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Effect of Adding Maleic Anhydride to Thermoplastic Elastomer Blends on the Rheological and Chemical Properties of Sustainable Asphalt

A. A. Ragab¹, Ibrahim M. Nassar^{1*}, Naglaa K. Rashwan², Ahmed S. Mansour¹

- ¹ Egyptian Petroleum Research Institute (EPRI), 1 Ahmed El-Zomor St., Nasr City, 11727, Cairo, Egypt
- ² Beni-Suef University, Faculty of Engineering, Department of Civil Engineering. Salah Salem St., Beni-Suef, 62521, Egypt

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Abstract

Thermoplastic elastomers (TPEs) have emerged as promising candidates for developing cost-effective asphalt materials with superior low-temperature performance, combining the attributes of vulcanized rubber with the processing ease of thermoplastics. In this study, a novel approach involved blending high-density polyethylene (HDPE) and natural rubber (NR) with and without compatibilizers (MA) as additives for modifying asphalt 60/70 at varying percentages (3%, 5%, 7%, and 10% wt/wt). The performance of polymer-modified asphalts (PMAs) was assessed through penetration index (PI), temperature susceptibility, shear stress/shear rate, dynamic viscosity, and mechanical properties under different conditions (air and water). The findings demonstrated that polymer addition to asphalt mitigates its thermal susceptibility, imparting increased elasticity. PMAs exhibited thixotropic behavior, high yield stress, excellent gunnability, and resistance to flow on vertical surfaces. Tensile shear strength in the blends increased with polymer content, with PE70/MA outperforming PE70. Both in water and air, PE70 and PE70/MA enhanced asphalt's mechanical properties, with air proving more effective. The optimal ratios for workability were identified as 7% and 5%. Notably, PMAs displayed higher tensile strength, indicating enhanced strain tolerance before failure (cracking). Moreover, the study highlighted the potential to evaluate asphalt mixture moisture susceptibility by comparing tensile strength under wet and dry conditions.

Keywords: Maleic anhydride; Thermoplastic; Elastomer; Blends; Rheological; Sustainable; Asphalt.

1. Introduction

Asphalt 60/70 is a modest material which has been easily influenced by temperature and long restoring time. So, there is a need to improve its in-service properties to overcome the problems occurred at low temperatures such as cracking and also occurred at elevated temperatures such as rutting ^[1]. The improvement in the asphalt properties allow us to expand the temperature operation ranges and enhance the deformational stability of asphalt that achieved by addition of polymers or any other modifier as polymer wastes ^[2-5]. Using of polymers for modification of asphalt mostly changes the in-service properties of asphalt pavement to be more stable and stiffer at elevated temperatures and more flexible at low temperatures ^[68]. One of the most popular and widely used polymers is the thermoplastic elastomer ^[9]. These materials have garnered significant attention in the industry due to their ability to amalgamate the attributes of vulcanized rubber with the facile processing characteristics of thermoplastics ^[10-15]. Among TPEs, styrene-butadiene-styrene copolymer (SBS) stands out as a widely used copolymer for asphalt modification, owing to its favorable compatibility with asphalt, workability, and high performance. Despite these advantages, challenges such as poor oxidation resistance arising from double bonds in the SBS backbone and high cost limit its selection for modifying asphalt properties. ^[16].

