ISSN: 0975-766X
CODEN: IJPTFI
Available Online through ***Research Article***
www.ijptonline.com

THE DESTRUCTION OF POLYMER MODIFIED BINDER AND PRESCRIPTION FACTORS HER DETERMINING

Marina Alekseevna Vysotskaya*, Svetlana YuryevnaShekhovtsova, Oleg NikolaevichKindeev
Belgorod State Technological University named after V.G. Shukhov,
Russia, 308012, Belgorod, Kostyukov Street, 46.

Received on 09-08-2016 *Accepted on 05-09-2016*

Abstract

In General, the aging of the bitumen, this process proceeding in several stages: the first stage is technological or "short-term aging", including the preparation of bitumen production and asphalt mix, the second operational period laid asphalt pavement or "long term aging".The work considers factors prescription, such as type of bitumen, polymer, plasticizer, have a significant effect on the destruction of polymer modified binder (PMB),(aging and bundle). It is established that ceteris paribus the decisive contribution to the destructiveprocesses makes a plasticizer and bitumen. At the preparation of a polymer modified binder it is necessary to carefully approach the compatibility of the components. Were analyzed the processes occurring in the system "bitumen-polymer" on different lifecycles.

Keywords: Polymer modified binder, plasticizer, destruction, aging.

Introduction

The most intensive aging process of bitumen occur on the technological stage. With free access of air in bitumen is dominated by destructive processes associated with the accumulation of free radicals and, as consequence, reduction in the content of oils, the accumulation of asphaltenes [1]. Thus in the process of thermal-oxidative aging of bitumen is changed not only their group composition, and group composition of oils and resins: the molecular weight of the resins increases and the molecular weight and of the ability to dissolve of the oil decreases. The described processes are accompanied by profound chemical transformations resulting in the change of group composition of bitumen's and their technical characteristics [2, 3]. Despite such obvious negative characteristics – the propensity to aging, increase brittle properties increase over time, etc., inherent in all organic substances, bitumen is a material with many useful consumer properties, which determines the breadth of it applications. The harsh of transport realities of our time, has identified the need for development and widespread introduction of a new kind of modification of bitumen

with various polymers to increase the stability of coatings for non-rigid pavements for roads to plastic and fatigue deformation. Most often this is called a polymer modified binder (PMB) [1, 5].

Overview of the problem

In the process of preparing a PMB bitumen acts as a complex and multi-component solvent for the polymer. The intensity of dissolution and homogenization of the system "bitumen – polymer" is influenced by a number of factors, including: the quality and nature of the original bitumen, plasticizer, structure and molecular weight of macromolecules of the polymer, its dispersion, and the technology of preparation and use of PBB the consumer. Ideally, in the process of making high-quality and homogeneous polymer-modified binder should be performed by a combination of factors: selected bitumen of appropriate quality, the technological operations should proceed at the lowest possible temperature and time of homogenization of the components of the modified binder, with the absence of bitumen in the phase of the smallest granules are no dissolved polymer.

Practically all PMB, on the spot production of asphalt mixture, passes through the following stages:

- preparation of PMB – the association of the binder and the polymer;
- "maturation" - the formation of the spatial grid of the polymer in the bitumen;
- storage of ready PBB from the manufacturer;
- loading into trucks;
- transportation to the consumer;
- drain and storage at the plant;
- production of asphalt mix.

The total duration of stages depending on the distance of transportation and weather conditions, as well as the technical capabilities of the consumer, may be up to several days. All this at each technological stage influences the quality of the binder, and intensifies the processes of destruction of a PMB, as evidenced by a number of research works [6-9]. Which found that the high temperature and duration of cooking process and storage cause the aging process of the PMB.

Material and Methods

We used a range of bitumen: BNDU 60, "LUKOIL-Nizhegorodnefteorgsintez" Norsi, Gazprom Moscow NPZ bitumen BND 90/130, "LUKOIL-Nizhegorodnefteorgsintez – BND 90/130, "Slavneft-YANOS – BNDU 100/130 Biturox. Polymers: Kraton D 1101, Shell company and SBS L 30-01A manufacturer Voronezhsintezkauchuk.

