ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 7, pp. 1310−1313. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © R.Z. Shakhnazarli, N.Ya. Ishchenko, Kh.G. Nazaraliev, B.A. Mamedov, A.M. Guliev, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 7, pp. 1213−1217.

MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Polymer–Bitumen Compounds with Crumb Rubber, Secondary Polyethylene, and Polyamide Fiber Waste

R. Z. Shakhnazarli, N. Ya. Ishchenko, Kh. G. Nazaraliev, B. A. Mamedov, and A. M. Guliev

Institute of Polymeric Materials, National Academy of Sciences of Azerbaijan, Sumgait, Azerbaijan

Received March 4, 2009

Abstract—The physicomechanical characteristics of a bitumen compound modified with secondary polyethylene, polyamide fiber waste, and crumb rubber were examined.

DOI: 10.1134/S1070427209070283

Petroleum bitumens have a fairly complex composition, being disperse systems. The bitumen binder used in road building should meet the modern requirements. As a rule, to obtain a high-quality bitumen binder, the bitumen is subjected to modification. Both individual compounds and oligomeric and polymeric products are used as modifiers [1]. In the development of new polymeric composite materials, utilization of secondary raw materials is promising from both economical and environmental viewpoints [2, 3]. In particular, one of modifying additives used is crumb rubber (CR) produced from worn automobile tires after appropriate processing. Crumb rubber is a cheap and readily available filler. Its performance is due to good elasticity, resistance to frost and light, and other useful properties. In addition, such filler contains a large amount of antioxidants, which enhances its resistance to thermal oxidative degradation [4, 5].

In this study we examined the properties of bitumen compounds prepared with secondary polyethylene (SPE), polyamide fiber waster (PFW), and CR as fillers. The CR was taken both as reclaim and in the modified form.

To determine the optimal formula of polymer–bitumen compounds, we primarily examined the effect of CR, SPE, and PFW on their properties.

We found that introduction of CR into bitumen enhances the elasticity of the compounds but decreases the ring-and-ball softening point. Addition of CR also decreases the strain and enhances the crack resistance of the pavement. Introduction of 5.0–20.0% SPE leads to an increase in the ultimate strength to 0.82 MPa and in the ring-and-ball softening point from 35 to 67°C (Table 1).

In so doing, the needle penetration and the extensibility decrease, i.e., the strength properties of bitumen

Table 1. Properties of a bitumen compound modified by SPE

Parameter	Parameter value at indicated SPE content, wt %				
	0	5.0	10.0	15.0	20.0
Ultimate tensile strength, MPa	0.03	0.102	0.48	0.61	0.82
Needle penetration, 0.1 mm units:					
at 25°C	64	43	27	11	1.7
at 0°C	29	16.3	12	4.3	0.8
Extensibility, cm:					
at 25°C	65.5	59.4	55.3	42.1	37.3
at 0°C	22.0	21.0	20.4	19.8	16.4
Fraas brittle point, °C	–20	–21	23	–24	–27
Ring-and-ball softening point, °C	53	55	57.4	62	67
Adhesion to mineral filler, %	23	27	28	28	31

Table 2. Influence of temperature and time of mixing of SPE with bitumen on the properties of the polymer–bitumen compound

Parameter	Parameter value at indicated mixing temperature, °C (5 h)				Parameter value at indicated mixing time, h (160°C)			
	140	150	160	170	3	4	5	6
Ultimate tensile strength, MPa	0.30	0.49	0.61	0.62	0.45	0.52	0.61	0.61
Relative elongation, %	1–1.5	1.5–2	2–3	3.0	2.0	2.5	2–3	2–3
Needle penetration, 0.1 mm units:								
at 25°C	41	30	11	10	42	35	11.2	11.0
at 0°C	15.8	12	4.3	4.1	8.2	4.8	4.2	4.1
Extensibility, cm:								
at 25°C	58.6	50.4	42.1	41.0	54.5	58.8	42.0	42.0
at 0°C	21.3	20.7	19.8	19.1	21.0	20.2	19.7	19.8
Fraas brittle point, °C	–20	–22	–24	–25	–21	–23	–24	–24
Ring-and-ball softening point, °C	56.0	58.5	62.0	63.0	55.4	57.6	62.1	62.0
Adhesion to mineral filler, %	23	26	28	29	22	25	28	29

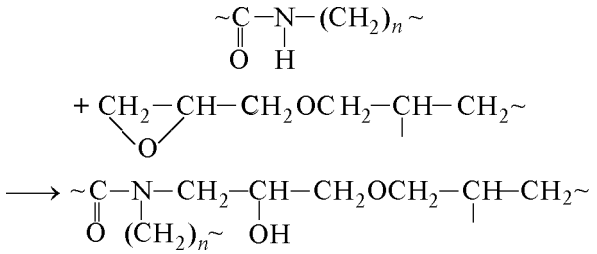
compounds are improved. This is due to the fact that SPE macromolecules contain a certain amount of functional groups enhancing the interaction between the bitumen and polymeric matrix and hence making the composite material more resistant to deformations. We also examined how the physicomechanical properties of a polymeric compound prepared from 85% bitumen and 15% SPE depend on the temperature and time of mixing of SPE with petroleum bitumen (Table 2).

