

Regulation of Colloidal Structure and Adhesion-Strength Properties of Bitumen Insulating Materials

Ruslan Alimovich Kemalov*, Alim Feyzrahmanovich Kemalov and
Rashid Ildusovich Khusnutdinov

Kazan Federal University, Kremlyovskaya St. 18, 420008, Kazan, Russian Federation, Russia; RuslanchKemalov@gmail.com, AlimFeyzrahmanovich1900@gmail.com, Rashid.Ildusovich2001@yahoo.com

Abstract

Background: The main objective of study is to develop a BIM to prevent for a long time the processes of electrochemical corrosion. So, in this paper physico-chemical material provided to control at different stages of the technological process.

Methods: The regulation of composite bituminous material properties are carried out in accordance with the main provisions of physicochemical mechanics. In this paper it is regulated by directional adjustment of their spatial dispersion structure and the change of the disperse phase particle sizes. **Results:** In accordance with the modern concepts, oil and oil products are considered as complex polymolecular dispersion systems differing by the ratio of components that are included into supramolecular structures, solvation shells, forming "a complex structural unit" (CSU). The association of molecules, the appearance of supramolecular SSS structures takes place due to the intermolecular forces of reacting molecules. Among the most common ways of colloid - chemical dispersion of bituminous materials is the compounding technology of highly molecular compounds, such as elastomer - an atactic polypropylene (APP), stereo irregular: $[-CH_2-CH(CH_3)-]_n$. In this paper a novel approach developed for regulating the colloidal structure and adhesion-strength properties of bitumen insulating materials to achieve its optimal performance. **Conclusion:** Polymer bitumen have a wide range of operating temperatures up to 100 °C. With the addition of elastomers in bitumen, its viscosity increases and its elasticity improves.

Keywords: Bitumen Insulation Material, Dispersion State of Polymer Systems, Elastomer, Strength, Particle Size

1. Introduction

The introduction of new technological processes, the increase of production efficiency and product quality, the intensification and reconstruction of existing petrochemical plants depend not only on construction materials in use¹⁻⁸, but also on the correct choice of corrosion-resistant materials for their protection⁹⁻¹². Most materials used in industry and the corresponding equipment, instruments are unstable in the environment, i.e. corrode. The extension of their operation period will save million tons of metal and reduce the cost of their production. Metal structural materials are particularly susceptible to destruction¹³⁻¹⁶.

2. Experimental

APP - atactic polypropylene polymer provides bitumen with the properties of plastic. The material with such an additive acquires a high resistance to sunlight and an excellent heat resistance. According to physical and chemical characteristics APP refers to thermoplastics, based materials, which are used where the resistance of bitumen - polymer compositions (BPC) to high temperatures (from -15 to +130 °C) and increased solar radiation is important. This is explained by the properties of APP and the structure of a well-mixed bitumen-polymer mixture. Being plastic, APP has low elasticity, but the fatigue resistance under cyclic loading due to the use of polyester

*Author for correspondence

bases, is sufficiently large. Due to their high dimensional stability and an excellent adhesion they are perfect fillers bitumen-polymer materials^{9–11}.

Solvent choice substantiation. It was determined that aromatic base solvents for bituminous insulating materials (BIM), in particular the fractions of xylenes, benzene-toluene mixtures, as well as various solvents boiling upto 150–160 C make an influence on the adsorption process^{12,13}. For example, aromatic hydrocarbons, ketones, ethers and esters with a basic nature, promote the adsorption of a film former in the acid sites of the dispersed phase (asphaltenes, the particles of pigments and fillers, in particular polymers).

The development of polymer and bitumen combining technology. At the creation of BIM the task of a relatively cheap and available materials modification is set, as the petroleum bitumen is by more expensive and scarce polymers to produce a composite material with the predominant polymer properties. The technology of bitumens and polymers combination depends not only on the state of bitumen (melt, emulsion, solution) but on the type of polymer, the polymer solution and its viscosity. The technological modes of BIM obtaining depend on the choice of combination method. Polymer and bitumen qualities determine their structure in the process of combination, the degree of dispersion, and hence the composition obtaining structure, its uniformity and the time required to obtain a homogeneous composition at these combination conditions (temperature and shift direction). The selected combination conditions shall exclude or minimize the thermal degradation of bitumen and polymer. To this end, the temperatures of the complete APP dissolution in xylene (Table 1) were determined and the gradual combination of polymer with bitumen is selected.