As plasticizers were considered: fuel oil M-100, industrial oil I-40, Athol 1101 for the preparation of the PBB, and two of plasticizer No. 1 and No. 2 do not have trade names. Selection of compositions of PMB and study of the properties of PMB was performed according to standard method Destructive indicators of the PBB depending on used of plasticizer, polymer and bitumen, manifested in delamination of the binder was studied by delamination in tube when heated at 180 °C for 72 hours.

The intensity of aging of the PMB, was estimated by loss of mass after heating, the change in the softening temperature according to standard methodics and methodic TFOT. In general, the efficiency of dissolution of the polymer in the bitumen depends on: molecular weight of the polymer;the size of the particles polymer;viscosity of the original bitumen and its group composition; temperature preparation of a PMB;duration mixing of the binder; In work was made, that the molecular mass, temperature mode preparation and duration mixing values unchanged. The variation happened by the viscosity of the original bitumen and the particle size of the polymer. For the experiment we used the bitumen BNDU 60 "LUKOIL - Nizhegorodnefteorgsintez" and polymers: Kraton D 1101 and SBS L 30 - 01A. It is obvious that to obtain effective PMB 60 of bitumen with a penetration of 64 mm^{-1} is not possible. Will be observe the shortage of light fractions for swelling and dissolution of polymer in binder. In this regard, stood the actual question about the necessity of using a plasticizer in the composition of the bitumen. Currently, the range of plasticizers is quite wide. In addition, each has a different effect on the properties of bitumen in different amounts.

Results and Discussion

To assess the influence of different plasticizers on the properties of bitumen and determine his then necessary quantities in the composition of the bitumen were injected different plasticizer in an amount of from 0 to 5%. Then determine the viscosity of bitumen, softening point and mass loss after warming. The data obtained are presented in tables 1-3.

Table 1 - Dynamics of change of conditional viscosity of bitumen from of the type and content of plasticizer.

Typeofplasticizer	The content of plasticizer in the bitumen, %					
	0	1	2	3	4	5
Fueloil M-100 (1)	63	75	81	85	91	97
Oil I-40 (2)		68	77	80	80	96
Esol (3)		66	77	82	86	96

Plasticizer 1 (4)		77	87	95	100	95
Plasticizer 2 (5)		72	80	92	93	85

Table 2 - Dynamics of change in weight of bitumen and plasticizer after heating.

Typeofplasticizer	The content of plasticizer in the bitumen, %					
	0	1	2	3	4	5
Fueloil M-100 (1)	0,4	0.4	0.4	0.5	0.6	0.6
Oil I-40 (2)		0.6	0.8	0.8	1.2	1.6
Esol (3)		0.4	0.4	0.7	0.9	0.9
Plasticizer 1 (4)		0.5	0.5	0.6	0.7	0.8
Plasticizer 2 (5)		0,.7	0.7	0.7	0.8	1.0

Table-3: Dynamics of changes in the softening point of the bitumen from the appearance and content of plasticizer.

Typeofplasticizer	The content of plasticizer in the bitumen, %					
	0	1	2	3	4	5
Fueloil M-100 (1)	53	51	50	50	49	49
Oil I-40 (2)		51	50	49	49	48
Esol (3)		51	50	48	48	48
Plasticizer 1 (4)		51	50	48	48	49
Plasticizer 2 (5)		51	50	48	48	49

The main purpose of the experiment by liquefying the bitumen to go out on his penetration at a temperature of 25^{o}C in the range of 85-90 mm^{-1} at which becomes possible dissolution and homogenization of the polymer. In parallel evaluated the influence of the plasticizer on the softening temperature, because the plasticizer should not significantly reduce this figure. As noted earlier, the plasticizer should not be volatile. The presence of considerable number of volatile components, in the composition of the binder determines the high rate their evaporation during warming up, which is an indicator of the tendency of the binder to aging and contributes to more significantly alter the softening temperature. Based on the obtained dependency graph was built, figure 1. In accordance with a pattern, the optimum

content of plasticizer in the bitumen amounted to: Fuel oil M-100 - 3.5%; Oil-40 - 4.5% ;Azol – 3.5%; Plasticizer №1 - 2.5%; Plasticizer № 2 – 3%. In accordance with the data of table 2, the maximum intensity changes in the mass of sample binder characterized the samples, plasticized with oil industrial. Minimum indicator characterized plasticizers from fuel oil and the plasticizer № 1. Changing the softening temperature, regardless of the type and quantity of plasticizer has not changed significantly. Specified the concentration of plasticizer were used for further selection of the composition of PMB 60. Selection was carried out using two different polymers. To work were taken linear SBS. The data obtained are presented in figures 2, 3.

