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Novel modification of soft asphalt for use in infrastructure applications

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ABSTRACT

Asphalt penetration grade 60/70 can not be used in coating applications for its long curing time at ordinary temperature and for its brittleness at very cold temperature. This material is very cheap as compared to blown asphalt that usually used in industrial applications. This research aims to use soft asphalt in coating applications via using rubber nanoparticles in its modification to overcome the undesired properties. The rubber nanoparticles were prepared in lab via emulsification of natural rubber with a suitable emulsifying agent. The nanoparticles were added to asphalt in percentages ranging from 3 to 10%w/w. The prepared samples were tested physically, mechanically and the thermal behaviour was also detected. In addition, morphological investigation has been performed using SEM and TEM, where these results confirmed a good dispersion of the rubber nanoparticles in the asphaltic matrix. Overall, the results show that this specific modifier is the best -so far- in the modification of soft asphalt to suit the industerial applications in different climate conditions. Moreover, this modification approach is simple and cost effective which is suitable to produce a low cost industrial material that has a wide range of infrastructure applications.

KEYWORDS

Asphalt modification;
Rubber nanoparticles;
Coating and emulsification.

INTRODUCTION

As a viscoelastic material, bitumen exhibits both elastic and viscous components of response and displays both a temperature and time-dependent relationship between applied stresses and resultant strains[1]. However, a key drawback is its high susceptibility to temperature. At low temperatures, asphalt is rigid and brittle, at room temperature it is flexible, and at higher temperatures, it flows. The chemistry of bitumen is most often defined in terms of fractions obtained by chromatography, e.g. saturates, resins, aromatics and asphaltenes fractions (SARAs), or in terms of maltenes and asphaltenes contents, the maltenes being the de-asphaltenated portion of bitumen. Each SARAs fraction is a mixture with a complexity, aromaticity, heteroatom content, and molecular weight that increase in the order of S < A < R < As[2]. Bitumen exhibits a glass transition around -20 °C, although it varies in a very wide range from +5 °C down to -40 °C depending essentially on the crude origin and somewhat less on the process[3, 4]. The transition range typically spans 30 to 45 °C and -20 °C corresponds to the typical midpoint value[5]. Therefore, on a thermodynamical standpoint, bitumen is a very viscous liquid at room temperature.

From a product design point of view, the most important group of bituminous products are modified bitumens, which are obtained as a result of the addition of a polymer into the bitumen, by using physical mixing or chemical reaction[6]. The purpose of bitumen modification with polymers is to achieve the desired engineering properties, such as increased shear modulus and reduced plastic flow at high temperatures and/or increased resistance to thermal fracture at low temperatures.

From a physicochemical point of view, bitumen modifiers can be classified into two main categories: passive (e.g. thermoplastics elastomers, plastomers, and crumb tire rubber) and active or reactive polymers (e.g. polymer containing reactive groups as: anhydride, isocyanate, epoxide, etc.). Thus, whereas passive modifiers are physically mixed with bitumen, reactive polymers are designed to react with some bitumen compounds to produce chemical modifications, and consequently becoming a part of the resulting binder structure[7, 8].

Natural rubber (cis-1, 4-polyisoprene) is a kind of polymers using for modifying of the asphalt properties. It has an outstanding resilience and tensile strength, as well as low heat build-up. In addition, natural rubber latex has excellent tack (that is, the ability to stick to itself and to other materials), which makes it best suited for pressure-sensitive adhesives, and excellent water resistance (whereas some synthetics absorb water)[9]. Some properties that are advantages such as stability, elasticity and fatigue resistance will be the better supplementary to asphalt properties and aging is extended which can be help to save budget of maintenance the road paving[10]. Mixing asphalt with rubber has been testing for a long time. Nair et al[11] had studied the improvement of asphalt properties by using fumigated rubber to reduce molecule by dissolving rubber into Fluxing oil until it became Liquid Natural Rubber, LNR, and then it had been mixed with asphalt cement by heating. It was found that adding LNR provided reduction of ductility and increased the softening point depending on the ratio of rubber to asphalt used to mix. On the other hand, Fermando et al[12] had carried on improvement asphalt properties by various kinds of natural rubber latex such as field latex, concentrated latex, and skim latex. Shelburne et al[13] used powdered natural rubber, powdered reclaimed rubber mixed into asphalt.

