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# Interfacial role and properties in model composites: fracture surfaces by scanning electron microscopy

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The fracture surfaces of glass sphere-filled polyethylene model composites with varying degrees of interfacial modification were examined by scanning electron microscopy. The micrographs give a qualitative view of the bonding process and the nature of the region of modified matrix surrounding the glass spheres. Adhesive failure is seen for the unmodified composites, and also for the composites with near monolayer modification. At higher degrees of interfacial modification a layer of bound modified matrix is formed around the glass surface and the failure is cohesive. The micrographs demonstrate that the properties of the modified interfacial layer are dependent on the volume fraction of glass. The micrographs also show that the mechanism of bonding the matrix to the glass surface is through the thermally activated azide moiety.

## 1. Introduction

Scanning electron microscopy (SEM) is useful in obtaining a qualitative view of morphological changes in polymers. SEM is often used to examine polymer fracture surfaces, particularly where multiphase systems (e.g. composites, blends, networks) are involved. SEM has found particular use in identifying the failure mechanism between matrix and reinforcement phases in polymer composites and numerous examples can be found in the literature [1–5].

Often a conclusion is drawn from the nature of the fracture surface as to whether there is adhesion between the polymer and the reinforcement surface. In fact, the locus of failure in a multicomponent system is dependent on a number of criteria which include, but are not exclusively limited to, the presence or lack of adhesive bonds. The scanning electron micrographs presented in this paper provide a qualitative view of the effects of interfacial modification in composites of glass-reinforced polyethylene. The locus of failure and the amount of bound polyethylene after fracture is studied as a function of controlled interfacial modification. The dynamic-mechanical properties of these composites have also been examined [6].

## 2. Experimental details

Composites of glass sphere-reinforced high-density polyethylene (HDPE) were prepared by milling at 170° C for 15 min on an open two-roll mill and compression moulding into 0.30 cm thick plates under standard conditions at 190° C. Standard conditions include a pressure of 300 MPa and a cooling rate of 40° C min$^{-1}$. The glass spheres (no. 5000, Potters Industries) had an average particle size 10 to 13 $\mu$m and a B.E.T. surface area of 0.3 m$^2$ g$^{-1}$. The linear polyethylene (Stamylan 9089F, DSM) was a high-purity grade HDPE with a density of 0.963 g cm$^{-3}$ at 25° C and 0.760 g cm$^{-3}$ at 190° C, the weight average molecular weight $M_w = 6 \times 10^4$, and the melt index MI = 8 g/10 min. Experimental composite volume fractions were calculated at 25° C and were measured by thermogravimetric analysis (TGA) (TGS-2, Perkin Elmer). The glass reinforcement was chemically modified to produce a reactive azide group on its surface. This was accomplished by washing the glass in 0.5 N HCl to leach ions and increase the surface concentration of $SiO_2$ followed by reaction of the glass with an azido-functional alkoxysilane (AZ-CUP$^{TM}$ MC, Hercules Inc.) in methylene chloride or aqueous methanol. For most samples the azide moiety was allowed to react to completion during the compounding and moulding operations.

Composites of polypropylene (Stamylon P 16M10, DSM) and mica (Suzorite 200 HK, Martin-Marietta) with a particle diameter of approximately 1 $\mu$m and a B.E.T. surface area of 1.7 m$^2$ g$^{-1}$ were compounded similarly to the glass-filled polyethylene.

Scanning electron micrographs were recorded on a Philips scanning electron microscope at an applied voltage of 30.0 kV and magnifications from × 750 to × 12 500. The fracture surfaces were coated

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with evaporated gold prior to insertion into the microscope.

## 3. Results

Figs 1 to 7 show the scanning electron micrographs of the fracture surfaces of composites modified with increasing surface loadings of an azido-functional trialkoxysilane. The chemistry and use of azido-functional trialkoxysilanes as coupling agents can be found elsewhere [6–8]. The surface loadings are described as the number of equivalent molecular layers. This is an approximation based on the assumption that each azido-functional silane molecule occupies 1.5 $\mathrm{nm}^2$ surface. The actual concentration values range from 0.29 mg azido-functional silane solution per gramme glass (1 equivalent molecular layer) to 25 mg azido-functional silane solution per gramme glass (100 equivalent molecular layers) where the silane solution is 50 vol % active material. Although they are now shown here, glass samples with 0.1 and 0.5 equivalent molecular layers have also been studied.

In Figs 1 to 7, micrograph A represents a magnification of ×3000 and micrograph B represents a magnification of ×12 500. The micrographs show a progression of changes in the locus of fracture. The composite specimens were fractured at −196° C. In Fig. 1 with no surface modification the glass surface appears clean without the presence of any observable bonded polyethylene. The locus of fracture failure is at the equator of the spheres and the failure through the polyethylene is relatively brittle as would be expected at the temperature of fracture. In Fig. 7 at the highest level of surface modification examined (100 equivalent molecular layers), the locus of fracture failure has moved to the poles of the glass spheres and is completely through the matrix material. Figs 1 and 7 are typical of micrographs commonly used to demonstrate the difference between adhesive and cohesive failure.

Fig. 2 represents levels of surface modification at one equivalent molecular layer. The glass samples treated with less than monomolecular equivalent layer also showed the same trend. Similar to Fig. 1, the fracture occurs near the sphere equator and the surface of the glass appears not to bind any matrix material. These specimens would all be typically classed as showing adhesive failure; however, extraction experiments reported elsewhere [6] show that in each of these composites there was a measurable level of polyethylene bound to the glass surface. Fourier transform-infrared (FT-IR) spectra of these extracted glass surfaces [6] showed that the amount of bound polyethylene was equal in each of these samples even though the level of surface modification varied from 0.1 to 1 equivalent molecular layer. There was also a small and equivalent rise in the composite modulus of these samples over the unmodified control as detailed previously [6]. Therefore, it is not surprising that there is no fundamental observable difference among the samples with less than 1 equivalent molecular layer of silane. A few very small random islands of matrix material are apparent on the glass surface with close inspection of Figs 1b and 2b. They would appear to be artefacts of the fracture and have nothing to do with the controlled interfacial modification. It should be noted that because bonding to the glass surface takes place in the samples shown in Fig. 2, the lack of observable difference in the micrographs between the control and these samples is simply because the morphology of the bound material in these samples does not provide sufficient contrast to be seen by the scanning electron microscope.

Fig. 3 represents the first micrograph in the series where there is an observable difference in the glass surface after fracture due to interfacial modification. Fracture still occurs near the equator of the spheres and the failure mechanism would still be classically described as adhesive. However, there are many observable differences. Comparison of Figs 2b and 3b shows that there is spatial continuity at the glass/polyethylene interface in Fig. 3b where at the lower surface modifications the fracture produces some dewetting of the matrix from the glass surface, leaving a gap between the matrix and glass sphere. Relatively uniformly dispersed islands or nodules of matrix cover the exposed surface in Fig. 3b. Close inspection of Fig. 3b gives some indication of a morphology with less contrast on the glass surface at a level below the island formation. The individual nodules of islands are about 100 nm diameter and are spaced at distance from 0.25 to 1 $\mu$m from each other. The nodules are formed as a result of ductile failure of the polyethylene at points where the polyethylene is bound to the surface.

