

POLYMER MODIFIED BITUMEN

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Introduction

Bitumen is a complex hydrocarbon material which is used for road construction and production of bitumen adhesives, waterproofing coatings and roof bitumen membranes. Bitumen is a good material for these application, but not perfect [1-3]. Especially, in road construction the increasing number of vehicles on the roads, have enforced the need to develop methods improving the basic physico-mechanical and rheological properties of the bitumen binders such as: the strength and fatigue life (resistance to cracking and permanent deformation - rutting), the temperature sensitivity in a wide range of viscoelasticity (difference between softening point and brittle point should be as great as possible) and the service life of asphalt pavements (wear resistance and fatigue). This forced the bitumen producers to look for a new material and technological solutions that would improve the properties of bitumen, so that they meet the needs of the market, both in technical and economic terms. In this paper we present the benefits of using polymers as an asphalt modifiers, especially the low molecular weight reactive compounds, which are capable of forming polymer network with bitumen "in situ" in the process of its modification.

Bitumen modified by elastomer and thermoplastic

Currently the best-known and widely used methods of improving the quality and performance properties of the bitumen is their modification with the polymers. Among the polymeric modifiers currently used on an industrial scale, the most widespread are the "passive" modifiers, such as copolymer of styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), ethylene–vinyl acetate rubber (EVA), polyethylene (PE), and atactic polypropylene (APP). Those kind of modifiers are only physically mixed with bitumen and due to this some improvement of bitumen properties is the result of only the physical interactions with bitumen. [2-3]

For economic reasons, producers of bitumen for their modification also use the polymer wastes from the recycling processes of plastic products. In this field the crumb rubber (CR), which are obtained from waste tyres, proved to be the most effective modifier. Unfortunately, the modification of bitumen with CR increases the viscosity of bitumen. Beside this the rubberized bitumen is not stable during a storage at high temperature, which significantly limits the scope of its use in roads construction [1-2]. In the table 1 are presented the most popular polymers which are used to modify bitumen at the industrial scale and their influence on the properties of modified bitumen.

Unfortunately the modification of the bitumen with virgin polymers is still limited by high cost of modifiers, low ageing resistance of modified bitumen and their low resistance to heat, oxidation and ultraviolet radiation (UV). As shown in Table 1, modifiers formed from the polymer wastes also do not meet the intended expectations. Beside this the very important problem in the modification of bitumen with these kinds of polymers is also a low compatibility of them with bitumen what causes the poor storage stability of polymer modified bitumen [3-4].

The properties of bitumen modified by different kind of polymers [2-3]

Type of polymer	Examples	Advantages	Disadvantages
Elastomer	SBS, SIS	<ul style="list-style-type: none"> • improvement of the elasticity (rutting resistance), • improvement of the temperature sensitivity, 	<ul style="list-style-type: none"> • problem with the compatibility with some bitumen, • low resistance to heat, UV radiation, oxidation, • relatively high cost
	Crumb Rubber	<ul style="list-style-type: none"> • improvement of the elasticity (rutting resistance), • low cost, • improvement of the temperature sensitivity, 	<ul style="list-style-type: none"> • instable at storage, • high viscosity, • low resistance to heat and oxidation,
Thermoplastic	PP, PE	<ul style="list-style-type: none"> • improvement of the resistance to high temperature • low cost 	<ul style="list-style-type: none"> • lack of flexibility • instable at storage,

From our research work it follows that, the overcoming the basic problems of currently used polymeric bitumen modifiers might be solved by using the low molecular weight “active” modifiers which react in chemical way with compounds of bitumen. These kind of modifiers can be used in modification process of bitumen in low amount (below 1 wt. %) and with their use it is possible to form "in situ", during the modification process, the polymer network, which significantly changes the physico-mechanical and rheological properties of the bitumen [1].

Active modifiers of bitumen

In the structure of bitumen, can be distinguished the presence of chemical groups such as $>NH$, $-OH$, $-SH$ and $-COOH$ (Fig.1). For this reason bitumen is reactive to compounds that have isocyanate groups (diisocyanates, poliisocyanates and urethane prepolymers with free isocyanate groups) [5-8].

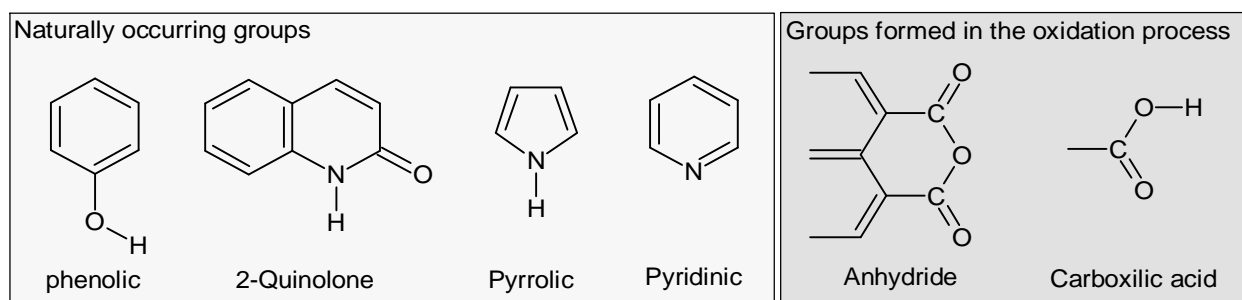


Fig. 1 Functional groups present in bitumen structure [9].

