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Preparation and characterisation of modified reclaimed asphalt using nanoemulsion acrylate terpolymer

Abstract

Purpose – Investigate the best methods of utilisation of reclaimed asphalt pavements (RAP) in Egypt, in order to determine the effect of using 100% RAP instead of using virgin aggregates and asphalt. Investigate the effect of thermoplastic elastomer polymer as asphalt modifier. Also, improve the mechanical and physical characteristics and consequently improving the quality of asphalt paving, increasing the service life of asphalt-paving and reducing costs.

Design/methodology/approach –Nano acrylate terpolymers were prepared with different % (wt.) of and were characterised by Fourier Transforms Infrared (FTIR), for molecular weight (M_w), by Thermo Gravimetric Analysis (TGA) and by Transmission Electron Microscopy (TEM). A 4% (wt.) of the prepared nanoemulsion terpolymer was mixed with virgin asphalt as a polymer modifier, to improve and reuse of the Reclaimed Asphalt Pavement (RAP). The modified binder was tested. The tests conducted include penetration, kinematic viscosity, softening point and specific gravity. Application of Marshall mix design types; Hot Mix Asphalt (HMA), Warm Mix Asphalt (WMA) and Cold in place Recycled (CIR). Four different mix designs used; control mix contained virgin asphalt by HMA, and the other three mix designs were PMA by HMA, WMA and CIR.

Findings – The research results showed that using 4 wt. % of the prepared nanoemulsion terpolymer to produce hot mix asphalt (HMA) and warm mix asphalt (WMA) achieved higher stability compared to the control mix and cold in place recycled (CIR).

Research limitations/implications – This paper discusses the preparation and the characterisation of nanoemulsion and its application in reclaimed asphalt pavements in order to enhance and improve the RAP quality.

Practical implications – Nano-acrylate terpolymer can be used as a new polymer to modify asphalt to achieve the required specifications for reclaimed asphalt pavements (RAP).

Originality/value – According to the most recent surveys, Europe produced 265 tonnes of asphalt for road applications in 2014, while the amount of available Reclaimed Asphalt Pavement (RAP) was more than 50 tonnes. The use of RAP in new blended mixes reduces the need of neat asphalt, making RAP recycling economically attractive.

Keywords: Acrylate terpolymer; Reclaimed asphalt pavement; Modified asphalt; Hot mix asphalt; Warm mix asphalt; Cold in place recycled

Introduction

Reclaimed Asphalt Pavement (RAP) is comprised of aggregates and asphalt binder from Hot Mix Asphalt (HMA) mixtures that have been removed and reclaimed from an existing pavement. The aggregates in the RAP are typically coated with aged (oxidised) asphalt binder (Hansen *et al.*, 2013; Bulatović *et al.*, 2014). RAP has been used successfully in surface HMA mixtures since the 1970s at percentages generally around 20%. A concern associated with the use of higher RAP contents is that the resultant mixture might become too stiff and consequently be prone to failures in the field (Bonaquist, 2005; McDaniel *et al.*, 2007). The increased stiffness is due to the aged binder in the RAP. The major factor contributing to the increase in stiffness of asphalt concrete mixtures over time is the oxidation of the asphalt binder at the molecular level (Glover *et al.*, 2009). With increases in the price of asphalt cement and subsequent price fluctuations, the industry has further amplified its recycling efforts. Most recently, with the drastic increases in the cost of asphalt cement, the use of RAP has become another 'black gold' (Johnson *et al.*, 2010; Giani *et al.*, 2015). The hot mix asphalt industry is constantly seeking technological improvements to produce sustainable, cost effective, and environmentally friendly mixes (Bowers *et al.*, 2014). A logical approach to achieving such mixtures is to use readily available recycled materials such as Reclaimed Asphalt Pavements (RAP). Also, to advance environmental stewardship, the industry has been using Warm Mix Asphalt (WMA) technologies that allow for the production of asphalt mixtures at temperatures in the range of 17°C to 54°C (30°F to 100°F), lower than typical hot mix asphalt (Mogawer *et al.*, 2011), where Cold In-place Recycling (CIR) is the process and treatment with bituminous and/or chemical additives of existing HMA pavements without heating to produce a restored pavement layer (Zhang *et al.*, 2013). Rejuvenating additives can be used to counteract the stiffness of the RAP binder, therefore enabling the use of RAP in HMA. It has been documented that rejuvenating agents can be polymers, copolymers and terpolymers because of their absorptive properties to revitalise the properties of the RAP binder (Gudimettla *et al.*, 2003). Polymer modification of bitumen has increasingly become more popular for asphalt pavements, particularly in the United States. The modification of the bitumen has shown to increase rutting resistance, decrease fatigue damage, and reduce the potential for moisture damage.

Polyphosphoric acid (PPA) is one of many additives used to modify and enhance paving grade asphalt. The first patent describing asphalt modification with PPA was published in 1973. Since the early 1990s, PPA has also been successfully used across the United States in combination with various polymer modifiers (Thomas Bennett, Jean-Valery Martin, 2012). The effects of reclaimed asphalt pavement (RAP) binders collected from two different sources (RAP-A and RAP-S) on Superpave Performance Grade (PG), rutting and fatigue performance of a Polymer Modified Binder (PMB) was studied and evaluated (Dharamveer et al., 2018). The addition of PPA alone or in combination with other polymers can successfully increase rutting and fatigue resistance while minimizing stripping potential similar to polymer modified bitumen. Studies have also indicated that the addition of PPA may aid in reducing age hardening and oxidative age related stiffening of bitumen and mixtures containing PPA (Baumgardner, G., 2009). Nanoemulsion terpolymers which have very small particles and used as an asphalt modifier are introduced into asphalt mixtures through HMA, WMA or CIR. Many properties of polymers such as process ability, electrical properties, chemical, thermal, mechanical and environmental stability, affect their suitability and reliability as protective organic coatings (Abd El-Wahab *et al.*, 2013). Recently, modified reclaimed asphalt by using styrene – butyl acrylate nanoemulsion copolymer was prepared and evaluated. The study also investigates the effect of thermoplastic elastomer polymer as asphalt modifier. Also, improve the mechanical and physical characteristics and hence improving the quality asphalt paving, increase asphalt-paving age and reduce the cost. The prepared nanoemulsion copolymer was mixed with virgin asphalt as a polymer modifier, to improve and reuse of the RAP. The modified binder was tested. The tests conducted include penetration, kinematic viscosity, softening point and specific gravity (Ahmed G. Sark, A. M. Nasser, H. Abd El-Wahab, M. Abd El-Fattah and Abdelzaher E. A. Mostafa, 2018). Compatibility between polymer and asphalt should be high enough to avoid separation phase. Vinyl acetate bu-acrylate vinyl ester of versatic acid is one of the terpolymers which has been used to improve the properties of asphalt pavements (Mangiafico *et al.*, 2014). The present study is a part of a wider research on performances and durability of asphalt mixtures made with RAP (Brovelli *et al.*, 2015). The research is divided into three stages. In the first stage, the asphalt was extracted from RAP and its solid materials evaluated. In the second stage, vinyl acetate bu-acrylate vinyl ester of versatic acid terpolymer was prepared and its physical characteristics of the nanoemulsion polymer were analysed via Fourier Transform InfraRed (FTIR), molecular weight measurement, Thermo Gravimetric Analysis (TGA), and Transmission Electron Microscopy (TEM) (Hashemi *et al.*, 2013). The terpolymer was then added to the virgin asphalt to improve the asphalt characteristics (Khezri*et al.*, 2012). Application of Marshall Stability forms the last stage of the experimental investigation. The asphalt was applied as HMA, WMA and CIR Asphalt which conforms to Marshall properties are showing high resistance to stresses caused by high loads, high working temperatures and low temperatures due to weather conditions. HMA design using virgin asphalt as a control mix and hot mixes using the virgin asphalt (Tapsoba *et al.*, 2014). The effects of polymer modified asphalt of RAP with prepared nanoemulsion physical properties have been widely investigated (Hoppe *et al.*, 2015). The objective of the research was to comprehensively characterise RAP mixtures in terms of performances of asphalt mixtures and asphalts by observing Marshall characteristics out of mix designs (Kriz *et al.*, 2014). The objective of the research was to comprehensively characterise RAP mixtures in terms of performances of asphalt mixtures and asphalts by observing Marshall characteristics out of mix designs (Li *et al.*, 2016). In this study, Marshall stability and flow obtained and air voids, voids in mineral aggregate, unit weight and voids filled with asphalt were calculated and shown in curves to define the optimum asphalt content and the best percentage addition of polymer to the virgin asphalt (Liu *et al.*, 2012).

Experimental

Materials

All the chemicals used during the project were sourced either locally, or from international companies, and were used without modification. Vinyl acetate (VAM), Vinyl Versatate (®VeoVa10), butyl acrylate (BuAc), acrylic acid (AA) and acrylamide (AAm), were used as essential monomers and supplied by the Sigma-Aldrich Company, USA. Potassium persulphate (KPS), sodium acetate, were supplied by the Sigma-Aldrich Company, USA. Nonylphenol Ethoxylate (NP30) and sodiumlauryl sulphate (SLS), was imported from the BASF Chemical Company. Ammonium hydroxide (NH_4OH) pH control It was obtained from El Naser Pharmaceutical, Chemical Company, The reclaimed asphalt pavement (RAP) used in this study was obtained from a highway pavement in Cairo – Alexandria road, Asphalt cement of penetration grade 60/70 produced from EL-Nasr Petroleum Company in Suez city, Egypt.

