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Shear Controlled Morphology of Rubber/Organoclay Nanocomposites and Dynamic Mechanical Analysis

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Summary: Styrene butadiene rubber/layered silicate composites were prepared using clays modified with alkyl ammonium salts of different structure. The influence of modifier structure and compounding conditions on the extent of exfoliation/intercalation of the silicates was investigated by electron microscopy and dynamic mechanical analysis. With increasing exfoliation the glass transition temperature is lowered and the stability of the filler network is enhanced.

Introduction

In the last few years layered silicates have attracted much interest as fillers with potential for novel applications. The clays are modified via cation exchange with ammonium salts to yield organophilic clays (OC) and to make them compatible with polymers. During mixing the polymer chains can penetrate into the gallery between the layers and under the action of shear forces the aggregates can be transformed into smaller intercalated stacks of layers or even exfoliated to single layers leading to polymer/silicate nanocomposites (NC). Due to the ultrafine dispersion and high aspect ratio of the OC the NC exhibit superior strength, moduli, higher heat distortion temperatures and improved water and gas barrier properties compared to conventional isotropic fillers as silica or carbon black, especially when the layers are exfoliated into single layers.[1, 2] A large number of papers deals with mechanical properties of NC with polyamide[3], polypropylene[4], epoxy resins[5] and rubber[6,7]. This work focuses on the generation of styrene butadiene rubber (SBR)/Organoclay composites with different types of OC and investigations on the influence of the filler dispersion on dynamic mechanical relaxation. The T_g dependence and a relaxation process due to filler network destruction are investigated in terms of exfoliation degree. The influence of shear forces during compounding on the filler dispersion is also discussed.

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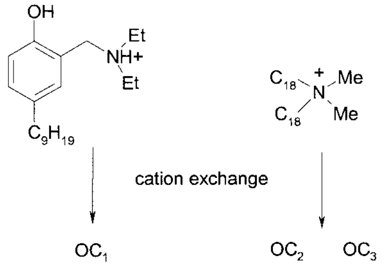
Experimental

To prepare nanocomposites with SBR (BUNA SL 18-0, 18% styrene content, $M_w \approx 400.000$ g/mol, Bayer AG) as matrix polymer three different organically modified clays were used. The modification takes place via a exchange of the intergallery cations of the layered silicate against ammonium cations and results in OC_1, OC_2 (Nanofil, Südchemie AG) and OC_3 (Nanomer I.42E, Nanocor). The clay used for the preparation of OC_1[6] is a synthetic hectorite (Somasif ME 100, Coop Chemical), OC_2 and OC_3 are based on montmorollinite. The only difference of the latter ones is the intergallery distance determined by X-ray scattering, OC_1 has a spacing of 2.7 nm between two silicate layers, OC_2 3.1 nm and in the case of OC_3 it is 3.6 nm. The particle size of the OC is about 10-25 µm.



For compounding with SBR an internal mixer (Haake Rheocord 90, Banbury rotors) was used. SBR, vulcanization chemicals (1.5 phr sulfur, 2,5 phr N-Cyclohexyl-2-benzothiazole sulfene amide (CBS), Bayer AG, 4 phr zinc oxide, 2 phr stearic acid) and the organoclay (30 phr, which is equal to 15 wt% inorganic content) were mixed at temperatures of 80-90°C for 10 minutes. For further improvement of filler dispersion the mixing was followed by a treatment on a roll mill at 80°C for 10 min. After compounding the products were vulcanized for 50 min at 160° C in a hot stage press (Collin).

Dynamic mechanical analysis (DMA) was performed on a Rheometrics RSA II in film fixture geometry (1 mm x 6 mm x 22 mm) at a frequency of 1Hz and 0.1 % strain from -80 °C to 120 °C.

Transmission electron micrographs were taken from ultrathin sections cryo-ultramicrotomed at -100 °C with a Reichert Ultracut E using a LEO 912 Omega operating at a voltage of 120 kV and a slow scan camera.

Influence of organoclay structure on intercalation/exfoliation

Vaia et al. described a lattice model of polymer melt intercalation in organoclays where they separated the free energy change upon mixing into an energy change due to new intermolecular interactions and a combinatorial entropy change associated with conformational changes of the polymer and the modifier.[8] When the polymer diffuses into the galleries between the silicate layers it loses conformational freedom due to confinement between the layers which can be compensated partly by enhanced conformational freedom of the modifier chains and more efficiently by the energy gain through favourable interactions between polymer/modifier and polymer/silicate. If the energy gain is smaller than the entropic loss the polymer chains do not diffuse into the galleries. In the case of favourable enthalpic interactions intercalation and exfoliation under the combined action of thermodynamic and shear forces is possible. The morphology image of the composite containing OC_1 shows that intercalation of the polymer is prevented (figure 1), whereas nanocomposites with intercalated and exfoliated structures are generated with OC_2 and OC_3 (figure 2). The favoured diffusion into the OC galleries in the second case probably occurs because of a larger initial entropy gain of the modifier due to the longer alkyl chains. In the first case the entropy barrier opposing diffusion cannot be compensated by the assumed favourable interactions between the phenolic group of OC_1 and the phenyl ring of SBR.