However natural rubber (cis-1, 4-polyisoprene) has been emulsified to form a stable colloid that was then crosslinked in the nano scale forming stable, elastic, resilient nano rubber particles for toughening of brittle materials. The particle size control, degree of crosslinking, colloidal stability, and toughening properties of polyisoprene make it an important industrial polymer, suitable for use in many applications[14].

The present research aims to use penetration grade asphalt 60/70 (which is not used in roofing or coating applications) in preparation of modified asphaltic material using rubber nanoparticls for use in infrastructure applications to produce an attractive material has low cost and superior characteristics as compared to oxidized asphalt that commercially used. The produced material can help in increasing the application fields of soft asphalt especially at very low temperatures.

EXEPRIMENTAL

Materials used

Asphalt cement

Local virgin asphalt cement of penetration grade (AC 60/70) produced by El-Nasr Petroleum Company in Suez, Egypt.

Chemicals

Polyisoprene (NR; Narobien), Divinylbenzene as crosslinker was dried and vacuum distilled over calcium hydride. palmitic acid, benzoyl peroxide (BPO), potassium hydroxide KOH, Hydrochloric acid, Toluene and Methanol.

Experimental procedure

The testing program included the following steps.

Characterization of virgin asphalt 60/70

- The virgin asphalt sample was tested for penetration (ASTM D5), softening point (ASTM D36), specific gravity (ASTM D70) and Brookfield viscosity (ASTM D4402). Also, the sample was chemically analyzed after it separated into asphaltene and maltene fractions using n-heptane insoluble.[15 & 16]. The results are illustrated in TABLE 1. Thermal gravimetric analysis (TGA) as shown in Figure (2A) was carried out using SDTQ 600 thermo-gravimetric analyzer (TA-USA) to test the thermal stability of the virgin asphalt sample in the temperature range of 25 to 800^{o}C with a heating rate of 10^{o}C/min under dynamic nitrogen gas.

- The temperatures susceptibility of virgin asphalt sample was expressed in term of penetration index (P.I) using the penetration (@ 25ºC) and softening point values. P.I can be calculated using the following equation[16]:

$$P.I = \frac{1952 - 500 \times \log(\text{pen } 25) - 20 \times SP^*}{50 - \log(\text{pen } 25) - SP - 120}$$

Where SP softening point, °C Pen 25= penetration value at 25°C

Synthesis and characterization of rubber nanoparticle (RNP).

- The natural rubber nano-particles (RNP) were synthesized by emulsification of NR macro molecules. In this manner, 5.0 g of NR was dissolved in 50 mL of toluene containing 5-7 wt% of divinylbenzene or isoprene as a crosslinker and 5 % (by wt) of palmitic acid were added to the reactants. About 1.0 wt% of benzoyl peroxide as a free radical initiator was added. In the second step, the whole organic phase was slowly added to a vigorously stirred solution of KOH soluble in 100 mL of deionized H_2O until that the final emulsion has a p^H slightly alkaline. The stirring was strongly continued for 30 min and then, the emulsion was homogenized by sonification for 30 min in an ultrasonic processor homogenizer operating at 300 bar under nitrogen. The flask was purged with N_2 for 30 min before rising the temperature to 90^{o}C. The processing time ranged from 2 to 6 hrs depending on the viscosity of the previously prepared samples and consequently on the molecular weight of the used rubber. The product was coagulated by HCl/methanol, re-dispersed in chloroform and precipitated with

TABLE 1 : Characteristics of virgin asphalt sample used (AC)

Characteristics	AC	SP*
Physical characteristics		
penetration (@ 25C^o, 100g,5s)0.1mm	62	60/70
Softening point (ring and ball)C^o	50.6	45/55
Specific gravity (@ 25 C^o)using a pycnometer	1.02	NS**
Flash and fire points (Cleveland Open Cup) C^o	+250	+250
Ductility (@ 25 C^o , 5cm/min.) cm	+150	+150
Brookfield viscosity (@60 C^o)*** c.P	7.85	NS**
Penetration Index (P.I)	-0.51	-2: +2
Heavy metal analysis		
Nickle (ppm)	18.0	
Vanadium (ppm)	251.4	
Separation of polymer, (163 C^o), 48 hrs		
Difference in softening point from top and bottom, C^o (****)(15)	1	
Chemical composition		
Maltene (wt %)	77.2	
Asphaltene (wt %)	22.8	

