Particle size dependence of the Young's modulus of filled polymers: 2. Annealing and solid-state nuclear magnetic resonance experiments

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Experimental results are reported from which it appears that in the case of polymer filled with silane-treated glass beads the Young's modulus is, in accordance with present theory, independent of the particle size of the filler. However, if pure glass beads are used as filler, the Young's modulus appears to be significantly dependent on the particle size. In a previous report a hypothetical explanation was given for this behaviour. It was assumed that, owing to the free filler surface offered to the polymer in the case of the untreated glass beads, the morphology of the polymer matrix adjacent to the filler particles is different from that of the bulk of the material. The results of annealing and solid-state nuclear magnetic resonance experiments reported here appear to support this hypothesis.

(Keywords: polystyrene–glass bead composites; filler particle size dependence; Young's modulus; solid-state nuclear magnetic resonance; morphology)

INTRODUCTION

The Young's modulus of a composite material has been the subject of many investigations and a number of equations have been derived which predict this property with varying accuracy[1–5]. In these studies the polymer is considered as an isotropic, structureless material and in that case the Young's modulus of the polymer filled with spherical particles should be independent of the size of the particles.

However, in a previous report experimental results have been discussed which show that in certain cases the Young's modulus is, in fact, dependent on the particle size of the filler[6]. Similar results have also been reported by other investigations[5,7–14]. In the same report[6] a number of explanations have been discussed, of which all but one could be ruled out. The remaining explanation is based on the assumption of a particular morphology of the matrix material, caused by the presence of the filler particles.

Because of the tentative character of this explanation, in the present report experiments will be discussed which were performed in order to sustain the validity of this hypothesis. In this study one representative type of composite material was investigated extensively.

EXPERIMENTAL

Polystyrene (Styron 634, Dow Chemical) was used as matrix material. Three types of glass beads differing in their average particle diameter were used as filler materials: glass beads of 4 μm (Louwers, range 1–10 μm), 30 μm (Tamson, range 10–50 μm) and 100 μm (Tamson, range 80–110 μm) diameter, respectively.

Two series of composites were produced. In the first series pure glass beads were used as the filler material and in the second series the glass beads were pretreated with a vinylbenzyltrimethoxysilane (Z6032, Dow Corning)[15–17] in order to obtain a chemical bonding of the glass beads to the polymer matrix.

The coupling agent was applied in the following pretreatment. To a suspension of 100 g of glass beads in 200 ml of methanol, 30 ml of Z6032 and 2 ml of concentrated hydrochloric acid were added. This mixture was stirred for 1 h, after which it was centrifuged to obtain a sediment of glass beads. The sediment was washed with 200 ml of methanol, centrifuged again and pre-dried at room temperature. The glass beads were dried for 1 h under vacuum at 130°C.

The polymer and respective fillers were mixed on a two-roll mill at 190°C. The filler content was varied in the range of 0 to 25 vol%. Test samples were machined from compression-moulded sheets. The standard annealing procedure consisted of a heat treatment at 80°C for a period of 24 h. However, in one set of experiments the annealing period was increased to 15, 50 and 100 days respectively. After the annealing procedure the samples were stored at room temperature for at least two days before testing.

The tensile tests were performed on an Instron tensile tester equipped with an extensometer ($l_0 = 50$ mm). The strain rate was 0.02 min^{-1}. All mechanical properties were estimated as the average of the results of at least five test samples.

Solid-state ^{13}C n.m.r. experiments were performed with a Bruker CXP-300 spectrometer at 75.47 MHz. Cylindrical samples were machined from the materials in such a way that the cylinders fitted in the alumina rotors for the double-air-bearing MAS probe of the

CXP-300. The samples were spun at $\sim 3500\,Hz$ in order to avoid overlap of the backbone signals in the ^{13}C n.m.r. spectrum with spinning sidebands from the aromatic part of the system[18]. A contact time of 1 ms was used for the cross-polarization excitation of the ^{13}C n.m.r. signals[19].