Methods and techniques

Preparation of vinyl acetate–butyl acrylate–vinyl ester of versatic acid terpolymer (El-Sherif *et al.*, 2017)

The co-polymerization of VAM, VeoVa 10 and BuAc**,** was carried out in a water bath, with the material being refluxed in a 1000ml three-necked flask equipped with a stirrer and having a gas inlet system. The oxygen was removed by purging nitrogen through the mixture for at least 30 minutes. Then 80.5 ml of distilled water was introduced into a glass reactor with 2.2 g Sodium lauryl sulphate (SLS) & SULFOPON 12 G as anionic surfactants. Then 0.4 g of NP30 non-ionic surfactant was added and this was followed by 8 ml of distilled water and 0.1gm of Potassium persulfate (KPS) as the initiator. The mixture was stirred under nitrogen atmosphere at 80°C. The SLS dissolved in distilled water (2.2 g in 59.6 g), was then mixed with different ratios of VAM, VeoVa 10 and BuAc, according to polymer type, using vigorous stirring with the homogenizer at room temperature for 30 min. The 10% of obtained pre-emulsion was charged into the reactor for 30 min as a seeding stage, and then there was a 30 min wait before the 0.1 g KPS initiator, dissolved in 17 ml distilled water, was gradually added. The 2% AA and the 0.4 NP30 were mixed with the remaining 90% pre-emulsion, using the homogenizer, and this was charged into the reactor within a 3 hour period. The reaction was allowed to proceed under continuous stirring at 80 rpm and then the temperature was raised to 83 °C. At the end of the pre-emulsion addition, the temperature was raised from 83 to 85°C for 1 hour to complete the polymerization reaction. The prepared emulsion was then cooled to 40°C and the pH adjusted to pH 8 using an aqueous solution of ammonia.

(Take in Table I)

(Take in Scheme 1)

Characteristics of vinyl acetate-butyl acrylate–vinyl ester of versatic acid terpolymer

Fourier transform infrared (FTIR), Transmission electron microscopy (TEM), Thermogravimetric analysis (TGA) and Molecular weight (Mwt) were employed to characterise the prepared nanoemulsion terpolymer. These characterisations were carried out at the Egyptian National Research Centre.

Preparation of the modified asphalt

The calculated amount of virgin asphalt was heated to a temperature not more than 90°C. Surfactant NP_9 was added at 10 wt. % of the virgin asphalt to improve the durability of the extracted asphalt. The nanoemulsion terpolymer was added slowly at 80°C – 90°C at 2, 4 and 6 wt. % of asphalt. Vinyl acetate-butyl acrylate–vinyl ester versatic acid terpolymer was mixed with a high-speed mixer at 2000 rpm for 2 hours. The end point was determined visually. The virgin and the polymer modified asphalt samples (PMAs) were characterised by conventional asphalt tests including Penetration Test (ASTMD5–06), Softening Point Test (ASTMD36–06), Specific Gravity (ASTMD70–09), and Kinematic Viscosity Test (ASTMD2170–10).

Preparation of asphalt paving mix design samples

The asphalt paving mixes were prepared using the Marshall test method (ASTM D-6927–15 and AASHTO T-245–2012) including three types of design: hot mix asphalt (HMA), warm mix asphalt (WMA) and cold in place recycled (CIR). For each compacted sample of the asphalt paving mix, the stability and flow were measured while the unit weight and air voids were calculated to define the optimum asphalt content. In this step, hot mix asphalt sample using the virgin material and the modified asphalt sample were prepared using the Marshall test procedure. All of the mixes were designed according to the Egyptian Specification (ESP) limits for dense graded hot mix asphalt (Dense–Graded 4D) for binder course knowing that;

Mix 1: "control mix"; it consists of virgin asphalt AC added to RAP by HMA.

Mix2: it consists of PMA, with 4 wt. % vinyl acetate-bu-acrylate-Vinyl ester of versatic acid terpolymer added to RAP by HMA.

Mix 3: it consists of PMA, with 4 wt. % vinyl acetate-bu-acrylate-Vinyl ester of versatic acid terpolymer added to RAP by WMA.

Mix 4: it consists of PMA, with 4 wt. % vinyl acetate-bu-acrylate-Vinyl ester of versatic acid terpolymer added to RAP by CIR.

Characteristics of the solid materials

The solid materials were obtained after the extraction of asphalt from RAP and tested for sieve analysis (ASTMC136–14), resistance to abrasion using a Los Angeles machine (ASTMC131– 14) and bulk specific gravity (ASTMC128–15 and 127–15 respectively). Tables II and III show the sieve analysis results and physical properties of the fine and of the coarse aggregates, the result obtained was found to comply with the standard requirements.

(Take in Tables V and VI)

Characterisation of prepared polymers

a. Fourier transform infrared (FT-IR)

The FT-IR analysis of the dried polymer samples was carried out using a JASCO FTIR 6100 in the range of 4000 – 400 cm-1.

b. Gel permeation chromatography (GPC).

The weight-average (Mw), and number-average (Mn) molecular weights, were determined using an Agilent 1100 series gel permeation chromatography (GPC) system, equipped with a G1362A refractive index detector with 100-104-105 A° ultra styragel columns. Polystyrene was used as a standard. THF was used as an eluent with a flow rate of 1ml min^{1}.

c. Thermo gravimetric analysis (TGA).

TGA analysis was performed using a Shimadzu TGA – 50 thermo gravimetric analyser (Columbia, EUA) using a nitrogen atmosphere and a heating rate of 10 ˚C /min over the temperature range between room temperature and 600˚C.

d. Transmission electron microscopy (TEM)

The morphology of the copolymer particles was examined using transmission electron microscopy (TEM). In TEM the dry sample was transferred into ultra-high vacuum and exposed to a high energy beam of electrons (100 keV). In an ideal case, a lateral resolution of around 1nm is achievable. To perform a TEM analysis, the latex was diluted with distilled water, with a drop of the diluted latex being placed on a carbon – coated grid and dried in a dissector. Then 1 – 2 drops of a 0.8 wt. % aqueous solution of phosphor tungstic acid (PTA) was used to stain the particles. The shape and particle size distribution of the nanoparticles were determined using a JEOL-JEM-1011 transmission electron microscope.

Viscosity

The consistency of the flexographic inks was assessed by utilizing a Ford viscosity cup number 4 at 25°C by filling the cup with the fluid under test, and recording the time taken for the material to run through the standard openings.

Characterization of polymer modified asphalt

Standard test method for penetration of PMA

The penetration test is an empirical measure of asphalt consistency. The penetration of a bituminous material is the distance in tenths of a millimetre that a standard needle penetrates of temperature, load, and time. In the test, the sample is melted and cooled under controlled condition then a container of asphalt cement is heated to the standard test temperature 77 ^{o}F (25^{o}C) in a temperature controlled water bath. The prescribed needle, plus a standard load weight up to 100 g is allowed to bear on the surface of the asphalt cement for 5 seconds. The distance, in units of 0.1mm, which the needle penetrates into the asphalt cement is the penetration value.

Standard test method for kinematic viscosity of asphalts (bitumens)

This test method covers procedures for the determination of kinematic viscosity of asphalt cements at 135°C [275°F]. In this test, the time is measured for a fixed volume of the preheated sample to flow through the capillary of a calibrated glass capillary Viscometer under an accurately reproducible head and at a closely controlled temperature. The kinematic viscosity is then calculated by multiplying the efflux time in seconds by the Viscometer calibration factor.

Standard test method for softening point of bitumen (ring-and-ball apparatus)

This method covers the determination of the softening point of asphalt (bitumen), in the range 30 to 175°C (85 to 347°F) using the ring and ball apparatus in a water or oil bath. In this test, a steel ball of specified weight approximately 2.5 g is placed upon a disk of sample contained within a horizontal, shouldered, and metal ring of specified dimensions. The assembly is heated in the bath at a uniform and prescribed rate and the softening point taken as the temperature at which the sample becomes soft enough to allow the ball, enveloped in the sample material, to fall a distance of 1 inch (25.4mm).

Standard test method for specific gravity of semi-solid bituminous materials (Pycnometer method)

In this test, the sample is placed in a calibrated pycnometer, which are weighed, and then the remaining volume is filled with water. The filled pycnometer is brought to the test temperature, and weighed. The density of the sample is calculated from its mass and the mass of water displaced by the sample in the filled pycnometer. The sample is heated with care, and stirring to prevent local overheating, then enough sample is poured into the clean dry, and warmed pycnometer to fill it about three fourths of its capacity. The beaker is removed from the water bath if necessary, to allow the pycnometer to remain in the water bath for a period of not less than

30 min. The pycnometer is removed from the bath, then dried and weighed. The relative density (specific gravity) is calculated at the nearest 0.001 as follows:

Relative density = (C-A) / [(B-A) - (D-C)]

Where:

A = mass of pycnometer (plus stopper), g

B = mass of pycnometer filled with water, g

C = mass of pycnometer partially filled with asphalt, g and

D = mass of pycnometer plus asphalt plus water. g

Mix design

In this step, the asphalt paving mixes were prepared using the Marshall test method [ASTM D 6927 – 15 & AASHTO T245 – 97 (2008)] for application with three different mix designs which include, hot mix asphalt (HMA), warm mix asphalt (WMA), and cold in place (CIP).

