

Processing and mechanical performance of SBS block copolymer/layered silicate nanocomposites

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Short Title: Mechanical performance of SBS Nanocomposites

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ABSTRACT

Nanocomposites based on a SBS triblock copolymer and organomodified layered silicates were prepared by solution casting followed by melt shearing. The dispersion of the nanofiller in the polymer matrix and its influence on the mechanical behavior of the composites were determined by means of different microscopic techniques, tensile testing, dynamic mechanical analysis and microindentation hardness measurements. It was found that the procedure used for the composite preparation was suitable to obtain optimum dispersion of the nanofiller. A significant improvement in the Young's modulus was observed at a filler content of 10 wt.-% while the other tensile properties remained unchanged. As demonstrated by microhardness measurements, the mechanical reinforcement was verified by a parallel increase in hardness with increasing filler content.

Keywords: SBS block copolymer, nanocomposite, layered silicate, mechanical properties, nanostructure, electron microscopy

1. INTRODUCTION

The design of nanostructured polymers with specific mechanical and functional properties is an important objective in modern materials science and engineering [1]. Thus, there is a growing interest in the field of nanostructured polymeric materials due to their promising mechanical and functional properties. The mechanical properties are determined mainly by the molecular parameters as well as the structural details (morphology) of the polymers and their response to the applied load. Hence, to design polymeric materials possessing a desired property profile, it is essential to develop a suitable morphology aimed at specific micromechanical processes of deformation. Within this context, in recent years, there has been a rapidly growing trend for the incorporation of inorganic fillers into the polymer matrix to enhance one or several physical properties. In particular, high aspect ratio fillers with platelets thickness in the range of a few nanometers (so called ‘nanofiller’) such as layered silicates have been used to increase the stiffness and strength of amorphous and semicrystalline polymers without compromising the toughness properties [2]. Other nanofillers include: alkaline earth metal salts, alumina, silica, polyhedral oligomeric silsesquioxanes (POSS), carbon nanotubes and even Fullerenes [2-11]. The trend in the application of nanofillers has been to ‘achieve large effects with the aid of small particles’. Unfortunately, one often achieves an improvement in stiffness of the polymer at a cost of ductility. Experience shows that the deterioration of mechanical ductility of the polymeric materials by addition of nanofiller is based on the lack of affinity between the filler and the polymer, leading to the formation of agglomerates of critical sizes which may cause a premature failure of the composites. Therefore, the common practice of polymer-based nanocomposite technology has been to modify the filler surface so as to promote interaction with the polymer matrix (see [12] for recent review).

The aim of the present study is to report about some model experiments concerning the dispersion of layered silicate nanofiller within a nanostructured polymer. To avoid difficulties

arising from different crystallization parameters and processing histories, microphase-separated lamellar polystyrene-block-polybutadiene-polystyrene (SBS) triblock copolymer has been used, in which the nanostructured morphology lies in the amorphous state at a molecular scale. The choice of lamellar morphology is justified by the high ductility of the polymer so that the effect of the filler on the ductility of the polymer can be analyzed.

2. EXPERIMENTAL

2.1 Materials

The polymer used in this study is a commercial polystyrene-block-polybutadiene-block-polystyrene (SBS) triblock copolymer of Dexco Polymers (Trade name: Vector 6507). The number average molecular weight (M_n) and polydispersity index (M_w/M_n) of the block copolymer determined by gel permeation chromatography are 80 kg/mol and 1.15, respectively. The polystyrene (PS) weight content of the copolymer is 43.5% (as provided by the supplier).

The Montmorillonite type layered silicate “Nanofil 32” supplied by Sued Chemie AG was used as a filler. This silicate is organomodified by benzyltrimethyl ammonium chloride.

2.2 Sample Preparation

The polymer was dissolved in p.a. chloroform as to form a homogeneous solution. The solution concentration was 10 wt.%. A suspension of layered silicate in the same solvent was prepared. Both mixtures were poured into a conical flask, treated with an “Ultraturrax” disperser for 5 min (about 20.000 r/min), following an ultrasound treatment for 30 min. The mixture was stirred for 24 h at room temperature. The concentration of filler in the final mixture was 30 wt.-%. The solvent was allowed to evaporate in about 48 hours. The remaining film was dried in air for three days. The film was, then, granulated and dried in a vacuum oven at 80°C for three days in order to remove the residual solvent.