N.B: (*) Standard Specification for "General Authority for Roads, Bridges and Land Transportation in Egypt. Item No 102.1; (**) Not specified; (***) Shear rate 80 s^{-1}, Spindle No. 40& RPM= 20 using Brook Field viscometer (modelDV- 111+ programmable rheometer); (****) According to literature, maxim difference is 2

TABLE 2 : Physical characteristics of PMAs

Characteristics	AC	PAMs			
		3%	5%	7%	10%
- penetration (at 25Cº, 100g,5s)0.1mm	62	42	28	23	17
- Softening point (ring and ball)Cº	50.6	56	64	68	73
- Specific gravity (at 25 Cº)	1.02	1.027	1.033	1.038	1.042
- Brookfield viscosity (at 60 Cº)* c.p	7.85	45	95	142.1	275.4
- Penetration Index	-0. 51	-0.21	0.38	0.64	0.85

methanol to remove the surfactant before the material was dried for overnight.

Dynamic light scattering (DLS) measurements[17]

Particle size distributions and volume-average diameters of the RNP and PMAs samples were determined with a Coulter LS 230. This analyzer uses the principles of light scattering, based on both Fraunhofer and Mie theories. Moreover, the range of detectable particle sizes is extended to the submicron region (lower size limit: 50 nm of diameter).

Transmission electron microscopy (TEM)

Transmission Electron Microscopy for RNP and PMAs samples were performed at 120 kv using model JEOL JEM 1200 EXII equipped with a video camera, a Gatan Bioscan 792 camera and a high resolution Tietz F224 camera and a PGT Prism light element detector RNP and PMAs samples. Samples were prepared by dipping the grid in a dilute asphalt modified with RNP and RNP solution (before curing) followed by evaporating the solvent which affords a very thin film for TEM analysis.

Modification of asphalt with RNP

In this step, the calculated amount of asphalt was heated up to 180 ± 5 ºC in a small container until it soften and become pourable. The calculated amounts of rubber nanoparticls (RNP) depending on the addition percents as 3%, 5%, 7% and 10% (of the weight of the base asphalt) were gradually added to molten asphalt in a constant rate as 5 gr/ min under high shear mixer rotating at 2000 rpm for 2 hrs until the blends became essentially homogenous. The prepared samples were tested for compatibility test using Shell method[16]. The results of characteristics of PMAs are illustrated in TABLE 2.

Characterization and evaluation of polymer modified asphalt samples prepared

Physical characteristic

The prepared PMAs were physically characterized as previously mentioned in testing program step no.1. Also, DLS and TEM for RNP and PMAs are represented as in Figure 1 (A&B), 2 (A&B) respectively. TGA analyses are represented as in Figure (3 (A-E)). SEM photographs have been observed using scanning electron microscopy (SEM; Philips) as shown in Figure (4 (A-E)).

Bending test

Mandrel test (ASTM E 522) was used to evaluate the flexibility and the resistance to cracking for the organic coatings on the substrates of sheet metal. In this way, the coating materials were applied at a uniform thickness by using the bursh in one direction for one time to panels of sheet metal. After complete curing, the coated panels were bent over a mandrel and the resistance to cracking of the coating was determined. Coatings attached to substrates are elongated when the substrates are bent during the manufacture of articles or when the articles are abused in service. Conical mandrel bend tester is applicable also to determine the extensibility of asphalt coatings on metal panels which are clamped in position and formed round the conical mandrel by rotating the roller frame. The panels were examined to evaluate crack resistance detachment from the metal substrate of coated surface which was coated with epoxy under standard condition.

