JST: Engineering and Technology for Sustainable Development
Volume 32, Issue 2, April 2022, 016-023

Synthesis of Fatty Acid Amide from Waste Cooking Oil as an Additive for Asphalt Binder

Nguyen Anh Vu*, Nguyen Han Long, Nghiem Thi Thuong
Hanoi University of Science and Technology, Hanoi, Vietnam
**Email: vu.nguyenanh@hust.edu.vn*

Abstract

Organic additives, i.e., fatty acid amide compounds, are typically used to reduce the viscosity of asphalt mixture at high-temperatures working operation. Present work focuses on preparing fatty acid amide from waste cooking oil and its characterization as an additive for bitumen. The role of synthesized fatty acid amide as an additive for bitumen was tested on the bitumen 60/70 penetration grade sample. The fatty acid amide was synthesized and characterized by FT-IR and NMR spectroscopy. It showed that the fatty acid amide was successfully prepared from the waste cooking oil due to the presence of the characteristic functional groups. The binders made from fatty acid amide and bitumen with different content of fatty acid amide were prepared and tested. It demonstrated that the kinetic viscosity of the binder reduced by 23 % at 0.7 wt% additive concentration at 140 ºC. Moreover, the penetration and softening point of the binder was also improved, which enhance the binder's physical properties when used at target temperatures.

Keywords: Viscosity, binder, organic additive and bitumen

1. Introduction

Asphalt mixing is the most common process in the construction industry. It is the process of mixing adhesive and aggregates. There are three standard asphalt mixing techniques: Hot Asphalt Concrete – Hot Mix Asphalt (HMA), warm Asphalt concrete – Warm Mix Asphalt (WMA), and cold Asphalt Concrete – Cold Mix Asphalt (CMA) [1]. HMA technology requires large energy consumption for transportation, causing emissions of hydrocarbon pollution, directly affecting the health of workers and operations, while, WMA technology allows the asphalt mixture to operate stably, with good physical properties, reducing construction time and creating a safe working environment for workers. The emission reduction, smog, and smell also allow the asphalt production station and the mixture of asphalt materials to be placed near the construction area, reducing the shipping distance, avoiding traffic jams and reducing the cost of transportation.

HMA is a high-temperature mixing process of 155-165 ºC. It leads to the use of more heat-burning and adversely affects the environment [2]. WMA was produced at a lower temperature than the HMA mixture from about 28-45 ºC, with the technical specification is equivalent to HMA. WMA technology is one of the critical solutions contributing to the global warming depreciation and the construction and maintenance of roads in many countries worldwide [3,4]. The announcement showed that the exhaust emissions by HMA contain polycyclic aromatic hydrocarbons (PAH) and some substances that adversely affect reproductive health and the likelihood of carcinogenic. With WMA technology, the toxic gas is reduced by 50 % compared to the HMA technology. Furthermore, the energy consumption of WMA technology is 60 % compared to the HMA.

So far, WMA technology can be classified into three main categories: (1) foam generation technology, in which the foaming caused by water is put into the asphalt concrete mixture during mixing, (2) organic additives which reduces the viscosity of asphalt binder (3) chemical additives which create coatings aimed at reducing the surface tension of the aggregate [5].

A long chain of hydrocarbon atoms usually forms organic additives, and it can reduce the viscosity of the asphalt binder when it is heated to its melting point. Organic additives have a long carbon chain larger than C45. The longer the carbon chain, the higher the melting point [6]. Currently, there are several types of organic additives used in WMA technology, such as Fischer-Tropsch Wax [7, 8], Montan Wax [2, 9].

Waste cooking oil, a by-product from cooking and frying activities, could be used as a good rejuvenator since it contains lighter oil fractions similar to asphalt. Every year, a lot of waste cooling oil is generated. Waste cooking oil disposal is a primary concern since it may cause environmental and municipal problems. Thus, recycling waste cooking oil in asphalt binder may be helpful for sustainable development [10-13].

