Modular mobility investigation of polymer binder bitumen

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Abstract. This paper is aimed to obtain polymer binder bitumen for the road applications with improved properties. Objectives included studying the degradation of crumb rubber during devulcanization in melted petroleum bitumen for its modification and resulted structural properties of bitumen. Using equilibrium swelling technique reduced density of the polymer chains was observed and analysis of sol-gel fractions showed a significant decrease in gel fraction. Under selected method of devulcanization 64% of the backbone rubber remained. With the $^{1}$H NMR relaxation method the reduction of bitumen molecular mobility was observed due to thickening of its light fractions. The effectiveness of devulcanization was optimized using a new agent in a powder form and vacuum application. The developed binder has an improved spectrum of physical and technical properties such as softening point temperature, hardness, elasticity, frost resistance, low temperature characteristics.

1. Introduction

Modification of bitumen polymers is an effective way to obtain high performance technology of building materials on the basis of organic binder. High relative cost of thermoplastic elastomers and rubbers hinders their widespread application for bitumen properties improvements.

At the same time the problem of used car tyre recycling is well known all over the world. Today the main usage of crumb rubber, produced by grinding of old tyres is to mix it with thermoplastics and thermosets [1-2] to reduce the cost of raw polymer blends, but crumb rubber degrades such mixtures’ properties to some extent.

Direct modification of bitumen crumb rubber (CR) is considered ineffective, as it acts in bitumen as filler, causing swelling and forming elasticity centers, but does not create a polymer grid. “The dry” additional procedure method of crumb rubber in asphalt concrete mixture is considered unsatisfactory [3]. Therefore, to implement the properties of polymer in bitumen the rubber crumb must be devulcanized, making cross-linked polymer into linear (or branched) and therefore soluble.

We have developed a chemical method of rubber devulcanization for bitumen modification, where devulcanization is performed directly in bitumen. It should be noted that unlike devulcanization in solvents used for rubber regeneration [4], in this case there is no need to allocate a dissolved rubber
from the solvent, since the purpose of crumb rubber devulcanization in bitumen is to obtain bitumen-polymer binder.

The composition included bitumen BND 90/130 (100 wt. parts), crumb rubber (20 wt. parts), devulcanizing agent (0.06 – 0.7 wt. parts). The technology of producing bitumen – polymer composition was addressed. Preparation of the bitumen-polymer compositions was performed in the following way: bitumen was heated in the reactor to a temperature 90°C with constant stirring, rubber crumb and devulcanizing agent were introduced sequentially, after vacuum was applied in the reactor with temperature rise to 220 °C. The stirring time was 1.5 hours.

In this mode bitumen was modified with the rubber crumb. We used Neozon D (naphthyl-2) - a secondary aromatic amine (Figure1) - as a devulcanizing agent.

Our experiments demonstrated that neozon D is an effective agent for devulcanization; it reduced a gel fraction to 35 % and grid circuit density by 5.5 fold. The resulted molecular weight of rubber in asphalt is more than 60 % of the original weight; therefore rubber degradation presumably occurs mainly by sulfur links.

The developed devulcanization technology of crumb rubber in asphalt environment allows obtaining a composite polymeric bitumen binder with enhanced technical properties. However the implementation of the composition obtained is hampered by the lack of opportunity to provide vacuum processing in manufacturing. So, we have produced the similar composition using the same technology in rotor – pulsation apparatus.

According to GOST 39 – 79 “Naphtam – 2. Specification” neozon D can be manufactured both in powder form and in form of crumbling flakes. Experiments indicate that the form of neozon D affects the efficiency of vulcanization.

The main properties of polymer modified bitumen (PMB) are represented in Table 1.

| Composition | Softening temperature, °C | Penetration n0, 0,1 mm | Penetration n100, 0,1 mm | Ductility δ50, cm | Ductility δ100, cm | Elasticity δσ, % | Elasticity δ0, % | Flexibility, °C | Penetration index |
|-------------|--------------------------|------------------------|--------------------------|-------------------|-------------------|----------------|----------------|----------------|-----------------|
| Bitumen 90/130 | 44                       | 97                     | 50                       | 95                | 0                 | 13             | -              | 5              | -1.2            |
| Bitumen 90/130+20% CR | 58                      | 56                     | 15                       | 14                | 0.5               | 55             | 65             | -5             | -1.2            |
| Bitumen 90/130+20% CR+0,1% powder neozone, vacuum BND | 76                       | 45                     | 36                       | 9,7               | 5                 | 83             | 73             | -25            | 3.5             |
| Bitumen 90/130+20% CR+0,1% powder neozone, RPA BND | 68                       | 55                     | 40                       | 10                | 4                 | 78             | 72             | -20            | 2.8             |
| Bitumen 90/130+20% CR+0,1% flakes neozone, RPA BND | 67                       | 58                     | 44                       | 13                | 3.3               | 74             | 73             | -20            | 2.7             |
As seen from the Table 1, the best performance composition was obtained in vacuum. Powder neozon D was the most effective devulcanizing agent.