Immediately following the cross-polarization, a well defined $\pi/2$ pulse was applied. A second $\pi/2$ pulse was applied after a variable delay. Subsequently, the free induction decay was sampled and stored. The pulse cycle described above is, in fact, an inversion–recovery type of experiment with cross-polarization excitation. Usually, 300–320 free induction decays, sweep width 17 kHz, were accumulated and stored in 1 kbyte of memory. After exponential weighing (line broadening typically 10–20 Hz), zero-filling to 8 kbyte was applied, followed by Fourier transformation and phase correction.

Typical spectra, measured at ambient temperature, are shown in *Figure 1*. Three ^{13}C n.m.r. signals can be distinguished: one for the coinciding backbone resonances ($\sim 40\,ppm$) and two for the aromatic parts (at about 145.5 ppm for the *ipso* position, and at 127.3 ppm for the remaining five overlapping carbons). However, the results of the signal of the *ipso* position are not very accurate and therefore they are left out.

For each sample eight different delay times, from 1 to 300 s, were applied in one series of experiments. The total measurement time typically amounted to about 65 h. The resulting peak heights of the three signals *versus* pulse interval times were analysed in terms of mono-exponential decays. This is an approximation because any solid sample is inhomogeneous. The agreement

Figure 1 Typical inversion–recovery ^{13}C n.m.r. relaxation experiment. The signals marked 'ssb' are artifacts (spinning sidebands of the aromatic parts, caused by the large magnetic anisotropy) at various delay times

between repeated experiments was generally gratifying for the three resonances.

$T_{1\rho}$ (^{13}C) values were also determined for some samples using standard procedures[20]. Usually, 24 different experiments of 500 transients each and with carbon spin lock times ranging from 1 to 30 ms were combined (pulse interval times of 3 s). The contact time was 0.7 ms and $|B_1|$ was 10 G. Mono-exponential analysis of the curves of signal amplitude *versus* spin lock time were applied.

RESULTS

Young's modulus

In a previous study[6], experimental results were reported for the determination of the Young's moduli of PS filled with untreated glass beads of various sizes at different filler contents. In *Figure 2* these data are compared with the results of experiments in which the glass beads were pretreated with the adhesion promotor Z6032. Within experimental error, Young's modulus is dependent on particle size of untreated glass beads but shows no dependence in the case of chemically adhering glass beads.

In the same report[6] a comparison was made between the experimental results of the Young's modulus of PS filled with untreated glass beads, and calculations according to the modified Kerner equation[5]. It appeared that the calculated Young's moduli were slightly higher than the experimental results of the 30 μm glass bead composites. From this it is obvious that in the case of PS filled with chemically adhering glass beads the experimental results agree well with the predictions of the modified Kerner equation (see *Figure 2*).

Annealing experiments

In the preceding report[6] an explanation is proposed for the particle size dependence of the Young's modulus of a composite, where it is assumed that the morphology of the polymer adjacent to the filler particles is changed by the presence of the particles. In order to gain more insight into this problem, a series of annealing experiments was performed. During annealing a sample is heated to a temperature just under its glass transition temperature for a few hours. Two processes are likely to occur. Because of the increased mobility of the polymer molecules at the elevated temperature, the thermal stresses in the composite can be reduced and/or the morphology of the matrix material can be affected. The composites that were subjected to the annealing experiments were PS filled with 20 vol% of untreated glass beads of the three different sizes, and a pure PS reference material. Samples of these materials were kept at $80 \pm 1°C$ for a period of 1, 15, 50 and 100 days respectively. At room temperature the Young's modulus, the dewetting stress of the 30 μm and the 100 μm glass-bead-filled samples[21], and the molecular weight of the polymer (M_n and M_w) were determined.

