

Compatibility Studies of Mixed Thermoplastic Rubber with Road Bitumen

Dmitry Makarov*, Damir Ayupov, Asia Murafa and Vadim Khozin

The Kazan State University of Architecture and Building Construction 420043, Russia, Kazan, Zelenaya Street No., 1

Abstract: This paper is devoted to the study of bitumen compatibility with mixed thermoplastic rubber designed for its modification which is three polymer mixture. Unlike most popular bitumen modifiers based on butadiene and styrene copolymers having unsaturated main chain, the proposed polymer is composed of components with saturated hydrocarbon main chain. Thus, the increased weather resistance is provided for the products and designs based on modified bitumen. The solubility of mixed thermoplastic rubber and its components separately is studied.

Keywords: bitumen, bitumen modification, mixed thermoplastic rubber, polymer bitumen, weather resistance.

INTRODUCTION

The increasing demands for performance properties, particularly for bitumen-based materials durability call for its modification. The main disadvantages of bitumen: intense atmospheric aging and narrow temperature range of plasticity due to its chemical nature.

The considerable commercial interest for polymer modified bitumen appeared since the late 1970s [1]. It is generally accepted that the high temperature sensitivity of unmodified bitumen providing rut appearance on asphalt roads in summer and winter low temperature brittleness of coatings is significantly limited by its use [2], while bitumen modified polymer additive allows to produce composite materials with improved consumer properties [3]. A perfect modifier shall also be easily combined with bitumen, as well as be resistant to UV radiation [4]. Good solubility of used polymer additives in melt bitumen allows homogenization without the use of plasticizers and carbon solvents [5]. It is believed that synthetic thermoplastic rubber is the most effective among bitumen modifiers by the complex of technological and operational properties meeting the abovementioned requirements. However, the most used block copolymers among synthetic thermoplastic rubbers of styrene and butadiene (SBS polymers) have several disadvantages, including poor resistance to climatic influences [6]. In this regard, the following goal was set: to create thermoplastic rubber (TPR), which has SBS advantages, but without its disadvantages and developing maximum modifying effect.

Low-viscosity bitumen, comprising of petrolene fraction with the domination of paraffin-naphthenic oils is commonly used for roads. It is to concluded that bitumen modifier should be well dissolved in this fraction and, hence, be nonpolar.

The main prerequisites for TPR development were the original properties of their components: ethylene-propylene rubber (EPR) has a good elasticity, frost resistance, ultraviolet (UV) radiation and ozone resistance, and high-density polyethylene (HDPE) has high resistance to UV and ozone, heat resistance, good strength, but insufficient frost resistance. Both polymers (EPR and HDPE) belong to non-polar polymers and therefore should be well combined with such bitumen as BND-90/130. Furthermore, it was noted [7] that polyolefins comprising of bitumen-polymer binders are less prone to the crystallinity, rather than in pure form, that should have a positive effect on the compatibility of selected polymer with bitumen. The composition of the mixed thermoplastic rubber should be added by isoprene rubber, which, as it is known [8], will improve the adhesion of modified bitumen to the reinforced basis and mineral fillers.

The combination of these polymers allows for TPR improvement which will be without EPR, HDPE and especially SIR deficiencies.

It is known [9] that the maximum modifying effect of bitumen is exhibited by polymers which are well compatible and soluble in bitumen. Therefore, the studies to assess the compatibility with BND-90/130 TPR and BN-70/30 bitumen were conducted.

METHODS

The process of bitumen and polymers combination is reduced essentially to the physical-chemical interaction of the latter with petrolenes, the final outcome of which depends, on the one hand, on the degree of thermodynamic compatibility which is connected with the chemical nature and the molecular weight of polymer, and on the other hand it is connected with the temperature and intensity of mechanical mixing (dispersing). True polymer solutions in bitumen ensuring the system stability over time, may be formed in the presence of thermodynamic affinity between the components characterized by similarity (or equality) of

*Address correspondence to this author at the Kazan State University of Architecture and Building Construction 420043, Russia, Kazan, Zelenaya Street No. 1; Tel: (843) 510-47-34; Fax: (843) 238-39-13; E-mail: makarov@kgasu.ru

bitumen solubility parameters - $[\delta_1]$ and $[\delta_2]$ polymer. At.