2. Nuclear magnetic resonance study of free induction decay relaxation

The measurements were carried out at the Physics of Molecular Systems Department in Kazan Federal University using NMR analyser “Chromatec Proton -20M”. Resonance operating frequency on proton was 20 GHz, the detailed device specifications can be found online at (http://www.chromatec.ru/products/main/nmr/proton20m/).

Maltene fractions contribute strongly to H¹ NMR signal because of their significant presence and bitumen and higher hydrogen content (compared with asphaltenes and resins). H¹ NMR experiments provide qualitative information about molecular mobility of hydrogen containing molecules and structures due to complex composition of bitumen.

The asphaltene fraction of bitumen in the NMR experiment is characterized by a complex form of free induction decay (FID), consisting of “solid” Gaussian component and Lorentzian recession component [5].

Resins and n-paraffins crystalline fraction, found in heavy crude oil (bitumen) may also contribute into Gaussian component [6].

Low molecular uncrystallized fraction of bitumen contributed to Lorentz component of FID. The decomposition into three components was used in processing of the experimental data: two exponentially decaying with time (Lorentzian components) with large T_a, T_b relaxation times and solid-state Gaussian component with a quadratic dependence on time inside the exponential function with smaller relaxation time T_c.

Thus, the experimental FID were fitted with formula:

\[ A(t) = A(0) \left( p_c \exp\left(-\frac{t^2}{T_{2c}^2}\right) + p_b \exp\left(-\frac{t}{T_{2b}}\right) + p_a \exp\left(-\frac{t}{T_{2a}}\right) \right) \]  

(1)

Where \( p_a \), \( p_b \), \( p_c \) – fractions, and \( T_a \), \( T_b \), \( T_c \), - corresponding fractions of slowly and rapidly relaxing Lorentzian component and “Gaussian” solid component respectively.

Because of short time constant \( T_c \) is close to dead time the apparent proportion of solid component in the NMR signal is substantially less than the true proton proportion of this component. However, in terms of technological properties of bitumen, it is much more interesting to obtain information about the “fluid” fraction and therefore the analysis of Gaussian signal component is beyond the scope of this paper.

Because of a lower molecular weight and higher mobility, the slowly relaxing FID components are to a great extent responsible for the contribution in proton signal of maltene fraction.

Neozone affects the bitumen – polymer binders’ structure as shown in Figure 2.
Figure 2. FID curves of free induction of the developed systems over time.

Black – BND 90/130
Red – the optimal composition of flake neozone in RPA
Green – the optimal composition of powder neozone in RPA

FID for bitumen with RK (green triangles) differs little from the FID of pure bitumen (black squares). In the presence of neozone (red circles) the slope of the “tail” of free induction decay is markedly increased, indicating a decrease in molecular mobility of uncrystallized low molecular weight components of bitumen.

By introducing powder form of neozone relaxation time of slowly relaxing component “a” decreased from 255 ms to 220 ms, and also its fraction was diminished from 30 % to 22 %. Relaxation times for “b” and “c” components remained constant, but their fractions increased from 34 % to 38 % and from 36 % to 40 % respectively.

Presence of devulcanizing agent leads to reduced molecular mobility due to better swelling of devulcanization product. Figure 3 illustrates the greater efficiency of powder form neozone over flake one.
Figure 3. Free induction decay curves of the developed compounds.

Black – BND 90/130
Red – the optimal composition of flake neozone in RPA
Green – the optimal composition of powder neozone in RPA

In the presence of powder form of neozone the “tail” steepness of FID decay increases to a greater extent in comparison to flake form of neozone.
Vacuum effect is observed in Figure 4.

Figure 4. Effect of vacuum on FID curves of developed systems.
Black – BND 90/130
Green – optimal composition with powder neozone prepared in RPA
Red – optimal composition with powder neozone prepared in vacuum

For a product with vacuum application the contribution of slowly relaxing components “a” is reduced to 14 % comparing to 24 % at ADP of “b” component increases from 41 % to 50 %.

Relaxation times and the solid component’s fractions are not sensitive to the method of processing. Thus, bitumen-polymer binder with the best performance was obtained in vacuum with the application of powder-like neozone.

3. Conclusions
The experimental results suggest the following conclusions:

1. To implement the properties of polymer in bitumen the rubber crumb must be devulcanized, making cross-linked polymer into linear (or branched) and therefore soluble.
2. Because of a lower molecular weight and higher mobility, the slowly relaxing FID components are to a great extent responsible for the contribution in proton signal of maltene fraction.
3. Degradation of sulfur cross-links increases when neozone is added. Presence of devulcanizing agent leads to reduced molecular mobility due to better swelling of devulcanization product
4. Resulting bitumen-compositions possess improved properties such as softening point, hardness, elasticity, resistance to frost, low temperature characteristics.
5. Devulcanization by powder form of devulcanizing agent is more effective than by flake form.
6. Using vacuum improves rubber crumb devulcanization in melted bitumen.

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