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Structure and Properties of Nanocomposites Based on SBS Block Copolymer and Alumina

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Summary: The addition of inorganic filler into commodity plastics has a long history. Today, polymer composites based on nanosized filler are popular among polymer scientists from academia and industries due to their ability to enhance a number of physical properties. In this work, we investigate the dispersion and reinforcing effect of alumina nanoparticles using a polystyrene-polybutadiene based block copolymer (SBS) and organically modified alumina nanofiller. With the aid of solution casting procedures, polymer composites with good dispersion of nanoparticles could be produced. It has been demonstrated that with suitably coated nanoparticles, polymer composites with optimum dispersion of nanofiller ensuring marked reinforcement effect can be achieved.

Keywords: alumina nanoparticles; electron microscopy; polymer nanocomposites; SBS block copolymer

Introduction

Block copolymers belong to the family of heterogeneous soft matter, in which the molecules self-assemble into a large variety of periodic nanostructures via intramolecular phase separation.[1–3] The periodicity of these structures lies in the same order as the gyration radius of macromolecules. The type and the size-scale of these nanostructures are controlled by various parameters such as molecular weight, composition, molecular architectures etc. [1–6] A precise control of these structures enables to tailor their mechanical properties over a wide range.[7,8]

The reason of continuously increasing interest for these materials over the last few decades is their potential application in nanotechnology such as templating of various nano-objects.[2] The studies on various block copolymer systems have enabled not only the understanding of complex self-assembly phenomena in general but also triggered the development of materials having properties relevant for specific applications.[2] Many of the physical properties of nanostructured block copolymer systems are generally controlled by the nature, dimension and orientation of morphologies, and the latter may be significantly altered by molecular architectures[5,6] and processing conditions.[8,9] Therefore, it is a subject of practical importance to study a correlation between processing parameters, morphology and end-use properties of these materials.

Styrene-butadiene based block copolymers (SBS) with a butadiene content of up to about 30% have gained a permanent place in the area of transparent and high impact materials over the last 30 years.[7] Typical applications are high-quality, crystal-clear, sparkling packaging with high toughness, for example for menus and deserts, cups for cold-drink dispensers, freezer boxes, shower cubicles, and applications in medical technology and toys.

Like other impact-modified thermoplastics, the hard/soft phase volume ratio affects

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some characteristic mechanical properties in contradictory ways. For example, with increasing butadiene content, the elongation at break and the fracture energy increase while the modulus of elasticity, heat resistance and tensile strength drop. It is to be noted that the mechanical properties of SBS are dictated primarily by the nature of nanostructures provided that the centre rubber block is anchored on both the ends by glassy polystyrene (PS) domains.[7,8]

SBS block copolymers are frequently blended with general purpose polystyrene (GPPS) for cost reasons and/or for specific production of a defined polymer. For example, a combination of relatively high stiffness with ductility can only be achieved this way [7,8] and not by strong reduction of the butadiene content. Another option to increase the stiffness without sacrificing the ductility of the block copolymer would be to introduce inorganic nanoparticles, where the compatibility and dispersion of the filler are most important issues concerning the mechanical properties.

The addition of inorganic filler into commodity plastics has a long history. Primarily those fillers were added to reduce the price, but today polymer scientists concentrate more on other aspects such as reinforcing effect, flame retardancy, controlling the rheological properties etc. Of particular interest are the polymer composites based on nanosized fillers. The great advantage of nanofillers can be achieved only if the particles are finely dispersed in the polymer matrix. The latter requires a suitable surface treatment of the inorganic nanoparticles so that the dispersion of the particles and hence the effective reinforcement are warranted. The common nanofiller used currently include layered silicates, alkaline earth metal compounds, carbon nanotubes, silica particles etc. There is a huge number of articles on polymer based nanocomposites (for relevant reviews see[10–13]) which often claim that all the mechanical properties are simultaneously enhanced in such composites. However, in reality, one often encounters the doubtful reports especially on toughness enhancement of polymers.

The aim of this work is to conduct model experiments on dispersion of alumina nanoparticles into a polymer matrix (using amorphous polymers that can be easily dissolved in an organic solvent such as chloroform) and its effect on mechanical properties of the polymer.

