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# Rheological properties of synthesised additives in hot mix asphalt

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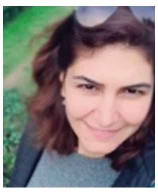

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**Subject review**

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**Rheological properties of synthesised additives in hot mix asphalt**

In civil engineering, pavement, which is a mixture of aggregate and bitumen, is the layer most affected by traffic loads. Thus, problems, such as cracking, rutting, fatigue, aging, and moisture damage occur in the asphalt pavement layer throughout its service life. Such problems are generally caused by the increase in the number of heavily loaded vehicles, design and construction errors, and climate and environmental conditions. Scientists and engineers are continuously working on improving the performance of asphalt pavements. Particularly, recent studies have focused on improving multiple properties of asphalt simultaneously by chemically synthesising a novel material in the laboratory. This study aims to present a review of the effects of chemically synthesised additives on the performance of asphalt binders and mixtures. The findings of this study show that these new additives had a significant effect on the rheological properties of asphalt, such as rutting, elasticity, and fatigue life, when used in appropriate proportions. This study is expected to serve as a reference and guide for future studies on the production of new synthesised additives as asphalt modifiers.

**Key words:**
**asphalt, modification, novel additives, rheology, road performance**

**Pregledni rad**

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**Reološka svojstva sintetiziranih aditiva u vrućoj asfaltnoj mješavini**

Asfaltni kolnik je dio kolničke kostrukcije koji je pod najvećim utjecajem prometnog opterećenja. Stoga se u slojevima asfaltnog kolnika tijekom njegova trajanja javljaju oštećenja poput pukotina, kolotraga, zamora materijala, starenja te oštećenja uzrokovanih vlagom. Uzroci takvih oštećenja većinom su povećanje broja teških vozila, pogreške pri projektiranju i izvođenju te klimatski i okolišni uvjeti. Znanstvenici i inženjeri kontinuirano rade na poboljšanju svojstava asfaltnih kolnika. Nedavna istraživanja usmjerena su na poboljšanje svojstava asfaltnih mješavina kemijskom sintezom novog materijala u laboratoriju. Cilj je ovog rada prikazati pregled stanja u području učinaka kemijski sintetiziranih aditiva na svojstva asfaltnih mješavina i veziva. Rezultati ovog istraživanja pokazuju da su ti novi aditivi pri upotrebi u odgovarajućim omjerima imali značajan učinak na reološka svojstva asfaltnih mješavina, kao što su kolotrazi, elastičnost i otpornost na zamor. Očekuje se da će ovo istraživanje poslužiti kao referenca i vodič za buduća istraživanja o proizvodnji novih sintetiziranih aditiva kao modifikatora asfaltnih mješavina.

**Ključne riječi:**
**asfalt, modifikacija, novi aditivi, reologija, ponašanje kolničkih konstrukcija**

## 1. Introduction

The deterioration of asphalt pavements is caused by changing climatic conditions, rapid population growth owing to the increase in living standards that resulted from industrial development and excessive traffic volumes to which road superstructures are exposed. These deteriorations can be rutting at high temperatures, fatigue at medium temperatures, and cracks at low temperatures. Studies have focused on asphalt modification by wide variety of additives to the bituminous binders or mixtures to reduce the occurrence of these deformations, improve the performance characteristics of asphalt pavements, and increase road quality and life. A summary of some of the relevant studies in the literature is given below.

Styrene-butadiene-styrene (SBS) is a thermoplastic elastomer additive that is commonly used in bitumen modification. The elasticity of bitumen was increased by SBS additives [1-3], thereby improving the fatigue and cracking behaviour [4, 5], enhancing the high temperature stability of the binder by increasing the complex shear modulus [6, 7] and improving its rutting resistance [8-10]. However, as a result of SBS addition, bitumen could suffer from loss of penetration and strength at high temperatures [1], and the flow values of the SBS-modified mixtures are higher than those without it [11]. Ethylene-vinyl-acetate (EVA) is a plastomeric asphalt modifier contributing to the physical [12-14] and rheological [15] properties of asphalt, improving fatigue cracks in road pavements at low temperatures [16-18], and increasing asphalt viscosity at high temperatures [19-21]. Bitumen modification with SBS and EVA polymers improved the traditional properties of asphalt [11] and increased rutting resistance [22]. The high temperature storage stability of asphalt modified with styrene-butadiene rubber (SBR) can be significantly improved with the addition of polyphosphoric acid (PPA). Moreover, the addition of sulfur to asphalt modified with PPA and SBR can improve the rutting resistance and physical properties at low temperature as well as the rheological properties and adhesion [23-25]. It has been reported that the rheological properties and adhesion asphalt that has been modified with PPA and SBR improved by adding sulfur [23-25]. It has been reported that low density polyethylene (LDPE) improved the low temperature property of asphalt, and the cracking resistance of asphalt decreased as the LDPE concentration increased [26-28]. Although the mixing time and temperature of the bitumen binder modified with high density polyethylene (HDPE) increased as the Marshall Stability and elasticity modulus values increase [29-32], the polymer phase separated from the asphalt and became unsuitable for road applications after a short-term storage at high temperatures [33]. Adding ground or crumb waste car tires to the bituminous binder had a significant effect on the viscosity and low temperature crack resistance of the binder [34-37], improved the coating performance [38, 39], resulted in permanent deformation and high temperature properties, [40] and reduced road-maintenance costs and noise [41,42]. Modifying asphalt binders with commercially purchased wax improved fluidity, rheological properties [43, 44], and performance of asphalt mixes at high temperatures [47]. Moreover, it had a positive effect against short-term aging [45, 46]. According to the results of the tests performed using five different fibres (i.e., polyacrylanitrile fibre, lignin fibre, asbestos fibre, and two polyester fibres) in bitumen modification, the dynamic shear modulus improved with the resistance of bitumen to rutting and flow [48]. Waste cooking oils added to aged asphalt binders have shown properties similar to the original physical and rheological properties of the binder [49-51]. Additionally, it increased the deterioration temperature of the asphalt binder [52] and caused the binder to lose its elasticity after a certain amount of oil addition (2 %) [53]. Bio-based oils have been increasingly popular in bitumen modification owing to their sustainability and positive effects. Studies have shown that using bio-oils in asphalt modification improved the high temperature performance of the binders, increased their viscosity, deformation resistance, low temperature crack resistance, and temperature sensitivity [54-58]. Addition of furan resin produced from furfural obtained by acidic hydrolysis of vegetable waste and activated carbon components obtained by vacuum pyrolysis of hazelnut shell reduced the temperature sensitivity of asphalt and improved its rheological properties [59, 60]. Nanomaterials, which form the basis of nano technology, have unique properties, such as high temperature sensitivity, high ductility, large surface area, high tensile strength, and low electrical resistance [61-64]. With these properties, the application areas of nano materials are considerably wide. Recently, they are being used as an additive in asphalt modification. The most used nanomaterials for asphalt modification are carbon nanotubes, nanowires, nanofibres, and nanoceramics [65]. Modifying asphalt with nano-titanium dioxide (nano-$TiO_2$) reduced its ductility and increased its softening point [66, 67], rutting resistance, and aging resistance [68]. Nano- montrmorillonite (nano-MMT) is a type of clay that has been used in many studies on asphalt modification [69-71]. The addition of nano-MMT improved the softening point and viscosity of asphalt by improving its physical and rheological properties [72] and rutting strength and reduced its phase angle [73-77]. Nano-zinc oxide (nano-ZnO) increased fatigue performance, resisted thermal and photo oxidation, and improved fatigue performance [78-80] of asphalt, while nano-calcium carbonate (nano-$CaCO_3$) improved its high and low temperature properties, storage stability, and aging resistance [81]. Moreover, carbon nanoparticles/fibres have been reported to improve the rheological properties of asphalt, increase its resistance to fatigue and thermal cracks, and improve its rutting resistance [82-84]. It has been noted that nano-silica improves the consistency and resistance of asphalt against permanent deformations and increases performance against fatigue [85, 86], while the modification of asphalt using nano-ceramic waste increased softening point and rutting resistance and decreased temperature sensitivity [87]. Epoxy resin reduced asphalt viscosity, softening point, and temperature sensitivity and increased rutting resistance [88-90]. However, it adversely affected the cracking resistance at low temperatures [91]. The modification of asphalt with various oils, including corn, palm kernel and soybean oils, has been reported to have a positive effect on fatigue and low temperature behaviour, increase workability at low temperatures, and is a regenerative substance for recycled asphalt [92, 93]. The resistance to workability and fatigue strength of asphalts can be increased by using recycled oils in asphalt modification [94, 95]. However, if the amount of oil used as a modifier is more than a certain ratio, the resistance to wheel marks decreases [96]. Asphalt modified with waste polymers has increased elasticity at low temperatures, increased resistance to rutting [97, 98] and had no effect on the performance of asphalt at low temperatures [99]. However, the additives used in the above mentioned studies are expensive, consume large amounts of energy, cause environmental pollution during the modification process, and require special mixing facilities; thus, new, cost-effective, and environmentally friendly additives to modify asphalt have been the focus of many ongoing research with new additives being continuously studied to improve asphalt properties.

This study aims to review the published research in this area and summarise the contribution of synthesised additives to the asphalt and asphalt mixtures. First, we summarise the effects of the traditional test methods, such as penetration, softening point, and ductility tests, on the physical properties, such as viscosity, dynamic shear modulus, and low temperature properties of the binder. In addition, the performance of newly synthesised additives in asphalt mixtures is also summarised. Furthermore, the summary is extended to include the structural characterisation properties of the synthesised novel additives.

## 2. Synthesis and preparation of new additives

Many different additives are used to increase the performance of asphalt, which is generally used as an organic binder for waterproofing and moisture resistance and as a corrosion protection agent in road pavements. Recently, polymers have been the most commonly used additives to extend the life of asphalt. While various polymer modifiers improve the coating performance of asphalt, the general incompatibility of polymers with asphalt negatively affects the material by causing composite delamination [100].

Compared to polymers, synthesised additives are not only dispersed in the bitumen matrix but can also chemically react with the bitumen during modification, resulting in new properties. In addition, chemical reagents can influence the performance at low additive rates, thus, reducing costs.

Chemical synthesis is the process of artificially obtaining a new product with two or more substances through chemical reactions using safe and widely available reagents, industrial by-products, and environmentally harmless wastes. According to the desired properties in bitumen modification, new additives are obtained from these products under laboratory conditions. Various methods, catalysts and solvents are applied based on the reagents used in the synthesis.

### 2.1. Organic-based additives

Organic compounds are mostly hydrogen-containing carbon compounds. The carbon (C) atom can easily form new compounds by establishing a covalent bond with metals, such as oxygen (O), nitrogen (N), and sulfur (S). Generally, organic reactions are slow and require energy, usually in the form of heat [102].