The study aimed to evaluate the effect of organic

ISSN 2734-9381
https://doi.org/10.51316/jst.157.etsd.2022.32.2.3
Received: October 4, 2021; accepted: March 13, 2022

additives on the properties of the binder, in which the organic additive was synthesized from waste cooking oil. For this purpose, a grade 60/70 bitumen from Shell was characterized before and after adding additives.

2. Experiment

2.1. Materials

Waste cooking oil used in this work is waste sunflower oil (SO). Acid sulfuric, methanol, toluene, acetone, diethyl amine, NaOH and CaO were analytical grade.

In this study a population bitumen produced from Shell with 60/70 penetration was selected. The properties of the bitumen was evaluated to understand its behavior and susceptibility to modification. The original properties values of the bitumen grade are used as control.

2.2. Synthesis of Fatty Acid Amide Additive

The additive, a fatty acid amide (FAA), was synthesized from waste cooking oil following by procedure shown in Fig. 1. First, the waste SO was pretreated by filteration to remove the sediment. After that, it was mixed with methanol (1:1 volume ratio). KOH was then added into the mixture with the percentage of 2 wt% of the total weight. The reaction was under reflux for 12 hours at 60 ºC. After completion, the mixture was separated into two layers. The product was recovered by extraction to remove the glycerin layer. Next, the excess of H_2SO_4 was washed until it was removed entirely. The obtained fatty acid methyl ester (FAME) was dried at 80 ºC.

To prepare FAA, the as-prepared FAME was allowed to react with diethyl amine in the presence of a CaO as a catalyst [14]. Next, the FAME and diethyl amine were added into a reaction vessel in the presence of the appropriate amount of NaOH/CaO catalyst (2 wt% of the total weight). The reaction was carried out for 1.5 hours at 110 ºC. After that, the product in liquid form was separated from the catalyst and washed by recrystallization in toluene/acetone solvent (7:3 volume ratios) at 5 ºC. Finally, the product was purified by centrifugation to obtain the pure product, called fatty acid amide (FAA). The FAA, then, was used as an additive to prepare various blends with a bitumen 60/70 penetration grade at different concentrations.

The synthesized FAA, FAME were characterized with FT-IR (JASCO 4600) to identify the functional groups. The measurements were carried out at room temperature, from 400 to 4000 cm^{-1}, with a resolution of 4 cm^{-1}. The product, FAME, was further characterized by solid-state NMR spectroscopy (JNM 400 MHz FT-NMR, JEOL) to verify the chemical structure. The solid-state NMR was performed with a CP/MAS probe at a spinning rate of 6 kHz. The number of scans is 1000.

