

MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

**Compatibility of Olefinic Thermoelastoplastics
with Oxidized Bitumens
of Various Colloidal Structures**

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Abstract—The compatibility of oxidized bitumens of types I and III with blended olefinic thermoelastoplastics was studied by calorimetry, viscometry, and atomic-force microscopy. Improvement of process characteristics of modified products based on bitumens is associated with different mechanisms of formation of their structure.

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Petroleum bitumens [1] modified with polymers are widely used in road building and civil engineering thanks to high plasticity and the capability to withstand without failure the effect of low temperatures, temperature changes, and various deformation loads. As a rule, the main goal of modification is the development of a compound with prevalent polymer properties and process characteristics preserved throughout the operation life. To this end, a polymer in a bitumen should be uniformly distributed, should uniformly swell, and should form a dense elastomeric network [2]. It was found empirically that the compatibility of a polymer and a bitumen (formation of solutions or disperse composite materials) depends on the content and quality of the polymer added, of asphaltenes, and of the oil fraction of bitumen [3]. The problem of mixing and compatibility of a polymer with a bitumen is always important when preparing high-quality polymer–bitumen blends and is solved individually depending on the composition and properties of the polymers and bitumens used.

In this study we examined the effect exerted by the colloidal structure of bitumen on its compatibility with blended olefinic thermoelastoplastics (OTEPS).

EXPERIMENTAL

We performed our experiments with samples of oxidized bitumens of different grades. Sample no. 1 was prepared by oxidation of tar from Central Asian crude; sample no. 2, by oxidation and subsequent compounding of tars from Romashkino crude (Tatarstan); and sample no. 3, by oxidation of tar from commercial West Siberian crude (Table 1). To prepare modified products, we used blended thermoelastoplastic of TPM grade [TU (Technical Specification) 2211-001-9305691–2006], consisting of SKEPT-40, HDPE 273-79, and I40 industrial oil. The physicomachanical characteristics of the initial bitumens and modified products based on them, determined according to GOST (State Standard) 2678–94, are given in Table 1.

The phase composition of bitumens and compounds and the enthalpy of mixing of the polymer with a bitumen were determined with a C80 calorimeter (Setaram) equipped with a reversing device. The bitumen sample weight was 50 mg, and the temperature was scanned from 20 to 200°C at a rate of 1 deg min⁻¹. Blending of the bitumen with a polymer (7 wt %) under industrial and laboratory conditions was performed at

Table 1. Physicomechanical characteristics of oxidized bitumens and modified products based on them

Sample no.	Bitumen grade	Oxidized bitumen			Modified bitumen			$\Delta T_2/\Delta T_1$
		ring-and-ball softening point, °C	brittle point, °C	working temperature range ΔT_1 , °C	ring-and-ball softening point, °C	brittle point, °C	working temperature range ΔT_1 , °C	
1	BNK90/30	90	-15	105	110	-25	135	1.3
2	BND90/130	48	-9	57	95	-26	121	2.1
3	BNK45/190	46	-16	62	101	-26	127	2.0

180°C. The calorimeter was calibrated by the Joule effect and the melting point of indium. The uncertainty of the temperature measurement did not exceed 0.1°C. As the melting point of the crystalline phase we took the temperature of the minimum in the thermal effect of melting.

The morphology of the surface of bitumen films was studied in air by atomic-force microscopy (AFM) in the tapping and phase contrast modes. We used a Solver P47 scanning probe microscope (maximal scanning area $50 \times 50 \mu\text{m}$) (NT-MDT, Zelenograd, Russia). As microprobes we used cantilevers of NSG-11 and NSG-20 grades with a rigidity constant of 48 N m^{-1} (NT-MDT).

The structural-rheological properties were studied with a Rheotest-2 rotary viscometer with a coaxial cylindrical unit, using cylinder H. The sample volume was 17 cm^3 . Measurements were performed in the shear rate interval $0.17\text{--}146 \text{ s}^{-1}$ at temperatures from 45 to 130°C.

