



Addition of Polyurethane in the reformation of Bitumen

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Abstract

In the current research, the addition of Polyurethane in the process of reforming the Bitumen has been investigated. The construction engineers are concern about the asphaltic damages and consume too much money in order to maintenance of asphaltic roads. There are many efforts in order to enhance the resistance and the age of asphalt including the improvement of Bitumen's characteristics. It is common to use polymers in order to reform the Bitumen's characteristics. Thermoplastic Elastomers and reactive polymers are the families of polymers which have impressive effects on the characteristics of Bitumen. TPU and PU were used as modifier additive in Bitumen. Bitumen penetration test, softening point, TFO, PAV,DSR,BBR and FTIR on the modified samples with different forms of Polyurethane have been done in the current research. The achieved findings showed that Polyurethane decreased the penetration degree and even it increases the softening point of Bitumen. The mentioned modified Bitumen had the following characteristics: high viscosity and less sensitivity. Polyurethane also has increased the temperature of base Bitumen's performance and its resistance towards the transformation. In an average temperature, the modified Bitumen has better performance than fatigue of base Bitumen. Although the Polyurethane has a little positive effect on the Bitumen's performance, it couldn't add any positive performance to Bitumen in low temperature. The results of FTIR test showed, the Polyurethane bonds determined the chemical structures.

Keywords: Bitumen, Polyurethane, Isocyanate, polyol, Bitumen's foam



Introduction

Today, trains and subways are the most important transportation systems in the world. In fact, the function and safety of these systems is dependant to the railways which the mentioned device is moving on. The presence of disadvantages causes some human and financial losses to the transportation system. It is necessary to have safety in the lines of railway system. The first event which was related to the reformation of Bitumen returns to 1843. The experimental project related to the reformation of Bitumen is related to 1930 in Europe. In 1950s, usage of NEOPRENE/LATEX was begun as a material for reformation of Bitumen in North America [1]. In 1963, the first roads with modified Bitumen in France were made in order to determine the behavior of modified Bitumen using natural and artificial rubbers [2]. In the late 1970s, Europe was pioneer about Bitumen's reformation than America. One of the most important reasons was requirement of guarantee representation by the European contractors in order to continuance of pavement's life which had direct relationship with the increasing of primary costs [12,13]. This high primary cost in the execution of modified asphaltic makes its consumption limited. In the mid 1980s, the European technology represented some modern polymers which developed the consumption of polymeric Bitumens in America. In the current research, addition of Polyurethane has been investigated in the process of reforming Bitumen. Traffic loads and environmental factors are the most important parameters in the process of making damages in the asphaltic pavement. Traffic loads causes some damages such as rutting, and environmental factors like temperature are the most important parameters of cryogenic crack. Traffic loads is able to create some tension stress, compression stress, and shear stress or even the combination of these but it depends on some parameters such as load size, temperature, stiffness, thickness and surface. Generally, repetition of these stresses and strains lead to destroy the pavement. In fact fatigue cracks are tiny cracks which are developed as a form of cracks derived from fatigue. Since the خستگی event is mostly occurred in the bitumen phase related to the asphalt mixture, so we can use tests which are related to the fatigue bitumen [3].

Statement of the problem

Every year, there has been considered too much expenses for repairs and maintenance of roads. Most of these expenses are related to the repairmen of cracks which are created on the pavements. The presence of crack on the pavements is the main important reason of its low performance. There are some types of cracks such as reflective, contraction and fatigue. Cracks are created because of different factors such as traffic load, temperature changes, and sediment of the layers. Basically, the main important parameter is temperature changing and even the traffic load leads to develop the size of crack. In high temperatures, rutting is the main important reason for the damage of asphalt concrete. However, the existence of crack on the asphalt pavement is occurred in low temperatures, because asphalt has brittleness behavior in the low temperatures. This leads to create crack without deformation of asphalt. Cracking in pavement is one of the most important failure



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modes and is one of the main factors in reducing the level of servicing of pavement. Of all types of cracks, reflexive traction, contraction and fatigue can be mentioned. Turcks are created by various factors such as traffic load, temperature variations, and the layers of the lower layers. Basically, the main cause of cracking is temperature variation, and traffic will spill over and spread further. At high temperatures, cracking is the main mode of failure in concrete asphaltic, but cracking in asphalt pavement usually occurs at low temperatures because the asphalt finds crisp behavior at low temperatures and this causes the unpaved asphalt Too much cracked. Also, low temperatures make bitumen harder in asphalt concrete and, as a result, reduce fatigue life. One of the main ways to increase the capacity of asphalt to withstand failures is to provide quality materials and to improve the properties of bitumen. Bitumen properties modify the bitumen with better elastic and viscous properties, as well as higher shear modulus and hence better performance. Many additives from different families, including polymers (elastomers, plastomers and reactive polymers), fibers, fillers, nanomaterials, etc., are used to improve the properties and performance of bitumen in asphalt mixtures. In this study, the use of polyurethane polymeric material as a bituminous reformer additive against fatigue phenomena should be considered. In addition, the effect of this additive on the bitumen chemical structure was investigated by the Fourier Infrared Spectrometry (FIR) test, as well as its effect on bituminousness against long-lasting deformation at high temperatures and cold curing trays at low temperature and bitumen thermal sensitivity. Polyurethane is the general name of polymers with urethane bonds. Urethane bonds form the reaction of the isocyanate group with polyals. In polyals, groups such as hydroxyl (OH), which has active hydrogen, react with an isocyanate group and produce urethane bonds.

