

EVALUATION OF THE INFLUENCE OF NANOMETRIC FILLERS ON THE PROPERTIES OF NBR COMPOUNDS

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INTRODUCTION

The use of nanometric scale fillers in Nitrile-Butadiene Rubber (NBR) compounds is oriented towards the obtention of physical properties similar or superior to those obtained with carbon black, in applications where the colour black is not required. In most of the investigations carried out with nanoclays, their incorporation to the elastomeric matrix involves a previous treatment for changing their hydrophilic nature to organophilic^[1,2], and only few researchers use the clay unmodified assuring a good filler-matrix interaction by means of coupling agents^[3]. Based on all these previous aspects, this study had the purpose of investigating the influence of adding untreated bentonite to NBR compounds with special attention on filler content, coupling agent type, and comparing the final properties to a compound filled with carbon black.

EXPERIMENTAL

NBR with 32.7% acrylonitrile content and bentonites Optibent CP and Milbond-TX were used. Polyethylene glycol (PEG 6000) and Vinyl-trimetoxisilane (Z-6300) were employed as coupling agents. All formulations (Table 1) were prepared using a Banbury® internal mixer and then passed through a milling roll for banding. Rheometric characteristics, tensile properties, tear strength, hardness and abrasion resistance were studied for all NBR compounds.

Table 1: NBR formulations

| Formulation | F1 | F2 | F3 | F4 | F5 | F6 | F7 |
|--|-----|-----|-----|-----|-----|-----|-----|
| NBR [phr] | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Zinc oxide [phr] | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| Stearic acid [phr] | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Milbond-TX® [phr] | - | - | - | - | 10 | 10 | - |
| Optibent CP® [phr] | - | 10 | 20 | 30 | - | - | - |
| TBBS [phr] | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 |
| Sulphur [phr] | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Polyethylene glycol (PEG 6000) [% of filler] | - | - | - | - | - | 10 | - |
| Vinyltrimetoxisilane (Z-6300) [% of filler] | - | 10 | 10 | 10 | 10 | - | - |
| Carbon black N330 [phr] | - | - | - | - | - | - | 20 |

RESULTS AND DISCUSSION

Table 2 shows the cure characteristics of all NBR formulations evaluated. The addition of filler originated in all cases an increase on torque, and this increase was even more notorious when filler content increased. Besides, for all the formulations with bentonite, the scorch time (t_{s2}) and curing time (t_{90}) increased with respect to the unfilled NBR (F1). However, this tendency was not observed with carbon black, due to its organic nature that permits a better interaction with the rubbery matrix, hence activating the curing process. With respect to the coupling agent used, it seems that for silane the curing process is slightly slower and starts

later. If filler nature is compared, one can see that carbon black is superior with respect to cure index.

Table 2: Cure characteristics of NBR formulations

| Formulation | M_L [dN.m] | M_H [dN.m] | t_{s2} [s] | t_{90} [s] | Cure index [s^{-1}] |
|-------------|--------------|--------------|--------------|--------------|-------------------------|
| F1 | 0.25 | 6.33 | 124 | 556 | 0.23 |
| F2 | 0.42 | 9.35 | 147 | 637 | 0.20 |
| F3 | 0.50 | 10.32 | 135 | 709 | 0.17 |
| F4 | 0.60 | 11.86 | 111 | 670 | 0.18 |
| F5 | 0.41 | 8.63 | 203 | 712 | 0.20 |
| F6 | 0.31 | 7.33 | 155 | 586 | 0.23 |
| F7 | 0.72 | 9.71 | 85 | 268 | 0.55 |

Table 3 shows all physical properties evaluated. With respect to tensile and tear properties, these properties increased with the presence of a filler, independently of its nature, and when the filler content increased. The influence of the nature of the coupling agent was also noticed since better performance was obtained with Z-6300 (F5) with respect to PEG (F6). When comparing the effect of bentonite (F3) and carbon black (F7), one can see that the latter provided higher tensile (σ_r) and tear strength (TS) due to better filler-matrix interactions, hence higher reinforcing effect. Concerning hardness, it is evident that Shore A hardness increases when adding fillers. Nonetheless, the nature of the coupling agent did not affect this property. With respect to the abrasion resistance, one can see that the abraded volume decreased when filler was present. In addition, the maximum abrasion resistance was obtained with 20 phr of carbon black (F7); however, this value is equivalent to a formulation with 30 phr of bentonite (F4). The abrasion resistance in presence of coupling agents (F5, F6) was deficient in both cases, but once again, the silane (F5) showed better performance compared to PEG 6000.

Table 3: Physical properties of NBR formulations

| Formulation | ϵ_r [%] | σ_r [MPa] | TS [KN/m] | Shore A | Volume loss [mm^3/mg] |
|-------------|------------------|------------------|------------|---------|---------------------------|
| 1 | 432 ± 20 | 2.9 ± 0.2 | 18.1 ± 0.2 | 48 ± 1 | 94 ± 4 |
| 2 | 409 ± 9 | 4.4 ± 0.1 | 25.4 ± 0.7 | 52 ± 1 | 82 ± 7 |
| 3 | 424 ± 3 | 5.5 ± 0.1 | 32.0 ± 0.7 | 55 ± 1 | 81 ± 2 |
| 4 | 439 ± 13 | 7.5 ± 0.2 | 39.0 ± 1.0 | 60 ± 1 | 72 ± 5 |
| 5 | 476 ± 17 | 3.8 ± 0.2 | 22.3 ± 0.4 | 52 ± 1 | 112 ± 15 |
| 6 | 453 ± 16 | 3.1 ± 0.1 | 19.3 ± 0.3 | 50 ± 1 | 136 ± 18 |
| 7 | 435 ± 25 | 13 ± 1 | 61.2 ± 0.8 | 59 ± 1 | 71 ± 2 |

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