Competitive thermoplastic elastomers (TPEs) show promise for asphalt modification, with maleic anhydride and irradiation methods employed to enhance compatibility [17-18]. Thermoplastic elastomers are categorized into six main types: styrenic thermoplastic elastomers, combinations of hard polymers and elastomers, multiblock copolymers, ionomers, graft copolymers, and core-shell morphologies. The properties of these elastomers are influenced by the mixing of two or more distinct polymeric phases, where, in some instances, the phases are not chemically bonded but may be linked through block or graft copolymerization ^[19]. Increasing the softening point, making penetration less effected by temperature, increasing the ductility (especially at low temperatures), making asphalt less susceptible to elastic reverse deformation, enhanced expansion of the working temperature range and adhesion of asphalt to mineral fillers of asphalt concrete are desirable modifications of a paving asphalt ^[20]. Elastoplastics are not all compatible with asphalt and their compatibility depends on the chemical composition of both asphalt and Elasto-plastics. The using of a novel polyurethane thermoplastic elastomer (PUTE) as an asphalt modifier was studied. The results indicated that the PUTE modified asphalt mixture has better performance in low-temperature property and moisture stability than the SBS modified asphalt mixture, whereas the PUTE modified asphalt mixture has worse high-temperature property than the SBS modified asphalt mixture ^[21]. Thermoplastic elastic PP/NBR Mixtures of 3, 5, 7 and 10% were added with and without the use of PP-MA to improve the properties of the asphalt. From the results, we find that adding polymers to asphalt reduces its heat susceptibility at different temperatures as the asphalt becomes more flexible. It was also found that PMAs have higher tensile strength which means that the asphalt can withstand higher strains before failure (i.e. crushing) ^[22].

Study the properties of bitumen are modified by blend TPEs was done. It is established that their introduction leads to a considerable increase in the softening point and frost resistance, as well as a drop in the penetration and water sorption. Moreover, it is found that the effect of TPEs grows with increase in their solubility in the aliphatic component of the maltenes fraction of bitumen ^[23].

For this paper, flexible thermoplastic blends (HDPE/NR at 3, 5, 7, and 10w/wt ratios) are used with 10wt/ wt maleic anhydride as a compatible device for good compatibility of blends to achieve asphalt favorite properties. Mixtures of PMAs were evaluated by physical characterization such as (temperature susceptibility, routine analysis and PI), yield stress, dynamic viscosity and in air and water as different mediums we study the mechanical properties (such as elongation, shear strength and tensile strength).

The results indicated that adding polymers to asphalt reduces its heat susceptibility at temperatures and ensures greater stability of its properties as the asphalt becomes more flexible. By increasing the percentage of polymer added, there are improvements in the physical and rheological properties of the final product. The rheological data of PMAs indicates its low flow on surfaces thixotropic property, good vertical flowability. Also, the tensile shear strength (N/cm3) of the obtained mixtures increased with the concentration ratio of polymer content using HDPE70/MA more than using HDPE70 only so, the TEPs addition (HDPE70& HDPE70/MA) enhance the engineering properties of virgin asphalt 60/70 in various mediums but in the air is the best. Finally, polymer modified asphalt mixtures have higher tensile strength which means higher stress is provided before failure (i.e. cracking). In addition, the sensitivity of asphalt samples to moisture can be assessed by comparing asphalt mixtures tensile strengths of exposed to different conditions.

2. Experiments and evaluation methods

2.1. Chemicals and asphalt used

Egyptian asphalt penetration grade (60/70) produced by Al-Nasr Petroleum Company in Suez, Egypt, high density polyethylene, natural rubber, maleic anhydride for preparation of these materials: HDPE70/ NR30, HDPE70/NR30/10% MA were prepared according to Motawie *et al.*^[24].

2.2. Characterization and preparation procedure

2.2.1. Characterization of unmodified asphalt

The sample of original asphalt tested as described in Table 1 according to ASTM D36 softening point, (ASTM D5) penetration, ASTM D4402 Brookfield viscosity, ASTM D3297 n-heptane insoluble and specific gravity (ASTM D70). Table 1 showed the results.

Penetration (mm) 25°C	Ductility, cm	Kinematic vis- cosity 135°C, cSt	Absolute vis- cosity 60°C	Softening point, °C	Specific gravity, g/cm ³
63	+150	256	1070	51	1.1733
API	Penetration temperature susceptibility	Penetration in- dex	Specific heat Btu pound/°F	Thermal con- ductivity	
-11.33	0.0281	-0.49	0.383	0.6379	
Wax %	Oil %	Resin %	Asphaltene %		
6.88	28.90	55.10	16.41%		

Table 1. Physical and chemical properties of asphalt samples AC 60/70 used for modification.