3- Methodology

3-1 materials

-bitumen

The choice of bitumen's type is related to some important parameters. Hence, some factors such as atmospheric conditions, type of traffic and its amount, stone material and the way of execution of pavement. Regarding this, we need less bitumen for preparing the asphalt mixture if the average annual temperature of one region is low and even the number of transportation devices is little. The bitumen which was used in this research was bitumen 85/100 which was the production of Pasargad Oil Company.

Table1. Characteristics of pure bitumen

parameters	unit	standard	Findings
Penetration degree	0.1	ASTM D5	92



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Softening point	° c	ASTM D36	46.4
Ductility characteristic	cm	ASTM D113	More than 100
Flash point	° c	ASTM D70	232
Special weight	Gr/cm ³	ASTM D2024	1.02

-polymer

Two types of Polyurethane have been used in the current research in order to modifying the bitumen. The mentioned Elastomeric thermoplastic Polyurethane is a kind of thermoplastic which has both Elastomeric characteristics and high hardness with A65 value on the basis of polyester with mechanical features.

Table2. TPU's characteristics

parameters	Findings/ unit	standard
Special weight	Gr/cm ³ 1.19	DIN53479
Hardness test	66 A	DIN 53505
Tensile strength 50% 100% 300%	1.8 N/mm ² 2.7 N/mm ² 5 N/mm ²	DIN 53504
Tensile strength	NN/mm ² 30.7	DIN 53504
Strain failure	880%	DIN 53504
Tearing strength	45 N/mm	DIN 53515
Softening point	63° C	ISO 306



Another form of consuming Polyurethane is functional group which is derived from the MDI family with active Hydrogen. Another name of them is Polyol. The primary materials of Polyurethane are used in preparing the thermoplastic foams. Isocyanate KABONATE 401 and consuming Polyol K-FLEX 3673 are represented in table 3 from Kaboodan Company in Iran.

Table3. Characteristics of primary materials of synthesis Polyurethane

parameters	unit	Polyol K- FLEX 3673	Isocyanate KABNATE 401	Standard
Appearance characteristics	---	White liquid	Brown liquid	445 ASTMD
Viscosity in 25° C	mPa.s	1400±200	65±15	891 ASTMD
Special weight	Gr/cm ³	1.02±0.01	1.18±0.03	5155 ASTMD
NCO percentage	%	---	29±1	---
OH value	---	36-41	---	---

2-3 sample preparation process

The cutting machine mixture was used in order to mix and homogenize the polymer and bitumen and even preparing the modified samples with TPU. The model of this machine is L4RT and the used TPU was mixed through weight percent of 3, 5, and 7 added to bitumen. The mentioned additional was in the temperature of 175± 5°c with 4000 rpm speed about 1 hour. Figure 1 is a sample of cutting machine mixture with L4RT model.



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Figure1. Cutting mixture machine with L4RT model

Four blades blender machine in Rheomix 4500 model was used in order to synthesize the Polyurethane using primary Isocyanate and Polyol. This machine was made in Germany. The process of mixing was done in the speed of 2000 rpm in the conditions written in table4. This process of mixing with modified bitumen and Polyurethane foam with high cutting mixture including Polytron 6000 equipped by PT-DA 3030/2 and four blades made in Kinmatica Company. The view of mixing system is shown in figure2. Synthesized Polyurethane in weight percent of 3, 5 and 7 were added to bitumen in order to provide modified bitumen. The mixing temperature of polymer based on the recent research was determined as $90\pm 1^\circ\text{C}$ [52, 58]. The process of mixing the polymer and bitumen with the speed of 4000 rpm by means of Polytron 6000 system and 2500 rpm speed using four blades blender for one hour was done. 2 weight percent of bitumen and water were added to the modified bitumen using Polyurethane about 45 minutes in the same temperature and the speed of mixing [52].