Martinez et al. [103] synthesised an organic asphalt modifier bearing six furan rings and four formyl groups. As a result of a series of chemical processes, six different substances were synthesised from 5-hydroxymethylfurfural, 2-formylthiophene, 5-formyl furanboronic acid and 5-bromo-2-formylfuran by cross-linking and Suzuki reactions. Six new substances were synthesised as asphalt modifiers and the effects of these additives on the asphalt performance were investigated. First, the intermediate 3 was formed by a cross-linking reaction between 5-formyl furanboronic acid and 5-bromo-2-formyl furan. Then, compound 8 was obtained from the Corey-Fuchs reaction [104] of the intermediate 3. Subsequently, compound 8 underwent a palladium catalysed cross-coupling reaction with 5-formyl furanboronic acid to form compound 7 containing six furan rings and four formyl groups. The chemical name of the synthesised modifier was 2,2′-Bis [2,2-di (5-formyl-2-furyl) vinyl] -5,5′-bifuryl. The modification was carried out with the new additive in a ratio of 1 % to the bitumen weight.

Arslan et al. [105] synthesised the calcium (Ca) compound and boric acid with abietic acid composed of hydrocarbons for an asphalt modifier. The synthesis apparatus consisted of a magnetic stirring heater, a spherical three-necked flask reactor, and a reflux condenser. CaO was added to the abietic acid in the oil and catalysed using sulfuric acid ($H_2SO_4$) at 150°C and the synthesis was carried out with the aid of a magnetic stirrer and a heater. The ratio of resin and oil was 3:7. Ethyl alcohol was added at the end of the experiment to ensure the dissolution of the formed substances. The same procedure was applied to the boric acid compound. As a result of the synthesis, an organic-based calcium compound (OBCC) and organic-based boric acid compound (OBBAC) were obtained separately. The modification was carried out by adding the synthesised additives to the bitumen at the rates of 1 %, 2 %, 3 %, 5 %, and 10 %.

Çubuk et al. [106] synthesised a magnesium compound to be used as an asphalt modifier. First, magnesium oxide (MgO) was powdered and mixed in an oil under laboratory conditions. The mixture was added to the resin-oil mixture in the reactor by distillation. The additive containing 0.0474 g of Mg metal was synthesised in 1 mL of the obtained solution. The modification was carried out by adding the synthesised Mg compound in a ratio of 0.1 % to the heated bitumen.

Arslan et al. [107] synthesised three different asphalt modifiers using the same synthesis process as in their previous study [105]. However, they used resin instead of abietic acid. Different metal oxides, such as MgO for organic-based magnesium compound (OBMAGC), $MnO_2$ for organic-based manganese compound (OBMANC), and ZnO for organic-based zinc compound (OBZC), were added to the resin-oil mixture separately, and sulfuric acid was used as the catalyst. The ratio of resin and oil used as a source of abietic acid was added at different values according to metal oxides. The resin-oil ratio was 7.5:17, 2.6:6.5, and 2.6:6 for OBMAGC, OBMANC, and OBZC, respectively. Ethanol was added at the end of the experiment to dissolute the formed substances [106]. The three additives obtained were added to the bitumen separately at the rates of 1 %, 2 %, 3 %, 5 %, and 10 %, and their modification was carried out.

## 2.2. Boron-containing additives

Boron is found as a compound in water, soil, and rocks, and is used in various fields, such as the pharmaceutical and glass industries [108]. In 1982, boron was chemically mixed with asphalt. Glass fibre particles chemically reacted with an orthoester of organic metal compounds, and the resulting borate reaction product was used in asphalt modification [109]. Arslan et al. [110] synthesised triethyleneglycol based polyboron (TEGPB) as a new asphalt modifier under laboratory conditions. They used a reactor equipped with a condenser and a magnetic stirrer heater. Additionally, 150 g of triethylene glycol with 99 % purity and a molecular weight of 150.18 g/mol was heated in the reactor. Then, 0.75 mL of sulfuric acid was added as the catalyst and mixed with a magnetic stirrer. When the temperature reached 70 °C, 90 g boric acid (purity≥99 %) was slowly added and the mixing-heating processes continued. The synthesis took 30 min at 120 °C using a magnetic stirring heater. The modification was carried out by adding the obtained TEGPB modifier to the bitumen in the ratios of 1 %, 2 %, 3 %, and 5 %. Two new bitumen modifiers were obtained from the same synthesis process using monoethylene and diethyleneglycol rather than triethyleneglycol [111]. Calisici et al. [112] produced a new modifier from diethyleneglycol using similar chemical procedures and examined the effects of the modifier on asphalt modification. The two modifiers obtained were added to the bitumen in the same proportions of the TEGPB modifier and modified separately.

Oruc et al. [113] chemically synthesised four new boron-containing asphalt modifiers in the laboratory. Alkyl groups containing different amounts of carbon atoms (ethyl, butyl, and octyl) were used in the chemical structure of the new modifiers. Alkyl groups are used because asphalt, which has a hydrocarbon structure, can achieve a stronger electrostatic effect with such modifiers. The composition used in the additive compound-1 [4-(3-hyroxypropyl) -3-methyl-1H-1,2,4-triazole-5 (4H) -one] and compound-2 [ethyl 2- (4- (3 -hydroxypropyl) -3-methyl-5-oxo-4,5-dihdyro-1H-1,2,4-triazol-1-yl) acetate] was obtained using the methods described in [114-116]. A drop of concentrated sulfuric acid was added as the catalyst to a mixture of 0.01 mol of compound-2, 0.02 mol of alcohol (ethanol, h-butanol, and 1-octanol) and 0.01 mol of boric acid. The mixture was refluxed at 140-160 °C for 4-6 h. After the mixture was cooled, pure ethanol was added to the mixture. Then, the alcohol was removed from the mixture by evaporation. As a result, a new boron-containing adhesive compound-3 additive was obtained. The common name of compound-3 was "ethyl2- (4- (3- ((dialcoxboranyl) oxy) propyl) -3-methyl-5-oxo-4,5-dihydro-1H-1,2,4-triazole- 1 -il) acetate". Compound-3 type additives were obtained because of the reaction with various chain lengths between compound-2 and the alcohols [R-OH]. The R-OH groups were R: a ($H_3CH_2C$-), b ($H_3CH_2CH_2C$-), c ($H_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2C$-), and d ($H_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2C$- ($H_2SO_4$ catalyser)). As a result of the chemical reaction between compound-2 shown in "a" instead of R and ethyl ($H_3CH_2C$- containing two carbons), the resulting compound was called triazole borate ester ethanol (TBEE). As a result of the chemical reaction between compound-2 shown in "b" rather than R and butyl ($H_3CH_2CH_2CH_2C$- containing four carbons), the resulting compound was called triazole borate ester butanol (TBEB). The resulting compound from the chemical reaction between compound-2 and octyl ($H_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2C_2$, containing eight carbons) shown in "c" instead of R, was called triazole borate ester octanol (TBEO). As a result of the chemical reaction between compound-2 and octyl ($H_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2C$- containing eight carbons) shown in "d" instead of R in the sulfuric acid catalyst, the given compound was called the triazole borate ester octanol-sulfuric acid (TBEOSA) additive. The modification process was carried out by adding four different modified bitumens containing boron in a ratio of 1 % of their weight to the bitumen.

Oruc et al. [117] synthesised an asphalt modifier from three different components, such as ethyl- (E) -2-(1-ethoxyethylidene) hydrazine-1-carboxylate, 2) 4-(3-bromopropyl) -5-methyl-2,4-dihydro-3H-1,2,4-triazole-3 -one and 3) 4- (3-hydroxypropyl) -5-methyl-2,4-dihydro-3H-1,2,4-triazole-3-one, using the methods previously described in [12-15]. A drop of concentrated sulfuric acid was added to a mixture of compound-3, boric acid, and 1,2-dihydroxypropane. Then, the mixture was refluxed for 18 h at 300 °C. The systematic name of the cyclicborate ester (CBE) component formed was 5-methyl-4- (3 - ((4-methyl-1,3,2-dioxaborolan-2-yl) oxy) propyl) -2,4-dihydro-3H -1,2,4-triazol-3-one. The modification was carried out by adding CBE in a ratio of 1 % of its weight to the bitumen.

## 2.3. Succinimide additives

Succinimides with the formula (CH2) 2 (CO) 2NH, are white, solid, and organic compounds. They are used in various organic syntheses, industrial silver-plating processes, and in pharmaceutical industry. Succinimides are also used to form covalent bonds between proteins or peptides and plastics, which is useful in different assay techniques [118].

Kumar et al. [119] synthesised three different asphalt modifiers, such as DDSA-TETA, DDSA-TEPA, and DDSA-PEHA, with high polarity from the succinimide compound. The modifiers were synthesised by a simple reflux reaction between dodecenylsuccinic anhydride (DDSA) and triethylenetramine (TETA), and tetraethylenepentiamine (TEPA) and pentaethylamine (PEPA), respectively. For the DDSA-TETA asphalt modifier, 5.33 g (20 mmol) of DDSA and 2.92 g (20 mmol) of TETA were blended in a 250 mL three-bare round bottle with 50 mL of toluene. The content was heated with stirring at 130 °C for 6 h. All treatments were carried out in a nitrogen atmosphere to prevent the decomposition of the reactants. Finally, the mixture was cooled. Then, the toluene was removed using a rota-evaporator. The additive was left to dry in an oven at 100 °C overnight. As a result, DDSA-TETA, a semi solid brown coloured compound, was obtained. Similarly, TEPA (3.79 g) and PEPA (4.65 g) were used in the place of TETA to obtain DDSA-TEPA and DDSA-PEHA, respectively. The efficiencies of the three modifiers were 7.50 g for DDSA-TETA, 8.14 g for DDSA-TEPA, and 9.04 g for DDSA-PEHA. The modification was carried out by adding additive concentrations to the bitumen at 1.5-6.0 % by weight.

## 2.4. Waste-based additives

Recycling enables wastes to be used in various production processes as raw materials, reducing the amount of waste and unnecessary use of resources. Waste materials used in various sectors are chemically synthesised and used as asphalt modifiers.

Padhan et al. [120] synthesised two different modifiers through chemical conversion from PET waste to increase the slip resistance of asphalt. The waste PET polymers were cleaned, cut into small pieces, and dried at an ambient temperature. The test apparatus consisted of a three-necked 500 mL round-bottom flask equipped with a heating mantle, overhead stirrer, water condenser, nitrogen gas sparging tube, and thermo wellpocket containing a thermometer. Moreover, 30 g PET, 100 mL xylene, and 60 g polyamine (PET-A for tetraethylenepentamine and PET-B for triethylenetetramines) were separately added to the three-necked flask. A current of dry nitrogen was constantly maintained and the mixture was heated at 130-140 °C to reflux. After 8 h, the solution turned homogeneous and the polyaminesfany and glycols that did not go into reaction were recovered under vacuum when the PET decomposition was finalized. The resulting product was a semi-viscous liquid at ambient temperature. The modification was carried out by adding PET-A and PET-B additives at a rate of 0.5 % by weight to the bitumen.

Parvez et al. [121] obtained a new asphalt modifier by binding essential oil ash (OFA) to the carboxylic group under laboratory conditions. OFA is a black powder-type waste material that results from the use of crude and residual oil in power generation. First, the OFA was washed to remove the oil and sand. Then, it was dried at 105 °C to evaporate the water on it. $H_2SO_4$ and $HNO_3$ solutions were prepared at a ratio of 3:1 to OFA. An ash sample of 200 g was placed in the oven, and the solution was slowly poured onto it. The acid ash mixture turned into a liquid solution, which was then placed in a magnetic stirrer assembly containing the OFA/acid solution. The reaction continued for 12 h at a rate of 1000 rpm at 165 °C. The mixture diluted with deionized water was filtered through a vacuum filter to distinguish the unreacted substances. The filtered mixture was dried at 90 °C. As a result, an OFA-COOH modifier was obtained. The modification was carried out by adding the OFA-COOH additive at a rate of 4 % by weight to bitumen.

