Microindentation Hardness of Nanostructured Thermoplastic Materials

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Summary: The micromechanical behaviour of various thermoplastics based nanocomposites was investigated with the aid of the microindentation technique. The materials studied were microphase separated styrene-butadiene block copolymer systems and several thermoplastics reinforced with nano-sized fillers having variable dimensionality. It was found that the microhardness behaviour of the nanocomposites studied was strongly influenced by the dimensionalities of the filler. Due to large surface to volume-ratio one- and two-dimensional fillers exhibit a far better reinforcing behaviour than the three dimensional ones. In case of nanostructured block copolymers, the microhardness is not determined by the total polystyrene (PS)/polybutadiene (PB) composition alone but diminishes gradually in presence of freely standing dangling polybutadiene chains even if the morphology of the systems remains unaltered.

Keywords: Nanocomposites, block copolymers, nanofiller, microphase separation

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Introduction

Polymeric nanocomposites have been the object of intensive scientific and technological interest due to their promising mechanical, optical, barrier and various other functional properties.^[1-6] Within this context, nanomaterials of various kinds (viz. those based on inorganic filler, organic/inorganic hybrid filler, and even multi-component polymer/polymer composites) have been studied intensively in recent years [references !].

A great deal of research efforts have been made in order to understand the structure-properties correlation in those materials and to exploit their properties to full extent. It has been found that there are some specific aspects related to the interface and interphase formation in those materials which contribute to their smart property profile. Different scattering and microscopic techniques have been used to characterize those aspects in the nanocomposites.^[7-10] (Please add reference 10a)

As mentioned above, there is a large number of research articles devoted to mechanical, electrical and functional properties of nanocomposite materials. It has been demonstrated that the excellent mechanical performance of these materials relies mainly on the extremely large surface area of the filler at hand. The introduction of small amount of nanofiller into the polymer matrix can cause a large improvement in the micromechanical properties [20]. Thus, one has the opportunity of developing strong materials with low density (Recall that the density of the filler is quite high, but the amount is too small; thus the change in density of whole polymer is rather negligible). Of course, in addition to improved mechanical properties, the nanocomposites are endowed with other advantages such as low permeability to gases and moisture, low flammability, high thermal stability and high chemical resistance (Please, add references).

Recent studies have demonstrated that microindentation techniques provide very direct and reliable information on the structure and properties of nanostructured materials, including semi-crystalline polymers^[11,12], block copolymers^[13-17] and inorganic particles filled nanocomposites.^[18-21]

The aim of this study is two-fold:

- 1) To analyse the correlation between the microhardness behaviour and nanostructured morphology with special reference to the effect of molecular coupling
- 2) To examine the influence of filler dimensionality on the properties of thermoplastics based nanocomposites.

Experimental

Materials

The materials used in this study were obtained through collaboration with different research groups including:

- a). Styrene/butadiene block copolymer systems. The samples are polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) block copolymers having linear and star shaped architectures. The samples were kindly provided by Kraton Polymers, Houston, TX. The blends of those polymers with polystyrene-*block*-polybutadiene (SB) diblocks and boehmite nanofiller (three-dimensional, 3D filler) will be studied. The Boehmite naofiller was supplied by Sasol Chemical Company, Hamburg.
- b). Polymethyl-methacrylate (PMMA)/Silica nanocomposites (3D filler), kindly supplied by Röhm, Darmstadt.
- c). Nylon 6/Layered silicate nanocomposites (2D filler). The injection moulded samples were kindly provided by Pro. Sung Chul Kim, KAIST, Korea.
- d). The isotactic polypropylene (PP)/multiwall carbon nanotubes (MWCNT) nanocomposites prepared by the so-called *in situ* polymerization was provided by Dr. Andreas Funck, University of Hamburg (Harburg).

The characteristic properties of the samples used in this study will be mentioned below when discussing the results.

