

THE INFLUENCES OF ALTERING THE MIXING CONDITIONS ON THE PROPERTIES OF POLYMER MODIFIED BITUMEN: AN OVERVIEW

Derya KAYA ÖZDEMİR *

Ali TOPAL *

Burak ŞENGÖZ *

Received: 31.03.2020; revised: 18.04.2020; accepted: 30.04.2020

Abstract: Modification of bitumen by different modifiers, causes the morphological, rheological and chemical characterisation differences related to the following three main factors: the type of the polymer, bitumen components and blending conditions. Manufacturing conditions can be investigated in several groups such as; mixing temperature, duration of mixing and shear rate (mixing speed). These manufacturing conditions are the key parameters, since they act an important role on the properties of the final product. These key parameters and their effects have always been an interesting topic for the researchers, because they may have some consequences like aging of the sample, degradation of the polymer or sometimes less absorption of the polymer by bitumen etc. This study aims to present the influences of mixing conditions on different properties of the bituminous mixtures with the help of reviewing the previous studies in the literature.

Keywords: Polymer Modified bitumen, Mixing conditions, Key parameters, Shear rate, Duration of mixing, Mixing temperature

Karıştırma Koşullarının Polimer Modifiye Bitümün Özellikleri Üzerindeki Etkileri: Genel Bir Bakış

Öz: Bitümün farklı polimerler ile modifikasyonu, polimerin tipi, bitüm bileşenleri ve karışım koşulları gibi faktörlere bağlı olarak, reolojik ve kimyasal karakterizasyon farklılıklarına neden olur. Anahtar parametreler olarak da adlandırılabilen karışım koşulları; karıştırma sıcaklığı, karıştırma süresi, kesme oranı (karıştırma hızı) gibi alt başlıklarla incelenebilir. Polimer Modifiye Bitüm (PMB) karışım koşulları, ya da diğer bir deyişle anahtar parametreler, malzemenin yaşlanma özellikleri, polimerin degradasyonu ya da polimerin bitüm tarafından emilimi gibi PMB karakterizasyonu üzerinde önemli etkilere sahiptir ve bu sebeple araştırmacılar için her zaman ilgi çekici bir konu olmuştur. Bu çalışma, literatürde şimdiye kadar gerçekleştirilmiş ve PMB'nin üretiminde karışım koşullarının etkisini ortaya koyan yayınların derlemesini sunarak anahtar parametrelerin önemini ortaya koymayı amaçlamaktadır.

Anahtar Kelimeler: Polimer Modifiye Bitüm, Karışım koşulları, Anahtar parametreler, Kayma oranı, Karıştırma süresi, Karıştırma sıcaklığı

*Dokuz Eylül University, Faculty of Engineering, Department of Civil Engineering, 35160, Buca, Izmir, Turkey
Correspondence Author: Derya Kaya Özdemir (d.kaya@deu.edu.tr)

1. INTRODUCTION

Modification of bitumen by modifiers, causes the morphological, rheological and chemical characterisation differences related to the following five factors: the type of the polymer, bitumen components and blending conditions in terms of the temperature, shearing rates or mixing durations. Blending conditions, which can be named as key parameters, are effective on the polymer dispersion, phase separation and most importantly the aging of the bitumen. Mixing polymer with bitumen for longer duration or higher shear rates caused the bitumen to be oxidised, because it directly affects the interaction of the oxygen with the bitumen. These key parameters and their effects have always been an interesting topic for the researchers, because they may have some consequences like aging of the sample, degradation of the polymer or sometimes less absorption of the polymer by bitumen etc.

It is well known that, the mixing conditions have some influences on the characteristics of Polymer Modified Bitumen (PMB) samples. Characterisation in materials science can be explained as the process of materials' structural, chemical, thermal, physical, morphological etc. properties investigation (Sam et al., 2009). For bituminous materials most common characterisations techniques can be investigated in four groups which are; physical, rheological, chemical and structural (Yu et al., 2011). Material characterisations have been examined for centuries. Nowadays, it is possible to study, not only micro and also macro characteristics of the materials, with the help of developing technology. Evaluation of the different characteristics of the bituminous mixtures depending on the manufacturing conditions is a very common approach. For this reason, before spotting the mixing conditions influences on the final product, it is a good idea to discuss the characterisation types, experiments or the devices used for the characterisations.