Guru et al. [122] synthesised a new asphalt modifier consisting of sugar beet molasses and boron oxide under laboratory conditions. Sugar beet molasses are organic wastes obtained from raw sugar during the refining process and are thick, dark brown in colour with a sugar content of approximately 50 %. The test apparatus consisted of a spherical three-necked flask, reactor, reflux condenser, and heating mantle with a magnetic stirrer. The ratio of the molasses to boron oxide used in the reaction was 5.2:1. In the reaction, the molasses first reacted with the sulfuric acid catalyst, and then boron oxide was added to the mixture. The mixture was mixed in a magnetic stirrer for 20 min at 90 °C, and water vapor was observed during the reaction. At the end of the reaction, a plastic, dense, and paste-like molasses-based boron oxide (MBOC) was obtained. The modification was carried out by adding the MBOC additive between 1-10 % by weight to the bitumen.

Padhan et al. [123] produced a new asphalt modifier from waste PET. The setup and test process of the new additive was the same as those used in the other modifiers, such as PET-A and PET-B. Moreover, 50 g of waste PET flakes and 100 g of ethanol amine chemicals were subjected to aminolysis reaction for 8 h in a magnetic stirrer heater. As the flakes completely disappeared, the mixtures became homogeneous. The product was filtered, and a white crystalline powder called BHETA was obtained. Then, 97 % bitumen, 1 % MDI, and 2 % BHETA additives were heated and mixed for 2 h and the BHETA-based polyurethane modifier was obtained.

Leng [124] synthesised an asphalt modifier to be used together with reclaimed asphalt pavement by aminolysis method from waste PET bottles in the laboratory. Waste plastic bottles were collected and their labels removed and cleaned using the solution. The cleaned PET bottles were dried and cut into small pieces of approximately 5 mm and dried at 80 °C for 4 h. The test apparatuses consisted of a three-necked 500 mL round-bottom flask equipped with a heating mantle, overhead stirrer, water condenser, nitrogen gas sparging tube, and thermo wellpocket containing a thermometer. The bottle was filled with 30 g of PET and extra triethylenetetramine (TETA) in the presence of nitrogen gas. The mixture was heated to reflux for 2 h at 130 °C and 140 °C. The mixture became homogenous when the PET breakdown was finished. After the reaction was complete, the polyamines and glycols were recovered under vacuum. The final product is a residue that can be quantitatively recovered at ambient temperatures. The modification was carried out with the PET waste residue at a ratio of 2 % to the bitumen weight. Then, 2 % PET modified binder was mixed with 15 %, 25 %, and 40 % RAP

**Table 1. Conventional physical properties of base asphalts**

| Svojstvo | Martinez et al. [103] | Arslan et al. [110] | Cubuk et al. [106] | Oruc et al. [113] | Guru et al. [122] | Calisici et al. [112] |
|---|---|---|---|---|---|---|
| Penetration (0.1 mm) | 65 | 62 | 62 | 57 | 67 | 51 |
| Viscosity [Pa·s] | 0.41 | 0.316 | 0.280 | 0.413 | 0.261 | 0.316 |
| Softening point [°C] | 50 | 48.4 | 49.2 | 50 | 49 | 47.5 |
| Ductility [mm] | - | 63.5 | - | 100+ | 100+ | - |
| Binder type | 60-70 | 50-70 | 50-70 | 50-70 | 50-70 | 50-70 |

**Table 2. Recommended mixing temperature, duration, and speed**

| Studies | Additives | Temperature [°C] | Duration [min] | Speed [revolutions/min] |
|---|---|---|---|---|
| Arslan et al. (2011) | TEGPB | 110 | 5 | 1300 |
| Arslan et al. (2012) | OBBC<br>OBBAC | 140 | 10 | 1300 |
| Cubuk et al. (2013) | Organic-based magnesium compound | 110 | 20 | First 400 revolutions/min and then, 1300 revolutions/min |
| Arslan et al. (2013) | OBMAGC<br>OBMANC<br>OBZC | 140 | 10 | 1300 |
| Arslan et al. (2014) | MEGPC<br>DEGPC | 110 | 5 | 1300 |
| Oruc et al. (2016) | Four boron-containing additives | 150 | 15 | 800 |
| Oruc i Yilmaz (2016) | CBE | 150 | 15 | 1000 |
| Guru et al. (2017) | MBOC | 120 | 15 | 1300 |
| Kumar et al. (2018) | DDSA-TETA<br>DDSA-TEPA<br>DDSA-PEHA | 140 | 60 | - |

binders. Padhan [125] adopted the aminolysis process applied to PET wastes in previous studies and obtained asphalt modifier in laboratory conditions. As a result of the chemical process, a substance called bis (2-hydroxy ethylene) terephthalamide was obtained.

### 2.5. Asphalt

In most studies, only one type of asphalt was used. Oruc et al. [119] and Guru et al. [122] utilised 50/70 penetration grade bitumen to analyse the property changes of the modified asphalt, while Padhan et al. [120] selected PG 58-19 as the control asphalt binder. The conventional physical properties of original asphalts are listed in Table 1.

In their study, Martinez et al. [103] employed two different sources of asphalt binders, including B 60/70 and B 80/100. In general, it was observed that most of the studies used B 50/70 class bitumen [105, 106, 110].

## 3. Mixing procedures of the new additives used to modify asphalt

Asphalt is a temperature-sensitive material in which higher temperatures accelerate its aging rate, leading to the deterioration of the durability of the asphalt binder**.** The temperature during the preparation of asphalt should not be considerably high. Thus, balancing the temperature of producing uniformly dispersed nano-modified composites and reducing the aging degree of virgin asphalt is an important issue that must be addressed [100].

In terms of the mixing time, a long duration is required to ensure that the additives are homogeneously dispersed in the asphalt. However, a longer mixing time can also lead to higher energy consumption and waste. An optimal mixing speed is required to ensure an adequate distribution of the synthesised additives. However, exceeding the high speed can destroy the structure of the synthesised additives. Table 2 summarises the temperature,

time, and speed that were used to produce modified asphalt with synthesised additives in various studies.
Table 2 shows the temperature, duration, and speed utilized by various researchers to ensure the uniform diffusion of the synthesised materials. From the table, it is seen that the mixing conditions used to produce different types of additives for the modification of asphalt significantly vary. The temperatures varied from 110 °C to 150 °C, with 140 °C as the most common temperature. A total of 5 min was used to mix the triethylene glycol-based polyboron compound (TEGBPC) with asphalt [110].

## 4. Techniques used in synthesised additives to modify asphalt and determine mix performance

Asphalt is widely used as a binder in pavement engineering. However, asphalt is also a viscoelastic material and its temperature sensitivity and fatigue resistance must be improved. Additionally, it is a combined material containing aggregate, asphalt binder, and air voids. HMA mixtures, which affect the strength, durability, stiffness, rutting, fatigue life, and moisture damage properties, have been widely utilised in road pavements. The addition of synthesised additives to asphalt mentioned in Section 2 greatly affects its binding properties. Penetration, softening point, and ductility tests are used as traditional tests to determine the base properties of binders. Additionally, rheological tests, including viscosity, rutting, and crack resistance parameter tests, are applied to predict the performance of asphalt binders.

### 4.1. Conventional tests

Penetration test experimentally determines the consistency of asphalt. It is defined as the depth at which the needle penetrates the asphalt sample of 100 g at 25 °C for 5 s (ASTM D5) [126]. A high penetration value indicates that the bituminous binder is soft and less viscous. The conventional test aims to determine the hardness and consistency of the bituminous material [117]. The softening point test experimentally measures the susceptibility of the asphalt to temperature and the temperature at which the asphalt starts to flow. For this experiment, steel balls (3.5 g/unit) are put into the asphalt sample placed in a standard ring. Then, these samples are heated in a water bath at 5 °C/min. The softening point is the recorded temperature at which the balls touch the basement plaque covering the rings (ASTM D36) [127]. Ductility is defined as the length (in cm unit') that a standard briquette can be pulled from asphalt cement without breaking at a specified temperature and acceleration. The bonding capability of asphalt is dependent on its ductility. A highly ductile asphalt is extremely useful [117]. Ductility is determined by filling the ductility device with water at a certain temperature and horizontally pulling the asphalt sample at an acceleration of 5 cm/min (ASTM D113) [128]. The Nicholson stripping test, which is a static, visual assessment method applied to uncompacted asphalt mixtures, is performed as per ASTM D1664 [129]. The stripping resistance of each mixture is visually determined and recorded as the ratio of non-stripped aggregate surface area to the total aggregate surface area and gives an indication regarding the adhesion force at the asphalt-aggregate interface [107].

### 4.2. Superpave tests

A Brookfield rotational viscometer (RV) can be used to determine the viscosity of the binder between 90 °C and 180 °C (ASTM D 4402) [130]. A cylindrical spindle (no.29) is immersed in the asphalt sample and rotated at a constant speed at testing temperature. The torque required for the rotation of the spindle is measured and converted to viscosity in Pa.s by the rheometer. Two samples are tested and if the difference between the two exceeds 2 %, a third test is conducted. The rolling thin film oven test (RTFOT) is used to characterise the aging of bitumen during the manufacturing process. For the test, each bottle is filled with 35 g of bituminous binder and rotated for 75 min along the vertical axis at 15 revolutions per min. During the rotation, air is supplied to the bottles with the help of an air blower located at the bottom of the test device at a flow of 4000 ± 200 mL/min (ASTM D 2872) [131]. The evaluation of aging characteristics is carried out by penetration, softening point, ductility, and dynamic shear rheometer (DSR) tests. To determine long-term aging features, a pressure aging vessel (PAV) test is performed on the samples that are obtained through the RTFOT experiment. The PAV test is carried out at 100 °C under a pressure of 2.1 MPa for 20 h (ASTM D6521) [132]. After this process, the samples are prepared for DSR and bending beam rheometer (BBR) tests. The DSR test is performed at 22 °C, 25 °C, and 28 °C to determine fatigue resistance ($G^{*}.\sin\delta$). In the DSR experiment, the gap between 8-mm-diameter parallel plates is set at 2 mm. The DSR test can be used to measure both the viscosity and elasticity of asphalt binders at intermediate to high temperatures based on the complex shear modulus ($G^{*}$) and phase angle ($\delta$) (AASHTO T 315) [133]. Unaged and RTFO-aged binders are tested with a 25-mm-diameter plate at a 1000 μm gap. Moreover, PAV-aged binders are tested with an 8-mm-diameter plate at a 2000 μm gap. The DSR test represents the resistance of the asphalt binder to permanent deformation and fatigue cracking. The BBR test can be used to plot the creep stiffness of asphalt binders versus the loading time. The results of the test show the relationship between temperature and asphalt binders and indicate the stress relaxation when a constant load (0.98 kN) is applied on the asphalt beam (AASHTO TP1) [134].

### 4.3. Marshall test

The Marshall test is an empirical test in which compacted asphalt specimens with a diameter of 100 mm and a height of 63.5 mm are immersed in water at 60 °C for 30-40 min. Then, they are loaded using curved steel loading plates at a constant compression rate of 51 mm/min till they break (ASTM 1559) [135].

