

Effect of surfactant treated Boehmite nanoparticles on properties of block copolymers

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Abstract. Effectiveness of a reinforcement of a polymer is known to depend on the strength of the interfaces between that reinforcement and the matrix. We have used as matrices polystyrene and a styrene/butadiene/styrene (SBS) copolymer and as the reinforcement the ceramic Boehmite γ -AlO(OH). We have applied Boehmite both untreated as well as treated with sulfonic acid based surfactants with different alkyl groups. As expected, the coupling agents improve the adhesion between the polymers and the ceramic filler. The presence of Boehmite as well as the treatments affect the glass transition temperatures determined by dynamic mechanical analysis, nanoindentation hardness $h_{\text{nanoindent}}$ as well as Vickers microhardness h_{Vickers} . For SBS and SBS-containing composites the ratio $h_{\text{nanoindent}}/h_{\text{Vickers}}$ is a constant.

Keywords: polymer reinforcement, Boehmite, surface modification, polystyrene, styrene/butadiene/styrene, Vickers hardness, nanoindentation hardness

1. INTRODUCTION

There is a large variety of polymer-based materials (PBMs). Some of them are created for improvement of electrical, tribological or acoustic properties but the majority is developed to achieve better mechanical properties [1 - 3]. Among classes of PBMs we have block copolymers in which the constituents are microphase separated into ordered nanostructures [4]. This allows a fairly wide range of properties that can be varied.

A composite material is made out of two or more parts, each of which gives certain properties. Wood is a natural composite, which has fibers that provide strength and is held together by a matrix [5]. Aerospace industry uses many composites in airplanes such as the American F-22 where carbon fibers are embedded in a epoxy matrix [6].

Most composites currently made are macrocomposites or microcomposites. In fiber-reinforced ones, the fibers have strong effects on certain properties but less effect on some other properties. For example, if we measure the glass transition temperature T_g of an epoxy with and without fibers in it, that transition temperature of the epoxy resin does not change [7].

Recently people have begun making nanocomposites containing particles with diameters measured in nm [8]. Such materials can also be used for instance in food packaging since they produce a good barrier to gases - what allows longer storage times. Other avenues of research in nanocomposites are electrical and thermal conductivities and body armor for soldiers and police. In our work, we investigated how a series of modified nano-particles affects certain properties of thermoplastics.

The T_g is known to be an indicator for changes in material properties [9 - 11]. It actually represents a region in which the transition takes place; for convenience a single number is used. We decided to track T_g values of a series of materials made with nano-particles of Boehmite, an aluminium oxide hydroxide (γ -AlO(OH)) mineral. These nanoparticles were used both untreated as well as treated with sulfonic acid based surfactants with different alkyl groups. As matrices we have used polystyrene/polybutadiene/polystyrene

(SBS) triblock copolymers. They behave as cross-linked elastomers at ambient conditions, are procesable at elevated temperatures, while their properties can be tuned by changing the composition of the constituents and their molecular architectures [12]. For comparison we have investigated also the corresponding nanocomposites of polystyrene (PS) homopolymer.

The best way to measure the T_g is by dynamic mechanical analysis (DMA) due to high sensitivity of this technique [9 - 11]. We have also performed microindentation meaasurements as representative for tribology of the material as well as determined Vickers hardness.

2. EXPERIMENTAL

2.1 Materials

Polystyrene sample is a commercial product of BASF SE, Ludwigshafen, Germany, under the trade name of PS 158k and has a number average molecular weight of $8.20 \cdot 10^4$ g/mol and the polydispersity index $M_w/M_n = 2.30$, where M_w is the weight-average molecular mass while M_n is the number-average molecular mass. The SBS copolymer, to be called below ST3, is a star block copolymer also supplied by BASF SE. It contains 74 wt. % polystyrene and 26 wt. % polybutadiene and has $M_n = 8.57 \cdot 10^4$ g/mol whereby the polydispersity index is 2.10. The sample was synthesized by butyl lithium initiated anionic polymerization; more details of the synthesis have been provided in [12].