Fig. 4a shows the first micrograph in this series where the failure would be considered cohesive. The plane of fracture has moved away from the equator of the sphere, at an angle approximately 10° from the equator. Fig. 4b shows an underlying morphology of polyethylene covering the entire glass surface similar to what was seen in Fig. 3b. In addition, there are now larger domains of polyethylene bound to the surface as opposed to the individual nodules seen in Fig. 3b. Fig. 5 illustrates what might be considered complete cohesive failure. These appear to be large domains of polyethylene covering the entire glass surface. The fracture plane now intersects the spheres approximately 45° from the equator.

In Fig. 6a, very few glass sphere surfaces are visible, indicating further movement of the fracture plane toward the sphere poles. From visual inspection of the micrographs, the fracture plane can be assigned as occurring at the poles of the spheres or 90° from the equator. In Fig. 7 at the highest loading of surface modification, there is little or no fundamental difference in the fracture surface from the example in Fig. 6.

In addition to modifying the interface in the glass-filled polyethylene composites with increasing concentrations of the azido-functional silane, experiments were performed to modify the organization or structure of this interface. Fig. 8 shows the micrographs of samples prepared with 20 equivalent molecular layers of the azido-functional silane. Prior to incorporation in the matrix polyethylene, the modified glass surface was slurried in *n*-hexane for 10 min followed by repetitive washings with *n*-hexane. The glass was filtered

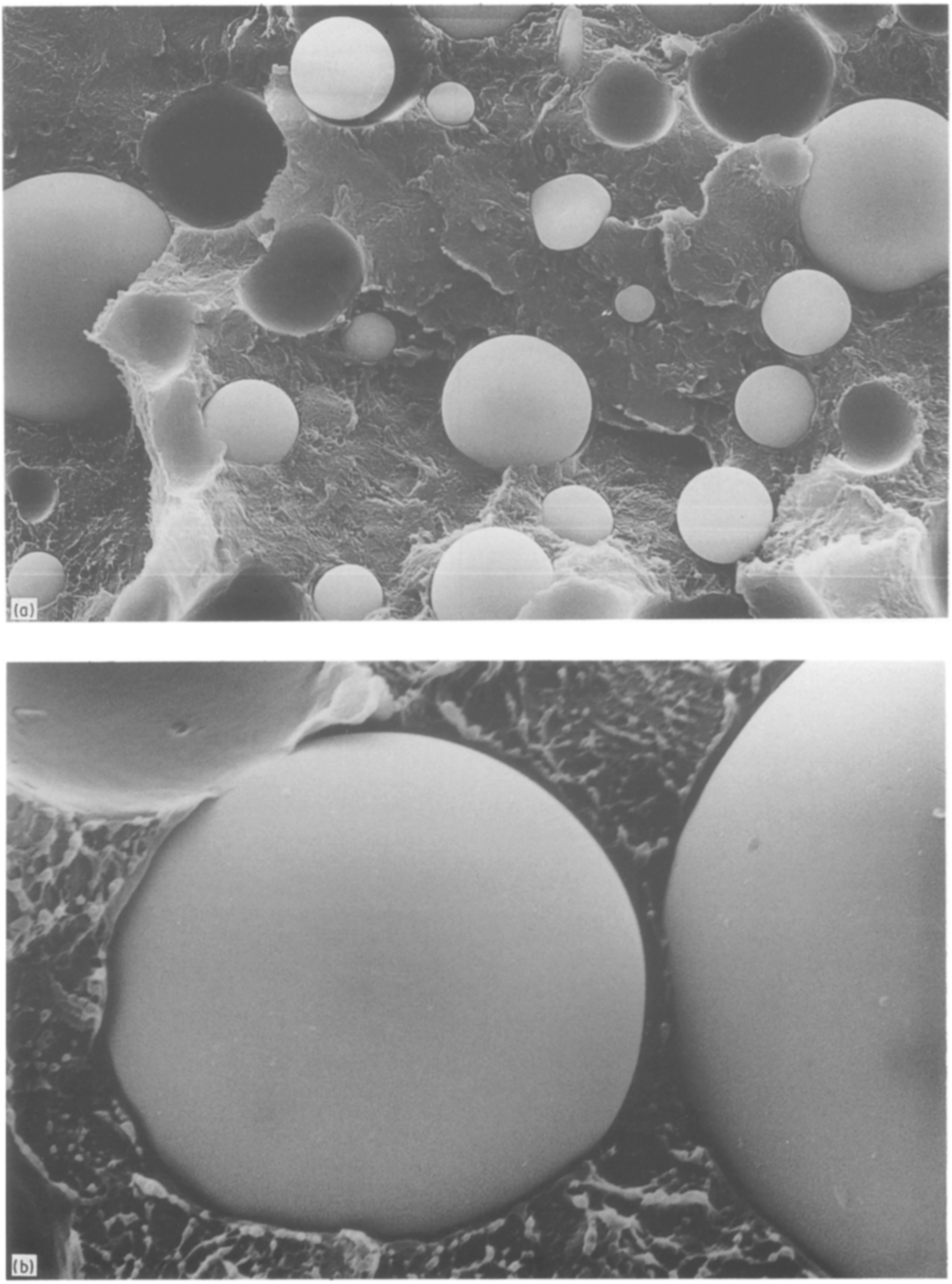

*Figure 1* Scanning electron micrographs of glass/polyethylene composite fracture surface without interfacial modification at magnifications of (a) × 3000 and (b) × 12 500. All figures reduced to 66.66% for reproduction.

and air dried at room temperature. The micrographs demonstrate a different failure mechanism and fracture surface than was observed in Fig. 6 for the 20 equivalent layer modification. The fracture plane is located near the equator rather than the poles and Fig. 8b shows that islands or nodules of polyethylene remain on the glass after fracture, similar to, but more numerous than, those seen in Fig. 3b.

Fig. 9 illustrates the fracture surface after another variation of the interfacial structure. Prior to incorporation in the matrix polyethylene, the glass spheres were modified with 20 equivalent molecular layers of the azido-functional silane deposited from a solution of aqueous methanol (0.75 g deionized water, 50 ml methanol) unlike the specimens shown in Figs 1 to 5, which were treated by methylene chloride solution.