In *Figure 3* the Young's moduli of the different materials are plotted as a function of the annealing time. The Young's moduli of the PS reference and of PS filled with 30 μm glass beads appear to be independent of the annealing time. But in the case of the 4 μm glass-bead-filled PS the Young's modulus tends to decrease with increasing annealing time, until at an annealing time of about 50 days a constant level is reached.
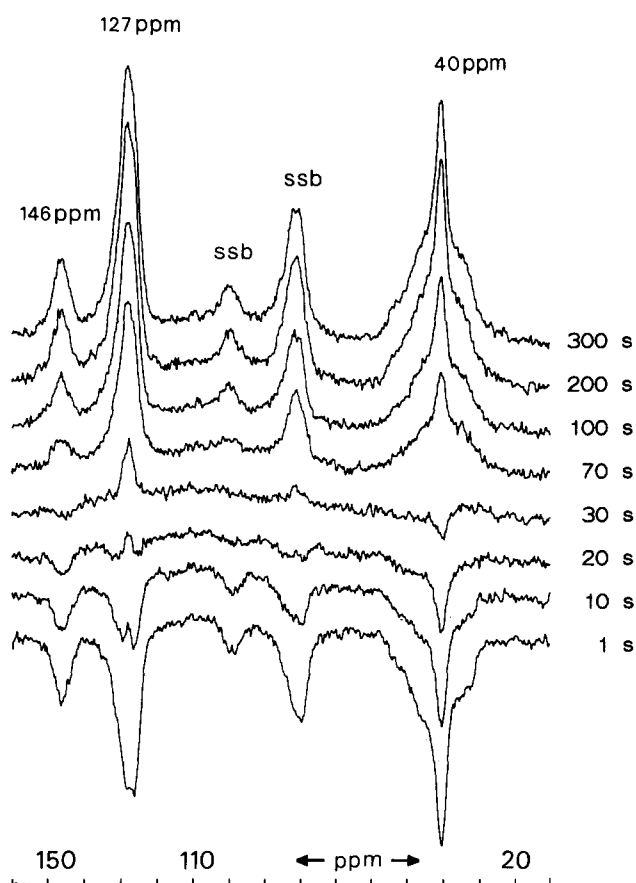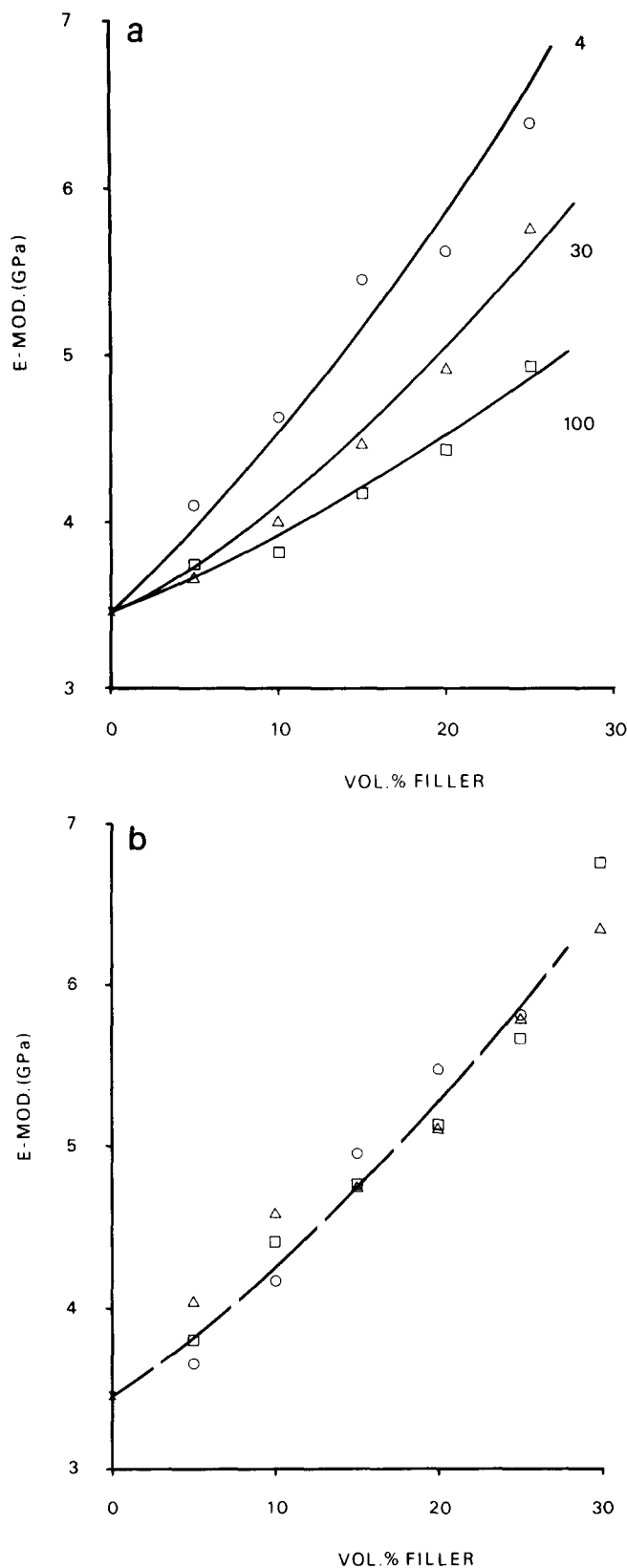
Figure 2 The experimentally determined Young's moduli of PS filled with glass beads of different particle sizes as a function of the filler content: (a) untreated glass beads; (b) silane-treated glass beads. The broken curve represents the Kerner prediction