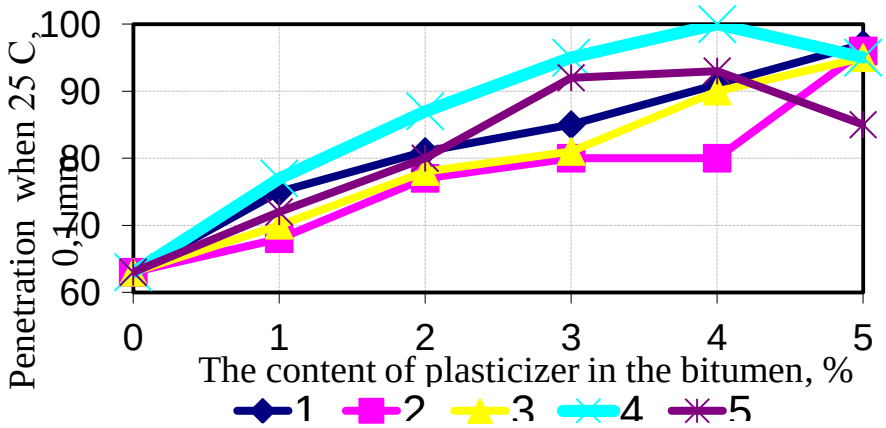

Figure 1 - Determining the optimum content of plasticizer in the bitumen.

As seen from figures 2 and 3, variation of the polymer was carried out in the interval of 2.8-3.8%. However, to obtain a binder on the penetration corresponding PMB 60 it did not work in all cases. By reason the high viscosity of the original bitumen and, obviously, the presence of small content of light fractions malthenes involved in the swelling and dissolution of the polymer, to enter into the higher content of the polymer was not possible. The most effective formulations of PMB 60 and their indicators properties are presented in table 4.

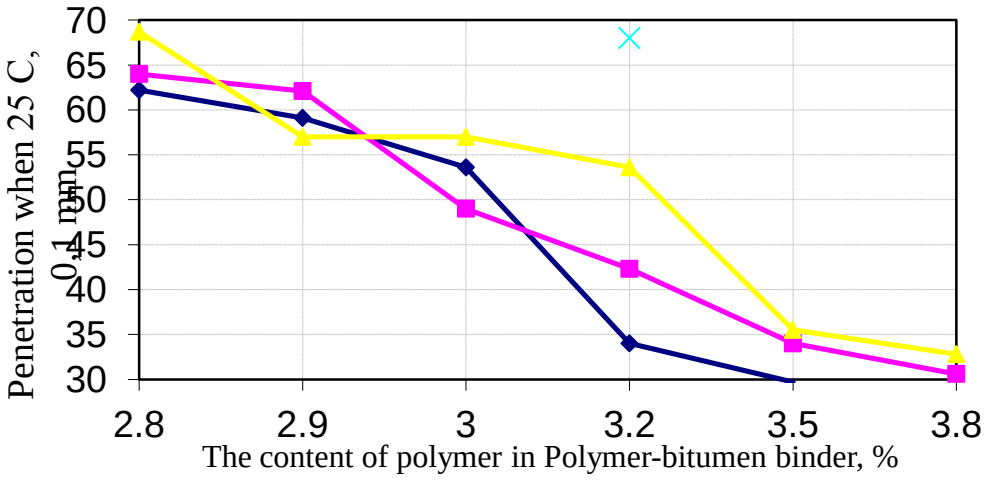

Figure 2 - Determination of the optimal content of polymer SBS L 30-01 A.

