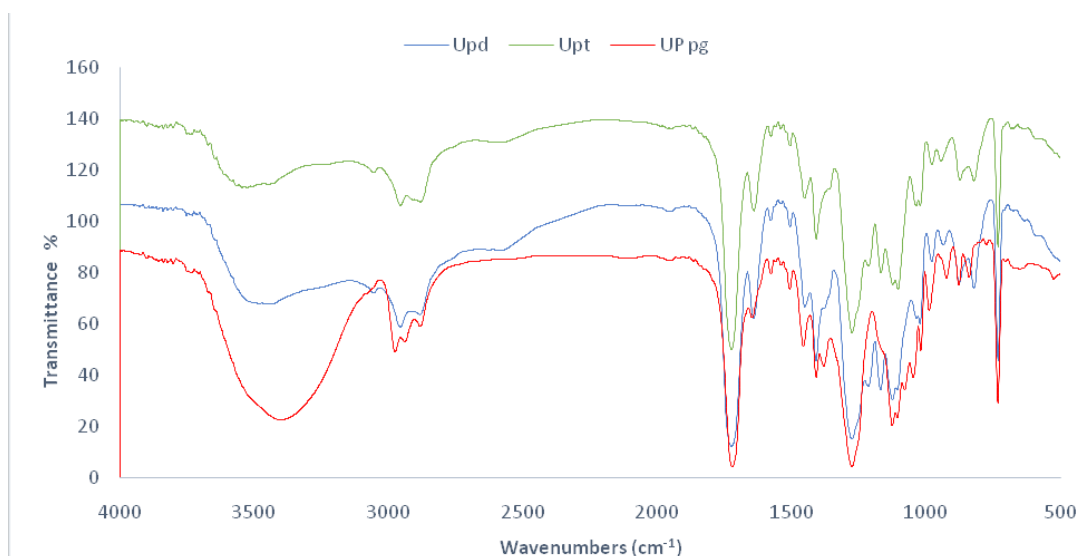


Fig. 5. FTIR Spectra of UPd, UPt and UP pg.

Molecular Weight result of Unsaturated polyester resins

The molecular weight obtained valuee results of Unsaturated polyester resins are presented in Table 2 and shows that the molecular weight increases in the order of UP pg > UPt > UPd. This increase is due to the longer chain glycolized products as it falls in the same order Gpg > GT > GD as previously mentioned in section 3.2.2.1.

Thermal Gravimetric Analysis (TGA).

Figure 6 shows TGA curves of UPd, UPt and UP pg. Comparison between the prepared unsaturated polyesters (UPd, UPt and UP pg.), shows that UP pg has the highest mass loss, which decreases in the order of UPt < UPd < UP pg. This indicates that UPt is the highest stable polyester prepared [26,15].