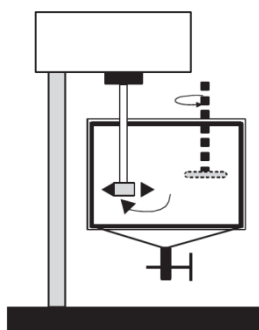


Figure2. kinmatica mixing system and temperature control chamber

3-3 naming samples

Samples are named in table 4 with their abbreviations



Table4. Abbreviations for samples

samples	Additive percent	Samples' abbreviations
Test bitumen	---	CB
Modifies bitumen with TPU	3	BTPU3
	5	BTPU5
	7	BTUP7
Modified bitumen with synthesized Polyurethane	3	BPU3
	5	BPU5
	7	BPU7
Polyurethane bitumen foam including weight percent of synthesized Polyurethane and 2 percents water	3	BF3
	5	BF5
	7	BF7

3-4 programs of tests

In the current research, the following tests have been done on the basis of ASTM and AASHTO instruction in order to determine the characteristics, behavior and performance of unmodified bitumen in high and average and even low temperatures.

-Penetration test

According to ASTM D5 standard, pure bitumen and modified ones were used in order to execute the penetration test about 1 hour with 25 degree centigrade. After that the plates of samples were located under the penetrometer device. The amount of penetration of pin with 100 gram weight about 5 seconds was written with 0.1 accuracy. The penetration test was done in the Technical and Soil Mechanics Laboratory Branch of Tehran.

-softening point test

According to the ASTM D 36 standard, pure bitumen and modified bitumen were used in order to execute the softening point test. Regarding this, almost two rings which were purred in the bitumen were selected in order to measure the softening point of bitumen. After cooling the mentioned



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sample, we put them on the plate contains distilled water with 4 °C. The water container was heated in order to pass the bullets from the bitumen's layer. The mentioned temperature was related to two rings including readable bitumen with the softening point average. The softening point test was done in Technical and Soil Mechanics Laboratory Branch of Tehran.

-FTIR test

FTIR test is used for determine and analysis of polymers' structures. This test was done by means of Equinox 55 machine belonged to Broker Company of Germany in Iran Polymer and Petrochemical Institute .In the current research, FTIR was used in order to determine the chemical structure of TPU, synthesized Polyurethane and polymeric modified bitumen. TPU polymer was cut to thin film using press under the condition of spectroscopy synthesized Polyurethane and the modified bitumen were located on the prepared tablets using KBr powder.

-temperature scan test

TPR was done in order to investigate the performance of bitumen in the intermediate temperature (13-31), in order to control the related parameter to the permanent deformation. According to the ASTM standard, the samples were under RTFO conditions in order to apply short ageing in 163° C for 85 minutes. Also we put the bitumen under the conditions of PAV based on ASTM D6521 standard for 20 hours in 100° c under 2.1 mpa pressures. The conditions of aging in both long time and short time were executed in Technical and Soil Mechanics Laboratory Branch of Tehran. Based on the AASHTO TP5 standard within the 10 rad/s frequency under the strain of 1% . Temperature scan test according to AASHTO TP5 standard at frequency rad / s10 Hz (1.6) at strain 1% and with increase in temperature at ° C / min1 by DSR device, MCP 300 model of Antonpar Company available at Iran Polymer and Petrochemical Research Institute The image is shown in figure 1. The diameter and thickness of the samples examined at an average temperature of 8 and 2 mm, and the diameter and thickness of the samples were at a high temperature of 25 and 1 mm Is.



Figure3. shear reometer dynamic- model MCR300



- BBR test

According to the standard 6648ASTM D, the BBR test was performed to determine the bitumen performance at low temperature on the bitumen samples after applying RTFO and PAV conditions. According to the standard, the temperatures of the test are 6-, 12- and 18-degrees Celsius, and the test is repeated on each sample twice. The results of this experiment on the samples are two stiffness parameters and bitumen stiffness variations with time during loading (m). The loading takes place within 60 seconds. The appropriate range of two parameters for optimal bitumen performance at low temperatures is $G^* > 0.3$ and $S < 300\text{MPa}$

4. Analysis and results

1-4 investigating the results of temperature scan test in high temperature

The results of the temperature scanning experiment on the samples at high temperatures (42-48 ° C) are presented in this section, which has been analyzed. The results of bitumen performance at high temperatures in both aged and aged conditions are discussed. By performing a temperature scanning experiment on old samples in RTFO and obtaining G^* and δ values, the $G^* / \sin\delta$ parameter was calculated at high temperatures. Increasing the $G^* / \sin\delta$ means reducing the exhausted energy or doing the job and eventually reducing the deformation during loading. For an impure bitumen state, $G^* / \sin\delta > 1\text{KPa}$ and for an aged state, $G^* / \sin\delta > 2.2\text{KPa}$ should be. It should also be kept in mind that every ° C increase in bitumen temperature is considered as an increase in functional class.