In order to improve the dispersion of the layered silicate by shearing forces the dry composites were extruded at 140°C for 15 min under nitrogen using a counter-rotating Haake Miniextruder. Finally, the sample was compression molded at 200°C and 200 bar to prepare specimens for further experiments.

The composites, having varying filler contents, were prepared by diluting the composite with pure SBS copolymer via solution blending using chloroform as solvent. The resulting films including pure SBS film were dried at room temperature for several days and annealed at 120°C for 24 hrs to equilibrate the block copolymer nanostructures. The thickness of the films was about 0.4 mm.

2.3 Mechanical Testing

Miniaturized tensile bars having a total length of 50 mm were punched out of the films prepared as described above. The tensile bars, with their measuring length 30 mm, were strained at a cross-head speed of 50 mm/min at 23°C using a Zwick universal tensile machine. At least 5 experiments were carried out for each sample.

For the measurement of the Young's modulus as a function of temperature, the composites were subjected to dynamic mechanical analysis (DMA) in the tensile mode using a Qualimeter Explorer 500 N DMTA equipment. The heating rate was set to 1K/min and frequency of deformation was 1Hz.

The microindentation hardness (H) of the composites was determined by using a Leitz Microhardness Tester equipped with Vickers square based pyramidal indenter [13]. The indenter penetrates the sample surface at a given load, P , for 6 s. The diagonal of the residual impression, d , after load release, is measured using an optical microscope. The microhardness H , was derived from the expression:

$$H=kP/d^2, \quad (1)$$

where k is a geometric factor equal to 1.854. The H values were calculated from an average of at least 10 indentations.

2.4 Microscopic Techniques

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were used to visualize the structural details of the composites. For the SEM studies, the composites were first cooled to liquid nitrogen temperature and broken by brittle fracture. The freshly prepared fracture surfaces were coated with thin carbon film to avoid charging and irradiation damage during SEM inspection. For the TEM analysis, ultrathin sections (ca. 80 nm thick) were ultramicrotomed from a piece of bulk specimen using a diamond knife at cryogenic temperature. Prior to the TEM studies, the ultra-thin sections of some of the samples were treated with osmium tetroxide (OsO_4) vapor for several hours at room temperature in order to selectively stain the polybutadiene (PB) phase.

3. RESULTS AND DISCUSSION

3.1 Filler dispersion and composite morphology

The filler morphology as well the structure of the SBS/layered silicate composite were characterized by means of electron microscopic techniques. To gain an overview about the level of the filler dispersion and the filler size distribution, scanning electron microscopy (SEM) was employed. Fig. 1 shows the SEM micrographs of a fracture surface of a 30 wt.-% layered silicate composite after extrusion. For this particular study, the so-called BSE (back scattered electrons) mode was employed. Here the marked variations in the scattering of electrons by different phases reflect the material contrast in the electron micrographs. One of the advantages in using SEM is that it allows the inspection of the filler dispersion and morphology of much larger sample areas than in the case of transmission electron microscopy.

In the SEM micrographs studied, the regions with higher electron density (i.e. the silicates) appear brighter while the areas with lower electron density (i.e. the organic polymer) are darker. Thus, the white dots (up to about a micron in diameter), which are well dispersed in the polymer matrix, represent the aggregates of the layered silicate. Taking into consideration that 30 wt.-% layered silicate is mixed with the polymer, one can only see a very small amount of filler as large aggregates. Therefore, it can be concluded that the major part of the filler is efficiently dispersed so that all the aggregates are less than 1 micron in diameter. Nevertheless, based on the SEM results, it can be expected that, for an optimum amount of filler, the aggregation tendency can be reduced and a reinforcement effect in the mechanical behavior may be expected.

Figure 1.