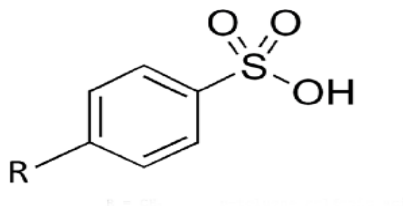
The Boehmite nanofillers were supplied by Sasol Chemical Company. A characteristics of the fillers used is presented in Table 1.

Table 1. Characteristics of the nanofillers use in this study

Properties/Filler	Disperal OS1	Disperal OS2	Disperal HP 14
Surface treatment	p-toluenesulfonic acid	alkylbenzenesulfonic acid	undecanoic acid
Average crystal size	10 nm	10 nm	-

Particles shape	spherical	spherical	needlelike
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The general chemical structure of the surfactants used can be represented as:



where R is either the $-\text{CH}_3$ group or a mixture of C_{10} to C_{13} straight chain alkyl groups for the sulfonic acids. Undecanoic acid is a simple straight chained carboxylic acid.

The components were mixed in a Brabender mixer for 5 minutes and compression molded at the pressure of 120 bar at 200°C for 5 minutes. This part of work was done in Halle. Following is the list of materials made:

Table 2. Compositions of materials

Base polymer	Filler type and wt. content
ST3	-
ST3	5 wt. % OS1
ST3	5 wt. % OS2
ST3	5 wt. % HP14
PS	-
ST3/PS (80/20)	-
ST3/PS (80/20)	5 wt. % OS1
ST3 + PS (80/20 by weight)	5 wt. % OS2
ST3 + PS (80/20 by weight)	5 wt. % HP14

We prepared specimens for testing at North Texas from the samples made in Halle. Samples were cut into multiple strips and then measured with a micrometer to two decimal places in length, width, and thickness.

2.2 Electron microscopy analysis of the samples

The block copolymer and some of the blends and nanocomposites were investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). For the TEM analyses, the specimens were prepared by ultramicrotomy of each sample following by staining with osmium tetroxide vapor so that the double bond containing butadiene phase appears darker in the TEM micrographs. The ultrathin sections were investigated by 120 kV LEO 912 TEM. For the SEM analyses of the samples, each sample was cryo-fractured using liquid nitrogen and the fracture surface was coated with a thin film of carbon. The specimens were investigated by means of JEOL-JSM 6300 SEM in back scattered electron (BSE) imaging mode.

2.3 Dynamic mechanical analysis (DMA)

We loaded the samples into a PerkinElmer DMA 8000™ machine with the single cantilever fixture. The technique has been described by one of us [9 - 11]. We studied the materials over temperatures ranging from -125°C to +150°C. The DMA was cooled using liquid nitrogen. The samples were run at three frequencies of 0.1, 1.0, and 10.0 Hz and with 0.050 mm of applied strain. The temperature of transitions was calculated following the procedures of the ASTM discussed by Seyler [13].

2.4 Nanoindentation hardness and Vickers hardness

The indentation is made on the surface, creating a unique load-depth curve for the specific sample. Using the tangential slope of the curve and the indenter tip geometry, the software calculates the indentation hardness. The indents may be visually inspected using an integrated, synchronized optical microscope. A TTX-NHT S/N: 50-00155 from CSM Instruments, Neuchatel, Switzerland, fitted with a diamond Berkovich indenter (B-K59), an approach speed of 5000 nm/min with a delta slope contact of 25 % was used. Data was collected at 10.0 Hz with a linear loading and unloading rate of 100 mN/min to a maximum of 50 mN. A pause of 6 s between cycles was used.

Vickers microhardness h_{Vickers} was determined using a dynamic microhardness measurement device, HMV-M Shimadzu Micro Hardness Tester Model M3 from Shimadzu Co., Kyoto, Japan. Microindentations were made using a 300 g load. The hold-

ing time after completion of the indentation was 5 s. Five indentations were made for each sample. Each mean value of the Vickers microhardness was calculated from five tests using the formula:

$$h_{Vickers} = 1854.4P/d^2 \quad (1)$$

Here P is the load in g while d is the mean diagonal of the indentation in μm . While the resulting value has dimensions, it is customary to list the Vickers microhardness as if it were a dimensionless quantity [14, 15].