Indirect Tensile Strength Test (IDT) –AASHTO (T 322-03)

The indirect tensile strength test equipment of Materials laboratory, faculty of Engineering – Mattaria - Helwan University, was employed. The compression test machine was used for this test as well as for Marshall Test. The difference between this test and Marshall Test is only in the procedures of test. Marshall Test specimens were also used for this test having a diameter of about 100 mm (4.0 inch) and a height from 62 to 69 mm. The indirect tensile strength is the maximum strength resistance in (kg/cm^2) which the standard test specimen develops at a specified test temperature when subjected to load by standardized procedure. Normally, test temperature ranges between (-30 to +30 ^{o}C). In this study the test temperature was selected as +25 ^{o}C. Test procedure can be summarized in the following steps:

1) The test specimens were immersed in a water bath at 25 ^{o}C for 60 minutes before testing. The plate of the testing head was cleaned and guide rods were lubricated with a thin film of oil so that upper test plate would slide freely.
2) Marshall Specimenwere tested in compression machine by a constant strain rate 10 mm per minute (10 mm / minute) until failure occurred. The point of failure is defined by the maximum load obtained and the failure shape occurred in. The load in Newton required to produce the failure of the specimen at 25 °C was recorded.

3) The measured load value at failure (P) in Newton, the thickness of specimen (H) in mm and the specimen diameter (D) in mm were used to calculate the ITS values (St) by using the following equation:

$$St = 2P / (\pi * H * D)\ [N/mm^2].$$

Deformation test (rutting) Hamburg wheel tracking

The wheel tracking equipment of Materials laboratory, faculty of Engineering – Mattaria - Helwan University, was employed. Permanent deformation or rutting of asphalt mixtures is a distress that occurs at high pavement temperatures under loaded conditions. As the pavement temperature increases, the asphalt mixture becomes softer and is more susceptible to movement under load. Permanent deformation occurs when the asphalt mixture deforms under load and then does not recover to its original, un-deformed position. Over time, permanent deformation can lead to channelization or rutting

1- A laboratory – compacted specimen of asphalt mixture, or a core taken from a compacted pavement is repetitively loaded using a reciprocating steel wheel. The specimen is submerged in a temperature – controlled water bath at a temperature specified by the agency. The deformation of the specimen, caused by the wheel loading, is measured.
2- The impression is plotted as a function of the number of wheel passes. An abrupt increase in the rate of deformation may coincide with stripping of the asphalt binder from aggregate in the asphalt mixture specimen.

Results and discussion

Characterisation of nanoemulsion terpolymer

Fourier transform infrared (FTIR)

FTIR spectra shown in Figure1 indicates the presence of the following groups: the carbonyl group C=O double bonds appear in the region of 1731.8 cm^{-1}; the band at 2965.7 cm^{-1} is specific of aliphatic hydrocarbon of butyl acrylate and vinyl acetate; whereas the band at 3368 cm^{-1} is due to –OH group and $-NH_2$ of acrylamide.

(Take in Figure 1)

Molecular weight (Mwt)

Mwt results for vinyl acetate–bu-acrylate–vinyl ester of versatic acid terpolymer shown in Figure 2 illustrates that, the relative time (RT) is 0.78–4.45, where Mwt average is 1073 and the mass over the charge number of ions is 50.00–1100.00. The M.wt of the prepared polymers has a direct relationship with particle size. The range of MWT "Mn" is 1.7×10^3. The pH, solid content, particle size, viscosity and the molecular weight results as the Characterization of the prepared VAM, VeoVa 10 and Bu terpolymer are represented in Table II.

(Take in Table 2)

Thermo gravimetric analysis (*TGA*)

The TGA shown in Figure 3 demonstrates that, the decomposition temperature of the prepared nanoemulsion terpolymer is between 310 - 450°C; the weight loss of 15, 50 and 90 % were at 298, 338 and 460°C, respectively. The recorded the weight residual at 600°C was 5.4 %.

(Take in Figure 3)

(Take in Table 3)

Transmission electron microscopy (*TEM*)

Figure 4 shows the TEM of the vinyl acrylate–butyl acrylate–Vinyl ester of versatic acid terpolymer. It's clear from the figure that the diameters of the observed particles of the polymer range between 1.0 µm and 100nm. The implication here is that the progressive emulsion of the polymer improved the structure and robustness of the polymer. All particles are spherical and consist of a core from vinyl acetate–butyl acrylate–Vinyl ester of versatic acid. It's clear from the image that the particles are spherical in shape without any deformation with a narrow particle size distribution, the diameter of most particles were between 164 – 214nm.

(Take in Figure 4)

Modification of asphalt

Table IV illustrates the physical characteristics of the virgin asphalt and of the modified asphalt with 2, 4 and 6 wt.% vinyl acrylate–butyl acrylate–Vinyl ester of versatic acid terpolymer. The obtained results showed that the modification of asphalt with vinyl acrylate–butyl acrylate–Vinyl ester of versatic acid terpolymer produced a binder hardener than the virgin sample, as it has lower penetration and higher kinematic viscosity and softening point. This may be attributed to this type of polymer which produces a fine dispersion of the polymer in molten (solvating) phase with no disturbance of the asphalt structure, as it is a thermoplastic and a flexible polyolefin which does not contain any double bonds. Generally, the polymer creates a network to the asphalt molecule.

The obtained data also showed that the penetration, the softening point, and the kinematic viscosity of the modified asphalt improved by incorporation of different wt. % of the prepared emulsion terpolymer, as the obtained results are within the specified criteria, where the specific gravity is used to define the weight or density as compared to the density of an equal volume of water at a specified temperature.

(Take in Table VI)

Evaluation of characteristics of the prepared samples

In accordance with the Egyptian standard, the optimum asphalt content of the AC mixture was determined using the Marshall mix design methodology using different mix design types shown as follows.

Vinyl acrylate–butyl acrylate–Vinyl ester of versatic acid terpolymer was prepared and mixed with virgin asphalt in three different percentages using 2, 4 and 6 wt. %terpolymer. The best results obtained from the application using Marshall design was 4%. The application of the Marshall design included three types namely, hot mix asphalt, warm mix asphalt and cold in place recycled. However, all mixtures met the Egyptian Specifications for Road. Air void content, stability and other characteristics are illustrated in Table V and Figures 5–12. Comparing to the control Mix 1, the following results could be observed;

a) The optimum asphalt content increased compared to the control mix (0.017 % for WMA), and decreased (0.05% for HMA and 0.117% for CIR);
b) The stability of the control mix increased from 1050 Kg to 1550 Kg for WMA, where its increased to 1420 Kg for HMA and decreased to 725 Kg for CIR;
c) Marshall stiffness of the prepared mixes increased from 86.06 for control mix to 113.6 and 119.2 Kg/Inch for HMA and WMA respectively, this is due to the increase of stability and decrease in flow values where Marshall stiffness is not required for CIR;
d) The air voids decreased from 4.8 % to 4.5 % for HMA and increased to 4.9% for WMA and 10.37% for CIR;
e) The voids in mineral aggregates decreased from 15.25% to 15.0% for HMA and increased to 15.4% and 20.11% for WMA and CIR respectively, and

f) The voids filled with asphalt increased from 68.52% to 70.06% for HMA and decreased for WMA to 67.0%.

(Take in Table VII)

(Take in Figures 5-12)

Conclusions

The asphalt modified with terpolymer composition complies with the requirements of the Egyptian Standard Specification and has characteristics that are typical of those that use special polymer modifier: vinyl acrylate–butyl acrylate – vinyl ester of versatic acid terpolymer. This study focused on evaluating the effects of polymer on modification of reclaimed asphalt pavement in order to improve the quality of paving and reduce the cost of asphalt using three different mix designs. In this study, the effect of using RAP mixtures was evaluated using a Marshall mix design by three different types HMA, WMA, and CIR.

In this research, a content of 4 wt. % of vinyl acrylate–butyl acrylate–Vinyl ester of versatic acid terpolymer was used as a polymer modified asphalt PMA while applying Marshall mix design as HMA, WMA and CIP. The research results show a change in stability. The milled asphalt mixture that contained 3.88% asphalt, the optimum asphalt content was ranging between 1.506 – 1.73 %, which designate the polymer amount ranged between 0.06 – 0.066 %. All mix types of HMA, WMA and CIP have achieved the required specifications for stability and all other requirements and this will allow the production of an asphalt mix giving a higher performance and longer service life accordingly.

The research achieved using nanoemulsion terpolymer as RAP modified with required quality according to required specifications.

The application of the Marshall design for the control mix and the modified mixes showed that:

- The optimum asphalt content was decreased for Mixes 2 and 4 from 5.503 to 5.453 and 5.386%, while increased for Mix 3 to 5.520%. This may be due to the effect of the Sasobit material used in WMA and the effect of terpolymer as a flexible terpolymer causing the adhesive effects of asphalt to increase.
- The stability, increased for Mixes 2 and 3 to 1420 and 1550 Kg respectively, then decreased

for Mix 4 to 725 Kg compared to 1050 Kg for the control Mix 1 at percentages of 35.2 and 47.6. Such an increase in stability for Mixes 2 and 3 is due to the nature of mix design used.

