Nanomodified bitumen composites: solvation shells and rheology

E.V. Korolev, S.S. Inozemtcev & V.A. Smirnov
Moscow State University of Civil Engineering, Moscow, Russian Federation

ABSTRACT: Nanotechnology is now taking the worthy place in material science. One of the most effective nanomodification methods consists in formation of extra layers at the phase boundary either by means of chemical treatment or appropriate selection of preparation technology. The latter can lead to formation of solvation shells which stabilize disperse system and improve operational properties of resulting building material. At present, despite the numerous models for viscosity of disperse systems, there is no commonly accepted method which allows estimation of the thickness of solvation shells on the basis of rheological experiments. In the present work theoretical and experimental studies concerning origination and parameters of solvation shells on the surface of fine filler are performed. It is shown that proposed rheological method allows adequate estimation of the thickness of solvation shells.

1 INTRODUCTION AND PRIOR WORK

Current demands for advanced road construction materials lead to shift of primary research direction towards lower spatial level of constructional composites. Particular effects at micro- and nanoscale levels of bituminous and sulfur-bituminous mixtures are of most importance during structure formation of such disperse systems.

The state of nanotechnology in material science is adequately reflected in (Gupta et al. 2010): "nanomaterials are an important subset of nanotechnology". Strictly speaking, the nanotechnology was always employed in material science; it is only during last decades application of relevant methods becomes deliberate and systematic.

Concerning building materials for road construction, the modern trends of nanotechnology are mostly applications of high aspect ratio nanoscale filler platelets – layered silicates. Rheological properties of bitumen binder with admixture of clays and organoclays were studied in numerous research works. It was shown that due to the addition of organomodified montmorillonite a number of physical properties can be enhanced (Jahromi et al. 2009), including resistance to rutting (Tao et al. 2010). It is discovered (Markanday et al. 2010) that bitumen systems with ethylene-vinyl acetate and organoclay are characterized by improved thermomechanical properties. Operational characteristics of bitumen-clay systems modified by styrene-butadiene-styrene copolymer are subject to optimization in (Galooyak et al. 2010).

Dedicated chapters about application of organoclays are also in (Gupta et al. 2010).

Though positive prospective effect of organoclay to bitumen binder is certain, there are also several drawbacks. Admixture of 2D nanoparticles requires proper selection of homogenization methods (that are usually chemical surface treatments to make the clay more compatible with matrix material). Special measures for increasing the stability of mixes must also be taken (Galooyak et al. 2010).

This is why in our earlier research works we had proposed different type of nanomodification. The proposed method is based on the assumption that surface treatment of fine filler is by itself can lead to significant enhancement of performance. Thus, while using 2D nanoplatelets is expedient, it is also not always necessary for some groups of fillers and treatment agents; in case of sulfur-based constructional composite, butadiene oligomers can successfully be used (Korolev et al. 2012). Moreover, since bitumen is a microheterogeneous system formed from primary (several nanometers in size) and complex (20-60 nm in size) structural units, for which the uniformity of system is disrupted when a mineral filler is introduced (Korolev et al. 1993), appropriate selection of preparation technology can lead to formation of bitumen absorption layer which stabilizes disperse system and/or leads to improved operational properties of resulting asphalt concrete. In most cases, formation of oriented layers of bitumen is mostly due to physical sorption (Inozemtcev et al. 2014).

The aim of the present work is to perform theoretical and experimental studies concerning origination and parameters of solvation shells on the surface of fine filler. The shells can be formed either by fractions of bitumen (asphaltenes), or by nanomodifier with high molecular mass.

2 THEORETICAL STUDIES

Predominant influence of the fine filler to microstructure of asphalt concrete is mostly due to large area of the phase boundary. Despite the relatively low amount of fine filler, total surface of its area are maximal among areas of other disperse phases. There is a simple way to demonstrate this. For the given specific surface $S_{s,i}$, density ρ_i and volume V_i of the i-th disperse phase, surface area can be expressed as:

$$S_{f,i} = S_{s,i} \rho_i V_i = \frac{1}{V} S_{s,i} \rho_i v_i, \quad i = \overline{1, N},$$

where, V – volume of the composition, v_i – volumetric fraction of the i-th phase, N – number of disperse phases.

Specific surface of the spherical particles:

$$S_s = \frac{6}{\rho d}.$$

Thus, for the area we get:

$$S_{f,i} = \frac{1}{V} \frac{6}{\rho_i d_i} \rho_i v_i = \frac{1}{V} \frac{6 v_i}{d_i}.$$

Total area of all phases is equal to sum:

$$S_f = \sum_{i=1}^{N} S_{f,i} = \frac{6}{V} \sum_{i=1}^{N} \frac{v_i}{d_i}.$$

Therefore, relative area of the i-th phase can be expressed in form:

$$\delta S_i = \frac{S_{f,i}}{S_f} = \frac{v_i}{d_i} \left(\sum_{j=1}^{N} \frac{v_j}{d_j} \right)^{-1}; \quad (1)$$

it can easily be verified that equality

$$\sum_{i=1}^{N} \delta S_i = 1$$

holds for the obtained values.