3. Electron microscopy results for unindented samples

In Figure 1 we show a typical nanostructured morphology of the block copolymer (ST3) and ST3/PS (80/20) blend. The pure block copolymer shows a bicontinuous network of glassy PS phase and rubbery butadiene-rich phase. The addition of 20 wt. % PS leads to formation of droplets of PS embedded in a soft block copolymer matrix – as reported before by some of us [16].

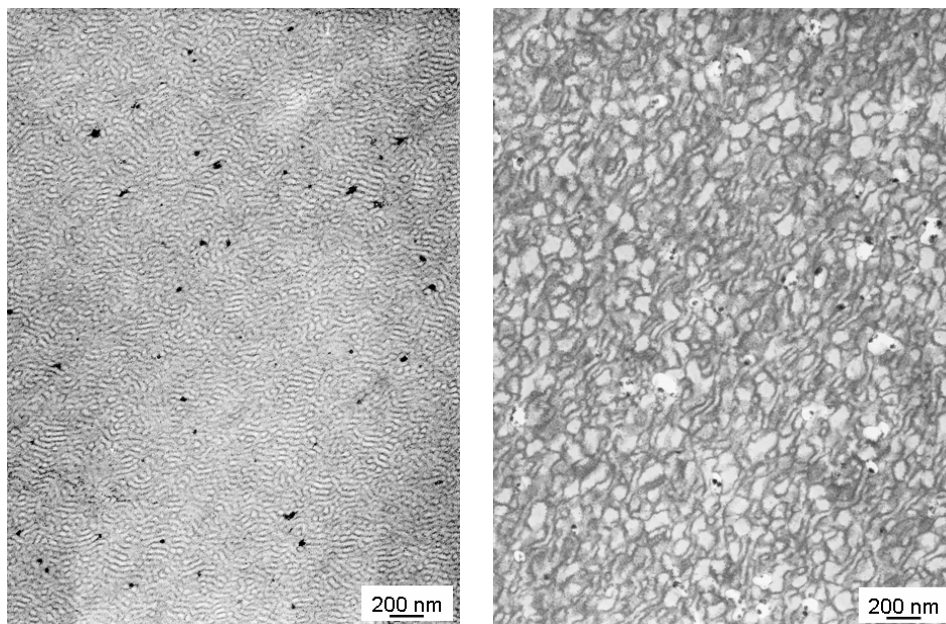


Figure 1. TEM micrographs of the pure star block copolymer (left) and ST3/PS (80/20) blend (right); osmium tetroxide staining renders the butadiene rich phase appear dark in the images.

Nanocomposite materials based on the pure block copolymer (ST3) and those based on ST3 + PS blends show a similar distribution of the filler particles in the polymeric matrix. As an example, Figure 2 shows SEMicrographs of the ST3/PS (80/20) blend comprising 5 wt.% of OS1 nanofiller (Fig. 2a), OS2 (Fig. 2b) and HP14 (Fig. 2c). As mentioned above, we have used the BSE mode. In general, higher atomic numbers of the atoms result in higher efficiency of BSE electrons emission leading to a brighter contrast in the micrographs. Thus, in our case the brighter regions in the micrographs represent the inorganic fillers rather than the low atomic mass elements present in the organic polymer.

An inspection of the SEM images of the samples easily reveals that the blend containing HP13 as a filler contain large filler aggregates whereas the blend comprising O1 exhibits smaller inorganic particles. The blend with OS2 shows no clear appearance of the filler; we infer we are dealing here with uniform distribution of the filler without aggregation.