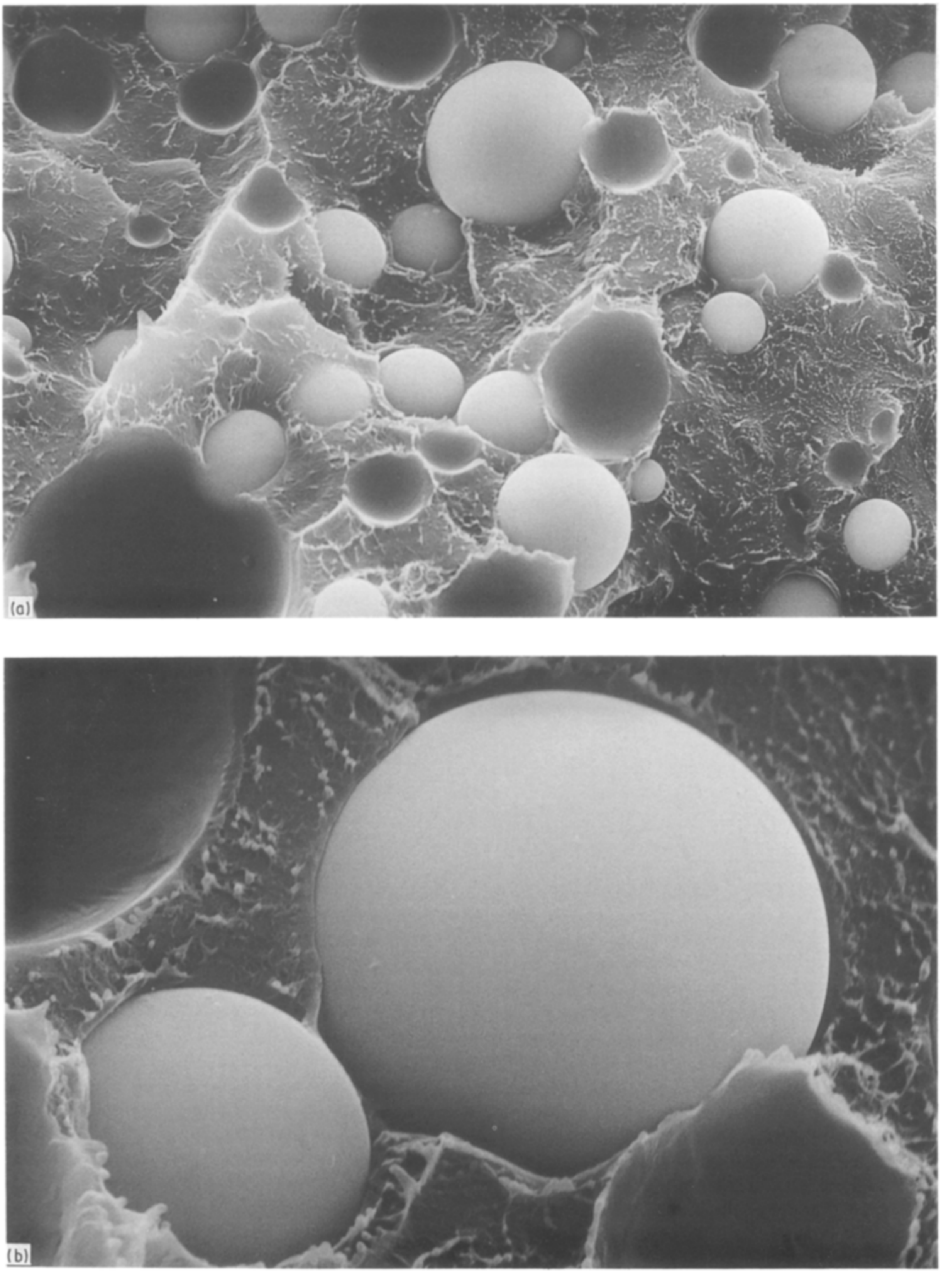

*Figure 2* Scanning electron micrographs of glass/polyethylene composite fracture surface with glass modified by 1 equivalent molecular layer of azido-functional silane at magnifications of (a) × 3000 and (b) × 12 500.

This is different from the specimen shown in Fig. 6 only in the carrier solvent and the small amount of water used. In Fig. 9a, the fracture plane is near but not at the equator of the sphere. Fig. 9b shows that the glass surface is well covered with matrix polyethylene at the fracture surface.

Figs 10 and 11 demonstrate the effect of the total volume fraction of glass on the fracture surfaces. The specimens in Figs 10 and 11 are 50 vol % glass at 25° C. In Figs 5 and 6 at the same level of surface modification, the samples were 20 vol % glass at 25° C. Figs 10 and 5 contain glass with the 10 equivalent molecular layers of surface modification. The fracture plane in Fig. 10a at about 30° from the equator is