Previously [4], based on data on the component composition and process characteristics of bitumen sample nos. 1 and 2, we suggested that bitumen no. 1 has a gel structure (type I [1]) and bitumen no. 2, a sol-gel structure (type III). The coagulation structure in bitumen no. 1 is formed by interaction of asphaltene aggregates with each other [5, 6]. Relatively low content of asphaltenes in bitumen sample no. 3 (18.8 wt %), high content of the oil fraction (46.0 wt %), and high penetration (19 mm) suggest formation in this bitumen of a structure close to type III. The suggested colloidal structures of bitumens are confirmed by characteristics of their rheological behavior [7].

Introduction of a modifier in an amount of 7 wt % considerably improves the technological characteristics of oxidized bitumens, appreciably decreasing the brittle

point and increasing the softening point determined by the ring-and-ball method (Table 1). Modified bitumen no. 1 with the structure of type I is still characterized by the widest interval of operation temperatures. However, the modifier performance evaluated from the ratio of the operation temperature intervals of the bitumens before and after the modification increases in going from type I bitumen to type III bitumen (Table 1), i.e., the modifier performance is higher in type III bitumens, apparently, owing to their better compatibility [8]. The mechanism of the action of OTEP modifier of TPM grade in bitumens with different colloidal structures was examined by studying the phase structure of bitumen-polymer compounds by calorimetry, viscometry, and AFM.

OTEP modifier of TPM grade is a blend of synthetic ethylene-propylene rubbers (SKEPT) differing in the polypropylene content with high-density polyethylene (HDPE) and mineral oils. According to DSC, the modifier contained HDPE crystallites with the melting point of 128.9°C and enthalpy of melting of 42.4 J g^{-1} , and also polypropylene crystallites with the melting points of 167.3 and 174°C and the total enthalpy of melting of 6.9 J g^{-1} . In the AFM image of the modifier surface, one can distinguish crystallites with a width of 400 to 800 nm and a length of up to $2 \mu\text{m}$, combined in coarser formations with the width from 2 to $3 \mu\text{m}$.

Polymer-bitumen compounds are physical blends (solutions or dispersions) [2]. High-temperature blending of bitumen with polymers of any chemical nature involves emulsification of the softened polymer in liquid bitumen, followed by partial swelling or complete dissolution. The extent of the polymer dispersion in bitumen under equal other conditions is determined by the chemical nature and molecular weight of the polymer, chemical composition of bitumen, and ratio of

the blend components. Differences in the mechanisms of blending of bitumens with the modifier of TPM grade were proved by DSC: blending at 180°C of modifier with bitumen no. 1 is a one-step process, and blending with modifier no. 2, a two-step process (Fig. 1). The two-step character of the process with bitumen no. 2 suggests that emulsification of the modifier is accompanied by its swelling due to adsorption of bitumen components.

According to DSC data, modified bitumens contain a crystalline phase of HDPE melting in the temperature interval 117.4–121.9°C. The 7–12°C lower melting point of HDPE in the modified bitumens compared to the neat modifier is due to formation of smaller crystallites, defects in the crystal lattices, and various surface effects [9]. Recalculation of the thermal effect of HDPE melting in bitumens considering the modifier content shows that a part of components of the crystalline phase of HDPE dissolves in the dispersion medium of the bitumen.

The structural features of modified bitumens were revealed in comparative analysis of the rheological characteristics of polymer–bitumen compounds. The coagulation structure of bitumen no. 1 is confirmed by a slight change in the viscosity in the temperature interval 20–100°C [7]. In the modified bitumen, the temperature sensitivity of the viscosity in this temperature interval is also low, suggesting preservation of the coagulation structure of bitumen in the modification product.

