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RESEARCH ARTICLE

Investigation of effects of Cocamide Diethanolamide chemical on physical and rheological properties of bituminous binder

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ABSTRACT In this study, bituminous binder was modified with Cocamide Diethanolamide chemical, a non-ionic surfactant, and the physical and rheological properties of modified binders were investigated. In addition, Cocamide Diethanolamide has been used for the first time to modify bituminous binder, and this situation makes the study distinctive. Bituminous binder was modified more than once with the chemical by changing modification parameters and using certain additive ratios (1%, 3%, and 5%). The effects of different modification parameters and chemical additive on modified samples were investigated with conventional bitumen tests (softening point, penetration, ductility) and Superpave tests (rotational viscometer, rolling thin film oven test, pressure aging vessel, dynamic shear rheometer, bending beam rheometer). In addition, the structural characteristics of the reference binder and modified samples were examined by X-ray diffraction, Fourier Transform Infrared Spectroscopy, scanning electron microscopy, and energy dispersive X-ray spectroscopy. The examinations showed that Cocamide Diethanolamide softens bituminous binder and lowers processing temperatures. In addition, compared to reference binder, rutting resistances of modified bituminous binders decreased with the increase of additive ratio. However, modification with Cocamide Diethanolamide increased the resistance to fatigue cracks and thermal cracks.

KEYWORDS Cocamide Diethanolamide, bitumen modification, rheology, Superpave tests

1 Introduction

Although bituminous hot mixtures contain a relatively small amount of bituminous binder, this material plays an important role in achieving the expected performance from pavements. Bituminous binder exhibits variable behaviors depending on climate and environmental conditions because of its thermoplastic structure [1]. These variable behaviors cause decreases in the performance of the pavement. These decreases in the performance cause deformations in the pavement. Deformations in the form of rutting, fatigue cracks, and thermal cracks are the most common deformations that occur mainly due to bituminous binder properties. To prevent these deformations, the pavements should be constructed by using bituminous binders which have the proper performance grade (PG). The climate and traffic conditions of the region where the pavement will be constructed should be considered, too [2].

Another way to prevent deformations and improve pavement performance is the modification of bituminous binders with various additives. Polymers are one of the most used additive materials for the modification of bituminous binders [3–6], and usage of many types of them (including their wastes) can be seen in the literature [5–16]. It is known that the modification of bituminous binders with polymers increases the deformation resistance of flexible pavements. However, improvement of the bituminous binder or mixture performance is also possible with the usage of different types of additives such as nanomaterials [17–22], fillers [23–28], waste and recycled materials [29–38], geopolymers [39,40], fibers [41–44], organic-based compounds [1,45–48] and chemicals [49–54]. According to the results of the different

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studies in literature, it can be said that usage of these additives affected the physical, mechanical, and rheological properties of bituminous binder or performance of hot mix asphalt (HMA). For example, modification of bituminous binder using additives such as polymers and surfactants is known to increase the deformation resistance of flexible pavements [45]. The usage of various nanomaterials for modification in different studies has provided an increase in the rutting resistance of the bituminous binders [19]. In another study, it has been expressed that the usage of bituminous binders modified with fillers can increase high-temperature performance and resistance to water, cracking, and fatigue of HMA [28]. In addition to these, waste and recycled materials are used more and more in the pavement. Because the usage of these materials both improves pavement properties and contributes to the prevention of environmental pollution [30]. Although geopolymers, one of the additives mentioned above, have been introduced to use in asphalt pavements in recent years, it is stated that this additive is important in terms of environment, sustainability, and economy [39]. Since various fibers have different properties from each other, it was observed that they could create different effects on bituminous binders due to their usage in bitumen modification [41,44]. It has been seen that many different organic-based compounds used in the modification of bituminous binders reduce problems arising from moisture which causes a significant decrease in stripping resistance. In addition, tests have shown that organic-based compounds soften the bituminous binder. Even if such additives did not contribute positively to the high-temperature performance of the bituminous binder, they have improved rheological properties of binder at low temperatures [1,47]. In another study, phospholipids have been used as additives in modification to improve the high-temperature mechanical properties of bituminous binder and the adhesion efficiency to aggregate surfaces. In terms of adhesion efficiency, it has been found that the bituminous binder modified with phospholipids in liquid form gives better results than that with phospholipids in powder form [49]. In addition to all these, in some cases, it may be necessary to use two or more additives together to improve the properties of the bituminous binder/HMA or provide more than one benefit at the same time [55–60]. In addition to the additives mentioned so far, it is considered that surfactant additives are also suitable for modification of bituminous binders as they can also meet the mentioned expectations while protecting the mechanical properties of the mixture.

Surfactants are chemical compounds with a surface activity that lowers the interfacial or surface tension when dissolved in a liquid. In the case of mixing them with bituminous binders, the same mechanism also steps in and causes a decrease in the surface tension of the binders. Another factor that affects the surface tension is the temperature. As the temperature increases, the intermolecular attraction forces decrease and this means that the surface tension decreases. It is known that high temperatures are required for bituminous binders to become usable in HMA. The intermolecular attraction forces and hence surface tensions of bituminous binders reduce even more with the effect of both high temperature and surfactant addition. Thus, as the viscosity of bituminous binders modified with surfactants also decreases, the bituminous binders become workable at lower temperatures. In addition, surfactants act as a dispersing agent for asphaltenes which is one of the main components that causes the bituminous binder to have high viscosity. In a study that used four different types of surfactants, it was found that the interaction of anionic surfactants with asphaltenes is productive, and this interaction can reduce aggregation of asphaltenes [61]. Again, this means that a reduction in viscosity of bituminous binder can occur. Therefore, the interest in research studies conducted on the usage of surfactants to modify the bitumen is increasing. Considering the studies on this context, it can be seen that organic compounds which are derived from alkyl benzene and have both hydrophobic and hydrophilic properties (amphiphilic), have been recognized as a forceful surfactant that can be effective on asphaltene structures in bitumen. The usability of such an additive named linear alkyl benzene sulfonic acid (LABSA) with the aim of bitumen modification and its effects on the rheological properties of bitumen at different temperatures were evaluated. Consequently, this anionic surfactant increased the resistance of bitumen to rutting, fatigue, and low-temperature cracks [62]. The effects of usage rates of another anionic surfactant with the same properties (amphiphilic) to the behaviour of modified bitumen were also investigated. Regardless of the mixing temperature, rheologic and thermomechanical properties of modified samples improved as the surfactant additive rate increased [63]. Rediset, which is another surfactant additive, decreased the viscosity of the bitumen; accordingly, it decreased the mixing and compaction temperatures of HMA. It was also found that this additive affects positively the bonding between bitumen and aggregates at medium and high temperatures [64]. In addition to this, researchers have found that the effects of Rediset on the high-temperature properties of bituminous binders depend on binder type, additive rate, and loading type [65]. Another surfactant-based chemical additive which was used in bitumen modification has decreased the surface free energy, and like Rediset, this additive has also increased the adhesion between bituminous binder and aggregates [66]. When it comes to reducing of viscosity, surfactant warm mix additives come into prominence. A study analyzed the effects of a surfactant warm mix additive on the physical and rheological properties of high-viscosity asphalt. The results showed that the additive increased the workability of high-viscosity asphalt by reducing the viscosity. In addition, the rate of the surfactant warm mix additive may affect the performance of the high-viscosity asphalt at critical temperatures. So, it is emphasized that the rate of this type of additive should be determined carefully. It was also found that such additives can slightly increase the lubrication between the asphalt molecules, allowing the bitumen to cover the aggregates more easily [67,68].

Surfactants are sometimes used in line with different purposes in bitumen modification. In this sense, the usability of different surfactant additives as rejuvenator agents on aged bituminous binders was examined. According to the obtained results, it has been seen that certain rates of these surfactant additives can be used for the rejuvenation of aged bituminous binders [69,70]. In another study, three different non-emulsifiable bituminous binders were tried to make emulsifiable by using three different additives; one of them was a surfactant. It was indicated that the surfactant additive used in this study may provide that the binder can be emulsifiable if used for the appropriate bituminous binder [71].