- Marshall stiffness of the prepared mixes increased from 86.06 for control Mix1 to 113.6, 119.2 for Mixes 2 and 3 at percentages of 32.0 and 38.5, respectively. This is due to the increase of stability and the decrease in flow values of the asphalt mixes.
- The percentage of air voids in the mix for Mix 2 decreased from 4.8 to 4.5% and increased for Mixes 3 and 4 from 4.8 to 4.9 and 10.37% respectively. This is due to the increase in stability of mixes in addition to the compatibility and flexibility of polymer samples and the type of the Marshall design used.
- The percentage air voids in the mineral materials decreased for Mix 2 from 15.25 to 15.0 and increased for Mix 3 to 15.4 and Mix 4 to 20.11 respectively. All of these results may be due to the effect of compatibility of asphalt and the nature of the polymer which in turn affects the adhesion power between the solid materials and the asphalt.
- All Marshall mix design types HMA, WMA and CIR using PMA achieved the required specifications for Egyptian Standard Specification.
- The addition of 4 wt.% vinyl acetate–butyl acrylate–vinyl ester of versatic acid terpolymer produced a WMA that has good Marshall stability as well as gives more desirable general characteristics of the modified asphalt than HMA and CIR.
- Added polymer amount for modification of asphalt range between 0.06% for CIR, 0.063% for HMA, and 0.066% for WMA.

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Table I Recipe of vinyl acetate-butyl acrylate– vinyl ester of versatic acid nanoemulsion terpolymer

Components	**Wt. %**	**Wt. (g)**
Vinyl acetate monomer VAM	40	200
Butyl acrylate BuA	3.75	18.75
Vinyl ester of Versatic acid (VeoVa)	5.25	26.25
Sodium lauryl ether sulphate (SLS)	0.4	2
Ethoxylated Nonyl Phenol (NP_{30})	2.2	11
Potassium per sulphate (KPS)	0.75	3.75
Sodium acetate ($C_2H_3O_2Na$)	0.6	3
Acrylamide (AA)	4	20
Dist. H_2O	43.05	215.25

Table II **Characterization of the prepared VAM, VeoVa 10 and BuAc nanoemulsion terpolymer**

Properties	Standard	Prepared polymer
	ASTM	The sample
pH		7.5
Solid Content (%)	D2369	50
Particle size (nm)	TEM	164-214
Brookfield Viscosity RVT #50 rpm, (cps)	D 2196	2000
Molecular weight	Mn*10^3(g/mole)	1.7

Table III TGA data of the synthesized polymer.

Run	% weight loss at various temperature ( ) °C				Decomposition temperature range (°C)	T (°C^{15})	T (°C^{50})	T (°C^{90})	T (°C^{max})
	200	300	400	Max ( ) °C					
Polymer	15	50	90	94.6	310 - 450	298	338	460	398

Table IV The sieve analysis for RAP according to the Egyptian Standard Specifications

Sieve Size	Gradation before extraction % Passing	Gradation after extraction % Passing	Limits of the binder mix Egyptian Standard Specification (Dense –Graded 4D),2008
37.5 mm (1½")	100	100	-------
25.0 mm (1")	100	100	80 – 100
19.1 mm (¾")	84.1	88.5	70 – 90
12.5 mm (½")	76.4	80.3	-------
9.5 mm (⅜")	68.4	72.1	55 – 75
4.75mm #4	54.3	59.7	45 – 62
2.36mm #8	39.2	43.8	35 – 50
0.6mm #30	19.5	24.6	19 – 30
0.3 mm #50	11.4	14.5	13 – 23
0.15mm #100	2.4	8.2	7 – 15
0.075mm #200	0.45	3.3	0 – 8
Asphalt content %	3.88%		3.5 – 7.0

Table V The physical properties of the aggregate

Property	AASHTO Test Method	Coarse Aggregate		Fine Aggregate	Mineral Filler	AASHTO Specification
		Agg. (1)	Agg. (2)			
Los Angeles Abrasion (Loss wt. %)	T 96 – 83	19.2	18.4	-----	------	Max. 40 %
Bulk specific gravity G_{sb}	T 85 – 85	2.50	2.478	2.65	2.701	------
Apparent specific gravity	T 85 – 85	2.62	2.615	------	------	------
Specific gravity SSD	T 85 – 85	2.684	2.679	------	------	------
Water absorption (wt. %)	T 85 – 85	1.16	1.17	------	------	Max. 5 %
Stripping	T 85 – 85	>95 %	>95 %	------	------	>95 %

Table VI The physical characteristics of the used asphalt

Physical characteristics	Virgin AC	Terpolymer wt.%			ESP
		2	4	6	
Penetration (at 25˚C, 100g, 5s) 0.1mm	63	63	65	68	60/70
Softening point (ring & ball) ˚ C	46.5	49	51	54	45/55
Specific gravity (at 25/25) ˚C using a pycnometer	1.02	1.044	1.092	1.111	Not specified
Kinematic viscosity (at 135˚C) cSt	380	520	610	885	> 320

Table VII Marshall Characteristics of the prepared asphalt mixes

Characteristics	Mix Number				Egyptian Standard Specification Limits for Binder Course
	Control Mix (1)	(HMA) (2)	(WMA) (3)	(CIR) (4)	
Optimum asphalt content Before Extraction (%)		3.88			
Optimum Asphalt Content (%)	5.503	5.453	5.520	5.386	Not specified
Stability of the mix (kg)	1050	1420	1550	725	Min 700 Kg
Unit weight of the mix (gm/cm^3)	2.308	2.310	2.300	2.170	Not specified
Flow of the mix (0.01 inch)	12.2	12.5	13.0	11.6	8 – 16
Air voids of the mix (%) Va	4.8	4.5	4.9	--	3 – 8
Air voids of the mix CIR (%) Va	--	--	--	10.37	9 – 14
Voids in Mineral Agg (%) VMA	15.25	15.0	15.4	20.11	Min 15 %
Voids Filled with Asphalt (%) VFA	68.52	70.06	67.0	Not required	60 – 70
Marshall stiffness Kg/in	86.06	113.6	119.2	Not required	Not specified
Virgin asphalt added to RAP (%)	1.623	1.573	1.64	1.506	Not specified
Polymer Modified Asphalt wt.%	0.0	0.063	0.066	0.060	Not specified

Scheme 1 Chemical structure of terpolymer components

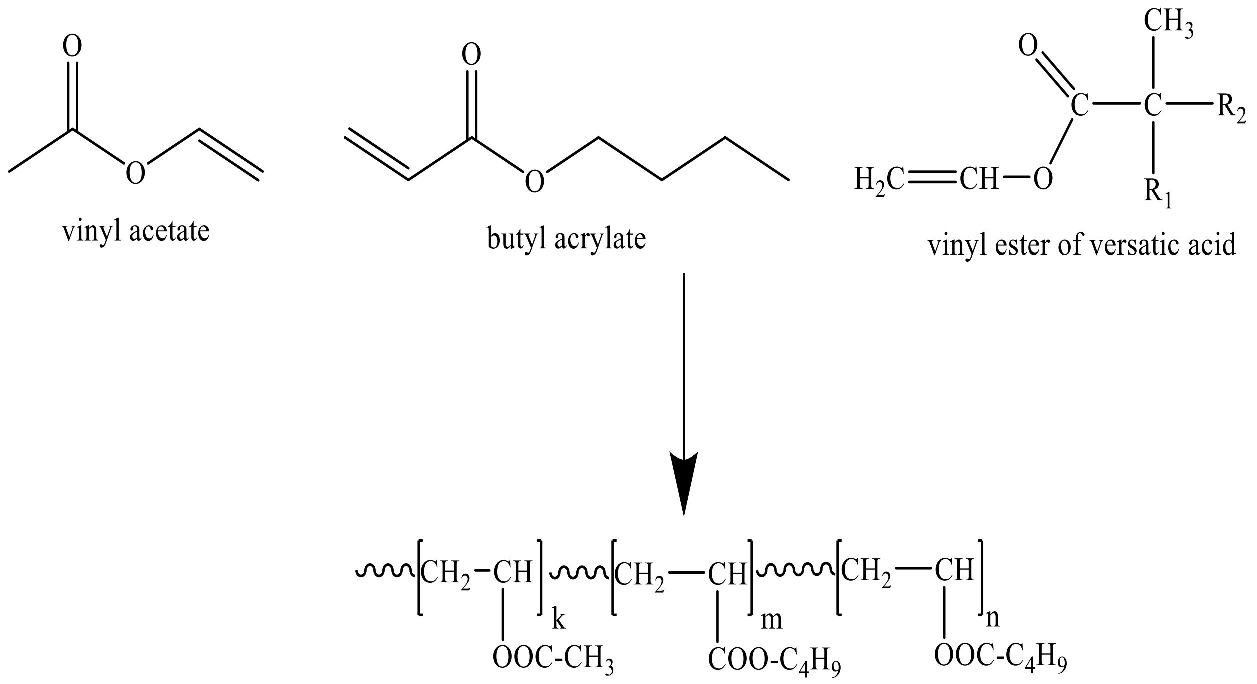


Figure 1 FTIR spectra of the prepared vinyl acrylate–butyl acrylate– vinyl ester of versatic acid terpolymer