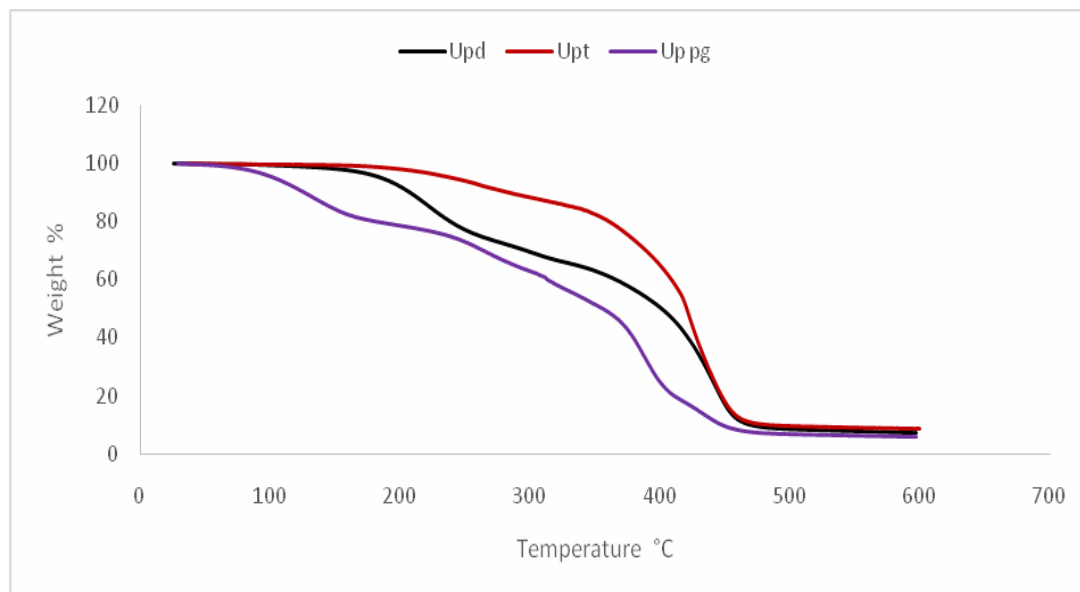


Fig. 6. TGA Curves of UPd, UPt and UP pg.

TABLE 2. Molecular weights of the prepared unsaturated polyesters

Sample name	Molecular weight
UPd	2396
UPt	5743
UP pg	10350

Physical characteristics of virgin and prepared polymer modified binders.

Table 3 illustrates the effect of different percentages of all modifiers addition ranging from 2 to 8% (w/w) on the physical properties of the binder. Also, SARA fractions and colloidal stability index are presented in Table 4.

Penetration test results:

- Generally, and comparing to virgin asphalt characteristics, the penetration values of asphalt decreased significantly by adding the three prepared modifiers and by increasing the percentage of each modifier added namely; UPd, UPt and UP_(pg). The decrease is due to the crosslinking which occurs due to the possible chemical reaction between asphalt the added modifiers.
- The decrease was found to be much more using UP_(pg) modifier added and decreases in the order of UP_(pg) > UPt > UPd. This is

due to the nature of the prepared modifiers as using the longer chain of glycolised products led to higher Mn, and that long chains of the glycolised products improves flexibility of the prepared UPR which affected the properties of the prepared asphalt samples. for example, when 4% of each modifier added to asphalt, the penetration decreased by 34.9 %, 30.2 % and 27 % for UP_(pg), UPt and UPd respectively.

Softening point test results:

- The softening point values of the prepared asphalt samples comparing to virgin asphalt as illustrated in Table 3 increased significantly by adding the three prepared modifiers and by increasing the percentage of each modifier added namely; UPd, UPt and UP_(pg). The increase is due to the crosslinking which occurs due to the possible chemical reaction between asphalt the added modifiers.

TABLE 3. physical properties of virgin asphalt (AC) and polymer modified asphalt samples.

Sample	Penetration (0.1 mm) at 25 °C	Softening Point (°C)	Ductility (cm) at 25 °C	Specific gravity at 25 °C	Penetration index (PI)
Virgin asphalt	63	46	+100	1.019	- 1.742
AC + 2% UPd	53	57	+100	1.021	0.556
AC + 4% UPd	46	63	+100	1.029	1.396
AC + 6% UPd	39	69	+100	1.031	2.042
AC + 8% UPd	32	73	+100	1.039	2.213
AC + 2% UPt	54	60	+100	1.021	1.223
AC + 4% UPt	44	64	+100	1.030	1.470
AC + 6% UPt	37	71	+100	1.037	2.239
AC + 8% UPt	28	75	+100	1.043	2.214
AC + 2% UP(pg)	49	62	+100	1.038	1.365
AC + 4% UP(pg)	41	67	+100	1.051	1.829
AC + 6% UP(pg)	34	71	+100	1.075	2.043
AC + 8% UP(pg)	25	76	+100	1.089	2.117

TABLE 4. SARA fractions analysis of virgin asphalt (AC) and polymer modified asphalt samples.

