

NANOCLAY FILLER DISLOCATION AND COMPATIBILIZATION EFFECT IN HETEROGENEOUS POLYMER BLENDS

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Introduction

The capability of nanoclay for the enhancement of application properties of polymer blends is strongly dependent on the degree of clay dispersion, which - on the other hand - depends on the clay structure and its chemical modification, viscosity and polarity of the polymer matrix as well as the processing conditions [1,2]. It was found that the addition of nanoclay into heterogeneous polymer blends can improve the compatibility of the polymeric components, and also a refinement of the phase morphology of heterogeneous blends was detected [3,4]. Also on the dislocation of nanoparticles between the blend phases during mixing has been reported [5].

The goal of the work what about is reported here was the investigation of nanoclay dispersion, the dislocation of nanoclay particles in rubber blend phases as well as the compatibilizing effect of nanoclay in heterogeneous rubber blends. The electrical conductance measured directly, i.e. *in situ*, during the mixing process was used to monitor the dispersion of nanofillers and to describe the change of phase morphology of the rubber blends [6]. By this method monitoring of the intercalation and exfoliation processes of nanoclay in polymer, especially rubber, became possible. In contrast to the conductance of CB or CNT filled rubber compounds, which is characterized by electron transport, the online measured electrical conductance of polymer-clay composites has an ionic nature due to the release of the quaternary ammonium cations, which are available in the clay galleries. A close correlation between the online conductance chart and the kinetics of clay dispersion has been observed empirically [7]. The dislocation of nanoclay from one to another rubber phase as well as the compatibilizing effect of the clay expressed especially in a drastic refinement of the isle-matrix phase morphology was visualized by AFM and correlated to the online measured electrical conductance curves during mixing of HNBR/NR blends.

Experimental

Hydrogenated nitrile butadiene rubber (HNBR) Zeptol 2030L (Zeon Deutschland) and natural rubber (NR) SMR10 (Standard Malaysian Rubber) were used as polymer blend components. As nanofiller Organoclay Nanofil[®] 9 (Süd-Chemie) and Luperox 101 (Atofina Chemicals) as crosslinking agent for the rubber matrix were used. In the first mixing step NR was mixed with nanoclay in an internal mixer Rheomix (Thermo

Haake) at an initial chamber temperature of 50 °C to produce a NR-nanoclay masterbatch. In the second step, HNBR was mixed with the NR-nanoclay masterbatch at the same mixing conditions to get a filled 50/50 HNBR/NR blend with a clay concentration of 5 phr. For comparison purpose, an unfilled 50/50 HNBR/NR was prepared. During mixing the electrical conductance of the batch was measured by means of a coupled conductivity-temperature sensor. The in such a way online measured electrical conductance (OMEC) was recorded in dependence on time. Simultaneously, samples were taken out of the mixing chamber after different mixing times for the characterization of dispersion kinetics of the nanoclay. The mixtures were compression-molded and vulcanized at 170°C. AFM investigations were performed to characterize the phase morphology and filler distribution. Thermogravimetric analysis (TGA) after solvent extraction of NR was applied for determination of the phase specific filler content.

Results and Discussion

Figure 1 shows the OMEC of the unfilled HNBR/NR blend, NR-nanoclay masterbatch and HNBR/(NR-nanoclay masterbatch) blend in dependence on mixing time. As expected the conductance values of the NR-nanoclay masterbatch is very low and lies below the

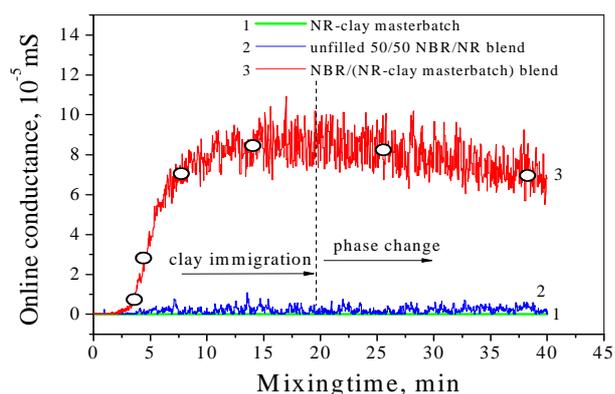


Fig. 1 Online conductance of the unfilled HNBR/NR blend (1), NR-nanoclay masterbatch (2) and HNBR/(NR-nanoclay masterbatch) blend (3) in dependence on mixing time.

measuring range of the equipment (curve 1). The conductance curve of the unfilled 50/50 HNBR/NR blend (curve 2) is also low but it is determined by the polar HNBR phase. When mixing HNBR with NR-nanoclay masterbatch the OMEC of the HNBR/(NR-nanoclay masterbatch) blend (curve 3) shows a drastic

increase of the conductance level compared to the unfilled HNBR/NR blend. The increase of electrical conductance is caused by the release of ions out of the intercalated as well as exfoliated nanoclay tactoids. The course of the first part of curve 3 is determined by the dislocation of clay from the NR into the HNBR phase and the phase morphology development proceeding during the mixing process. In the course of the mixing process the nanoclay loading in the NR phase decreases from 5 phr at the start of mixing to less than 1 phr after a mixing time of 40 min. Simultaneously, the clay loading in the HNBR phase increases from zero to 4 phr (Fig. 2).

