

## Microstructural Characterization of Bitumen/Montmorillonite/Isocyanate Composites by Atomic Force Microscopy

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**Abstract :** Asphaltic bitumen has been largely used in both industrial and civil engineering, mostly in pavement construction and roofing membrane manufacture. However, bitumen as such is greatly susceptible to temperature variations, and dramatically changes its in-service behavior from a viscoelastic liquid, at medium-high temperatures, to a brittle solid at low temperatures. Bitumen modification prevents these problems and imparts improved performance. Isocyanates like polymeric MDI (mixture of 4,4'-diphenylmethane di-isocyanate, 2,4' and 2,2' isomers, and higher homologues) have shown to remarkably enhance bitumen properties at the highest in-service temperatures expected. This comes from the reaction between the -NCO pendant groups of the oligomer and the most polar groups of asphaltenes and resins in bitumen. In addition, oxygen diffusion and/or UV radiation may provoke bitumen hardening and ageing. With the purpose of minimizing these effects, nano-layered-silicates (nanoclays) are increasingly being added to bitumen formulations. Montmorillonites, a type of naturally occurring mineral, may produce a nanometer scale dispersion which improves bitumen thermal, mechanical and barrier properties. In order to increase their lipophilicity, these nanoclays are normally treated so that organic cations substitute the inorganic cations located in their intergallery spacing. In the present work, the combined effect of polymeric MDI and the commercial montmorillonite Cloisite® 20A was evaluated. A selected bitumen with penetration within the range 160/220 was modified with 10 wt.% Cloisite® 20A and 2 wt.% polymeric MDI, and the resulting ternary composites were characterized by linear rheology, X-ray diffraction (XRD) and Atomic Force Microscopy (AFM). The rheological tests evidenced a notable solid-like behavior at the highest temperatures studied when bitumen was just loaded with 10 wt.% Cloisite® 20A and high-shear blended for 20 minutes. However, if polymeric MDI was involved, the sequence of addition exerted a decisive control on the linear rheology of the final ternary composites. Hence, in bitumen/Cloisite® 20A/polymeric MDI formulations, the previous solid-like behavior disappeared. By contrast, an inversion in the order of addition (bitumen/polymeric MDI/ Cloisite® 20A) enhanced further the solid-like behavior imparted by the nanoclay. In order to gain a better understanding of the factors that govern the linear rheology of these ternary composites, a morphological and microstructural characterization based on XRD and AFM was conducted. XRD demonstrated the existence of clay stacks intercalated by bitumen molecules to some degree. However, the XRD technique cannot provide detailed information on the extent of nanoclay delamination, unless the entire fraction has effectively been fully delaminated (situation in which no peak is observed). Furthermore, XRD was unable to provide precise knowledge neither about the spatial distribution of the intercalated/exfoliated platelets nor about the presence of other structures at larger length scales. In contrast, AFM proved its power at providing conclusive information on the morphology of the composites at the nanometer scale and at revealing the structural modification that yielded the rheological properties observed. It was concluded that high-shear blending brought about a nanoclay-reinforced network. As for the bitumen/Cloisite® 20A/polymeric MDI formulations, the solid-like behavior was destroyed as a result of the agglomeration of the nanoclay platelets promoted by chemical reactions.

**Keywords :** Atomic Force Microscopy, bitumen, composite, isocyanate, montmorillonite.

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