$$\delta_1 - \delta_2 = 0,$$

i.e. $\delta_1 = \delta_2$

the full heat of mixing makes

$$\Delta H = V_1 * V_2 (\delta_1 - \delta_2)^2 = 0$$

(V_1 is mixture volume, V_2 is polymer volume). In this case, the main role at dissolving is played by entropic factor. It is known that the polymer dissolution feature is a important role of entropy, because dissolution alters macromo-lecule conformation. But even at high affinity, polymer initially passes through a swelling step and its complete dissolution requires the system temperature increase and intensive mixing. The composition of oil bitumen includes both marginal and unsaturated hydrocarbons, aromatic and polycyclic compounds with different polarity and different values of solubility parameter. In particular, the bitumen $[\delta]$ is equal to 17.4 $(\text{MJ}/\text{m}^3)^{0.5}$, the saturated malthenes $[\delta]$ is equal to 14.3, the aromatic malthenes $[\delta]$ is equal to 18.0, and the resin $[\delta]$ is equal to 18.6 $(\text{MJ}/\text{m}^3)^{0.5}$. Let's note that the solubility parameters of saturated bitumen malthenes are close to the saturated hydrocarbon solvent parameters (15.1 $\text{MJ}/\text{Nm}^3)^{0.5}$ of n-heptane, aromatic malthenes - to aromatic

hydrocarbon solvents $(18.15 \text{ MJ}/\text{m}^3)^{0.5}$ of toluene. Therefore, when polymers are selected for making the bitumen-polymer compounds one may take into account in the first approximation the solubility data of a particular polymer as the basis in the hydrocarbon solvent or by oil swell. Thus, the bitumen compatibility with TPR was determined using toluene simulating the malthenes portion of bitumen.

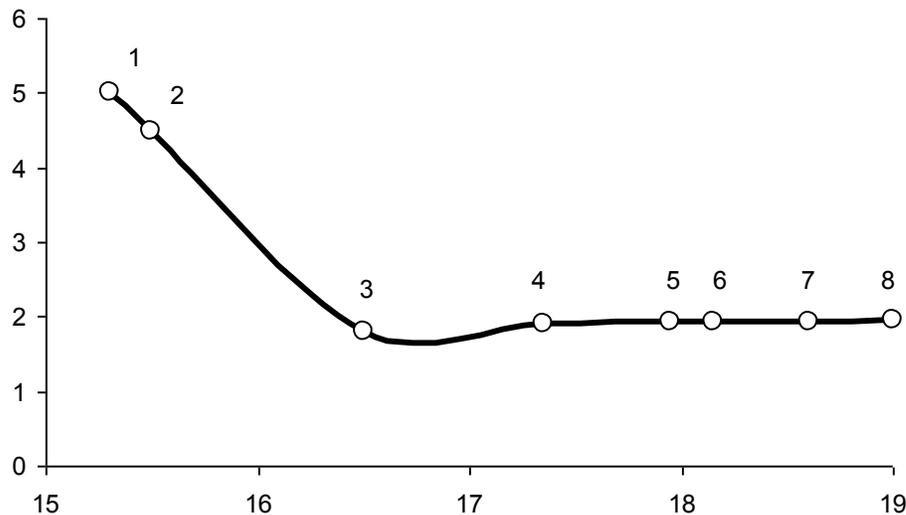
MAIN PART

In our work, the solubility parameter value was determined to assess the bitumen compatibility with mixed thermoplastic rubber. 10% solutions of thermoplastic rubber were prepared in hydrocarbon solvents. The time of a homogeneous solution formation was determined at the temperature of 25 °C. TPR dissolution (in corresponding solvent) period was used as a benchmark parameter. The data obtained are shown in Fig. (1), which demonstrate that the curves have a pronounced minimum at $\delta = 16,5$ $(\text{MJ}/\text{m}^3)^{0.5}$.

Dependence of dissolution period for mixed thermoplastic rubber on solvent type

Using the known data of solubility parameters [9] the TPR $[\delta]$ value was calculated to view the content of each component in TPR equal to 16.66 $(\text{MJ}/\text{m}^3)^{0.5}$. These results allow us to predict a good TPR solubility in saturated and aromatic bitumen petroleues.