- *Structural Characterisation*

The structural characteristics of bitumen can be analysed by Fourier Transform Infrared (FTIR) spectroscopy and Atomic Force Microscopy (AFM) investigations. FTIR spectroscopy enables to evaluate the chemical characteristics, while AFM assesses the microstructural properties of the sample. Infrared Spectroscopy has been one of the most important analytical techniques for scientists in recent years. The greatest developments in infrared systems have been the result of the introduction of Fourier-conversion spectrometers. In these methods, called FTIR, it is aimed to reduce the time, required to obtain data by using the interferometry and improved mathematical Fourier-transform (Berthomieu and Hienerwade, 2009).

AFM is one of the most common approaches in order to characterise the bituminous mixtures, in terms of morphologies. It is capable of measuring topographic features at the nanometer-scale or even at atomic-scale resolution. Moreover, AFM enables to understand bitumen's micro mechanical behaviour, such as phase separation, micro friction, micro abrasion etc. (Hou et al., 2017). Moreover, previous researches clarified that, microscale properties of the samples are directly related with the macro scale properties (Al-Rub et al., 2010; Mahboob et al., 2015). Aging has crucial importance on the microstructure and phase dispersion of the bituminous sample. The molecular structure depends on the aging, because of some chemical changing and degradation after oxidation (Wang and Liu, 2017; Zhang et al., 2011). Based on this point of view, it can be conceivable that, influences of mixing conditions, which will cause aging can be evaluated by AFM.

- *Rheological Characterisation*

Rheology is defined as the branch of physics that deals with the deformation and flow of matter, especially the non-Newtonian flow of liquids and the plastic flow of the solids. Rheometer is a device, which is employed to investigate the rheological characteristics of the bitumen at different temperatures or frequencies. Complex modulus (G^*) and phase angle (δ) values, which are obtained by rheometers, are directly related with the viscoelastic properties of the sample. Therefore, it is known that, either modification or aging of the sample, effects the rheological behaviour of the sample. By using complex modulus (G^*) and phase angle (δ), rutting parameter

($G^*/\sin(\delta)$), fatigue cracking - parameter ($G^* \cdot \sin(\delta)$), master curves, black diagrams, Cole-Cole plots, Zero Shear Viscosity (ZSV), Multiple Stress and Recovery (MSCR) values etc., can be investigated to evaluate the rheological properties of the bitumen (Kaya et al., 2019a). Moreover, aging characteristics of the binder might be obtained by rheological investigations because, bitumen becomes to be stiffer and have different rheological properties after aging.

- *Morphological Characterisations*

Fluorescence microscopy is used to study heterogeneous surfaces, where the components have different responses to the reflected lights. Oily fractions of the bitumen (like aromatics) have fluorescence properties, however resins and asphaltenes have no fluorescence responses under UV light (Lambert, 2005; Skoog and Leary, 1996). Neat bitumen itself has little emission, due to the fact that, all components are well mixed therefore, it cannot be observed under Optical Microscopy (OM) (Loeber et al., 1996). For this reason, it is very popular to investigate the effects of mixing conditions on the bituminous materials under OM. Fluorescence microscopy has been one of the most popular tool to investigate the morphological characterisation of PMB samples. Depending on the different coloured appearance of two phases (bitumen and polymer), it is easy to study the homogeneity and the dispersion of polymer into bitumen (Brûlé et al., 1988).

Another technique, which is common to obtain the morphological characteristics of PMB samples, is employing the Confocal Laser Scanning Microscopy (CLSM). CLSM is qualified of considering extremely localized fluorescence emissions and enables a thorough study of bitumen scale of asphalt observation (Handle et al., 2014). That capability of CLSM, allows to handle the microstructure of the bitumen (Bearsley et al., 2004; Forbes et al., 2001; Handle et al., 2012). Moreover, one of the biggest advantages of CLSM is that, it can be used to study the aging properties of PMB samples, by measuring the different fluorescence emission behaviour of the bitumen components. Additionally, it is possible to investigate polymer dispersion, compatibility and network formation by CLSM based on the interaction between the polymer and bitumen (Collins et al., 1991; Forbes et al., 2001; Handle et al., 2012; Lee et al., 1997; Newman, 1998; Rozeveld et al., 1997; Takamura and Heckmann, 1999).

