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Bitumen nanocomposites with improved performance

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HIGHLIGHTS

- Part of SBS can be effectively substituted by less costly CR.
- Clay nanocomposites show an outstanding improvement of mechanical properties.
- Clays act as compatibilizers between the two polymers and bitumen.

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ABSTRACT

Bitumen-clay nanocomposite binders with styrene-butadienestyrene triblock copolymer, SBS, and combinations of SBS and crumb rubber (CR) with different CR/SBS ratios have been synthesized and characterized. In addition to the binder, samples containing the binder and concrete sand (with a weight ratio 1:9) were prepared. The modified binders were studied in terms of filler dispersion, storage stability, mechanical performance and water susceptibility. We demonstrate that the samples containing nanoclays consistently outperform those based only on the polymer additives. We also find that nanocomposite samples based on a combination of SBS and CR are best, since in addition to other improvements they show excellent storage stability. Our work shows that substituting CR with SBS as a bitumen additive and combining it with inexpensive nanoclays leads to new materials with enhanced performance and improved stability for practical asphalt applications.

1. Introduction

Bitumen is used extensively for road surfacing and roofing materials. It is obtained from the distillation of crude oil and contains a chemically complex mixture, which is classified typically according to the polarity of the constituents roughly into asphaltenes and maltenes; maltenes can be further separated by chromatographic techniques to saturates, aromatics and resins which altogether are referred to as *SARA* (*Saturates, Aromatics, Resins and Asphaltenes*) [1,2]. A satisfactory description of bitumen as colloid is offered by Lesueur [3], who suggests that asphaltenes form micelles and are dispersed in maltenes stabilized by the polar fraction of the latter.

The primary use of bitumen is in asphalt, where it serves as the glue or binder mixed with mineral aggregate (stone or sand) particles. Recent advances for bitumen used for pavement applications include addition of various polymers in order to improve performance and reduce rutting, cracking and water susceptibility.

Styrene–butadiene–styrene triblock copolymers (SBS) have proved very effective as polymer additives in bitumen. SBS shows good dispersability with good final properties, though storage stability issues still need to be resolved [4,5]; the level of SBS addition in the bitumen matrix is limited to 3–6 wt%. The reason is that higher loadings improve further the properties but they lead to phase separation and settling during storage. In addition, the higher loadings lead to higher cost and are impractical [6]. Various attempts for stabilizing SBS modified binders have been reported in the last several years [7]. Wen et al. [8] added successfully sulfur to SBS improving storage stability of bitumen. Even earlier work starting as early as 1958 [9,10] describes a storage-stable SBS-modified asphalt by adding sulfur, though due to the excessive viscosity, the product could not be used in practice. Although the addition of sulfur has been exploited industrially for more than 30 years there still remain some issues; modified binders are more susceptible to oxidative aging. In addition hydrogen sulfide, a hazardous gas, can be generated during sulfur vulcanization. Another important drawback is poor recyclability, which might be caused

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by the chemical reactions of sulfur during the vulcanization process.

The use of nanoclays and other nanoparticles to improve the properties of polymers is already well documented [11,12]. Similarly, several have reported nanoclay-bitumen nanocomposites. Liu et al. [13] added organo-modified montmorillonites (O-MMT) to bitumen without any polymer additives and noticed that clays can improve the short-term aging behavior. However, the material still settled in long-term aging tests. A better aging behavior was reported later by Galooyak et al. but these researchers used an SBS modified bitumen as the matrix [14]. A combination of SBS and hydrophobic MMT [7,15] led to increased viscosity, higher stiffness and better rutting resistance though storage stability still remains a problem. Pamplona et al. [16] used organically modified vermiculite and montmorillonite and noticed that the binder modified by 2.5% of SBS and 2.5% of clays showed a similar behavior to the binder modified by 4.0% of SBS, which confirms that the nanoclays can serve as inexpensive substitutes for polymer additives. However, only the vermiculite based system showed improved storage stability.

Several papers report potential improvements to bitumen by using blends of polymers [17,18] as additives. Recently Munera and Ossa [19] using an experimental design analysis approach, have optimized the conditions of blending SBS, crumb rubber and a polyethylene wax (PW), aiming mainly at the reduction of production costs. Crumb rubber (CR), which is produced from recycling rubber tires, has been used for road applications in the US since the 1960s [20,21] while in Europe CR modified binders for pavement applications have been used extensively over the past 30 years [22]. CR is a promising additive especially for substituting part of SBS; considering that billions of tires are produced every year and a large part of them is eventually discarded without any further use, it is of considerable practical interest to substitute part of SBS with the less expensive CR without compromising performance [23]. Liang et al. [24] replaced part of SBS with crumb rubber to produce CR/SBS modified binders and noticed a significant improvement in failure temperature, moduli and viscosity, when the amount of SBS exceeded 1%. However, their CR/SBS-modified system shows obvious phase separation upon storing resulting from coalescence of SBS on the top of the sample and sedimentation of rubber particles at the bottom. González et al. [25] reported different additives such as SBS, polyoctenamer, wax and polyphosphoric acid to binders already modified with CR and although these additives increased the value of both storage and loss moduli, and decreased the value of the loss tangent, they couldn't prevent instability during binder storage at high temperature. Xiang et al. proved that the aging process of CR/SBS modified binder due to the simultaneous presence of CR and SBS, is different compared to the aging process of CR-bitumen and SBS-bitumen [26]. Diab et al. compared SBS modified binder to that modified by CR only and concluded that the former showed higher resistance to high strains and exhibited strong strain stiffening compared to the latter [27].