It is worth noting that the dissolution temperature of a polymer in a solvent increases with the polymer content increase. So for a polymer solution (PS) with the content of polymer 1% wt. the alignment temperature makes 50 C

Table 1. The dependence of complete dissolution temperature on the polymer content in the solution

Polymer name	Content in polymer solution, % wt.	The temperature of full polymer dissolution, °C
APP	1	50
	2	50
	4	60
	6	70

alignment, and for 4% wt., 6% wt. it makes 60 and 70 °C respectively. Thus, it is necessary to bring a higher quantity of heat in order to increase the physical-chemical affinity of the polymer and bitumen systems at their alignment.

Conductometric method of PR analysis (Coulter counter). The PR studied by us may be represented in the form of film-forming organic disperse system where discrete phase is presented by APP particles of colloidal sizes, and a solvent is presented by a dispersion medium. The dispersion analysis (DA) provides some presentation concerning APP particle distribution by their quantity and sizes depending on the polymer concentration in a solvent. The effectiveness of PR combination with bitumen is used to create BIM with optimal properties expressed by strength characteristics. Thus, the analysis of polymer solution dispersion system change determines the most effective APP content for its best combination with bitumen. A more complete understanding about PR dispersion system is provided by the distribution curve of the dispersed phase amount by particle sizes (Figure 1).

With the increase of APP particles up to 5 microns a monodisperse nature of the polymer system is revealed, expressed in a large number of particles with a certain size, for example, for the particles with the dimensions $r = 2$ and 3.17 microns, in a polymer solution containing a 2% PPA, the number $N = 13184$ and 12722 respectively. Further along the curve (Figure 1) the increase of particle size results to increase of a system polydispersity, which begins from the transition state with the borders according to the particle size from 4 microns to 12.7 microns. The polydispersity of the system is characterized by the increase of APP particle size differences within the average

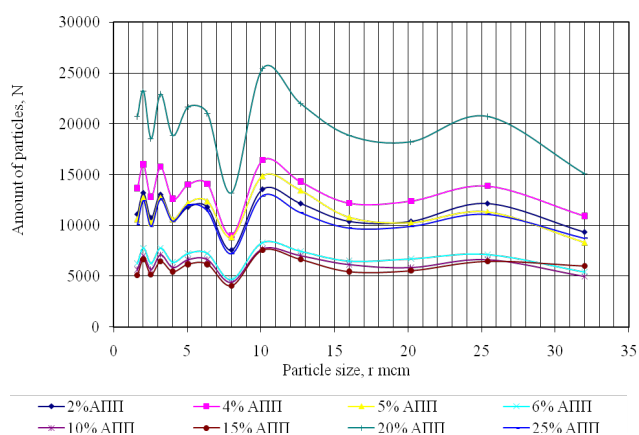


Figure 1. The curves of APP particle amount distribution by sizes.

amount: the r makes 12.7 - 32 microns for a polymer solution with a 2% content of APP, the amount $N = 11123$.

The gradient between the curves (Figure 1) relative to each other with the change of APP in PR content (%) by dispersed phase volume describes the processes of coagulation and dispersion (Figure 2).

During the PR preparation process APP dispersing takes place at heating in a dispersion medium with a colloidal system development the equilibrium of which is established as the result of cooling and the process of aggregation - the formation of larger particles (aggregates), consisting of smaller (primary) particle system takes place. The primary particles in such systems are joined by intermolecular forces directly or through a thin layer of a liquid dispersion medium as a result of weak intermolecular (van der Waals) attraction forces. Thus, the segment of 2% - 4% wt. on Figure 2 shows the increase in the number of particles associated with an increase of a polymer percentage content in a solution, and not related with the process of aggregation, because of APP small amount. On the contrary, a further increase of the polymer concentration, the section of 4% - 6%, leads to process of latent coagulation to form a sedimentation-stable system (Figure 2), followed by progressive enlargement of the particles (the increase of a unit size and weight) and the reduction of their number in the volume of a dispersion medium (Figure 3).