- The effect of TPU on the performance of bitumen in high temperature

The result of the temperature scan test on TPO-modified specimens is not in RTFO mode. According to the shape of maximum high temperature of bitumen BC (PG58-22), 61/83 ° C, this bitumen in dry weather due to this functional class does not perform well. By adding TPU polymer, this maximum high temperature for BTPU3, BTPU5 and BTPU7 bitrates increased to 233.6 ° C, 80.75 ° C and 81.88 ° C, respectively. Also, according to Fig. 3.3, after applying the aging maximum maximum temperature for PB bitumen was 58.15 ° C, and for modified samples, it was 60.75 ° C, 69.55 ° C and 69.69 ° C respectively, respectively. . Due to the temperatures obtained for the samples from the aged and aged conditions, the high temperature class of the CB function was obtained at a temperature of 58 ° C. The BTPU3 specimen has a maximum temperature of 60.75 ° C, but because it failed to display as high a function as a bit of control, its performance class is considered to be C58. The BTPU5 sample, with a maximum temperature of above 55/65 ° C, can add a category to the high temperature performance class of the base bitumen and has a performance rating of -64 ° C. Also, the BTPU7 sample with a maximum temperature of 74.79 ° C has two higher performance classes than the base bitumen and has a high operating temperature of 70 ° C. In fact, the increase of G^* and reduction of δ , which indicates increased stiffness and



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bituminous elasticity at a wider temperature, is the result of this, which is, in fact, the result of the creation of a polymer lock and chain in the bitumen matrix.

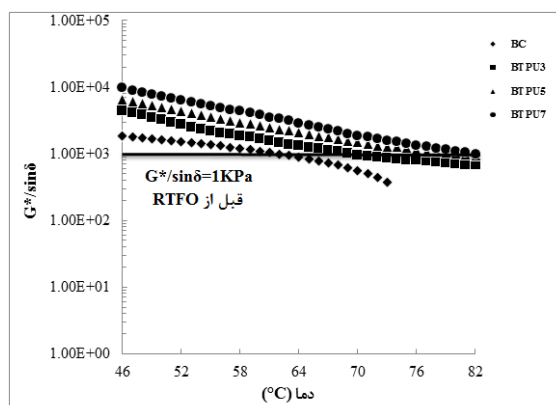


Figure4. the effect of temperature on the parameter $G^*/\sin\delta$ related to the modified bitumens with TPU in non-aging mode

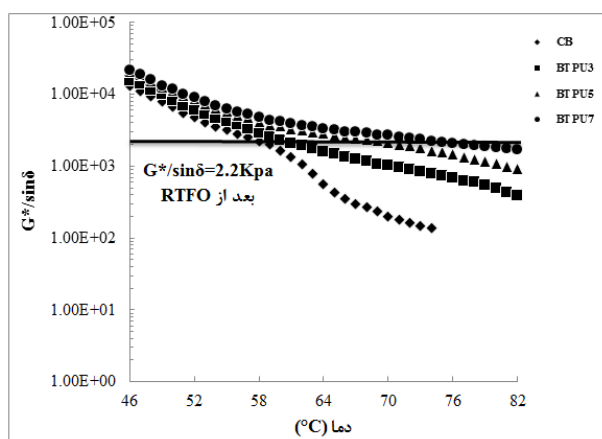


Figure5. the impact of temperature on parameter $G^*/\sin\delta$ related to the modified bitumens with TPU in aging mode

- The effect of synthesized polyurethane on the performance of bitumen in high temperatures

For samples modified with polyurethane synthesized in an aged and aged state, Figures 5-4 and 5-5 show that this modification also has a positive effect on the performance of bitumen at high temperatures, so that the maximum temperature The top of the samples for BPU3, BPU5 and BPU7 was 67.69°C , 70.83°C and 73.4°C for an aged state, 93.93°C , 70.69°C and 73.75°C respectively. According to the observed temperatures, the maximum temperature of the three modified samples is 63.9°C , 70.69°C , and 73.4°C . Due to the high operating temperatures of the modified specimens, BPU3 has failed to reach a higher level than the base bitumen and has a high -58°C . A sample of BPU5 with two grades above the base bitumen has a high performance



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class of 70 ° C. The BPU7 sample did not have a higher performance class than BPU5 and had a high operating temperature rating of about 70 ° C compared to BPU5. It should be kept in mind that these three samples have a larger $G^* / \sin\delta$ than the base bitumen at high temperatures and, with this parameter increasing resistance to permanent deformation, resistance to this phenomenon has increased and with increasing percentage of additive To bitumen, increasing resistance to permanent deformation has risen. Regarding the chemical structure, the NCO reaction in the polyurethane synthesized with the OH (OH) groups in the bitumen polar elements, such as asphaltene, should be considered, and the extent of the asphaltic chains in the bitumen has increased. [4] When asphaltene is present in bitumen, the viscosity of the bitumen is increased, which in fact causes increased rigidity of the bitumen, resulting in bitumen at higher temperatures viscous, and more resistant to permanent deformation. Modified samples for high temperature deformation due to the presence of strong hydrogen bonds formed by the reaction of the polymer and polar groups in them, require more energy to rupture, ie more energy must be introduced, so that the modified sample at temperature upset.