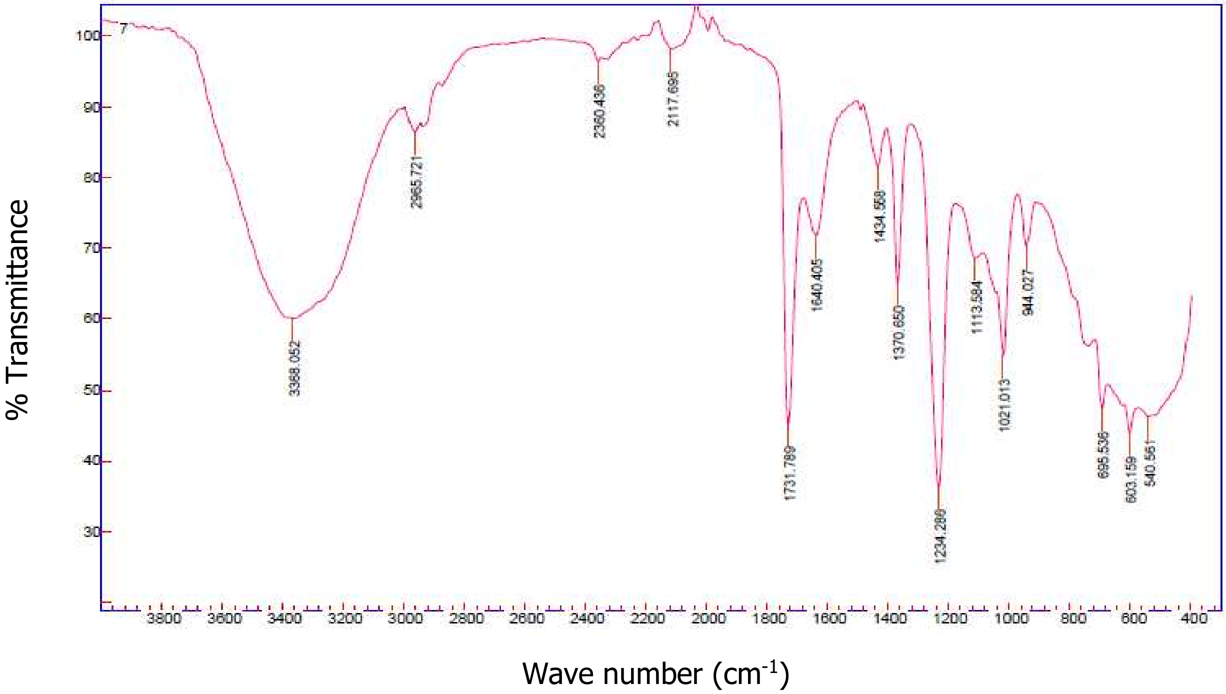


Figure 2 Molecular weight of the prepared vinyl acrylate–butyl acrylate–vinyl ester of versatic acid terpolymer

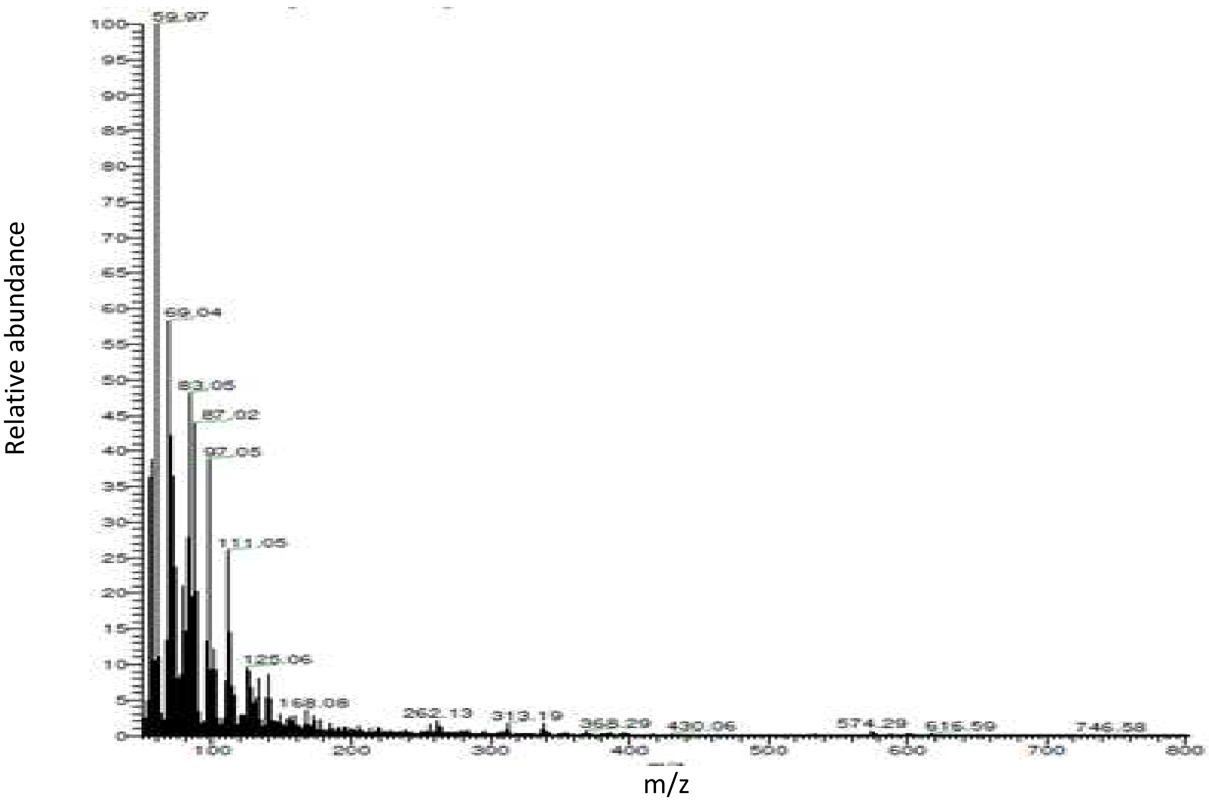


Figure 3 TGA of the prepared vinyl acrylate–butyl acrylate–vinyl ester of versatic acid terpolymer

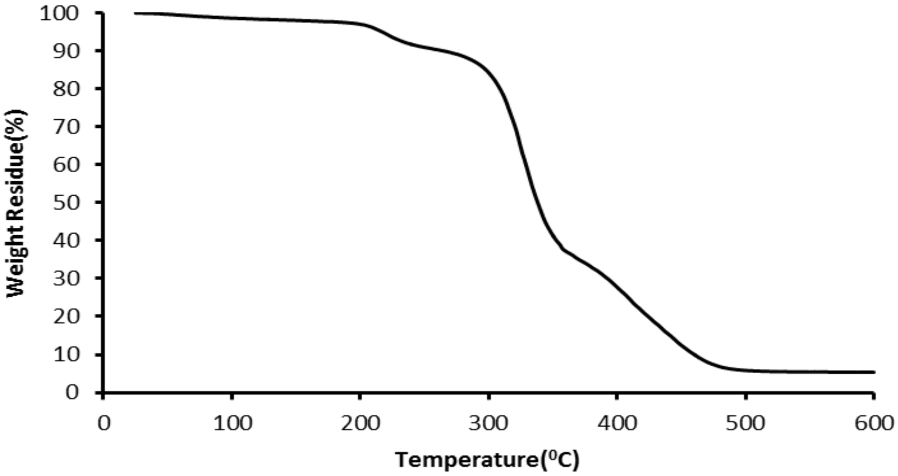
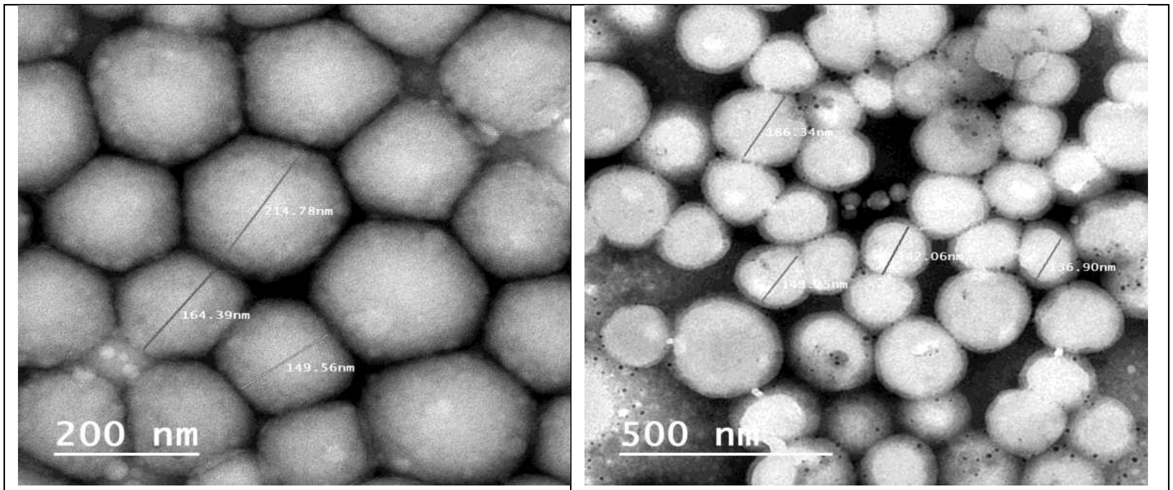


Figure (3.4) TGA curve for the prepared sample (Weight loss versus temperature range) for clarity the curve have been plotted
(0-100) °C.