The fine distribution of the major part of filler (in the form of nanoparticles) cannot be visualized by the SEM. TEM investigations were, therefore, conducted to examine the filler morphology and distribution of particles in a much smaller length scale. The sections were weakly stained by OsO_4 to make the microphase-separated block copolymer structures visible. The purpose of this experiment was to inspect whether the filler affects on the block copolymer domain orientation or the filler has a tendency to be localized in one of the phases. Fig. 2 illustrates the TEM micrographs of a composite containing 5 wt.-% layered silicate. The areas occupied by the layered silicates appear as dark strips while the dark dots are caused by the staining agent. Over the areas investigated by the TEM no large particle agglomeration was observed. Based on the TEM images, one can realize that the processing route used in the work mainly leads to a distribution of layered silicate filler into a bundle of several nanolayers (dark strips). It can be seen that there are several locations where the individual exfoliated layers (dark lines) are also present. In the bundles, the spacing between the layers is even much larger than the thickness of individual layers. This is an indication of

the incorporation of polymer chains into the gap between the inorganic layers (so called intercalation process).

This experiment was extended to other composites including those containing low molar mass polystyrene homopolymer (hPS). In the blends with polystyrene, where the thickness of PS lamellae increased due to the solubilization of hPS by the PS block lamellae, a morphology similar to the one presented in Fig. 2 was observed. For the composites containing a higher filler content, the agglomeration tendency increased, as expected, with the amount of filler.

Similar results were recently observed by Ha and Thomas in the composites of organomodified layered silicate [14]. In this case lamellae-forming polystyrene-block-polyisoprene-block-polystyrene (SIS) triblock copolymers developed after preparing samples via solution casting followed by roll-casting. As a result of shearing both the microphase-separated block copolymer nanostructures as well as the silicate nanolayers were aligned along the flow direction.

The composites used in this study, with sizes lying on the nanoscale (the aggregates being maximum up to 1 micrometer), can be described as nanocomposites. Hence, there are good reasons to expect an improvement in mechanical properties of the SBS/layered silicates nanocomposites according to the concept: 'small particles producing big effects'.

Figure 2.

3.2 Mechanical performance of nanocomposites

Tensile stress-strain curves of the composites having different amount of nanofiller are shown in Fig. 3. The SBS block copolymer used is a ductile polymer, as can be seen from the stress-strain curve. The addition of filler causes a slight increase to the yield stress of the composites. Moreover, there is a trend for the stress to increase with filler content, at a given strain, in the stress-strain curves. For a filler content of 5 wt.-%, the curve runs nearly identical with that of the pure block copolymer. The small decrease in strain at break lies

within the experimental error, i.e. the filler does not induce a decrease in the ductility of the polymer (in contrast to many other nanocomposites discussed in the literature). However, it is noteworthy the significant increase observed in the Young's modulus (see below).

For a filler content of 10 wt.-%, the reduction in strain at break is still not so high. At higher filler content, with increasing tendency of agglomeration, the ductility of the composites decreases. In such cases, the decrease in ductility is much lower than that reported in the literature for other polymer systems, too.

Figure 3.

Additional information on the stiffness and plastic deformation behaviour of polymeric materials can be obtained with the aid of microindentation hardness measurements [13]. The microhardness values can be correlated with the Young's modulus (elastic property) as well as with the yield stress (plastic deformation) of the materials [15].

The increasing yield stress of the composites with addition of nanofiller (see Fig. 3) can be justified by plotting indentation microhardness (H) of the composites as a function of filler content presented (see Fig. 4). The increase in hardness with increasing filler content can be correlated with the increasing stiffness (Young's modulus) and strength (yield stress) as observed in other polymer materials [15].

The bentonite mineral from which nanolayered silicate is produced is a hard material (H values higher than 1000 MPa). The H values of the investigated composites are much smaller than those predicted by the additivity of two components. This observation suggests that the elasto-plastic deformation behavior of the composites below the indenter is mainly controlled by the deformation of the matrix in the composition range studied. The low hardness values of the composites may be envisioned as being caused by the predominantly elastic behavior of the matrix SBS; i.e. the layered silicate platelets as well as their aggregates finely dispersed in the polymer matrix do not offer much mechanical resistance during the indentation process.

These observations are consistent with our earlier micromechanical results on polymer composites comprising hard filler dispersed in rubbery matrix [16, 17].

Figure 4.

Figure 5.

The modulus of elasticity is one of the important mechanical properties which characterizes the stiffness of the materials. The goal of most of the nanofiller reinforced plastics has been to enhance this property without deteriorating the other physical properties. It should be noted that due to natural yellowish color of Bentonite mineral the composites containing layered silicates have a faint yellow color. In the present study the composites with higher amount of filler also lost the usual high transparency of the SBS block copolymer. At lower filler concentration (e.g. 5 wt.-%) the yellowish color almost disappears; and the composite film becomes nearly as transparent as the pure block copolymer.