Sample	Asphaltene (%)	Saturate (%)	Aromatic (%)	Resin (%)	Colloidal stability index (C.I)
Virgin asphalt	21.02	11.60	35.68	31.70	0.4606
AC + 2% UPd	23.00	11.30	34.90	30.80	0.5220
AC + 4% UPd	27.00	11.10	34.00	27.90	0.6155
AC + 6% UPd	30.00	10.50	32.75	26.75	0.6807
AC + 8% UPd	35.00	9.80	31.00	24.20	0.8116
AC + 2% UPt	24.00	11.50	34.00	30.50	0.5503
AC + 4% UPt	29.00	11.20	32.80	27.00	0.6722
AC + 6% UPt	34.00	10.80	31.20	24.00	0.8116
AC + 8% UPt	38.00	10.10	29.90	22.00	0.9268
AC + 2% UP(pg)	26.00	11.20	34.45	28.35	0.5924
AC + 4% UP(pg)	31.00	10.80	32.50	25.70	0.7182
AC + 6% UP(pg)	35.00	10.40	30.10	24.50	0.8315
AC + 8% UP(pg)	40.00	9.80	28.60	21.60	0.9920

- The increase was found to be much more using UP_(pg) modifier added and increases in the order of UP_(pg) > UPt > UPd. This is due to the nature of the prepared modifiers as using the longer chain of glycolised products led to higher Mn, and that long chains of the glycolised products improves flexibility of the prepared UPR which affected the properties of the prepared asphalt samples. for example, when 4% of each modifier added to asphalt, the softening point values increased by 45.7 %, 39.1 % and 37% for UP_(pg), UPt and UPd respectively.

Specific gravity test results

As seen in Table 3 and comparing to virgin asphalt, the specific gravity values of all polymer modified asphalt samples increased significantly and increases in the order of UP_(pg) > UPt > UPd. This may be due to increase in asphaltene content as illustrated in Table 4.

Colloidal Stability Index.

The data in Table 4 and Fig. 7 show that colloidal system of virgin AC is nearly stable, emphasizing that PMAs using different percentages of each

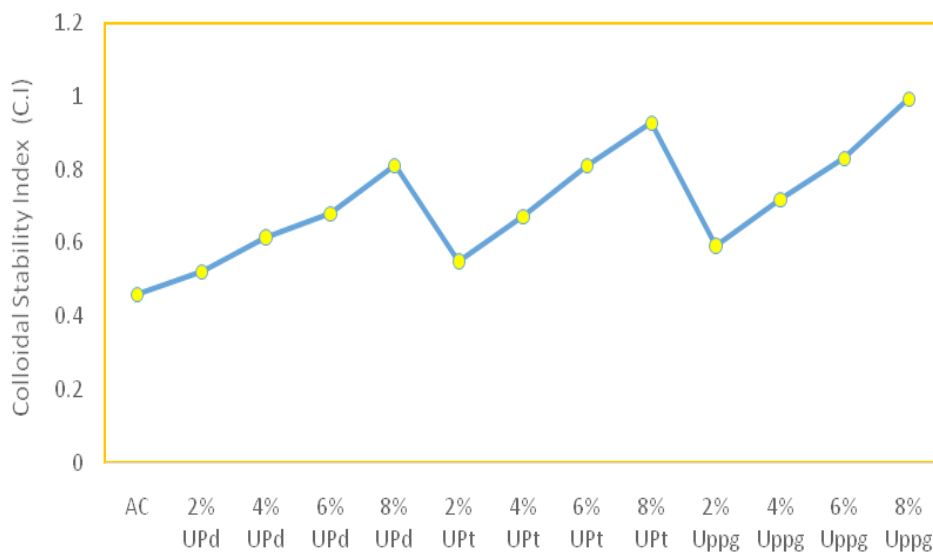


Fig. 7. Asphalt colloidal stability.

modifier (UPd, UPt and UP_(pg)) tend to be harder than virgin AC and increases in the order of: UPd < UPt < UP_(pg), this is attributed to the nature and the percentage of unsaturated polyester added which is affected with type of glycol used as previously mentioned, using the longer chain of glycolised products led to higher Mn, and that long chains of the glycolised products improves flexibility of the prepared UPR which affected the properties of the prepared asphalt samples.