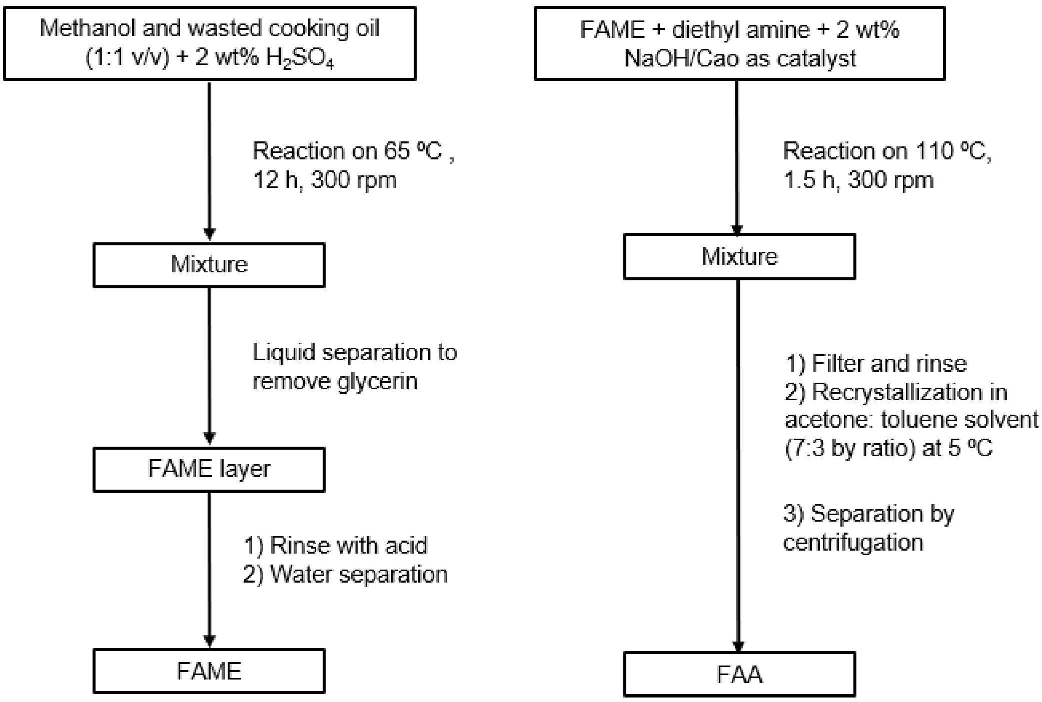

Fig. 1. Synthesis procedure of FAA from waste cooking oil

2.3. Characterization of Bitumen and Bitumen/Additive Blends

Bitumen/additive blends were prepared with the following procedure. The bitumen was pre-heated to form the liquid phase at 120 ºC in a glass cup. The additive was added into the bitumen liquid at 150 ºC with different concentrations (0.1; 0.2; 0.5; 1; 1.2; 1.5; 2 wt%) under continuous stirring (300 rpm) at constant temperature (150 ºC). The mixing was carried out at different stirring times, such as 15, 30, 45, 60, to 120 mins.

The characteristics of bitumen and bitumen/additive mixtures were assessed by following the standard tests. First, the needle penetration test was performed according to D5-20. Next, the softening point (ring and ball method) was determined following ASTM E28-18. Finally, the kinetic viscosity was measured following ASTM 2170-18 using Canon-350-456A viscometer.

3. Result and Discussion

3.1. FTIR Analysis of Synthesized FAA

Fig. 2 illustrates the image of the synthesized FAA from waste cooking oil. It could be seen that the FAA is a pale yellow solid, which is distinguished from the liquid form of waste cooking oil. That means the successful conversion of the waste cooking oil to FAA. FTIR spectra are used to identify the functional groups in the FAA during the preparation.

Fig. 3 shows FTIR spectrum for FAME and FAA. In the spectrum, there are several peaks appeared for both FAME and FAA.

In the IR spectrum of FAA, the peak vibrated at 1639 cm^{-1} corresponds to C=O (amide band) functional groups present in the amide structure. In the IR spectrum of FAME and compared to the IR spectrum of FAA, the peak located at 1742 cm^{-1} that denoted the C=O stretching vibration of the ester functional group has completely disappeared and been replaced by a vibration signal at 1639 cm^{-1}. The shift from the peak at 1742 cm^{-1} to the peak at 1639 cm^{-1} peak was similar to that reported in the previous work [11]. It is confirmed that FAA was successfully synthesized from FAME. The additional vibration peak at 3308 cm^{-1} indicated the stretching vibrations of N-H linkage. This may be due to the presence of residual diethyl amine.

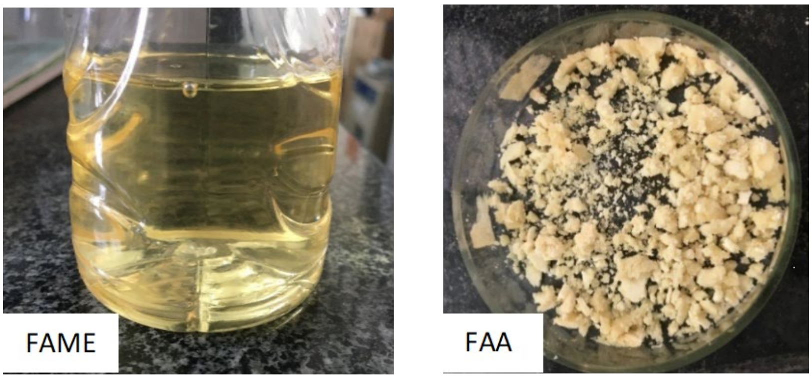

Fig. 2. Image of the synthesized fatty acid methyl ester (FAME) and fatty acid amide (FAA)