In some cases, surfactants are used together with other additives to modify bitumen. For example, the bituminous binder was modified by using a surfactant additive and polyurethane separately and together. Then modified samples were investigated thermally and chemically. Consequently, it has been determined that both of the modifiers are suitable for bitumen modification [72]. Similarly, the usage of surfactant additive and synthetic wax together with the aim of bitumen modification affected positively bitumen properties. Moreover, it has been determined that both of the additives can be used in asphalt mixtures, such as half-warm mix asphalt (HWMA) [73]. Another study includes examining the effects of two different surfactant additives on the rheological properties of binders modified with layered double hydroxides (LDHs). These additives improved the properties and behaviors of LDHs modified bitumen at low-temperature conditions [74]. Surfactant additives are commonly used to improve the engineering properties of foamed bitumen as well. Researchers have investigated the effects of using different foaming processes and varying surfactant additive rates on polymer-modified bitumen. The results showed that the usage of surfactant additives is beneficial in terms of high-temperature performance and fatigue resistance of foamed bitumen, as long as it does not exceed certain rates [75]. When two different surfactant additives were added to the natural rubber latex (NRL) modified bitumen, and the morphological and stability properties of the obtained samples were examined, it was seen that surfactants affected positively the homogeneity and stability properties of bitumen modified with NRL [76]. In addition, the rheological properties of bituminous binder modified with crumb rubber and stable surfactants have been investigated. The results obtained from the tests indicated that the modification with the surfactant additives affects positively the viscoelastic properties of the bituminous binder [77]. Crumb rubber and surfactant additive were also used together in the asphalt mixture. In the study implemented in this direction, the optimal sequence that can be used to include the mentioned additives to the asphalt mixture has been investigated. Consequently, it was indicated that first of all, the crumb rubber should be modified with surfactant, and then the modified crumb rubber should be added to the bitumen. It has been found that the asphalt mixture prepared with the modified bitumen obtained in this way provides the best performance [78].

To increase the stability of HMA and resistance to moisture, surfactants are frequently used [79]. Also, it is known that surfactants are reducing agents that allow the production of warm mix asphalt (WMA) at low temperatures [80]. In this context, researchers have investigated the effects of a surfactant additive on the WMA binder. According to obtained results, surfactant additive increased the temperature sensitivity and softness while improving the bituminous binder's low-temperature properties. Also, the workability of the mixture increased based on the decreases in mixing and compaction temperatures [81]. The effects of the usage of three types of surfactant additives which have different properties, and the usage rates of these additives on the behavior of WMA were also investigated. Again, the results of this study have shown that surfactant additives can help reduce the processing temperatures of the asphalt mixtures [82]. The effects of a surfactant additive (imidazoline) synthesized in the laboratory on the performance of asphalt mixtures and its suitability as an additive for the manufacturing of WMA were analyzed. It has been observed that the surfactant additive did not affect the physical properties of the bituminous binder too much, but it can cause a reduction in mixing temperature. In addition, this additive caused some reduction in low-temperature performance while it improved the high-temperature performance of asphalt mixtures. According to the findings, the imidazoline surfactant has been found to be a suitable additive for WMA [83]. In another study, the modification of bituminous binder was carried out by using organic surfactant additive and different methods. It has been aimed to decrease the processing temperatures of HMA with the use of surfactant additive and adapt a HMA plant to the manufacturing of WMA. As a result of the study, it was found that the usage of surfactant additive in WMA did not cause any adverse effects on the mechanical properties of pavement. The surfactant additive has improved the adhesion properties of the mixture and made the mixture workable easily at lower temperatures [80]. As a result of the modification of the bituminous binder with another surfactant, tetrachydropirymidupropyly (THPP), it has been understood that surfactants can also affect the properties of stone mastic asphalt (SMA). The increase in the amount of THPP added to the bituminous binder has decreased the moisture susceptibility of SMA. When the same surfactant additive was used in another study, it was observed that a minor difference occurred in the physical properties of modified binders [84,85].

Due to the properties of the existing surfactants and their possible effects on the rheological properties of the bituminous binders, the usage of surfactants to modify the bituminous binder can significantly change the binder and mixture performances. Even with a small increase in the surfactant ratio during modification, changes can occur in PG values of bituminous binders. A small amount of surfactant additive can increase the adhesion between aggregates and bituminous binder, even if it does not change the physical properties of the binder [86]. Considering the results of the studies reviewed, it was observed that the modification of bituminous binders with surfactants contributed mostly to improving their resistances to low temperatures.

Based on the existence of similar studies in the literature, it can be said that the materials and modification methods used to modify the bituminous binder are of great importance to improve the performance of binder and asphalt mixture. However, there is barely any research on the physical and rheological properties of the bituminous binders modified with non-ionic surfactants. It is thought that this study will contribute to the literature in this respect. In parallel with these, this study aimed to improve the performance of the bituminous binder by using Cocamide Diethanolamide (CDEA), which is a non-ionic surfactant. When selecting this chemical as additive material, it has been effective that the properties (such as chemical structure, behavior depending on the temperature) between chemical material and bituminous binder are similar. Also, the effects of modification parameters on the physical and rheological properties of the reference bituminous binder and the samples modified with CDEA were investigated. It was predicted that changes in the modification parameters would create a slight difference on the properties of bituminous binders. Decreasing the bitumen viscosity is another purpose of using CDEA chemical. Because potential decreases in viscosity provide reductions in mixing and compaction temperatures during the preparation of HMA, which means economic gain.

Following these purposes, modification of the bitumen, which has 50/70 penetration grade with CDEA, has been carried out by using different mixing parameters (mixing rates, modification temperatures, and times) and additive ratios (1%, 3%, and 5%). The effects of different parameters on the modification were investigated by conventional test methods (softening point, penetration, and ductility). According to the results of these tests, rheological evaluation of the samples in two test sets which are thought to exhibit the most consistent behaviors have been carried out with Superpave tests (rotational viscometer (RV), rolling thin film oven test (RTFOT), pressure aging vessel (PAV), dynamic shear rheometer (DSR), and bending beam rheometer (BBR)). Moreover, X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS) were used to obtain detailed information about mechanisms and the microscopic characteristics of reference binder and modified samples.

2 Materials and methods

2.1 Materials

CDEA material obtained from Şenol Chemical was used to modify 50/70 penetration graded bituminous binder supplied by Isparta Municipality.

2.1.1 Bituminous binder

50/70 penetration graded bituminous binder was supplied by Isparta Municipality. Penetration (TS EN 1426), softening point (TS EN 1427), ductility (TS EN 13589) and specific gravity (TS EN 15326 + A1) tests were performed to determine the physical properties of the bituminous binder. In addition, to determine the performance properties of bitumen, RV (ASTM D 4402), RTFO (TS EN 12607-1), PAV (TS EN 14769), DSR (TS EN 14770) and BBR (TS EN 14771) tests were carried out. Table 1 shows the average results of these tests for reference bituminous binder.

2.1.2 Cocamide Diethanolamide

CDEA material obtained from Şenol Chemical was used to modify bituminous binder. CDEA is known as a surfactant material and has the chemical formula in the way that $CH_3(CH_2)_nC(=O)N(CH_2CH_2OH)_2$. CDEA is a water-soluble derivative of a mixture of fatty acids obtained from coconut oils. It is a non-ionic material that increases viscosity and provides foam stabilization in anionic-based systems such as soaps, shampoos, cosmetics (Fig. 1).

It has been thought that CDEA will decrease the viscosity by thinning the bituminous binder because it is a smaller molecular material compared to bitumen which has a long-chain and high-flow resistance. The properties of CDEA chemical are shown in Table 2.

Table 1 Properties of bituminous binder

test	average result	standard
penetration (0.1 mm)	64	TS EN 1426
softening point (°C)	47.3	TS EN 1427
ductility (cm)	>100	TS EN 13589
RV (cP)	–	ASTM D 4402
135 °C	373	
165 °C	106.7	
specific gravity (g/cm^3)	1.021	TS EN 15326 + A1
RTFOT (loss in mass) (%)	0.0077	TS EN 12607-1
DSR (64 °C)	–	TS EN 14770
$G^*/\sin\delta$ (Pa)	1555.65	
phase angle (°)	88.23	
BBR (–18 °C)	–	TS EN 14771
stiffness (MPa)	232.7498	
m value	0.273	

Fig. 1 Cocamide Diethanolamide (CDEA).

