

Surface silanised nanoclays – Filler modifier for rubber compounds

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Abstract

Polymers filled with organically modified montmorillonite (MMT) have been attracting intensive research interest due to the potential benefits as highly active reinforcing filler or as an additive to reduce liquid and gas permeability. The introduction of these property-enhancements into the pure polymer matrix by the filler is directly related to the highly anisotropic structure of the layers of the smectic clays and the potentially very high surface accessible in case of complete exfoliation. However, the potential benefits from the large anisotropy of the clay-layers also pose the biggest challenge – assure a good dispersion. The desired dispersion state of the montmorillonite clays in polymers and elastomers typically is not achieved using standard rubber processing equipment, even in the case of best possible compatibilisation with organic modifiers, impairing their application as additives.

An alternative approach to overcome the dispersibility issue are synthesized layered silicates (SLS). Except Octosilicate, synthesized layered silicates are naturally occurring minerals (Magadiite, Kanemite, Kenyaite). Analogous to MMT the SLS require organic modification by ion-exchange with long-tailed cations resulting in an extension of the layer-spacing and compatibilisation with the rubber matrix facilitating the dispersion and exfoliation of the SLS-sheets. However, synthetic layered silicates (SLS) have some important differences to layered clay minerals: the former have interlayer silanol- and negatively charged sites SiO⁻ groups, whose ordering can be defined specifically, while the charged sites of clay minerals arises from isomorphous substitution within the layers and the exact position of these sites is very difficult to define [1]. Cation-exchange should therefore yield a more regular coverage of the silicate-layers with long-tailed cations and hence a better overall compatibilisation promoting intercalation and exfoliation. Synthetic layered silicates (SLS) are assumed to have in general a lower aspect ratio, i.e. the sheet extension is smaller than the one of the familiar mined layered clays, while maintaining the typical layer thickness of the individual sheets. Because the interaction energy between the layers of the clay scales also with the surface area, intercalation and exfoliation of SLS in apolar polymers should be easier.

We studied these materials for their potential as a reinforcing filler of elastomers. As a base polymer matrix we used a standard tire-tread mixture (70phr s-SBR, 30phr BR) together with the usual curing and antioxidant reagents and TESPT. Tensile tests showed an interesting synergism at high filler loadings (70-90 phr) of highly dispersible silica (HDS) and 3-5 phr SLC. Upon the addition of SLS to the base tire-tread mixture reinforced with HDS, the stress at 10% deformation was found to be lower by ca. 30% than the corresponding SLS-free mixture but higher at σ_{100} , σ_{200} , σ_{300} by 15-28%. Most interesting is that the MMT-compound does not show any additional reinforcement over the HDS-only compound, suggesting that the SLS-compound has a much better dispersion of the layered clays than the MMT-compound. Additionally, we show the beneficial effects of SLS- over MMT-additive on the dynamic mechanical properties in such a tire-tread mixture: improvement of the performance predictors for ice-wet-grip and rolling resistance by 35% without significantly impairing the wear and abrasion behavior in comparison with a reference compound. These effects were obtained using standard rubber processing equipment and industry-established silanization technology [2-4].

We reason that the performance gain is related to a much higher level of exfoliation of the synthetic layered silicates than montmorillonite. We present a detailed experimental study and develop a qualitative model of the effect of the additive on the reinforcing silica-filler network. [3]

References

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Figures