- *Thermal Characterisations*

Differential Scanning Calorimeter (DSC) or Modulated Differential Scanning Calorimeter (MDSC) and Thermogravimetric Analyser (TGA) are the most popular devices, which can be used for thermal analyses of PMB. DSC or MDSC is employed to characterise the physical/chemical properties, depending on the heat exchange such as Tg, heat capacity, chemical reactions or phase transition, like crystallization and melting (Soenen et al., 2014). Glass transition Temperature (Tg) is a distinctive feature of the polymeric materials. Modulated DSC (MDSC) is used in order to study the thermal behaviour of the polymer modified bitumen samples, as it is useful in the detection of overlapping Tg's (Reading et al., 1994). The distinct advantage of MDSC is that, it applies two simultaneous heating rates to the sample, a linear heating rate provides the total heat flow rate similar to standard or conventional DSC, but at the same time, a sinusoidal (modulated) heating rate provides a route to determine a fraction of the total heat flow. Bitumen has 4 different Tg corresponding the Tg's of saturates, aromatics, resins and asphaltene fractions. Therefore, PMB samples should have more than 4 Tg, depending on the polymer used for modification. Moreover, in some situations new Tg'(s) can arise/arises, from a phase of mixed compositions, which occurred by branching and cross linking between polymer and bitumen. Ageing evaluation can be done by DSC, since it allows to assess the asphaltenes fractions among the bitumen components.

Thermal gravimetric analysis is an experimental technique, which is useful for measuring the thermal stability of a material and extrapolate its maximum operating temperature above, which degradation starts to take place (Hatakeyama and Quinn, 1999). The thermal characterisation of bitumen is a very difficult investigation, because of the complex fractions of the bitumen (Yoon et al., 2009). In the literature, it can be found that, bitumen displays three major mass losses, first one because of the volatilization of light fractions (saturates and non-polar aromatics), second one

depending on the decompositions of resins and asphaltenes and the last one due to the asphaltene (Zhang et al., 2011).

2. THE EFFECTS OF MIXING CONDITIONS

In this section, the previous studies, dealing with the effects of mixing conditions, have been overlooked and presented depending on the different key parameters. The studies were handled as the effects of five sub grouped and they are: mixing duration, shear rate and mixing temperature.

2.1. The Effect of Mixing Duration

Haddadi et al (2008) investigated the importance of the mixing duration on the performance of bitumen, modified with different amount of EVA additive. They measured the penetration value by increasing the mixing duration up to four hours, for each sample. As a result, they deduced that, penetration value was decreased by the duration and at the end, after four hours, it became a constant value. Additionally, they did the same investigations for softening point and obtained the similar results. Therefore, they determined mixing duration as four hours for the speed of 300 rpm.

Larsen et al. (2009) investigated the aging effects of the mixing conditions on the structural characteristics of the sample. They examined two different styrene-butadiene-styrene (SBS) modified samples, one mixed for 90 mins while the other for 150 mins. They compared the absorbance values, which correspond to carbonyl group and butadiene blocks, to reveal the aging effects of longer mixing. Moreover, they could be able to conclude the degradation of SBS, after mixing at higher temperature and shearing rate depending on the FTIR investigations.

Kok et al. (2011), investigated the alteration of mixing duration on the softening point and rheological characteristics of the PMB samples. Based on the results, it was observed that, the increase of the mixing duration caused an increase on the softening point, viscosity and complex modulus values, due to the occurrence of oxidation. But, this effect is more distinct when the PMB produced by high shear rates.

Mohan et al. (2013) evaluated the different mixing duration of Ethylene Vinyl Acetate (EVA) modified bitumen on the conventional test results and the morphological characteristics of the sample. The effect of the mixing duration did not result significant changes in the conventional binder test results. However, slight changes were observed in the morphology.

Fang et al. (2014) studied the effects of mixing duration of waste polyethylene modified bitumen on high temperature storage stability, thermal and morphological characteristics of the sample. TGA, DSC and fluorescence microscopy were employed for the investigations. In this study, it was found that, phase segregation changed with the mixing duration, if the mixing temperature was not high enough. Moreover, morphologies of the samples were directly affected with the key parameters. Homogeneity of the polymer phase into the bitumen phase, increased with the increasing mixing duration. However, after a specific value, PMB polymer in the PMB became to agglomerate. On the other hand, this study validated that, key parameters had a little influence on the thermal characteristics of the sample. Additionally, they suggested the optimum key parameters of the blend.

Shaffii et al. (2017), completed a study, where they reported that, the increase of the mixing duration up to 45 mins, results in the decrease of softening point and the increase of penetration value, however more than 45 mins of mixing duration results in the increase of softening point and the decrease of penetration value. Furthermore, they concluded that, the increase in the mixing duration results in the lower resistance to the temperature susceptibility. But it changes by reversal, when the sample starts to oxidise, due to the higher mixing duration.