Figure 4 TEM for vinyl acrylate–butyl acrylate–vinyl ester of versatic acid terpolymer



Transmission electron micrographs of the prepared emulsion terpolymer (avg.149 214 nm)

Figure 5 Optimum asphalt content for all mixes

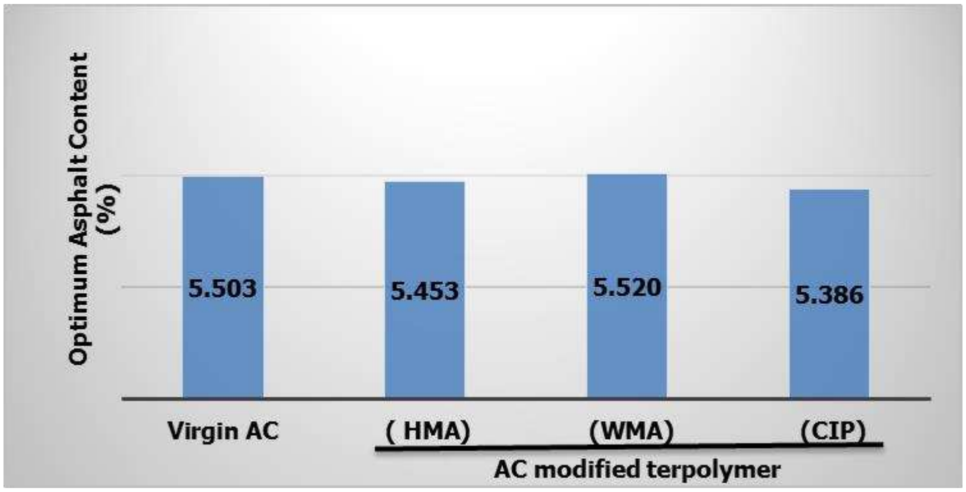
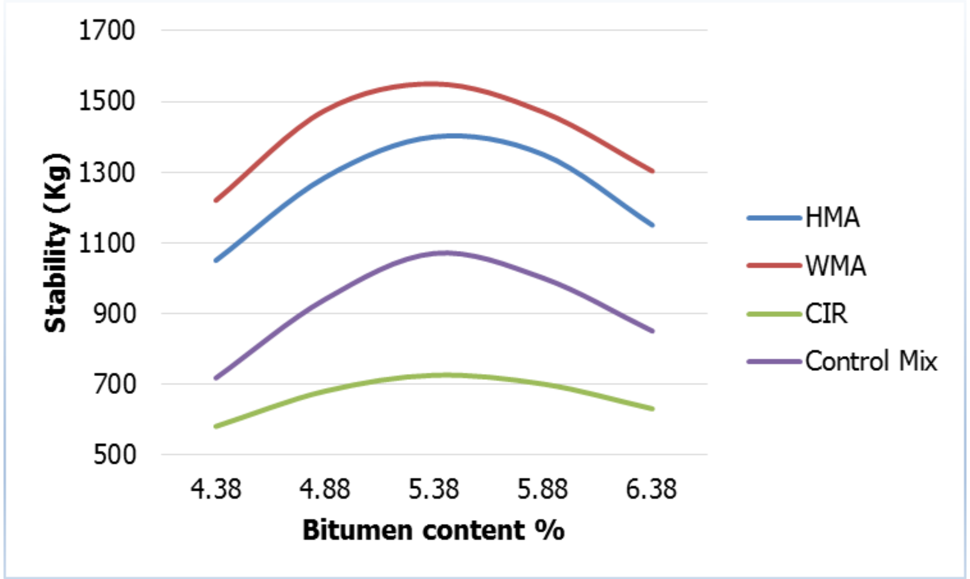
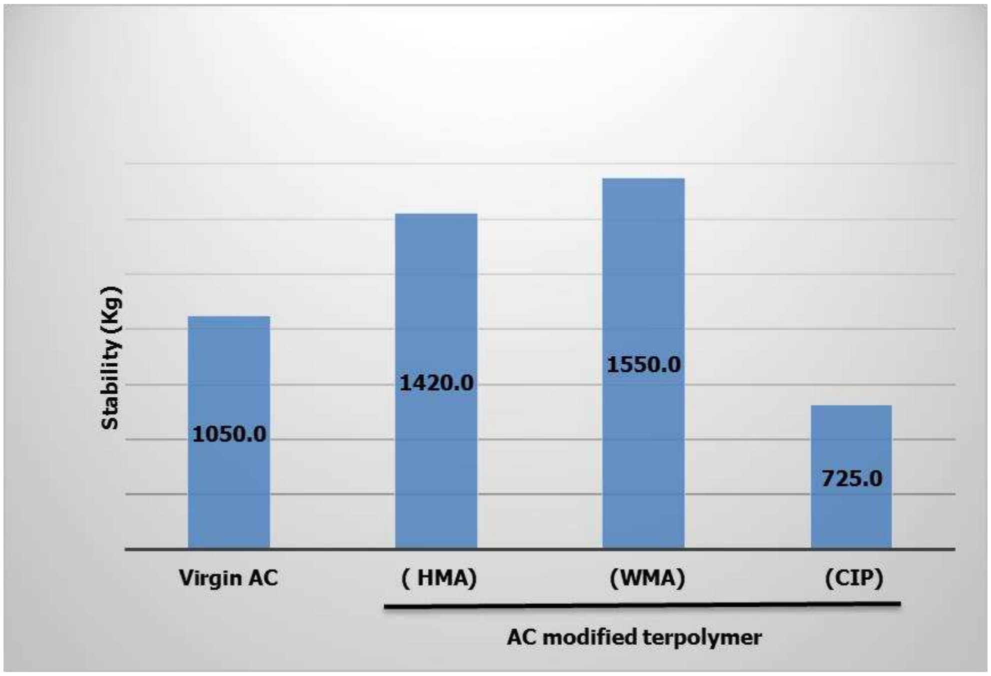