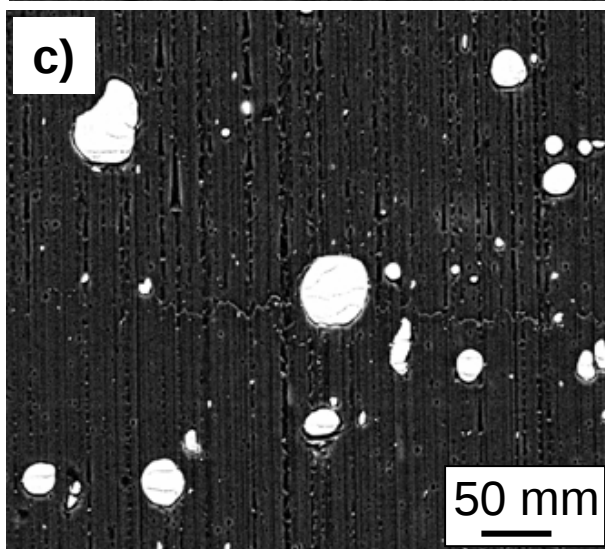
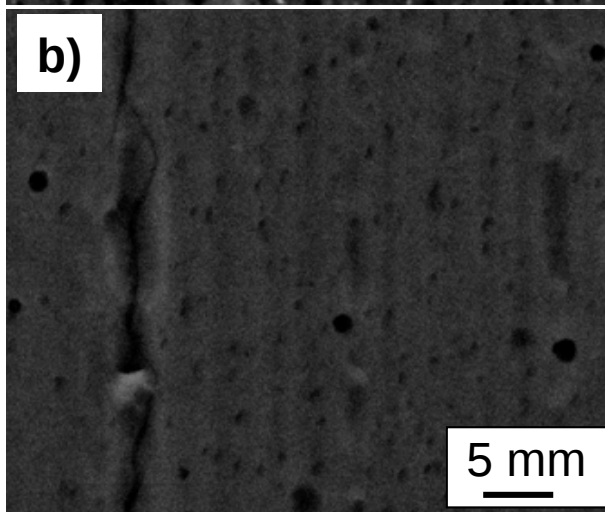
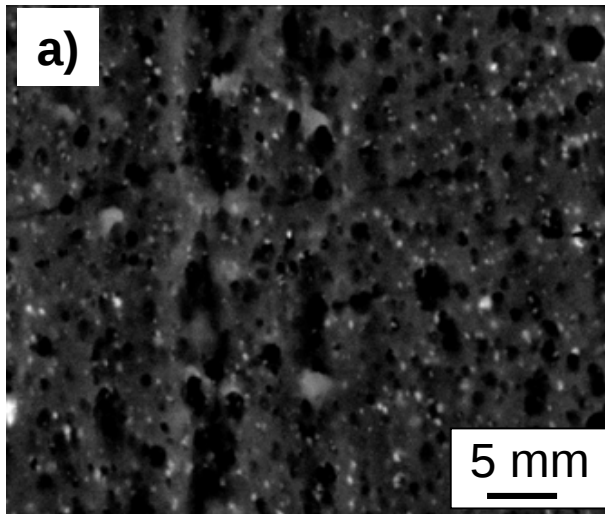


Figure 2. SEM micrographs of composites based on block copolymer/PS blends; a) ST3/PS (80/20) + 20 % OS1, b) ST3/PS (80/20) + 20 % OS2, and c) ST3/PS (80/20) + 20 % HP14

4. Dynamic mechanical analysis results

In DMA experiments a sinusoidal stress σ is applied as a function of time t :

$$\sigma(t) = \sigma_0 \sin(2\pi\nu t) \quad (2)$$

Here ν is the frequency in Hertz. The result of imposition of the sinusoidal load results in the following behavior of the strain ε :

$$\varepsilon(t) = \varepsilon_0 \sin(2\pi\nu t - \delta) \quad (3)$$

If the material is fully elastic, we have $\delta = 0$. In a viscoelastic material there always is a phase lag between stress and strain so that $\delta \neq 0$.

For a given deformation mode (such as the cantilever used by us) we have

$$\sigma/\varepsilon_0 = E^* = E' + iE'' \quad (4)$$

Here E^* is the complex modulus; $i = (-1)^{1/2}$. E' is the storage modulus, a measure of the solid-like (elastic) response of the material. E'' is called the loss modulus and corresponds to the liquid-like (viscous flow) response of the material. Since E'' represents energy dissipation, it is also a measure of the *energy converted to heat*. Namely, the heat H created is given by

$$H = \pi E'' \varepsilon_0^2 \quad (5)$$

The phase lag δ between stress and strain can be connected to the quantities featured in Eq. (4), namely

$$\tan \delta = E''/E' \quad (6)$$

An example of results so obtained is shown in Figure 3.