Key parameters are not only important at mixing stage, but also crucial during sample preparation process. In the literature, many studies were conducted to exhibit the importance of

the key parameters for sample preparation. For instance, Liu et al (2017) observed different morphological images under confocal laser scanning microscopy (CLSM) by altering the duration of curing for EVA modified bitumen. Initially, PMB samples have more homogenous morphologies, by increasing time, but after a specific duration, morphologies became to be phase separated. Additionally, they employed SEM for further morphological characterisation, to evaluate the effects of the curing time and the results agreed well with the results of CLSM.

Shaffie et al. (2018), studied the effects of the mixing duration on the physical properties of neat bitumen. According to the results, the higher the mixing duration, the higher the penetration value and the softening point of the sample. Moreover, they investigated the changes on the penetration indices of the sample, which is related with the temperature susceptibility. They concluded that, the increase in the mixing duration results in the higher resistance to the temperature susceptibility.

Babalghaith et al. (2019) examined the impacts of mixing time on the rheological properties of the PMB samples produced with different polymers. In the first place, the complex modulus of the PMB samples increased with the longer mixing duration, however after some point, it started to decrease depending on the aging. The same results were observed in another study conducted by Alsoliman (2010).

Kaya et al. (2020) investigated the effects of key parameters on the characteristics on the PMB with SBS. They used 2 different mixing duration as 15 mins and 45 mins and evaluate the differences on the chemical, thermal, morphological and rheological characteristics of the PMB. Chemical bonds of the samples were changed by not only SBS modification also the mixing conditions of the SBS with bitumen. Carbonyl index values, which are related to aging, increased together with the increment of mixing time. By the increase of mixing duration, the Aromatics index of PMB samples were decreased because of the decrease of the aromatic components by aging. The similar results were investigated by rheological characterisation. Because of the aging caused by longer mixing, the activation energy of the PMB samples mixed for 45 mins were higher than the ones produced by 15 mins of duration (Kaya et al., 2018; Kaya et al., 2019a). At the different study conducted by the same researcher, they investigated the effect of mixing duration on the morphological properties of the sample. Based on the result, the increment of the mixing duration yielded more homogeneously dispersed PMB (Kaya et al., 2019b).

2.2. The Effect of Shear Rate

Gingras et al. (2005) examined the effects of process parameters, which are temperature, rotor speed, dispersed phase content and bitumen grade, on the droplet size in bitumen emulsion. They obtained that, average droplet size is decreased with the increment of rotor speed.

Garcia-Morales et al. (2007), investigated the possible impacts of employing the high and low shear rate mixers during manufacturing the recycled EVA/LDPE modified bitumen. According to their findings, processing with the high shear device shortened the necessary mixing time. Moreover, the PMB samples produced with high shear rates contained higher volume of polymer depending on the increased swelling. However, the results also exhibited that, the samples manufactured by high shear device had unstable characteristics during storage at high temperatures.

Larsen et al. (2009) completed a similar study by investigating the effects of manufacturing conditions on the microstructural and rheological characteristics of the SBS modified bitumen. They used different mixing temperatures and shearing rates as key parameters and employed rotational viscosity, fluorescence microscopy, size exclusion chromatography and FTIR spectroscopy. Consequently, they observed that, key parameters effected the dispersion of SBS into bitumen and, higher shearing rate and temperature causes the degradation of SBS within the PMB sample. Moreover, they concluded that, all key parameters are interdependent of each other and dependent to polymer type and molecular weight or bitumen characteristics.

Kok et al. (2011), also evaluated the influences of the shear rate. They concluded that, up to 1000 rpm/min, shear rate did not have a significant impact on the softening point, viscosity and the complex modulus of the PMB samples. However, above 1000 rpm/min, the higher shear rate resulted in the increased softening point, viscosity and complex modulus.

Mohan et al. (2013) examined the possible effects of different shear rates on the conventional test results and morphology of the EVA modified bitumen. According to the test results, the higher shear rates provided a decrease in the penetration value and the distinct changes on the morphologies of the sample.

Ortega et al. (2015) compared the effects of shearing rates on PMB samples in their study. They employed two types of mixer: high shear (16000-18000 rpm) and low shear (800-1000 rpm), to manufacture the samples. Microstructural characteristics and rheological characteristics were investigated by AFM and oscillatory rheometer. Consequently, they clarified low shear mixing as “poor mixing condition” depending on the investigations.

Dehouche et al. (2016) considered the effects of five different manufacturing shearing rates from 750 rpm to 4500 rpm, on the morphological and physical properties of PMB samples, by employing Wide Angle X-Ray scattering (WAXS), AFM, DSC and FTIR. Significance of the manufacturing conditions was demonstrated by WAXS result, because, samples showed intercalated structures up to 2000 rpm. However, beyond 3000 rpm the behaviour of the sample changed into exfoliated structure. Moreover, height and the number of aromatic sheets in the bitumen was decreased with the accelerated shear rates, which can be associated with the oxidation. Based on the AFM results, they announced that, the amount of bee like structures were increased with the increasing shearing rates. On the other hand, crystalline index value was decreased for higher shearing rates.