It is seen that, the colloidal stability index increases by increasing asphaltene content. This refers to changing the nature of the prepared asphalt samples by changing the nature and the content of the modifier added. It is seen that, the colloidal stability index increases in the order of UP_(pg) > UPt > UPd which means the prepared asphalt samples more stable and harder than virgin asphalt due to their ability to form crosslinking between asphalt and the prepared unsaturated polyesters. The requirements of the colloidal stability index are given in Table 5.

Thermal gravimetric analysis of choice PMA sample.

TGA has been made for virgin and prepared asphalt samples containing 4% of each modifier and compared to virgin asphalt (AC) as shown in Fig. 8. As seen, generally the virgin and modified sample show the same thermal manner. virgin AC has the decomposition stage ranging from 240 to 492.35 °C with mass loss of 82.09 %.

This may explain that AC sample contains heavy metals, some non-hydrocarbon materials and asphaltene content, suggesting the decomposition of asphaltenes to produce coke. AC + 4 % UPd shows initial decomposition stage starting from 415.07 °C to 497.17 °C with mass loss value equal to 87.13 %. AC + 4 % UPd showed a very similar thermal behavior when compared to virgin AC. Also, 4 % UPt and showing decomposition stage starting from 428.30 °C to 492.22 °C with mass loss value equal to 89.10 %. while, AC+ 4% UP pg showing decomposition stage starting from 425.60 °C to 493.69 °C with mass loss value equal to 83.66 %.

Generally, the initial decomposition stage is arranged in the order of 4% UP(pg) > 4% UPt > 4% UPd > virgin AC and this is due to the chemical reaction between asphalt and unsaturated polyester from different Glycols added and the nature of the prepared modifiers as using the longer chain of glycolised products led to higher Mn, and that long chains of the glycolised products improves flexibility of the prepared UPR. By comparing these samples according to mass loss, it was found that 4% UPt has the highest mass loss and there is a decrease in this order of 4% UPt > 4% UPd > 4% UP pg > virgin AC. This may be attributed to that thermal stability decreased with increasing penetration index (P.I) [27, 28]. i.e., the presence of asphaltene decreased the decomposition temperatures and also mass loss

of asphalt. However, the rate of decomposition after initial decomposition temperature (IDT) has opposite effect. Bitumen with higher P.I decomposes slower after IDT than bitumen with lower P.I. [29]. the results nearly the same and this is due to formation of chemical network between asphalt and added modifiers.

Dynamic mechanical properties of virgin and PMAs:

The rheological properties of the virgin asphalt (AC) and the prepared polymer modified asphalt samples using different percentages of each modifier at different temperatures are illustrated in Table 6.

Complex Shear Modulus.

The complex shear modulus value (G^*) of the virgin and PMA using different contents of UPd, UPt, UP pg from 2% to 8% (W/W) at different temperatures is illustrated in Table 6 and shown in Fig. 9.

- The results obtained from Table 6 and Fig. 9 detected that for all samples, the G^* value decreases with increasing temperature, which

means that the stiffness of the prepared samples decreases This is due to the decrease in elastic manner of asphalt by raising temperature.

- At the same temperature, (G^*) value decreased with increasing percentage of polymer added. This is attributed to that each polymer has its own saturate content with asphalt after which a separation phenomenon occurs, The presence of 4% (W/W) content of each polymer was found to be most suitable for modifying asphalt as it has high (G^*) value [30].
- At the same modifier addition content, for example UPd, (G^*) value decreased with increasing temperature. For an example, at 4% UPd content addition, G^* value decreased from 5.48 at 58 °C to 0.53 (kPa) at 76 °C in a percent of 90.3 %.

Phase Angle (δ).