Dissolution time, 24 hours

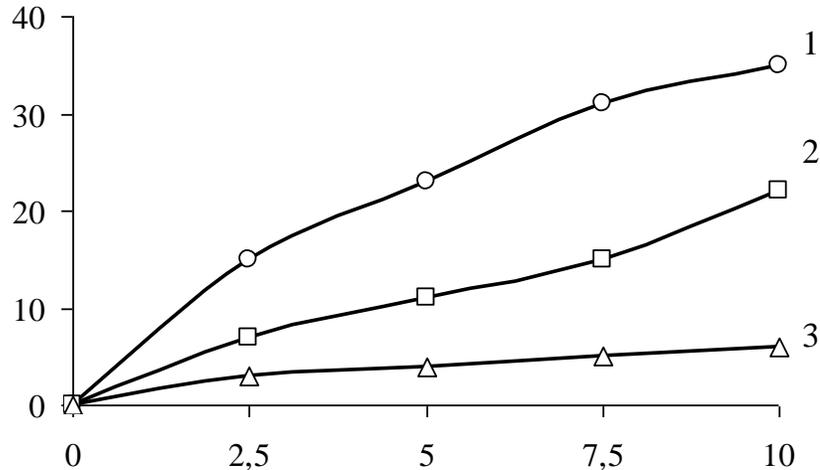


Solubility parameter $(\text{MJ}/\text{m}^3)^{0.5}$

- 1 - heptane (petrol);
- 2 - ethyl ester;
- 3 - Turpentine;
- 4 - Carbon tetrachloride;
- 5 - Meta-xylene;
- 6 - Toluene;
- 7 - Benzene;
- 8 - Chloroform.

Fig. (1). Dependence of dissolution period for mixed thermoplastic rubber on solvent type.

Dissolution time, h



Polymer concentration, %

1 – mixed TPR;

2 – SIR;

3 – EPR.

Fig. (2). Polymer dissolution concentration dependences in toluene at 25 °C.

It is known that not only the solubility parameter but also a number of other factors influence the polymer solubility: molecular weight, molecular weight distribution, crystallinity, etc. [9]. This should be considered when the compatibility of polymers with bitumen and their effect on modified bitumen properties is assessed.

The determination of dissolution rate of TPR separate components and TPR in different concentrations (2.5-10 %) was of interest. EPR, HDPE, SIR and TPR solutions were prepared in toluene at $t = 25\text{ °C}$ to do this. As Fig. (2) demonstrates, all the cases of polymer concentration increase show a toluene dissolution period increase.

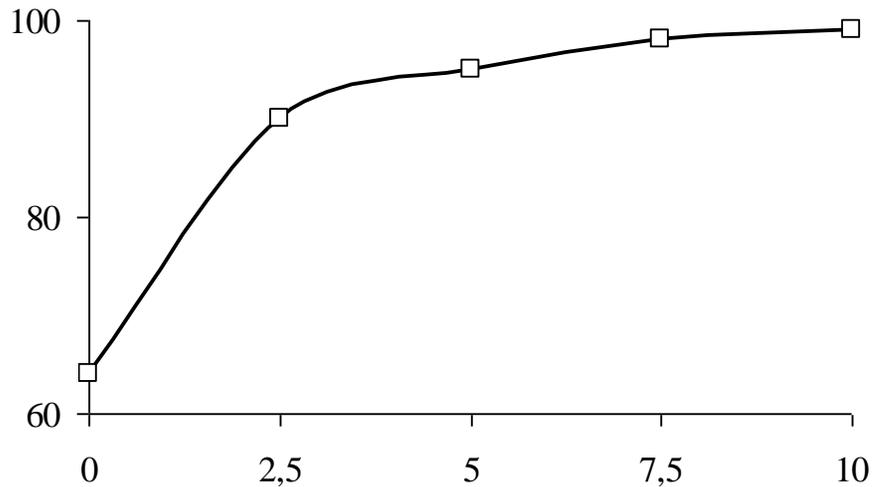
Polymer dissolution concentration dependences in toluene at 25 °C.

EPR has the best solubility. The increase of its concentration in toluene does not significantly affect the dissolution time. In the case of SIR and TPR especially the dissolution time is 2 and 3 times higher for EPR, respectively. Polyethylene in these conditions, i.e. at 25 °C is not soluble in toluene at all.