Table 2 shows that, as the mixing temperature is increased from 140 to 170°C, significant changes are observed in the properties of the composites (mixing time 5 h). The ultimate strength, relative elongation, ring-and-ball softening point, and adhesion to the mineral filler increase. At the same time, the needle penetration depth, Fraas brittle point, and extensibility of the polymer–bitumen compound decrease. Similar changes in properties of the composite occur when the time of mixing of SPE with bitumen is increased to 5 h (at 160°C). The results of these studies indicate that the best mixing, leading to more uniform distribution of SPE macromolecules in the polymer–bitumen compound, is attained at 160–170°C and mixing time of 5 h. As a result, a colloidal solution of SPE in bitumen with smaller size of polymer particles is formed, which ensures good physicochemical interaction of the components.

On introducing PFW into bitumen, the rigidity and strength of the resulting materials increase, which is very important for practice. The most important factors determining the properties of the composite material are the fiber size, shape, and length-to-diameter ratio (*L/D*), the extent of preservation of these parameters in the course of mixing and processing, the extent of dispersion, the adhesion, and the fiber content in the polymer matrix.

Introduction of polyamide fiber into a bitumen compound apparently favors uniform distribution of an applied load over separate fibers and inhibits crack propagation. Realization of such a mechanism obviously requires high adhesion between the fiber and bitumen surfaces. The adhesion between the matrix and PFW is usually enhanced when the fiber surface contains functional groups capable of interaction with bitumen.

To enhance the adhesion, PFW was treated with a solution of a dressing agent (epoxy oligomer containing Si or without it) in methyl ethyl ketone, after which the dressed PFW was heat-treated. The dressing followed by heat treatment involves the reaction of the amide group of the fiber with the oxirane ring of the epoxy olgiomer, with the formation of hydroxy groups. As a result, oligomer macromolecules become grafted to PFW:



Thus, PFW undergoes modification, and the surface energy of the modified PFW decreases compared to that of the initial PFW. The occurrence of such a chemical

reaction between SPW and epoxy oligomers was confirmed by comparative analysis of the IR spectra of the initial and dressed PFW samples. The results of fiber dressing are given in Table 3.

As seen from Table 3, as the dressing agent concentration in fiber treatment is increased, the ultimate tensile strength first appreciably increases and then decreases, which is due to improvement of the conditions for formation of chemical bonds on the fiber–bitumen phase boundary.

We also examined the influence of the fiber length on the physicomechanical properties of compounds based on PFW and bitumen binder. For this purpose, after appropriate dressing, we prepared PFW samples of length ~2.0, 4.0, 6.0, and 8.0 mm and determined some characteristics of the compounds obtained (Table 4). As can be seen, the best service characteristics are exhibited by compounds prepared with 4–6-mm-long fibers.

To examine the effect of CR on the physicomechanical properties of a polymer–bitumen compound, we prepared mixtures from bitumen and SPE with the addition of CR whose fine fractions are uniformly distributed in the bitumen matrix within 15–20 min and coarse fractions partially swell, additionally reinforcing the system. After that, PFW was introduced. Because in preparation of polymer–bitumen compounds crushed tire wastes consisting of CR and SPE in ~1 : 1 ratio were used, in preparation of asphalt concrete samples we used the same mixture.

Table 3. Influence of the content of dressed PFW on the properties of bitumen compounds

Compound composition	Ultimate strength, MPa	Relative elongation, %	T_s, °C
(a) + AGE,[a] wt %:			
3.0	1.83	25.3	
5.0	2.01	23.1	78
10.0	1.22	23.3	
(a) + purified AGE-based resin, wt %			
3.0	2.05	30.0	
5.0	2.31	32.0	80
10.0	1.38	23.0	
(a) + AGE oligomerization product, wt %:			
3.0	1.91	28.0	
5.0	2.29	33.0	79
10.0	1.28	22.0	
(a) + Si-resin,[b] wt %			
3.0	2.12	30.0	
5.0	2.51	35.0	80
10.0	2.48	33.0	

[a] AGE stands for allyl glycidyl ether, and T_s, for softening point.

[b] Product of AGE oligomerization in the presence of vinyltriethoxysilane.

To prepare asphalt compounds with improved properties, it would be advisable to introduce all the components (SPE, CR, PFW) into bitumen simultaneously. As the compatibility of PFW with bitumen and SPE is very low, it was appropriate first to mix petroleum bitumen with SPE to obtain modified bitumen.