The phase value (δ) values of the virgin and PMA using different contents of UPd, UPt, UP pg from 2% to 8% (W/W) at different temperatures are illustrated in Table 6 and shown in Fig. 10.

TABLE 5. Requirements of colloidal stability index.

I.c	0.5 – 2.7	Ic > 0.5	Ic < 0.22
State of Asphalt	Colloidal system is unstable	Asphalt becomes more harder	Asphalt becomes more Softer

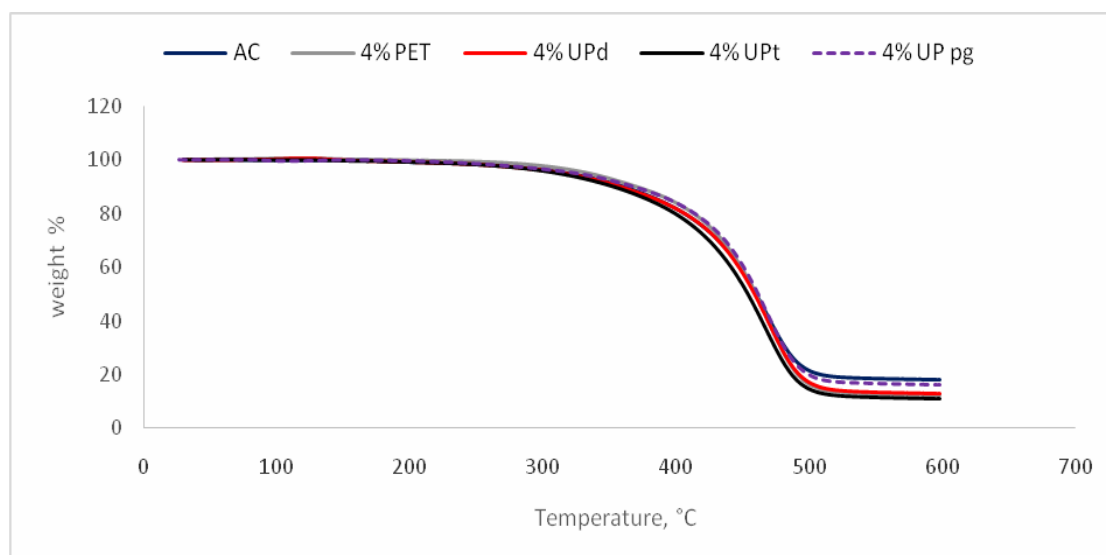


Fig. 8.TGA curves for virgin asphalt 60/70 and prepared PMA samples

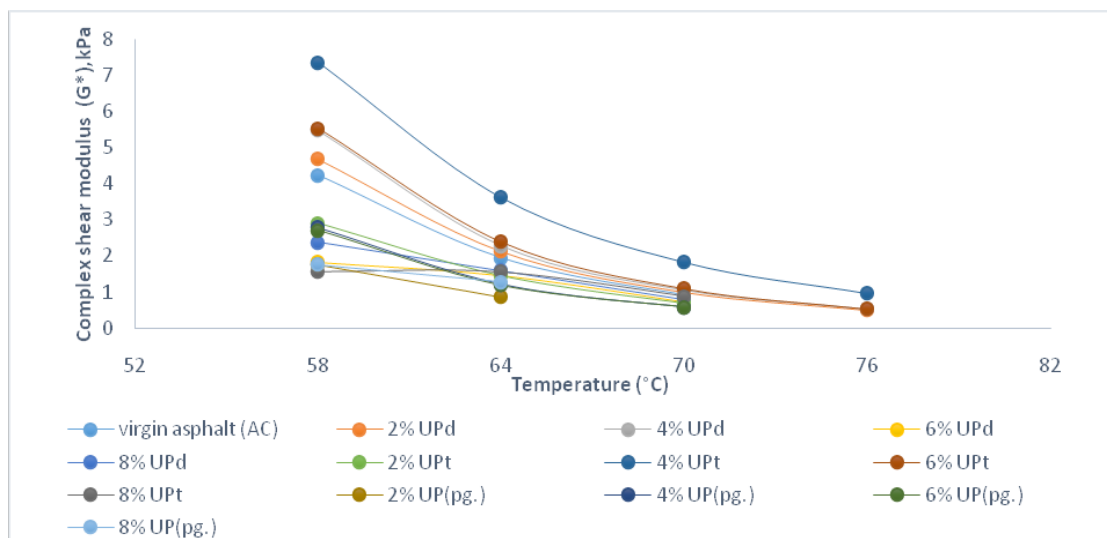


Fig. 9. The complex modulus of virgin asphalt (AC) and modified asphalt samples using different contents of UPd, UPt and UP pg at different aging states.

TABLE 6. Rheological properties of virgin asphalt and the prepared PMA using different contents of each modifier (UPd, UPt and UP_(pg)) at different temperatures.

Temperature	Virgin asphalt	AC + UPd				AC + UPt				AC + UP(pg)			
		2%	4%	6%	8%	2%	4%	6%	8%	2%	4%	6%	8%
Complex shear modulus (G*)													
58	4.229	4.68	5.48	1.82	2.37	2.905	7.360	5.527	1.566	1.763	2.792	2.702	1.763
64	1.937	2.13	2.28	1.46	1.59	1.461	3.620	2.395	1.554	0.860	1.204	1.198	1.271
70	0.916	1.00	1.06	0.722	0.78	0.697	1.817	1.092	0.875		0.578	0.572	
76	-----	0.49	0.53	-----	-----		0.957	0.537	-----				
Phase angel (δ)													
58	84.5	83.7	83.5	81.9	81.9	84.7	81.3	82.8	79.6	86.6	86.7	86.6	86.6
64	86.1	85.4	85.2	84.1	84.2	86.2	83.4	84.6	82.4	87.8	87.8	87.7	87.6
70	87.4	86.8	86.6	85.8	85.9	87.5	85.1	86.2	84.6		88.7	88.6	
76		87.9	87.7				86.4	87.4					
Rutting factor (G* / sin δ)													
58	4.25	4.71	5.52	1.84	2.39	2.92	7.45	5.57	1.59	1.77	2.80	2.71	1.77
64	1.94	2.14	2.29	1.47	1.60	1.46	3.64	2.41	1.57	0.86	1.21	1.20	1.27