2.2.2. Processing and testing of HDPE/NR mixtures

Variable weight ratio HDPE/NR blends were obtained in the presence and non-presence of MA as specification with the Brabender plastic system (PL 2100, 350S). First, PE was added to the plastic Brabender order preheated to 180°C for 2 min, the tested compatibility apparatus was incorporated, and NR was finally added. Mixing temperature 180°C; keep stirring for 6 minutes at 60 rpm.

HDPE modified with malic acid (MA-HDPE) as a stabilizer obtained with MA, addition of dicumyl peroxide (3 parts) and benzoquinone (0.75 parts) at 180°C.

2.2.3.	Viscoelastic	properties	of prepared	materials
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Parameter	Description	Formula
Tensile strength	The maximum load that a mate- rial can support without fractur- ing when subjected to tension, divided by the original cross- sectional area of the material, is known as tensile strength [25-26].	Tensile Strength (TS)=(L/T.W) x 10 MPa (2) where: L is the load in kgf, its significance for causing a break; W Width of the sample in millimeters; T sample thickness in mm
<u>Fracture strain</u>	Fracture strain or tensile elonga- tion at break, is the ratio be- tween increased length and ini- tial length after breakage of the tested specimen at a controlled temperature.	Elongation $\epsilon = (\Delta L/L) \times 100$ (3) where: » ΔL : Final Length; L: Initial Length Elongation at Break is measured in % (% of elongation vs. initial size when break occurs).
Young's Modulus	The ratio of tensile stress (σ) to tensile strain (ϵ).	Young's modulus = Stress/Strain=MPa (4)
Hardness	The ability of a material to resist deformation, as determined by a standard test where the surface resistance to indentation is measured.	ASTM-D 2240 Model 306 L type A durometer. (Shore A) is used to express the unit of hard- ness

2.2.4. Preparation of modified asphalt via HDPE70 and HDPE70/MA

This stage we use HDPE70 + 10% MA and HDPE70 (3, 5, 7 and 10 % wt). In suitable containers, samples are prepared with a stirring speed of 3000 rpm. At a temperature of $180 \pm 1^{\circ}$ C, the polymer is added at a rate of 5 g/min. Stirring continues after complete addition of polymer for two hours ^[27-28].

Parameter	Description	Formula		
Penetration index (PI) and tem- perature susceptibility;	The value of PI ranges from around -3 for high temperature Asphalt is sensitive to approxi- mately +7 for extremely low el- evation susceptible (high PI) bi- tumen	*log P = AT + K (5) where: A is the temperature susceptibility; *A= (log pen at T1-log pen at T2) / (T1-T2) P is penetration at temperature T; K is constant. ^[29] Value of A varies from 0.0015 to 0.06 *PI= $\{20 (1-25A)\} / (1+50A)$		
Rheology of asphalt	Rheology encompasses the ex- amination and assessment of the flow and enduring defor- mation of materials with time- temperature dependence, like bitumen, subjected to stress (typically shear stress or exten- sional stress) induced by the ap- plication of force.	Brookfield viscometer ASTM D4287, 1994); 		
Tensile shear strength τ and elongation measurements [30]	The strength of a material or component against the type of yield or structural failure when the material or component fails in shear ASTM D638-77a	$\tau = \frac{\sigma 1 - \sigma 3}{2}$ $\sigma 1$ is major principal stress and $\sigma 3$ is minor principal stress.		

2.2.5. Characterization of physiologically and rheological modified asphalt samples (PMAs)

3. Results and discussion

3.1. Elastic plastics blending process

3.1.1. Choosing the optimum ratios of HDPE/NR

In order to characterize the HDPE/NR mixture, different mixtures of HDPE and NR are required to study. Mixtures prepared from HDPE/NR and the mixing ratios are shown in Table 2. The mechanical properties of the prepared mixing samples were assessed, and the results are presented in Table 2.