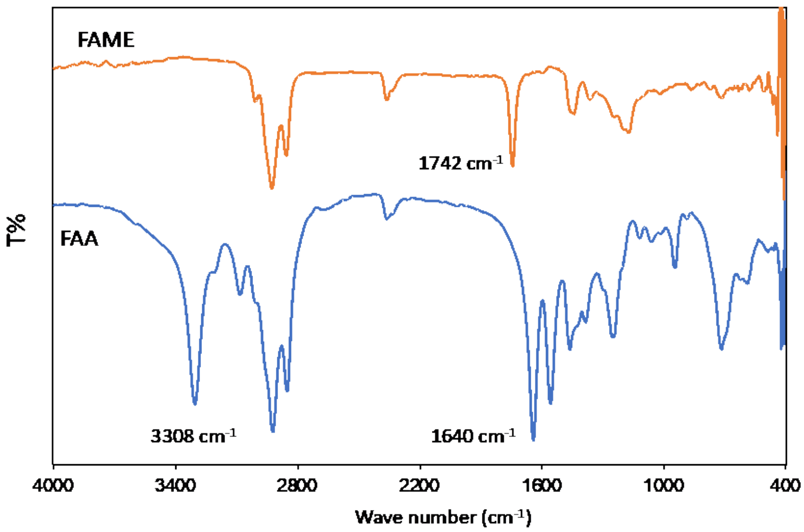

Fig. 3. FTIR spectra of fatty acid amide (FAA) and fatty acid methyl ester (FAME)

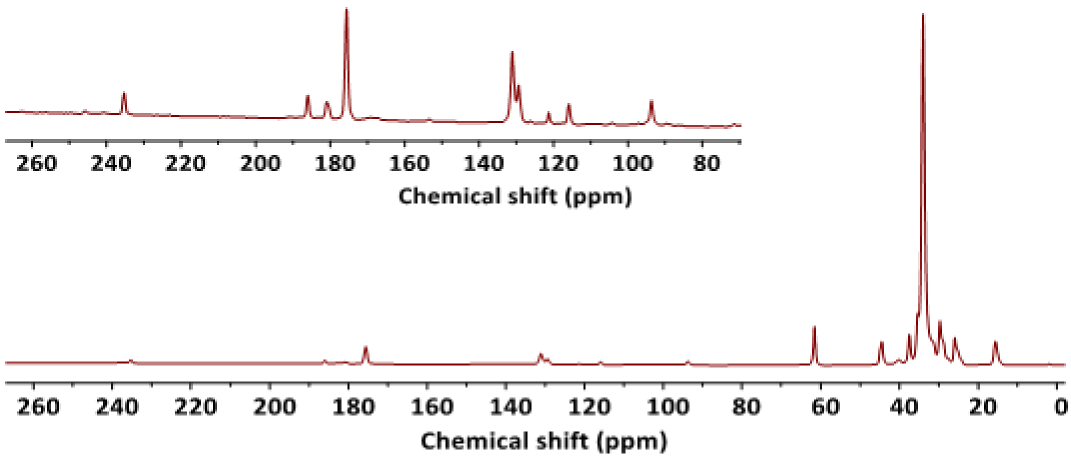

Fig. 4. ^{13}C-NMR CP/MAS of FAA

Table 1. Softening points and penetration for mixtures of bitumen 60/70 and FAA additive

Additive concentration (wt%)	Softening points (ºC)	Penetration (1/10 mm)/Δ (%)
0	47	61
0.1	47	61/0
0.2	48	58.7/3.7
0.3	53	52.3/14.2
0.5	57	49.3/19.1
0.7	58	48.2/20.1
1	59	47.8/21.6