Table 2 Properties of CDEA chemical

property	value
boiling point (°C)	169–275
melting point (°C)	23–35
specific gravity (g/cm^3)	0.976–0.99
pH (1% solution)	9

2.2 Bitumen modification

While preparing CDEA modified binders, a temperature-controlled, high-shear mixer was used. Modifying bituminous binder with chemical at certain additive ratios (1%, 3%, and 5%) was carried out by changing the modification temperature, time, and rate parameters. Table 3 shows the test sets and changing parameters.

Table 3 Test sets and changing parameters

test set	additive ratio	modification temperature (°C)	modification time (min)	mixing speed (r/min)
1	1%	155	30	1000
	3%			
	5%			
2	1%		60	
	3%			
	5%			
3	1%		90	
	3%			
	5%			
4	1%	165	30	
	3%			
	5%			
5	1%		60	
	3%			
	5%			
6	1%		90	
	3%			
	5%			
7	1%	155	30	2000
	3%			
	5%			
8	1%		60	
	3%			
	5%			
9	1%		90	
	3%			
	5%			
10	1%	165	30	
	3%			
	5%			
11	1%		60	
	3%			
	5%			
12	1%		90	
	3%			
	5%			

2.3 Test methods

2.3.1 Conventional test methods

The effects of different parameters on modified samples were investigated by softening point, penetration, and ductility tests.

2.3.2 Superpave test methods

The effects of modification with CDEA on rheological properties of the bituminous binder were investigated by RV, RTFOT, PAV, DSR, and BBR tests.

2.3.2.1 Rotational viscometer

In the RV test, the torque required to rotate a cylindrical spindle immersed in the bituminous binder at a constant temperature and speed is measured and converted to viscosity in Pa·s [87]. The RV test informs about the workability of the bituminous binder. The test was carried out by using Brookfield Viscometer, according to ASTM D 4402 standard. The viscosity or torque measurements are taken during 3 min in 1 min intervals, and the arithmetic mean of these measurements is recorded as the viscosity value of the sample. The viscosity at 135 °C should not exceed 3 Pa·s for the original binders [88].

2.3.2.2 Aging processes with rolling thin film oven test and pressure aging vessel

RTFOT represents the short-term aging of the bituminous binder with the effect of high temperature and air flow during mixing and compaction. During the test, a thin film of bitumen is continuously rotated around the inner surface of glass bottles for 75 min in an oven which has 163 °C temperature. At the same time, hot air is injected into the bottles. After the test, the loss in mass of the sample is due to the evaporation of volatile components in the bitumen. An increase in the mass means that the binder has reacted with oxygen [87]. The test is carried out according to TS EN 12607-1 standard. At the end of the test, the samples are removed from the oven, and the two bottles are allowed to cool for approximately 1 h to determine the mass losses that have occurred. Samples in the other six bottles are stored for use in tests to determine the effects of aging.

The PAV test is used to estimate changes in bitumen properties during the service life of the pavement. This test ensures that aging of the samples which has been short-term aged by RTFOT in laboratory conditions for 20 h under high temperature and pressure. After this aging process, bitumen samples are used in DSR and BBR tests [87].

2.3.2.3 Dynamic Shear Rheometer

The DSR test is used to evaluate the stiffness and viscoelastic behavior of bituminous binders at medium and high service temperatures. DSR determines the resistance to rutting at high service temperatures during the early periods of pavement life. Also, this test evaluates resistance to fatigue cracks at the later periods of service life [87,88]. During the DSR test, a thin bituminous binder sample is placed between two parallel plates. The bottom plate is fixed, but the upper plate oscillates to the left and right at a frequency of 10 rad/s (1.59 Hz) to create a shearing motion [89,90]. In addition to the original bituminous binders, short-term aged and long-term aged bituminous binders can also be subjected to the DSR test. The test was carried out according to the TS EN 14770 standard.

2.3.2.4 Bending Beam Rheometer

The BBR is described as a simple device that measures how much deviation in a bitumen beam under constant load at temperatures corresponding to low service temperatures where bitumen acts as an elastic solid [87]. This test measures the creep stiffness parameter which is a measure of the resistance of bitumen to constant loading and the creep ratio parameter, also known as “*m* value”. The creep ratio parameter gives an idea about how the stiffness of bitumen changes as the load is applied. The BBR test is carried out according to TS EN 14771 standard.

2.3.3 Characterization and measurement

SEM/EDS was used to analyze the changes in the surface morphology of the reference binder and CDEA modified samples. This analysis was carried out by using the FEI Quanta FEG 250 device with high magnification and superior resolution characteristics. SEM images were taken at low vacuum mode and a voltage of 10 kV.

The XRD patterns of reference binder and CDEA modified samples were obtained by using Bruker D8 Advance Twin-Twin diffractometer (Bruker Corporation, Germany). Samples were examined with CuKα radiation (λ = 154060 Å) at 40 kV, 40 mA, and at room temperature. The data were collected at a scattering angle of 2θ from 10° to 80° with 0.01° step size and 2°/min scan speed.

The FTIR was performed to investigate the chemical and structural status of samples, and FTIR data was obtained by using Jasco FT/IR-4700. Spectra of samples were measured at wavelengths which are changed from 4000 to 400 cm^{-1}. The accumulation value is 32, the scanning speed is 2 mm/s, and the spectral resolution is 4 cm^{-1}.

3 Results and discussion

3.1 Results of conventional bitumen tests

To determine the consistency of samples, softening point, penetration, and ductility tests have been applied on the reference bituminous binder and all modified samples. In this section, results of the tests carried out to examine the properties of CDEA modified bituminous binders comprised using different parameters, and the effect of changes in modification parameters on these properties are discussed.

The results obtained from the softening point tests were examined in four steps as test sets that have different modification times but the same modification rates and temperatures. Representations of the results as graphical are available in Fig. 2.

As can be seen from the graphs, the softening point temperatures decreased according to the reference binder as the CDEA ratio increased for each test set. A similar trend for softening point test was observed in some studies using surfactants with different properties [67,73]. In fact, in a study using different additives, the addition of surfactant to the aged bituminous binder gave the best softening results [70]. In this study, especially, when samples modified with 5% CDEA additive, are compared to the reference binder, a decrease between 7.4%–10.78% in softening point values can be seen. Also, it is evident that, changes in the modification parameters do not affect this decrease, but may create differences between sets. For both modification rates, in sets prepared with 5% additive ratio at 155 °C, the period of time needed to see the maximum decrease in softening point temperature is 60 min. Similarly, for 165 °C modification temperature, the softening point values are affected by a modification time of 30 min. Accordingly, in the softening point test, independently from the modification rates, for 5% additive ratio, it can be said that bituminous binders which have been prepared at 155 °C for 60 min may be equivalent to binders prepared at 165 °C for 30 min.

The results obtained from the penetration tests were examined in four steps similar to the results of softening point tests. Representations of the results as graph are available in Fig. 3.