Experimental Part

Materials and Sample Preparation

The polymers used in this study were general purpose polystyrene (GPPS) and an SBS block copolymer. Both the polymers were supplied by BASF, Ludwigshafen. The SBS sample was a lamellae forming polystyrene-polybutadiene based triblock copolymer comprising asymmetric polystyrene (PS) outer blocks separated by a polystyrene-co-polybutadiene random copolymer (PS-co-PB) middle block. The total number average molecular weight (M_n) and the polydispersity index of the copolymer are 127,300 g/mol and 1.10, respectively. The morphology of this polymer has been discussed elsewhere.[14,15] The alumina nanoparticles used was organically modified boehmite nanoparticles (Disparal OS1) supplied by Sasol Germany GmbH, Hamburg.

The samples were prepared by solution casting. First, a calculated amount of filler was weighed out in a conical flask followed by preparation of suspension of the nanoparticles in chloroform. The mixture was vigorously shaken for about 10 minutes to prepare a homogeneous, clear suspension (see Fig. 1b). Then, the polymer was added to the suspension and allowed to dissolve in about 6 hours. The final concentration of the polymer solution was approximately 3% (w/v). Films, about 0.5 mm thick, were cast by evaporating the solvent in about two days followed by subsequent vacuum drying and annealing under reduced pressure for 24 hours at a temperature of 120 °C.

Fig. 1 presents the photographs of the containers with Boehmite powder (Fig. 1a)

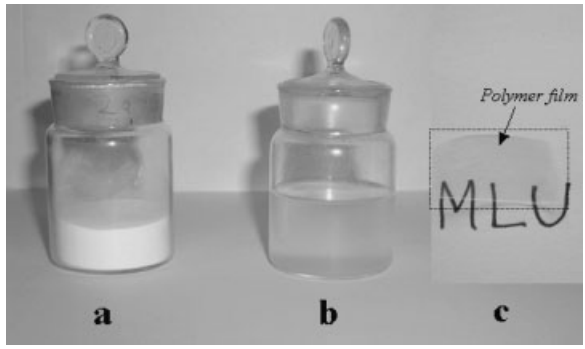

Figure 1.
Photographs showing as supplied boehmite powder (a), suspension of the nanoparticles in chloroform (b), and polystyrene film containing 5 wt.-% boehmite, which covers the upper half of the letters 'MLU'.

and the suspension (about 10% weight/volume) of the particles in chloroform (Fig. 1b). A small piece of polystyrene composite with 5 wt.-% Boehmite is also shown in Fig. 1c. One can notice that suspension of the alumina particles in chloroform is very clear indicating the absence of micron size particles and that the particle surface modification by an aromatic sulphonic acid was effective enough to ensure the good dispersion of the alumina particles in the organic solvent. The transparency of the resulting film (such as one in Fig. 1c) further supports the well dispersion of the fine alumina particles into the polymer matrix.

Microscopic Techniques

Transmission Electron Microscope (TEM, Leo 912) and *Atomic Force Microscope* (AFM; Dimension 3000, Digital Instruments, Ca) were used for the study of nanostructure of the polymers and their composites with Boehmite. *Scanning Electron Microscope* (SEM, Joel, JSM 6300) was used to study the fracture surface morphology of the composites.

Thin sectioning at cryo-temperature using an ultramicrotome (RMC, Drukker Inc.) equipped with a diamond knife (Diatome) served as the method to prepare specimens for both TEM and AFM. Thin sections, ca. 70 nm thick, were inspected by TEM while the remaining block was scanned by an AFM in tapping mode. Prior to the TEM studies, some of the polymer sections were stained by osmium tetroxide (OsO_4) to selectively stain the butadiene-rich phase of the block copolymer so as to uncover the block copolymer nanostructures.

Tensile Testing

Uniaxial tensile testing was used to characterise the mechanical deformation behaviour of the composites. Tensile bars of total length 80 mm were cut out of the solution cast films which were strained at 23 °C and at a cross-head speed of 50 mm/min using a Zwick universal tensile machine. At least 6 samples each were tested.

Results and Discussion

Morphological Characterisation

In this section, we discuss both the structure and the distribution of alumina particles in polymer matrix on the basis of TEM and AFM results.