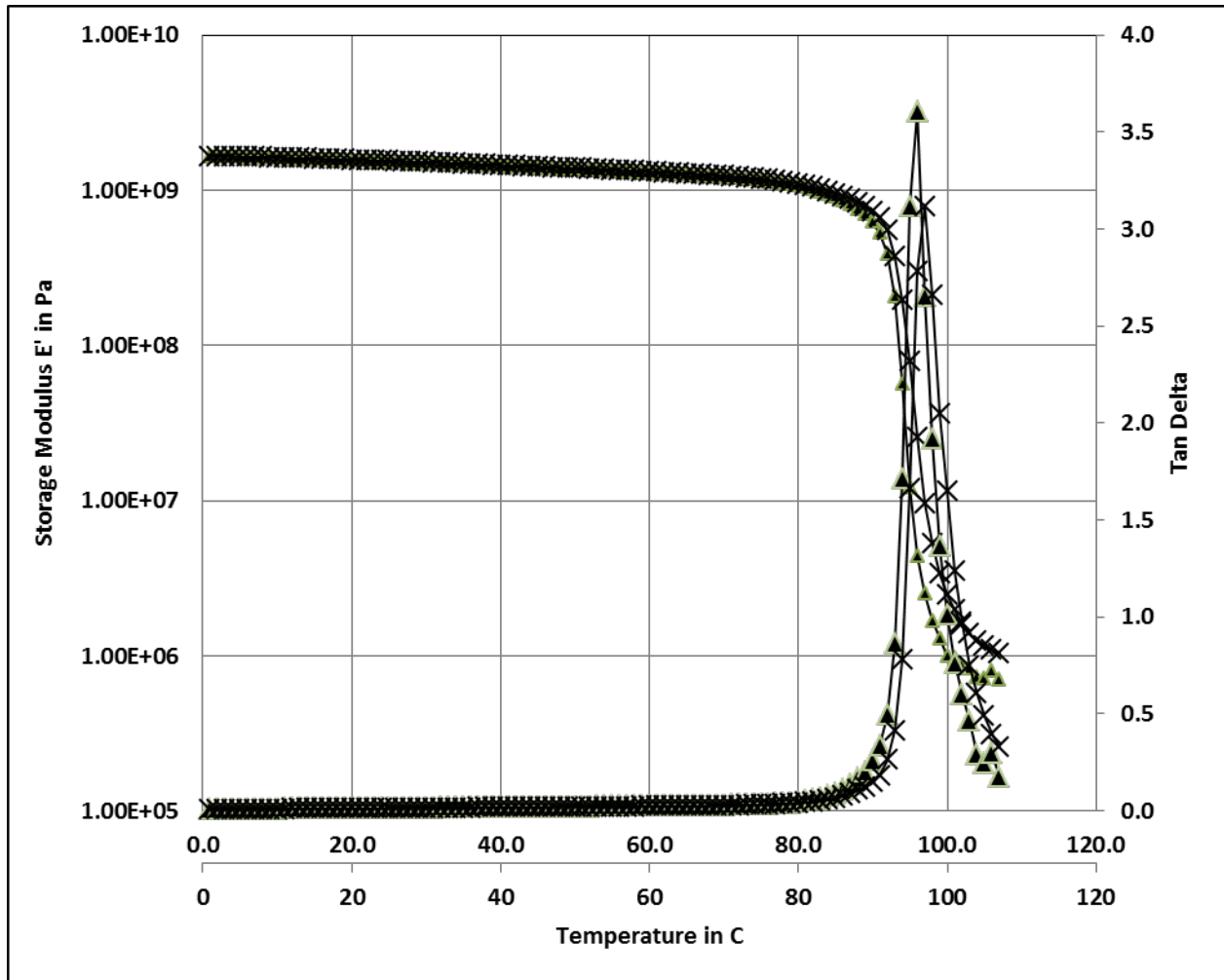


Figure 3. DMA results for polystyrene: only 2 frequencies are shown for clarity: 0.1 Hz (Δ) and 1.0 Hz (X). Note the shift in the major drop in E' and in the peak of tan δ with increased frequency. On the left the curves at the top which then descend at higher temperatures are those for E' ; the curves which on the left are close to the bottom but then at higher temperatures form peaks are for tan δ .