RESULTS AND DISCUSSION

Characteristics of virgin and modified asphalt samples

From TABLES (1&2) and Figures (1- 5) the following results were detected:-

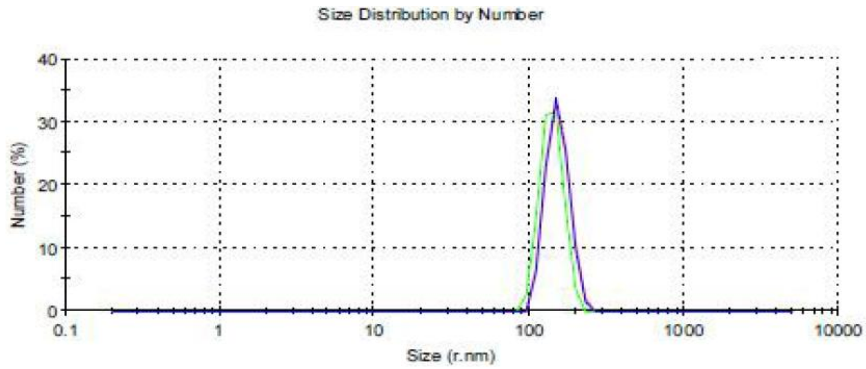

Figure 1A : Particle size distribution measured by light scattering of RNP

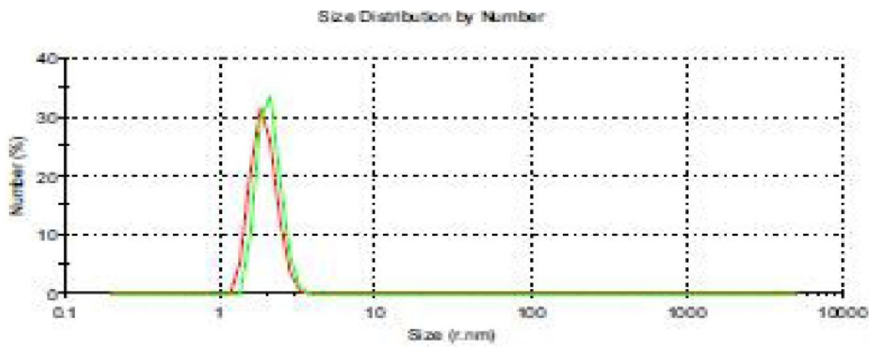

Figure 1B : Particle size distribution measured by light scattering of asphalt modified with 10%RNP

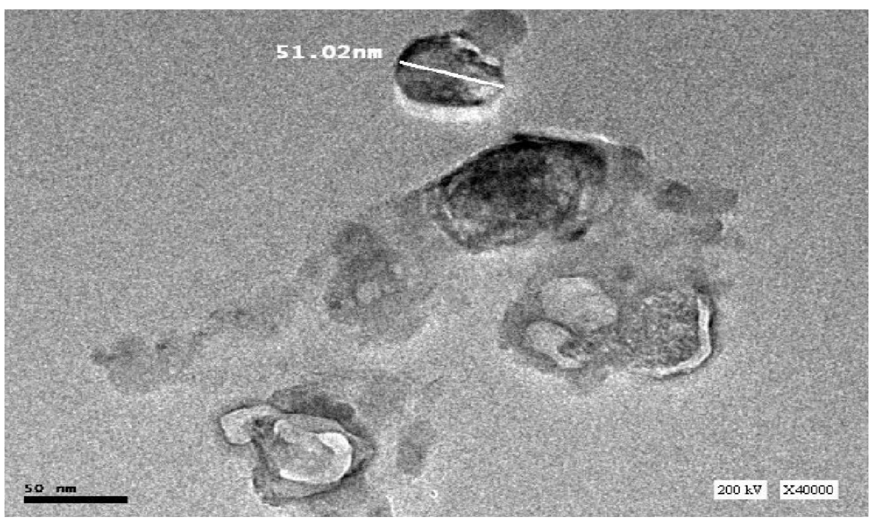

Figure (2A) : TEM of RNP

Physical characteristics of asphalt samples

Generally, data indicated in tables that the modified samples are more hardening than the virgin one as there was an increase in softening point, specific gravity and dynamic viscosities and decrease in penetration value with the addition indicated that increase in asphaltene percentage in sample.