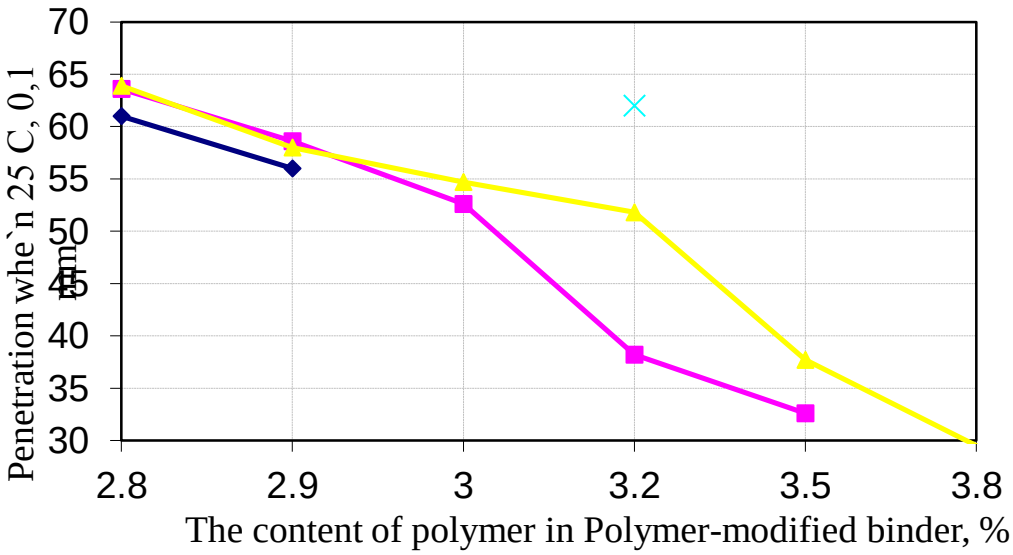

Figure 3 - Determination of optimum content of the polymer Kraton D 1101.

As the table shows, when using the polymer SBS L 30-01 A most effective formulations is obtained when working with the plasticizer №1. These formulations differ in the combination of useful properties such as substantial margin of penetration at temperatures of 25 and 0 °C, the highest, in the series, it should be noted an inverse correlation between the considered samples, temperature embrittlement and elongation. When working with this polymer, industrial oil as the plasticizer test is not passed.

If we consider a series of experiments with polymer Kraton D 1101, it must be noted the inverse relationship. With the use of industrial oils was obtained the most effective composition of the PMB. As the plasticizer fuel oil is not allowed to obtain the conditional binder.

Thus, we can conclude that by development of formulations of PMB need carefully approach the selection the aggregate system "bitumen-polymer - plasticizer" because there is a likelihood of their incompatibility.

This is evidenced by the data of table 5.

As can be seen, when studying the stability properties of the PMB after finding the tube, the maximum delamination is observed in samples prepared using with industrial oil and polymer Kraton D 1101.

Defective composition can be traced not only in the study of peelability in a tube, but also in the study of aging resistance. Aging resistance was determined by the method TFOT and to change the temperature of softening by this method and aging in the thin film.

The least proclivity to exercise defects are characterized samples prepared on Azol. In this case, the stratification and the difference in indicators is minimal, regardless of the polymer.

Table 4 - Indicators properties of matched formulations PMB 60.

Indicatorsproperties	Requirements PMB 60 GOST	SBSL 30-01A			KratonD 1101		
		Theratioplasticizer / polymer					
		Fueloil 3.5/2.8	Azol 3.5/2.8	Plasticizer 1 3.0/3.2	Azol 3.5/2.8	Oil 4.5/2.8	Plasticizer.1 3.0/3.2
The depth of needle penetration 0.1 mm 25℃ 0℃	>60 >32	 63 30	 65 33	 70 35	 64 32	 64 34	 63 32
Stretch , cm. 25℃ 0℃	 >25 >11	 32 12	 38 14	 55 13	 28 11	 26 13	 40 12
Thesofteningtemperature, ℃	>54	65	63	60	68	64	69
The brittleness temperature by Fraas, ℃	>-20	-22	-21	-23	-21	-24	-21
Uniformity	uniformly	uniformly	uniformly	uniformly	uniformly	uniformly	uniformly
Elasticity, % 25℃ 0℃	 >80 >70	-	 82 73	 86 70	 80 69	 67 53	 81 70

Table 5 - The propensity for destruction of matched formulations PMB -60.

