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The effects of mixing rate on morphology and physical properties of bitumen/organo-modified montmorillonite nanocomposites

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HIGHLIGHTS

- Bitumen/Cloisite 15A (3%) nanocomposites were prepared by melt compounding at various mixing rates from 750 to 4500 rpm and their morphology and physical properties were investigated.
- An exfoliated structure was observed in the bitumen nanocomposites beyond 3000 rpm.
- The bitumen nanocomposite exhibited improved rutting resistance and lower creep stiffness.

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ABSTRACT

The paper reports some experimental data on the effects of mixing rate on the morphology, carbonyl index (I_{CO}), rheological and viscoelastic properties of nanocomposite materials based on bitumen/organo-modified montmorillonite (OMMT) incorporated at 3 wt.%. The melt compounding process was carried out at 140 °C under various mixing rates, i.e. 750, 1500, 2000, 3000 and 4500 rpm. The results indicated through Wide angle X-ray scattering (WAXS) that up to 2000 rpm, bitumen/OMMT nanocomposites exhibited an intercalated structure whereas at 3000 rpm and more, an exfoliated structure was observed. Atomic force microscopy (AFM) showed an homogeneous dispersion of OMMT in the bituminous matrix accompanied with a decrease in the "bee like" structure, being however more pronounced at higher mixing rate. Differential scanning calorimetry (DSC) data indicated a decrease in the crystalline index (X_c) for both neat bitumen and bitumen nanocomposites with increasing the mixing rate. Complex viscosity (η^*) and complex modulus (G^*) were significantly improved compared to those of neat bitumen. Fourier transform infrared spectroscopy (FTIR) analysis showed a slight increase in the I_{CO} value of bitumen/OMMT nanocomposites, especially at 4500 rpm compared to that of neat bitumen, which remained almost constant.

1. Introduction

The top layer of a major road consists of an asphalt composite, which contains mainly bitumen and stone aggregates [1]. The use of bitumen is due to its good adhesion to mineral aggregates and also to its viscoelastic properties [2]. However, in service conditions, asphalt pavements are subjected to heavy loads and climatic factors such as high-temperature rutting and low temperature cracking which limit their applications and reduce their durability [3–5]. In this respect, it was reported that the ideal asphalt should possess both a high relative stiffness at high service temperature in order to avoid rutting and also a good adhesion between asphalt and aggregates in the presence of moisture reducing stripping [4]. Indeed, pavement distresses such as rutting could be reduced by using modified binders [5]. Several methods in terms of physical or chemical modifications were reported in the literature [6,7] aiming to improve the performances and durability of bitumen. Among these methods, the incorporation of a small amount of clays in road bitumen led to an improvement in the functional properties of the bituminous materials, i.e. increase in strength and fatigue and rutting resistance with enhanced ductility and durability [4,8]. As a matter of facts, Yu et al. [9] have reported that the incorporation of clay to bitumen induced an increase in softening point and viscosity, while ductility decreased being however, more pronounced for bitumen/OMMT nanocomposites due to the

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intercalated structure. Moreover, an increase in stiffness of the bituminous modified phase was also observed contributing to the improvement of the physical properties of bitumen [10]. On the other hand, a significant decrease in both viscosity aging index (VAI) and softening point after aging (ΔS) was noted compared to the neat bitumen indicating that the aging resistance of bitumen was significantly improved [10]. Moreover, the restricted effects of thermo-oxidative aging on dynamic rheological properties of bitumen/OMMT nanocomposites were also reported and explained as a result of the layered silicates barrier, which can prevent oxygen diffusion into the bituminous matrix [10–12]. Furthermore, Li et al. [13] have also indicated that OMMT could considerably improve the resistance of bitumen against both thermo-and photo-oxidation. But, in all cases, the improvement of properties of bitumen/clay nanocomposites was assessed only if some parameters were taken into account such as type and content of fillers [3–5,14,15], type of bitumen [13,16] organo-modification of clay [3,4,14], processing conditions, etc. As well known, one of the method commonly used to prepare bitumen/clay nanocomposites is by high shear mixing to ensure uniform distribution [8]. Although, several papers were published on the preparation methods and characterization of properties of bitumen/clay nanocomposites, the literature data is rather scarce about the processing parameter effects, in particular the mixing rate, which needs to be studied further. Therefore, this work aims to investigate the influence of mixing rate variation in the range comprised between 750 and 4500 rpm, on the morphology, carbonyl index, rheology and viscoelastic properties of bitumen/OMMT nanocomposites filled at 3 wt.%. The changes in morphology and material properties for both neat bitumen and bitumen/OMMT nanocomposites induced by the mixing rate, were evaluated by several techniques such as WAXS, AFM, DSC, FTIR, Dynamic Shear Rheometer (DSR) and Bending Beam Rheometer (BBR).

2. Experimental

2.1. Materials

The base bitumen used was provided by "Total" company (France) and commercialized under the grade 50/70 according to NF EN 12591 standard.

The main physical properties of the bitumen are penetration (at 25 °C 1/10 mm) = 58 (according to EN 1426) and softening point temperature = 49.6 °C (according to EN 1427). The OMMT used was provided by Southern Clay Product Inc. (USA), under the trade name Cloisite 15A. According to the manufacturer, Cloisite 15A was produced from Na-montmorillonite by ion exchange with an organic cation, i.e. a quaternary ammonium salt and dimethyl dehydrogenated tallow (2M2HT) with ca. 65% C18. 30% C16. 5% C14 and C.E.C. = 125 meq/100 g. The particle size distribution of Cloisite 15A used was 10% < 2 μm, 50% < 6 μm, 90% < 13 μm.