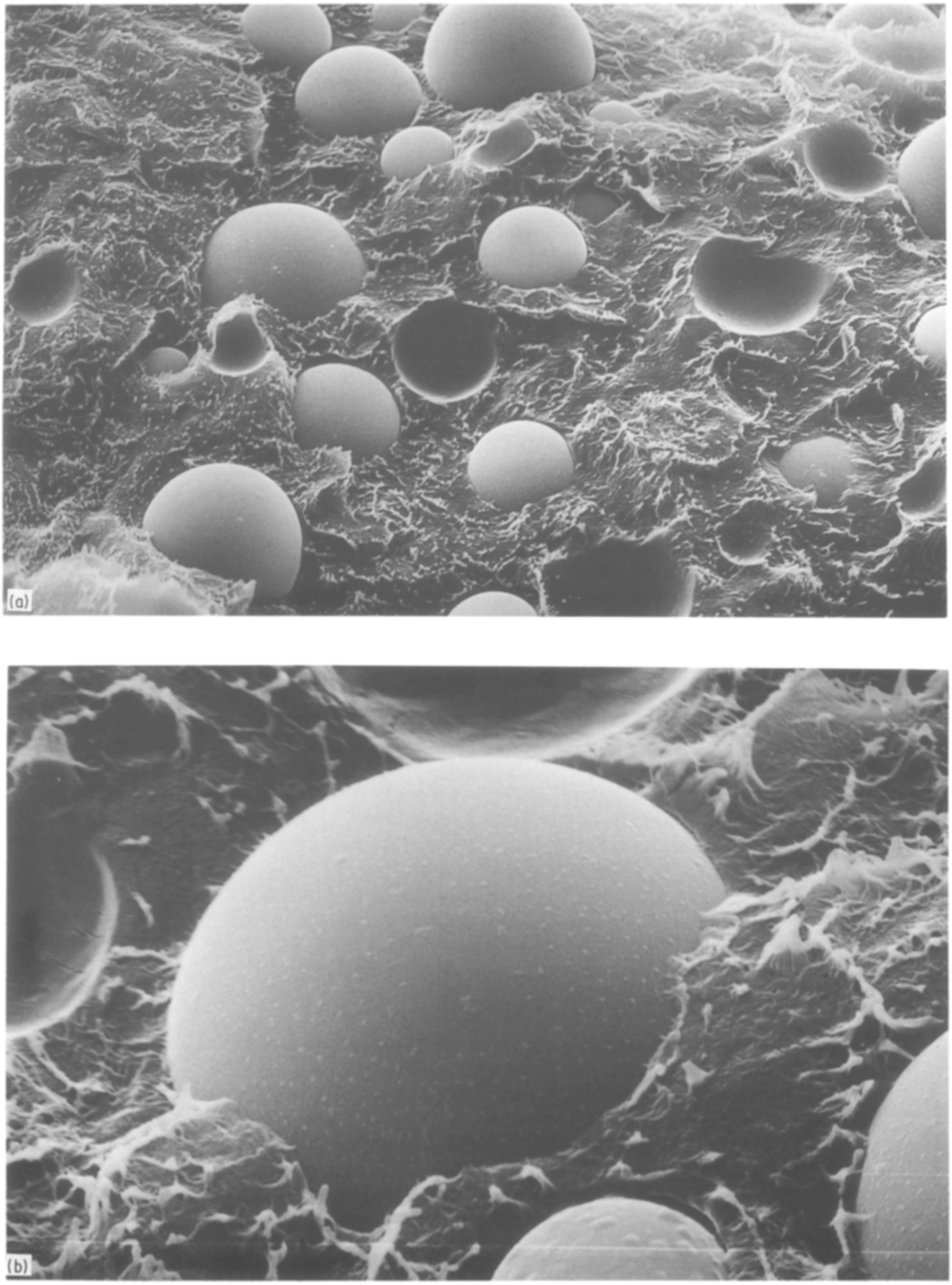

*Figure 3* Scanning electron micrographs of glass/polyethylene composite fracture surface with glass modified by 2 equivalent molecular layers of azido-functional silane at magnifications of (a) ×3000 and (b) ×12 500.

closer to the equator than in Fig. 5a and there is less matrix polyethylene bound to the exposed glass surface. The fracture surface in Fig. 10 resembles the fracture observed in Fig. 4 for the 5 equivalent layer modification. A similar comparison can be made between Figs 11 and 8 which both contain glass modified with 20 equivalent layers of the azido-functional silane. The fracture plane in Fig. 11a is located approximately 30° from the equator similar to Fig. 10a and quite different from the fracture at the poles in Fig. 6 at the same level and method of surface modification. The large difference is apparently caused by the different shear conditions produced while milling a 20 compared to 50 vol % glass composite.

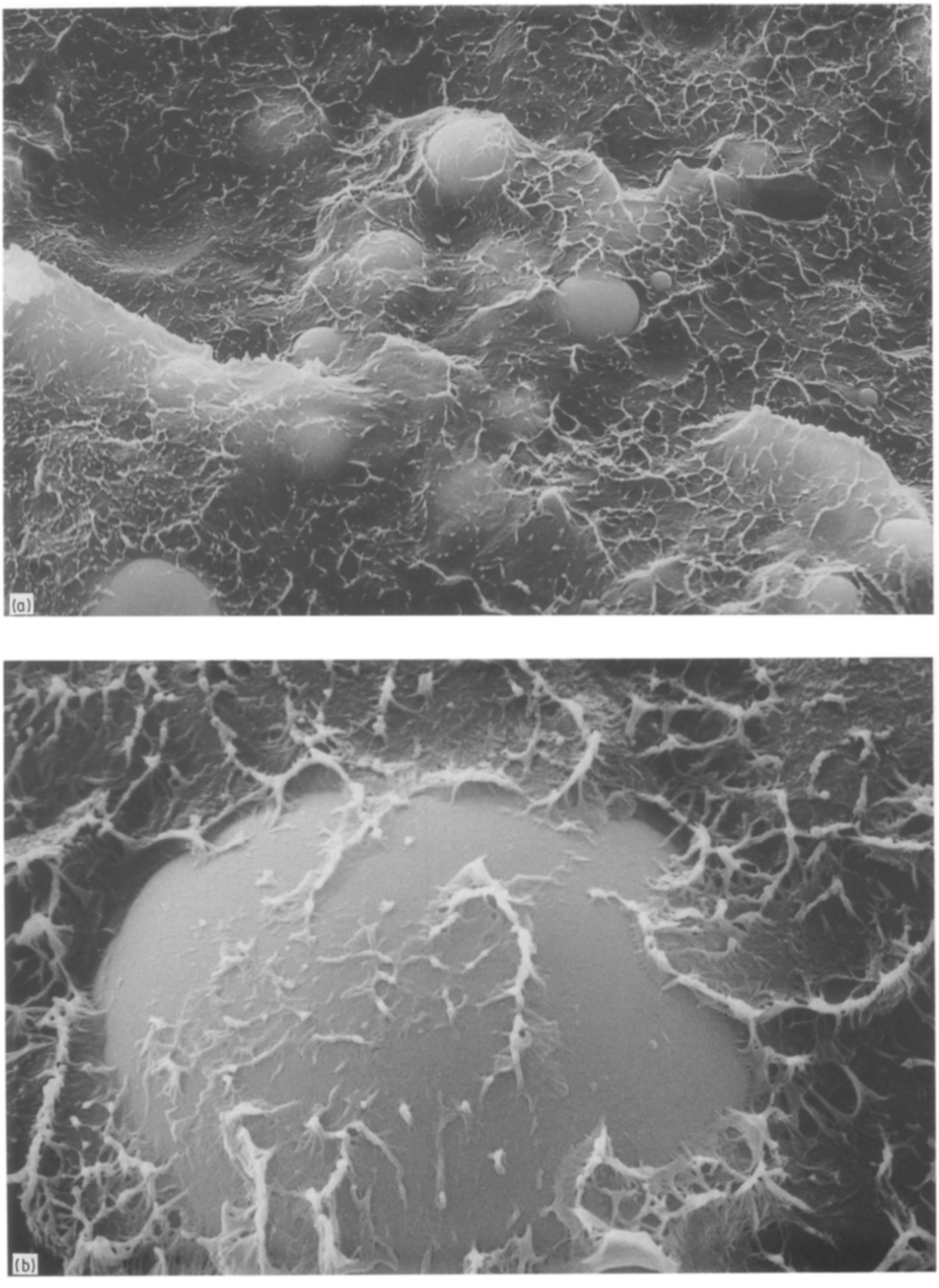

*Figure 4* Scanning electron micrographs of glass/polyethylene composite fracture surface with glass modified by 5 equivalent molecular layers of azido-functional silane at magnifications of (a) × 3000 and (b) × 12 500.