Table 2. Mechanical properties of HDPE/NR and PE70/10 MA binary blend samples with different ratios of blending

	Ratio H	DPE:NR	Tensile	Elongation	Absorbed	Young's	Hardnoss
Sample	PE	NR	strength (MPa)	at break (%)	energy (Kgf.mm)	modulus (MPa)	shore A
HDPE100	100	0	33.2	15.2	206.6	518.6	96
HDPE90	90	10	25.0	66.6	182.6	437.5	96
HDPE 80	80	20	21.3	80.1	164.9	366.3	96
HDPE 70	70	30	17.2	96.3	137.7	278.5	96
HDPE 60	60	40	13.7	69.8	75.5	219.6	95
HDPE 50	50	50	8.7	45.7	47.9	161.3	94
HDPE 40	40	60	7.1	41.9	25.6	91.7	90
HDPE 30	30	70	3.6	38.6	11.1	52.7	83
HDPE 20	20	80	2.7	244.9	5.3	28.1	75
HDPE 10	10	90	1.6	663.8	1.8	5.2	64
HDPE 0	0	100	0.8	1250.0	0.2	1.6	31
HDPE70/ 10% MA	70	30	20.3	75.0	217.6	576.0	99

The data indicates that HDPE exhibits the highest values for adsorbed energy, Young's modulus, and tensile strength, with the lowest value observed for elongation at fracture. On the other hand, NR shows the lowest values for tensile strength, absorbed energy, Young's modulus, and hardness, coupled with the highest value for elongation at break. As for NR, it gives the lowest values for the mentioned mechanical properties. These values reflect the difference between the very low crystalline content of amorphous NR and the high crystal content of HDPE ^[31]. The crystallinity of the HDPE/NR mixture was observed to be decreased by foundation of NR, from 55.3 for HDPE to 33.9 and 13.7 for both inclusion 30 and 70 w/w% NR.

HDPE phase strength is a major influence on the strength of HDPE/NR mixture, which in turn depends on how the mixture crystallizes, which is reduced by foundation of NR. With the increase of the NR content it is observed that HDPE/NR mixture reduces the absorbed energy and Young's modulus, which may be due to the presence of a soft rubbery phase and lower crystallinity of the HDPE phase. Thus, the crystal content of the mixture decreased ^[32]. It turns out that the presence of the rubber phase inhibits the growth of HDPE pellets in mixtures with rubber. It can also be inferred that a negative deviation in the energy absorbed, tensile strength and Young's modulus values for mixtures will appear, that is, the mixing properties fall below the additive line. Due to the poor interfacial adhesion between the non-polar HDPE phases and the polar NR phases results in negative deviation, which causes poor pressure transfer between the dispersed phase and the matrix. Obvious change in slope of this tensile formation curve is shown between formulations ranging from 50/50 to 30/70 HDPE/NR. Noticeable change in the composition curves of the mechanical properties was reported by Song *et al.* ^[33] for the system of PP/EPDM.

Elasticity usually depends on the particle size of the dispersed phase in immiscible mixtures. With the addition of NR the data indicate that the elongation at fracture slightly increases at proportions of 10, 20 and 30% in the area of the HDPE90, HDPE80 and HDPE70 mixture. NR of 30% can be considered as a plasticizer for HDPE/NR at this mixing ratio NR are small spheres, it is dispersed in the continuous phase of HDPE. Increasing NR from 30 to70 leads to an increase in particle size growth in the NR dispersed phase, which hinders mixing elasticity, this is evident by the continuous decrease in elongation values at fraction from HDPE70 to HDPE30. The larger particle size of the dispersed NR phase at higher rubber content caused a decrease in elongation at fracture and the weak surface adhesion between the polymers showed that the elongation at fracture decreased with the increase of the particle size in the phase of dispersed rubber for HDPE/NR mixtures. Poor interfacial adhesion reasons early disappointment due to the typical crack opening mechanism. Small, uniformly distributed particles are most effective in initiating and ending madness before it develops to catastrophic sizes. Over 70% increase in rubber content accompanied by a sharp increase in elongation at break with more NR added.

This high-pitched increase in elongation at break might be because of the unceasing phase of NR nature, which procedures a co-continuous assembly with the plastic phase; alike results were stated in the incident of the PP/EVA system ^[34].