2.2. Preparation of bitumen/OMMT nanocomposites

The modified bitumen was prepared using a high shear mixer (EUROSTAR, power control visc 6000). Initially, 400 g of bitumen were heated at 140 °C in a 2000 ml spherical flask until they become fluid. Then OMMT, which was steamed before use during 3 h at 105 °C, was added into bitumen at 3 wt.% based up on the literature data [10,12,13]. The mixture was blended for 60 min to ensure a uniform dispersion of the filler in the bituminous matrix. Various mixing rates were used, i.e. 750, 1500, 2000, 3000 and 4500 rpm. The neat bitumen was also processed at 750 and 4500 rpm and 140 °C for comparative purposes.

2.3. Techniques

2.3.1. Wide angle X-ray scattering (WAXS)

WAXS analysis was used to characterize the structure of the nanocomposite samples and to determine the interlayer spacing between stacked clay platelets [17]. WAXS experiments were performed by using XPERT-PRO MPD, PANalytical, Spinner PW3064 diffractometer with Cu Kα radiation (k = 0.154 nm, 40 kV, 40 mA) at room temperature. The first scan was from 1 to 8° to characterize the structure of the bitumen nanocomposite samples and the second one started from 1 to 40° to determine the crystallized fraction of bitumen in 0.05° steps at a scan speed of $0.013°s^{-1}$. WAXS was also used to evaluate the changes occurred in the crystallized fraction of the neat bitumen and bitumen nanocomposite samples induced by the mixing rate variation. Furthermore, WAXS provides internal structural information as well as the crystallite parameters towards the molecules associated with the aggregates contained in the asphaltene part [18], which are more polar than the maltenes due to the presence of reactive functional groups through which they can form aggregates.

According to the literature [19], the crystallized fraction of bitumen is mainly formed by crystalline wax and aromatics. The use of Braggs law [18,20] allows the determination of the distance between aromatic layers (dm) in the bitumen as shown in Eq. (1):

$$d_m = \frac{\lambda}{2sin\theta} \quad (1)$$

The average height of the aromatic layers (Lc) perpendicular to the plane was then calculated from Eq. (2):

$$Lc = \frac{0,9\lambda}{\omega cos\theta} \quad (2)$$

where, ω is the full width at half-maximum (FWHM). Finally, the number of aromatic sheets in a cluster (M) was determined from Eq. (3):

$$M = \left(\frac{Lc}{d_m}\right) + 1 \quad (3)$$

2.3.2. Atomic force microscopy (AFM)

AFM (Model Agilent 5500, Agilent Company, USA) was applied to investigate the morphology of bitumen. A hot liquid drop of bitumen at 140 °C was carefully placed on a 10 × 10 × 1 mm glass gill, then cooled to ambient temperature, covered by a glass cap to prevent dust pick-up and annealed for a minimum of 24 h before imaging [12,21]. Topographic images were scanned using a silicon probe. Cantilever was 125 μm long with curvature radius at 5–10 nm. The drive frequency was 400 kHz and the scan rate was 0.9 Hz. The test was operated in tapping mode.

The cantilever was excited into resonance oscillation with a piezoelectric driver. The oscillation amplitude is used as a feedback signal to measure topographic variations of the sample. AFM images were acquired at several locations on the sample surface. All the microphotographs show a 10 × 10 μm region.

2.3.3. Differential scanning calorimetry (DSC)

DSC measurements were carried out by using a Perkin-Elmer type Diamond differential scanning calorimeter with nitrogen as the purge gas at flow rate of 20 ml/min. Samples of almost 10 mg were analyzed in the temperature range −100 to +120 °C. To erase the thermal history, the first cooling and the second heating thermograms were recorded with the following heating rate: −10 °C/min in the first cooling step and 10 °C/min in the second heating scan. DSC was used to determine the percent crystallized fraction (% CF) and the glass transition temperature (Tg) of the bitumen samples taken as the point of inflection of the mid-height of the onset, and the end set of the curve. (% CF) was determined from Eq. (4)

$$\%CF = \frac{\Delta H_f}{\Delta H} \times 100 \quad (4)$$

where, ΔH_f is the enthalpy of fusion of the bitumen sample and ΔH_{100} corresponds to the bitumen of 100% crystallinity, i.e. 200 J/g [22–24]. The procedure to determine the %CF is described in Fig. 1, which shows the DSC thermogram of the control

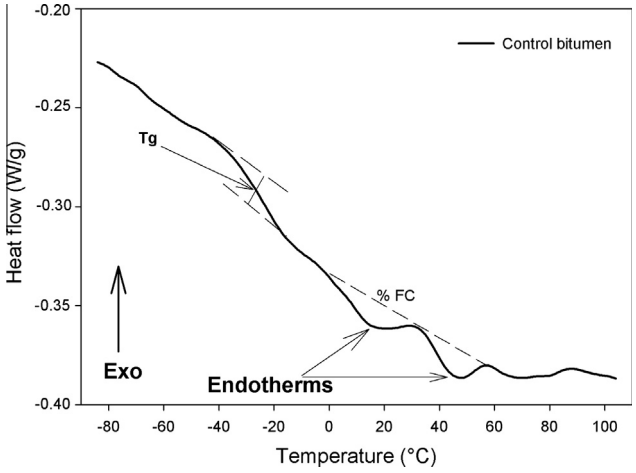

Fig. 1. DSC Thermogram of control bitumen recorded in the temperature range from −80 to +100 °C.