

Novel Nanoclay/MDI/bitumen composites: Thermomechanical characteristics

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Abstract—Bitumen, by-product resulting from the vacuum distillation of crude oil, is commonly utilized to provide waterproofing and protective coating, as well as for building applications. However, its high temperature susceptibility and aging may change may led to premature failure during service. In order to improve its performance, bitumen has normally been modified by the use of different kinds of additives, commonly polymers like SBS, EVA, etc. Polymers, when added to bitumen and properly mixed, improve its mechanical properties, decreasing its thermal susceptibility due to the shift of its effective glass transition temperature towards lower value.

Recently, layered silicates (nanoclays) have been used as bitumen modifiers due to their nanoscale characteristics. In this sense, bitumen with penetration grade of 162 dmm was used as base bitumen for modification with polymeric MDI (4,4'-diphenylmethane diisocyanate) and Cloisite 20A® (OMMT). On the one hand, the modification with MDI produced a slight increase in the elastic and viscous moduli, especially after 24 h curing. On the other hand, the addition of 10 wt.% OMMT on the MDI modified bitumen notably improved the viscoelastic performance, what is attributed to the structural reinforcing effect of the intercalated/exfoliated clay tactoids. This result can be attributed to the disruption of the clay-based reinforcing network, as a consequence of clay tactoid re-aggregation during blending, promoted by chemical interactions with MDI.

Keywords—Bitumen, isocyanate, nanoclay, intercalation, exfoliation

I. INTRODUCTION

BITUMEN is a complex mixture of different organic molecules, predominantly hydrocarbons with a small amount of structurally analogous heterocyclic species, along with functional groups containing sulphur, nitrogen and oxygen atoms [1]. Because of its good viscoelastic and waterproofing properties, it is used in a wide range of applications, mainly related to the fields of road and building construction.

However, the combination of loads, extreme temperatures and environmental factors (oxygen diffusion, UV radiation, etc.) may affect its properties during in-life service, leading to problems related to thermal susceptibility and ageing, like

high temperature rutting or low temperature cracking [1,4]. In order to improve its performance, bitumen has traditionally been modified by the addition of polymers (EVA, SBS, etc.) [1]. Recently, a growing interest has arisen in the physical modification of bitumen using layered silicates (nanoclays), due to their nanoscale characteristics, such as high aspect ratio [2]. Here, Montmorillonites are considered, which are a type of naturally occurring mineral consisting of layers of silica SiO₄ tetrahedron sheets bonded to alumina AlO₆ octahedron sheets, may produce a nanometer scale dispersion into a polymer matrix with significant improvement in its thermal, mechanical and barrier properties. In order to increase the degree of compatibility with bitumen, these nanoclays are normally subjected to an ion exchange process in which organic cations from a quaternary alkylammonium salt substitute the inorganic cations located in the gallery.

Lately, bitumen chemical modification by means of reactive polymers (anhydrides, isocyanates, epoxides, etc.) have been also performed

Both, nanoclay and chemical modification, have shown, when used separately, to improve bitumen performance and resistance against the previous factors, extending its in-life service. With this aim, the viscoelastic behavior of the binary blends bitumen/nanoclay and bitumen/MDI, along with the corresponding ternary composite bitumen/nanoclay/MDI has been investigated in this work.

II. MATERIALS AND METHODS

A. Materials

Bitumen with penetration grade of 162 dmm (EN 1426) and softening point of 32°C (EN 1427) was used as base bitumen for the modification. Polymeric MDI (4,4'-diphenylmethane diisocyanate) and Cloisite® 20A nanoclay ("C20A" hereafter) were employed as bitumen modifiers.

Cloisite® 20A ("C20A", hereafter), corresponds to an off-white, natural montmorillonite modified with N,N-dimethyl di-hydrogenated tallow (C14-C18) quaternary ammonium chloride. The cation exchange capacity is 92.6 meq/100 g clay and the hydrogenated tallow is composed of a combination of octadecyl (65 wt.%), hexadecyl (30 wt.%) and tetradecyl (5 wt.%) groups. Chemically, in addition to the organic cation between the platelets, clays naturally contain hydroxyl groups on the edge of the platelets, which are

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available for further interaction with other groups. Regarding particle specifications, the weight loss on ignition is 38 wt.%, with moisture content lower than 2 wt.%. Dry particle sizes range from values lower than 2 μm (10 vol.%), to lower than 13 μm (90 vol.%), with an average value of 8 μm . The platelets are approximately 1 nm in thickness, leading to aspect ratio values higher than 50, and according to XRD, the interlayer spacing is 2.42 nm.