Fig. 12 demonstrates that the changes noted in the fractured specimens with respect to locus of failure and the amount of bound polyethylene are caused by the thermally activated reaction between the azido-functional silane and the polyethylene matrix. Fig. 12a illustrates the fracture surface of a glass-filled polyethylene composite in which the glass was modified with 7.5 equivalent molecular layers of the azido-functional silane. The glass was incorporated into the polyethylene matrix by roll milling and pressing at 130° C. At this temperature, the reaction time of the azide group is approximately 70 h [9] and therefore, the reaction with the polyethylene should be negligible under these conditions. Fig. 12b shows the fracture

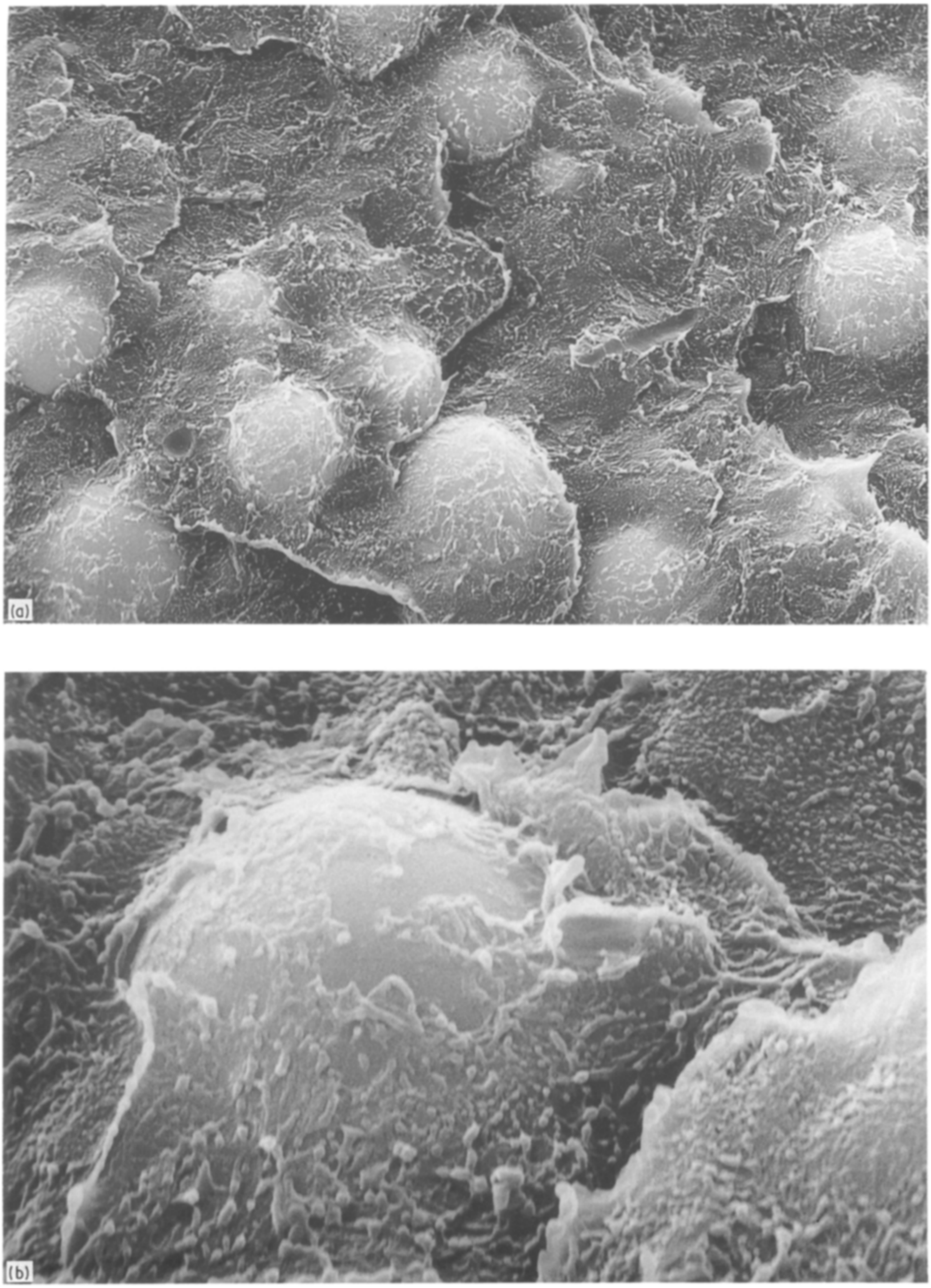

*Figure 5* Scanning electron micrographs of glass/polyethylene composite fracture surface with glass modified by 10 equivalent molecular layers of azido-functional silane at magnifications of (a) × 3000 and (b) × 12 500.

surface with the same modification to the glass surface after reacting the azide moiety in the presence of the polyethylene. Polyethylene bound to the glass surface is now evident. The same observation noted in Figs 10 and 11 concerning the effect of total volume fraction of glass explains why the amount of bound polyethylene in Fig. 12 appears to be less than at comparable surface modification levels in Figs 4 and 5.

Fig. 13 shows the effect of interfacial modification in mica-filled polypropylene. Fig. 13a is the unmodified sample and shows substantial mica flake pullout at the fracture surface. Fig. 13b demonstrates that