Fig. 5 shows the plot of storage modulus (E') determined by DMTA as a function of temperature, for the pure block copolymer and a composite containing 10 wt.-% layered silicate. Owing to the two-phase microphase-separated morphology the SBS block copolymer exhibits two glass temperature values (T_g) corresponding to two different homopolymer chains comprising the copolymer [18]. As a result, there are two temperature ranges in which the Young's modulus shows drastic changes: near $-100\text{ }^\circ\text{C}$ (close to polybutadiene T_g) and near $+100\text{ }^\circ\text{C}$ (close to polystyrene T_g). Because the sample was too soft and thin (approximately 0.4 mm) the Young's modulus could not be measured accurately at higher temperatures ($> 90\text{ }^\circ\text{C}$). However, the values of E' at the so called 'plateau region' are of importance, as this region corresponds to the temperature range in which the SBS block copolymers find applications. In the 'plateau region' the value of Young's modulus for the SBS/layered silicate composite is significantly higher than that of the pure SBS block copolymer

even at a low filler content (see Fig. 5). This result confirms that the exfoliation and fine dispersion of layered silicates particles comprising high aspect ratio nanoplatelets, which significantly contributes to the increase of the elastic modulus of the composites.

For the sake of comparison Fig. 5 also includes a SBS/20% PS015 blend (PS molecular weight of about 15k, here named as hPS). As the molecular weight of the added hPS is lower than that of the PS outer blocks of the block copolymer, the added hPS causes a swelling of the PS lamellae which makes the materials stiffer as compared to the pure block copolymer, a similar effect as with the layered silicate. This effect can also be seen at higher temperature when the pure block copolymer and the composite with layered silicate become soft, while the blend with PS015 is still mechanically stable. However, in the plateau region (service temperature range) the contribution to the storage modulus (E') is very low.

4. CONCLUSIONS

1. In this work, nanocomposites of a lamellar SBS triblock copolymer and organo-modified layered silicates were prepared by means of a two-step processing (solution blending followed by melt shearing procedure).
2. The two-step procedure used in the composite preparation was found to be very effective to ensure the fine distribution and exfoliation of the nanofiller. The solution blending presumably enhances the introduction of solvent as well as the polymer molecules into the gallery spaces (intercalation) thereby making the platelets separation easier during the melt shearing process.
3. The layered silicate filler was finely dispersed in the polymer matrix; many of the particles were exfoliated leading to the formation of individual layered silicate platelets. With increasing filler content, the tendency of larger aggregate formation increases. The optimum mechanical properties were reached for 5 wt.-% layered

silicates. A significant increase in Young's modulus without a cost of ductility was obtained.

4. The microhardness (H) of the composites increases with the filler content. The H values were, however, much lower than those expected from a two-component additivity law. The results suggest that the plastic deformation process is mainly controlled by the matrix even at high filler content (up to 30 wt.-% studied).
5. The present study further concentrates on the analysis of the effect of small amounts of filler (<5 wt.-%) with parallel optimization of the filler intercalation. The next strategy will involve the study of the effect of various organophilic modifications on the dispersion and physical properties of the composites. In future, these studies will be further extended to other amorphous systems, semicrystalline polymers and rubber toughened thermoplastics.

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FIGURE CAPTIONS

Figure 1. Lower (top) and higher (bottom) magnification SEM micrographs of fracture surfaces of SBS containing 30 wt.-% layered silicate; the SEM was operated in BSE mode.