Volumetric rates of the disperse phases can be determined a priori for the model of regular dense sphere packing with extra assumption

$$d_{i-1} \gg d_i, \quad i = \overline{2, N}.$$

For such a model the volume occupied by the i-th phase equals to:

$$V_1 = V \eta_p, \quad V_i = \left(1 - \sum_{j=1}^{i-1} V_j \right) \eta_p, \quad i = \overline{2, N}.$$

In case of three disperse phases and hexagonal lattice the volumetric rates will be 60%, 24% and 9% (binder occupies about 6% of space); for the cubic lattice they will be 52%, 23% and 12% (binder occupies about 11%).

Due to several reasons model of regular dense sphere packing only roughly corresponds to the asphalt concrete. The assumption about size ratio is incorrect for aggregate and coarse filler. Volumetric rate of aggregate is usually near 60%, and rates of coarse and fine fillers are near to 10% and 13%, respectively.

Relative areas of disperse phases obtained by (1) are presented in tables 1 & 2.

Table 1. Relative areas of disperse phases: cubic lattice.

Phase	Average grain size, mm	Volumetric rate, %	Relative area, %
Aggregate	5	52	0.8
Coarse filler	0.65	23	2.8
Fine filler	0.01	12	96

Table 2. Relative areas of disperse phases: real asphalt concrete.

Phase	Average grain size, mm	Volumetric rate, %	Relative area, %
Aggregate	5	60	0.9
Coarse filler	1.25	10	0.6
Fine filler	0.01	13	98

As it follows from Tables 1 & 2, surface area of the fine filler dominates both for real asphalt concrete and for approximate model. The difference between Tables 1 & 2 is in the second row; such difference noticeably affects rheology of composition.

A number of general considerations regarding interrelation between characteristic size and rheological properties of bituminous disperse systems with fine filler were former discussed in (Korolev et al. 2015), though obtained results allows neither determination, nor verification of shell size on the basis of rheological properties. It was also stated (Gladkikh et al. 2014) that dependence between mixture and rheology for bituminous system with aggregates can only be subject of numerical investigation.

It is well known that viscosity of bitumen in solvation shell (that is often called "structured bitumen") is several orders of magnitude higher than viscosity of ordinary bitumen. One of the first methods of determination of solvation shell thickness was proposed in (Bakhrakh et al. 1969). The method is based on classical model (Einstein 1911) for viscosity of medium with non-interacting solid spheres. While such a model is only appropriate for diluted systems (Willenbacher et al. 2013), the obtained dependence

$$h = \frac{1}{\rho_{f,N} S_{s,N}} \left(\frac{k}{k_m} - 1 \right) \quad (2)$$

(where, $\rho_{f,N}$ and $S_{s,N}$ – density and specific surface of the fine filler, k and k_m – empirically determined parameters in regression models which correspond to Einstein equation and were derived for bitumen and physical model system "filler-medium" without significant interaction on phase boundary) allowed adequate determination of the shell thickness (the results were in range 30-180 nm for temperatures 110-122 ^{0}C).

The drawback of the model presented in (Bakhrakh et al. 1969) is in assumption about identity in formation of layers for different dispersion mediums. In fact, comparative analysis does not involve idealized systems that can be described by Einstein model. Experimental determination of parameters k and k_m is hindered by necessity to use dispersion medium which is:

a) characterized by thermal dependence of viscosity similar to the dependence for bitumen;

b) inert to the surface of the fine filler (dispersion medium can be considered "inert" when contact angle is $\pi/2$: wetting does not change total energy of system).

The model (Bakhrakh et al. 1969) can be extended. Viscosity of disperse system is affected by several factors. Among others, there are volumetric rate of filler and shape of particles of the fine filler. During preparation of the hot mix asphalt the formation of two surface layers takes place. First (absorptive) layer is mostly due to physical-chemical interaction between bitumen, nanomodifier and filler. Second (kinetic) layer depends on both shape of the particles and viscosity of the dispersion medium. During experiment it is possible to directly measure the viscosity:

$$\eta_{ex} = \eta_0\left(1 + \alpha_0\left(v_f + \Delta v_f\right)\right), \tag{3}$$

where, η_{ex} and η_0 – viscosities of the disperse system and dispersion medium, α_0 – form factor of the particle ($\alpha_0 = 2.5$ for spherical particles), v_f – volumetric rate of the filler, Δv_f – estimated increment of the volumetric rate caused by absorption on the surface of filler:

$$\Delta v_f = \frac{\eta_{ex}\left(v_f\right) - \eta_0\left(1 + \alpha_0 v_f\right)}{v_f \alpha_0}. \tag{4}$$