Fig. (3). shows the dependence of HDPE phase state in toluene. You may notice that the critical solution temperature of polyethylene in toluene (VKTR) makes 95 °C. At 1-10% concentrations below VKTR temperature the solution turns

"Toluene-HDPE" system state diagram

T, °C



Polymer concentration, %

Fig. (3). "Toluene-HDPE" system state diagram.

in a two phase system. For Example, the polyethylene solubility in toluene is strongly dependent on temperature. At $t > 25^{\circ}\text{C}$ EPR, SIR and TPR-2 in toluene are solutions. The phase separation of these systems is likely to be observed below 25°C . The reduced rate TPR dissolution rate in toluene is obviously reasoned by the fact that there is HDPE in TPR composition. It seems that each of the bitumen components influences TPR dissolution in toluene. It is interesting to note the fact that the HDPE contained in TPR is dissolved in toluene and in bitumen, although the introduction reduces the TPR dissolution rate. However, it is known that mixed TPR is a mechanical mixture according to the authors [8]. Due to this, we can assume that its delamination is performed in good solvents. However, this is not observed. This allows the suggestion that the TPR is not purely a physical mixture.

According to the data presented in Fig. (4), the TPR dissolution rate is increased with temperature increase. It is also worthy to note the fact that the difference in TPR dissolution rates decreases when temperature increases. This is especially noticeable at the temperatures above 80°C , which is, as mentioned earlier, explained by HDPE phase transition from one state to another. With polymer concentration increase in a solvent, and the temperature decrease the dissolution time increases. The highest values are demonstrated at the concentrations of up to 2.5%.

Concentration dependences of mixed TRP dissolution in toluene from on dissolution temperature

Thus, the obtained data analysis shows that the greatest TRP dissolution and its components occurs at the concentrations of up to 2.5% in the solvent. At higher polymer content in toluene the turbidity of solutions is observed which indicates its incomplete dissolution.

Considering the above statement, it was interesting to study the effect of individual components on bitumen properties. Table 1 and Fig. (5) data show the effect of TPR individual components: EPR, SIR and HDPE at the concentrations of 5, 10 and 15% on the properties of BND-90/130 road bitumen.

Dependence of softening and fragility temperature on polymer concentration in bitumen

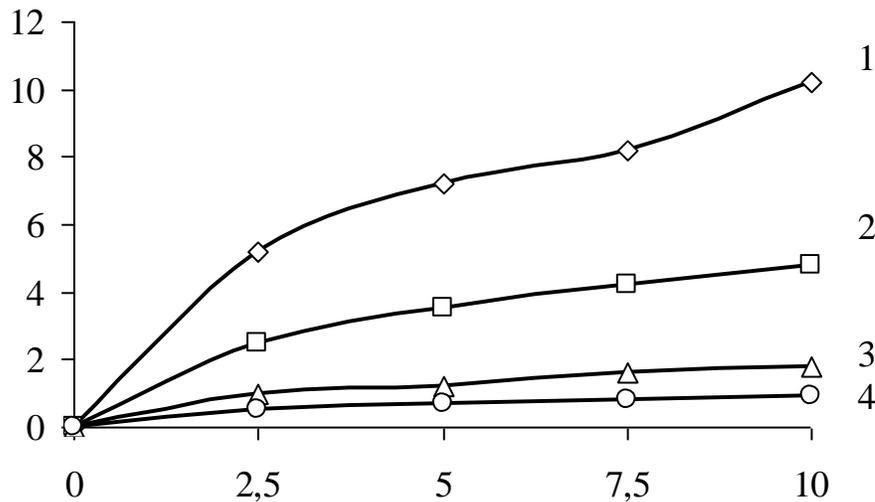
It is evident that the greatest influence on the BPK temperature range expansion is due to EPR and HDPE. When EPR concentrations in bitumen are increased from 5 to 15% the deformability interval of such BPK is increased from 75 to 120°C . It should be also noted that the EPR introduction in bitumen reduces the brittleness temperature by Fraasu to -46°C which is a greater extent compared to the SIR and HDPE.

Besides, EPR provides climatic influence resistance for bitumen polymer compositions [8]. However, bituminous compositions modified by EPR are weaker than the compositions modified by thermoplastic rubbers by dissolution speed in bitumen at the processing temperature.

Polyethylene-bitumen compositions with the increase of thermoplastic content up to 15% demonstrate a significant increase in heat resistance up to 115°C , which makes bitumen composition value significantly higher than the rate of bituminous compositions with EPR and SIR at the same level of bitumen content.