For the modified products based on bitumen nos. 2 and 3, in the temperature dependence of the viscosity in the interval 20–80°C there is a portion with a low temperature sensitivity (Fig. 2), which may be due to formation in these compounds of a three-dimensional structure similar to that formed in bitumens of the gel

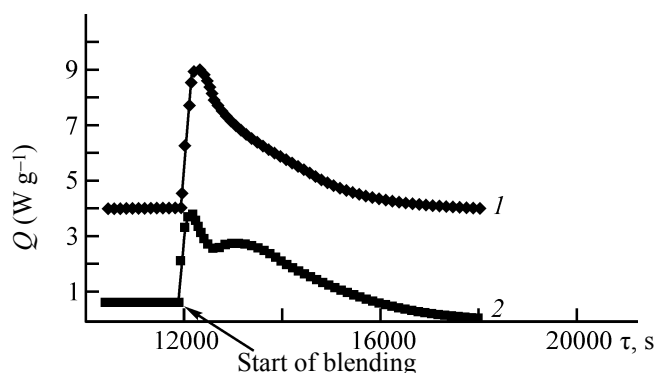


Fig. 1. Thermal effects Q of mixing of bitumen nos. (1) 1 and (2) 2 with OTEP modifier of TPM grade at 180°C (mean result of three experiments for each bitumen sample). (τ) Time.

type. The absence of such a portion in the temperature dependence of the viscosity of the initial bitumens and of bitumen no. 2 modified with HDPE only indicates that the formation of this structure is most probably due to the presence of SKEPT molecules.

The modifier introduced into bitumen affects either the properties of the dispersion medium (owing to dissolution or adsorption of components of the dispersion medium) or the content, composition, and properties of the dispersed phase. To examine the phase state of the modifier compounded with the bitumen, we analyzed the precipitate obtained by the standard procedure of isolating asphaltenes from petroleum products [10]. After dissolution of asphaltenes in benzene, a precipitate remains on the filter. Its relative weight for all the bitumens is about 4%. According to DSC data, the content and melting point of the crystalline phase in the precipitate on the filter, obtained from modified bitumen no. 1, are practically identical to the content and melting point of the crystalline phase in the initial modifier (Table 2), indicating that the interaction of the modifier with the bitumen components is insignificant. In the precipitate on the filter, obtained from modified bitumen nos. 2 and 3, the content of the HDPE crystalline phase is considerably (by a factor of almost 2.5) higher than its content in the OTEP modifier (Table 2), suggesting better interaction of SKEPT with the dispersion medium of the bitumen.

Comparative analysis of the AFM images of the surface of bitumen no. 2 before [11] and after modification (Fig. 3a) shows that the initial structure of the bitumen does not appreciably change upon

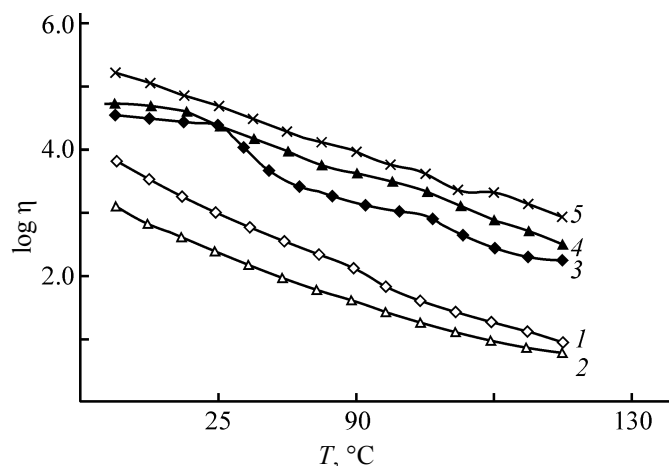


Fig. 2. Temperature dependence of the viscosity $\log \eta$ of oxidized bitumen nos. (1) 2 and (2) 3, of OTEP-modified bitumen nos. (3) 2 and (4) 3, and (5) of HDPE-modified bitumen no. 2.