If we substitute

$$v_f = N_f \frac{\pi}{6} d_f^3$$

into (4), we get

$$\Delta v = v_f\left[\left(\frac{d_f}{d_{f,0}}\right)^3 - 1\right].$$

Taking into account

$$d_f = d_{f,o} + 2h, \quad d_f = 6/S_u\rho_f,$$

the thickness of the solvation shell will be:

$$h = \frac{3}{S_{f,N}\rho_{f,N}}\left(\left(\frac{\eta_{ex}\left(v_f\right) - \eta_0}{v_f\eta_0} + 1\right)^{\frac{1}{3}} - 1\right). \tag{5}$$

If we take into consideration both shape of the particles and presence of the absorptive layer, than:

$$\left(\frac{d_f}{d_{f,0}}\right)^3 = \frac{1}{\alpha v_f}\left(\frac{\eta_{ex}\left(v_f\right)}{\eta_0} - 1\right),$$

and for thickness we get:

$$h = \frac{3}{S_{f,N}\rho_{f,N}}\left(\left(\frac{1}{\alpha v_f}\left(\frac{\eta_{ex}\left(v_f\right)}{\eta_0} - 1\right)\right)^{\frac{1}{3}} - 1\right). \tag{6}$$

Since thickness of the solvation shell is the sum

$$h = h_a + h_k,$$

where, h_a and h_k – thickness of the absorptive and kinetic layers, respectively, for the thickness of absorptive layer it can be derived from (5):

$$h_a = \frac{3}{S_{f,N}\rho_{f,N}}\left(\sqrt[3]{\frac{\eta_{ex}\left(v_f\right) - \eta_o}{v_f\alpha_0\eta_0} + 1} - \sqrt[3]{\frac{\eta'_{ex}\left(v_f\right) - \eta'_o}{v_f\alpha_0\eta'_0} + 1}\right), \tag{7}$$

and (6):

$$h_a = \frac{3}{S_{f,N}\rho_{f,N}}\left(\sqrt[3]{\frac{\eta_{ex}\left(v_f\right)}{\alpha v_f\eta_0} - \frac{1}{\alpha v_f}} - \sqrt[3]{\frac{\eta'_{ex}\left(v_f\right)}{\alpha'v_f\eta'_0} - \frac{1}{\alpha'v_f}}\right), \tag{8}$$

where apostrophe denotes model system. Viscosities and parameter α can be determined from the experimental studies.

3 EXPERIMENTAL SETUP

To determine the parameters required for calculations according to (5)-(8), we have performed series of experiments. Viscosity was measured for several bituminous and one model system. In the latter castor oil was used as a dispersion medium. The former were composed from BND 60/90 bitumen and four types of fine filler: fired diatomite (hereafter FDP), diatomite (DP), grinded quartz sand (QP) and grinded limestone (LP). For all types of fillers specific surface was 250 m^2/kg. Volumetric rate of filling was varied in range 0-0.02. Viscosity was measured on MCR 101 rotation rheometer. Rotation rate was 20 s^{-1}. Temperatures of the bituminous systems were varied in range 120-150 ^{0}C.

4 EXPERIMENTAL RESULTS

Experimental dependencies between temperature and viscosity ($v_f = 0.01 = const$) and volumetric rate of filler and viscosity ($T = 135$ ^{0}C $= const$) are presented on Figure 1 & 2.
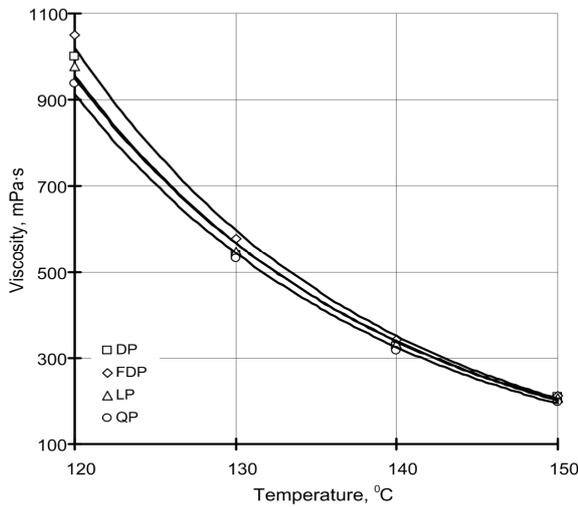
Figure 1. Dependencies between temperature and viscosity.
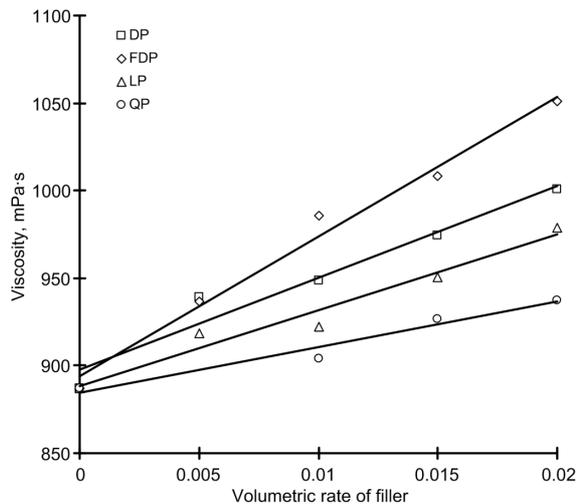
Figure 2. Dependencies between volumetric rate of filler and viscosity.