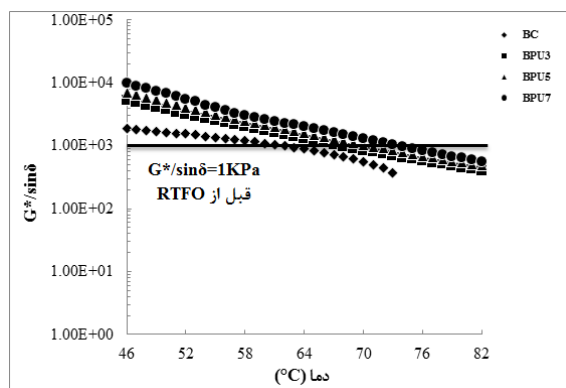


Figure6. The effect of temperature on the parameter $G^*/\sin\delta$ related to the modified bitumens with synthesized Polyurethane in non-aging mode

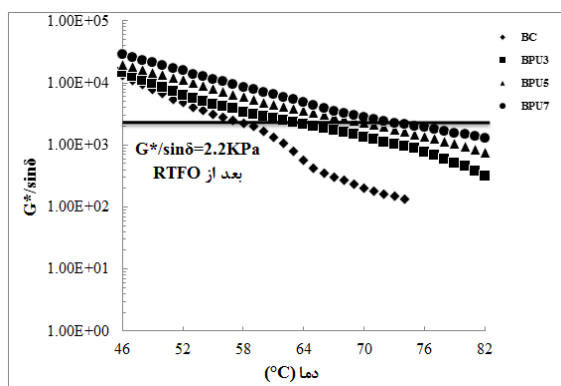


Figure7. The effect of temperature on the $G^*/\sin\delta$ parameters related to the modified bitumens with synthesized Polyurethan in aging mode

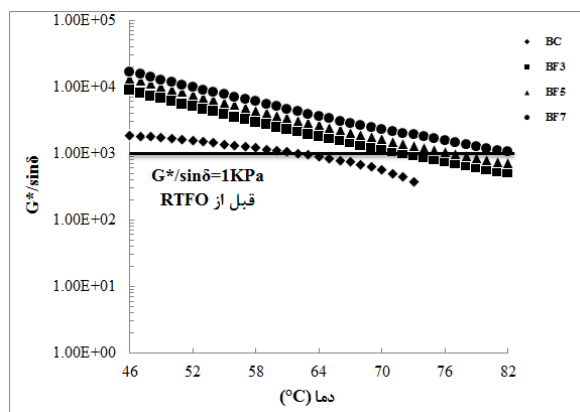


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- The effect of synthesized Polyurethane and water on the performance of bitumen in high temperature

In this section, the results of the polyurethane foam render at high temperatures are presented. Regarding the shape, which shows the changes in the parameter $G^* / \sin\delta$ relative to the high temperatures in the aged and aged state, it is observed that the maximum temperature of the samples of BF3 and BF5 in the aged state is respectively C55 / 71 and ° 77/76. The BF7 sample in an aged state has a high operating temperature of 83.85 ° C, which is remarkable and has exceeded the upper limit of the operating temperature range of 82 ° C. Also, these samples were in an aged state with a maximum temperature of 61.44 ° C, 72.51 ° C and 79.55 ° C. According to these, maximum BF3, BF5 and BF7 temperatures were 61.44 ° C, 72.51 ° C and 72.55 ° C respectively. The BF3 sample has a similar performance rating of 58 ° C relative to the base bitumen and BF5 showing two higher temperature classes than the base bitumen with a high operating temperature rating of 70 ° C. The BF7 also has a high operating temperature range of 76 ° C with three higher temperature classes. The significant increase in G^* in these samples and their significant reduction in δ resulted in an increase in $G^* / \sin\delta$ associated with persistent deformation. In fact, as G^* increases, the rigidity of the bitumen is higher and the δ decreases, the bitumen elastic property will increase. The occurrence of these two cases after the correction of bitumen with the additive has led to an increase in the parameter $G^* / \sin\delta$, which in fact increases this parameter causing the amorphous reduction of energy, or the work carried out under the loading, and consequently resistance to the change phenomenon Permanent shape increases. In the process of producing polyurethane bitumen foam, when polyurethane is synthesized, which is initially added to bitumen, the NCO reacts with OH or NH in asphaltene or resin and increases their amplitude. Increasing the asphalt content raises the viscosity of the bitumen and renders it more rigid, making it viscose higher at higher temperatures and resistant to permanent deformation. Subsequently, by adding 2% water to this set, H₂O reacts with free isocyanates (NCO) and produces NH₂. This creates a new hydrogen bond that has very strong bonds, provides a more rigid structure to the bitumen, resulting in more resistance to permanent deformation in polyurethane bitumen foam.