On the basis of the descents of E' and of peaks of tan δ we have obtained T_g values which for the frequency of 1.0 Hz are summarized in Table 3:

Table 3. Glass transition temperatures from DMA results.

Materials	T_g
ST3	106.5

ST3 +5 % OS1		108.0
ST3 +5 % OS2		110.2
ST3 + 5 % HP14		109.1
Pure PS		128.5
ST3 + 20 % PS		111.3
ST3 + 20 % PS + 5 % OS1		114.1
ST3 + 20 % PS + 5 % OS2		111.7
ST3 + 20 % PS + 5 % HP14		111.9

We note that brittleness of materials B is inversely proportional to the value of storage modulus E' at 1.0 Hz [17, 18] and also that PS is much more brittle than most polymers [17].

As seen in Figure 3, at the higher frequency of 1.0 Hz the glass transition shifts to a higher temperature. In general, materials resist deformation. At a lower frequency a material has more time to adapt to a stress wave defined by Eq. (2). At a higher frequency there is less time for adaptation, hence the material shows more resistance to the force applied. Since above T_g there is more adaptability to deformation, at a higher frequency ν we have T_g shifting to a higher value.

Consider results for ST3 reinforced in turn with OS1, OS2 and HP14. Addition of 5 wt. % OS1 increases the T_g by 1.5°C. Addition of the same concentration of OS2 increases the T_g by 3.7°C, more than a double effect. Addition of HP14 produces a shift by 2.6°C. We recall the order of uniformity of the filler distribution in the matrix found by SEM: the best for OS2, intermediate for HP14, the worst for OS1. Thus, more uniform filler distribution results in more 'cooperation' of the filler with the matrix and larger ΔT_g effects.

Now consider now pure polymers and the blend of ST3 and PS containing 20 wt. % of the latter. Clearly the T_g value for the blend is much closer to that of pure ST3 than to that of PS. Thus, the presence of PS does not have much effect on the glass transition temperature.

In turn, consider ternary systems formed so that to ST3 + PS blend in the weight proportion 80/20 different forms of Boehmite have been added, each time 5 wt. %. Thus, the value to be used in comparisons is $T_g = 111.3^\circ\text{C}$ for the un-reinforced blend. Here OS1 affects the T_g more than OS2. One possible explanation is strong interaction of OS2 with PS.

Finally, consider ST3 and PS with 5 % HP14 added. Here the effect of the additive amounts to $\Delta T_g = + 2.6^\circ\text{C}$ for the former and $\Delta T_g = - 16.6^\circ\text{C}$ for the latter. In other words, Boehmite HP14 acts as a reinforcement for the copolymer but as a plasticizer for PS. Given that for PS we have the very high value $10^{10}\text{B}/[\%\cdot\text{Pa}] = 8.78$ [17], this effect is not surprising. We recall the results for low density polyethylene (LDPE) reinforced with Boehmite [19]. LDPE has $10^{10}\text{B}/[\%\cdot\text{Pa}] = 0.132$ [17]. Static and dynamic friction values of LDPE are lowered by the presence of Boehmite, an effect explained by lubricating action of $-\text{OH}$ groups of Boehmite on the LDPE surface [19]. Grafting of coupling agents on the surface of Boehmite enhances the friction lowering effect; Kopczynska and Ehrenstein [20] stress the importance of interfaces for properties of multiphase materials. In the same LDPE + Boehmite system in the molten state we have found lowering of viscosity with addition of Boehmite [21] - this against the general tendency of solid ceramic additives of increasing viscosity. This unusual effect is caused also by application of coupling agents which cause attachment of polymer fibrils to Boehmite particles. As a result of good adhesion between the polymer matrix and the mineral filler, the polymer melt with filler flows more uniformly, thus exhibiting a lower viscosity despite adding the solid filler. Thus, a fairly coherent image of effects of Boehmite on behavior of polymers seems to emerge.