Figure 6 Stability results for all mixes

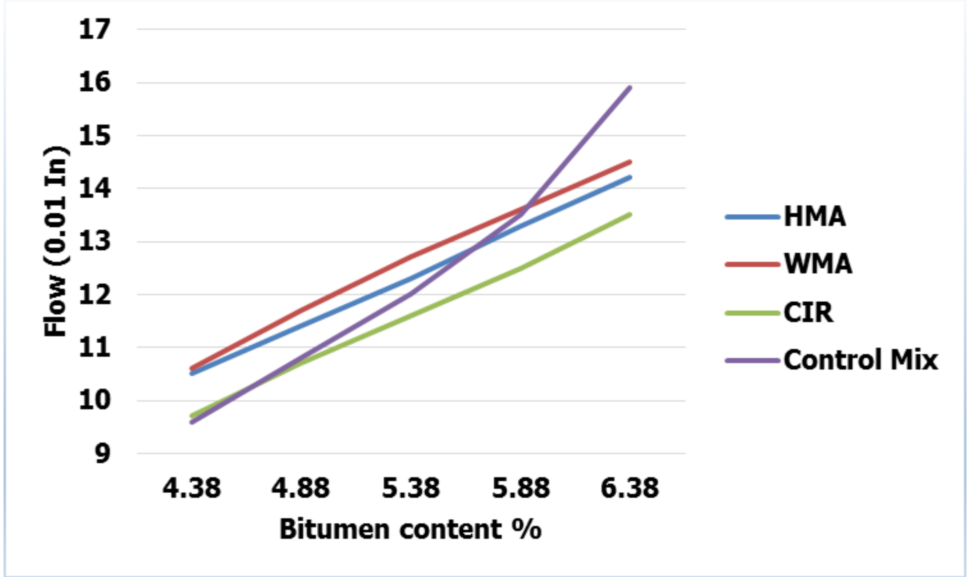


(a) Stability profiles

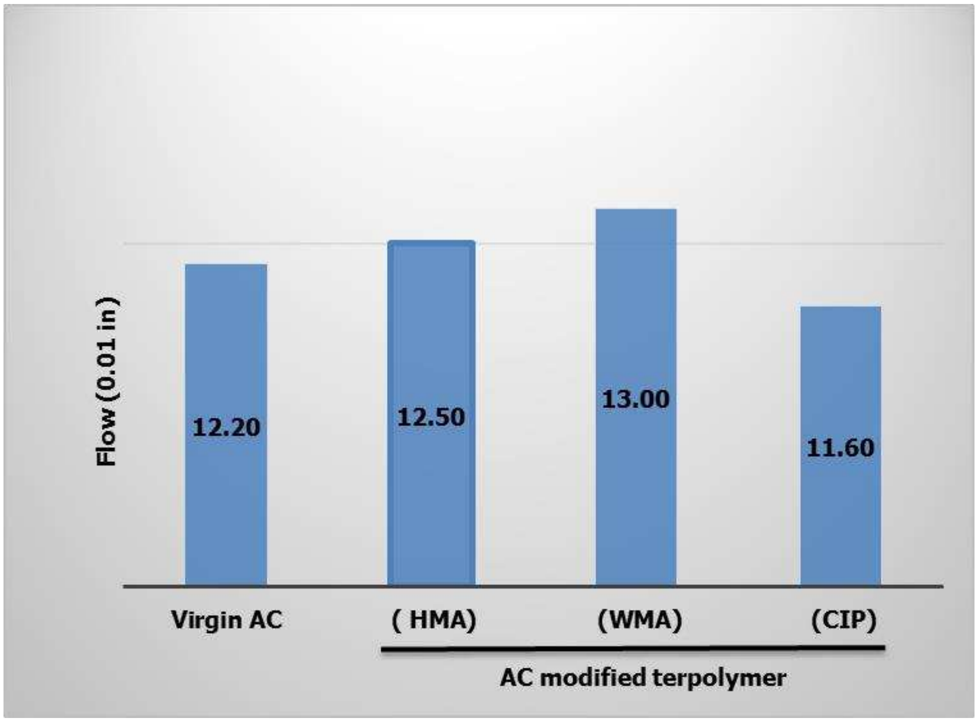


(b) Optimum stabilities

Figure 7 Flow results for all mixes

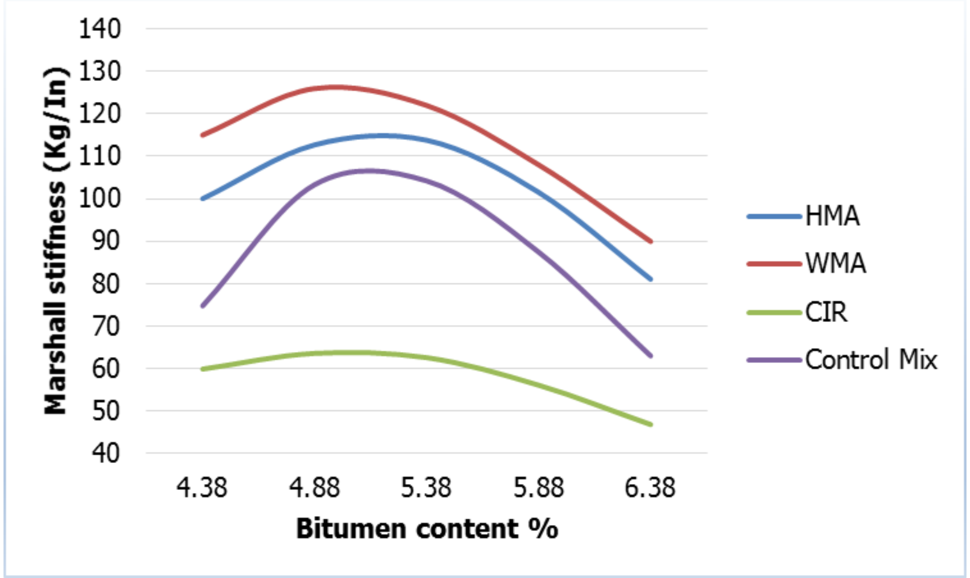


(a) Flow profiles

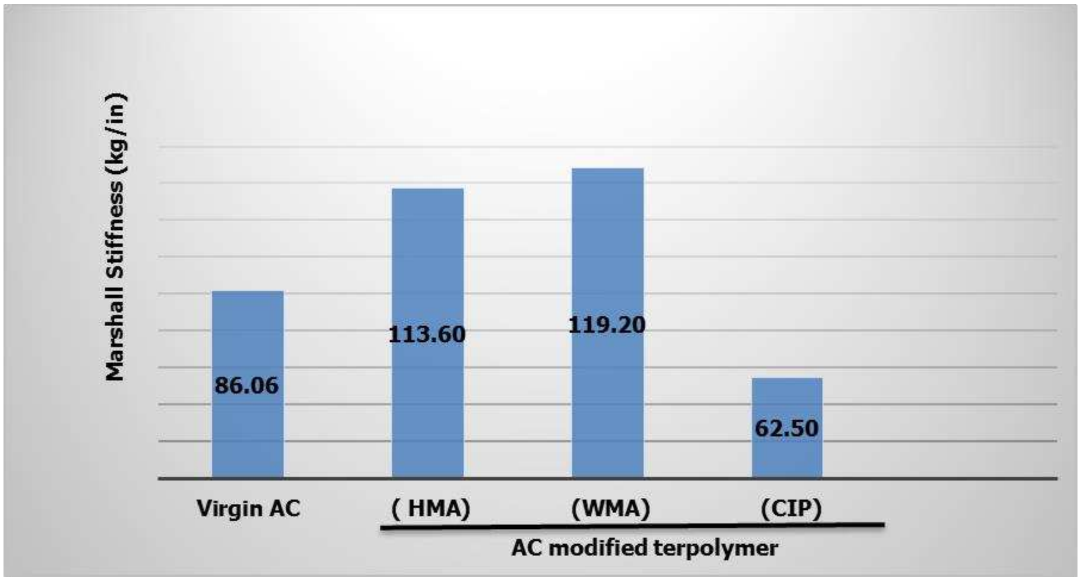


(b) Optimum flow values

Figure 8 Marshallstiffness results for all mixes

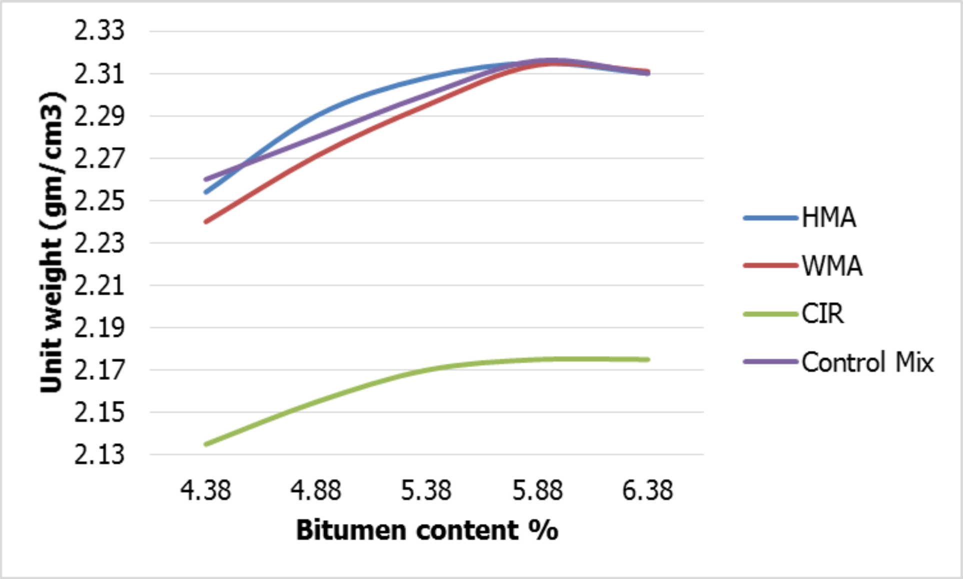


(a) Marshall stiffness profiles

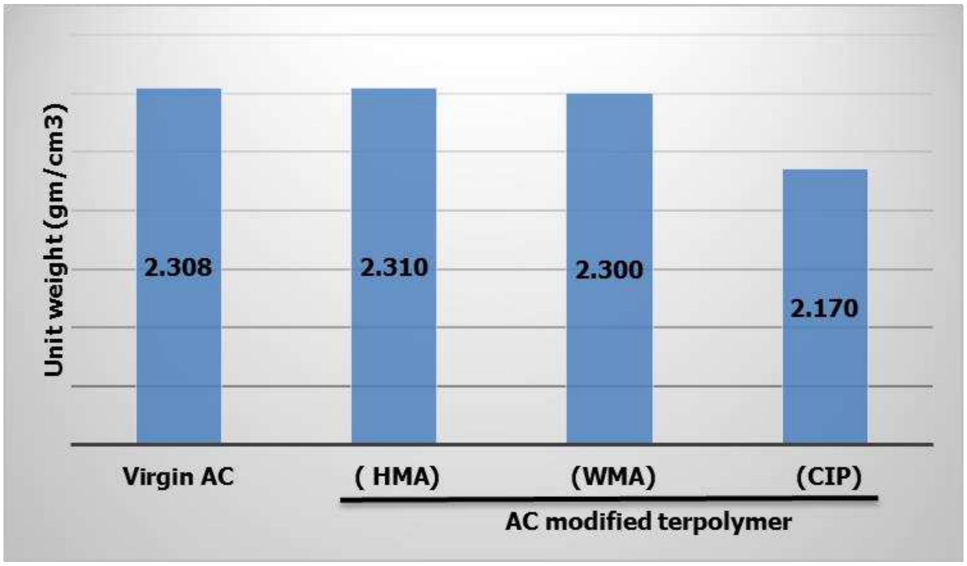


(b) Optimum Marshall stiffness values

Figure 9 Unit weight results for all mixes

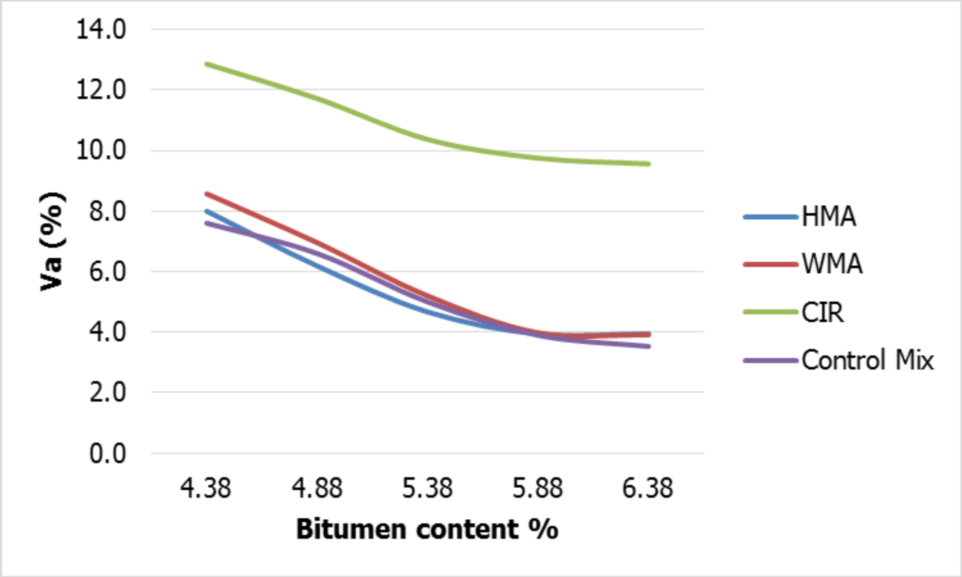


(a) Unit weight profiles