70	0.92	1.01	1.06	0.72	0.78	0.70	1.82	1.09	0.88		0.58	0.57	
76		0.50	0.53				0.96	0.54					

- The phase angle (δ) values increases with increasing the temperature due to the increase of the plasticity (viscous manner) of asphalt.
- At the same temperature (δ) value decreases with increasing the polymer content. This is due to the decrease in deformation resistance.
- At the same modifier addition content, for example UPd, (δ) value increases by increasing temperature. for example, 4 % UPd, (δ) value increased from 83.5° at 58 °C to 87.7 ° at 76 °C in a percent of 5 % as a result of decrease in resistance of asphalt to deformation against the applied load.
- Also, the presence of 4% (W/W) content of each polymer was found to be most suitable for modifying asphalt.

Superpave Rutting Resistance Parameter ($G^*/\sin \delta$).

The rutting parameter ($G^*/\sin \delta$) is considered as previously mentioned the Superpave rutting parameter. The rutting parameter values of the virgin and PMA using different contents of UPd, UPt, UP pg from 2% to 8 % (W/W) at different temperatures are illustrated in Table 6 and shown in Fig. 11.

- Generally, the rutting parameter ($G^*/\sin \delta$) values of the prepared PMA samples comparing to virgin asphalt decreases with increasing the temperature and increasing the percentage of the prepared unsaturated

polyester added. This is due to the viscoelastic properties of asphalt as its viscosity changes with temperature and as well as to a decrease in its stiffness.

- At the same modifier addition content, for example 4% UPd, ($G^*/\sin \delta$) value decreased from 5.52 at 58 °C to 0.53 kPa at 76 °C.