Increasing the RNP content from 3 to 10 wt % produced more hardness asphalt samples. This is attributed to the nature and accordingly the chemical molecular composition of the RNP used. The formation of modified samples may be explained by that, when RNP (which is a macromolecule with long chain and three-dimensional network) mixed with asphalt which is composed of hard, and large molecules polar aromatic material dispersed in saturated paraffin materials, will cause difficulty to soften the mixture. As a result of asphalt modification, its cohesion and elasticity are both enhanced. At higher

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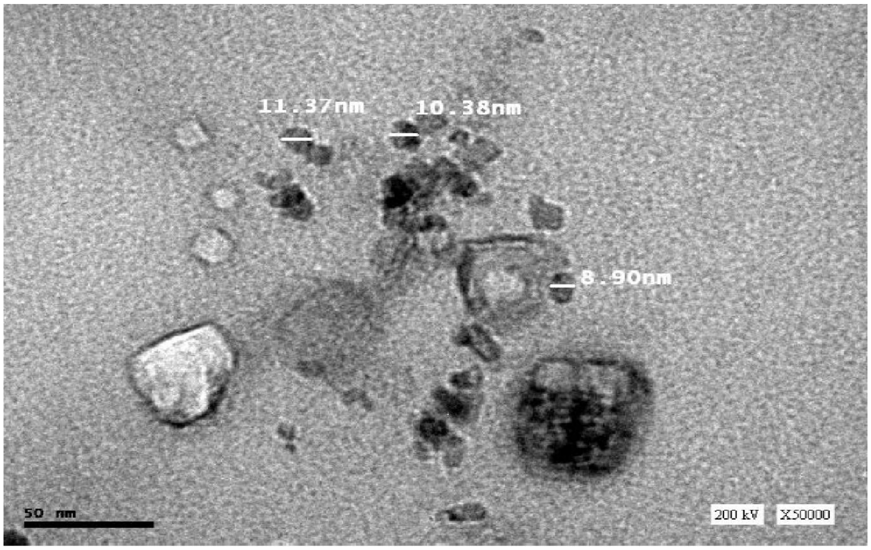