### 4.4. Advanced test

In both civil and pavement engineering, effective macro-scale techniques are employed to characterise the materials. However, there are still many problems related to the usage of macro-scale techniques that are not clearly understood and are yet to be solved [100].
There are many techniques for determining the structural characterisation of both asphalt and modified binders. The most common of these are Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM).

#### 4.4.1. Fourier transform infrared spectroscopy

FT-IR is a technique that can analyse samples qualitatively and quantitatively. Thus, it is widely used in industries, such as medicine, chemistry, mining, oil, coal, customs, gemstone, and forensic identification. The bonding characteristics of the tested materials can be obtained according to the main bands of the FT-IR spectra [100].

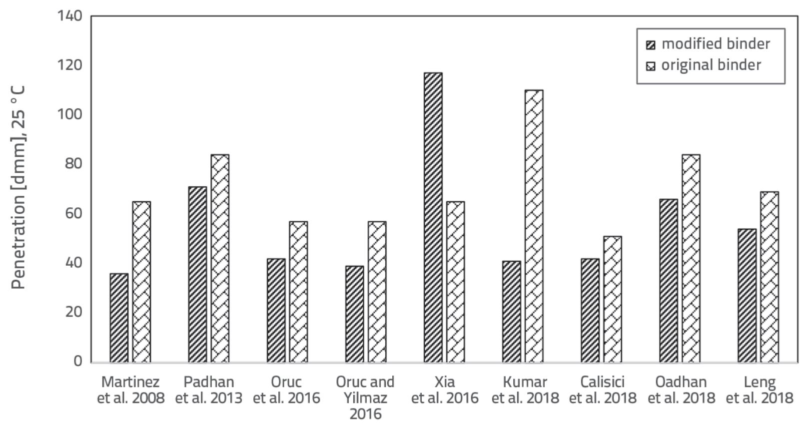


**Figure 1. Penetration values of the modified asphalt binders**

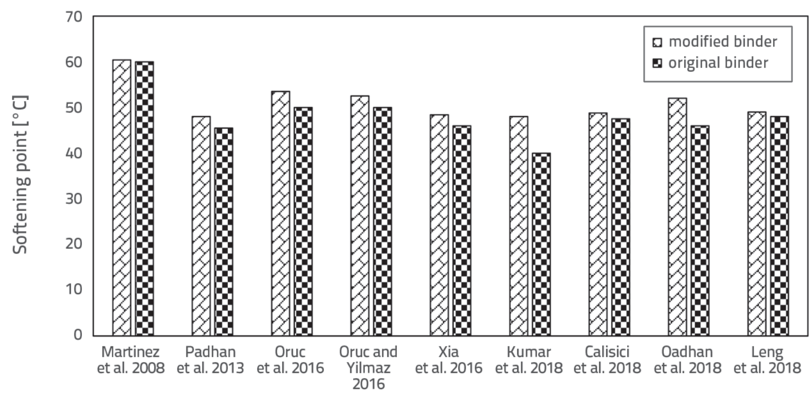


**Figure 2. Softening point of the modified asphalt binders**

#### 4.4.2. Scanning electron microscopy

Electron microscopy is the bombardment of electron on a sample and capturing of the reflected electrons or radiated electrons out of the sample. The morphologies of original binders, modified asphalt binders, and modified asphalt mixtures can be observed from SEM images. Therefore, SEM can help understand the microstructure of composites and the failure mechanism of asphalt materials [100].

## 5. Performance properties

### 5.1. Asphalt performance

#### 5.1.1 Effect of synthesised additives on the physical properties of asphalt

The physical properties of the new additive-modified binders and the base asphalt are shown in Figures 1 and 2, respectively. A 63 % decrease in the penetration value is observed compared to the original binder in the study conducted by Kumar et al. [119].
According to Figure 2, studies reported an increase in softening point compared to that of the original binder. The highest increase (20 %) in the softening point was determined in the study by Kumar et al. [119]. In addition, the change in the softening point was found to be below 1 % in the study conducted by Martinez et al. [103] .

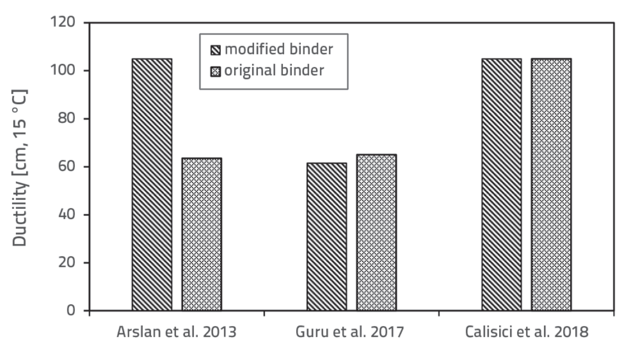


**Figure 3. Ductility test results of the modified binders**

Figure 3 presents the ductility test results for the new synthesised additive-modified binders and original binder.

The ductility test was carried out at 15°C in few studies [107, 112, 122]. In the study by Guru et al. [122], the elongation of the modified bitumen decreased by 6 % compared to the original bitumen. In addition, another study [112] reported no change in the amount of elongation.

The Nicholson stripping test is designed to evaluate the effects of additives on the stripping resistance of asphalt mixtures. Stripping occurs because of the loss of adhesion at the bitumen-aggregate interface due to moisture [136]. Figure 4 shows the Nicholson stripping test results of the original asphalt and 3 % OBMAGC modified asphalt. The adhesive bond between bitumen and aggregate strengthened and stripping resistance significantly improved with the usage of novel additives such as OBCC, MEGPC, OBMAGC, and PET residues [124].

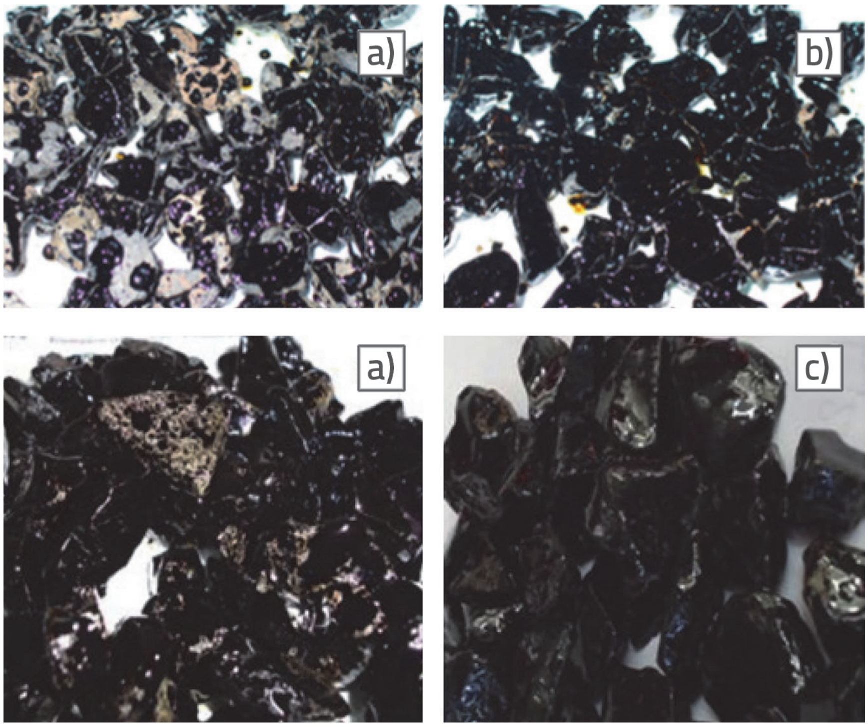


**Figure 4. Nicholson stripping test results for: a) original asphalt; b) modified asphalt with 3 % (w/w) OBMAGC; c) modified asphalt with 2 % (w/w) PET residue**

### 5.1.2. Effects of the new additives on the viscosity of asphalt

The rotational viscometer test is carried out to determine the workability of asphalt binders during pumping and mixing. An increase in viscosity indicates an increase in the resistance against rutting [137]. Moreover, the viscosity value at 135°C should not exceed 3000 cP to maintain the workability at an appropriate level.

Guru et al. [122] determined that the viscosity of original asphalt increased when the concentration of MBOC was increased at all temperatures, indicating that the addition of MBOC makes bitumen stiffer. A previous study [105] reported that the mixing temperature could be decreased up to 4.7°C and 11.4°C using OBCC and OBBAC, respectively. Similarly, Arslan et al. [110] reported that TEGPB addition increased the viscosity of the original bitumen at all temperatures, implying better rutting resistance of the modified bitumen. In their study, the viscosity increments by TEGPB addition varied from 0.4 % to 24.3 %.

### 5.1.3. Rutting and fatigue resistance

$G^*/\sin\delta$ is defined as the rutting factor of the asphalt binder in the Superpave asphalt binder specification. A high $G^*/\sin\delta$ value indicates a strong rutting performance of the modified asphalt binder at high temperatures. Figure 5 shows the $G^*$ values of the different synthesised additives. There is a considerably small change in $G^*$ value compared to the original asphalt binder modified with 2 % DEGPC [112]. Another study [117] found that the CBE-modified asphalt binder had a substantial change in the complex shear modulus compared to the original asphalt.

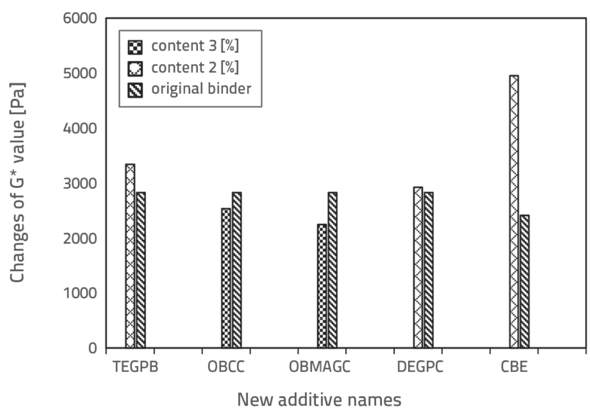


**Figure 5. $G^*$ values of the synthesised additives**

It can be concluded from figure 6 that changes similar to the observations from figure 5 were reported in the rutting factor by Cubuk [112] and Guru et al. [122]. In addition, Oruc and Yilmaz [117] achieved the most significant results in terms of the rutting factor.

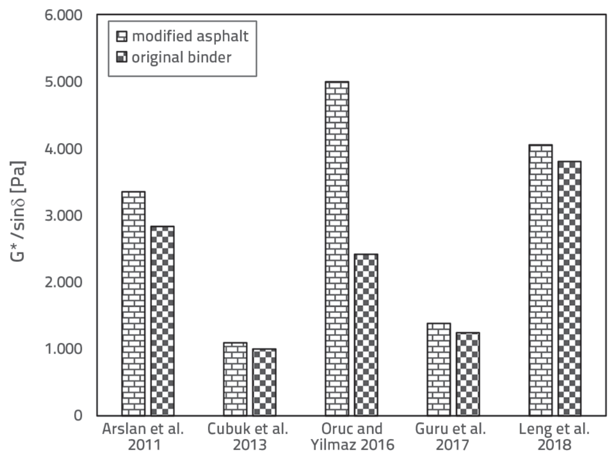


**Figure 6. G*/sinδ of the modified binders**

### 5.1.4. Low temperature crack resistance

The creep rate (m) and creep stiffness (S) values are shown in Figures 7 and 8, respectively. According to the Superpave specification, creep stiffness values must not be more than 300 MPa. This is because, when the value is higher, the binder exhibits brittle behaviour, and more cracking occurs at low temperatures. Additionally, the creep rate must be a minimum of 0.300 and a high m-value indicates a decreased stiffness [117].