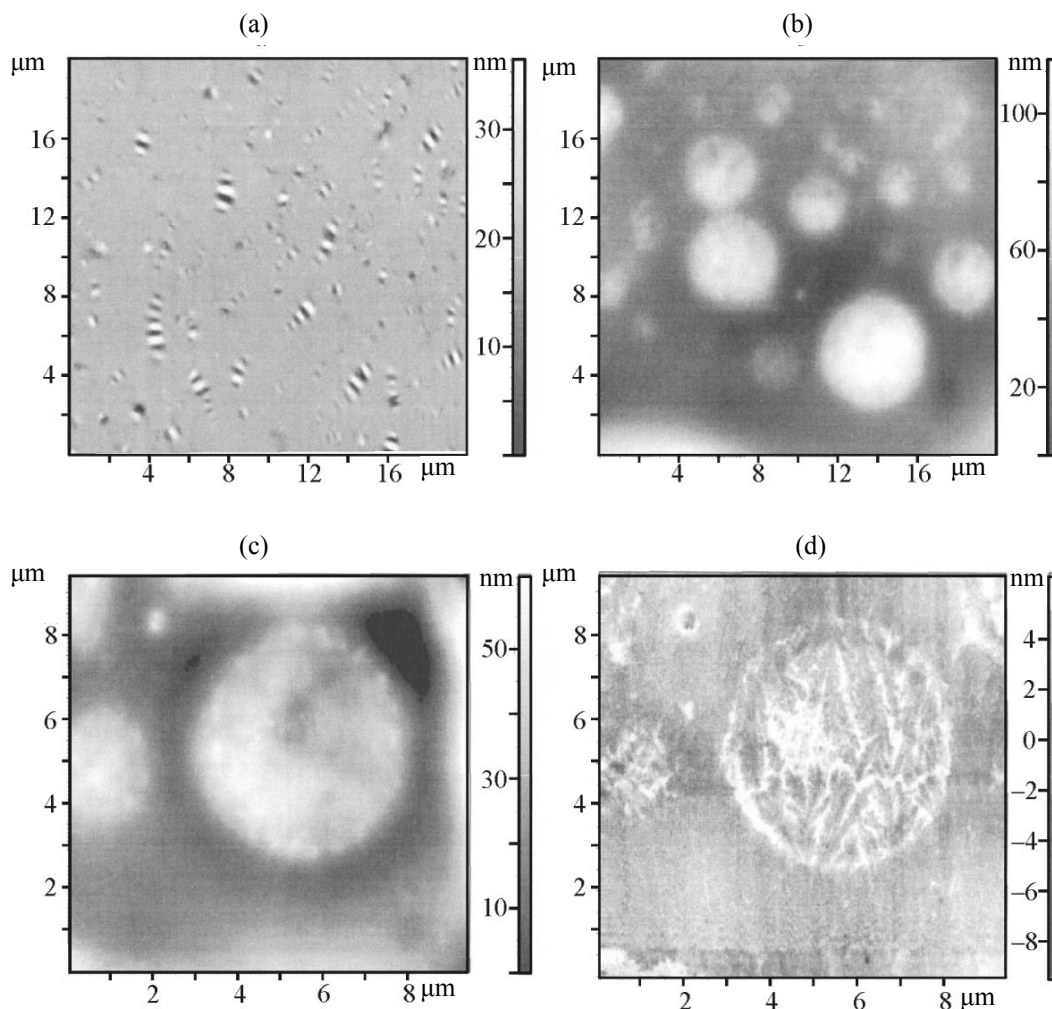


Fig. 3. AFM images of modified bitumen nos. (b–d) 1 and (a) 2, taken in the (a–c) tapping and (d) phase contrast modes.

introducing the modifier, only the so-called catana phase formed by resin–asphaltene components decreases in size [12]. Introduction of the modifier into bitumen no. 1 leads to changes in the topography of the bitumen surface: The catana phase disappears, and globules of various sizes, distributed nonuniformly and not connected with each other, appear (Fig. 3b).