Indicatorname	Requirements PMB 60 GOST, EN	SBS L 30-01A			KratonD1101		
		exactrelationplasticizer/ polymer					
		Fueloil 3.5/2.8	Azol 3.5/2.8	Plasticizer .1 3.0/3.2	Azol 3.5/2.8	Oil 4.5/2.8	Plasticizer .1 3.0/3.2
Peelabilityintube							
-brittleness temperature by Fraas, *°C* top pipe/the lower partpipe	-	-22/-23	-21/-21	-21/-24	-21/-22	-26/-18	-23/-19
-softening point by ring and ball, *°C* toppipe/ the lower part pipe	5	65/63	64/62	60/63	6767	58/66	68/67
Resistance to delamination :							
- Δembrittlement temperature, ℃	-	1	0	3	1	8	4
- Δ the softening temperature,	5	2	2	3	0	8	1
Δ the softening temperature after warming up , ℃	5	3	3	5	2	12	6
The resistance to aging, method TFOT							
the change in mass, %	-	0.6	0.8	0.9	0.9	1.5	1.0
the softening temperature, *°C*	-	2	3	4	3	11	5

In the next phase of work investigated the effects of bitumen on the performance of PMB properties. There is an established opinion that PMB should be prepared without plasticizer. For this selected bitumen less viscous, with penetration not less than 100 mm^{-1}, this corresponds to the Marche BND 90/130 or its derivatives.

In the present work for the preparation of PMB 60 was chosen three different the manufacturer of the binder. Indicators of initial bitumen's are presented in table 6.

Table 6 – Characteristics of bitumen different manufacturers.

Indicatorname	Differenttypesheavyresidue		
	BND 90/130	BND 90/130 NORSI	BNDU 100/130 Biturox
Manufacturer	GazpromMoscow	"LUKOIL-Nizhegorodnefteorgsintez"	"Slavneft-YANOS"
The depth of needle penetration 0.1 мм,			
25°*C*	101	106	108
0°*C*	28	28	30
Elongation, cm, at a temperature :			
25°*C*	98	100	100
0°*C*	5.8	6.1	5.2
Softening point by ring and ball,℃	46	45	45
The brittleness temperature by Fraas,℃	-27	-28	-28
The change in softening point by ring and ball,℃	5	5	5
Penetrationindex	-0.6	- 0.6	- 0.6

On the basis of these bitumen's and polymer SBS L 30-01A samples were prepared PMB 60. Indicators properties are presented in table 7.

As you can see, presents compositions meet the requirements. The difference is that when using the bitumen Moscow the content of the polymer, which can accommodate the system slightly lower, by 0.5%. In the context of c than, at the PMB on this binder minimum indicators from considered series. Such as: softening point, brittleness and elasticity at all temperatures. Obviously, this can be explained by the difference in the group composition of the studied bitumen's. Binders, prepared on the Norsi and Biturox characterized by high indicators completely corresponding with the requirements of normative documents. Interesting data were obtained in the study of destructive processes, table 8.

Table 7: Indicators properties of PMB 60 on different bitumen.

Indicatorname	PMB 60			Requirements PMB 60 GOST
	BND 90/130	BND 90/130 NORSI	BNDU 100/130 Biturox	
Manufacturerofbitumen	Gazp-romMos-cow	"LUKOIL-Nizhegorodneft eorgsin-tez"	"Slavneft-YANOS"	
The content of the polymer	3,5	4	4	
The depth of needle penetration 0.1 мм,				
25°C	64	67	66	60
0°C	32	36	33	32
Elongation, cm, at a temperature :				
25°C	43	45	43	25
0°C	13	18	15	11
Softening point by ring and ball, *°C*	62	68	67	54
The brittleness temperature byFraas,*°C*	-24	-27	-26	-20
The change in softening point by ring and ball,*°C*	5	3	4	5
Elasticity, %, not less, at a temperature				
25°C	84	89	86	80
0°C	73	77	75	70

Table 8 - Propensity to destruction of selected formulations PMB 60 on different bitumen's.