Bagshaw et al. (2019) investigated the influences of different shear rates on the properties of nano-clay bitumen nanocomposites. As a result of their study, they concluded that, higher shear rates resulted in increased dispersion and exfoliation of the nanomer particles. However, rheological analyses showed that, altering the shear rates does not change the rheological properties of the sample significantly.

In the studies of Kaya et al. (2018, 2019a, 2019b, 2020), where they evaluated the effects of high and low shear rates on the characteristics of SBS modified bitumen, the influences of SBS copolymer was more revealed by the increment of shear rate. They clarified this with the increment of absorbance of bitumen oily component by SBS with the help of higher mixing speed. The morphological images of PMB obtained by OM proved the higher SBS phase in the blend, which is produced by 3000 rpm compared to the one by 1000 rpm. Similar result were found by the FTIR analyses. The more butadiene components revealed with the help of using 3000 rpm compared the 1000 rpm.

2.3. The Effect of Mixing Temperature

Determining the mixing temperature requires precise work, because the temperature must be high enough to melt polymer and the bitumen, but not too high to prevent the oxidation (Shenoy, 2000). Wegan (2001) investigated the high and low mixing temperature on the properties of PMB by considering the inclusion of the polymer inside the bitumen and the homogeneity of the blend. Depending on the morphological images obtained by this study, it was concluded that, low mixing temperature provides better inclusion-of the polymer while, high mixing temperatures causes the inhomogeneous blend.

Gingras et al. (2005) did not investigate only the effects of shear-rate but also the mixing temperature. As a result, they obtained the increased droplet size with the decrement of the temperature.

Martin-Alfonso et. al (2009) studied the mixing temperature of bitumen with Polyethylene-Glycol functionalised with polymeric Methylene diphenyl diisocyanate (MDI-PEG). Atomic Force Microscopy (AFM), Thermogravimetric analyses (TGA) and thin layer chromatography

(TLC-FID) were employed to highlight the effects of mixing temperature on the reaction, between the polymer and bitumen fractions. They determined that, increased mixing temperature provides 3D polymer-bitumen network and reaction ability, however, it also causes polymer degradation.

Dogan and Bayramli (2009) conducted a study about the processing temperature of the PMB samples containing three different types of polymers; LDPE, EVA and SBS. They chose 2 different mixing temperatures (150°C and 180°C) and compared the morphological, mechanical, rheological and thermal conductivity of the final products. Consequently, they determined that, processing temperature had a little influence on the characteristics of the samples.

Different study, which was done by Navarro et al. (2007), presented the influences of mixing temperature on the rheological characteristics of crumb tire rubber modified bitumen. As a result, they observed that higher mixing temperatures yielded an increase of dissolved/dispersed rubber.

Kok et al. (2011) studied the influences of mixing temperature along with the mixing duration and shear rates. As a result, they found that, higher mixing temperature does not have a clear effect on the softening point, viscosity and complex modulus, when the PMB samples produced by the low shear rates or mixing duration.

Shaffie et al. (2018) also investigated the mixing temperature effects on the conventional test results of the sample. The increase of the mixing temperature had the similar results with the increase of the mixing duration. Samples produced by higher mixing temperatures resulted in higher penetration values, lower softening point and temperature susceptibility up to a certain value. Above 180°C, when the bitumen starts to be oxidised, the increase of the mixing temperature created a decrease in the penetration value and increase in the softening point and the temperature susceptibility.

3. CONCLUSION

This study aims to present the importance of the mixing conditions and their effects on the characteristics of the PMB samples. Mixing conditions, in other words key parameters, are evaluated under three groups as mixing temperature, mixing duration and shearing rate. Depending on the literature review, the following results have been found as a result of this study;

- The influences of the mixing conditions on different properties of the bituminous mixtures can be investigated by rheological, morphological, chemical and structural characterisation.
- Mixing conditions can be named as the key parameters since, they affect the characteristics of the final product. Determining the necessary and sufficient mixing conditions are not only crucial on the manufacturing stage of the PMB, but also during the sample preparation phase before doing characterisations of the sample.
- Key parameters are interdependent of each other but dependent to the type of polymer used for modification or the chemical and physical properties of the bitumen.
- Mixing duration as a key parameter may cause aging or agglomeration of the sample, if selected longer than it should be, on the other hand it is important to have a sufficient mixing duration to obtain a homogenous PMB samples.
- Using higher shear rates than needed during the PMB manufacturing may cause oxidation of the bitumen. However, decreasing the shear rate, effects the absorbance of the polymer by the bitumen. For that reason, it needs special attention to determine the shearing rate among the mixing conditions.
- Mixing temperature should be determined by considering the melting point of both the polymer and the bitumen. Also, previous studies have shown that, using high mixing

temperature causes some damages on both the polymer and the bitumen because of the oxidation. Therefore, selected mixing temperature should enable the melting of the bitumen and the polymer, but avoid the aging of the sample.