As can be seen from the graphs, the penetration values have increased according to the reference binder as the CDEA ratio increases for each test set. Similarly, in various studies evaluating the physical properties of modified bituminous binders, it can be observed that the addition of surfactant additives generally increases penetration [67,70,73,79,83]. In the penetration tests performed on the reference binder and all samples, it can be observed that the penetration values increased by 56.25% to 100% for the highest additive ratio and this rate of increase was closer to 100% for many samples. Also, it was evident that changes in modification parameters do not affect this increase but may create differences between sets. For both modification temperatures, in sets prepared with a 5% additive ratio at 1000 r/min, the period of time needed to see the

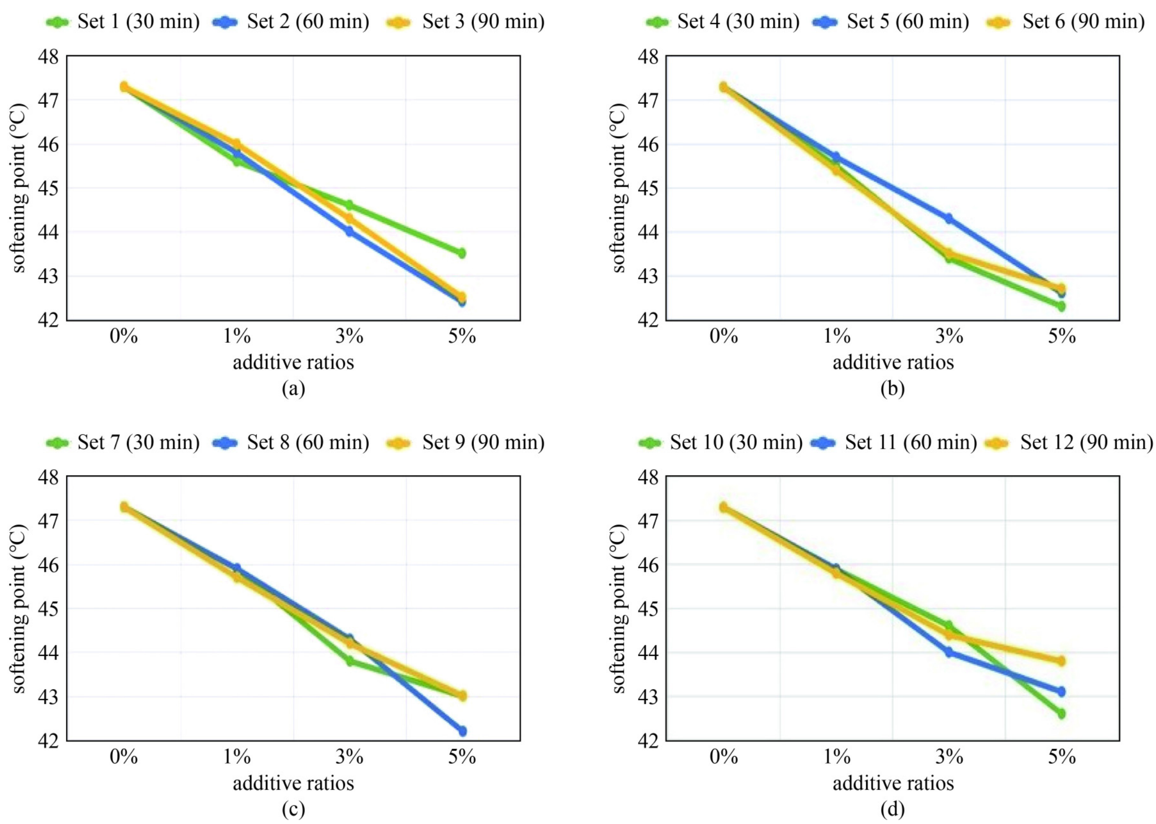

Fig. 2 Softening point test results of (a) 1000 r/min and 155 °C; (b) 1000 r/min and 165 °C; (c) 2000 r/min and 155 °C; (d) 2000 r/min and 165 °C.

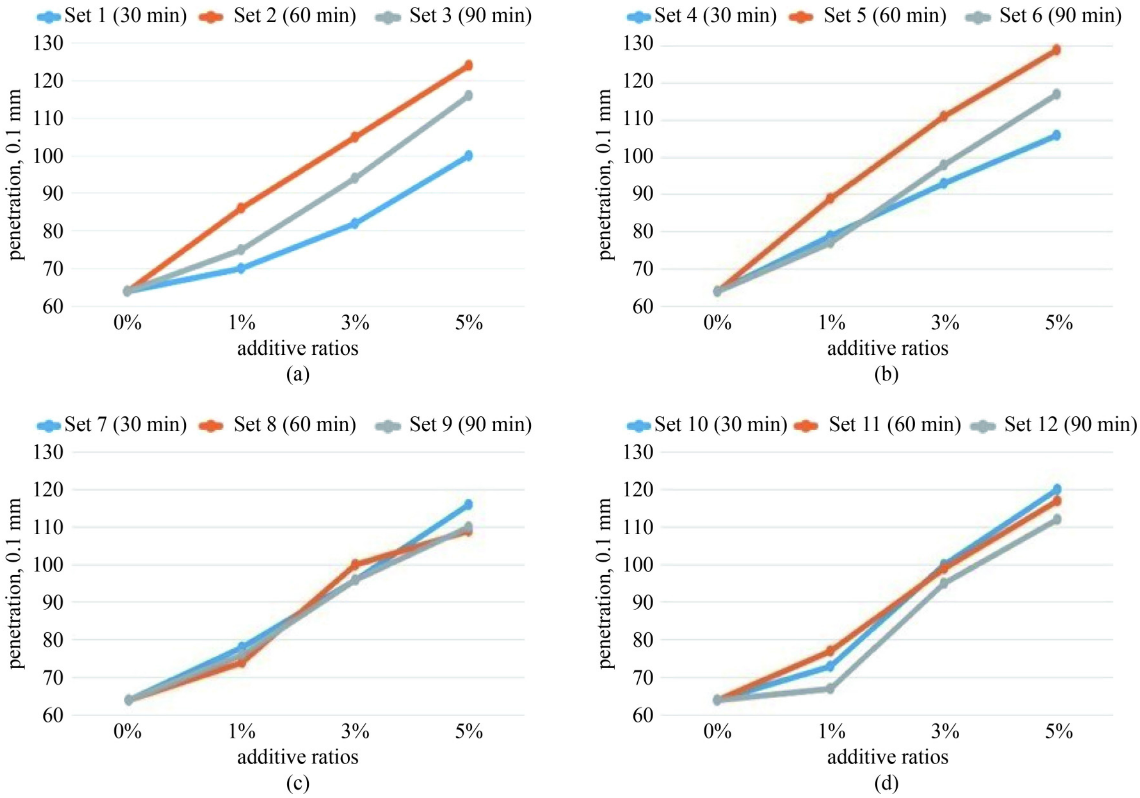

Fig. 3 Penetration test results of (a) 1000 r/min and 155 °C; (b) 1000 r/min and 165 °C; (c) 2000 r/min and 155 °C; (d) 2000 r/min and 165 °C.

maximum increase in penetration values is 60 min. Similarly, at 2000 r/min modification rate, penetration values are affected by a modification time of 30 min. Accordingly, in the penetration test, independently from the modification temperatures, for a 5% additive ratio, it can be said that bituminous binders which have been prepared at 1000 r/min for 60 min may be equivalent to binders prepared at 2000 r/min for 30 min.

According to the results of ductility tests, the reference bituminous binder and all modified samples have indicated elongation without breakage by exceeding the specification limit value of 100 cm at 25 °C. This means that the reference bitumen and all modified samples can indicate durability under the tensile effects caused by traffic on the pavement. When the ductility test results in different studies are examined, it can be understood that the increases or decreases in ductility change according to the type and the amount of surfactant additive used [67,68,83].

According to the data obtained so far, the results of conventional tests are consistent with each other. It is known that bituminous binders with low softening point and high penetration values can be used for pavement construction in cold regions. So, considering these results, it can be said that bituminous binders modified with CDEA are suitable for cold climatic regions. Additionally, for the bituminous binders modified with 5% CDEA, which is the highest additive ratio in each test set, it has been found that the parameters which affect the softening point values are the modification time and temperature. Similarly, it has been found that the parameters which affect the penetration values are the modification time and rate.

In parallel with these results, it was desired to determine the effects of additive on the rheological properties of bitumen. Therefore, among the 12 test sets, the 2nd and 10th sets were chosen. Because the consistency decreases of these two sets are the most and coherent among the 12 test sets. Additionally, these sets have been considered to be suitable for comparison with each other because of having different modification parameters. To determine also the effects of additive on the rheological properties of bitumen, Superpave performance tests were performed on all samples included in 2nd and 10th sets.