It can be clearly deduced from all the above data for the mechanical properties of all HDPE/NR mix ratio; The HDPE70 sample with the HDPE/NR blending ratio (70/30) has the greatest reasonable wanted mixture of mechanical properties meaning high values of tensile strength, energy absorbent, youth modulus and hardness along with a high value of elasticity. It is remarkable that any other sample will have a deficiency of one or more values of mechanical properties compared to HDPE70.

3.1.2. Effect of addition maleic anhydride as a compatibilizer on blends ^[24]

In Table 2, the results indicate the variance of tensile strength, elongation at break, energy absorption, youth modulus and hardness of 70/30 of HDPE/NR mixture and copolymers with the presence of the compatibility device.

For copolymers compatible with MA-HDPE, tensile strength increasing may be payable to an increase in the dipole interaction between the MA-HDPE and NR phases, which increases the interfacial adhesion between the HDPE and NR phases, although there is no decrease in

particle size with Increasing the concentration of MA-HDPE elsewhere 1%. Mixtures tensile strength can be determined by Coran's equation wherever MA-HDPE and Ph-PE are found to be aligners in the HDPE/NR system. With increasing concentration of the conformer, the province size of the dispersed NR phase decreases, monitored by flattening at higher concentrations, which is an indicator of interfacial saturation. According to the theories of Noolandi and Hong, there are predictions of a linear decrease in surface tension with a volume fraction consistent with lower concentrations of CMC. It has been shown that the experimental data agree with these theories, given the fact that the interfacial tension is directly proportional to the field size.

The energy absorbed, Young's modulus, and hardness of the mixture exhibit an exponential increase with the addition of compatibility agents. The rate of increase in these parameters is found to be proportional to the number of moles of H_2O_2 added per mole of oil in the epoxidation process. MA-HDPE, used as a stabilizer, yields the highest values for energy absorption, Young's modulus, and hardness. However, the values of elongation at break show a notable decrease with the addition of MA as a stabilizer, and further reduction in elongation at breakage is observed with the addition of more MA.

3.1.3. Reaction mechanism of compatibilization process

In the synthesis of a graft-compatible copolymer (HDPE-MA) enhancing the biocompatibility of HDPE-MA, maleic anhydride serves as the primary monomer for reactive compatibility. This graft copolymer, acting as an emulsifier at the interface, effectively diminishes interfacial tension. The process involves grafting maleic anhydride (MA) groups onto the HDPE series backbone, resulting in the formation of MA-HDPE grafted polyethylene, as depicted in Scheme (1) ^[24].

3.2. Modification of asphalt using prepared blend and evaluation of PMAs

Characteristics of all PMA materials: o 3, 5, 7 and 10% HDPE70 and HDPE70/MA will be revealed as follows: In Table 1, with the polymer modification, the properties and performance of asphalt 60/70 change dramatically.



MA modified PE

Scheme 1. Maleic anhydride (MA) reaction with polyethylene (PE) to produce maleic anhydride modified polyethylene (MA-PE)

3.2.1. The ability to resist climate change by calculating penetration indexes

In general, the modified samples showed increased rigidity compared to the original sample, as evidenced by increased dynamic viscosity, softening point, specific gravity and a decrease in the penetration value as in Table 3 and Figure 2. the addition of HDPE70/MA results in greater stiffness compared to the use of HDPE70 alone, as indicated in Tables 4 and 5. The combined impact of incorporating both HDPE70 and HDPE70/MA into the asphalt contributes to this outcome. Additionally, the hardness is greater in the case of HDPE70/MA compared to HDPE70 (Tables 4 and 5). Increasing HDPE70 ratios (3%, 5%, 7%, and 10% w/w) led to a significant reduction in PMA penetration by 32.26%, 54.8%, 62.9%, and 72.6%, respectively, and softening point decreased by 10.67%, 26.48%, 34.4%, and 44.27%, respectively, compared to unmodified asphalt. At 60°C the dynamic viscosity increased by 338.5, 393.0, 456.4, 892 and the values of 6.7, 73.24 and 258.53 respectively at 130°C. The penetration index increased from -0.51 to -0.21, 0.38, 0.65 and 0.85, respectively and in the same way increased specific gravity.