In the case of PS filled with 100 μm glass beads an initial increase of the Young's modulus is found with increasing annealing time, but again, after annealing for about 50 days, a constant level is reached. At this level the Young's moduli of the 4 μm, 30 μm and 100 μm glass bead composites are all equal, and in agreement with the

prediction according to the modified Kerner equation (see previous subsection headed 'Young's modulus').

As mentioned before, the changes in the Young's modulus caused by the annealing procedure have to be connected with changes in the thermal stresses within the material and/or changes in the morphology of the polymer matrix, provided of course that the molecular structure is not affected (e.g. by degradation). In order to check this last point the molecular weight of the polymer was determined as a function of the annealing time. It appears from *Table 1* that the molecular structure is unchanged.

Data on the thermal stress within glass-bead-filled PS can be obtained from the dewetting stress of the material[21]. The dewetting stress is determined by a first term which depends on the thermal stress and a second term which depends, among other things, on the radius of the filler particles.

In *Table 2* the experimentally determined dewetting stresses of 30 μm and 100 μm glass-bead-filled PS are listed as a function of the annealing time. Data on PS filled with 4 μm glass beads are not included, since the dewetting stress of this material cannot be determined[21]. From *Table 2* it appears that the dewetting stress of both materials is independent of the annealing time. Therefore, it has to be concluded that in this case the thermal stress of the polymer matrix is not affected by the annealing procedure.

For this reason the final conclusion of the annealing experiments is that the dependence of Young's moduli of 4 μm and 100 μm glass-bead-filled PS on the annealing
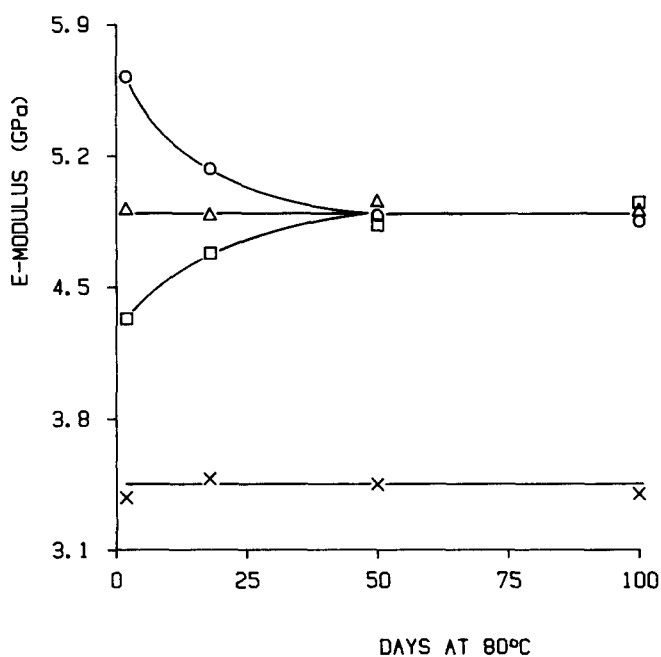

Figure 3 The Young's modulus of PS filled with 20 vol% of 4 μm (O), 30 μm (△) and 100 μm (□) glass beads and a PS reference (x) as a function of the annealing time