Polymeric MDI (4,4'-diphenylmethane diisocyanate), supplied by T.H. Tecnic (Spain). It consists of an oligomeric mixture of 4,4'-diphenylmethane diisocyanate, 2,4' and 2,2' isomers, and condensation products with more than two aromatic rings. A typical polymeric MDI contains approximately 50 wt.% pure MDI, 30 wt.% tri-isocyanate, 10 wt.% tetra-isocyanate, 5 wt.% penta-isocyanate and 5 wt.% higher homologues. The polymeric MDI used is characterized by an -NCO content of 30 wt.%

Formulations were prepared by melt blending. In ternary blends, bitumen was first heated at 150°C and 10 wt.% C20A was added and low-shear blended for 10 min. Afterwards, an Ultraturrax™ high-shear mixer was used for 20 minutes to ensure the adequate dispersion of the nanoclay (a sample of this bitumen/nanoclay blend was taken for testing at this point). Thereafter, 2 wt.% polymeric MDI was added and low-shear blended for 24h. In bitumen/MDI binary blends, bitumen was first heated at 150°C and 2 wt.% polymeric MDI was added and low-shear blended for 24h. In both procedures, samples were also taken 1h after MDI addition.

B. Methods

Oscillatory shear temperature sweep tests within the linear viscoelastic range, at 10 rad/s, were conducted at a heating rate of 1 °C/min, on a Physica MCR-301 rheometer (Anton Paar, Austria).

Strains were specifically selected in every case to ensure a linear viscoelastic response within the entire temperature interval tested. Smooth plate-and-plate geometry with 25 mm diameter and a gap size of 1-2 mm was used for the whole set of samples.

III. RESULTS AND DISCUSSION

As depicted in Fig. 1, neat bitumen exhibits terminal-flow-shaped curves, typical of materials with prevailing viscous behavior. The addition of MDI to neat bitumen leads to the same viscoelastic behavior, greatly influenced by the curing time. Hence, 1 h curing provokes a marked increase in both dynamic moduli, mainly attributed to the reactive interaction between isocyanate groups in MDI and pendant active hydrogen groups present in some fractions of bitumen [5]. Extending curing time up to 24 hours seems to promote the mentioned reactive interaction to a greater extent, likely giving rise to new urea/urethane linkages, thus increasing the structural complexity. This results in a greater viscoelastic response, especially in relation to the elastic component,

while maintaining a prevailing viscous behavior in the overall response.

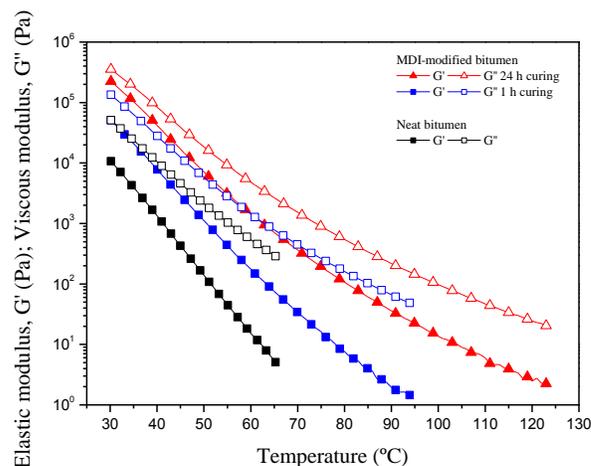


Fig. 1 Temperature sweep tests in oscillatory shear, at 10 rad/s, for neat and MDI-modified bitumen.