In Figure 7, the creep rates increased in the binders modified with the new synthesised additives. The highest increase was reported by Arslan et al. [107]. From figure 8, the creep stiffness closest to that of the original asphalt was obtained by Arslan et al. [111] and Oruc [117]. The reported stiffness values were below 300 MPa and within the specification limits.

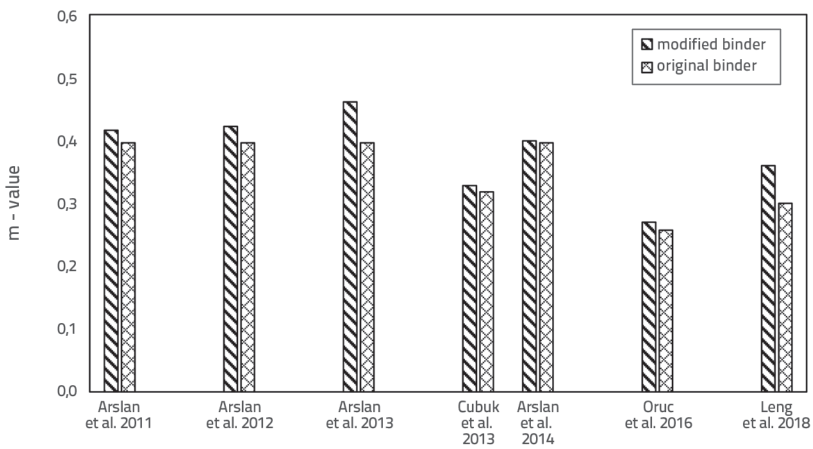


**Figure 7. m-values of the modified binders**

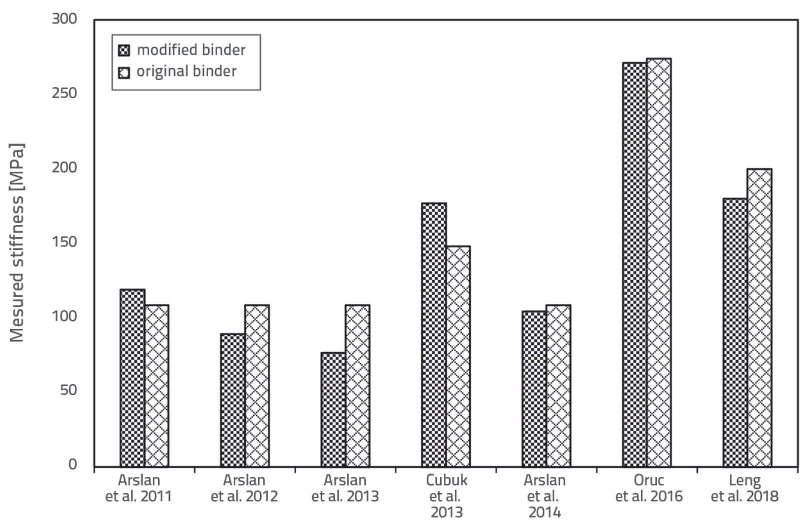


**Figure 8. S values of the modified binders**

## 5.2. Asphalt mixture performance

The effects of novel additives on the mechanical properties of asphalt mixtures can be detected through Marshall tests. Marshall stability is the measure of resistance of asphalt mixtures against permanent deformations, such as rutting, collapsing, and ondulation. Low stability can cause the occurrence of such issues and vice versa for high stability. However, high stability can decrease the flexibility of pavements, resulting in cracks.

It has been confirmed that asphalt mixtures modified with synthesised additives (OBBC, OBBAC, OBMAGC, MEGPC, and DEPGC) have better potential to resist permanent deformation and exhibit an enhancement of high-temperature performance [105-106, 111-112]. Table 3 summarises the Marshall stability test results and it is seen that the modified mixtures exhibited higher stability values. In addition, there was a decrease in the voids in the mineral aggregate (VMA) values compared to the original mixture. Calisici et al. [112] reported a 28 % decrease in the VMA value.

## 5.3. Chemical characterisation of synthesised additives

A study of the structure of synthesised additives requires the use of various advanced analytical techniques to explore the chemical composition and modification mechanisms of the additives. The SEM and FT-IR techniques provide detailed information regarding the changes in the modified asphalt.

**Table 3. Marshall test results of the original and modified mixtures**

| Studies | Stability -modified mixture [kN] | VMA - modified mixture [%] | Stability -original mixture [kN] | VMA - original mixture [%] |
|---|---|---|---|---|
| Arslan et al. (2012) | 866.89 | 13.84 | 815.35 | 14.34 |
| Arslan et al. (2013) | 793.59 | 14.13 | 762.73 | 14.27 |
| Arslan et al. (2014) | 985.4 | 13.90 | 908.30 | 14.17 |
| Calisici et al. (2018) | 1000 | 10.15 | 900 | 14.15 |

### 5.3.1. FT-IR analysis

FT-IR analyses provide information regarding the presence of new functional groups and changes in the bonds of chemically synthesised additives [138]. When the FT-IR spectrum of the PET-A additive was observed, an ester peak disappeared at 1735 cm$^{-1}$, and amide peaks were found at 1637 and 1547 cm$^{-1}$ for TEPA. Similarly, peaks of 1637 and 1544 cm$^{-1}$ were observed for the TETA amide in the PET-B additive [120]. Parvez et al. [121] bound a carboxyl group to the OFA waste and conducted a FT-IR analysis over the peaks of the carboxylic acid. They reported a C=O band at 1742.37 cm$^{-1}$, a C-C band at 1261.9 cm$^{-1}$, and an O-H functional group band at 1365.4 cm$^{-1}$.
Oruc et al. [117] observed C-H spectral band peaks at 2920 and 2851 cm$^{-1}$ for triazole borate ester (TBEO$_{SA}$) additives. The C=O spectral band caused by triazole rings was observed at a peak of 1740 cm$^{-1}$ and the B-O strain band was observed at a peak of 1163 cm$^{-1}$.
Kumar et al. [119] investigated the peak values of carbon and nitrogen bonds for asphalt modifiers containing succinimide and determined a strong N-H band at the peak of 1140 cm$^{-1}$ and a C-N band at 3290 cm$^{-1}$.
Calisici et al. [112] used FT-IR to investigate the oxidation of aged asphalt with modified asphalt aged under laboratory conditions. The carbonyl and sulphoxide regions of the 2 % DEGPB asphalt aged in the laboratory and aged asphalt were compared. They determined that the original aged asphalt had a more increased sulphoxide zone compared to the DEGPB aged asphalt. The same result was obtained in the carbonyl group. The DEGPB asphalt modifier increased the aging resistance.

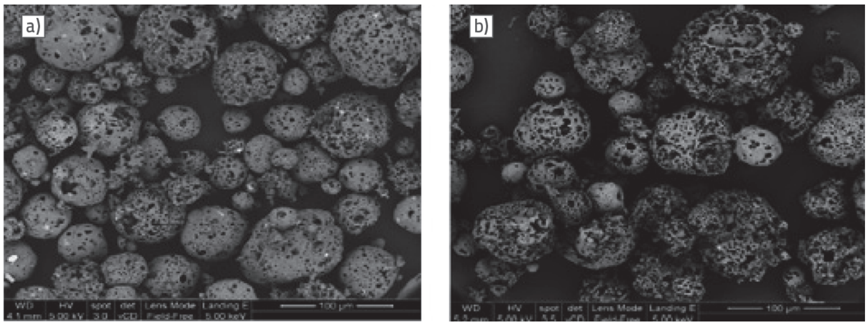

Figure 9. SEM/EDS analysis of the OFA samples [121]

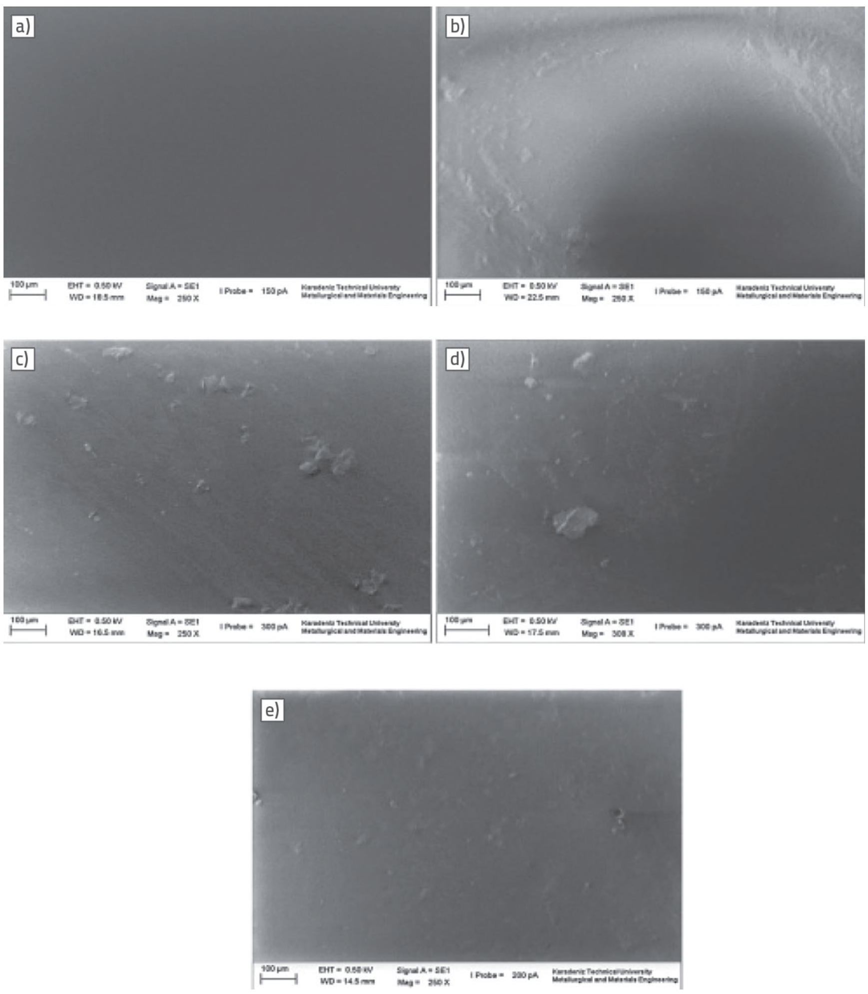

Figure 10. SEM of the: a) base asphalt; b) 1 % TBEE; c) 1 % TBEB; d) 1 % TBEO; e) 1 % TBEO$_{SA}$, according [117]

#### 5.3.2. SEM analysis

The microstructure of original binders, synthesised asphalt modifiers, and modified asphalt can be obtained from SEM images. In the study by Parvez et al. [121], the proportions of the substances in the additive were investigated using both SEM and EDS techniques. The amount of oxygen was examined before and after the carboxylated group was attached. The oxygen/carbon ratio provides the oxygen content. They obtained an oxygen/carbon ratio of 0.087 that increased to 0.283 after synthesis. Figure 9 shows the SEM images before and after the synthesis.