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Figure8. the effect of temperature on the $G^*/\sin\delta$ parameters related to the foams of Polyurethane bitumens in the non-aging mode

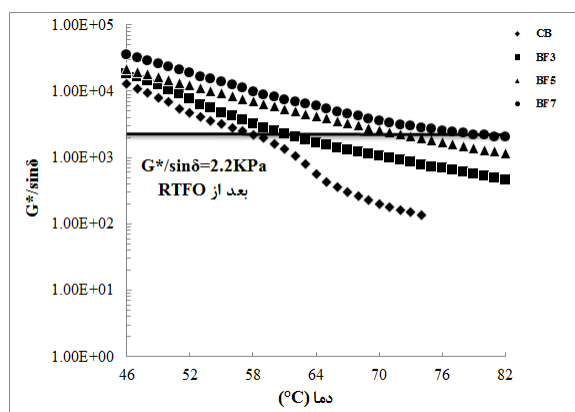


Figure9. the effect of temperature on $G^*/\sin\delta$ parameters related to the foams of Polyurethane bitumens in the aging mode

2-4 investigating the results of BBR test in low temperature

The flexural bending test (BBR) was used to test the performance of the samples at low temperature after RTFO and PAV conditions. Experiments were carried out at 3 temperature temperatures of -6°C , -12°C and -18°C . The results of this experiment on the samples are two parameters S and m . The appropriate range of two parameters for optimal bitumen performance at low temperatures is $S > 0.3$ and $S < 300\text{MPa}$. In this section, the control of bitumen is synthesized, polyurethane-modified bitumen and polyurethane bitumen foam have been investigated.

- The effect of synthesize Polyurethane on the performance of bitumen in lower temperature

It can be seen from Figures 10 and 11 that BPU3 bitumen, which contains 3% polyurethane, has a low temperature of -46.4°C , which is lower than the maximum low temperature of bitumen control BC of 13.71°C , Has had better performance. BPU5 and BPU7 bitumen have the maximum temperatures of -75°C - 14°C and -0.45°C , respectively, which have a lower operating temperature, due to the slightly less rust hardening of the modified bitumen than the control bitumen Which has somehow increased elasticity. At these temperatures, both the stiffness condition $< 300\text{MPa}$ and $m > 0.3$ are established. At the same time, the modified specimens have a lower operating temperature than the control pitch, they could not add a functional low temperature grade to the base bitumen and remained at a low temperature level of -22°C .

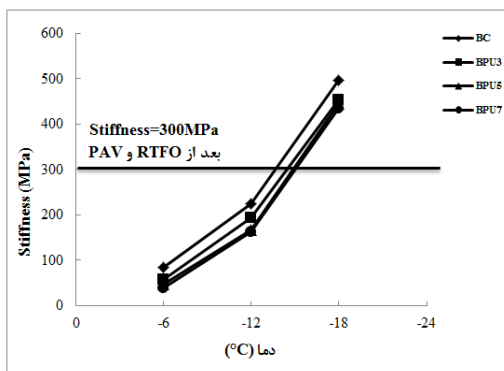


Figure10. the effect of temperature on the hardness of test bitumen and modified bitumens with synthesized Polyurethane

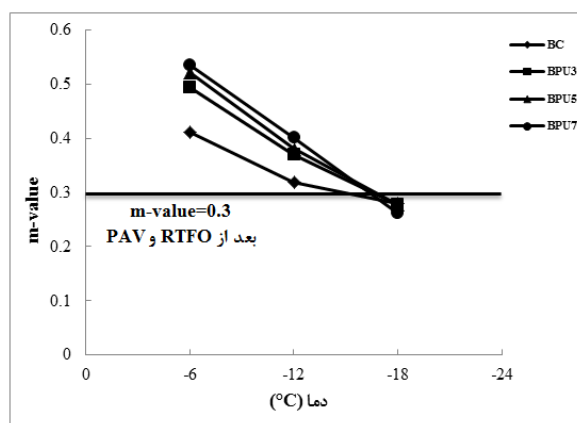


Figure11. the effect of temperature on the value of m in the test bitumen and modified bitumens with synthesized Polyurethane

- The effect of synthesized Polyurethane and water on the performance of bitumen in low temperature

According to Figs. 12 and 13, the results of an experimental rheometer test on polyurethane bitumen foam show that the maximum low temperatures associated with BF3, BF5 and BF7 samples were 14.55 ° C, C87 / 14- and C-89/14, which is more favorable than the maximum low temperature of the control pitch is 13.71 ° C. But at 18 ° C the modified samples, such as pitch, have a value of less than 0.3 and creep hardness greater than 300 MPa, which indicates that they are not able to react at that temperature. Also, these samples could not add as low as a low-performance grade to the base bitumen, and have a low temperature performance class similar to -22 ° C.