Asphalt sample	Penetration 0.01 mm 25 °C	Ductility cm	Kinematic viscosity 135 °C, C.st	Absolute viscosity 60 °C	Softening point °C	Specific gravity gm/cm³	(1) API	2* PTS	Id *E	*4 C, Btu pound per °F	*5 thermal con- ductivity	Dynamic viscosity mpa.s, 60 °C 1198.08 S-1
3	44	129	375	1645	56	1.023	8.563	0.0361	0.21	0.385	0.653	1176.54
5	28	120	435	1732	64	1.091	7.713	0.0281	0.38	0.377	0.667	1560.69
7	23	80	450	1820	68	1.143	3.008	0.0547	0.64	0.232	0.834	2201.12
10	17	50	495	1921	73	1.151	1.254	0.0201	0.85	0.2291	1.021	3301.56
	With MA											
3	42	125	450	1720	56	1.024	6.415	0.0344	0.21	0.360	0.748	1350.23
5	27	115	503	1850	72	1.028	2.568	0.0305	2.38	0.342	0.862	1820.36
7	17	75	560	1930	80	1.030	0.652	0.025	3.12	0.202	1.025	2830.56
10	7	30	630	2140	88	1.032	1.542	0.0184	4.3	0.160	1.458	7238.14

Table 3. Physical properties of PMAs using HDPE70 and HDPE70/MA.

*2 - penetration temperature susceptibility; *3 - penetration index; *4 - Specific heat; *5 - Thermal conductivity







Fig. 2. Physical properties PMAs using prepared TPEs with MA.

With the addition of HDPE70/MA as 3, 5, 7 and 10% and due to the chemical molecular structure of HDPE70/MA which reacts with asphaltene in the matrix, the penetration decreased by 32.3, 56.45, 72.6 and 88.7%, the softening point increased by 10.87, 42.29, 58.1 and 73.9%, respectively. At 60°C the dynamic viscosity increased by 473.0, 546.4, 678.5, 1036.5, and 8.6, 68.24, 196.53, 221.64, respectively at 130°C. Penetration index increased from -0.51 to -0.21, 2.83, 3.18 and 4.3, respectively, the specific gravity also increased.

3.2.2. Effect of thermoplastic elastomers (TPEs) blends on temperature susceptibility

By calculating the PI values the temperature sensitivity of the modified samples was checked. PI values also increased from -0.51 for unmodified asphalt to -0.21, 0.38, 0.64, and 0.85 for 3, 5, 7 and 10% of HDPE70 content respectively and -0.21, 2.83 & 3.12 and 4.3 for 3, 5, 7 and 10% of HDPE70/MA content respectively as in Table 3 and Figure 3 compared with unmodified asphalt.



Fig.3. Changes in the viscosity of PMA using HDPE70.

The resistance of asphalt samples to cracking at low temperatures in the case of using rubber materials with the increase in PI. It is evident that the hardness and stability of samples modified for addition of HDPE70/MA are observed and not if HDPE70 is used. It is now confirmed that PI is a fairly strong indicator to classify the rheological behavior of asphalt as PI < 2 denotes asphalt gel while PI > 0 is typical in sol. It was observed that blown asphalt usually contained PI < 1 when straight asphalt had -1 > PI > +1. Only very sensitive materials such as coal tar gave a PI > 1.

3.2.3. Rheological behavior of samples modified with different temperatures

3.2.3.1. Changes in the viscosity of the modified samples under different temperatures

Temperature change as harsh conditions the coating may be exposed to clearly affect the viscosity of all samples. It can be seen from Figures 4 and 5, regardless of the type of polymer added and its value, that the viscosity values decrease with increasing test temperature. An increase in both viscous and elastic modulus is observed under temperatures from 60 to 150°C with increasing polymer content.





Fig. 4. Changes in the viscosity of PMA using HDPE70/MA.