3.2. NMR Analysis of Synthesized FAA

The structural characteristic of the fatty acid amide functional groups was further investigated by using an NMR solid-state. Fig. 4 shows ^{13}C-NMR CP/MAS spectra for FAA. The signals correspond to methylene carbons in the long alkyl chain of fatty acid appeared at around 22-34 ppm (aliphatic methylene carbons, $-CH_2-$). The two signals at 16 and 41 ppm were assigned to the methyl and methylene carbons linked to C=C bonds, respectively. Also, the signals at 129 and 130 ppm belong to methine (=CH) and quaternary (=C-) carbon atoms of the C=C bond [12]. These results suggested FAA contains unsaturated fatty acid. The ^{13}C-signal that appeared at 61 ppm may be assigned to carbon atom linking to -OH group, derived from the ring opening of epoxidized C=C groups. The ^{13}C-signal at 175 ppm was given to the carbon atom of C=O (amide) [11]. The signal at 181-186 ppm may be assigned to the carbon atom of the residual carboxyl group of fatty acids. These assignments gave more precise evidence about the structure of FAA, which was synthesized from FAME.

3.3. Characterization of Synthesized FAA as Additive for Asphalt Binder

3.3.1. Effect of additive concentrations

Table 1 shows the softening points and needle penetration for bitumen/FAA additive blends at different additive concentrations. The result shows that the penetration of samples decreased when increasing additive concentration. In contrast, the softening point of the blends slightly increased with an increase in the concentration of additives. Since the softening point value gives the critical information for the binder at summertime and characterizes the temperature at which the bitumen starts flowing. Therefore, the increase in the softening point suggests the modified bitumen could work at the high-temperature condition.

Viscosity is a property that is used to characterize the shear resistance of the binder with an external force and a specified rotation using a viscometer. Fig. 5 shows the effect of temperature on the kinetic viscosity of the binder at different additive concentrations. As can be seen, there is a decrease in the binder viscosity with the temperature at all studied additive concentrations. At each temperature, the binder kinetic viscosity also decreased as concentration increased from 0 to 1.5 wt%. At 145 ºC, there are a slight decrease and difference in the binder viscosity of all the samples. Meaning that, at a temperature higher than 145 ºC, the effect of additive concentration in decreasing the binder viscosity is not so significant.

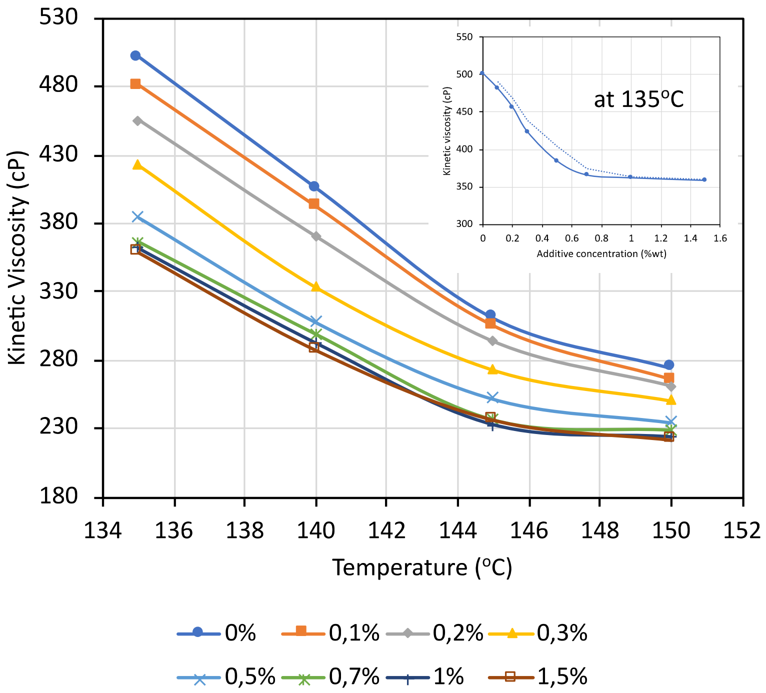

Fig. 5. Effect of temperature to kinetic viscosity at different additive concentrations