As a result, mixing conditions, also known as key parameters, is crucial for the rheological, thermal, morphological or structural characteristics of the PMB. For this reason, it is important to evaluate the different combination of mixing conditions before manufacturing, in order to have PMB sample with the desired properties.

REFERENCES

1. Al-Rub, R. K. A., Darabi, M. K., Little, D. N. and Masad, E. A. (2010). A micro-damage healing model that improves prediction of fatigue life in asphalt mixes. *International Journal of Engineering Science*, 48(11), 966-990. doi:10.1016/j.ijengsci.2010.09.016
2. Alsoliman, H. A. 2010 Engineering characteristics of local polymer modified asphalt mixtures, *Doctoral Thesis*, King Saud University, Riyadh.
3. Babalghaith, A. M., Koting, S., Sulong, N. H. R. and Karim, M. R. (2019). Optimization of mixing time for polymer modified asphalt. In *IOP Conference Series: Materials Science and Engineering*, 512(1), 1-8. doi:10.1088/1757-899x/512/1/012030
4. Bagshaw, S. A., Kemmitt, T., Waterland, M. and Brooke, S. (2019). Effect of blending conditions on nano-clay bitumen nanocomposite properties. *Road Materials and Pavement Design*, 20(8), 1735-1756. doi: 10.1080/14680629.2018.1468802
5. Bearsley, S., Forbes, A. and G. Haverkamp, R. (2004). Direct observation of the asphaltene structure in paving-grade bitumen using confocal laser-scanning microscopy. *Journal of Microscopy*, 215(2), 149-155. doi:10.1111/j.0022-2720.2004.01373.x
6. Berthomieu, C. and Hienerwadel, R. (2009). Fourier transform infrared (FTIR) spectroscopy. *Photosynthesis research*, 101(2-3), 157-170. doi:10.1007/s11120-009-9439-x
7. Brûlé, B., Brion, Y. and Tanguy, A. (1988). Paving asphalt polymer blends: Relationships between composition, structure and properties, *Proc Assoc Asphalt Paving Technologists*, 57, 41-64.
8. Collins, J., Bouldin, M., Gelles, R. and Berker, A. (1991). Improved performance of paving asphalts by polymer modification. *Journal of the Association of Asphalt Paving Technologists*, 60, 43-79.
9. Dehouche, N., Kaci, M. and Mouillet, V. (2016). The effects of mixing rate on morphology and physical properties of bitumen/organo-modified montmorillonite nanocomposites. *Construction and Building Materials*, 114, 76-86. doi: 10.1016/j.conbuildmat.2016.03.151
10. Doğan, M. and Bayramli, E. (2009). Effect of polymer additives and process temperature on the physical properties of bitumen-based composites. *Journal of Applied Polymer Science*, 113(4), 2331-2338. doi: 10.1002/app.30280
11. Fang, C., Liu, P., Yu, R. and Liu, X. (2014). Preparation process to affect stability in waste polyethylene-modified bitumen. *Construction and Building Materials*, 54, 320-325. doi: 10.1016/j.conbuildmat.2013.12.071
12. Forbes, A., Haverkamp, R. G., Robertson, T., Bryant, J. and Bearsley, S. (2001). Studies of the microstructure of polymer-modified bitumen emulsions using confocal laser scanning microscopy. *Journal of Microscopy*, 204(3), 252-257.