Figure (2B) : TEM of asphalt modified with RNP

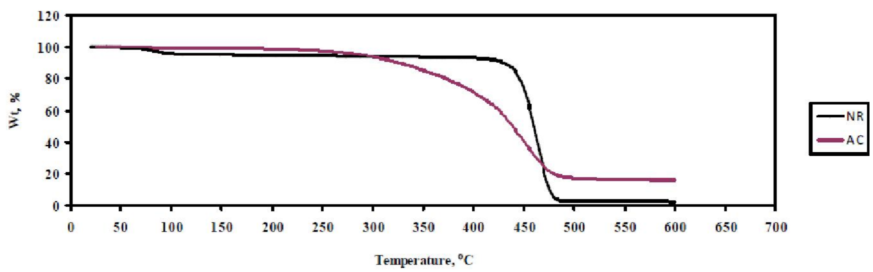

Figure (3A) : TGA curves of AC and RNP

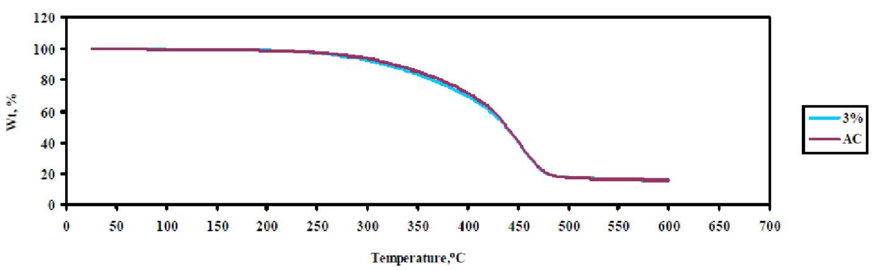

Figure (3B) : TGA curves of AC modified with 3%RNP

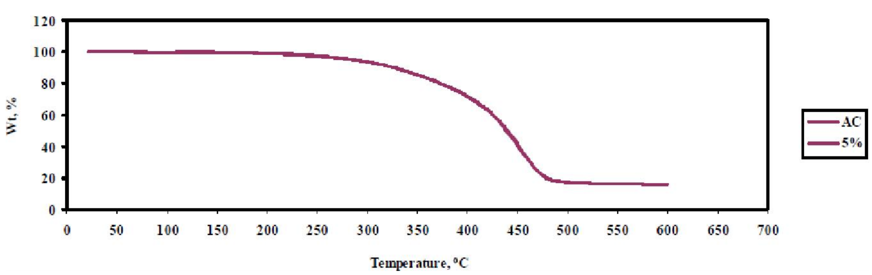

Figure (3C) : TGA curves of AC modified with 5%RNP

service temperatures, the stiffness modulus of polymer phase is higher than that of matrix. These reinforcing properties of the polymer phase contribute to the increase in viscosity. At low temperatures, the stiffness modulus of the dispersed phase is lower than that of the matrix, which reduces its brittleness. Consequently, the dispersed polymer phase enhances the engineering properties of asphalt in terms of viscosity, softening point and toughness[18].