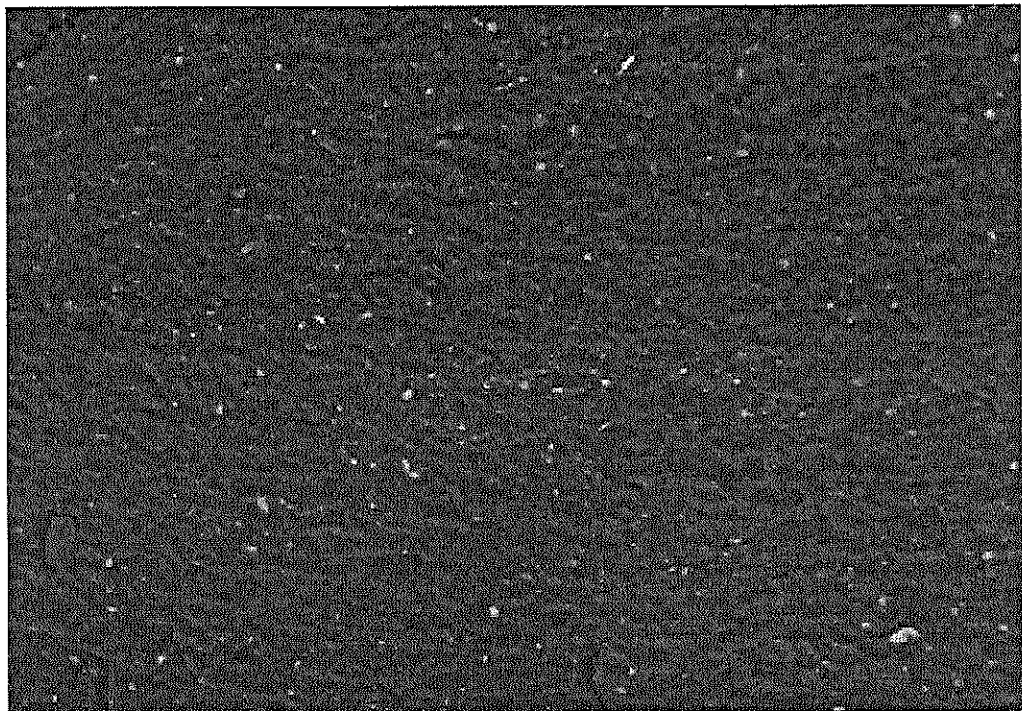
Figure 2. Lower (top) and higher (bottom) magnification TEM micrographs of a composite containing 5 wt.-% layered silicate.

Figure 3. Tensile stress-strain curves of SBS/layered silicate composites with various filler contents; tensile testing at 23°C at a cross-head speed of 50 mm/min.

Figure 4. Plot of Microhardness (H) against filler weight fraction for the investigated composites.

Figure 5. Storage Young's modulus of SBS/10% layered silicate composite as compared with that of a pure SBS block copolymer and SBS/20 wt.-% PS015 blend.