Indicatorname	Requirements PMB 60 GOST, EN	Polymer-modified binder - 60 on the bitumen		
		BND 90/130	BND 90/130 NORSI	BND-U 100/130 Biturox
Peelabilityintube				
-brittleness temperature by Fraas,*°C* top pipe/the lower partpipe	-	-24/-22	-27/-26	-23/-29
-softening point by ring and ball, *°C* toppipe/ the lower part pipe	5	62/60	68/68	68/54
Resistance to delamination :				
- Δembrittlement temperature, *°C*	-	2	1	6
- Δ the softening temperature	5	2	0	14

Δthe softening temperature after warming up, °*C*	5	4	3	5
The resistance to aging, method TFOT				
the change in mass, %	-	5	3	7
the softening temperature, °*C*	-	4	2	12

As you can see, the worst results were obtained in the preparation of PMB on Biturox binder. This applies both to the stratification of the binder when tested in the tube and the propensity to aging. PMB performed on the bitumen of Moscow, in spite of not high quality in accordance with standard indicators in the research process, destructive of the indicators establish itself better and meet the requirements of GOST and EN [3, 10].

The best indicators, at all stages of the experiment established itself samples prepared on the bitumen Norsi.

Obviously, such difference in the properties of the binders modified by polymer related to the quality of bitumen used and their group composition. Moscow bitumen has a significant amount of asphaltenes. It is known that asphaltenes in relation to polymers are competing system, which explains the smaller content of the polymer in the PMB.

The bitumen Norsi contain a significant the number multanovas part, which acts as a plasticizer for the polymer when their association. Biturox characterized by not constancy of the colloid disperse phase and the content of additional impurities that have a negative impact on the stability properties and in particular sovmestimosti with polymer class styrene-butadiene-styrene.

Conclusions

As can be seen, the presence of a plasticizing component in the binder, in some cases, is a prerequisite to achieving the quality of a PMB. However, it should be noted that the plasticizer makes the main contribution to the processes of destruction, manifested in the form of stratification and aging, evaluation of which was performed by changing the mass of the binder and the softening temperature after warm-up. Therefore, one of the fundamental requirements to the plasticizers should be a property - as long as possible save the indicators in perfect execution up to the end of the term of use of the composition. Thus, can conclude that by development formulations of PMB need carefully approach the selection the totality of the system "bitumen - polymer - plasticizer" because there is a likelihood of incompatibility, or use special techniques aimed at reducing their competing abilities.

Acknowledgments

The work was carried out within the state task of the Ministry of education and science of the Russian Federation №1950, as well as the project of strategic development of BSTU named after. V. G. Shukhova.

References

1. Ayupov, D.A.andA.V. Murafa, 2009. Modified bituminous binders in construction.Building materials. 8(12): 50-51.
2. Vysotskaya M.A., D.A.Kuznetsov, S.Y.Rusina, and E.V.Chevtaeva,2 013. Experience and Prospects of Nanomodification Using in Production of Composites Based on Organic Binders.5th International Conference NANOCON 2013 – Brno, ChechRepablik, EU.
3. Polyakova, V.I. andS.V. Polyakova, 2013. Peculiarities of production and application of polymer-bitumen binders in road construction. Roads and bridges, 3(12): 277 - 298
4. GOST R 52056-2003. Binders polymer-bitumen road on the basis of block copolymers. Introduction. 01.01.2004. M.: Publishing house of standards, 23 p., 2003.
5. Quintero, L.S. andL.E. Sanabria,2012. Analysis of Colombian Bitumen Modified With a Nanocomposite.Journal of Testing and Evaluation (JTE), vol. 40, issue 7, pp: 93-97,
6. Lucash, E.A.,Kuznetsov, D.A. andM.V. Babanin, 2013. Efficient asphalt mixture using modified fillers. Bulletin of the Belgorod state technological University named after. V. G. Shukhov, 6(6), pp: 57-60.
7. Vysotskaya, M.A. andM.Y.Fedorov, 2013. Development of the nanomodified filler for asphalt concrete mixtures. Bulletin of the Belgorod state technological University named after. V. G. Shukhov, 6(6), pp: 61-65.
8. Vysotskaya,M.A. andS.Y.Rusina, 2014. About the prospects of using nanotubes in the preparation of polymer-asphalt binder. Roads & bridges, 2(2): 171-187.
9. Khozin, V.G.,and R.K. Nizamov, 2009.Polymer nanocomposites for construction purposes, Building materials, 8(12): 32-35.
10. EN 133399,2013.Determining stability of modified bitumen.Introduction. 01.01.2015. M.: Publishing house of standards, pp:12.

Corresponding Author:

Marina Alekseevna Vysotskaya*,