5. Nanoindentation and Vickers hardness results

In instrumented indentation testing, an indenter tip normal to the sample surface is driven into the sample by applying an increasing load up to some preset value. The load is then gradually released until partial or complete relaxation of the material occurs. During both the loading and unloading cycles, the applied force and penetration depth into the material are recorded, and a load-displacement curve is created. Using the features of this curve such as slope and testing parameters such as contact area of the tip,

we can determine nanoindentation hardness. Namely, the local hardness $h_{nanoindent}$ can be calculated as [22]:

$$h_{nanoindent} = P/A \quad (7)$$

where P is the load applied to the test surface and A is the projected contact area at that load. If the material were fully elastic [22 - 24] – which viscoelastic materials never are by definition – we could also calculate Young's modulus. Surprisingly, the method developed by Doerner and Nix in 1986 [22] is often referred to in the literature as "the Oliver and Pharr method" in spite of the fact that Oliver and Pharr papers on the subject appeared several years later [23, 24] than the original paper by Doerner and Nix.

As described in Section 2.3, we have also determined Vickers microhardness numbers. In this method the values obtained are independent of the size of the indenter. The results obtained are presented in Table 4.

Table 4. Indentation hardness and Vickers hardness

Property	ST3	ST3 + HP14	ST3 + OS1	ST3 + OS2
Indentation hardness / MPa	18.4	31.1	129.3	17.6
Vickers hardness	1.70	2.88	11.97	1.62

Interestingly, the OS1 filler which is the most aggregated provides much stronger resistance to the indenter than the other fillers which are distributed more uniformly in the matrix. This applies to both the indentation hardness and the Vickers hardness. Again the SEM results are useful for understanding these results.

One would expect that the two kinds of hardness could be related, as already suggested in [15]. On the basis of the above results, we have assumed a simple proportionality:

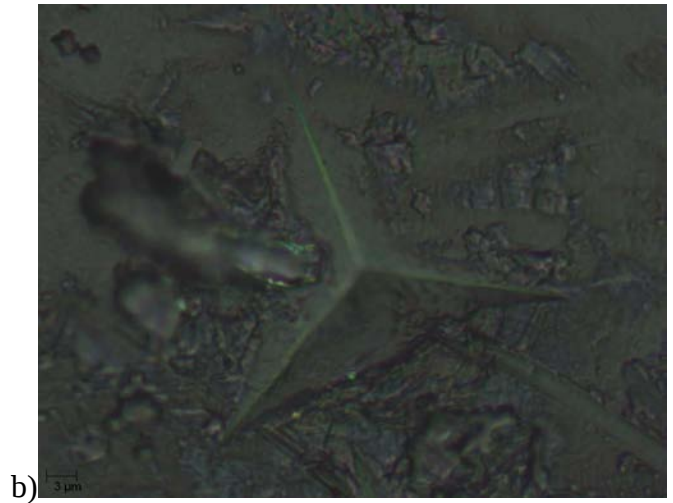
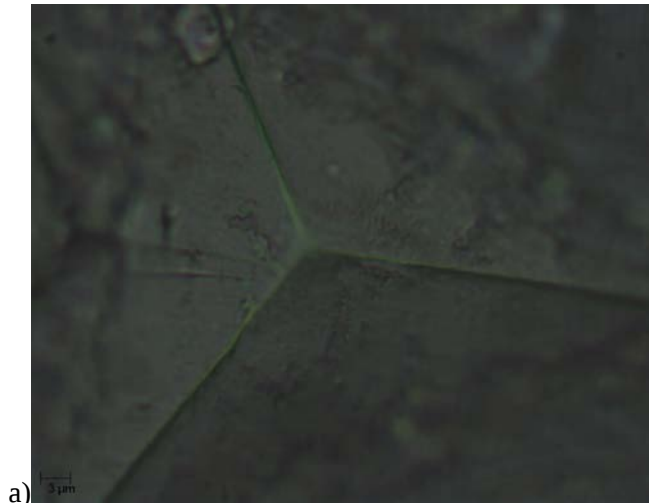
$$h_{nanoindent} = C_h \cdot h_{Vickers} \quad (8)$$

Calculations from the data in Table 2 for the series based on the ST3 copolymer with various reinforcements or without a reinforcement give us the numerical value $c_h = 10.82$. The subscript h stands for hardness. The average deviation from that number is only 0.025.

