**Investigation on the Limiting Oxygen Index of bitumen-organoclay nanocomposites**

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**Highlights**

* Two clays were used to obtain exfoliated or intercalated bitumen nanocomposites
* A reduction of the limiting oxygen index LOI was observed on bitumen mixtures
* TGA analysis showed strong variations in the decomposition kinetic of the bitumen
* Organoclays significantly interact with the binder, modifying its colloidal structure

**1. Introduction**

Bitumen is a complex mixture of hydrocarbons that are quite flammable and tend to produce smoke and poisonous gases while burning. This is an important aspect in the case of fire events in highway tunnels. Organoclays are well-known fire retardants in the polymer field and have been recently introduced in bituminous binders. The effect of native and organo-modified clays on the fire resistance has been evaluated [1–4], but the chemical-physical interaction mechanism between bitumen and clay has not been investigated yet. Therefore, the main object of this study is to provide a first insight in this direction. For this reason, two organoclays with different degree of interaction with a base bitumen were used in order to obtain both exfoliated and intercalated nanocomposites. The blends were characterized by WAXD, Brookfield viscosity, LOI test and TGA analysis.

**2. Methods**

The two clays were Cloisite 20A and Cloisite 30B (referred as 20A and 30B) from Southern Clay Products and derive from a sodium montmorillonite by treatment with dimethyl-dihydrogenated-tallow ammonium chloride (20A), and methyl-tallow-bis-2-hydroxyethyl ammonium chloride (30B). Bitumen is a 50/70 penetration grade base bitumen, referred as B, kindly furnished by Eni. Bitumen-clay mixtures were prepared with a high shear mixer Silverson L5T at 4000 rpm, 140 °C for 30 minutes. Wide angle X-ray diffraction (WAXD) was made in reflection mode by a Siemens D500 Krystalloflex 810 apparatus, with a wavelength of 0.1542 nm at a scan rate of 2.0 °/min. Viscosity was measured at 135 °C by a Brookfield viscometer. Thermo-Gravimetric Analysis (TGA) was performed in air using a Q500 by TA Instruments. The LOI test was performed by LOI-Smoke-230, from Dynisco & Alpha Technologies, USA.

**3. Results and discussion**

From WAXD, after mixing with bitumen, 20A has an intercalated structure with interlayer distance of 4.3 nm and 30B has a prevailingly exfoliated structure (Fig. 1). In the case of polymer nanocomposites, clay exfoliation means high interaction between the matrix and the filler, good interfacial adhesion, increased viscosity. Moreover, exfoliation improves the flame retardant properties of the materials because the delaminated platelets produce a labyrinth path to oxygen diffusion, thus decreasing the combustion kinetic. Surprisingly, the B/30B mixtures, which have a dominating exfoliated structure, did not show a significant viscosity increasing (Table 1). On the contrary, B/20A mixtures, which have an intercalated structure, showed a high increase in the binder viscosity. Both clays decrease the LOI value (Table 1) and this effect is more pronounced with clay 20A. The TGA derivative weight curves as a function of temperature are reported in   
Figure 2 for B, B/20A-4 and B/30B-4. The TGA spectra are significantly altered with respect to base bitumen even in the presence of small clay quantities. Moreover, there seems to be a direct correlation between LOI and the weight loss path of the binders.

 

**Figure 1.** WAXD of B, 20A, 30B, B/20A-4 and B/30B-4. **Figure 2.** TGA derivative weight curves as a function of   
 temperature for B, B/30A-4 and B/20A-4

**Table 1** – LOI, viscosity and TGA data for the binary mixes.

|  |  |  |  |
| --- | --- | --- | --- |
| **Blend** | **Clay content**  **(wt %)** | **LOI** | **Viscosity (135 °C, cP)** |
| **B** | 0 | 28 | 450 |
| **B/20A-2** | 2 | 26 | 608 |
| **B/20A-4** | 4 | 25 | 2304 |
| **B/20A-8** | 8 | 22 | 17000 |
| **B/30B-2** | 2 | 28 | 471 |
| **B/30B-4** | 4 | 29 | 542 |
| **B/30B-8** | 8 | 24 | 850 |

**4. Conclusions**

The organoclays significantly interact with the binder, thus modifying its colloidal structure. This effect prevails on the above-mentioned labyrinth-effect related to the presence of exfoliated or intercalated platelets in the bitumen matrix.

**References**

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