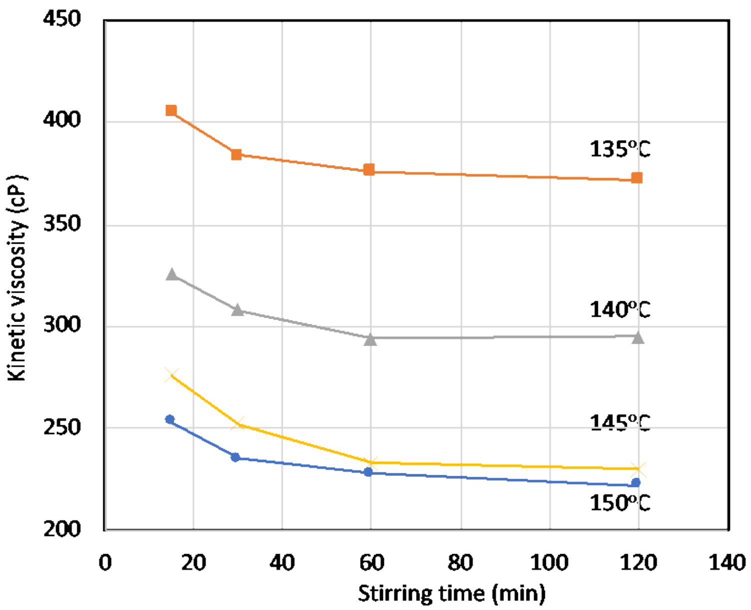

Fig. 6. Effect of temperature to kinetic viscosity at different stirring times

Fig. 5 also illustrated the impact of additive concentrations on the kinetic viscosity of the binders at 135 ºC. The binder viscosity decreased until the additive concentration of 0.7 wt% reached constant from 0.7 wt% to 1.5 wt%. Therefore, the suitable concentration of the additive was 0.7 wt%. The reduction of viscosity at 0.7 wt% additive concentration measured at 150 ºC was about 38% (from 370 cP to 230 cP). In previous work [15], the viscosity was found to reduce about 22 % at 2 wt% of oil additive measured at 150 ºC. This result showed that the FAA additive prepared in our work exhibited a better effect on the viscosity reduction that was observed for waste cooking oil additive in the literatures [15,16]. The reduction of the asphalt viscosity by adding FAA additive allows the asphalt to attain a proper viscosity to coat the aggregate and compact asphalt mixture at lower temperatures.

3.3.2. Effect of stirring time

The viscosity of the bitumen/additive mixture at 0.5 wt% at various temperatures at different stirring times were measured to determine the optimum stirring time for the preparation of the bitumen/additive mixture. The stirring times were varied from 15, 30, 60, to 120 mins at 135-150 ºC and a stirring speed of 150 rpm. The results are shown in Fig. 6. The other physical properties, such as penentration, softening points, are also determined to determine the best stirring time.

Fig. 6 shows the effect of stirring time on the kinetic viscosity of the bitumen/FAA additive at various temperatures. It is seen that the viscosity of the mixture decreased when increasing the stirring time from 15 mins to 60 mins, and it was slowly decreased when stirring time was prolonged to 120 mins. Therefore, 60 mins was a suitable stirring time for preparing the bitumen/FAA mixture to get the lowest viscosity at all studied temperatures.

The effect of stirring time on the softening point of the modified bitumen is illustrated in Fig. 7. The softening point gradually decreased as increasing stirring time, and it was almost constant from 60 mins to 120 mins of stirring. Thus, it shows that the appropriate stirring time is determined to be 60 mins.

Fig. 8 illustrates the change in penetration of the bitumen at 0.5 wt% and 1.0 wt% additive concentration with stirring time. The penetration of the binders at 0.5 wt% and 1.0 wt% slightly increased at stirring time from 15 to 60 mins. After that, it constantly reached a stirring time of 120 mins. Hence, the suitable stirring time is determined to be 60 mins to get good penetration.