3.2 Results of Superpave tests

According to the results obtained from the conventional bitumen tests, Superpave performance tests (RV, RTFOT, PAV, DSR and BBR) were performed on all the samples included in the 2nd and 10th sets. Because, as stated in the previous section, it has been thought that samples that constitute these two sets have given the best results in terms of consistency and are suitable for comparison with each other. This section discusses the results of the tests carried out to examine the rheological properties of CDEA modified bituminous binders.

3.2.1 Rotational viscometer test

RV test has been performed to determine the mixing and compaction temperatures and temperature ranges of bituminous binders. Two temperature values, 135 and 165 °C, have been used as test temperatures. For both the 2nd and 10th test sets, it was observed that both the mixing/compaction temperatures and the temperature ranges decreased with the increasing of additive ratio. These decreases show that the workability of bituminous binders modified with CDEA is higher than that of the reference binder. Similar studies in the literature have also suggested that surfactant additives reduce viscosity [70,73,75,79], even if they are sometimes less effective [68]. It was also stated that in some studies, the decreases in viscosity also lead to decreases in the mixing and compaction temperatures of the samples, resulting in an improvement in the workability of the asphalt [64,67,83].

According to the reference binder, the changes in viscosity of the samples included in Set 2 and Set 10 can be seen in Fig. 4. Also, changes that occurred in mixing and compaction temperatures have been given in Table 4.

Accordingly, if Set 2 and Set 10 are considered together, for both 1% and 3% additive ratios, it can be said that Set 2 has decreased mixing and compaction temperatures more than Set 10. However, for a 5% additive ratio, it can be seen that the mixing and compaction temperatures have decreased to almost the same level for both sets. Therefore, it can be concluded that changes in the modification parameters have little or no effect on the additive ratio of 5%. Generally, the mixing temperatures of Set 2 and Set 10 samples have approximately decreased at the rate of 6%, according to the reference binder. Similarly, the compaction temperatures have approximately decreased at the rate of 11%. These decreases mean that the workability of the materials has increased, and energy saving has been provided in conjunction with this. So, this will result in a reduction in cost, too.

3.2.2 Dynamic shear rheometer test

In the DSR test, test parameters are controlled by a computer program, and the results are recorded. Depending on the relationship between applied stress and deformation, G^* (complex shear modulus) and δ (phase angle) values are calculated by the program. In this test, while $G^*/\sin\delta$ value is known as the rutting factor, the $G^*\cdot\sin\delta$ value is known as the fatigue factor. This test has been carried out by using unaged, short-term aged, and long-term aged bituminous binders. $G^*/\sin\delta$ values of the unaged and short-term aged samples at high temperatures have been determined, and their resistances to the rutting have been investigated. Also, based on $G^*\cdot\sin\delta$ values, bituminous binders aged with PAV have been used to evaluate the resistance of the samples to fatigue cracks at moderate temperatures. Thus, interpretations have been made about the medium and high temperature performances of the samples.

The graphical representation of $G^*/\sin\delta$ and phase angle values obtained from DSR tests performed on the unaged samples is shown in Fig. 5.

From these graphs, it can be seen that the phase angle

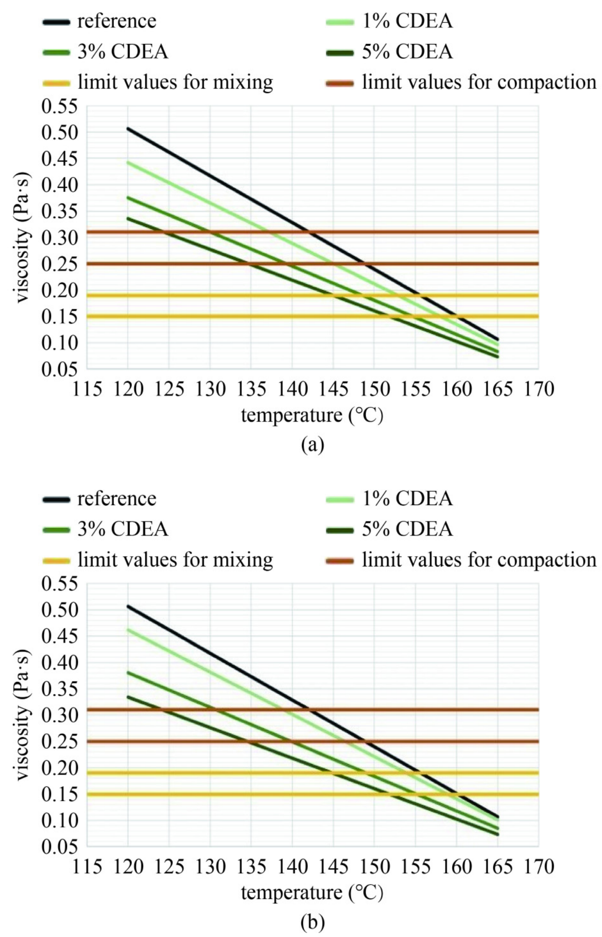

Fig. 4 RV test results of (a) Set 2; (b) Set 10.

Table 4 Changes in mixing and compaction temperatures

sample	additive ratio	mixing temperature (°C)	compaction temperature (°C)
reference binder	–	157.9	145.5
Set 2	1%	155.5	141.2
Set 2	3%	151.6	134.7
Set 2	5%	148.5	129.6
Set 10	1%	156.3	142.6
Set 10	3%	152.1	135.3
Set 10	5%	148.4	129.3

increases and approaches 90° with the increase of temperature for all samples. This tendency to approach indicates that samples behave viscous. For all samples, as the temperature increases, the $G^*/\sin\delta$ values, which means resistance to the rutting, have decreased. In addition, all modified samples have a lower rutting resistance compared to the reference binder. The specification limit value of 1.00 kPa (1000 Pa) has been provided at 64 °C for the reference binder and Set 2 and Set 10 samples which have an additive ratio of 1%. However, at 64 °C, Set 2 and Set 10 samples which have additive ratios of 3% and 5%, have dropped below the specification limit value.

$G^*/\sin\delta$ and phase angle values obtained from DSR tests performed on samples aged with RTFOT are shown in Fig. 6.

As can be seen from the graph, the phase angles of all modified samples are higher than the reference binder at all temperature values. In other words, the viscous behavior tendency of all samples exposed to short-term aging is higher than the reference binder. If the two sets are evaluated independently, it can be said that the increase of the temperature and additive ratio in the samples increases the phase angle values. According to Fig. 6, $G^*/\sin\delta$ values of all samples aged with RTFOT have decreased with increasing temperature. When modified bituminous binders which RTFOT aged are compared with the reference bitumen, it can be seen that all modified samples exhibit lower rutting resistance after aging. The specification limit value of 2.20 kPa (2200 Pa) for short-term aged binders has been provided at 64 °C for the reference binder and Set 2 and Set 10 samples with an additive ratio of 1%. Again at 64 °C, Set 2 and Set 10 samples with additive ratios of 3% and 5% have dropped below the specification limit value. So, 58 °C is the critical temperature value for these samples in terms of rutting.

When the studies in the literature reviewed, it has been seen that the effects of different surfactant additives on rutting resistances (i.e., high-temperature performances) of bituminous binders can vary. For example, some additives provided a complete improvement in terms of high-temperature performances for both binder and asphalt mixture [64,83]. However, in certain studies, it was stated that the high-temperature performances of binders were affected negatively for unaged samples as the surfactant additive ratio increased [62,68,75]. As for some additives, they have not had significant effects on this property [79]. In addition to these, some of the surfactants also decreased the resistance of unaged or

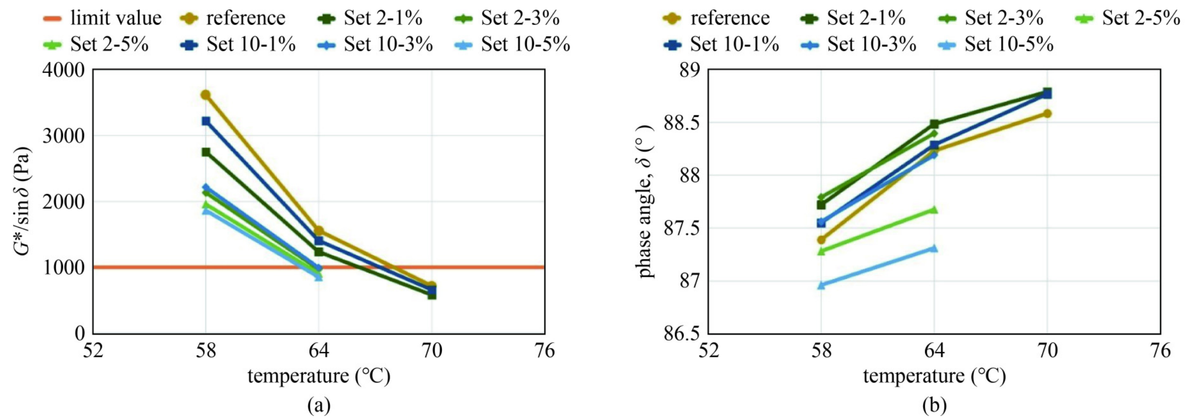

Fig. 5 (a) $G^*/\sin\delta$ and (b) phase angle values for unaged samples.