Fig. 2 shows the TEM micrographs of GPPS/5 wt.-% boehmite composite. The thin section of the sample was investigated by TEM without any treatment (unlike usual TEM studies of polymers) where the alumina particles, owing to their higher electron density than that of polymer matrix, scatter electrons to much higher extent and appear dark in the TEM images. In the low magnification TEM micrograph

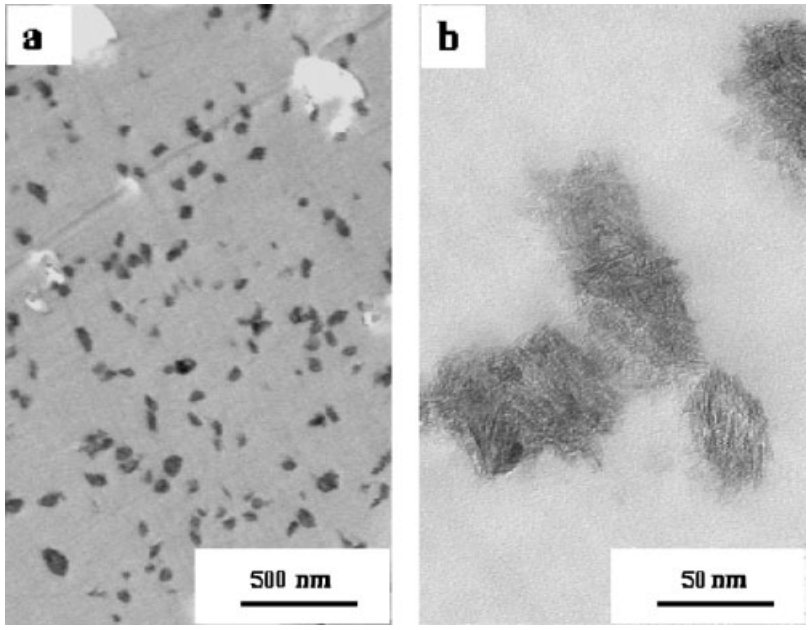

Figure 2.
Lower (a) and higher (b) magnifications of TEM micrographs showing the morphology of GPPS/5 wt.-% boehmite nanoparticles.

(Fig. 2a) one can see well dispersed alumina particles whose size ranges from about 10 nm to 100 nm. Therefore the particles can be regarded as nanoparticles. On the other hand, the higher magnification micrograph (Fig. 2b) shows the details of structure of alumina particles. It can be noticed that the particles are not necessarily spherical in shape and, as expected, have well defined interface with the polymer matrix.

Each nanoparticle depicts a crystalline texture comprising lamellae-like crystals arranged in a staple-like fashion. The thickness of the crystal lies in the range of 3–5 nm. The structure of crystals is similar to that of native boehmite. The size scale of these nanostructures is approximately one order lower than that of the block copolymer nanostructures.[3] Therefore, by optimising the processing parameters, one might be able to introduce the particles selectively into one of the block copolymer phases to achieve the so called 'nano-reinforcement effect'.

Fig. 3 illustrates the representative TEM micrographs of SBS/boehmite nanocomposites containing various amounts of nanofiller. On going from Fig. 3a to Fig. 3c, the concentration of the nanofiller increases. In the same order, the number of aggregates decreases and their size increases. For the composite containing 5 wt.-% alumina, the size of the particles is in the same range as for GPPS (compare Fig. 2a and Fig. 3a), although the nanoparticles in the block copolymer seem to be smaller. The increasing aggregate size with increasing filler content results from the fact that, in spite of the organophilic modification, the particles have their affinity towards themselves rather than to the polymers. At higher filler concentration, some of the particles reach a size of over 200 nm (see Fig. 2c). It suggests that the tendency of the particle agglomeration, which is not necessarily favourable for nano-reinforcement of the polymers, increases with higher feeding of the filler into the polymer matrix.