Conclusion

Utilization of waste polyethylene terephthalate for synthesis of unsaturated polyesters (UP) with different nature and different molecular weights using different glycols such as diethylene glycol (DEG), Triethylene Glycol (TEG) and propylene glycol (PG) to be used as modifiers for asphalt modification.

- The prepared unsaturated polyesters (UPd, UPt and UP_(pg)) makes crosslinking with asphalt leading to formation of polymer modified asphalt with improved nature and performance.
- The colloidal stability index differs with changing the nature and the percentage of the added polymer.
- The results of the colloidal stability of the prepared asphalt samples indicates the increasing the stability compared to the virgin sample.
- The modified asphalt samples show a higher resistance toward dynamic, rheological and

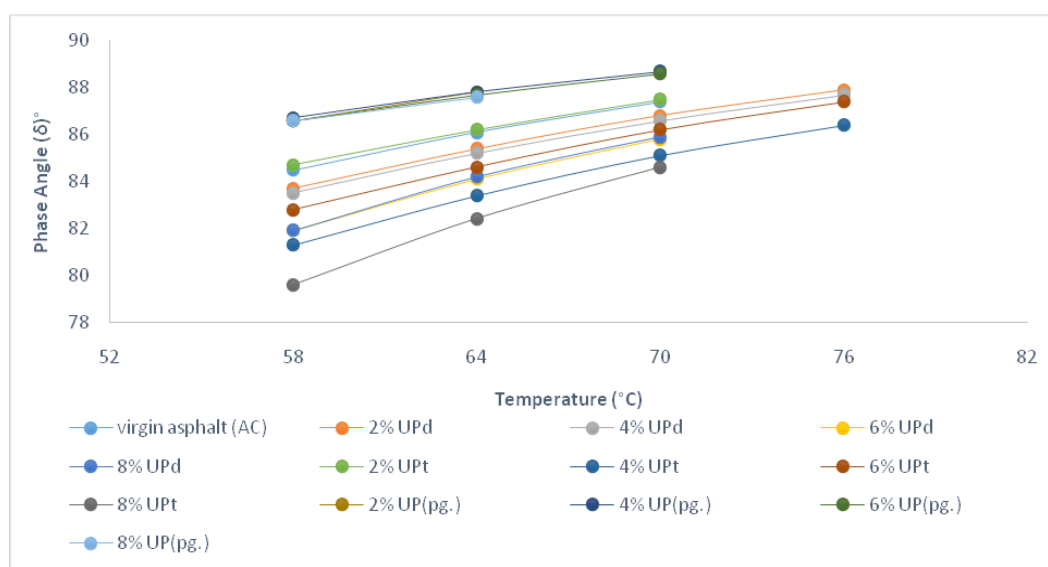


Fig. 10. The phase angle of virgin asphalt (AC) and modified asphalt samples using different contents of UPd, UPt and UP pg at different aging states.