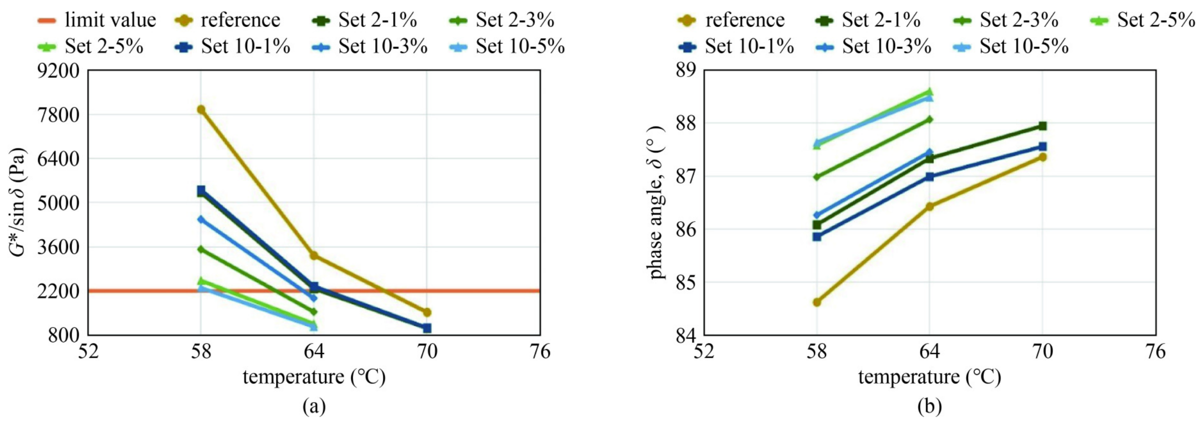

Fig. 6 (a) $G^*/\sin\delta$ and (b) phase angle values for samples aged with RTFOT.

aged bituminous binders to high-temperature [74,75]. These differences in rutting resistance behaviors are thought to be due to the different physical and chemical interactions between binders and surfactants.

Since the CDEA additive causes the softening of bitumen at lower temperatures, it is thought that the resistance to rutting of unaged and short-term aged samples has decreased under the effect of high temperature. As the amount of the CDEA additive increased, the high-temperature PG of the bituminous binder has changed. According to the results of the DSR tests, for high temperatures, the PG of the original binder and bituminous binders modified with 1% CDEA were determined as PG 64-Y. Similarly, PG of binders modified with 3% and 5% CDEA were obtained as PG 58-Y.

The DSR test has been performed on samples aged with PAV to determine the resistance of bituminous binders to fatigue cracks at moderate temperatures. The graphical representation of the obtained $G^{*}\cdot\sin\delta$ and phase angle values is shown in Fig. 7.

The graph shows that the phase angle values increase with increasing temperature for all samples. The minimum phase angle values have been obtained at 10 °C for samples containing 3% additive. As the temperature decreases, $G^{*}\cdot\sin\delta$ values of all samples aged with PAV have increased. Bituminous binders with low $G^{*}\cdot\sin\delta$ values are known to be more resistant to fatigue cracks, and in the specification, it is desired that the maximum value of $G^{*}\cdot\sin\delta$ is 5000 kPa. As can be seen from the graph, at 22 °C, where the data is available for all samples, the reference bitumen has the highest $G^{*}\cdot\sin\delta$ value. In addition, Set 2 and Set 10 samples containing 3% additive have minimum $G^{*}\cdot\sin\delta$ values and have put up the highest resistance to the formation of the fatigue cracks at moderate temperatures. The samples with the 3% additive ratio that showed the highest resistance to fatigue cracks have reached the limit value desired in the specification below 13 °C. This means that when compared to the reference binder, bituminous binder modified with 3% CDEA is resistant to the formation of fatigue cracks even at a lower temperature as 9–10 °C.

It is known that binders exceeding the specification limit value specified for $G^{*}\cdot\sin\delta$ are considered to be extremely hard in terms of fatigue behavior and have less resistance to fatigue cracks. Accordingly, as it softened the bitumen, it can be said that the 3% CDEA additive may have increased the resistance to fatigue cracks. Even though the 5% CDEA additive reduced the softening point temperature more, the loss of volatile materials even during short-term aging for this ratio has been considerably higher compared to the samples modified with 3% CDEA. Therefore, it is considered that binders modified with 5% CDEA are weaker in terms of resistance to fatigue cracks due to their hardening more during long-term aging. In general, all samples modified with CDEA are more resistant to fatigue cracks than the reference binder. It has also been observed that different surfactants also increase the resistance to fatigue cracks [62,64]. However, as in the present study, an increase in the surfactant additive content may adversely affect the resistance of the bituminous binders to fatigue cracks [75].

3.2.3 Bending beam rheometer test

To determine the resistance of bituminous binders to thermal cracking, samples that have been aged with PAV were subjected to BBR test. This test determines the creep stiffness which is one of the properties of bituminous binders. Creep stiffness is of capital importance to determining the resistance of the pavement to thermal cracks. It has been known that bituminous binders with low creep stiffness or high creep ratio put up higher resistance to thermal cracks.

When the studies in the literature reviewed, it has been seen that the thermal cracking performances of bituminous binders modified with different surfactant additives can vary. Some of the additives did not contribute to preventing thermal crack formation [64]. Contrary to this, some surfactant additives have positive effects on the

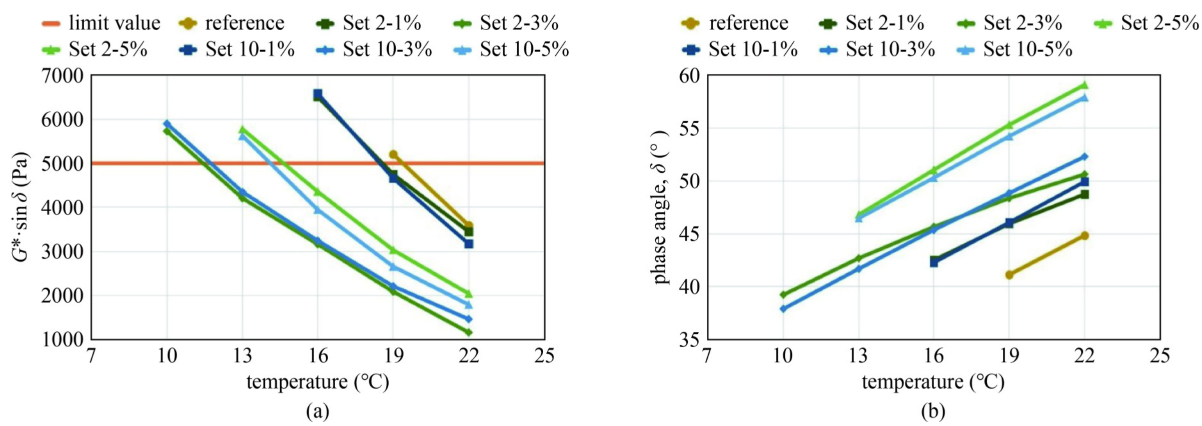

Fig. 7 (a) $G^{*}\cdot\sin\delta$ and (b) phase angle values for samples aged with PAV.

low-temperature properties of the binders, which are directly related to thermal cracking resistance, rather than the high-temperature properties [74]. Various studies stated that the usage of surfactants in certain ratios has generally increased the thermal cracking resistance of bituminous binders [62,67,70]. However, thermal cracking resistance of bituminous binders can be affected negatively by surfactant additives sometimes [75]. These differences in thermal cracking resistance behaviors are thought to be due to the different physical and chemical interactions between binders and surfactants.