Temperature susceptibility of all asphalt samples

The temperature susceptibility of the modified

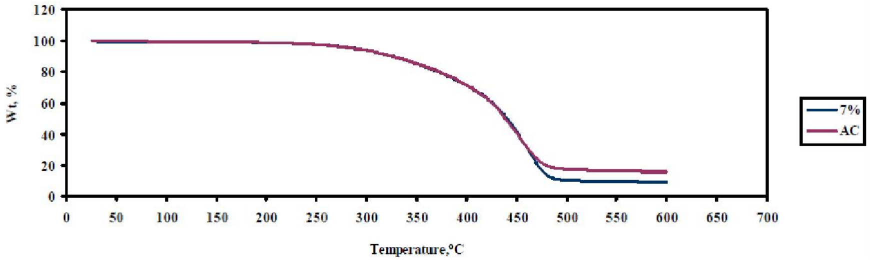

Figure (3D) : TGA curves of AC modified with 7%RNP

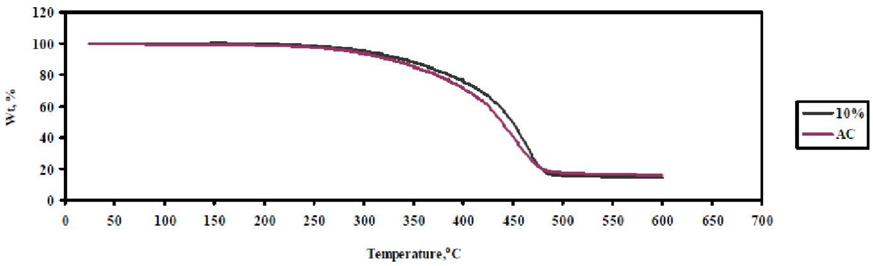

Figure (3E) : TGA curves of AC modified with 10%RNP

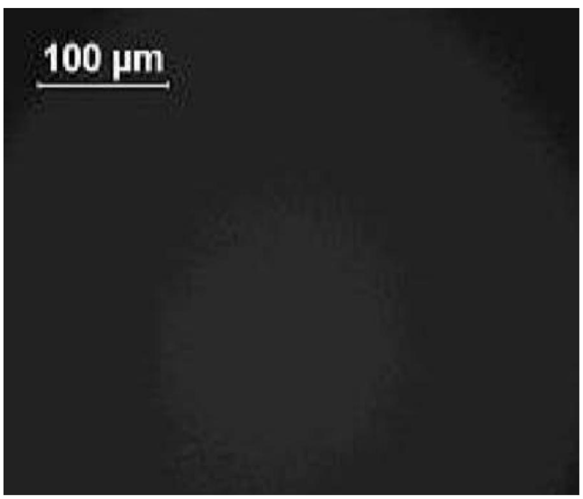

Figure (4A) : SEM of virgin AC

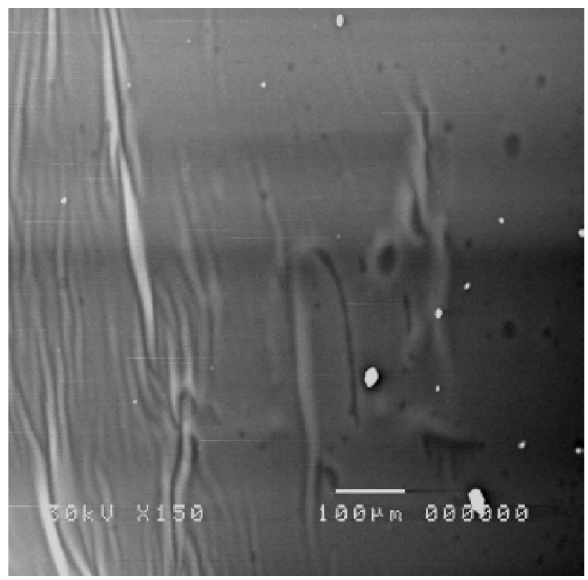

Figure (4B) : SEM of AC modified with 3% RNP

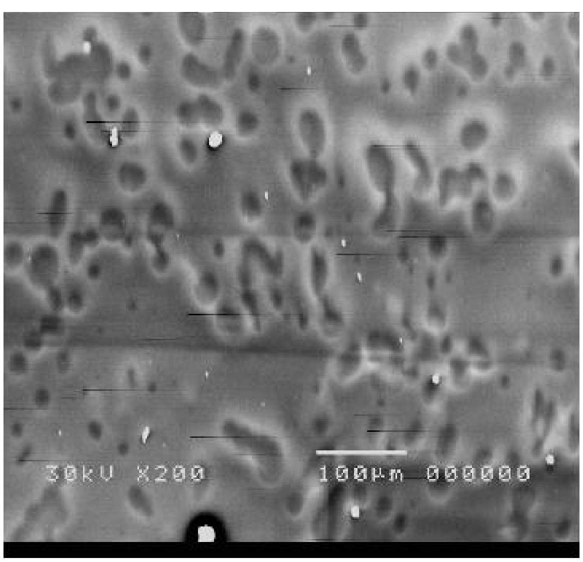

Figure (4C):SEM of AC modified with 5% RNP

bitumen was investigated. The results showed the more P.I (penetration index) which indicated that increase in asphaltene content therefore, the less temperature susceptibility. Effect of asphaltene content on temperature susceptibility was also studied. It was found that by increasing the penetration index (P.I) the temperature susceptibility decreased[19].

From TABLE (2) it is obviously that, the modification of asphalt reduces the temperature susceptibility of the virgin asphalt as the P.I values increase.

Also, the increase in P.I will increase the resistance of asphalt samples to cracking at low temperature[20].

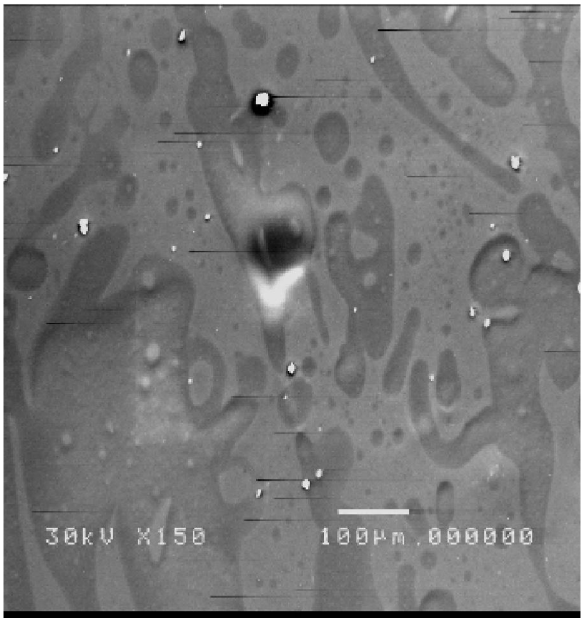

Figure (4D) : SEM of AC modified with 7% RNP

DLS measurement

Figure 1 (A, B) shows that the rubber nanoparticles and asphalt modified prepared samples using RNP have a sizes distribution by number about 152.8 and 2.08 respectively.

Transmission electron microscopy (TEM)

Figures 2A, 2B show that the size of particles in case of RNP larger than that in case of asphalt modified with RNP. According to the nature of bitumen which early described as a colloidal dispersion of asphaltenes micelles in the maltenes,[21] this nature of bitumen prevent the coagulation of RNP and cause good particles dispersion.