For a more complete understanding of APP concentration influence on the change of unit size in a polymer solution the Figure 2 shall be supplemented. For this

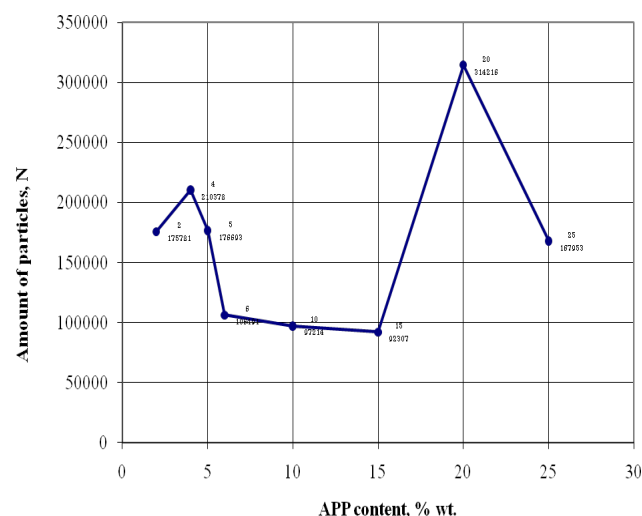


Figure 2. The dependence of the total number of particles on APP content (in %).

purpose the particles were selected corresponding to the monodispersity and polydispersity of the system (Figure 1), respectively $r = 2,52$ mcm and $r = 20,2$ mcm. Then, the dependence on the percentage content of a polymer is developed with the number of particles provided by Figure 3.

Thus, the interval of 6–15 % wt. (Figure 2) corresponds to the boundaries of a polymer solution polydispersed system (Figure 1), wherein the particles have different sizes, and represents orthokinetic coagulation - the buildup of small particles to larger ones (Figure 4), which causes an increase in the number of large particles (20.2 microns) as compared to small ones (2.52 microns) (Figure 3, Figure 4).

On the interval of APP 15–20% wt., on the dependence curve of the total volume of particles on the

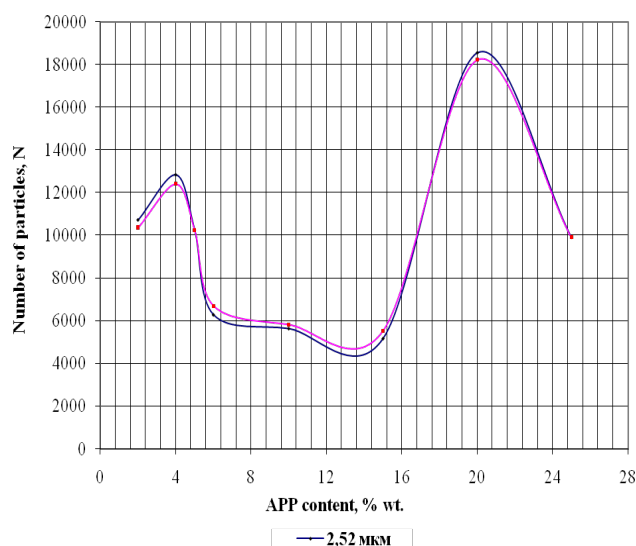


Figure 3. The dependence of the number of particles of a certain size from APP content (in %).

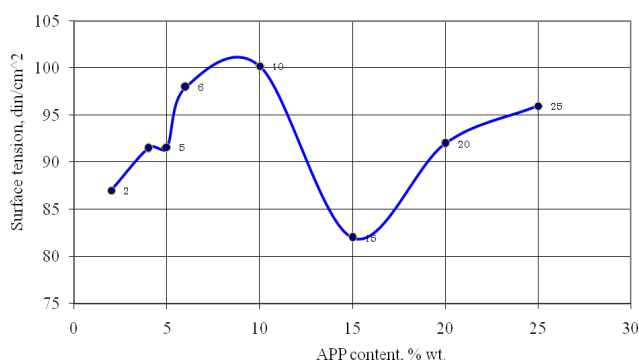


Figure 4. Surface tension change with the increasing APP content (in %)