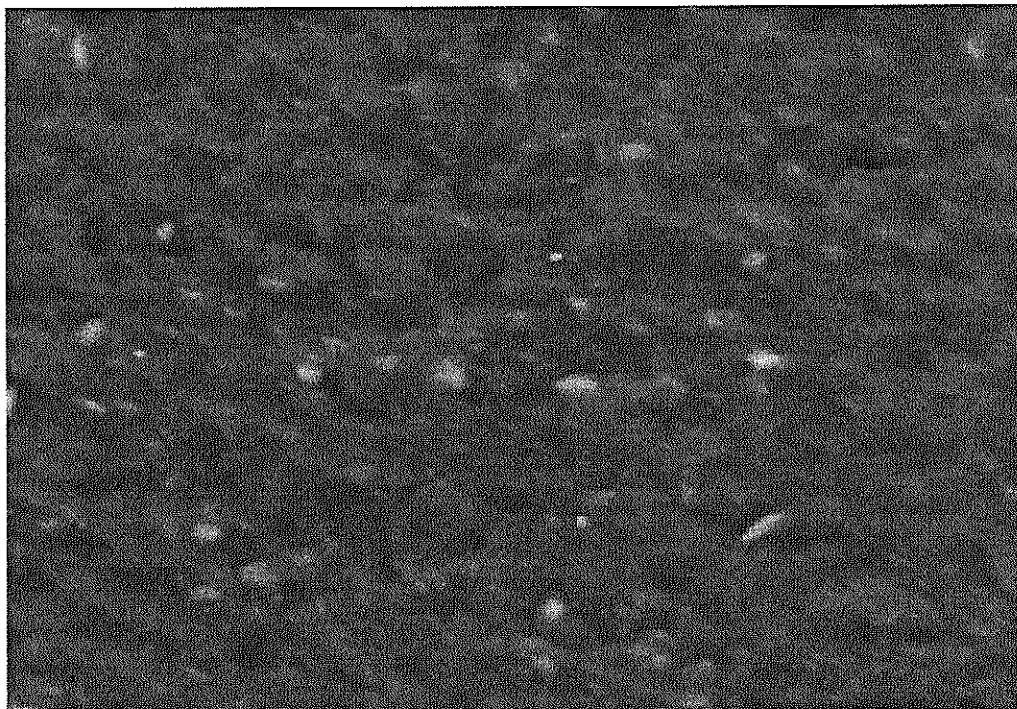
Figure 1



00011188

— 30 μm

JEOL



00011189

— 5 μm

JEOL

Figure 2

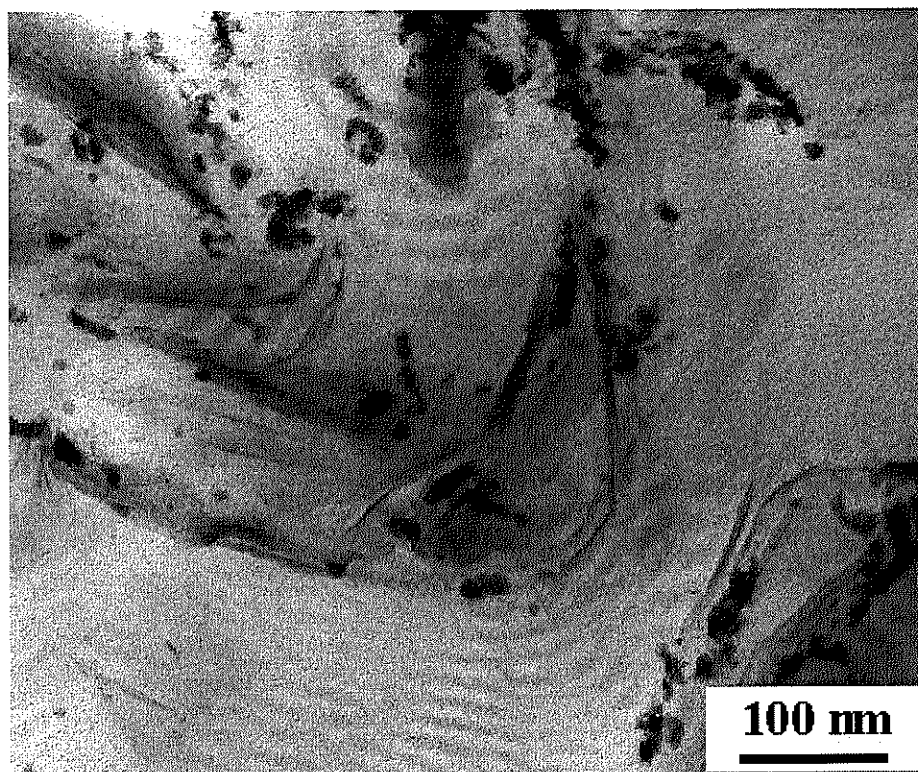
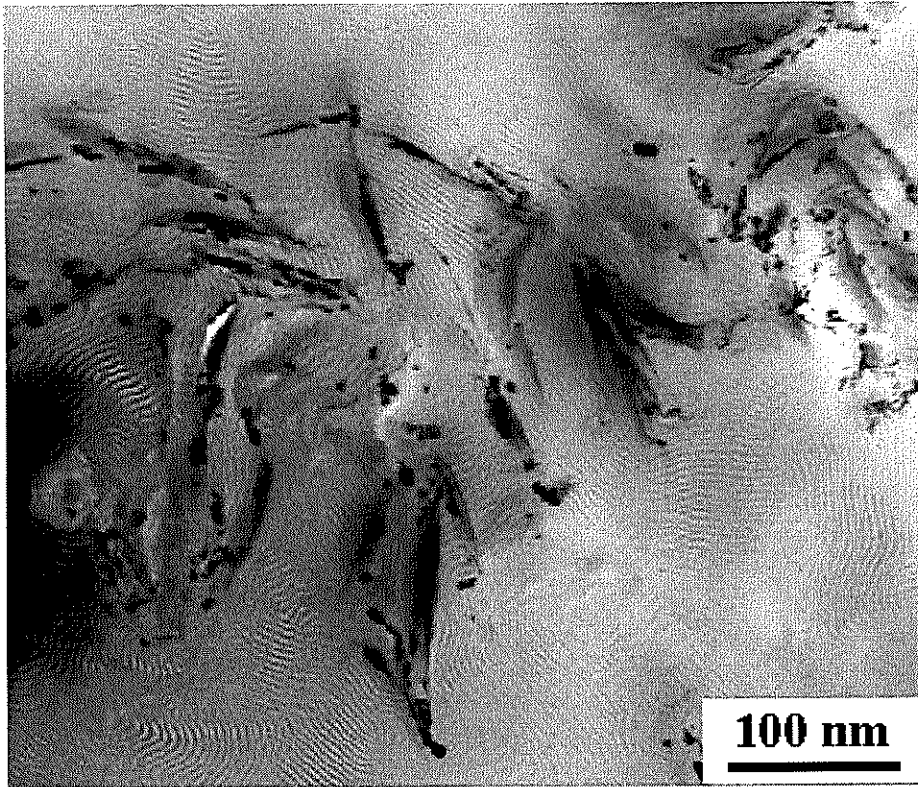


