

# Effect of MPS-modified bentonite on filler network structure, rheological behaviour and cure kinetics of rubber compounds

Z. Mičicová, S. Božeková, I. Labaj, J. Vršková, P. Skalková, M. Pajtášová

This study investigates the effect of bentonite modified with (3-Trimethoxysilyl)propyl methacrylate (MPS) on the dynamic filler network, rheological behaviour, and cure kinetics of rubber compounds. Bentonite was surface-modified using different concentrations of MPS to improve filler–rubber interactions and enhance its applicability as a partial replacement for carbon black. The modified bentonites were characterized by FTIR, TG and EDX analyses, while the viscoelastic and curing behaviour of the rubber compounds was evaluated using a Rubber Process Analyzer (RPA).

Bentonite was surface-modified using (3-Trimethoxysilyl)propyl methacrylate at concentrations of 0.5, 2.5 and 5 wt.%. The modification was carried out in an ethanol/water medium under mildly acidic conditions. The suspension was stirred for 2 h at 35°C, followed by centrifugation, ethanol washing and drying at 80°C for 12 h. EDX analysis (Table 1) showed that the elemental composition of bentonite remained relatively unchanged after MPS modification. Minor variations in  $\text{CaO}$ ,  $\text{SO}_3$  and  $\text{K}_2\text{O}$  contents suggest surface interactions between the silane and bentonite structure without the formation of significant impurities.

The FTIR spectra (Fig. 1) of raw and MPS-modified bentonites show absorption bands in the range of 3700–3200  $\text{cm}^{-1}$  corresponding to the stretching vibrations of structural OH groups and bound water in the smectite structure. The band at 1638  $\text{cm}^{-1}$  is assigned to OH deformation vibrations of interlayer water, while the band at 1036  $\text{cm}^{-1}$  corresponds to Si–O stretching vibrations. The appearance of absorption bands in the region of 2950–2850  $\text{cm}^{-1}$ , assigned to C–H stretching vibrations of MPS organic groups, confirms the successful surface modification of bentonite. A decrease in the intensity of OH-related bands after modification indicates reduced interlayer water content and interactions between the silane and bentonite surface.

The TG curves (Fig. 2) of the prepared samples show mass losses attributed to the dehydration process occurring at low temperatures (30–300°C), followed by dehydroxylation of the smectite structure at intermediate temperatures (350–750°C). Differences in the thermal behaviour of the modified bentonites were observed after MPS treatment. The modified samples exhibiting higher weight losses are probably associated with the presence of grafted organic silane groups on the bentonite surface, while the lower weight loss observed for one of the modified samples may be related to a reduced amount of interlayer and adsorbed water after surface modification.

The calculated apparent activation energy values (Table 2) demonstrated that filler incorporation significantly influenced the curing behavior of the investigated rubber compounds. All filled systems exhibited higher  $E_a$  values compared to the unfilled rubber compound, confirming that the presence of filler modifies the vulcanization environment and affects polymer chain mobility. Among the investigated systems, the M/Ben/0.5 compound exhibited the highest apparent activation energy, which may be associated with enhanced filler–rubber interactions and more restricted chain mobility after MPS modification of bentonite. The rheological measurements presented in Fig. 3 revealed a decrease in complex viscosity with increasing frequency for all investigated compounds, indicating typical shear-thinning behavior of rubber systems. The MPS-modified bentonite systems exhibited slightly higher complex viscosity at low frequencies compared to the unmodified bentonite-filled compound, suggesting moderately enhanced filler–rubber interactions.

The strain sweep measurements shown in Fig. 4 confirmed the development of a stronger dynamic filler network in the MPS-modified systems. Compared to the unmodified bentonite-filled compound, the MPS-modified systems exhibited higher Payne effect values, indicating improved filler networking and enhanced filler–rubber interactions. Overall, the obtained results confirm the significant influence of MPS-modified bentonite on the rheological behavior and curing characteristics of rubber compounds.