Fig.5. Elasticity modulus of PMAs HDPE70/MA at 80° C.

Due to the presence of HDPE/NR particles, the viscosity of PMAs samples as shown in Figures 4 and 5 recorded a very significant decrease compared to the unmodified sample because it causes an improvement in the rheological properties of the unmodified asphalt. HDPE70 / MA HDPE70 with percentages 3, 5, 7 and 10% w/w The dynamic viscosity in at 60°C decreases by 100, 200, 225, 250%, 300, 350, 360 and 600% respectively and decreases Dynamic viscosity at 47, 50, 52, 53, 20, 30, 43 and 45, respectively, at 130°C. The addition of polymer resulted in an increase in the viscosity of the asphalt and samples containing compatibility agents, which have a plasticizing effect, showed a higher viscosity than pure asphalt ^[35]. Because the MA-HDPE present as a stabilizer in HDPE70/MA forms a very strong network with the asphalt causing the asphalt to become very viscous, there are significant differences between the two modifiers.

3.2.3.2. Elasticity modulus of PMAs

Unmodified asphalt and PMA samples are considered as non-Newtonian materials, indicating that their stress rates do not align proportionally with the applied shear stress, as illustrated in Figures 6-9. So the viscosity of these fluids will change with the change in the shear rate. Therefore, the experimental factors encompassing the viscometer model, spindle and velocity impact the apparent viscosity of the non-Newtonian fluid. A non-Newtonian flow is visualized by by envisioning the fluid as a blend of particles characterized by varied. The force necessary to propel particles through flow, contingent on their size, shape, and cohesion, may differ. The alignment variations can lead to varying force requirements to sustain motion at distinct shear rates. There are several types of non-Newtonian flow behavior, characterized by the way that fluid viscosity changes in response to changes in shear rate. Because of the increase in the dipolar interaction between the MA-HDPE phase and the NR, which leads to an elevation in the interfacial adhesion between the HDPE and NR phases as shown in Figures 6-9, it is observed that there is an increase with the increasing level of polymer addition in the range of 3, 5 and 7 and 10% w/w for both HDPE70 and HDPE70/MA modulus and a significant increase in modulus of elasticity If using HDPE70/MA, this bond should prevent phase separation and improve storage stability ^[27].



Fig.6. Elasticity modulus of PMAs HDPE70/MA at Fig.7. Elasticity modulus of PMAs using HDPE70 at 130°C.









Fig.8. Elasticity modulus of PMAs HDPE70 at 130°C.

Fig.9.The tensile strength ratio (TSR) using TPEs in air.

3.2.4. The tensile shear strength values of PMAs using HDPE70 and HDPE70/MA

According to Chapuis et al. ^[36] the tensile strength of the hot mixture is associated to fatigue cracking. The purpose of the tensile strength test is to assess the stress potential of asphalt mixtures and the susceptibility to moisture.

Asphalt can withstand higher strains before failure (i.e. crushing) the higher the tensile strength. In addition, by comparing the tensile strength of asphalt mixtures exposed to wet and dry conditions the wettability of the asphalt mixture can be evaluated. The shear tensile strength values measured for various materialism air and water give an intriguing behavior which is evident from Figures 10-13 and Table 4.

With the increase in the percentage of polymer added, the tensile shear strength of all materials increases slightly. Compared with those based on PE70 without MA PMAs utilizing PE70/MA demonstrate improved tensile strength. When comparing PMAs in both air and water, the order of increased tensile shear strength is observed as follows:10% Polymer > 7% > 5% > 3%. The tensile strength ratio (TSR) ^[37] for water-conditioned samples is presented in Figures 10-12 and Table 4. The TSR value is calculated as follows:

Tensile strength ratio=Tensile strength of conditioned sample/Tensile strength of the dry sample

Table 4. Tensile shear strength, (N/cm^3) and elongation (El., %) for PMAs with HDPE70 & HDPE70/10% MA after 24 hours immersion in different media, at room temperature.