introduction of a polymer (Figure 2), the spontaneous decomposition of aggregates (Figure 4) takes place on a par with increasing polymer concentration (which, of course, also increases the volume of the particles) formed by the accumulation of agglomerated colloidal particles on smaller colloids or individual primary particles. The plot on Figure 3 corresponding to this segment has an intersection of the two curves which shows that there are more particles with a size of 2.52 microns as compared to the particles whose size is 20.2 microns with increasing concentration of APP, the process of peptization takes place. The segment of 20-25% wt. on Figure 2 begins with a period of 20% wt. of APP which can be taken conditionally for coagulation threshold, as the inclusion of minor amounts of APP above this point leads to the aggregation of the colloidal system (Figure 2). Thus, the optimum content of APP in a solvent makes 2-4 wt.%, because of a small number of particles.

In order to determine the optimal content of APP in a solvent it is necessary to set a number of requirements to a polymer solution, which will provide the most effective combination of the latter with the bitumen. The purpose of such a combination is the getting of BIM with the specified performance characteristics^{9,11,12,17}. Based on the foregoing, we proposed the following requirements for the PR:

1. PR sufficient affinity with bitumen (Hildebrandt parameter)
2. The smallest particle size of polymer macromolecules. An indispensable condition for the diffusion process and a uniform distribution of the polymer in the bitumen.
3. The polymer shall be resistant to aggregation and sedimentation in the presence of a solvent upon introduction into bitumen.
4. During the formation of the coating, with the removal of a solvent, it is necessary that the process of bitumen disperse system structuring is carried out directly with the polymer and the formation of a gel like structure.

The first requirement is satisfied by the solvent nature. The second requirement, according to dispersion analysis, is satisfied by PR with APP concentration of 2% and 4% by wt. (Figure 1) with dominating amount of particles with the size $r = 2$ mcm and 3.17 mcm. At 2 - 4% wt. of APP content the third requirement is observed due to a large number (excess) of solvent. The fourth requirement is met as the result of further conducted strength

tests. Consequently, the most effective PR is the solution containing 2 - 4% wt. of APP.

PR surface tension connection with the quantity and the size of APP particles. The surface layer of PR is largely conditioned by APP particle amount and sizes. The resultant of intermolecular forces in the PR surface layer is not compensated and directed into the phase with a greater force of cohesion forming the surface tension. Thus, an effective distribution of APP in bitumen at the introduction of PR a minimum value of surface tension is necessary. The determination of surface tension was performed by drop weight breaking from the end of a vertical tube (stalagmometer). The experimental data are presented in Table 2, Figure 4.

The initial increase of the surface tension (ST) is conditioned by the presence of APP particles in the surface layer, a further increase in ST is associated with the increase in density caused by the large diameter of the molecule at their aggregation. The decrease of surface tension with APP content of 10 - 15% by weight (Figure 4) occurs as a consequent reduction in the amount of particles during the process of orthokinetic coagulation (Figure 2). A further increase in ST by 15 - 25% of wt. is related to an equivalent increase in small and large sizes and the amount of APP particles (Figure 3).

Thus, the most suitable polymer solutions for the insertion into the bitumen with 2% and 15% wt. content of APP characterized by a low surface tension. However, it should be noted that the 15% of PR contain APP particles in the form of large size aggregates (Figure 2).

2.1 The Relation of Dispersive PR Analysis with Dynamic Viscosity

Coagulation dispersive structure (DS) of the polymer solution is formed in the presence of APP dispersed phase after the collision of particles in Brownian motion at heating and subsequent cooling. The dispersion structure is a disordered spatial network in the dispersion system (frame) formed by the particles of the dispersed phase in the process of coagulation. The structural grid may occupy in this case from a few hundredths of % to a few dozens of % from a system volume, based on a polymer content.

Table 2. PR surface tension

APP, % wt.	2	4	5	6	10	15	20	25
Surface tension, din/cm ²	87	91,5	91,6	98	100,2	82	92	96

Thus, the formation of coagulant DS is accompanied by the increase of dynamic viscosity and gelation.