Techniques

Microhardness measurements were carried out using a Leitz microhardness tester. A Vickers square-based diamond indenter having an opening angle of 136° was employed. To minimise the creep of the sample under the indenter, indentation periods of 6 seconds were used. The details about the procedure for the microhardness measurements may be found elsewhere.^[11] The microhardness is based on the measurement of the residual impression made by a sharp indenter upon the application of a given load with the aid of integrated optical microscope. The hardness value is defined as^[11]:

$$H = k \frac{P}{d^2} \quad (1)$$

where P is the applied load in N, d the diagonal of the impression in m, and k the geometric factor equal to 1.854. The H values were derived from an average of at least 10 indentations.

Figure 1: Scheme showing the sample preparation and hardness measurement of the samples using a Leitz microindenter.

Prior to the indentation measurements, the samples (having thickness 0.5 mm – 1 mm) were cut in appropriate size (about 1 cm x 1 cm) and glued onto the glass slide. The indentation experiments were carried out at room temperature (25° C), see Fig. 1

Transmission Electron Microscopy (TEM, Leo 912 operating at acceleration voltage of 120 kV)) was used to visualize the structural details of the composites. Ultra-thin sections (ca. 80 nm thick) were ultramicrotomed from a piece of bulk specimen using a diamond knife at room temperature. Prior to the TEM studies, the ultra-thin sections of some of the samples were treated with osmium tetroxide (OsO_4) vapour for several hours at cryogenic temperature in order to selectively stain one of the phases present in the polymer compound.

Results and Discussion

Morphology-Microhardness Correlation in Block Copolymer Systems

It is well known that the block copolymers comprising two or more incompatible polymer chains undergo the so called microphase separation upon cooling slowly from the melt or by allowing the solvent to evaporate from their solutions.^[22-25] Examples of practical significance are represented by block copolymers comprising polystyrene (PS) and polydienes (such as polybutadiene, PB and polyisoprene, PI). Owing to the wide separation between the glass transition temperatures of the constituent polymers and the presence of glassy (hard) domains in combination with adjacent soft rubbery phase, such polymers, under the condition of well organized microphase separated morphology, may be regarded as well as nanocomposite materials. Fig. 2 illustrates the TEM micrograph of a SBS triblock copolymer (named as SBS- I in this work) in which the lamellar nanostructure becomes clearly visible. It should be noted that the polystyrene (bright layers in Fig.2) and polybutadiene (dark appearing layers) are arranged in an ordered array whose

periodicity is approximately 30 nm. The apparent local alignment of the lamellae is simply accidental as the sample in the bulk state reveals a polygranular morphology. The orientation of the lamellae is one order below that of the size of indenter, and hence does not lead to anisotropic microhardness behaviour.

The blends of SBS-S48 with polystyrene-*block*-polybutadiene (SB diblock copolymer; weight average molar mass 49 kDa) were prepared via solution casting using toluene as solvent and subsequent vacuum drying and annealing. As the molar mass of the diblock copolymer is approximately the half of the triblock copolymer, the styrene/butadiene composition remains unaltered in the blends irrespective of the amount of the diblock copolymer contained in the blends.

Since the ratio of the molar mass of the corresponding blocks of the block copolymers at hand is approximately the unity, considering the miscibility criteria for the block copolymer blends developed in different diblock mixtures ^[25], the blends studied in this work should develop a uniform morphology (i.e., the lamellar structure without an appreciable change in the long period). Hence, it can be expected that the microhardness of the binary block copolymer systems should not change irrespective of the triblock/triblock weight fractions.

Fig. 3a shows the microhardness variation of the investigated blends as a function of the SB diblock content. The pure triblock copolymer shows a microhardness of about 10 MPa. With the addition of the SB diblock copolymer having a nearly identical chemical composition as the triblock copolymer, a clear the trend of decreasing hardness with increasing the diblock content is found, contrasting the expectation. This observation does not follow the hardness additivity law ^[11].

Figure 2: TEM micrograph of SBS-I having polystyrene weight fraction of 0.48, weight average molar mass of 98 kDa; the polybutadiene phase appears dark due to staining by osmium tetroxide.