Table 1 Number-average molar mass (M_n) and weight-average molar mass (M_w) of the PS matrix as a function of the annealing time

Annealing time (days)	1	15	50	100
M_n ($\times 10^3$)	97	98	96	98
M_w ($\times 10^3$)	264	261	263	265

Table 2 The dewetting stress of PS filled with 30 μm glass beads ($\sigma_D(30\mu)$) and of PS filled with 100 μm glass beads ($\sigma_D(100\mu)$) as a function of the annealing time

Annealing time (days)	1	15	50	100
$\sigma_D(30\mu)$ (MPa)	11.2	11.3	11.5	11.3
$\sigma_D(100\mu)$ (MPa)	6.6	6.7	6.7	6.6

time points to a changing morphology of the polymer matrix during the process of annealing.

Solid-state n.m.r.

More detailed information about the behaviour of the polymer matrix of composites can be obtained from solid-state ^{13}C n.m.r. experiments. In particular, the spin–lattice relaxation parameter T_1 and spin–lattice relaxation in the rotating frame $T_{1\rho}$ are of interest in this study because they provide information about the mobility of the polymer molecules. The spin–lattice relaxation parameters characterize the timescale of the process by which an excited spin system reaches thermal equilibrium with its surroundings. They are usually dependent on the temperature and the resonance frequency[19,20,22-26].

The results of the solid-state ^{13}C n.m.r. T_1 experiments are shown in *Table 3*. It appears that in the case of the material filled with adhering glass beads and in the case of the untreated glass bead composites which were annealed for 100 days, the parameter T_1 is independent of the particle size of the filler. In these cases also the Young's modulus is independent of the filler particle size.

On the other hand, the relaxation times of composites filled with untreated glass beads that were annealed for only 1 day show a different pattern. The T_1 values of the 4 μm glass-bead-filled material are larger than the T_1 values of the 30 μm and the 100 μm glass-bead-filled material, which are each about equal to T_1 for reference PS.

Veeman et al.[27] demonstrated that a larger T_1 is caused by a lower mobility of the polymer molecules, i.e. in their case the correlation times of the molecular mobilities were longer than those corresponding with the extreme narrowing condition. A similar situation prevails in the present case as was shown by a comparison of T_1 values measured for ^{1}C n.m.r. at 75 MHz and at 50 MHz (7.1 T and 5.4 T respectively). At the lower frequency smaller T_1 values were found. It therefore turns out that, on average, the polymer molecules of the PS filled with 4 μm glass beads have a lower mobility on the megahertz timescale than the molecules of the 30 μm and the 100 μm glass bead composites or the reference PS.

The results in *Table 3* show that the overall mobilities of the aromatic rings and of the main skeleton carbons differ in all samples investigated here. In the present study the signals of the methine and the methylene carbons overlap to such an extent that deconvolution as demonstrated for other cases[28] is not feasible. However, from the spectra of a typical T_1 series, as shown in *Figure 1*, it appears that the T_1 values for the two signals do not differ widely, the methine carbon possessing a slightly larger value.

Schaefer et al.[28] described the occurrence of large-amplitude ring flips in a part (about 10%) of polystyrene. These motions are characterized by small

T_1 values: about 60 ms, close to the T_1 in the extreme narrowing limit (25 ms at 1.4 T, see ref. 28). The 'main' overall T_1 is found to be about 25 s in their case. In a magnetization decay curve, the contributions of small T_1 values will be manifest in the initial part of the total decay, which will show a typical two-exponential behaviour. In the present case we compared the first half of the magnetization decay with the second half and we found no significantly different results. In some cases additional T_1 experiments were carried out with pulse delay times between 0.1 and 5 s. This leads to the conclusion that in the present case no high-frequency, large-amplitude ring flips are detected. On the other hand, the aromatic carbons possess a higher mobility than the main-chain carbons (see above). This difference could be ascribed to low-frequency, small-amplitude ring motions as in ref. 28.