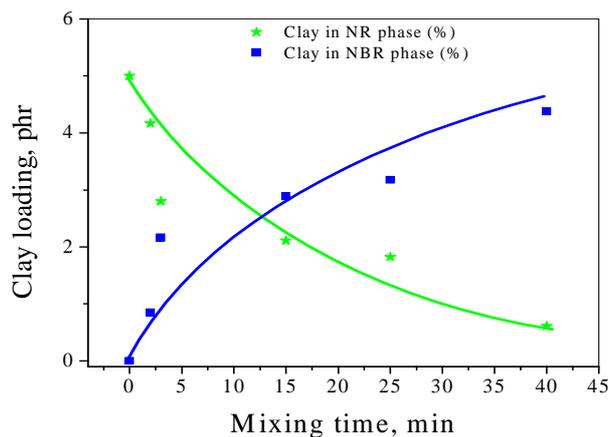


Fig. 2 Nanoclay distribution determined by extraction experiments and TGA as a function of mixing time (HNBR/NR ratio 50/50, 5 phr nanoclay)

The dislocation of nanoclay from the NR phase to the HNBR phase is caused by the enhanced interaction between HNBR and clay in comparison to the interaction between NR and clay. The clay immigration was visualized by AFM images (Fig. 3). After two minutes mixing time (Fig. 3a) most of the nanoclay (black agglomerates) is still visible in the NR phase (light area). With increasing mixing time the nonpolar NR chains, which contacted primarily the clay surface, are replaced now more and more by the polar HNBR molecules. In this period the HNBR appears as a continuous phase (Fig. 3b) which facilitates the good ionic conductivity of the blend. After that time period the continuous HNBR phase starts to be divided into disperse domains making the motion of ionic species through the blend volume difficult that is expressed in the subsequent decay of the online conductance (see Fig. 1). The extent of the conductance decay correlates with the change of the HNBR domains. In the period from 25 min to 40 min the diameter of NBR domain reduces to 1 μm (Fig. 3d) and the online conductance is dropping from $8.26 \cdot 10^{-5}$ mS to $6.86 \cdot 10^{-5}$ mS (Fig. 1).

Because of the polar interactions between HNBR polymer and nanoclay the HNBR molecules start to intercalate and exfoliate the nanoclay preferentially. With the transfer of the nanoclay out of the nonpolar

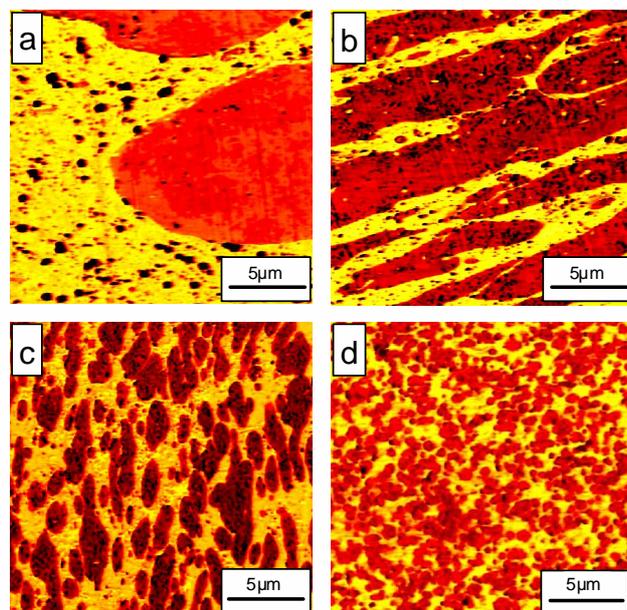


Fig. 3 Development of blend morphology and nanoclay dislocation in HNBR/(NR-clay masterbatch) blend in dependence on mixing time, a: 2 min, b: 5 min, c: 25 min, d: 40 min. HNBR/NR ratio 50/50, 5 phr nanoclay.

NR into the HNBR phase via the interface between both polymers the interfacial tension in the filled blend system is changed drastically. Furthermore, the exfoliated clay platelets effectuate that coalescence processes cannot run in that way as it would be possible without the presence of nanoclay. Hence, the disperse phase undergoes a refinement process and the phase morphology is changed markedly.

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