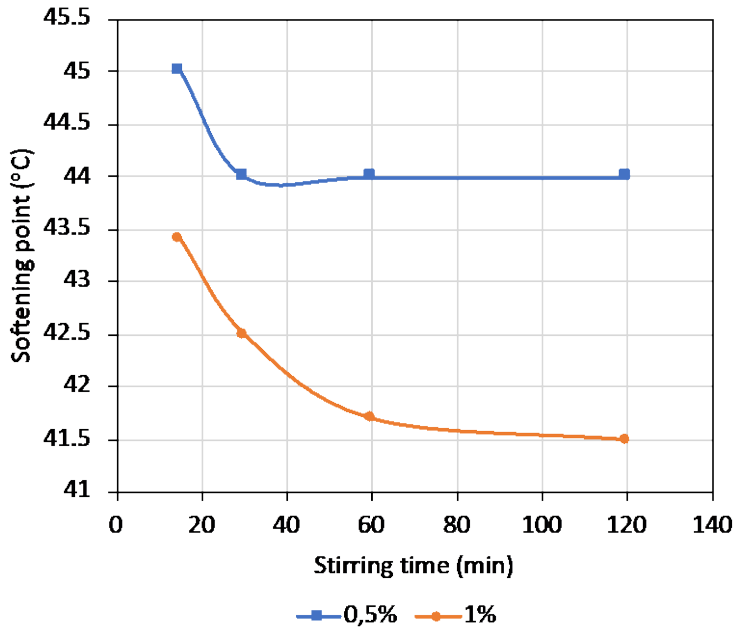

Fig. 7. Effect of stirring times to softening point

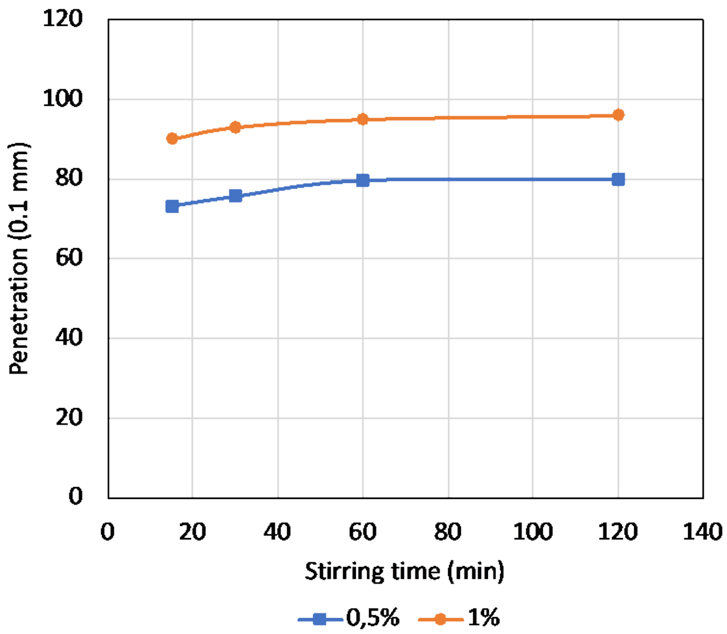

Fig. 8. Effect of stirring times to the needle penetration

4. Conclusion

This research studied the effect of FAA synthesized from waste cooking oil as an additive for bitumen 60/70 penetration grade. Several conventional tests were used to evaluate the viscosity, penetration, and softening point of the products. When the concentration of additive increased, the softening point slightly increased; however, the penetration decreased. The other important parameter of the evaluation of bitumen properties is viscosity. The FAA additives changed the binder viscosity to lower values, primarily to the original bitumen viscosity. In particular, the binder viscosity is reduced by 23% at 140 °C with 0.7 wt% of additive. Thus, it concluded that the final asphalt mixture's workability and properties could be enhanced by the additives prepared from waste products such as waste cooking oil.

References

[1] EAPA. The Use of Warm Mix Asphalt-EAPA Position Paper. European Asphalt Pavement Association, 2010. https://eapa.org/wp-content/uploads/2018/07/EAPA-paper-Warm-Mix-Asphalt-version-2014-1.pdf

[2] J. D'Angelo, E. Harm, J. Bartoszek, G. Baumgardner, M. Corrigan, J. Cowsert, T. Harman, M. Jamshidi, W. Jones, D. Newcomb, B. D. Prowell, R. Sines, B. Yeaton, Warm-Mix Asphalt: European Practice. Report No.FHWA-PL08-007, Alexandria, USA, 2008.