In the present study we demonstrate a new family of clay nanocomposites based on bitumen modified by CR/SBS. We explore binders based on low polymer content additives and a total of 3 wt% clay. The new compositions appear to avoid many of the shortcomings described above. The nanoclays act synergistically with the polymer additives and thus requiring less polymer. As a result, the addition of nanoclays, which are inexpensive and readily blended in the matrix, leads to a remarkable improvement of properties both at ambient and elevated temperatures, and a stable system under storage conditions. In addition to the hugely practical applications in bitumen systems, the work could guide further research in substituting copolymers and other polymer additives (SBS, EVA, and others) with the lower cost and recyclable crumb rubber taking advantage of the stabilization effect of inorganic nanoparticles and providing systems with both environmental and economic benefits.

2. Experimental

2.1. Materials

Bitumen grade PG 64-22 (Suit-Kote Corporation), poly(styrene-b-butadiene-b-styrene) (SBS) with 30 wt% of styrene, density 0.94 g/mL at 25 °C, viscosity 8.5 poise (Sigma-Aldrich) and crumb rubber (CR) prepared from waste tires using ambient temperature grinding (30-mesh, Crumb Rubber Manufacturers, CRM) were used as received. Cloisite 20A (herein referred to as 20A), a montmorillonite modified with dimethyl dehydrogenated tallow alkylammonium was obtained from Southern Clay Products with a specific gravity 1.77 g/ml and bulk density 0.118 g/ml. Concrete sand with particle size less than 0.84 mm (0.0331 inches) was used as received.

2.2. Sample preparation

Samples were prepared using a VWR 14215-268 General Purpose Mixer at 185 °C and a mixing time of 2.5 h. Initially, base bitumen was heated to 185 °C and SBS was gradually added; addition of CR followed and the mixture was stirred for an additional 1.5 h. After that, clay was added and the mixture was stirred for an additional 1 h at the same temperature.

In order to evaluate the effect of polymers and clays in bitumen's final performance, base bitumen was subjected to the same thermal treatment as the PMB (polymer modified bitumen) blends and was used as reference. The concentration of SBS ranged from 0.5 to 3.0%wt., for CR from 0 to 2.5%wt, whereas clay 20A level was either 0% or 3.0% wt. All PMB combinations prepared and characterized are shown in Table 1. Binder (PMB) and concrete sand (uniform sized) (with a weight ratio 1:9) were mixed at 185 °C for 2 h until a homogeneous mixture was obtained and samples for testing were hot pressed at 150 °C for 15 min.

2.2.1. Rheological measurements

Rheological measurements were carried out on an Anton-Paar rheometer using frequency sweeps from 0.1 to 100 rad/s at 25 °C and 60 °C in the linear viscoelastic region, using parallel plate geometry with a diameter of 25 mm. The final gap was adjusted to 1 mm and before each measurement the samples were kept at 100 °C for 15 min.

2.2.2. SEM, TEM microscopy, fluorescence microscopy

Surface morphology was observed through a field emission scanning electron microscope (FE-SEM, Tescan Mira3). Before imaging, samples were dried and sputter-coated with a layer of carbon (Denton Vacuum BTT-IV). Specimens for Transmission

Table 1
Codes for polymer/clay modified bitumen samples.

Binders	
#1	Bitumen treated at 185 °C for 2.5 h
#2	3.0%wt SBS/Bitumen
#3	3.0%wt 20A, 3.0%wt SBS/Bitumen
#4	2.0%wt SBS, 1.0%wt CR/Bitumen
#5	3.0%wt 20A, 2%wt SBS, 1.0%wt CR/Bitumen
#6	2.5%wt SBS, 0.5%wt CR/Bitumen
#7	3.0%wt 20A, 2.5%wt SBS, 0.5%wt CR/Bitumen
#8	1.5%wt SBS, 2.5%wt CR /Bitumen
#9	3.0%wt 20A, 1.5%wt SBS, 2.5%wt CR/Bitumen
#10	1.5%wt SBS, 1.5%wt CR/Bitumen
#11	3.0%wt 20A, 1.5%wt SBS, 1.5%wt CR/Bitumen