We recall that the Vickers hardness has also been related by an equation to the total groove area in scratch resistance testing [25]. The total groove area consists of the internal area (deeper than the surface) and the external area of two top ridges along the groove (above the surface).

6. Morphology of indented surfaces

In Figure 4 we show some of the SEMicrographs of indented surfaces of several samples. The samples were prepared by sputter coating the specimens with thin films of gold after completion of the indentation tests.



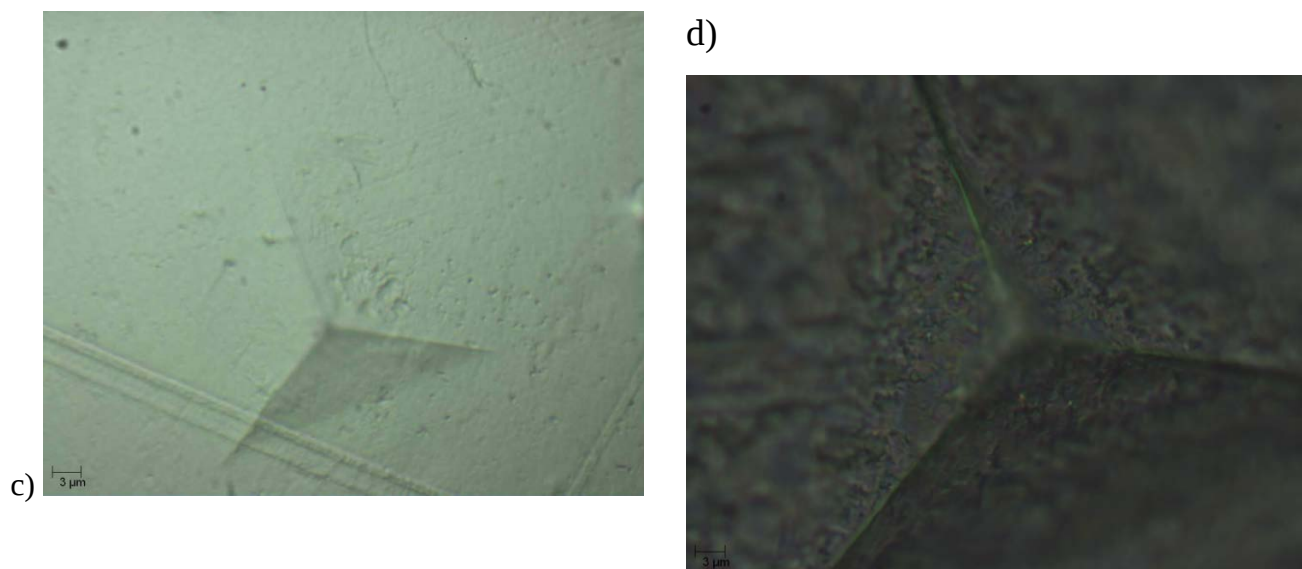


Figure 4. SEM micrographs of indented surfaces of some of the investigated samples; a) ST3, b) ST3 + 5 % HP 14, c) ST3 + 5 % OS1 and d) ST3 + 5 % OS2.

It is apparent that the surface of the composite containing the unmodified Boehmite is considerable more textured than those of composites with modified Boehmite. This supports our earlier conclusion that the coupling agents improve the adhesion of the polymers to Boehmite.

A wide variety of nanocomposites has been investigated before [26 - 40]. As already noted, the fact that our SBS block copolymer exhibits microphase-separated morphologies [40] provides additional maneuverability of properties.

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