

Network Formation and Properties of Asphalt Modified with Styrene-Butadiene-Styrene and Crosslinked by two Different Crosslinking Agents

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ABSTRACT

As the use of modified asphalt binders grows in popularity worldwide, modified binders (systems) are designed empirically through trial and error.

Sulfur is generally employed as a vulcanizing agent for the stabilization of asphalt blends containing dispersed particles of unsaturated rubber. The presence of sulfur can stabilize the polymer through the creation of a weak three-dimensional (3D) network, and can lead to enhanced thermo-rheological properties in the Polymer Modified Asphalt binders (PMAs). This alternative approach uses a “new generation” of crosslinkers capable of producing stable polymer modified asphalt blends, and of reducing hydrogen sulfide emissions and the risk of gelation. It seems that the new generation of crosslinkers uses a different mechanism to form a 3D network. Naturally, these differences can play a crucial role in the formulation of new types of modified asphalt binders, especially for special applications.

This work investigates the influence of a new generation of crosslinking agents on the engineering properties of soft conventional asphalt modified by a Styrene-Butadiene-Styrene (SBS) copolymer. The Superpave™ binder specification was used in this work, as were rheological investigations in the linear and in non-linear viscoelastic regions. The results were compared with PMAs crosslinked with sulfur.

RÉSUMÉ

À mesure que la popularité des liants à base de bitumes modifiés augmente dans le monde entier, ces liants modifiés (formulations) sont conçus de manière empirique par essais et erreurs.

Le soufre est généralement utilisé comme agent de vulcanisation pour la stabilisation de mélanges d'asphalte contenant des particules dispersées d'élastomère insaturé. La présence de soufre peut stabiliser le polymère grâce à la création d'un réseau tridimensionnel (3D) faible, ce qui peut améliorer les propriétés thermo-rhéologiques des liants à base d'asphalte modifiés par des polymères (PMA). Cette approche alternative utilise une "nouvelle génération" d'agents de réticulation capables de produire des mélanges de bitumes modifiés par polymères stables et de réduire les émissions de sulfure d'hydrogène et le risque de gélification. Il semble que cette nouvelle génération d'agents de réticulation utilise un mécanisme différent pour former un réseau 3D. Naturellement, ces différences peuvent jouer un rôle crucial dans la formulation de nouveaux types de liants à base de bitume modifié, en particulier pour des applications spéciales.

Cette étude examine l'influence d'une nouvelle génération d'agents de réticulation sur les propriétés rhéologiques de bitume conventionnel mou modifié par un copolymère Styrene-Butadiène-Styrene (SBS). La spécification Superpave a été utilisée dans ce travail, de même que pour les études rhéologiques dans les régions viscoélastiques linéaires et non linéaires. Les résultats ont été comparés aux PMA réticulés avec du soufre..

1.0 INTRODUCTION

Thermoplastic elastomeric block copolymers, especially Styrene-Butadiene-Styrene (SBS) copolymers, are commonly used in the asphalt industry. This subgroup of polymers is generally dispersed in asphalt under high shear. Small particles generate a larger polymer surface in the asphalt phase so that the contact between the components is increased [1-4]. SBS is, however, incompatible with asphalt that lacks proper stabilization. This incompatibility causes problems during isothermal storage, resulting in a separate polymer-rich phase [6, 7]. Sulfur has been employed as a vulcanizing agent to attempt to stabilize asphalt blends containing dispersed particles of unsaturated rubber. This effort was pioneered in North America by L. Zanzotto during the early 1980s, and was patented a decade later [7]. The presence of sulfur not only stabilizes the polymer with the creation of a weak three-dimensional (3D) network, but also leads to enhanced thermo-rheological properties of the Polymer modified Asphalts (PMAs) [8].

The crosslinking of unsaturated elastomers with sulfur is complicated from a chemical perspective due to a wide variety of parallel and subsequent chemical reactions that may result in substitutions, additions, or eliminations reactions. Both the original components of the crosslinking system and the products of their chemical conversion are present, impacting the vulcanization process. The unsaturated polymers generally contain multiple types of reactive functional groups like reactive hydrogen atoms or double bonds. Each of these may react at different speeds and through different mechanisms, thereby forming different byproducts or even different final products [9]. Side reactions such as isomerization and cyclization of elastomers can take place during vulcanization [10]. Several authors have also suggested that dehydrogenation of asphalt and subsequent recombination with radicals of sulfur may occur [11, 12].

The dynamic vulcanization technique can be used to prepare PMAs. Asphalt was blended together with polymer in a molten state in the first step of this continual process. After sufficient time elapsed, the vulcanizing agent (in this case sulfur) was added to the system to complete the second step. The vulcanization characteristics were studied, and it was observed that the curing time for PMAs was generally longer than that of rubber in the presence of a vulcanizing system containing the activators and other additives. The shapes of the vulcanization curves for both systems were found to be similar [13, 14].

Observation over time within temperature ranges of 140°C and below or 180°C and above showed either a decrease or a small increase in torque measured by strain-controlled rheometer. This indicates that either no network or a very weak network was created in the cured system, and supports the suggestion that the optimum vulcanization temperature range for PMAs is between 150 and 180°C [13, 14]. The vulcanization curve within the optimum temperature range can be divided into three zones [15].

Mutual interactions between the cured material components and the vulcanization system take place at the beginning of vulcanization (i.e., the induction period). The crosslinks are generally not formed in this stage. If the crosslinks are formed, it is only in small quantities. The duration of the induction period depends on both the type of vulcanization system and on the temperature of the process. The main curing occurs during the second stage via the rapid crosslinking of the rubber particles dispersed in the asphalt matrix. This leads to the creation of PMA vulcanizates as products of the third and final stage.

Prior to discussing the vulcanization of PMAs, it is useful to mention the basic principles of crosslinking unsaturated rubbers with sulfur. Vulcanizates with different properties can be obtained using different process parameters and different types and contents of accelerators during sulfur vulcanization. Vulcanizates comprised primarily of polysulfide bonds generally have good physico-mechanical properties and good resistance to fatigue [16] due to the network's ability to regroup and to dissipate under the influence of external stress without reducing the number of crosslinks. Theoretically, the stress relaxation