[3] A. Vaitkus, D. Cygas, A. Laurinavicius, Z. Perveneckas, Analysis and evaluation of possibilites for the use of warm mix asphalt in Lithuania. Baltic J. Road Bridge Eng. 2009, 4(2), pp. 80-86. https://doi.org/10.3846/1822-427X.2009.4.80-86

[4] N. Bueche, Warm asphalt bituminous mixtures with regards to energy, Emissions and Performance Young Researchers Seminar (YRS) LAVOC-CONF-2010-002, Torino, Italy, 2009.

[5] A. Vaitkus, V. Vorobjovas, L. Ziliut, The research on the use of warm mix asphalt for asphalt pavement structures, Road Department, Vilnius Gediminas Technical University, Vilnius, Lithuani, 2009.

[6] G. C. Hurley, B. D. Prowell, Evaluation of evotherm for use in warm mix asphalt. national center for asphalt technology. Report 06-02. Auburn University, Auburn, USA, 2006.

[7] J. G. Speight, Chapter 1 - nomenclature and terminology, Editor(s): James G. Speight, Asphalt Materials Science and Technology, Butterworth-Heinemann, 2016, pp. 3-43. https://doi.org/10.1016/B978-0-12-800273-5.00001-5

[8] X.Y. Huang, B.Y. Li, Mixing temperature design and properties evaluation for SMA-13 mixture. IOP Conf. Ser.: Mater. Sci. Eng, 2017, 167, pp. 012057. https://doi.org/10.1088/1757-899X/167/1/012057

[9] H.M.R.D Silva, J.R.M. Oliveira, C.I.G. Ferreira, P.A.A. Pereira, Assessment of the performance of warm mix asphalts in road pavements. Int. J. Pavement Res. Technol. 2010, 3(3), pp. 119-127.

[10] M.C. Rubio, G. Martínez, L. Baena, F. Moreno, Warm mix asphalt: An overview. J. Clean. Prod, 2012, 24, pp. 78-84. https://doi.org/10.1016/j.jclepro.2011.11.053

[11] B.J. Daniela, P. J. Youngblood, J. C. Martinez. Synthesis and characterization of fatty acid amides from commercial vegetable oils and primary alkyl amines for phase change material applications, ACS

Sustainable chemistry and Engineering 2020 8(36), pp. 13683-13691. https://doi.org/10.1021/acssuschemeng.0c03626

[12] P. Caputo, A. A. Abe, V. Loise, M. Porto, P. Calandra, R. Angelico, C. O. Rossi, The role of additives in warm mix asphalt technology: an insight into their mechanisms of improving an emerging technology, Nanomaterials. 2020, 10, pp. 1202. https://doi.org/10.3390/nano10061202

[13] C. Rodrigues, S. Capitao, L. Picado-Santos, A. Almeida, Full recycling of asphalt concrete with waste cooking oil as rejuvenator and LDPE from urban waste as binder modifier, Sustainability. 2020, 12, pp. 8222. https://doi.org/10.3390/su12198222

[14] J. Zhang, D. Cai, S. Wang, Y. Tang, Z. Zhang, Y. Liu, X. Gao. efficient method for the synthesis of fatty acid amide from soybean oil methyl ester catalysed by modified CaO, The Canadian Journal off Chemical Engineering. 2014, 92, pp. 871–875. https://doi.org/10.1002/cjce.21948

[15] W. N. A. Wan Azahar, M. Bujang, R.P. Jaya, M.R. Hainin, A. Mohamed, N. Ngad, D.S. Jayanti, The potential of waste cooking oil as bio-asphalt for alternative binder - An overview, Jurnal Teknologi. 2016, 78, pp. 111-116. https://doi.org/10.11113/jt.v78.8007

[16] M. Zargar, E. Ahmadinia, H. Asli and M.R. Karim. Investigation of the possibility of using waste cooking oil as a rejuvenating agent for aged bitumen, Journal of Hazardous Materials. 2012, 233–234, pp. 254–258.

https://doi.org/10.1016/j.jhazmat.2012.06.021