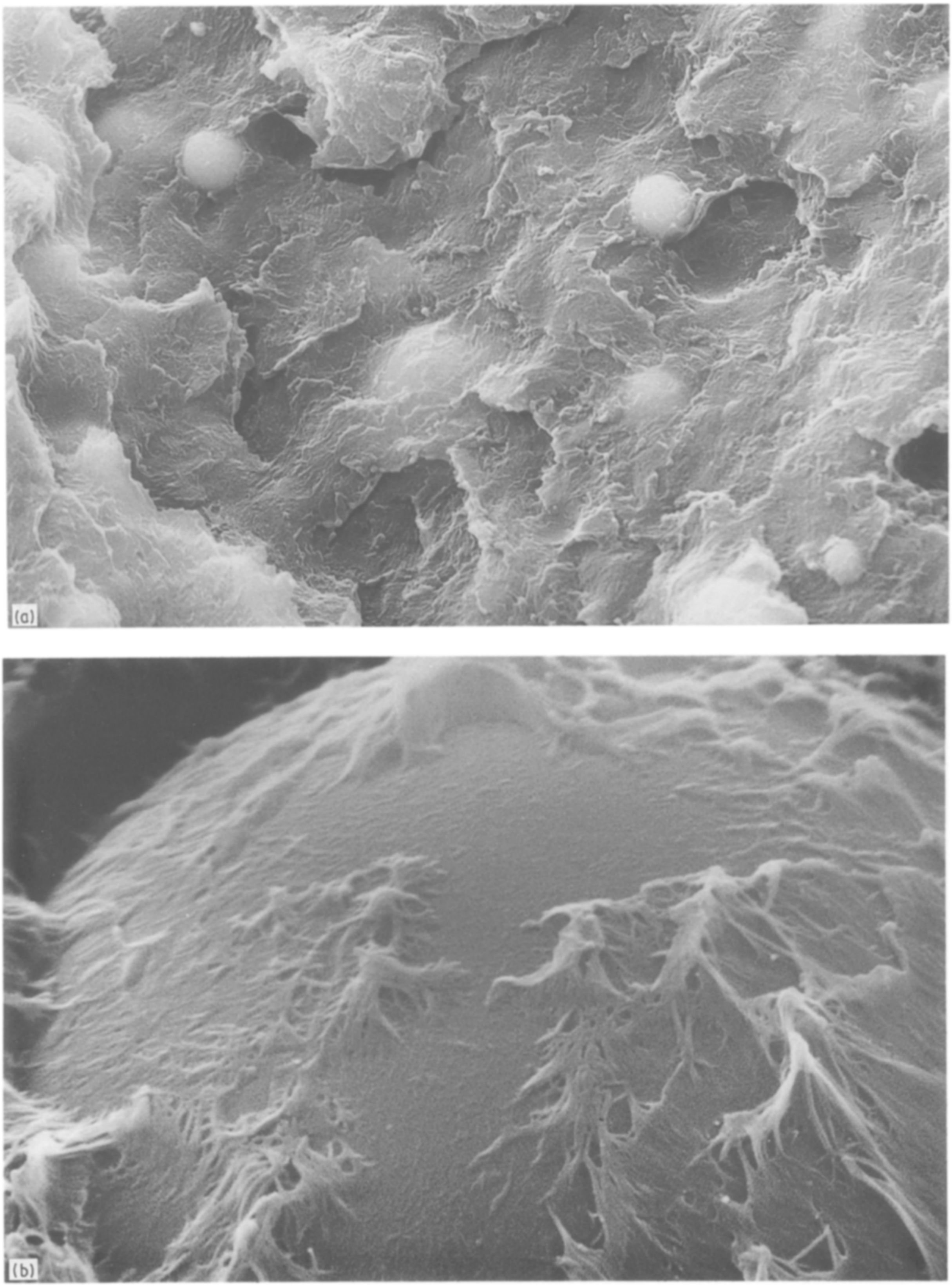

*Figure 6* Scanning electron micrographs of glass/polyethylene composite fracture surface with glass modified by 20 equivalent molecular layers of azido-functional silane at magnifications of (a) ×3000 and (b) ×12 500.

after interfacial modification at approximately 10 equivalent molecular layers, the fracture surface shows less flake surface indicating fracture through the flakes as opposed to fracture along the interface with polypropylene.

## 4. Discussion

Figs 1 to 7 reveal the effects and transitions in the interfacial modification of composites by alkoxysilane coupling agents. The spherical glass-filled polyethylene represents an ideal composite material because the constituents are well defined, well characterized, and can be theoretically modelled [6]. It can be concluded from these micrographs that there are at least two major types of interfacial bonding in this system. First, there is polyethylene chemically bonded directly

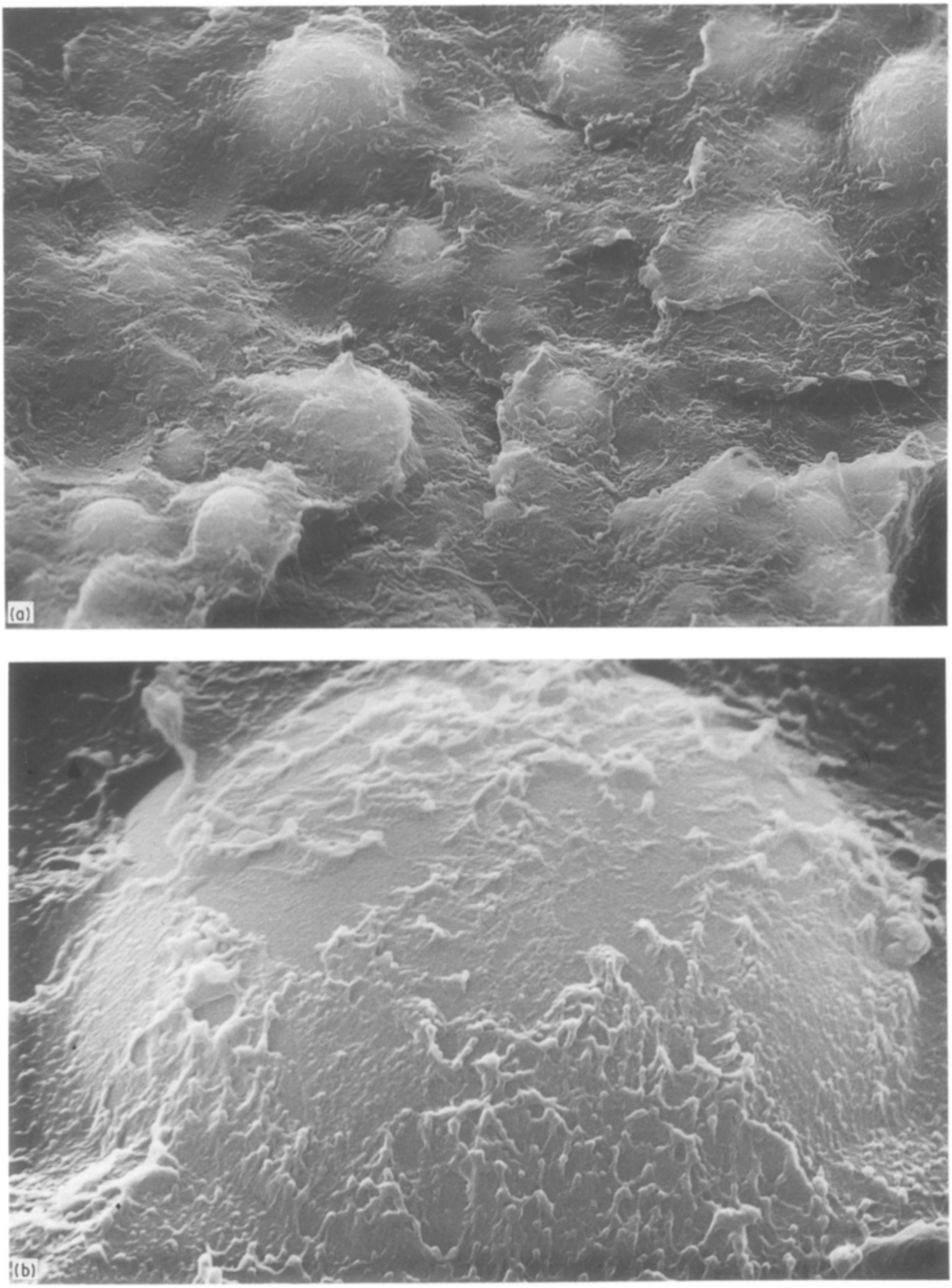

*Figure 7* Scanning electron micrographs of glass/polyethylene composite fracture surface with glass modified by 100 equivalent molecular layers of azido-functional silane at magnifications of (a) ×3000 and (b) ×12 500.

to the glass surface through a bridging silane molecule. This type of bonding is evident in Figs 2 and 3 even though there is presumably insufficient contrast to observe the bound polyethylene in Fig. 2. The polyethylene directly bonded to the glass surface does not affect the locus of fracture in the composites and has only an extremely small influence on the dynamic-mechanical properties of the composite [6].