It is to be noted that the internal particle morphology remains unchanged independent of the composite composition, i.e. the particles have structures identical to that

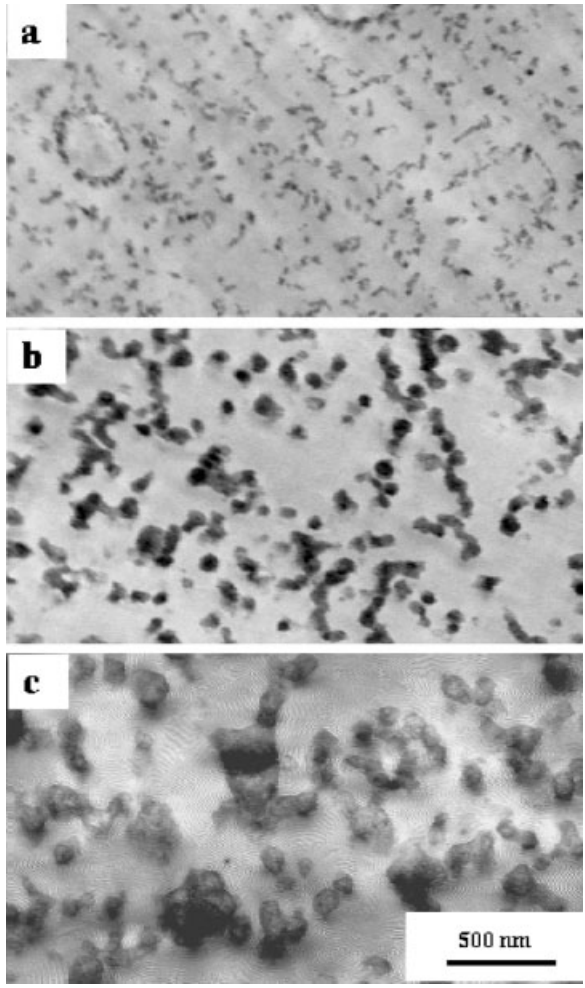

Figure 3.
TEM micrographs showing the morphology of SBS/boehmite nanocomposites containing different weight fraction of boehmite: a) 5%, b) 20% and c) 40%.

observed in Fig. 2b regardless of how much filler is incorporated into the polymer.

The TEM micrograph in Fig. 3c shows both alumina particles and the morphology of the surrounding matrix. The section was stained with OsO_4 vapour to expose the morphological details of the polymer matrix. As expected, the lamellar morphology of the matrix remains unaffected by the incorporated nanoparticles owing to organisation of the particles in larger aggregates. The effect of nanoparticles on the microphase separation behaviour will be the object of a future publication.[16]

AFM phase images of the SBS/alumina nanocomposite samples (studied by TEM in Fig. 3) are presented in Fig. 4. As the local stiffness of the SBS copolymer and the alumina nanoparticles are very different, the nanomechanical properties of the composites are sensed by the AFM technique. Unlike for Fig. 3c, in particular, both the nanoparticles and the matrix morphology can be imaged with the aid of a single AFM probe.

Undoubtedly, the contrast in the AFM micrographs is largely dependent on the experimental conditions.[17] Under the given