In this study, the samples have been tested at two test temperatures, –18 and –24 °C. Compared to the reference binder, the minimum creep stiffness values have been obtained in samples modified with 5% CDEA for both of two sets and test temperatures. However, at –24 °C, in tests carried out by using reference binder, Set 2 samples modified with 1% and 3% CDEA and Set 10 samples modified with 1% CDEA, 300 MPa, which is the specification limit for creep stiffness, has been exceeded. Including the reference binder, none of the samples exceeded this specification limit at –18 °C. Nevertheless, the requirement to have a value greater than the creep ratio limit (0.300) stated in the specification has been only provided for samples modified with 5% CDEA at –18 °C for both sets. Although the creep stiffness requirement has been provided for other samples, the creep ratio requirement could not be met for these two temperature values. With the decrease in temperature value, it has been observed that the creep ratio was dropped below the specification limit value. Since the specification limit values were not provided for most of the samples at temperatures that the tests were carried out, additional investigations at higher temperatures are required for all samples. Creep stiffness and creep ratio values obtained in 60 s for all samples are shown in Fig. 8.

As can be seen from the graph, the creep stiffness values of the samples in both sets are lower than the reference binder at both test temperatures. In addition, creep stiffness has decreased with the increasing additive ratio. According to these results, it was seen that as the amount of CDEA additive increases, the bituminous binders would put up resistance to the thermal stresses that the pavement is gradually exposed at quite low temperatures. The Set 2 and Set 10 samples modified with 5% CDEA met the specification limit values at –18 °C. So, for low temperatures, the PG of these samples were determined as PG X-28. It is thought that, as a result of subjecting the remaining samples to the test at –12 °C, the specification limit values can also be met for them. So, it is estimated that the PG of the samples that did not meet the specification limit values will be PG X-22. According to the results obtained by evaluating the DSR and BBR tests together, the determined PG classifications for all of the samples are shown in Table 5.

3.3 Results of characterization

SEM/EDS, XRD and FTIR analyses were performed on reference binder and all the samples included in the 2nd and 10th sets to interpret the morphologic and chemical structures of reference binder and modified samples. In this section, the results of these analyses are discussed.

3.3.1 SEM/EDS analysis

SEM was used to analyze the compatibility and homogeneous dispersion of CDEA, which was added to the reference binder. In addition, the main elements of reference binder and CDEA modified samples were investigated by using EDS analysis. The surface images of the reference binder and samples which were modified with the different concentrations of CDEA are shown in Fig. 9 for Set 2 and Fig. 10 for Set 10.

It is thought that the white areas seen in figures indicate the presence of CDEA in bituminous binder. According to this, the dispersion of CDEA in bituminous binder is homogeneous for both of the sets. The change in morphology of the bituminous binder was increased by increasing CDEA concentration.

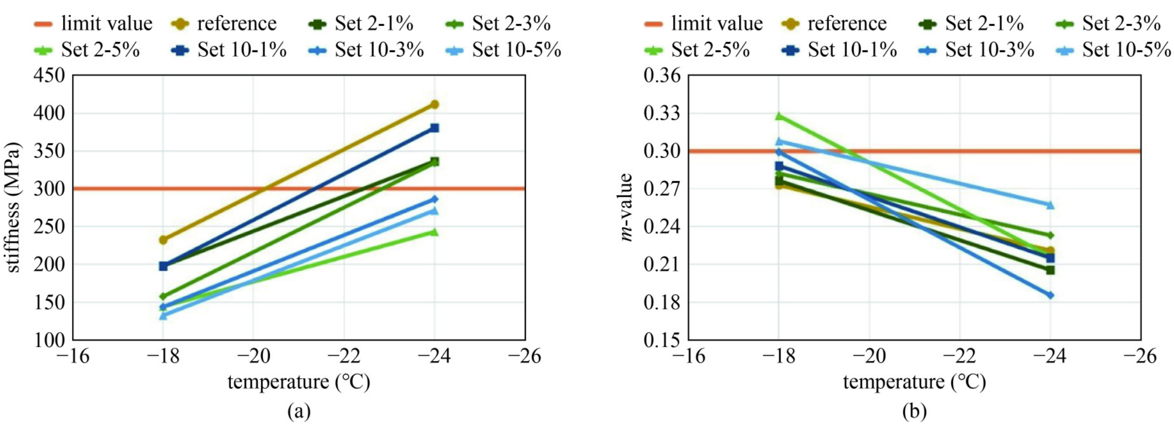

Fig. 8 (a) Creep stiffness and (b) creep ratio values obtained from the BBR test.

The chemical composition of the reference binder and CDEA modified samples can be seen in Table 6. The variation which is seen between carbon and oxygen atoms is thought to be due to the similar chemical structure of the bituminous binder and CDEA.

Table 5 PG classifications for all of the samples

sample	additive ratio	high temperature PG	intermediate temperature	low temperature PG	PG classification
reference binder	–	64	22	–12	64-22
Set 2	1%	64	19	–12	64-22
Set 2	3%	58	13	–12	58-22
Set 2	5%	58	16	–18	58-28
Set 10	1%	64	19	–12	64-22
Set 10	3%	58	13	–12	58-22
Set 10	5%	58	16	–18	58-28

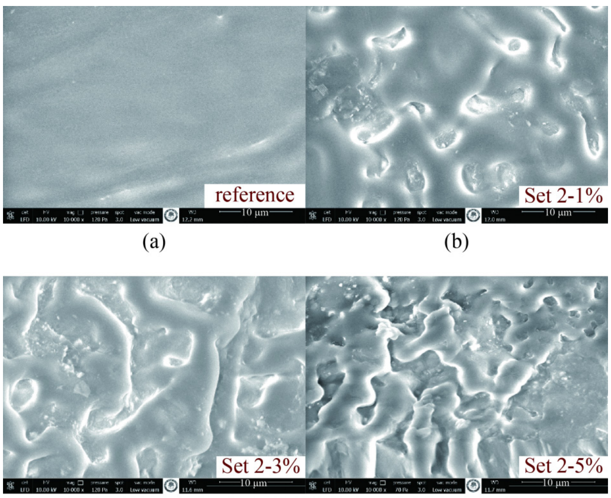

Fig. 9 SEM images of (a) reference binder and (b) Set 2 1%; (c) Set 2 3%; (d) Set 2 5% samples.

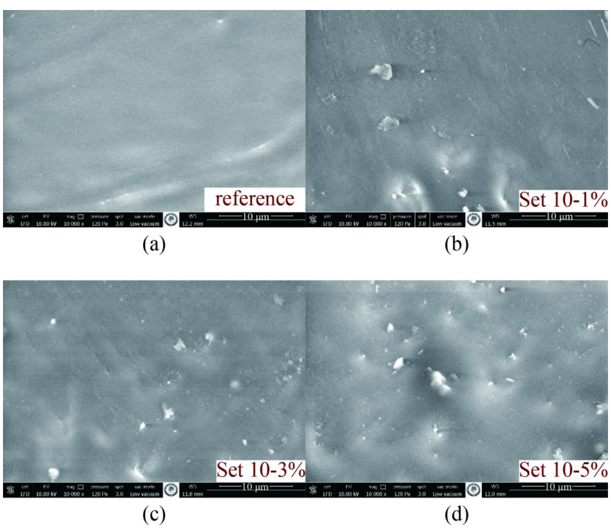

Fig. 10 SEM images of (a) reference binder and (b) Set 10-1%, (c) Set 10-3%, (d) Set 10-5% samples.