A second level of bound polyethylene is observed as a layer of increasing thickness adhering to the glass surface after fracture. This type of bound polyethylene is observable in Figs 4 to 7 and is caused by migration of monomeric or low molecular weight oligomers of the alkoxysilane into a region surrounding the glass. Upon reaction of the azide, the modified region is effectively cross-linked conceivably with chemical

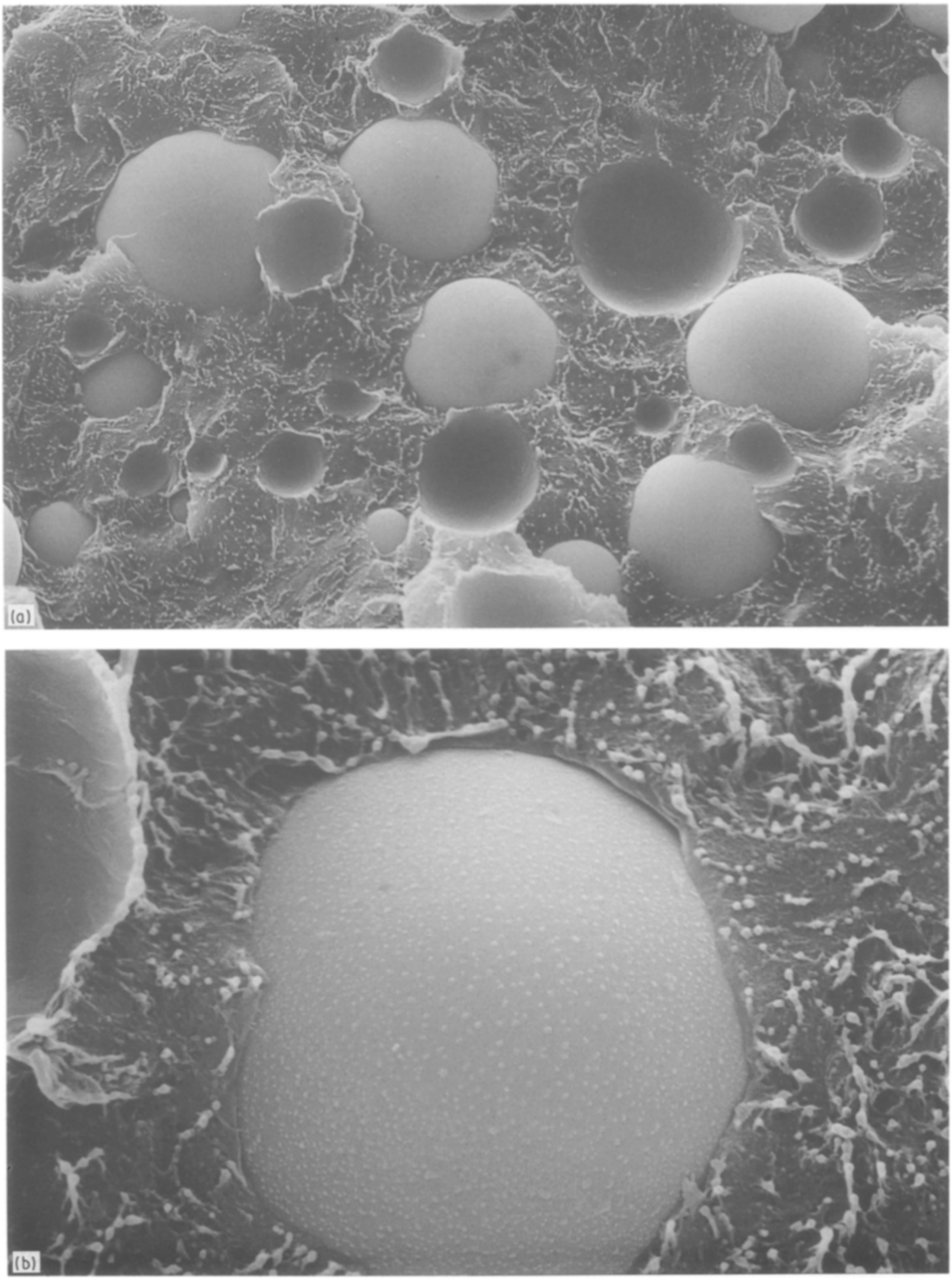

*Figure 8* Scanning electron micrographs of glass/polyethylene composite fracture surface with glass modified by 20 equivalent molecular layers of azido-functional silane and extracted with *n*-hexane at magnifications of (a) ×3000 and (b) ×12 500.

linkages all the way to the glass surface. This build-up of this type of layer drastically changes the locus of fracture and significantly changes the dynamic-mechanical properties of the composite [6].

Figs 8 and 9 further demonstrate the two levels of bound polyethylene previously described. In Fig. 8, any azido-functional silane which was not directly chemically bonded to the glass surface and, therefore, has possible mobility in the matrix has been removed by extraction with *n*-hexane. Therefore, all the polyethylene appearing on the glass surface after fracture presumably has direct bonds to the glass surface. Somewhat of a similar analogy is seen in Fig. 9 where mobile silane molecules have been eliminated by adding