13. García-Morales, M., Partal, P., Navarro, F. J., Martínez-Boza, F. J. and Gallegos, C. (2007). Processing, rheology, and storage stability of recycled EVA/LDPE modified bitumen. *Polymer Engineering & Science*, 47(2), 181-191. doi: 10.1002/pen.20697
14. Gingras, J., Tanguy, P., Mariotti, S. and Chaverot, P. (2005). Effect of process parameters on bitumen emulsions. *Chemical Engineering and Processing: Process Intensification*, 44(9), 979-986. doi:10.1016/j.cep.2005.01.003
15. Haddadi, S., Ghorbel, E. and Laradi, N. (2008). Effects of the manufacturing process on the performances of the bituminous binders modified with EVA. *Construction and Building Materials*, 22(6), 1212-1219. doi:10.1016/j.conbuildmat.2007.01.028
16. Handle, F., Füssl, J., Neudl, S., Grosseegger, D., Eberhardsteiner, L., Hofko, B., et al. (2014). Understanding the microstructure of bitumen: a CLSM and fluorescence approach to model bitumen ageing behavior. *The 12th ISAP International Conference on Asphalt Pavements*, Raleigh.
17. Handle, F., Grothe, H. and Neudl, S. (2012). Confocal laser scanning microscopy—observation of the microstructure of bitumen and asphalt concrete. *5th Eurasphalt & Eurobitume Congress*, Istanbul. Retrieved March 30, 2020, from https://publik.tuwien.ac.at/files/PubDat_211706.
18. Hatakeyama, T. and Quinn, F. (1999). *Thermal analysis*. Wiley, New York.
19. Hou, Y., Wang, L., Wang, D., Guo, M., Liu, P. and Yu, J. (2017). Characterization of bitumen micro-mechanical behaviors using AFM, phase dynamics theory and MD simulation. *Materials*, 10(208), 1-16. doi:10.3390/ma10020208
20. Kaya, D., Topal, A. and McNally, T. (2019a). Relationship between processing parameters and aging with the rheological behaviour of SBS modified bitumen. *Construction and Building Materials*, 221, 345-350. doi:10.1016/j.conbuildmat.2019.06.081
21. Kaya, D., Topal, A. and McNally, T. (2019b). Correlation of processing parameters and ageing with the phase morphology of styrene-butadiene-styrene block co-polymer modified bitumen. *Materials Research Express*, 6(10), 1-24. doi:10.1088/2053-1591/ab349c
22. Kaya, D., Topal, A., Sengoz B. and Aghazadeh, P. (2018). Short Term and Long Term Aging Performance Effects of Mixing Conditions on the Rheological Characteristics of Styrene-Butadiene-Styrene Modified Bitumen. *The 13th ISAP International Congress on Advances in Civil Engineering*, Izmir, Turkey.
23. Kaya, D., Topal, A., Gupta, J. and McNally, T. (2020). Aging effects on the composition and thermal properties of styrene-butadiene-styrene (SBS) modified bitumen. *Construction and Building Materials*, 235, 117450. doi:10.1016/j.conbuildmat.2019.117450
24. Kök, B. V., Yılmaz, M., Kuloğlu, N. and Alataş, T. (2011). Investigation of the Rheological Properties of SBS Modified Binder Produced by Different Methods. *Sigma*, 29, 272-288.
25. Lambert, J. B. (2005). The 2004 Edelstein award address, The deep history of chemistry. *Bulletin for the History of Chemistry*, 30, 1-9.
26. Larsen, D. O., Alessandrini, J. L., Bosch, A. and Cortizo, M. S. (2009). Micro-structural and rheological characteristics of SBS-asphalt blends during their manufacturing. *Construction and Building Materials*, 23(8), 2769-2774. doi:10.1016/j.conbuildmat.2009.03.008
27. Lee, Y., France, L. M. and Hawley, M. C. (1997). The effect of network formation on the rheological properties of SBR modified asphalt binders. *Rubber Chemistry and Technology*, 70(2), 256-263. doi:10.5254/1.3538430