Oruc et al. [117] utilised SEM images to understand the distribution of four new asphalt modifiers containing boron. Figure 10 shows the comparative images of the modified asphalt and the pure asphalt. The SEM micrographs of the 1 % TBEB/asphalt blend and the 1 % TBEO/asphalt blend were observed as two separate phases. In the 1 % TBEE/asphalt blend, there was a distant bond between the additive and asphalt. On the other hand, the 1 % $TBEO_{SA}$/asphalt blend had a better distribution.

## 6. Conclusions

Various factors, including the type and amount of additives, the synthesis process of the additive, and the technique of synthesis, influence the properties of the modified asphalt binder. This study focused on the formation processes of the synthesised additives, the amounts of the additives, and their rheological changes on the binder.

- The synthesised additives were classified into organic-based additives, boron-containing additives, succinimide additives, and waste-based additives. In general, modifiers based on the principle of forming a new substance accompanied by the catalyst of two different substances were added to the binders at different temperatures and mixing speeds. Synthesised additives do not require long-lasting modifications in high shear mixers similar to polymer additives. It was found that the synthesised additives could save both time and energy with the modifications made to standard mixers in a short time.
- It was observed that the binder hardened and the softening point increased when the synthesized additives were used as a modifier in the binder. This is an indication that most synthesised additives can reduce the temperature sensitivity of binders and give better rutting resistance with stiffness.
- The fragility and cracking potential of low temperatures were predicted to increase with the hardening of the binder. However, this was not the case with the synthesised additives. Low temperature cracking resistance did not decrease significantly in the modified asphalt.
- Asphalt mixtures made with synthesised additives can increase the performance in terms of stability.
- Information regarding the change in the peak values and the chemical location of the additive can be obtained using FT-IR technology, which shows the chemical structure of the synthesized substances; thus, proving that the modifiers had formed. SEM was insufficient in showing the distribution of synthesised additives in the binder. It is recommended to use advanced technological evaluation systems.

## REFERENCES


[1] Yildirim, Y.: Polymer Modified Asphalt Binders, Construction and Building Materials, 21 (2007), pp. 66-72.

[2] Collins, J.H., Bouldin, M.G., Gelles, R., Berker, A.: Improved Performance of Paving Asphalts and Polymer Modification, in Proceeding of the Association of Asphalt Paving Technologists, 60 (1991), pp. 43-79.

[3] Vonk, W.C., Van Gooswilligen, G.: Shell Laboratorium: Amsterdam, 8 (1991) 1.

[4] Aglan, H.: Poylmeric Additives and Their Role in Asphaltic Pavements Effect of Additive Type on the Fracture and Fatigue Behavior, Journal of Elastomers and Plastics, 25 (1993) 4, pp. 307-321.

[5] Airey, D.G.: Rheological Properties of Styrene Butadien Styrene Polymer Modified Road Bitumens, Fuel, 82 (2003), pp. 1709-1719.

[6] Weizhen, S., Peng, Y., Kaifu, H., Kejian, L., Daosheng, L., Feng, Y., Yi, W.: The Study of Producing SBS Modified Asphalt by Using Liaoshu High Viscous Crude Oil, Petroleum Science and Technology, 19 (2001) 9-10, pp. 1187–1196.

[7] Cortizo, S.M., Larsen, O.D., Bianchetto, H., Alessandrini, L.J.: Effect of The Thermal Degradation of SBS Copolymers During the Ageing of Modified Asphalts, Polymer Degradation and Stability, 86 (2004), pp. 275-282.

[8] Chen, J.S., Liao, M.C., Shiah, M.S.: Asphalt Modified by Styrene-Butadiene-Styrene Triblock Copolymer: Morphology and Model, Journal of Materials in Civil Engineering, 14(2002) 3, pp. 224-229.

[9] Şengul, E.C., Oruç, S., İskender, E., Aksoy, A.: Evaluation of SBS Modified Stone Mastic Asphalt Pavement Performance, Construction and Building Materials, 41 (2013), pp. 777–783.

[10] Zhao, X., Wang, S., Wang, Q, Yao, H.: Rheological and Structural Evolution of SBS Modified Asphalts Under Natural Weathering, Fuel, 184 (2016), pp. 242-247.

[11] Şengöz, B., Işıkyakar, G.: Evaluation of Properties and Microstructure of SBS and EVA Polymer Modified Bitumen, Costruction and Building Materials, 22 (2008), pp. 1897-1905.

[12] Isacsson, U., Lu, X.: Characterization of Bitumens Modified with SEBS, EVA and EBA Polymers, Journal of Materials Science, 34 (1999), . and 3737–3745.

[13] Panda, M., Mazumdar, M.: Engineering Properties of EVA-Modified Bitumen Binder For Paving Mixes, Journal of Materials in Civil Engineering, 11 (1999), pp. 131-137.

[14] Haddadi, S., Ghorbel, E, Laradi, N.: Effects of Manufacturing Process on the Performances of the Bituminous Binders Modified With EVA, Construction and Building Materials, 22 (2008), pp. 1212-1219

[15] Huseyin, A.I., Iqbal, H.M.: Al-Abdul-Wahhab, I. H., Influenceof Mw of LDPE and Vinyl Acetate Content of EVA on The Rheology of Polymer Modified Asphalt, Rheologica Acta, 45 (2005), pp. 92–104.

[16] Lu, X., Isacsson, U.: Artificial Aging of Polymer Modified Bitumens, Journal of Applied Polymer Science, 76 (2000), 12, pp. 1811-1824.

[17] Ameri, M., Mansourian, A., Sheikhmotevali, H.A.: Laboratory Evaluation of Ethylene Vinyl Acetate Modified Bitumens and Mixtures Based upon Performance Related Parameters, Construction and Building Materials, 40 (2013), pp. 438–447.

[18] Gonzalez, O., Munaz, M.E., Santamaria, A., Garcia-Morales, M., Navarra, F.J., Portal, P.: Rheology and Stability of Bitumen EVA Blends, European Polymer Journal, 40 (2004) 10, pp. 2365-2372.

[19] Liang, M., Ren, S., Fan, W., Xin, X., Shi, J, Lou, H.: Rheological Property and Stability of Polymer Modified Asphalt: Effect of Various Vinyl-Acetate Structures in EVA Copolymers, Construction adn Building Materials, 137 (2017), pp. 367-380.

[20] Brovelli, C., Hilliou, L., Hemar, Y., Pais, J., Percira, P, Crispino, M.: Rheological Characteristics of EVA Modified Bitumen and Their Correlations with Bitumen Concrete Properties, Construction and Building Materials, 48 (2013), pp. 1202-1208.

[21] Luo, W., Chen, J.: Preperation and Properties of Bitumen Modified by EVA Graft Copolymer, Construction and Building Materials, 25 (2011), pp. 1830-1835.

[22] Yılmaz, M., Kök, B.V., Alatas, T., ve Kuloğlu, N.: Determination of Strength of Mixtures Prepared with Pure and Modified Bitumen Against Permanent Deformations, 6th National Asphalt Symposium, November 2013, Ankara, pp. 32-39.

[23] Zhang, F., Yu, J.: The Research For High-Performance SBR Compound Modified Asphalt, Construction and Building Materials, 24 (2010) 3, pp. 410-418.

[24] Liang, P., Liang, M., Fan, W., Zhang, Y., Qian, C, Ren, S.: Improving Thermo-Rheological Behavior and Compatibility of SBR Modified Asphalt by Addition of Poylphosphoric Acid (PPA), Construction and Building Materials, 139 (2017), pp. 183-192.

[25] Zhang, F., Hu, C.: The Research for SBS and SBR Compound Modified Asphalt with Poylphosphoric Acid and Sulfur, Construction and Building Materials, 43 (2013), pp. 461-468.

[26] Jun, L., Yuxia, Z., Yuzhen, Z.: The research of GMA-g-LDPE Qinhuangdao Bitumen, Contruction and Building Materials, 22 (2008), pp. 1067-1073.

[27] Ho, S., Church, R., Klassen, K., Law, B., MacLeod, D., Zanzotto, L.: Study of Recycled Polyethylene Materials as Asphalt Modifiers, Canadian Journal of Civil Engineering, 33 (2006) 8, pp. 968-981.

[28] Othman, A.M.: Effect of Low-Density Polyethylene on Fracture Toughness of Asphalt Concrete Mixtures, Journal of Materials in Civil Engineering, 22 (2010) 10, pp. 1019-1024.

[29] Hinislioglu, S.: An Investigation on the Marshall and Resilient Characteristics of Asphalt Concrete with Bituminous Binder Modified with High Density Poylethylene, Istanbul Technical University, Doctorate Thesis, Institute of Science and Technology, Istanbul, 1998.

[30] Newman, J.K.J.: Dynamic Shear Rheological Properties of Polymer-Modified Asphalt Binder, Journal of Elastomers and Plastics, 30 (1998), pp. 245-263.

[31] Fawcett, A.H., McNally, T., McNally, G. M., Andrews, F., Clarke, J.: Blends of Bitumen with Polyethylenes, Polymer, 40 (1999) 23, pp. 6337-6349.

[32] Perez-Lepe, A., Martinez-Boza, F., Gallegos, C., Gonzalez, O., Pena, J.J., Munoz, M.E., Santamaria, A.: Influence of the Processing Conditions on the Rheological Behaviour of Polymer-Modified Bitumen, Fuel, 82 (2003), pp. 1339-1348.

[33] Perez-Lepe, A., Martinez-Boza, F.J., Attane, P., Gallegos, C.: Destabilization Mechanism of Polyethylene-Modified Bitumen, Journal of Applied Polymer Science, 100 (2006), pp. 260–267.

[34] Ge, D., Yan, K., You, Z, Xu, H.: Modification Mechanism of Asphalt Binder with Waste Tire Rubber and Recycled Polyethylene, Construction and Building Materials, 126 (2016), pp. 66-76.

[35] Liang, M., Xin, X., Fan, W., Sun, H., Yoo, Y, Xing, B.: Viscous Properties Modified Asphalt, Construction and Building Materials, 74 (2015), pp. 124-131.

[36] Lee, S.J., Akisetty, C.K, Amirkhanian, S.N.: The Effect of Crumb Rubber Modifier (CRM) on the Performance Properties of Rubberized Binders in HMA Pavements, Construction and Building Materials, 22 (2008) 7, pp. 1368-1376.

[37] Cao, W.: Study on Propeties of Recycled Tire Rubber Modified Asphalt Mixtures Using DRy Process, Construction and Building Materials, 21 (2007) 5, pp. 1011-1015.

[38] Daryl, M., Susanna, H., Ryan, W., Ludo, Z.: Study of Crumb Rubber Materials as Paving Asphalt Modifiers, Canadian Journal of Civil Engineering, 34 (2007), pp. 1276–1288.

[39] Gonzalez, V., Martinez-Boza, F., Navarro, F., Gallegos, C., Perez-Lepe, A., Paez, A.: Thermomechanical Properties of Bitumen Modified with Crumb Tire Rubber and Polymeric Additives, Fuel Processing Technology, 91 (2010), pp. 1033–1039.

[40] Moreno, F., Sol, M., Martin, J., Perez, M., Rubio, M.C.: The Effect of Crumb Rubber Modifier on The Resistance of Asphalt Mixes to Plastic Deformation, Materials and Design, 47 (2013), pp. 274–280.