However, in our research we proved that not every type of isocyanate compounds is suitable for bitumen modification. This conclusion was supported by the results of the research in which we compared the influence of two kinds of diisocyanates on the properties and stability of the bitumen modified by them. In these research we used as a modifier of bitumen the crystalline, solid 4,4'-Methylenebis(phenyl isocyanate) (solid-MDI), and liquid 4,4'-Methylenebis(phenyl

isocyanate) stabilized by carbodiimide (liquid-MDI). After the modification process the viscosity, softening point, penetration and stability tests were tested for all types of modified bitumen and the obtained results are shown in Table 2. Thermogravimetric analysis (TGA) of liquid-MDI and solid-MDI under air atmosphere was also performed to determine the degradation temperature of these diisocyanates (Fig. 2).

The TGA analysis of the diisocyanates showed that the more stable in the temperature of the bitumen modification is liquid-MDI, stabilized by carbodiimide. It should be emphasized that the initial degradation temperature of solid-MDI, corresponding to 2 wt.% of mass loss, is 130°C, which indicates that the modification process with this modifier should be conducted at much lower temperature than that used at industrial conditions (approx. 180°C).

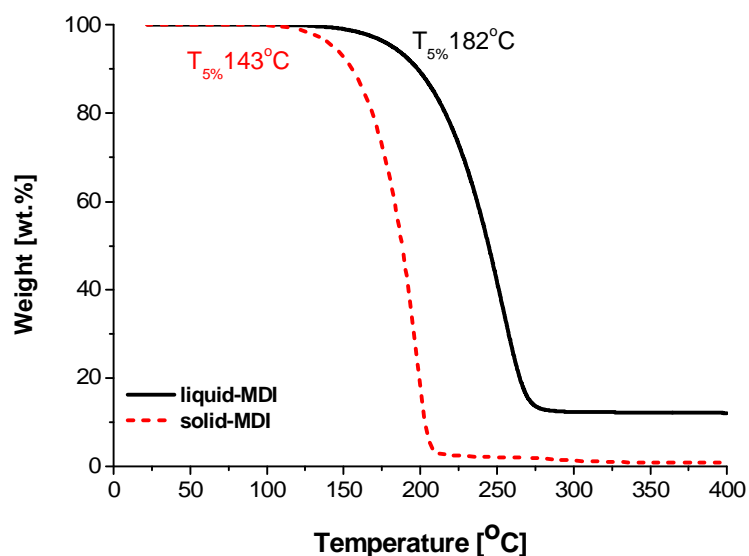


Fig. 2 Mass loss as a function of temperature for liquid-MDI and solid-MDI.

Table 2

The properties and stability of bitumen modified by solid and liquid MDI

Type of bitumen	Amount of modifier [wt.%]	Viscosity at 180 °C [Pas]	Penetration [0,1 mm]	Softening point [°C]	Stability at tube test	
					Difference in softening point [°C]	Difference in penetration [0,1 mm]
Pure bitumen	0.00	0.07	74	47.7	0.1	0
Bitumen/Solid-MDI	0.25	0.06	64	49.2	0.6	1
	0.50	0.08	61	51.1	0.6	3
	1.00	0.08	52	54.4	13.2	12
Bitumen/Liquid-MDI	0.25	0.06	69	49.6	0.1	1
	0.50	0.04	62	49.6	0.1	1
	1.00	0.04	53	50.6	0.7	1

According to the data given in Table 2 it can be concluded that under the influence of both types of diisocyanates, the properties of the bitumen are improved. In addition, the efficiency of the modification is comparable. However, significant differences can be pointed out in the

stability of bitumen, because the bitumen modified with solid-MDI used in the amount of 1 wt.% turned out to be unstable.

Conclusions

Based on the information and results presented in this work the following conclusions may be drawn:

- the best-known and widely used method of improving the quality and performance properties of the bitumen is their modification with the polymers,
- from the economical and environmental point of view the use of crumb rubber obtained from waste tyres to modify bitumen is the best solution to lower the cost of modified bitumen, unfortunately the rubberized asphalt is not stable during a storage at high temperature,
- the main disadvantages of currently used polymeric bitumen modifiers might be solved by using the low molecular weight “active” modifiers which react in chemical way with compounds of bitumen, but the ideal reactive modifier should be characterized by high thermal stability, proper for the industrial processing temperature.

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