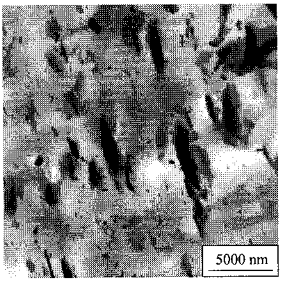


Figure 1: large silicate aggregates (OC_1) in SBR

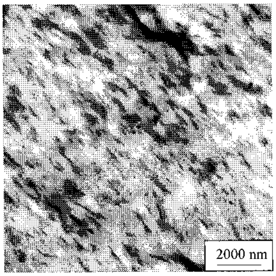


Figure 2: well dispersed silicate layers (OC_3) in SBR

Influence of shear forces on the extent of filler exfoliation

When high shear forces are applied during compounding, as it is the case on a roll mill, the shear stress supports the breakdown of larger silicate stacks into smaller ones. If the thermodynamic factors discussed above are favourable the shear stress and polymer diffusion into the galleries force the silicate layers to peel apart one by one. Fornes et al. recently proposed this mechanism for exfoliation under shear[9]. It is schematically shown in figure 3. A fan-shaped intermediate observed by TEM (figure 4) visualizes this mechanism.

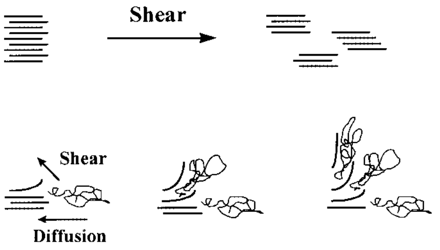


Figure 3: Schematic mechanism for exfoliation under shear[9]

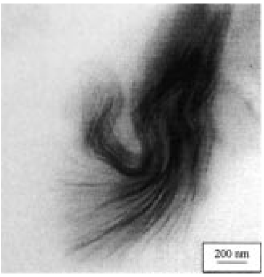


Figure 4: Silicate layers peel apart via a fan-shaped intermediate

The breakdown of large silicate aggregates (tactoids) into smaller stacks by virtue of greater shear forces can also be visualized by TEM images at different compounding stages. Figure 5 shows an image after compounding in an internal mixer where moderate shear forces are applied. After treatment on a roll mill under high shear stress large agglomerates are broken into smaller stacks (figure 6).

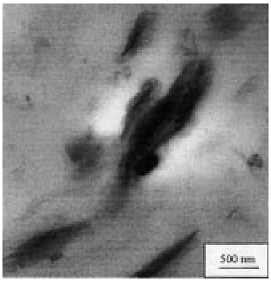


Figure 5: OC_2 in SBR matrix after compounding on an internal mixer

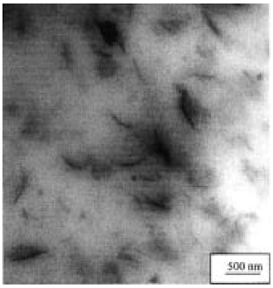


Figure 6: OC_2 in SBR matrix after compounding on a roll mill

Influence of filler dispersion on dynamic mechanical relaxation

First it is observed that the glass transition is shifted to lower temperature as the degree of intercalation/exfoliation increases (figure 7). When the silicate layers are exfoliated a greater amount of ammonium salt is at the silicate surface and acts as a plasticizer. The decrease of the tan δ peak with enhanced degree of intercalation/exfoliation is due to the greater amount of polymer included in intercalated stacks. This reduces the amount of polymer being deformed during strain oscillation and thus reduces the amount of dissipated energy.

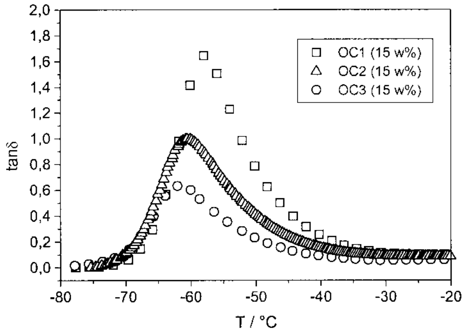


Figure 7: T_g dependence on filler dispersion

The additional relaxation process at higher temperatures can be related to the process associated with the breakdown and reformation of the filler network. The process is shifted to higher temperatures with increasing degree of exfoliation showing the greater perfection and stability of the network containing a larger number of exfoliated layers (figures 8 - 9). In conventional silica filled systems a much higher filler content is necessary to observe this relaxation process[10].

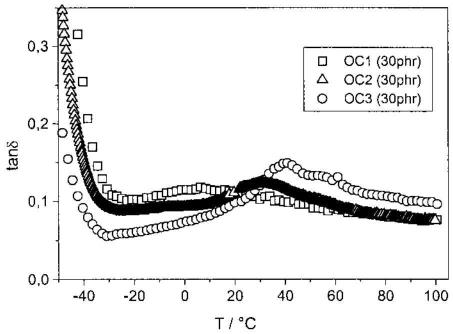


Figure 8: Temperature dependence of filler network relaxation on filler exfoliation

Both E' and tan δ show that exfoliation and expression of the filler network are increased with organoclay structure from $OC_1 \rightarrow OC_2 \rightarrow OC_3$.

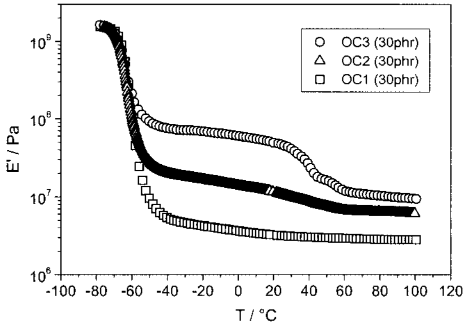


Figure 9: Temperature dependence of E' for organoclays with different degree of exfoliation

Conclusions

Introduction of a group with favourable modifier/polymer interactions into the modifier may not be sufficient for polymer intercalation if the length of the alkyl chain of the modifier is not long enough. If entropic and enthalpic interactions are favourable it is possible to improve exfoliation by increasing the shear stress during compounding. Exfoliation is shown to proceed via fan-shaped intermediates by TEM. DMA was proven to be a sensitive method to monitor the degree of exfoliation and intercalation by the depression of T_g and by the intensity and temperature dependence of the loss process at higher temperature originating from the relaxation of the filler network.

References

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