Fig. 3b shows the H versus SB diblock content plots for the mixtures of radial block copolymer/diblock mixtures. The radial block copolymer (named as SBS-II) used in this study is a symmetric star copolymer having four arms. This copolymer approximately has nearly identical chemical composition as the triblock copolymer and exhibits lamellar nanostructures as expected. Also in blends with the diblock copolymers (as in the case with SBS-I/SB mixtures) no alteration in the basic lamellar morphology is anticipated.

A closer look at Fig. 3 reveals that the micromechanical properties of the block copolymers are less affected by the presence of the diblock molecules up to 20 wt.-% of diblock copolymer. A significant change in the mechanical properties occurs when the diblock content is ≥ 30 wt.-%. In the case of sensitivity towards the presence of diblock copolymers, both triblock and star architectures exhibit the same trend in the microhardness variation.

Figure 3: Microhardness of the binary block copolymer blends as a function of SB diblock content; the broken line is meant for guiding the eye only; a) SBS-I/SB blends and b) . SBS-II/SB blends

Effect of Nanofiller Dimensionality on Microhardness Behaviour

After the microhardness analysis on styrenic block copolymers possessing lamellar morphology, we extend this study to systems embedding inorganic fillers. The objective is to vary systematically the size and shape of the filler from three dimensional (3D) through two dimensional (2D) to the one dimensional (1D) ones.

Fig. 4 depicts the morphology of a nanocomposite of a lamella forming SBS triblock copolymer (named as SBS-III in this work) with boehmite nanofiller. This system has been studied in detail with respect to its morphology, and tensile mechanical properties. ^[26] The dark, more or less spherical shaped inorganic particles are embedded in the organic polymer matrix. The average diameter of the filler is approximately 100 nm. It was found that the tendency to form larger particles is quite high for highly concentrated solution and quite low for low concentration solution. ^[26]

Figure 4: TEM micrographs of SBS-III and 40 wt-% boehmite; the thin sections were stained with osmium tetroxide.

The matrix polymer used is different from that presented in Fig. 2, the total polystyrene content being much higher in the present case. Thus a higher microhardness value is expected. Our previous studies demonstrated that the organophilic modified Boehmite nanoparticles are quite compatible with polystyrene and styrenic copolymer.^[26] In those systems, one could obtain an exceptionally high dispersion of the filler in the polymer matrix.

Fig. 5 shows the microhardness of this system as a function of nanofiller content. With addition of the nanofiller, the hardness of the composite materials increases almost linearly. As expected the H-value for SBS-II is higher (approximately 20 MPa) than that for SBS-I and SBS-II (approximately 10 MPa), which is related to the larger polystyrene content of the polymer SBS-III. For instance, the hardness of the composite doubles when the filler content approaches about 20 wt.-%.

Let us next examine the H-behaviour of an entirely different system containing 3D filler, namely polymethyl-methacrylate (PMMA)/silica nanocomposites. As in the previous case the samples for the microhardness measurements were prepared by solution casting procedures. The detailed characterization of the morphology-toughness relationship of these nanocomposites has been addressed in recent papers by Lach et al.^[27-29] It is demonstrated that the materials comprising exclusively of the interphase materials would be formed in those nanocomposites at higher silica nanofiller content beyond the percolation threshold with optimum dispersion of the nanofiller.^[27]

Figure 5: Microhardness of the SBS-II/Boehmite nanocomposites; a 3D filler system.

Fig. 6 shows the H versus silica nanofiller content plot of PMMA/silica nanocomposites. A representative TEM micrograph of a composite comprising 20 wt.-% filler is given in the insert. The quantification of the respective TEM micrograph makes it clear that the average diameter of the particle in this particular nanocomposite is approximately 25 nm. As in the previous case of 3D filler system (i.e. SBS/boehmite nanocomposites, see Fig. 5), the H-value of the composites increases almost linearly with the filler content. In this case the hardness increase of the polymer due to incorporation of the nanofiller is still less than that in the previous case. For instance, the H value of the composite comprising 20 wt.-% silica filler is approximately 1.4 times the H value for pure PMMA. It again suggests that the 3D filler only offers a limited extent of mechanical reinforcement.