The variations in $T_{1\rho}$ (^{13}C) upon addition of 4 μm glass beads are not larger than the experimental uncertainties (see *Table 4*). Measurements on a reference PS material at variable temperature showed that $T_{1\rho}$ (^{13}C) values decrease at least 25% upon raising the temperature from 300 to 330 K. This indicates that our measurements were not carried out in a motional minimum. On the other hand, the change in T_1 (^{13}C) upon addition of beads is small but significant and reproducible (see *Table 3*). Apparently, the influence of glass beads is mainly confined to motions with frequencies well above $\sim 10^4$ Hz. This could very well be motions of the 'first type' as described by Schaefer et al.[28]. Herein

Table 3 The three ^{13}C n.m.r. T_1 values at 75.47 MHz as a function of the particle size of the filler and the annealing time, for both untreated as well as for chemically adhering glass beads. The values of a PS reference are also included

		T_1 (s)	
Size (μm)	Annealing time (days)	127 ppm aromatic (± 1)[a]	40 ppm backbone (± 1)[a]
PS reference			
—	1	32	52
PS filled with 25 vol% of untreated glass beads			
4	1	38 (32[b])	58 (40[b])
30	1	32	51
100	1	31 (28[b])	52 (38[b])
4	100	31	52
100	100	31	50
PS filled with 25 vol% of adhering glass beads			
4	1	32	52
100	1	32	50

[a] Accuracy interval of the T_1 values
[b] ^{13}C n.m.r. T_1 values measured at 50 MHz

Table 4 The ^{13}C $T_{1\rho}$ values of pure PS and PS filled with 25 vol% of 4 μm glass beads (both annealed for 24 h) measured at 75 MHz. The rotating frame field strength was 10 G

	$T_{1\rho}$ (ms)	
	127 ppm (± 0.5)[a]	40 ppm (± 0.5)[a]
PS	5.9	3.6
PS (4 μm)	6.4	4.2

[a] Accuracy interval of the $T_{1\rho}$ values

low-frequency ring motions are coupled to main-chain reorientations, i.e. ring oscillations are restricted to those areas where the main-chain packing is not prohibitively tight. This also points to an influence of the glass beads on the polystyrene packing (cf. also the insensitivity towards annealing of the T_1 values in Schaefer's work to the significant influence found in the present study).

DISCUSSION

In the previous report[6] an explanation is derived for the particle size dependence of the Young's modulus of polymers filled with untreated spherical particles. The explanation is based on the assumption of a special morphology of the polymer matrix around the filler particles. During cooling from the processing temperature (190°C) to room temperature the filler particles are assumed to act as sites where thermal contraction is particularly favoured, which should cause the special morphology. Two extremes are treated: a polymer filled

Figure 4 Proposed morphology of the polymer matrix surrounding (a) very large particles and (b) very small particles. The hatched parts indicate the filler particles, the O, − and + indicate 'normal', 'low-modulus' and 'high-modulus' polymer material respectively. Note that the scales of the two figures are different

with very large particles, and a polymer filled with very small particles.

In the former case the filler particles are assumed to be surrounded by a layer of 'high-modulus' polymer, followed by a depletion zone of 'low-modulus' material. The bulk consists of 'normal' polymer. In *Figure 4a* this morphology is shown. In the case of the composite material filled with submicrometre particles (order of magnitude 0.01 μm) the interparticle distance is so small that a homogeneous matrix material of 'high-modulus' polymer is assumed to be created (see *Figure 4b*).

In the same report it is shown semiquantitatively that the special morphology, assuming a layer thickness of some micrometres, causes a relatively low Young's modulus in the case of composites filled with very large particles, and a relatively high Young's modulus in the case of composites filled with very small particles.

In the present study more experimental support is reported, sustaining this hypothesis. From the annealing experiments it can be concluded that indeed the morphology of the polymer matrix is responsible for the particle size dependence of Young's modulus.

This conclusion seems also in agreement with the present solid-state n.m.r. results. The effective mobility of the polymer matrix molecules in the megahertz range, as detected by ^{13}C n.m.r. T_1 values, depends on particle size and pretreatment of the filler.

In terms of the proposed morphology it can be concluded from both the annealing and n.m.r. experiments that the morphology of PS filled with untreated 30 μm and 100 μm glass beads should be of the type indicated in *Figure 4a*, whereas the morphology of the untreated 4 μm glass bead composites should be a combination of both types shown in *Figure 4*.