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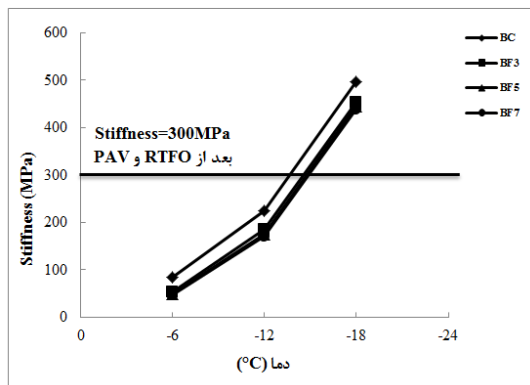


Figure12. the impact of temperature on the stiffness of test bitumen and foams of Polyurethane bitumen

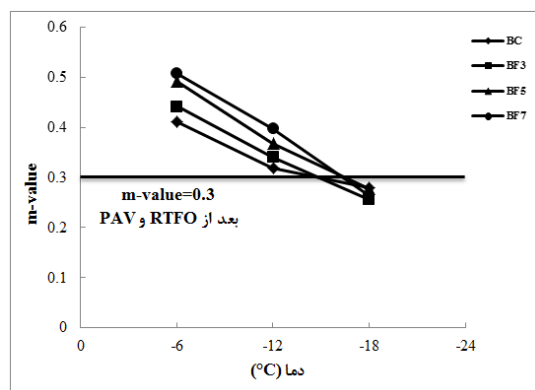


Figure13. the impact of temperature on the value of m in the test bitumen and foams of Polyurethane bitumen

3-4 classification of performance of modified bitumen with synthesized Polyurethane and foams of Polyurethane bitumen

For the classification of functional polyurethane modified bitumen and polyurethane bitumen foam, Table 5 was developed based on the results of high temperature and medium temperature scanning experiments and the rheometer test of bending beam at low temperature. As shown in the table, the samples have the same temperature at low temperatures and have different temperatures at high temperatures.

Table5. The impact of temperature on the performance of modified bitumen with synthesized Polyurethane and foams of Polyurethane

samples	Performance ranking



BC	PG58-22
BPU3	PG58-22
BPU5	PG70-22
BPU7	PG70-22
BF3	PG58-22
BF5	PG70-22
BF7	PG76-22

4-4 investigating the results of FTIR

By the execution of FTIR test, with the type of passing on the Isocyanate, Polyol, synthesized Polyurethane, basic bitumen and modified bitumen, we could recognize the structure of Isocyanate and investigated the presence of OH and NCO in the synthesized Polyurethane. According to figures 14 and 15, the NCO bond in the Isocyanate with wave number of 2268.88 cm^{-1} and OH in the Polyol with wave number 1726.33 cm^{-1} were illustrated. In fact, combination of bitumen with polar groups including Hydroxyl is existed. Figure 17 and 18 are related to the basic bitumen and modified bitumen with Polyurethane which show that in the range of modified bitumen, there is a bond related to the urethane bonds with 1720.97 cm^{-1} wave number which indicates the presence of urethane bonds in this sample. Maybe this bond is related to the reaction of free isocyanate with urethane bonds which are not observed in the basic bitumen. The spectrum in figure 18 indicates the urethane bonds in modified bitumen [5,6].

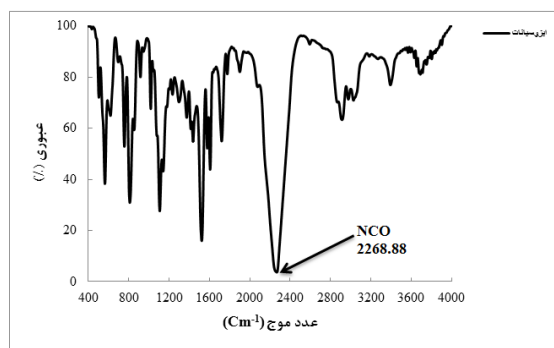


Figure14. Spectroscopy FTIR related to Isocyanate



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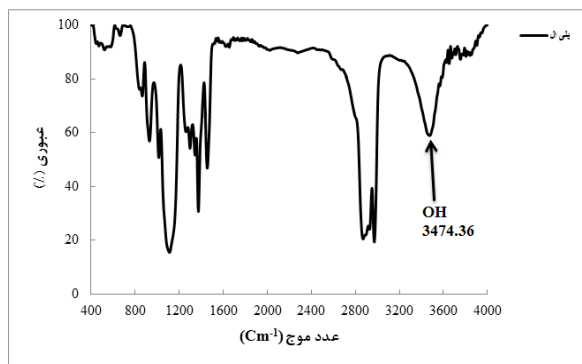