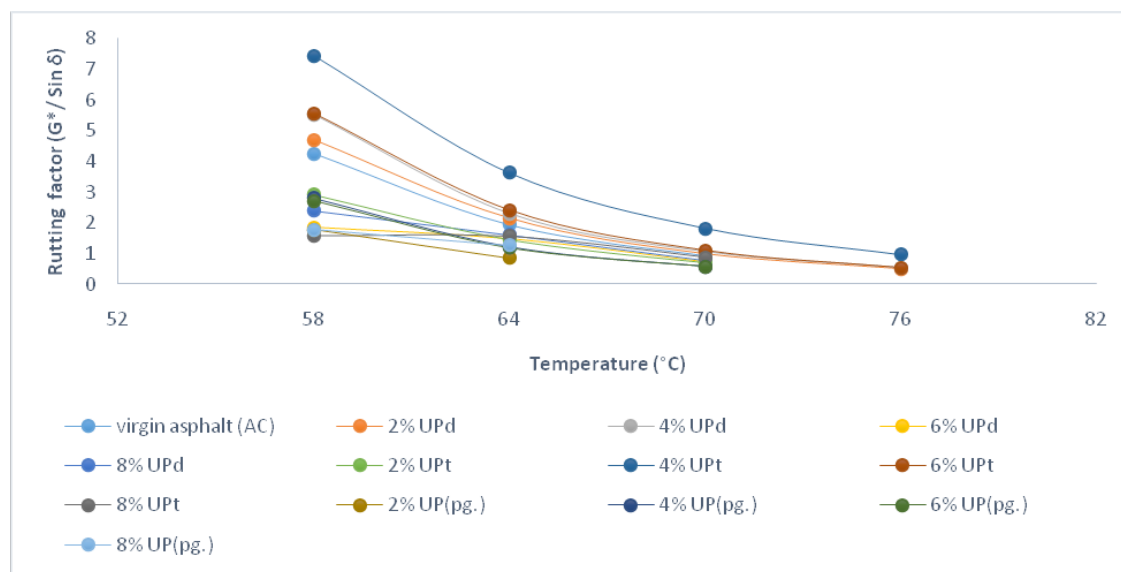


Fig. 11. The rutting factor of virgin asphalt (AC) and modified asphalt samples using different contents of UPd, UPt and UP pg at different aging states.

rutting properties according to the type and the percentage of the added polymer compared to the virgin sample.

- It is possible to prepare an eco-friendly asphalt using unsaturated polyesters synthesized from waste polyethylene terephthalate (WPET) Thus promoting the principles of sustainable development.

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الاستقرار الغروي والخصائص الميكانيكية الديناميكية للأسفلت المعدل بالبولىستر غير المشبع المحضر من مخلفات البولي إيثيلين تيريفثاللات

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يهدف هذا البحث إلى تحضير البولي استرات غير المشبعة (UP) من نفايات البولي إيثيلين تيريفثاللات (WPET) ودراسة آثارها على الثبات الغروي والخصائص الميكانيكية الديناميكية لعينات الإسفلت المعدلة المحضرة. ولتحقيق هذا الهدف، تم إعادة تدوير مخلفات البولي إيثيلين تيريفثاللات (WPET) كيميائياً من خلال تفاعل تحلل الغليكول باستخدام جليكولات مختلفة مثل داي إيثيلين جليكول (DEG)، وتراي إيثيلين جليكول (TEG) وبروبيلين جليكول (PG) بنسبة 1: 1, 2, 1 من وزن مخلفات البولي إيثيلين تيريفثاللات بشكل منفصل. ثم بعد ذلك يتم تحويل الأوليجومرات الناتجة من عملية تدوير مخلفات البولي إيثيلين تيريفثاللات إلى بوليستر غير مشبع (UP) عبر التفاعل مع المالتيك أنهيدريد. تم تقييم البولي استرات غير المشبعة المحضرة UPd و Upt و Uppg باستخدام الأشعة تحت الحمراء (FTIR) والأوزان الجزيئية (GPC) والثبات الحراري (TGA) ثم يتم إضافتها إلى الأسفلت 70/60 بنسب مئوية تتراوح بين 2٪ إلى 8٪ بالوزن باستخدام العملية الرطبة لتحضير عينات الإسفلت المعدل مع خصائص فيزيائية وهندسية مرغوبة. تم تقييم عينات الإسفلت المعدلة عن طريق الثبات الحراري باستخدام (TGA)، الخواص الفيزيائية والكيميائية باستخدام الاختبارات التقليدية، مؤشر الثبات الغروي بينما تم فحص خواصها الريولوجية باستخدام جهاز دابنامك شير ريوميتر (DSR) لتحديد مقاومة الصلابة و من العينات المحضرة. وقد أظهرت النتائج تحسناً في خواص الإسفلت التي أصبحت أكثر ثباتاً من ناحية الحرارة وثبات الغروي ومقاومة التشوه.