On the other hand, the modification of neat bitumen with 10 wt.% C20A gives rise to quite a different viscoelastic behavior, as depicted in Fig. 2. Thereby, both dynamic moduli show a significant increase, if compared to neat bitumen, with nearly coincident values of the elastic and viscous moduli in the low-to-intermediate range of temperature. As temperature rises, the viscoelastic patterns steadily decay up to a crossover point is reached, which defines a change in the viscoelastic response to mainly elastic. At greater temperatures, both moduli start flattening, tending to a plateau zone at the highest temperatures studied. The linear viscoelastic behavior observed hints at the formation of some kind of clay-based structural reinforcement [2], which contributes to maintain the overall viscoelastic response, even at temperatures at which viscoelastic partial contribution of the bituminous matrix decreases, as a consequence of softening.

As portrayed in Fig. 2, further addition of 2 wt.% MDI to the C20A/bitumen binary blend and curing for 1 hour barely affects the viscoelastic response of the system, with G'' slightly higher than G' in the low-to-intermediate temperature range, decreasing with temperature up to a crossover point, which sets the beginning of a flattening tendency towards a plateau zone, accompanied by a change in the linear viscoelastic behavior to mostly elastic at higher temperatures. Lower G' and G'' values than the previous system have been attributed to the development of some kind of agglomeration/re-aggregation between neighbor clay tactoids/platelets [3], which might lead to the reduction in the degree of dispersion, destabilizing the clay-based reinforcing structure of the bituminous matrix. A longer curing time of 24 hours provokes, at low-to-intermediate temperatures, a noticeable increase in both moduli. As temperature increases,

both moduli continuously decay, falling well below the other two systems at temperatures higher than 100 °C, approximately. This seemingly indicates the agglomeration/re-aggregation phenomena are promoted to a greater extent, likely favored by the NCO-involved reactions, which give rise to a further destabilization of the structural reinforcement provided by the clay-based network. Hence, this results in a worsening of the overall viscoelastic response of the composite, mainly governed by the partial contribution of the modified bituminous matrix, when this phase softens.

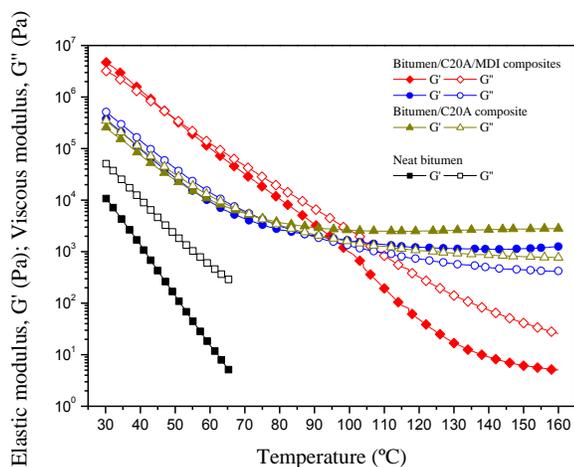


Fig. 2 Temperature sweep tests in oscillatory shear, at 10 rad/s, for neat and for bitumen/C20A and bitumen/C20A/MDI composites.

IV. CONCLUSIONS

The single addition of 2 wt.% MDI to bitumen yields an improvement in the viscoelastic response, favored by long curing times, with prevalence of the viscous response. This is mainly due to the development of a new and more complex microstructure, which stems from the formation of new urethane and urea bonds. On the other hand, the bitumen/C20A composite exhibits a marked enhancement of the viscoelastic response, which tends to a well-defined plateau zone at high temperatures, indicating the existence of some kind of clay-based network. If MDI is further added, both dynamic moduli are barely increased, showing slightly lower values than those of the binary system in the high temperature range, probably as a consequence of some kind of agglomeration/re-aggregation between neighbor clay tactoids/platelets [3]. A longer curing period of 24 hours further enhances the stiffness of the ternary blend, with an improved viscoelastic response at temperatures below that at which the modified bitumen phase softens. However, a worsening in the viscoelastic behavior (predominantly viscous) is clearly noticed as temperature is raised, which is attributed to the promotion of the agglomeration/re-aggregation of clay platelets/tactoids to a greater extent, further favored by the chemical interactions, with MDI acting as linking points.

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