[41] Rasoulzadeh, Y., Mortazavi, S., Yousefi, A., Khavanin, A.: Decreasing Polycyclic Aromatic Hydrocarbons Emission from Bitumen Using Alternative Bitumen Production Process, Journal of Hazardous Materials, 185 (2011), pp. 1156–1161.

[42] Cong, P., Chen, S., Yu, J.: Investigation of The Properties of Epoxy Resin Modified Asphalt Mixtures for Application to Orthotropic Bridge Decks, Journal of Applied Polymer Science, 121 (2011), pp. 2310–2316.

[43] Yi-qui, T., Lei, Z., Wei-qiang G., Meng, G.: Investigation of the Effects of Wax Additive on the Properties of Asphalt Binder, Construction and Building Materials, 36 (2012), pp. 578-584.

[44] Mrugula, F., Iwanski, M.: Resistance to Permanent Deformation of Asphalt Concrete with F-T Wax Modified Foamed Bitumen, Procedia Engineering, 108 (2015), pp. 459-466.

[45] Edwards, Y., Tasdemir, Y., Isacsson, U.: Rheological Effects of Commercial Waxes and Polyphosporic Acid in Bitumen 160/220-Low Temperature Performance, Fuel, 85 (2006) 7-8, pp. 989-997.

[46] Edwards, Y., Tasdemir, Y., Isacsson, U.: Rheological Effects of Commercial Waxes and Polyphosporic Acid in Bitumen160/220-High Temperature Performance, 21 (2007) 10, pp. 1899-1908.

[47] Tasdemir, Y.: High Temperature Properties of Wax Modified Binders and Asphalt Mixtures, Construction and Building Materials, 23 (2009), pp. 3220-3224.

[48] Chen, H., Xu, Q.: Experimental Study of Fibers in Stabilizing and Reinforcing Asphalt Binder, Fuel, 89 (2010) 7, pp. 1616-1622.

[49] Yilmaz, M, Yalcin, E.: The Effects of Using Different Bitumen Modifiers and Hydrated Lime Together on the Properties of Hot Mix Asphalts, Road Materials and Pavement Design, 17 (2016) 2, pp. 499-511.

[50] Asli, H., Ahmadinia, E., Zargar, M., Karim, M.R.: Investigation on Physical Properties of Waste Cooking Oil-Rejuvenated Bitumen Binder, Construction and Building Materials, 37 (2012), pp. 398-405.

[51] Zargar, M., Ahmadinia, E., Asli, H., Karim, M.R.: Investiagtion of the Possibility of Using Waste Cooking Oil as Rejuvenated Agent for Aged Bitumen, Journal of Hazardous Materials, 223 (2012), pp. 254-258.

[52] Azahar, W.M.A.W., Jaya, R.P., Hainin, M.R., Bujang, M.: Chemical Modification of Waste Cooking Oil to Improve the Physical and Rheological Properties of Asphalt Binder, Construction and Building Materials, 125 (2016), pp. 387-397.

[53] Maharaj, R., Maharaj, C.: Physical Properties of Low-Density Polyethylene, Polyvinylchloride and Used Engine Oil Modified Asphalt, Progress in Rubber Plastics and Recycling Technology, 31 (2015) 3, pp. 173-187.

[54] Yang, X, You, Z.: High Temperature Performance Evaulation of Bio-oil Modified Asphalt Binders Using the DSR and MSCR Tests, Construction and Building Materials, 76 (2015), pp. 380-387.

[55] Sun, Z., Yi, J., Huang, Y., Feng, D., Guo, C.: Properties of Asphalt Binder Modified by Bio-oil Derived from Waste Cooking Oil, Construction and Building Materials, 102 (2016), pp. 496-504.

[56] Gong, M., Yang, J, Zhang, J, Zhu, H., Tang, T.: Physical-Chemical Properties of Aged Asphalt Rejuvenated by Bio-oil Derived from Biodisel Residue, Construction and Building Materials, 105 (2016), pp. 35-45.

[57] Yang, X., You, Z., Dai, Q, Milss-Beale, J.: Mechanical Performance of Asphalt Mixtures Modified by Bio-oil Derived from Waste Wood Resources, Construction and Building Materials, 51 (2014), pp. 424-434.

[58] Zhang, R., You, Z., Wang, H., Ye, M., Yap, Y.K.: The Impact of Bio-oil as a Rejuvenator for Aged Asphalt Binder, Construction and Building Materials, 196 (2019), pp. 134-143.

[59] Bostancıoğlu M.: Development of Mechanical Properties of Chemical Products Obtained from Vegetable Wastes and Bituminous Hot Mixtures, Karadeniz Technical University, PhD Thesis, Institute of Science, Trabzon, 2012.

[60] Bostancıoğlu, M, Oruç, S.: Effect of Activated Carbon and Furan Resin on Asphalt Mixture Performance, Road Materials and Pavement Design, 17 (2016) 2, pp. 512-525.

[61] Simon, M.W., Stafford, K.T., Ou, D.L.: Nanoclay Reinforcement of Liquid Silicone Rubber. Journal of Inorganic and Organometalic Polymers and Materials, 18 (2008) 3, pp. 364-373.

[62] Yao, H., You, Z., Li, L., Lee, C. H., Wingard, D., Yap, Y. K.: Rheological Properties and Chemical Bonding of Asphalt Modified with Nanosilica, Journal of Materials Civil Engineering, 25 (2013) 11, pp. 1619-1630.

[63] Karahançer, Ş.: Investigating the Performance of Cuprous Oxide Nano Particle Modified Asphalt Binder and Hot Mix Asphalt, Construction and Building Materials, 212 (2019), pp. 698-706.

[64] Sun, L., Xin, X., Ren, J.: Asphalt Modification Using Nano Materials and Polymers Composite Considering High and Low Temperature Performance, Construction and Building Materials, 133 (2017), pp. 358-366.

[65] Li, R., Amirkhanian, S., You, Z, Huang, J.: Developments of Nano Materials and Technologies on Asphalt Materials - A review. Construction and Building Materials, 143(2017), pp. 633-648.

[66] Shafabakhsh, G., Mirabdolazimi, S.M., Sadeghnejad, S.: Evaluation the Effect of Nano-TiO2 on the Rutting and Fatigue Behavior of Asphalt Mixtures, Construction and Building Materials, 54 (2014), pp. 566-571.

[67] Qian, G., Yu, H., Gong, X., Zhao, L.: Impact of Nano-TiO2 on the NO2 Degradtion and Rheological Performance of Aphalt Pavement, Construction and Building Materials, 218 (2019), pp. 53-63.

[68] Nazari, H., Naderi, K., Nejad, F.M.: Improving Aging Resistance and Fatigue Performance of Asphalt Binders Using Inorganic Nano Particles, Construction and Building Materials, 170 (2018), pp. 592-602.

[69] Walters, R.C.: Enhancing Asphalt Binders's Rheological Behavior and Aging Susceptiblity Using Nano-Particles, North Carolina A&T State University, North Carolina, Greensboro, 2013.

[70] You, Z., Mills-Beale, J., Foley, J.M., Roy, S., Odegard, G.M., Dai, Q., Goh, S.W.: Nanoclay Modified Asphalt Materials; Preperation and Characterization, Construction and Building Materials, 25 (2011), pp. 1072-1078.

[71] Castillo, S.Z., Rivera-Armanta, J.L., Chavez-Cinco, M.Y., Salazar-Cruz, B.A., Mendoza-Martinez, A.M.: Physical and Rheological Properties of Asphalt Modified with SEBS/Montmorllilonite Nanocomposite, Construction and Building Materials, 106 (2016), pp. 349-356.

[72] Vargas, M.A., Moreno, L., Montiel, R., Manero, O., Vazquez, H.: Effects of Montmorillonite (Mt) and Two Different Organo-Mt Additives on the Performance of Asphalt, Applied Clay Science, 31 (2017) 4, pp. 424-430.

[73] Melo, J.V.S., Triches, G.: Evaluation of Properties and Fatigue Life Estimation of Asphalt Mixture Modified by Organophilic Nanoclay, Construction and Building Materials, 40 (2017), pp. 364-373.

[74] Landrus, D.D.: Effect of Nanoclay on Binder Rheology and HMA Rutting Resistance, University of North Dakota, North Dakota, Grand Forks, 2016.

[75] İskender, E.: Evaluation of Mechanical Properties of Nano-Clay Modified Asphalt Mixtures, Measurement, 93 (2016), pp. 359-371.

[76] Goh, S.W., Akin, M., You, Z., Shi, X.: Effect of Deicing Solution on the Tensile Strength of Micro or Nano-modified Asphalt Mixture. Construction and Building Materials, 25 (2011 1), pp. 195-200.

[77] Abdelrahman, M., Katti, D.R., Ghavibazoo, A., Upadhyay, H.B., Katti, K.S.: Engineering Physical Properties of Asphalt Binders Through Nano Clay-asphalt Interactions. Journal of Materials Civil Engineering, 26 (2014) 12, pp. 401-409.

[78] Zhu, C., Zhang, H., Shi, C., Li, S.: Effect of Nano-zinc Oxide and Organic Expanded Vermucilite on Rheological Properties of Different Bitumens Before and After Aging, Construction and Building Materials, 146 (2017), pp. 30-37.

[79] Xu, X., Guo, H., Wang, X., Zhang, M., Wang, Z., Yang, B.: Physical Properties and Anti-Aging Characteristics of Asphalt Modified with Nano-zinc Oxide Powder, Construction and Building Materials, 224 (2019), pp. 732-742.

[80] Zhang, H., Gao, Y., Gua, G., Zhao, B., Yu, J.: Effects of ZnO Particle Size on Properties of Asphalt and Asphalt Mixture, Construction and Building Materials, 159 (2018), pp. 578-586.

[81] Raufi, H.: Modification of Bituminous Binder and Asphalt Mixtures with Nano Materials, Dokuz Eylül University, Institute of Science, Master's Thesis, İzmir, 2018.

[82] Yao, H., You, Z., Li, L., Goh, S.W., Lee, C.H., Yap, Y.K., Shi, X.: Rheological Properties and Chemical Analysis of Nanoclay and Carbon Microfiber Modified Asphalt with Fourirer Transform Infrared Spectroscopy, Construction and Building Materials, 38 (2013), pp. 327-337.

[83] Nasubilin, A.G., Koltsova T., Nasibulina L.I., Anoshki, I.V., Semencha, A., Tolochko, O.V., Kauppinen, E.I.: A Novel Approach to Composite Preparation by Direct Synthesis of Carbon Nanomaterial on Matrix or Filler Particles, Acta Materialia, 61 (2013), pp. 1862-1871.

[84] Khattak, M.J., Khattab, A., Rivzi, H.R.: Characterization of Carbon Nano-fiber Modified Hot Mix Asphalt Mixtures, Construction and Building Materials, 40 (2013), pp. 738-745.

[85] Crucho, J.M.L., Neves, J.M.C., Capitao, S.V., Picato-Santos, L.G.: Mechanical Performance of Asphalt Concrete Modified with Nanoparticles: Nanosilica, Zero-valent Iron and Nanoclay, Construction and Building Materials, 181 (2018), pp. 309-318.