3.3.2 XRD analysis

The structural characteristics of reference binder and modified samples were investigated by using XRD. However, since even the smallest change on the materials affects the XRD analysis and the two sets evaluated in this study were prepared by using different parameters, the XRD results of the sets had to be interpreted separately. The analysis results of the CDEA chemical, reference binder, and CDEA modified samples are shown in Fig. 11 for CDEA, Fig. 12 for Set 2 and Fig. 13 for Set 10.

When the XRD pattern of CDEA chemical was examined, it can be said that the structure of this material is amorphous. According to Fig. 12, reference binder has a peak, indicating the crystal structure at 2θ = 22°. However, the sample of Set 2 with 1% CDEA shows semi-crystalline structure and tends to resemble the structure of the CDEA chemical. In addition, the crystallization tendency of the samples of Set 2 with 3% and 5% CDEA continues with the increase in the additive ratio.

Figure 13 shows that the crystal structure seen in the reference binder gets lost for the samples of Set 10 with 1% and 3% CDEA and for these samples, the structure was transformed to the amorphous. However, the crystallographic structure changed for Set 10 with the

Table 6 EDS analysis results of the samples

sample	additive ratio	carbon (wt.%)	oxygen (wt.%)	sulphur (wt.%)
reference binder	–	92.89	1.95	5.16
Set 2	1%	91.42	3.79	4.79
Set 2	3%	90.93	4.26	4.81
Set 2	5%	83.7	9.98	6.32
Set 10	1%	90.07	4.5	5.44
Set 10	3%	89.91	5.3	4.79
Set 10	5%	88.68	6.7	4.62

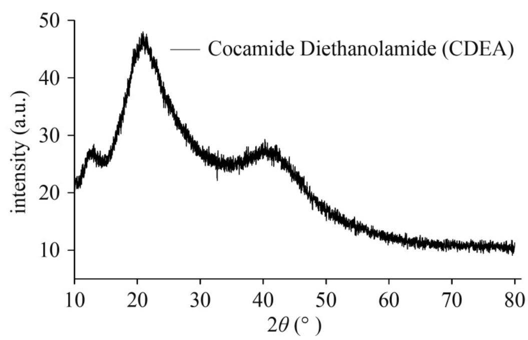

Fig. 11 XRD pattern of CDEA chemical.

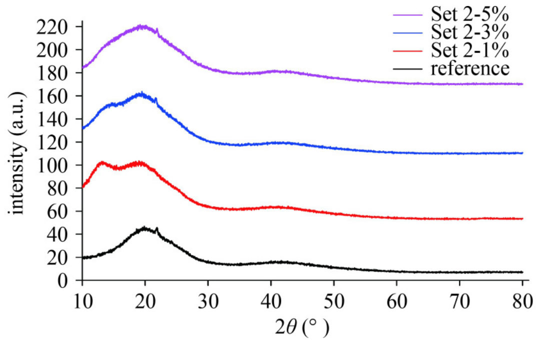

Fig. 12 XRD patterns of reference binder and Set 2 samples.

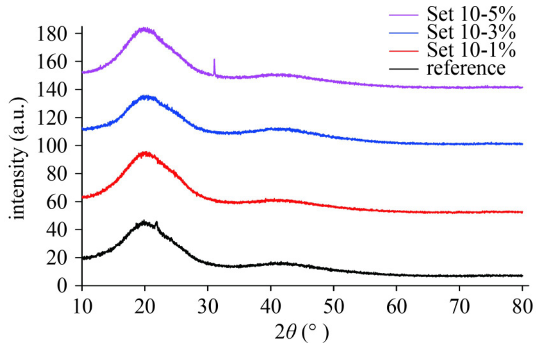

Fig. 13 XRD patterns of reference binder and Set 10 samples.

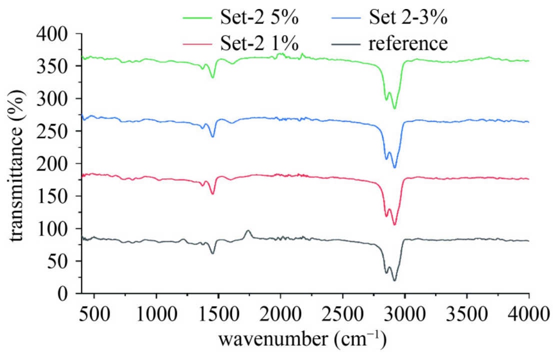

Fig. 14 IR spectra of reference binder and Set 2 samples.

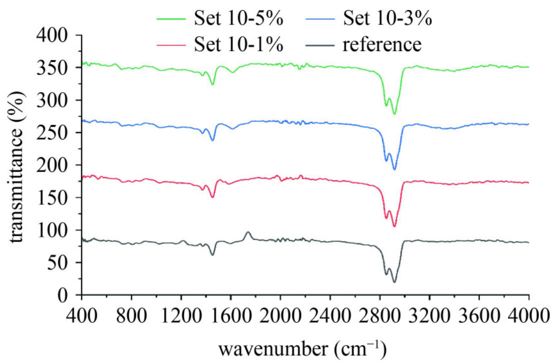

Fig. 15 IR spectra of reference binder and Set 10 samples.

usage of 5% CDEA. So, it can be said that the 5% CDEA ratio is the threshold value for Set 10. In addition, the presence of a relatively small amorphous structure about $2\theta \approx 40°$ for reference binder and samples of both sets is remarkable.

3.3.3 FTIR analysis

The chemical changes in the CDEA modified samples were investigated by using FTIR. Figures 14 and 15 demonstrate the IR spectra of Set 2 and Set 10 samples, respectively, according to the reference binder.

According to figures, peaks at 2919 and 2852 correspond to the C−H single bonds while the peaks that exist at about 1600 indicate the C=C double bond. In addition, the peaks at 1454–1371 cm^{-1} can correspond to C−H single bonds. When IR spectra of both sets were examined, it is seen that there is too little or no considerable change of peaks of reference binder and modified samples. The wavelength ranges which the bonds were seen remained more or less the same. These similarities between IR spectra of all samples are thought to be due to the similar chemical structure of the bituminous binder and CDEA.

4 Conclusions

In this study, the consistency and performance of bituminous binders which were modified under different conditions by using CDEA at 1%, 3%, and 5% ratios, have been investigated. The following conclusions can be drawn from the tests carried out.

1) As a result of the modification of bitumen with CDEA, compared to the reference binder, softening point temperatures of bituminous binders decreased, and penetration values increased. According to these results, it can be said that bituminous binders modified with CDEA are suitable for cold climatic regions.

2) According to the results of rotational viscosity tests performed on Set 2 and Set 10 samples, in accordance with the results of softening point and penetration tests, there is a decrease in viscosity for all samples of selected two sets.

3) The reason for these consistency changes is thought to be that the CDEA additive softens the bituminous binder by thinning it, because CDEA is a smaller molecular material compared to bitumen, which has a long-chain.

4) According to the results of the DSR tests performed at high temperatures, for all samples, as the temperature and amount of additive increase, resistance to the formation of rutting has decreased. In addition, at medium temperatures, all samples modified with CDEA are more resistant to fatigue cracks than the reference binder. The highest resistance to fatigue cracks was observed in binders with 3% CDEA additive.

5) According to the results of the BBR tests, it was seen

that as the amount of CDEA additive increases, the bituminous binders would put up resistance to the thermal cracks.

6) When the results of DSR and BBR tests are evaluated together, it can be seen that the binders especially modified with 3% and 5% CDEA, have caused changes in terms of the PG.

7) Chemical analysis results demonstrated that CDEA was suitable for the chemical structure of bitumen. The images obtained from the morphological analysis confirmed that the material was homogeneously distributed in the bitumen.

In summary, the usage of CDEA surfactant to modify the bituminous binder changed significantly the binder performance. Moreover, it was found that CDEA has decreased viscosity and accordingly mixing/compaction temperatures of bituminous binders. These reductions in temperature decrease energy cost and emission, thus obtaining significant environmental benefits. The results of this study have indicated that CDEA chemical, a non-ionic surfactant, is suitable for use as modification material because it has increased the performance of bituminous binder in many respects.

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