In order to perform the analysis of the dynamic viscosity, using the instrument “Reotest” the interesting states of PR dispersed system were determined (Figure 2) corresponding to 4, 10 and 20% of APP wt. The experimental data are presented in Table 3.

The curves have the general dependence: with the increase of a shear rate PR structural mesh loses its elasticity, which results to the reduction of dynamic viscosity under the influence of mechanical loading.

Then, with the increase of a shear rate in a colloidal system the compaction reactions occur between the polymer macromolecules which are the particles of APP after an intensive mixing, and consequently by the increase in dynamic viscosity.

The difference between the 4, 10 and 20% wt. in dynamic viscosity is characterized by the PR colloidal system state. Thus, the gradient according to the dynamic viscosity between 4 and 10% wt. is explained by the increased concentration of APP and the formation of large-sized units with a small amount of the polymer particles. A sharp drop in viscosity from 20% by wt. content of APP is caused by a large number of particles with a smaller size.

Assessment of BIM physical-mechanical properties of polymer solution prepared by introduction. Ultimately, the bitumen-polymer compositions were subjected to physical-mechanical tests in order to determine the optimum content of APP in bituminous insulating material composition.

Formulae of BIM compounds with the percentage content of APP to bitumen are presented in Table 4, Figure 5.

Then the prepared BIM were applied on substrates and were subjected to physical and chemical studies, which were conducted at the 3rd and the 5th day of curing.

Table 3. The values of kinematic viscosity for polymer dispersions.

APP content, wt. % in PR					
4		10		20	
Dr, c ⁻¹	η, MPa·s	Dr, c ⁻¹	η, MPa·s	Dr, c ⁻¹	η, MPa·s
437,4	1,289304	437,4	2,32086	437,4	0,644652
729	1,160712	729	1,547616	729	0,386904
1312	1,289304	1312	1,719072	1312	0,429768

Dr – shear rate, c⁻¹; η, – dynamic

Table 4. The developed compositions of BIM

Name	Xylene	Bitumen-2	APP	Dissolution temperature, °C
	Content, % wt.			
BIM 1	60	38	2	50
BIM 2	60	36	4	60
BIM 3	60	35	5	60
BIM 4	60	34	6	70
BIM 5	60	30	10	70
BIM 6	60	25	15	75
BIM 7	60	20	20	78
BIM 8	60	15	25	80

viscosity, MPa·s

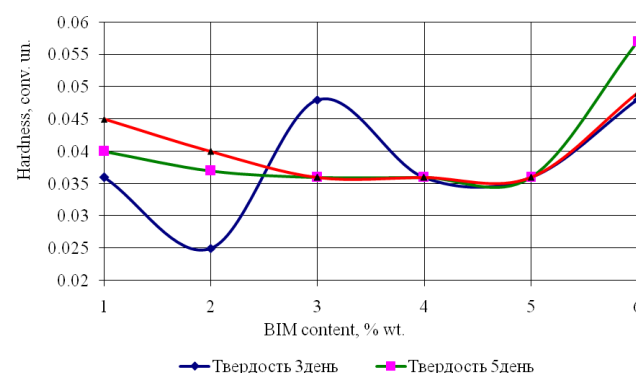


Figure 5. Cover hardness change in time.

With the increase of APP content in %, the decrease of adhesion-strength properties is observed. When APP content makes over 20% wt. the resulting film does not become dry, even after the expiry of the required retention time. From Figure 5. One may conclude that hardness increases with the curing time increase.

3. Conclusions

Results demonstrate that the optimum content of APP in BIM is 2% wt. Since at the introduction of APP more than 2% of wt. results in increasing of the crystallization degree for a filled film former expressed in the deterioration of the cohesive intermolecular interactions of bitumen with polymer. Also, it was founded that the adhesion-strength properties of hardness drop, are leading to the delamination of BIM with the violation of the coating adhesive bonds.

4. Conflict of Interest

The author confirms that the presented data do not contain any conflict of interest.

5. Acknowledgement

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