Figure15. Spectroscopy FTIR related to Polyol

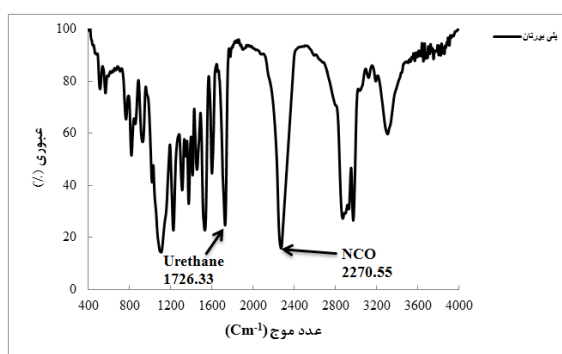


Figure16. spectroscopy FTIR related to Polyurethane

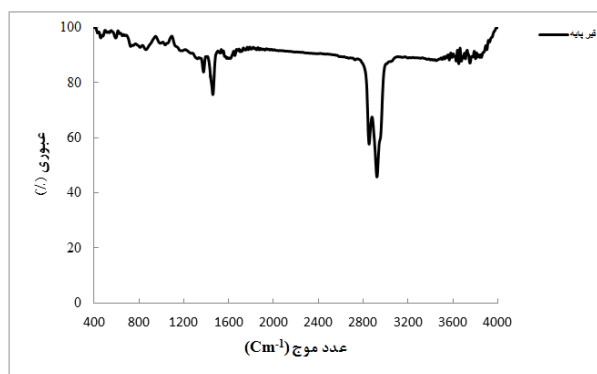


Figure17. spectroscopy FTIR related to base bitumen

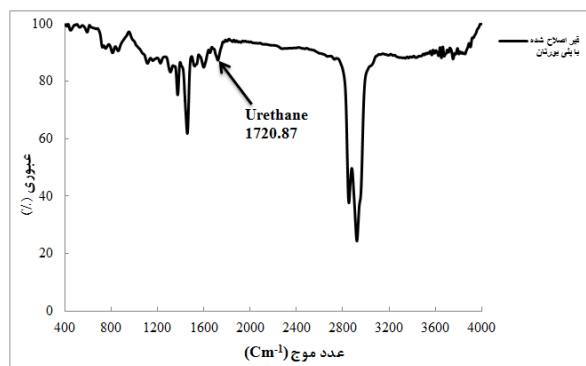


Figure18. spectroscopyFTIR related to the modified bitumen with Polyurethane

5. Conclusion

The additive of Polyurethane in the modifying of bitumen was investigated in the current research.

- The results of penetration degree showed that modifying of bitumen through Polyurethane led to decrease the penetration degree. Modified bitumen by TPU polymer and even synthesized Polyurethane and also bitumen's foam with lower penetration degree have more sustainability towards pressure and traffic loads. The trend of decreasing the penetration degree on the bitumens' foams more than other modified samples.
- Modified samples with TPU and synthesized Polyurethane have higher softening point than the test bitumen. However, the foams of bitumens especially BF7 had the highest softening point among the modified samples. In fact, it represents that the strength of bitumen and even its mixture towards the deformation change is increasing.
- By evaluation of PI index which represents the thermal sensitive of bitumen, we concluded that the test bitumen had the minimum penetration index and BF7 sample had the maximum penetration indexes which were -0.62 and 0.91 respectively. BF7 sample has the minimum amount thermal sensitivity. Increasing the weight percent of each polymer has positive effect in the thermal sensitivity of bitumen. The most minimum thermal sensitivity was related to the modified samples.
- According to the results of TPR test addition of TPU and synthesized Polyurethane and even preparation of bitumen's foam, it leads to increase the strength of base bitumen towards the deformation change. High temperature of test bitumen's performance with 58.15° C and the samples such as BTPU7, BPU7 and BF7 with 74.60, 73.46 and 79.55 centigrade degree. The mentioned samples added 2, 2 and 3 degree to the high degree of performance of base bitumen. Sample BTPU5 has two high temperatures performance with 60.55 degree close to 70 centigrade degree. However, it does not have two high



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performance degree rather than BPU5. According to the high performance degree, BBPU5 is similar to this. Comparing to similar weight percent, different forms of Polyurethane in bitumen, foams except BF3 have the most strength towards the deformation change. In the weight percent of 3 which was added to bitumen, BPU3 assigned the most value of strength for itself.

- Based on the chemical structure, adding the synthesized Polyurethane to bitumen, NCO has reaction with free Isocyanate with polar groups such as asphaltic with factor OH and lead to increase the asphalt chains. By the increasing of asphaltene on bitumen, the amount of viscosity increases and even the stiffness becomes increased. Also, when the amount of viscosity increases, the softening point of the bitumen increase and the penetration degree decreases. It may reduce the thermal sensitivity of bitumen and enhancing the strength towards the permanent deformation change.
- Production of Polyurethane from the modified bitumen with synthesized Polyurethane and water, leads to continuing the reactions, so that the water create new bond with free Isocyanate which lead to produce the NH₂. This kind of increasing for the powerful chains helps the enhancement in viscosity and stiffness of bitumen.
- Modified samples with synthesized Polyurethane and the foams of Polyurethane bitumen have shown better performance than the test bitumen. However, this kind of enhancement was not enough in order to add some range to the lower temperature. In fact, there are not too much changes in the reduction of hardness and enhancement of m value, so all these samples have low temperature performance with -22° c. in this regard, the minimum temperature is related to BPU7 which is equals with -15.04 centigrade degree.
- The results of FTIR showed that urethane bonds were taken place in the bitumen's matrix. The polar groups of bitumen including OH with synthesized Polyurethane had reaction with free Isocyanate and then the chains of asphalt were increased.

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