Comparison of the AFM images of the same area of the surface, taken in the topographic (Fig. 3c) and phase contrast (Fig. 3d) modes, shows that the globule surface has a fine structure characteristic of polymers. Thus, AFM images of modified bitumen nos. 1 and 2 confirm different mechanisms of their modification with olefinic thermoelastoplastics.

Table 2. Melting points and enthalpies of melting of PND and SKEPT crystallites in the modifier and in precipitates on the filter, obtained from modified bitumens

Sample	HDPE		SKEPT	
	T_m , °C	enthalpy of melting, J g ⁻¹	T_m , °C	enthalpy of melting, J g ⁻¹
Modifier	128.9	42.4	167.3; 174.0	6.9
No.1	128.5	36.0	170.5	6.8
No. 2	128.5	109.3	–	–
No. 3	126.9	121.3	166.8	1.6

CONCLUSIONS

(1) Modification of bitumens of types I and III with a blended olefinic thermoplastic of TPM grade was performed.

(2) The technological properties of bitumen of type I are improved owing to dissolution of the low-molecular-weight constituent of the modifier and to changes in the properties of the dispersion medium, with the coagulation structure of bitumen preserved.

(3) For bitumen of type III, the technological properties of the modified products are improved owing to swelling of the thermoelastoplastic and formation of fragments of the elastomeric network.

REFERENCES

1. Kolbanovskaya, A.S. and Mikhailov, V.V., *Dorozhnye bitumy* (Road Bitumens), Moscow: Transport, 1973.
2. Rozental', D.A., Tabolina, L.S., and Fedosova, V.A., *Modifikatsiya svoistv bitumov polimernymi dobavkami: Tematicheskii obzor TsNIITeneftekhimi* (Modification of Properties of Bitumens by Polymeric Additives: Topical Review of the Central Research Institute of Technical and Economical Studies in Petrochemical Industry), 1988, no. 6.
3. Gokhman, L.M., *Kompleksnye organicheskie vyazhu-shchie materialy na osnove bloksopolimerov tipa SBS: Uchebnoe posobie* (Complex Organic Binders Based on Block Copolymers of SBS Type: Textbook), Moscow: Ekon-Inform, 2004.
4. Frolov, I.N., Yusupova, T.N., Ganeeva, Yu.M., et al., *Neftegaz. Delo*, 2008, http://www.ogbus.ru/authors/Frolov/Frolov_1.pdf.
5. Pechenyi, B.G., *Kolloidn. Zh.*, 1970, vol. 32, no. 6, pp. 891–894.
6. Posadov, I.A., Rozental', D.A., Abramovich, G.V., and Borisova, L.A., *Kolloidn. Zh.*, 1985, vol. 37, no. 2, pp. 315–321.
7. Okhotnikova, E.S., Yusupova, T.N., Ganeeva, Yu.M., and Frolov, I.N., in *Sbornik materialov nauchno-prakticheskoi konferentsii "Neftegazopererabotka-2009"* (Coll. of Materials of Scientific and Practical Conf. "Oil Refinement and Gas Processing 2009"), Ufa, May 27, 2009, pp. 175–177.
8. Masson, J.F., Collins, P., Robertson, G., et al., *Energy Fuels*, 2003, vol. 17, pp. 714–724.
9. Fawcett, A.H., McNally, T., McNally, G.M., et al., *Polymer*, 1999, vol. 40, pp. 6337–6349.
10. Bogomolov, A.I., Temyanko, M.B., Khotyntseva, L.I., et al., *Sovremennye metody issledovaniya neftei* (Modern Methods for Studying Crude Oils), Leningrad: Nedra, 1984.
11. Ganeeva, Yu.M., Yusupova, T.N., and Romanov, G.V., *Dokl. Ross. Akad. Nauk*, 2009, vol. 426, no. 5, pp. 629–631.
12. Masson, J.-F., Leblond, V., and Margeson, J., *J. Microscopy*, 2006, vol. 221, pp. 17–29.