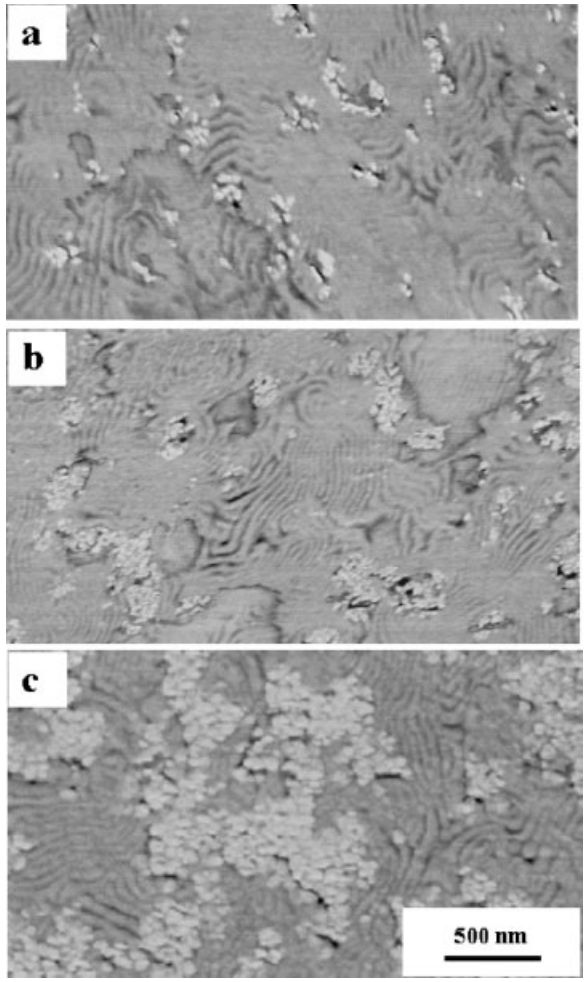

Figure 4.
Tapping mode AFM phase micrographs showing the morphology of SBS/boehmite nanocomposites containing different weight fraction of boehmite: a) 5%, b) 20% and c) 40%.

moderate tapping conditions, the relatively stiff alumina particles appear bright while the polymer matrix looks darker in the AFM micrographs. In addition to the particle morphology, the lamellar structure of the parent polymer can be observed, whose form and dimension remains unchanged. In line with the TEM results (see Fig. 3), the aggregates become larger with increasing alumina content. The internal details of particle morphology, however, cannot be resolved due to the fact that the needle-like crystals are much smaller than both the curvature radius of scanning AFM probe and the sample surface roughness.

Comparison of Fig. 3 and Fig. 4 reveals that the number of particles per unit area in AFM images is rather lower than in the corresponding TEM images. It is attributed to the fact that AFM imaging is restricted to the sample surface which only probes the particles residing on the surface or only a few nanometers beneath it. On the other hand, the TEM is a volume technique; as the electrons pass through the sections, the TEM may also record the particles situated beneath the section-surface.

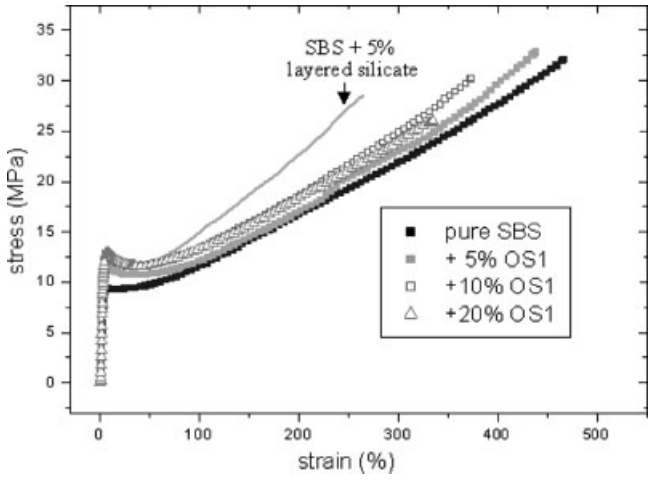

Figure 5.
Tensile stress-strain diagrams of SBS based Nanocomposites; tensile testing at 23 °C at a cross-head speed of 50 mm/min.

Deformation Behaviour of SBS/Boehmite Nanocomposites

Stress-strain curves of some of the SBS/boehmite composites determined by uniaxial tensile test are given in Fig. 5. For the purpose of comparison, the corresponding curve of an SBS/layered silicate composite (5 wt.-% of organically modified layered silicate) is also included. Irrespective of the type and content of the filler, the nature of the stress-strain curves does not change. This behaviour can be attributed to the fact that the basic matrix morphology persists in all the modifications as the properties of block copolymer systems are primarily determined by the nature of the microphase-separated structures.[7]

Characterised by large elongation at break, all the samples show relatively low yield stress (10–14 MPa) and high ductility. Although small, there is an increase of yield stress (σ_y) in the SBS/boehmite nanocomposites. At 5 wt.-% filler content, the value of σ_y increases slightly. However, surprisingly, it does not increase further with more filler content. In contrast, the strain at break drops drastically at higher boehmite content. This observation suggests that the agglomeration of the naoparticles leading to increase in filler domain size and interdomain distance affects negatively on the mechanical properties of the polymer nanocomposites. Hence, further attempts should be concentrated on more finer dispersion of the boehmite nano-crystals into the polymer matrix. For SBS/layered silicate composite, the stress level at each strain is higher but this composite shows much lower tensile strain similar to other polymer/layered silicate nanocomposites discussed in the literature.