Polyethylene has the greatest influence on the TPR and BPK properties. This is associated with close HDPE solubility parameters and saturated bitumen malthenes. Thus, a significant thermoplastic portion is dissolved in oil fraction

Dissolution time, h



Polymer concentration, %

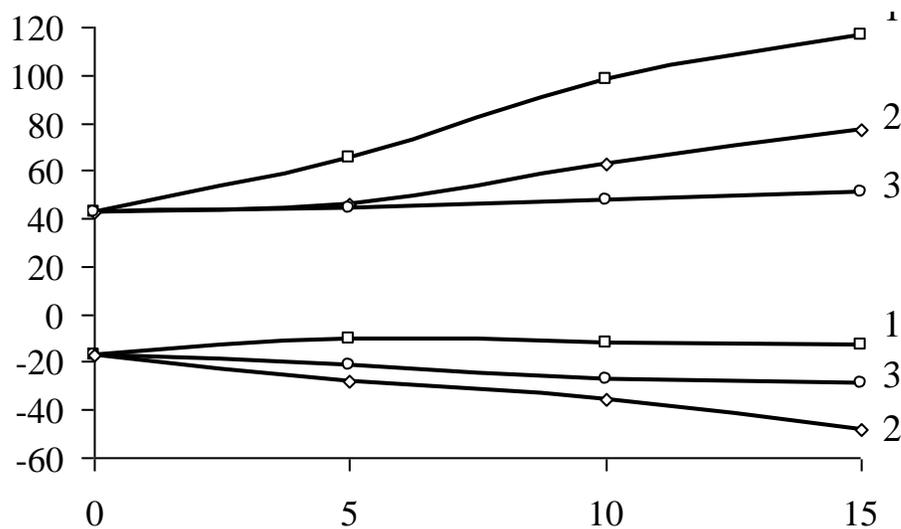
- 1 – dissolution at the temperature of 60°C ;
- 2 – dissolution at the temperature of 80°C ;
- 3 – dissolution at the temperature of 100°C ;
- 4 – dissolution at the temperature of 120°C .

Fig. (4). Concentration dependences of mixed TRP dissolution in toluene on dissolution temperature.

Table 1. BPK content and properties with separate TPR components.

Content	Plasticity Interval, °C	Penetration x 0,1 mm	
		25 °C	0 °C
BND-90/130	59	138	64
BND -90/130+5% EPR	75	102	58
BND -90/130+10% EPR	99	72	54
BND -90/130+15% EPR	120	67	49
BND -90/130+5% SIR	66	128	71
BND -90/130+10% SIR	76	112	80
BND -90/130+15% SIR	86	94	91
BND -90/130+5% HDPE	74	106	34
BND -90/130+10% HDPE	107	66	23
BND -90/130+15% HDPE	127	43	16

T, °C



Polymer concentration, %

1 – BND-90/130+ HDPE;

2 – BND-90/130+ EPR;

3 – BND-90/130+ SIR.

Fig. (5). Dependence of softening and fragility temperature on polymer concentration in bitumen.

modifying bitumen in general. It accelerates TPR dissolution in bitumen at processing temperatures (150-180 °C). It also enables TPR obtaining in granules or superfine powder. SIR and EPR additions into bitumen expands BPK plastic range, but to a lesser extent (Table 1 and Fig. (8)). SIR advantage is in its increased stickiness, which improves the cohesive strength of the filled BPK and also various substrate adhesion [8].

Introduction of elastomers in bitumen in all cases leads to a decrease in penetration value decrease. It should be noted that with its concentration increase, the decrease of this parameter occurs to a lesser degree than at HDPE use. This can be attributed to initial polymer properties: EPR and SIR have high low-temperature properties and HDPE has a good stiffness and crystallinity, but lacks frost resistance (Table 1).

CONCLUSION

The mixture modifier designed by Solomentsev A.B. [10] should be attributed to the plasticizing structuring additives and may be an alternative for the popular SBS polymers.

SUMMARY

Thus, the assessment of the main BPK properties modified by individual TPR components allowed to trace their influence on the bitumen properties. HDPE largely influences the heat resistance of modified systems, and low temperature bitumen properties improve EPR to a greater degree as expected. At that, this elastomer is resistant to ozone, radiation, UV [8], which suggests good BPK weather resistance using EPR.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

None declared.

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