28. Liu, Y., Zhang, J., Chen, R., Cai, J., Xi, Z. and Xie, H. (2017). Ethylene vinyl acetate copolymer modified epoxy asphalt binders: phase separation evolution and mechanical properties. *Construction and Building Materials*, 137, 55-65. doi:10.1016/j.conbuildmat.2017.01.081
29. Loeber, L., Sutton, O., Morel, J., Valleton, J. M. and Muller, G. (1996). New direct observations of asphalts and asphalt binders by scanning electron microscopy and atomic force microscopy. *Journal of Microscopy*, 182(1), 32-39. doi:10.1046/j.1365-2818.1996.134416.x
30. Mahboob Kanafi, M., Kuosmanen, A., Pellinen, T. K. and Tuononen, A. J. (2015). Macro- and micro-texture evolution of road pavements and correlation with friction. *International Journal of Pavement Engineering*, 16(2), 168-179. doi:10.1080/10298436.2014.937715
31. Martín-Alfonso, M., Partal, P., Navarro, F., García-Morales, M., Bordado, J. and Diogo, A. (2009). Effect of processing temperature on the bitumen/MDI-PEG reactivity. *Fuel Processing Technology*, 90(4), 525-530. doi:10.1016/j.fuproc.2009.01.007
32. Mohan, S. A., Woldekidan, M. F. and Qiu, J. (2013). Effects of mixing procedures on the properties of polymer modified bitumen. *In Proceedings of the International Conferences on the Bearing Capacity of Roads, Railways and Airfields*, 687-698.
33. Navarro, F., Partal, P., Martínez-Boza, F. and Gallegos, C. (2007). Influence of processing conditions on the rheological behavior of crumb tire rubber-modified bitumen. *Journal of Applied Polymer Science*, 104(3), 1683-1691. doi:10.1002/app.25800
34. Newman, J. K. (1998). Dynamic shear rheological properties of polymer-modified asphalt binders. *Journal of Elastomers & Plastics*, 30(3), 245-263. doi:10.1177/009524439803000305
35. Ortega, F., Navarro, F., García-Morales, M. and McNally, T. (2015). Thermo-mechanical behaviour and structure of novel bitumen/nanoclay/MDI composites. *Composites Part B: Engineering*, 76, 192-200. doi:10.1016/j.compositesb.2015.02.030
36. Reading, M., Luget, A. and Wilson, R. (1994). Modulated differential scanning calorimetry. *Thermochimica Acta*, 238, 295-307. doi:10.1016/s0040-6031(94)85215-4
37. Rozeveld, S. J., Shin, E. E., Bhurke, A., France, L. and Drzal, L. T. (1997). Network morphology of straight and polymer modified asphalt cements. *Microscopy Research and Technique*, 38(5), 529-543. doi:10.1002/(sici)1097-0029(19970901)38:5<529::aid-jemt11>3.0.co;2-o
38. Sam, Z., Lin, L. and Ashok, K. (2009). *Materials Characterization Techniques*. Taylor & Francis Group Cap, 7, 177-205.
39. Shaffie, E., Arshad, A. K., Alisibramulisi, A., Ahmad, J., Hashim, W., Abd Rahman, Z. and Jaya, R. P. (2018). Effect of mixing variables on physical properties of modified bitumen using natural rubber latex. *International Journal of Civil Engineering and Technology*, 9, 1812-1821.
40. Shafii, M. A., Veng, C. L. Y., Rais, N. M. and Ab Latif, A. (2017). Effect of blending temperature and blending time on physical properties of NRL-modified bitumen. *International Journal of Applied Engineering Research*, 12(13), 3844-3849.
41. Shenoy, A. (2001). Determination of the temperature for mixing aggregates with polymer-modified asphalts. *International Journal of Pavement Engineering*, 2(1), 33-47. doi:10.1080/10298430108901715
42. Skoog, D. and Leary, J. (1996). *Instrumentelle Analytik*. Springer Verlag, Berlin.

43. Soenen, H., Besamusca, J., Fischer, H. R., Poulikakos, L. D., Planche, J., Das, P. K., et al. (2014). Laboratory investigation of bitumen based on round robin DSC and AFM tests. *Materials and Structures*, 47(7), 1205-1220. doi:10.1617/s11527-013-0123-4
44. Takamura, K. and Heckmann, W. (1999). Polymer network formation in the emulsion residue recovered by forced air drying. *The 2nd International Symposium on Asphalt Emulsion Technology*. Retrieved March 30, 2020 from <https://s3.amazonaws.com/academia.edu.documents>.
45. Wang, M. and Liu, L. (2017). Investigation of microscale aging behavior of asphalt binders using atomic force microscopy. *Construction and Building Materials*, 135, 411-419. doi:10.1016/j.conbuildmat.2016.12.180
46. Wegan, V., (2001) "*Effect of Design Parameters on Polymer Modified Bituminous Mixtures*," Danish Road Institute
47. Yoon, S., Bhatt, S., Lee, W., Lee, H. Y., Jeong, S. Y., Baeg, J., et al. (2009). Separation and characterization of bitumen from Athabasca oil sand. *Korean Journal of Chemical Engineering*, 26(1), 64-71. doi:10.1007/s11814-009-0011-3
48. Yu, J.-Y., Feng, Z.-G., and Zhang, H.-L. (2011). *Ageing of polymer modified bitumen (PMB)*. In *Polymer modified bitumen* (pp. 264-297). Woodhead Publishing, Cambridge.
49. Zhang, H., Yu, J., Wang, H. and Xue, L. (2011). Investigation of microstructures and ultraviolet aging properties of organo-montmorillonite/SBS modified bitumen. *Materials Chemistry and Physics*, 129(3), 769-776. doi:10.1016/j.matchemphys.2011.04.078