To summarise the mechanical properties section, the addition of 5 wt.-% boehmite to the SBS copolymer leads to a gain in yield stress without lowering the strain at break. This improvement in mechanical performance is better than for the corresponding composites with organically modified layered silicate.

Concluding Remarks and Outlook

In this work, we have demonstrated that organophilic modified alumina nanoparticles can be easily incorporated into a polymer by solution casting procedure provided that the alumina particles form good suspension, and the polymer a good solution in a common solvent. Improvement in mechanical performance was observed at lower filler content (up to

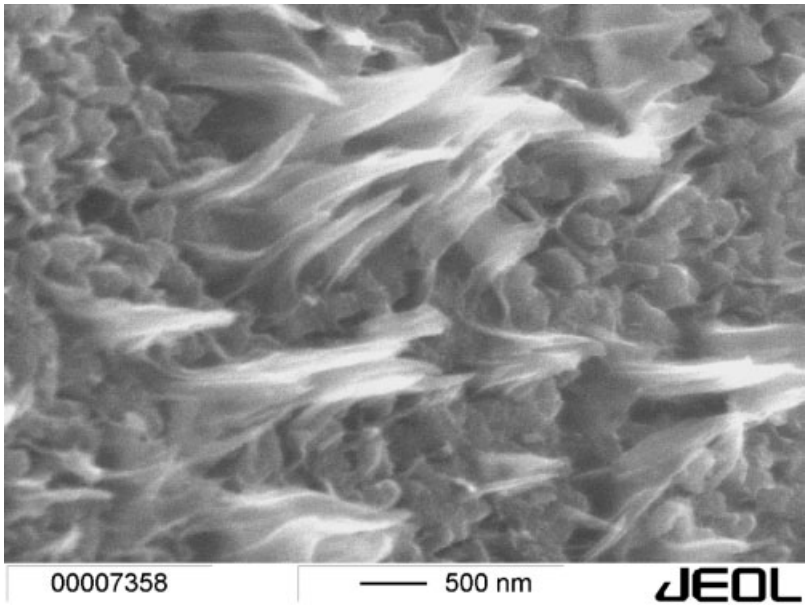

Figure 6.
An SEM micrograph showing fracture surface morphology of GPPS/50 wt.-% boehmite nanocomposite.

5 wt.-%) where the aggregate size was not more than 100 nm. At higher filler concentrations, the nanoparticles built larger agglomerates which were not favoured for the improved mechanical properties. The results, hence, indicates that the processing parameters have to be modified in such a way that one comes to still smaller size (practically approaching the size scale of individual boehmite crystal). In future, we will study the polymer composites with nanoparticles coated with paraffin-like molecules and process the composites under the influence of mechanical shearing.

Our preliminary examinations of GPPS based nanocomposites have demonstrated that the micromechanical properties of brittle polymers (such as polystyrene, polymethyl-methacrylate etc.) can be significantly altered by well dispersed nanoparticles. Fig. 6 shows, for instance, an SEM micrograph of GPPS/50 wt.-% boehmite composite after room temperature fracture of solution cast film. It is evident that there develops a dense texture of highly drawn polystyrene fibrils on the fracture surface. Normally, polystyrene homopolymer at room temperature is a brittle material and its fracture surface comprises the smooth terraces formed by uncontrolled propagation of the microcracks. Occasionally, small regions of drawn fibrils may also occur, which are correlated with the formation of deformation zones called crazes. However, in GPPS/boehmite composite, a large amount of highly drawn fibrils formed by plastic deformation of polystyrene strands situated between the alumina particles are observed on the fracture surface. In other words, the nanoparticles have initiated intensive flow processes in the surrounding polymer matrix. This observation suggests that, in the composite, the occurrence of local energy absorbing flow processes (which is typically crazing in glassy polymers such as polystyrene) occur rather intensively than in the neat polystyrene homopolymer. As a consequence, the composite may behave in more ductile manner than neat GPPS. Therefore, in future, besides the optimisation of filler size distribution in the polymer matrix, their effect on the microphase separation behaviour as well as the micromechanical processes of deformation will be investigated.

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