TGA analysis

Figure 3A shows TGA curves for virgin asphalt

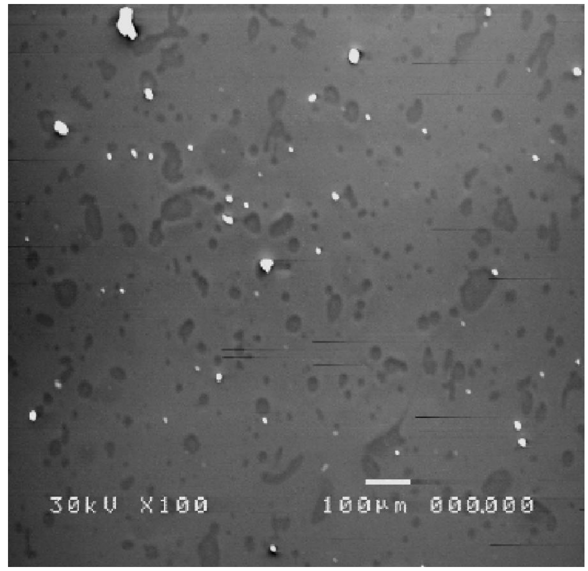

Figure (4E):SEM of AC modified with 10% RNP

60/70 (AC) sample and prepared rubber nanoparticle (RNP) and PMAs. AC showing decomposition stage from 290 to 490°C with mass loss of 84.17% suggesting the decomposition of asphaltenes to produce coke[6] while, RNP showing decomposition stage from 425 to 487°C with mass loss 97.72%.

Figures 3 (B- E) shows that PMAs samples showed a very similar thermal behavior when compared to virgin AC. For example, in case of using RNP modifier in percentages 3%and 5%, the complete weight loss decreased from 97.72 % to 84.26% and to 84.2% for modified asphalt samples respectively. This may be attributed to that thermal stability decreased with increasing P.I. In the other word, asphaltene decreased the decomposition temperatures and also char yield of bitumen. However, the rate of decomposition after initial decomposition temperature (IDT) has opposite effect. Bitumen with


Figure (5A) : Mandrel bend testing panel of virgin asphalt

Figure (5B) : Mandrel bend testing panel of asphalt modified with 10%RNP

Figurer (5C) : Mandrel bend testing panel of asphalt modified with 10%RNP, 3%RNP and AC virgin

higher P.I decomposes slower after IDT than bitumen with lower P.I.

SEM of PMAs

The SEM photos of the virgin and polymers modified blends are displayed in Figure (4 (A-E)). It was shown that;

The light phase in the picture represents the swollen polymer and the dark phase is the asphalt.

Small polymer spheres swollen by asphalt compatible fractions *(e.g.,* aromatic oils) are spread (dispersed phase) homogeneously in a continuous asphalt phase.

Polymer particles extensively spreading on PMA's surface lead to the decrease in engineering properties such as toughness and tenacity. This may be attributed to differences in molecular weight, polarity and structure.

A chemical dissimilarity exists between asphalt and polymer. The morphology of PMA samples is the result of the mutual interaction of polymer and asphalt, and, consequently, is influenced by asphalt composition and polymer nature and content. It is clear from Figure (D (1-5)) that, there is a good compatibility between asphalt and RNP.

Mandrel bending test

Based on ASTM D522 and from the corresponding elongation to such added values of the RNP, it is clear that when RNP content increased to 10%, the sample become completely flexible and no cracks appear as shown in Figures (5 (A-C)). Mandrel test clearly showed that incorporating 10 w% of nanorubber particles enhances the flexibility of the modified asphalt samples to the required value.

CONCLUSION

This research aims to use penetration grade asphalt 60/70 (which is not used in roofing or coating applications) in preparation of modified asphaltic material using rubber nanoparticls. The modified samples were tested for use in infrastructure applications to produce an attractive material has low cost and superior characteristics as compared to the commercially traditional material (oxidized asphalt)

To achieve this aim, 3- 10% of RNP were used in asphalt modifying, the obtained results showed that:

The mixes comply with the standards have reduced temperature susceptibility.

AC modified with 10% RNP become completely flexible and no crack appears with binding at very low temperatures.

The produced material can be used in infrastructure applications especially at very low temperatures.

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