By further reducing the dimensionality of the nanofiller (i.e. using 2D and 1D) and incorporating them after appropriate surface treatment into the polymer, the reinforcing effect may significantly differ as the 1D and 2D filler bear much larger surface area owing to their large aspect ratios. Fig. 7 collects the plots of H-values versus filler content measured in these systems having a high aspect ratio of filler.

Figure 6: Microhardness of the binary PMMA/silica nanocomposites; a 3D filler system; representative TEM image of composite containing 20 wt.% silica is given in the insert.

Fig. 7a illustrates the dependence of microhardness with filler content in the nanocomposites of polyamide 6 (PA6) with organo-modified layered silicate.^[28] The specimens for the microhardness measurement were taken from the middle of the injection moulded tensile bar (according to ISO 527). The measurements revealed that the mould had different hardness-values along and perpendicular to the injection direction, see Fig. 7a. The higher value of hardness along the injection direction can be correlated with the orientation of lamellar crystals due to action of shear forces towards the surface of the bar during the process of injection moulding. Fig. 7a also illustrates that the H-values show a large scattering, indicative of some non uniformity of the sample morphology towards the surface of the injection moulded bar. It is noteworthy that the value of microhardness shows a steep increase up to about 2.5 wt.-% filler after which the H values shows only the nominal increments. At this composition, the hardness of the sample increases from approximately 75 MPa to 120 MPa. This result implies that the optimum filler reinforcement in the nanocomposites with 2D filler is obtained for the filler loading equal to or less than 5 wt.-%.

In a recent study by Monami et al [ref. 31], it is found that the Nylon/clay nanocomposites do not show significant alteration in mechanical parameters such as yield strength, Young's modulus and hardness properties.^[29] The results were interpreted as a result of decreasing crystallinity of the sample caused by the incorporation of the filler. The

expected hardness decrease with decreasing crystallinity will compensate for the hardness increase due to the filler penetration. However, in our case, the crystallinity of the samples was not much affected by the nanofiller. Hence, the increase in hardness can be regarded mainly as a consequence of the reinforcement effect of the filler.

Figure 7: Microhardness of a) PA6/layered silicate (2D system) and b) iPP/MWCNT (1D system) as a function of filler content.

This suggestion is also supported by the microhardness indentation tests on isotactic polypropylene reinforced with multiwall carbon nanotubes (MWCNT), see Fig. 7b. The samples were prepared by oxidation of the carbon nanotubes followed by subsequent functionalization and *in situ* polymerisation of propylene.^[32,33] The study of the microhardness of the nanocomposites showed a similar steep increase in H up to about 2

wt.-% of MWCNTs after which the H values show large scattering at higher filler content. This is again an indication of the non-uniform distribution of the filler in the polymer matrix. This set of samples was also investigated using the depth sensitive measurement of hardness in the materials. ^[34] The H values were found to vary from place to place close to the surface and also from the surface towards the centre of the sample film indicating the inhomogeneous distribution of the filler into the polymer matrix.

Concluding Remarks

In this work we have utilized the microindentation technique to study the surface micromechanical properties (i.e. microhardness) of two sets of nanostructured polymeric materials: microphase-separated polystyrene/polybutadiene based block copolymer systems and inorganic nanofiller reinforced thermoplastics. The obtained results show that the microhardness behaviour of the microphase separated systems is primarily controlled by their morphology with an apparent effect of hardness reduction in the presence of freely hanging dangling chains in the microphases of the block copolymer. The 3D filler reinforced thermoplastics exhibit a linear hardness increase with filler weight fraction, although the increase in hardness was not too high. In contrast, the hardness values of 2D and 1D filler reinforced thermoplastics revealed a much steeper hardness increase up to about 2.5 wt-% filler beyond which the reinforcement effect was insignificant. It can be concluded that 2D and 1D fillers act as much stronger reinforcing agents owing to their extremely large surface area, increasing the interaction with the surrounding matrix. However, it should be kept in mind that the mechanical properties of the composites may become worse if the bonding between the matrix and filler is absent or too weak.

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