The remaining question is why the composites filled with silane-treated glass beads do not show a particle size dependence of the Young's modulus. This can be explained as follows.

It is possible that at the free glass surface, polymer molecules are adsorbed rather strongly and that new layers are accumulated in a way favourable for densification. It must be stressed that this densification is not caused by compression forces. Recall from part 1 that the net volume change in the neighbourhood of the particles is zero, as compression stresses are counteracted by tensile forces in the two other mutually perpendicular directions[6]. Moreover, these forces extend over a region proportional to the volume of the particles and should therefore not lead to a particle-size-dependent modulus. Also the adhesion strength cannot be important as long as the modulus is measured beneath the dewetting stress. However, polymers with totally different adhesion strength show the dependence of modulus on particle dimension. The effect must reflect the structural character of the matrix, independent of the particle dimension, such as the thickness of a layer of some micrometres of dense material. This kind of layer formation is well established for crystallizing materials such as polyamide, where at a metal–polymer interface *trans* crystallization takes place followed by spherulitic crystallization further into the matrix. Such a layer can extend for micrometres and is clearly visible under the microscope. It is suggested that this kind of ordering of polymer chains, albeit not so clear because the interfacial morphology is not so precisely formed, is responsible for the observed differences in the present study. The structure formed around the particles
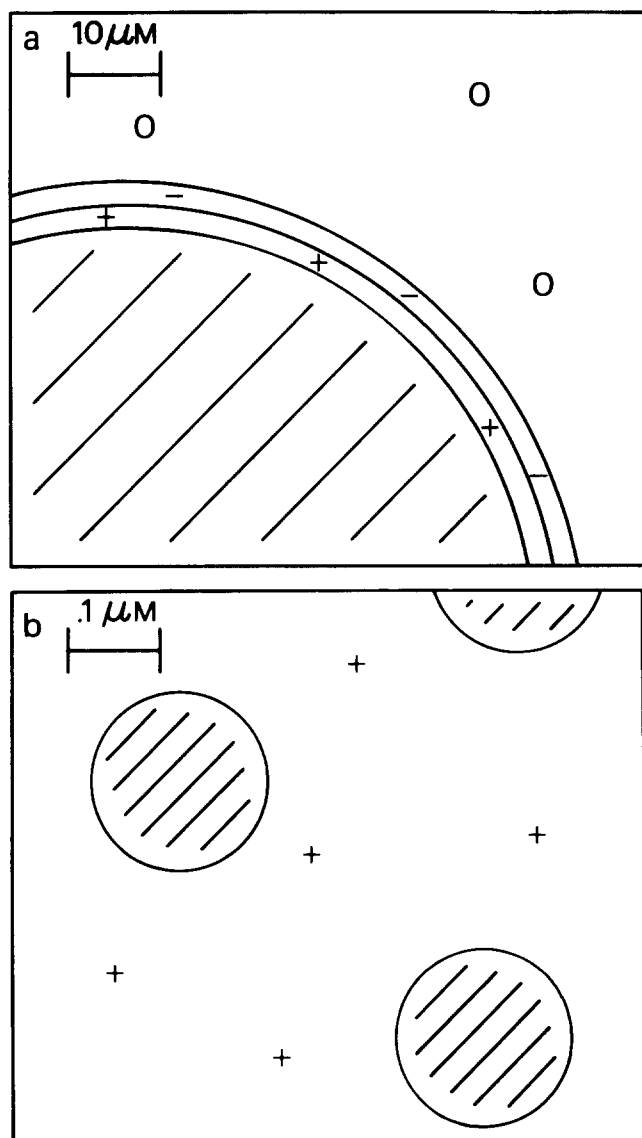
is essentially metastable in character, since it can be transformed to the normal PS morphology by annealing at 80°C over a period of weeks.

That a free surface of an inorganic substance is responsible for the effect is in agreement with the absence of any modulus variation for glass spheres covered with organofunctional silanes. These findings are in accordance with results on styrene-acrylonitrile copolymer (SAN) filled with glass beads coated respectively with adhesion or repulsion promotors, for which Young's modulus was invariant to particle size[29].

ACKNOWLEDGEMENTS

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