Sample	In	air	In H ₂ O		
	N/cm ³	EI, %	N/cm ³	EI, %	
HDPE70	825	40.4	800	80	
HDPE70 /MA	1370	41.7	1165	100	
3% HDPE70	420	60	523	140	
5% HDPE70	523	80	623	120	
7% HDPE70	795	100	795	100	
10% HDPE70	823	120	1180	80	
3% HDPE70/MA	623	80	573	160	
5% HDPE70/MA	707	100	1180	140	
7% HDPE70/MA	975	120	1225	120	
10% HDPE70/MA	1115	140	1295	100	



Fig.10. Effect of TPEs on Elongation of PMAs in air.



Fig. 12. Effect of TPEs on Elongation of PMAs in $\mathrm{H}_{2}\mathrm{O}.$



Fig.11.The tensile strength ratio (TSR) using TPEs in H_2O .

It is expected that unmodified samples will suffer moisture damage and exhibit lower tensile strength as compared to PMAs in the case of HDPE/NR blends with and without MA, so the TSR will have a value of less than 1.00; this phenomenon was noted in the control material. However, all polymer-modified asphalt samples exhibited TSR values exceeding 1.00 ^[38]. This indicates that the sample after modification has a higher tensile strength

Though, the results recorded that all polymer-modified asphalt samples showed TSR values greater than 1.00 ^[38]. This indicates that the sample after modification has a higher tensile strength. In general, it was determined that the addition of TEPs (HDPE70 & HDPE70/MA) would decrease the wettability of the mixture in most cases. Various additive ratios of HDPE70 and HDPE70/MA have shown a significant ability to improve the sample strength and fatigue properties, while enhancing ductility and hardness characteristics of engineering materials in several media.

4. Conclusion

This paper aims to use thermoplastics (TPEs), a category of copolymers or physical mixtures of polymers (usually plastics and rubber) containing materials with thermoplastic properties and are flexible in modified asphalt 60/70 to create a specialized asphalt material suitable for diverse infrastructure applications. TPE has attracted more interest in the industry because it combines the properties of vulcanized rubber with the ease of processing thermoplastics. The novel asphalt materials show cost-effectiveness and a great performance at lower temperatures. The study utilized HDPE/NR mixture with and without approvals (MA as additives to modify asphalt 60/70 in proportions of 3, 5, 7 and 10 w/w% and the results indicated that - HDPE and NR compatibility is poor and can be enhanced by adding compatibility devices. HDPE/NR mixtures (70/30 wt/wt%) were modified by addition of MA. Triple mixtures with the compatibility device (10 wt%) exhibited an improvement in the mechanical and rheological characteristics compared to the incompatible ones. Incorporating polymers into the asphalt reduces its heat susceptibility at temperatures, enhancing overall stability and flexibility. The progressive increase in polymer content correlates with improved asphalt properties, and 7% was chosen as the best suitable percentage according to its workability. Increasing the percentage of added polymers contributes to improving the properties of the asphalt, and 7% was chosen as the best suitable percentage according to its workability.

PMAs indicate that PMAs have thixotropic property and high yield stress, as indicated by rheological data. The modified samples showed low viscosity at high shear rate, and lack of flow at low shear rate which is very important for leak prevention and good workability and no flow on vertical surfaces. The use of HDPE70/MA gives the tensile shear strength (N/cm³) more than the use of HDPE70 with an increase with the polymer content added %. The use of TEPs (HDPE70 & HDPE70 / MA) improves the mechanical properties of virgin asphalt 60/70 in air by a higher value than in water. Samples of polymer modified asphalt have higher tensile strength, so before failure the asphalt can withstand higher strains. The wettability of an asphalt mixture can also be evaluated by comparing the tensile strength of asphalt mixtures exposed to wet and dry conditions.

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To whom correspondence should be addressed: prof. Ibrahim M. Nassar, Egyptian Petroleum Research Institute (EPRI), 1 Ahmed El-Zomor St., Nasr City, 11727, Cairo, Egypt, E-mail: <u>nassar_ibrahim@yahoo.com</u>