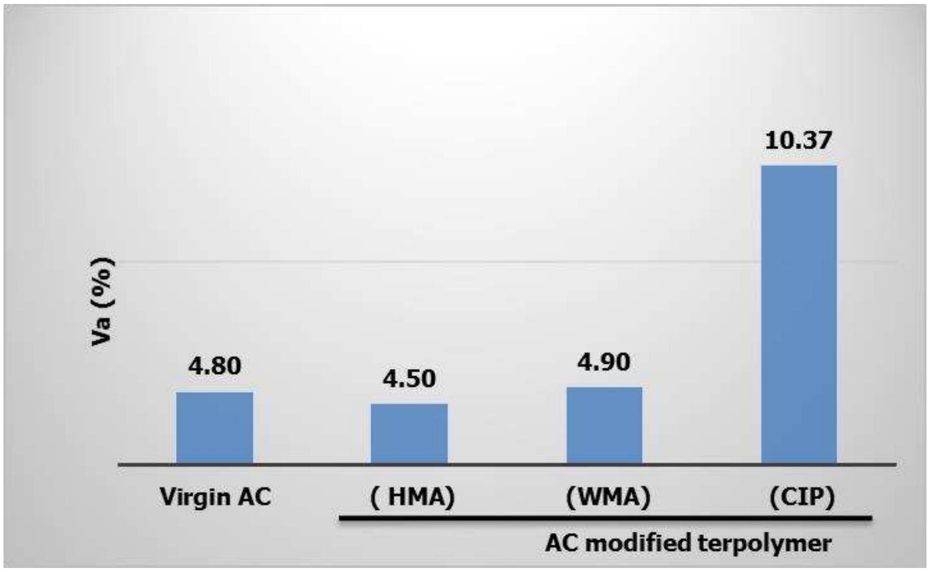


(b) Optimum unit weights

Figure 10 Air voids results for all mixes

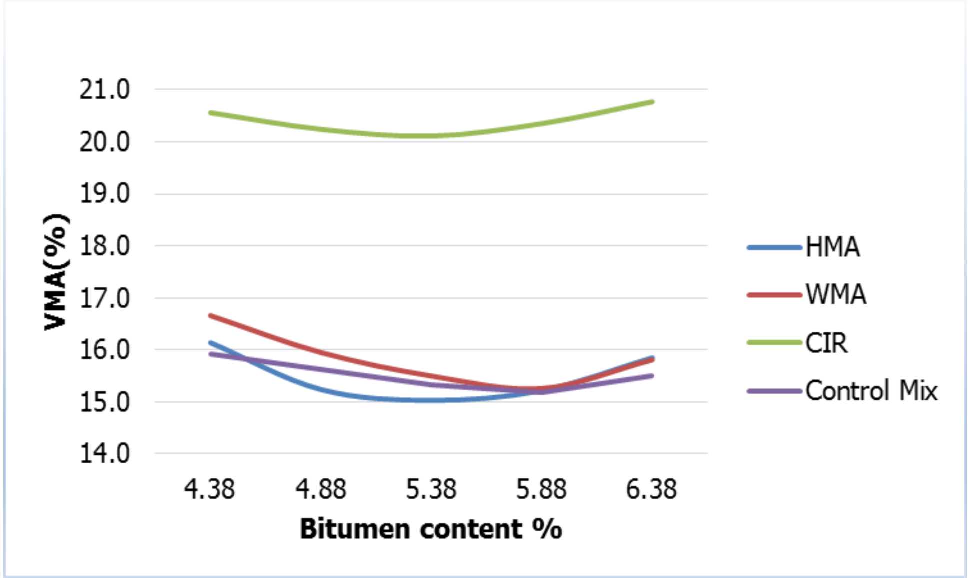


(a) Air void profiles

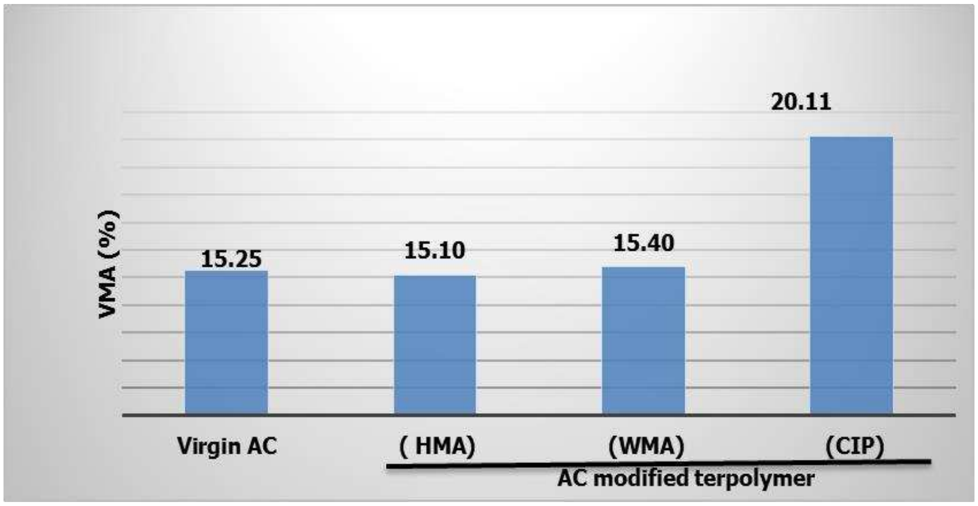


(b) Optimum air void values

Figure 11 Voids in mineral aggregate results for all mixes

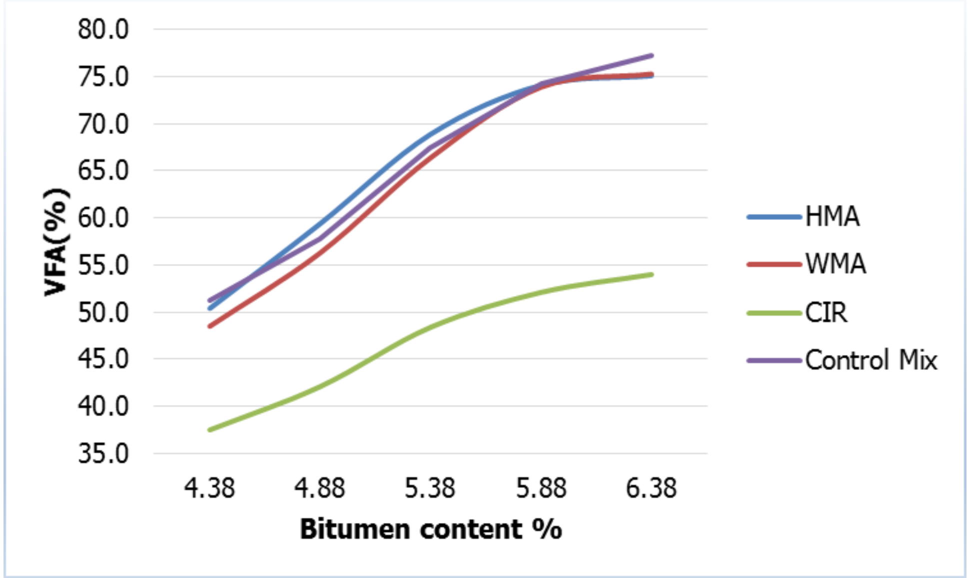


(a) Profiles of voids in mineral aggregates

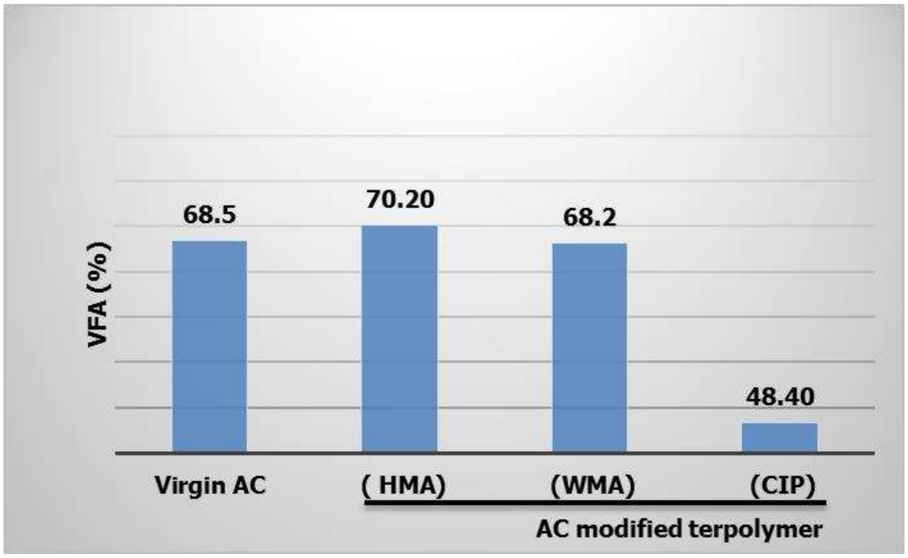


(b) Optimum values of voids in mineral aggregates

Figure 12 Voidsfilled with asphalt results for all mixes



(a) Profiles of voids filled with asphalt



(b) Optimum values of voids filled with asphalt