Series of experimental data similar to presented on Figure 2, upon completion of regression analysis, allowed to determine parameters for (5)-(8). Obtained values of the shell thickness are summarized in Table 3.

Table 3. Thickness of the solvation shell, nm

Type of filler	Temperature, ^{0}C			
	120	130	140	150
DP	378 ± 40	355 ± 30	225 ± 20	41 ± 10
FDP	219 ± 40	178 ± 30	55 ± 20	27 ± 10
LP	448 ± 40	413 ± 30	272 ± 20	106 ± 10
QP	285 ± 40	185 ± 30	48 ± 20	25 ± 10

The data presented in Table 3 are in good correspondence with values obtained by means of different other methods (Zlotarev 1995). It is also evident from Table 3 that traditional limestone-based filler requires higher amount of binder.

5 SUMMARY AND CONCLUSIONS

Solvation shells formed on the particles of the fine filler considerably affect both rheological properties of the asphalt mixtures and operational properties of the asphalt concrete. Despite the numerous models for viscosity of disperse systems (Willenbacher et al. 2013), there is no commonly accepted method which allows to estimate the thickness of such shells on the basis of rheological experiments.

In the present work we have proposed such a method. It is shown that obtained results correspond to values obtained by means of other methods.

REFERENCES

Bakhrakh, G.S. & Malinsky Yu.M. 1969. Estimation of the solvation shell thickness on the surface of mineral filler. *Colloid Journal,* (1): 21-24.

Einstein, A. 1906. Eine neue bestimmung der moleküldimensionen. *Annalen der Physik,* 19: 289-306.

Galooyak, S.S. Dabir, B. Nazarbeygi, A.E. & Moeini, A. 2010. Rheological properties and storage stability of bitumen/SBS/montmorillonite composites. *Construction and building materials,* 24 (3): 300–307.

Gladkikh V.A., Korolev E.V. & Smirnov V.A. 2014. Modeling of the sulfur-bituminous concrete mix compaction. *Advanced Materials Research,* 1040: 525-528

Gupta R.K. Kennel, E. & Kim, K.J. 2010. *Polymer nanocomposites handbook*. London: CRC Press.

Inozemtcev, S.S. & Korolev, E.V. 2014. Mineral carriers for nanoscale additives in bituminous concrete. *Advanced Materials Research,* 1040: 80-85.

Jahromi, S.G. & Khodaii, A. 2009. Effects of nanoclay on rheological properties of bitumen binder. *Construction and building materials,* 23(8): 2894-2904.

Korolev, E.V. Tarasov, R.V. Makarova L.V. & Smirnov, V.A. 2015. Model research of bitumen composition with nanoscale structural units. *Contemporary engineering sciences,* 8(9): 393-399.

Korolev, E.V., Smirnov, V.A. & Albakasov, A.I. 2012. Nanomodified composites with thermoplastic matrix. *Nanotechnologies in Construction* (4): 81-87.

Korolev, I.V. & Solomentsev, A.B. 1993. Features of component interaction in asphalt-mineral systems. *Chemistry and Technology of Fuels and Oils,* 29(4): 192-195.

Markanday, S.S. Stastna, J. Polacco, G, Filippi, S. Kazatchkov I. & Zanzotto L. 2010. Rheology of bitumen modified by EVA-organoclay nanocomposites. *Journal of Applied Polymer Science,* 118(1): 557-565.

Tao, Y,Y. Yu, J.Y. Li, B. & Feng, P.C. 2010. Effect of different montmorillonites on rheological properties of bitumen/clay nanocomposites. *Journal of Central South University of Technology,* 15(s1): 172-175.

Willenbacher, N. & Georgieva, K. 2013. Rheology of disperse systems, in *Product Design and Engineering: Formulation of Gels and Pastes*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA.

Zlotarev, V.A. 1995. Adhesion of bitumen on the surface of minerals: estimation. *Automotive roads,* (12): 13-15.