Figure 3

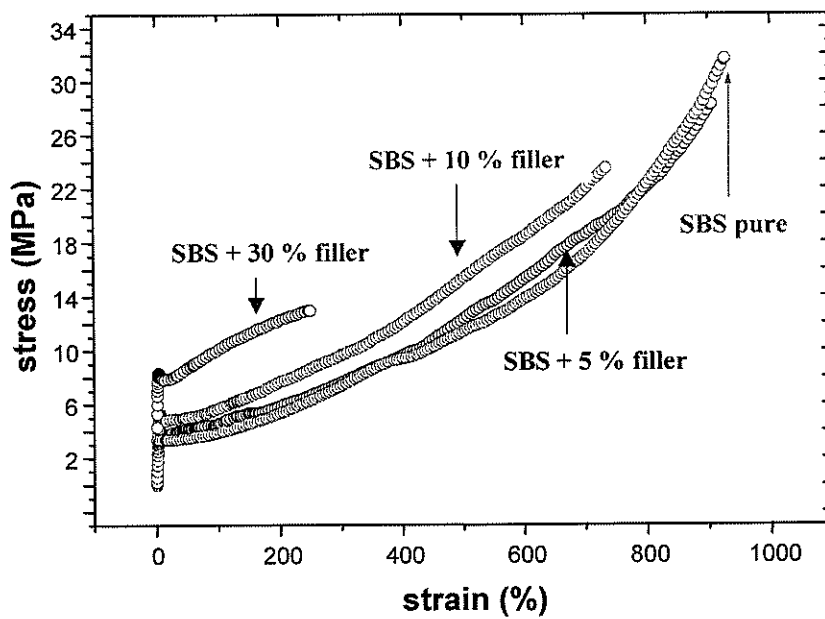


Figure 4

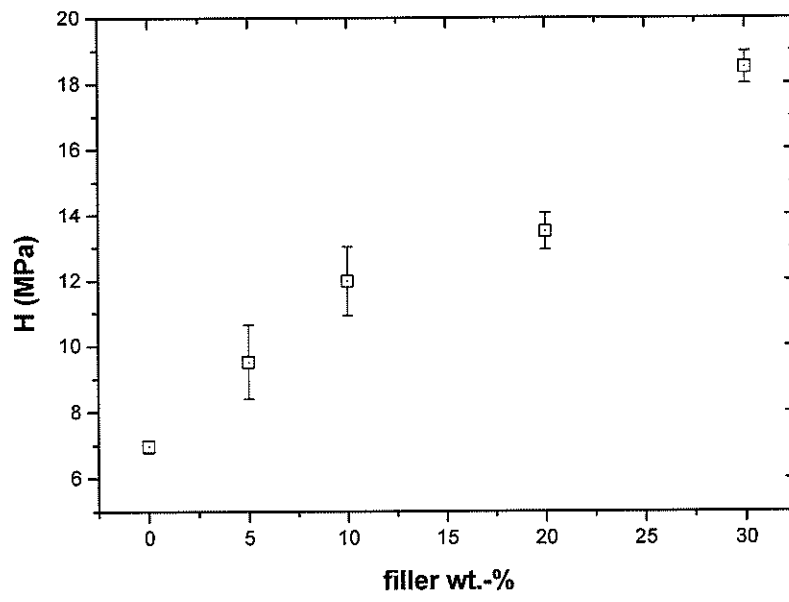


Figure 5