EXPERIMENTAL

To prepare crumb rubber, worn tires were cut in small pieces and then ground by an abrasive procedure. CR fractions of size 50–100 μm were obtained (the crumb size was determined by a sieve method). The crumb rubber was dried for 2 h at 60°C. To prepare reclaim, the finely divided CR was heat-treated at 300°C for 30 min.

Hydroxylation of crumb rubber was performed in the presence of a 0.3 M aqueous solution of potassium permanganate in a reactor with continuous stirring at approximately 60°C. After the reaction completion (pH reaches 9–10), the product was filtered off and thoroughly washed with water to remove MnO_2. The washed crumb was vacuum-dried at 80°C.

For dressing of polyamide fibers we prepared 5, 10, 20, 30, 40, and 50% solutions of a dressing agent in MEK. The fiber (10 g) was immersed in a solution of a dressing agent in MEK, after which it was removed and excess solution was allowed to drain. After drying the treatment was repeated two times more. The dressed fiber placed on aluminum foil was dried in an air thermostat at 70–80°C for 60 min.

Mixtures based on bitumen and SPE were prepared on rollers at 140–160°C for 15–20 min. Then vulcanized CR was added in an amount of 2–5 wt %, and the mixing was continued for an additional 15–20 min. To the resulting mixture, PFW was added in an amount of 10, 25, 50, and 75 wt %. Mixing of the dressed and cut fiber with the polymer–bitumen binder was performed in the pouring gate of a casting machine at 50–80°C. Samples of the compounds were tested on an RMI-60 tensile-testing machine.

Table 4. Influence of dressed PFW length on physicomechanical properties of compounds based on polymer–bitumen binder

Parameter	Parameter value at indicated fiber length, mm			
	2	4	6	8
Ultimate tensile strength, MPa	0.70	0.72	0.73	0.69
Ultimate compression strength,[a] MPa, at 20°C	5.5	5.9	6.2	5.6
Relative elongation, %	2.8	2.1	2.0	1.8
Needle penetration, 0.1 mm units:				
at 25°C	10	8	8	9
at 0°C	4.2	4.0	3.9	4.1
Extensibility, cm:				
at 25°C	48.1	51.1	50.5	43.5
at 0°C	19.6	20.3	21.1	19.9
Fraas brittle point, °C	–22	–23	–24	–24
Ring-and-ball softening point, °C	62	64	65	63
Adhesion to mineral filler, %	25	28	30	32

[a] Parameters for asphalt concrete of the following composition, wt proportion: bitumen 100, SPE 20, PFW 30, bentonite 50, and sand 400.

To prepare an asphalt concrete mix, PFW without treatment to remove rubber crumb was processed on rollers (fraction 1–2 mm) at 70–80°C for 10–15 min. Then mineral powder was added to the mixer, and the mixing was continued for 10–12 min. Then the temperature was raised to 100–110°C, bitumen modified with secondary polyethylene (polymer–bitumen compound) was added, and the mixing was continued until a uniform mass was obtained. After that, the calculated amount of sand was added in portions, and the charge was vigorously mixed. The temperature was elevated to 140–150°C, mixing was continued for an additional 20–30 min, and the mixture was pressed for 15 min at 180°C and a pressure of 200–250 atm. After cooling, the samples were subjected to physicomechanical and physicochemical tests.

CONCLUSIONS

(1) Addition of crumb rubber to the composite increases the adhesion of the binder both to components of the compound and to the mineral filler. The fibrous additive, reinforcing the binder, prevents its drainage, makes the system resistant to segregation in storage, and facilitates its transportation.

(2) Addition of secondary polyethylene to the composite enhances its strength and water resistance.

(3) The developed and prepared compounds with secondary products exhibit high service characteristics, are cheap, and can be used in building industry.

REFERENCES

1. Shakhnazarli, R.Z., Ishchenko, N.Ya., and Guliev, A.M., *Plast. Massy*, 2008, no. 12, pp. 44–45.
2. Goncharuk, G.P., Serenko, O.A., Nikitin, P.A., and Bazhenov, S.L., *Vysokomol. Soedin., Ser. A*, 2002, vol. 44, no. 8, pp. 1374–1379.
3. Kuznetsova, O.P., Zhorina, L.A., and Prut, E.V., *Vysokomol. Soedin., Ser. A*, 2004, vol. 46, no. 2, pp. 275–284.
4. Serenko, O.A., Goncharuk, G.P., Avinkin, V.S., et al., *Vysokomol. Soedin., Ser. A*, 2002, vol. 44, no. 8, pp. 1399–1404.
5. Savchenko, B.M., Grinen'ko, V.M., Pakharenko, A.V., et al., *Plast. Massy*, 2007, no. 1, pp. 31–33.