[86] Saltan, M., Terzi, S., Karahancer, S.: Performance Analysis of Nano Modified Bitumen and Hot Mix Asphalt, Construction and Building Materials, 173 (2018), pp. 228-237.

[87] Hussein, A.A., Jaya, R.P., Hassan, N.A., Yaacob, H., Huseien, G.F., Ibrahim, M.H.W.: Performance of Nanoceramic Powder on the Chemical and Physical Poperties of Bitumen, Construction and Building Materials, 156 (2017), pp. 496-505.

[88] Apostolidis, P., Li, X., Erkens, S., Scarpas, A.: Evaluation of Epoxy Modification in Bitumen, Construction and Building Materials, 208 (2019), pp. 361-368.

[89] Arafat, S., Kumar, N., Wasiuddin., N.M., Owhe, E.O., Lynam, J.G.: Sustainable Lignin to Enhance Asphalt Binder Oxidative Aging Properties and Mix Properties, Construction and Building Materials, 217 (2019), pp. 456-468.

[90] Çubuk, M., Gürü, M., Çubuk, M.K.: Improvement of Bitumen Performance with Epoxy Resin, Fuel, 88 (2009), pp. 1324-1328.

[91] Gaowang, Z., Hongliang, Z., Xinde, B., Hongzhi, Y.: Laboratory study on Performance of Bimaleimide/Unsaturated Polyester Resin Modified Asphalt, Construction and Building Materials, 179 (2018), pp. 576-586.

[92] Portugal, A.C., X., Lucena, L.C.F.L., Lucena, A.E.F.L., Costa, D.B., Lima, K.A.: Rheological Properties of Asphalt Binders Prepared with Maize Oil, Construction and Building Materials, 152 (2017), pp. 1015-1026.

[93] Alamawi, M.Y., Khairuddin, F.H., Yusoff, N.I.M., Badri, K., Ceylan, H.: Investigation on Physical, Thermal and Chemical Properties of Palm Kernel Oil Polyol Bio-based Binder as a Replacement for Bituminous Binder, Construction and Building Materials, 204 (2019), pp. 122-131.

[94] Cao, X., Wang, H., Cao, X. Sun, W., Zhu, H., Tang, B.: Investigation of Rheological and Chemical Properties Asphalt Binder Rejuvenated with Waste Vegatable Oil, Construction and Building Materials, 180 (2018), pp. 455-463.

[95] Sun, Z., Yi, J., Huang, Y., Feng, D., Guo, C.: Properties of Asphalt Binder Modified by Bio-oil Derived from Waste Cooking Oil, Construction and Building Materials, 102 (2016), pp. 496-504.

[96] Zhang, R., You, Z., Wang, H., Chen, X., Si, C., Pneg, C.: Using Bio-based Rejuvenator Derived from Waste to Wood Rcycle Old Asphalt, Construction and Building Materials, 189 (2018), pp. 568-575.

[97] Ahmedzade, P., Demirelli, K., Günay, T., Biryan, F., Alqudah, O.: Effects of Waste Polypropylene Additive on the Properties of Bituminous Binder, Procedia Manufacturing, 2 (2015), pp. 165-170.

[98] Yin, J., Wu, W.: Utilization of Waste Nylon Wire in Stone Matrix Asphalt Mixtures, Waste Management, 78 (2018), pp. 948-954.

[99] Köfteci, S., Ahmedzade, P., Kultayev, B.: Performance Evaluation of Bitumen Modified by Variosu Typeof Waste Plastics, Construction and Building Materials, 73 (2014), pp. 592-602.

[100] Li, R., Xiao, F., Amirkhnanian, S., You, Z, Huang, J.: Developments of Nano Materials and Technologies on Asphalt Materials, Construction and Building Materials, 143 (2017), pp. 633-648.

[101] https://www.britannica.com/science/chemical-reaction#ref49377

[102] Murray, P.R.S.: Principles of Organic Chemistry: a Modern and Comprehensive Text for Schoolsand Colleges, London, Heinemann Educational Books, 1997.

[103] Martinez, A., Paez, A, Martin, N.: Rheological Modification of Bitumens with New Poly-Functionalized Furfural Analogs, Fuel, 87 (2008), pp. 1149-1154.

[104] Corey, E.J., Fuchs, P.L.: Tetrahedron Lett, 36 (1972), pp. 3769-3772.

[105] Arslan, D., Gürü, M., Çubuk, M.K.: Performance Assessment of Organic-Based Synthetic Calcium and Boric Acid Modified Bitumens, Fuel, 102 (2012), pp. 766-772.

[106] Çubuk, M., Gürü, M., Çubuk, M.K., Arslan, D.: Improvement of Properties of Bitumen by Organic-Based Magnesium Additive, Journal of Faculty of Engineering and Architecture of Gazi University, 28 (2013) 2, pp. 257-264

[107] Arslan, D., Gürü, M., Çubuk, M.K.: Improvement of Hot Mix Asphalt Performance in Cold Regions by Orgnaic-Based Synthetic Compounds, Cold Regions Science and Technology, 85 (2013), pp. 250-255.

[108] Bakkalcı, A.C., Öz, E.: The Importance of Boron and Boron in Turkey, TISK (Confederation of Employers' Unions of Turkey) Academy 2 (2007) 4, pp. 248-268.

[109] Marzocchi, A., Roberts, G.M, Bolen, C.E.: Boron Modified Asphalts, United States Patent Office, Patent No: 4360473, 1982.

[110] Arslan, D., Gürü, M., Çubuk, M.K., Çubuk, M.: Construction and Building Materials, 25 (2011), pp. 3863-3868.

[111] Arslan, D., Gürü, M., Çubuk, M.K.: Preventing of Rutting and Crackings in the Bituminous Mixtures by Monoethylene and Diethylene Glycol Based Synthetic Polyboron Compounds, Construction and Building Materials, 50 (2014), pp. 102-107.

[112] Çalışıcı, M., Gürü, M., Çubuk, M.K., Cansız, O.F.: Improving the Aging Resistance of Bitumen by Addition of Polymer Based Diethylene Glycol, Construction and Building Materials, 169 (2018), pp. 283-288.

[113] Oruç, S., Yılmaz, B., Sancak, K.: Effect of Boron-Containing Additives on Rheological Properties of Asphalt Binder, Road Materialsand Pavement Desings, 2015, https://doi.org/10.1080/14680629.2015.1120228.

[114] İkizler, A.A., Sancak, K.: Synthesis of4-hydroxy-4, 5-dihydro-1, 2, 4-triazol-5-Ones., Monat SheftefurChemie, 123 (1992) 3, pp. 257–263.

[115] İkizler, A.A., Sancak, K.: Reaction of Ester Ethoxy Carbonyl Hydrazones with Aliphatic Diamines, Collection of Czechoslovak Chemical Communications, 60 (1995) 5, pp. 903–909.Ş

[116] Sancak, K., Unver, Y., Tanak, H., Degirmencioglu, I., Düğdü, E.E.M., İsik, Ş.: Thesynthesis of Some New Imidazoleand Triazole Derivatives: Crystal Structure and DFT-TDDFT Investigation on Electronic Structure, Journal of Inclusion Phenomena and Macrocyclic, 67 (2010) 3-4, pp. 325–334.

[117] Oruç, S., Yılmaz. B.: Improvement in performance Properities of Asphalt Using a Novel Boron-Containing Additive, Construction and Building Materials, 123 (2016), pp. 207-213.

[118] https://en.wikipedia.org/wiki/Succinimide

[119] Kumar, K., Singh, R.K., Kukrety, A., Singh, A., Maity, S.K., Srivastava, M., Atray, N., Ray, S.S.: Sythhesis of Succinimide Based Novel Additives for Viscosity Reduction of Bituminous Binder, Construction and Building Materials, 126 (2016), pp. 566-572.

[120] Padhan, R.K., Gupta, A.A., Badoni, R.P., Bhatnagar, A.K.: Poly (Ethylene Terephthalate) Waste Derived Chemicals as an Antistripping Additive for Bitumen- Sn Environment Friendly Approach for Disposal of Environmentally Hazardous Material, Polymer Degradation and Stability, 98 (2013), pp. 2592-2601.

[121] Parvez, M.A., Wahhab, H.I.A., Shawabkeh, R.A., Hussein, I.A.: Asphalt Modification Using Acid Treated Waste Oil Fly Ash, Construction and Building Materials, 70 (2014), pp. 201-209.

[122] Gürü, M., Çubuk, M.K., Arslan, D., Aminbakhsh, S.: Effects of Sugar Beet Molasses and Molasses-Based Boron Oxide Comound on Bitumen Properties, J. Mater. Civ. Eng., 29 (2017) 4, pp.1-1.

[123] Padhan, R.K., Gupta, A.A.: Preparation and Evaluation of Waste PET Derived Polyurethane Polymer Modified Bitumen Through in Situ Polymerization Reaction, Construction and Building Materials, 158 (2018), pp. 337-345.

[124] Leng, Z., Sreeram, A., Padhan, R.K., Tan, Z.: Value-added application of waste PET based additives in bituminous mixtures containing high percentage of reclaimed asphalt pavement (RAP), Journal of Cleaner Production, Volume 196 (2018), pp.615-625.

[125] Padhan, K.R., Leng, Z., Sreeram, A., Xu, X.: Compound modification of asphalt with styrene-butadiene-styrene and waste polyethylene terephthalate functionalized additives, Journal of Cleaner Production, 277 (2020), pp. 124286.

[126] ASTM D5-97: Standard Test Method for Penetration of Bituminous Materials, American Society for Testing and Materials, West Conshohocken (PA), USA, 1999.

[127] ASTM D36-95: Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus), American Society for Testing and Materials, West Conshohocken (PA), USA, 2000.

[128] ASTM D113-99: Standard Test Method for Ductility of Bituminous Materials, American Society for Testing and Materials, West Conshohocken (PA), USA, 1999.

[129] ASTM D 1664-80: Test Method for Coating and Stripping of Bitumen-Aggregate Mixtures, 1985.

[130] ASTM D4402-06: Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer, American Society for Testing and Materials, West Conshohocken (PA), USA, 2002.

[131] ASTM D2872: Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test), American Society for Testing and Materials, West Conshohocken (PA), USA, 2004.

[132] ASTM Standard D 6521-04: Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV), American Society for Testing and Materials, West Conshohocken (PA), USA, 2004.

[133] AASHTO T 315: Standard Method of Test for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR), 2012.

[134] American Association of State Highway and Transportation Officials, Standard Test Method for Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer (BBR), AASHTO Designation TP1, 1998.

[135] ASTM D 1559: Test Method for Resistance to Plastic Flow of Bituminous Mixtures Using Marshall Apparatus, 1998.

[136] Nicholson, V.: Adhesion tension in asphalt pavements, its significance and methods applicable in its determination, Journal of Association of Asphalt Paving Technologists, 3 (1932), pp. 28-49

[137] Ghuzlan, K., Al-Khateeb, G., Abu Damrah, A.: Using oil shale ash waste as a modifier for asphalt binders. Journal of Material Cycles and Waste Management, 15 (2013), pp. 522–529.

[138] Laçin, Ö., Dönmez, B.: Modifiye Hummers Yöntemi ile Elde Edilen Grafen Oksit Sentezleri İçin: Kısım3, Fourier Dönüşümlü Kızılötesi Spektroskopisi Analizi", Avrupa Bilim ve Teknoloji Dergisi, (2021), pp.985-989.