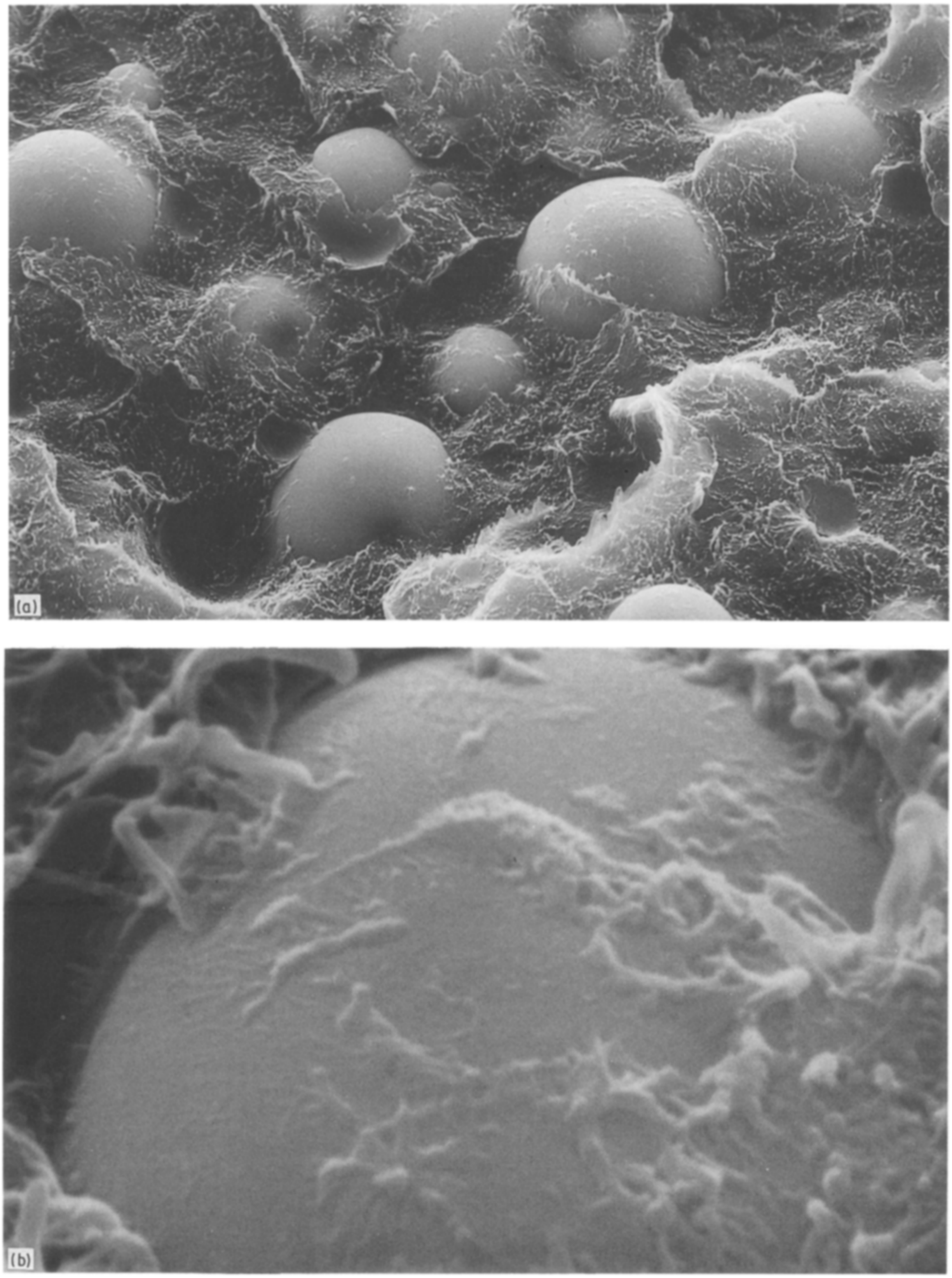

*Figure 9* Scanning electron micrographs of glass/polyethylene composite fracture surface with glass modified by 20 equivalent molecular layers of azido-functional silane from aqueous methanol at magnifications of (a) ×3000 and (b) ×12 500.

water to the reaction between the alkoxysilane and the glass surface. This causes complete hydrolysis and subsequent condensation of the alkoxysilane, resulting in a functionalized polysilsesquioxane network on the glass surface. It is unlikely that this network can be penetrated by molten polyethylene to any great extent and therefore, the thermally induced azide reaction is likely to be mostly interfacial at the boundary between the silsesquioxane network and the matrix polyethylene. In this case, the morphology of the bound polyethylene is different than seen in Fig. 8 because the effective substrates are different (i.e. glass rather than polysilsesquioxane) yet the amount of chemically bound polyethylene measured by FT-IR

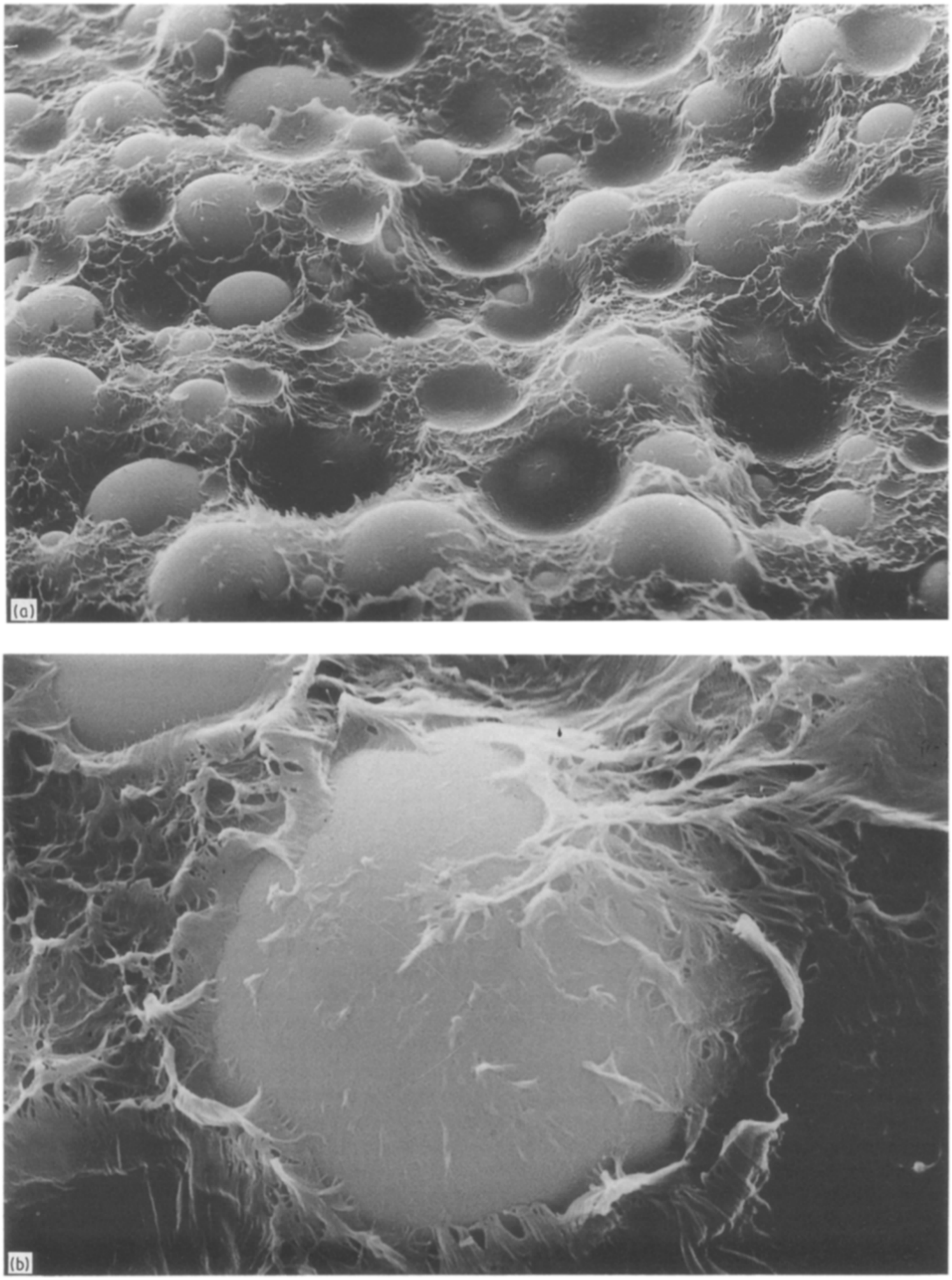

*Figure 10* Scanning electron micrographs of glass/polyethylene composite fracture surface with 50 vol % glass modified by 10 equivalent molecular layers of azido-functional silane at magnifications of (a) ×3000 and (b) ×12 500.

after solvent extraction of the bulk matrix is similar [10].

Figs 10 and 11 show the strong influence of total volume fraction of glass on the fracture surfaces. Because the build-up of the interfacial layer seen in Figs 4 to 7 is dependent on the migration of silane molecules, it might be expected that conditions which regulate the migration of these molecules (e.g. diffusion, mixing) would effect the final composite properties. The stress field near the glass surface during the milling process is dependent on the total volume fraction of glass and therefore, the migration of silane molecules into the matrix should be greater at the higher volume fraction. Figs 10 and 11 indicate

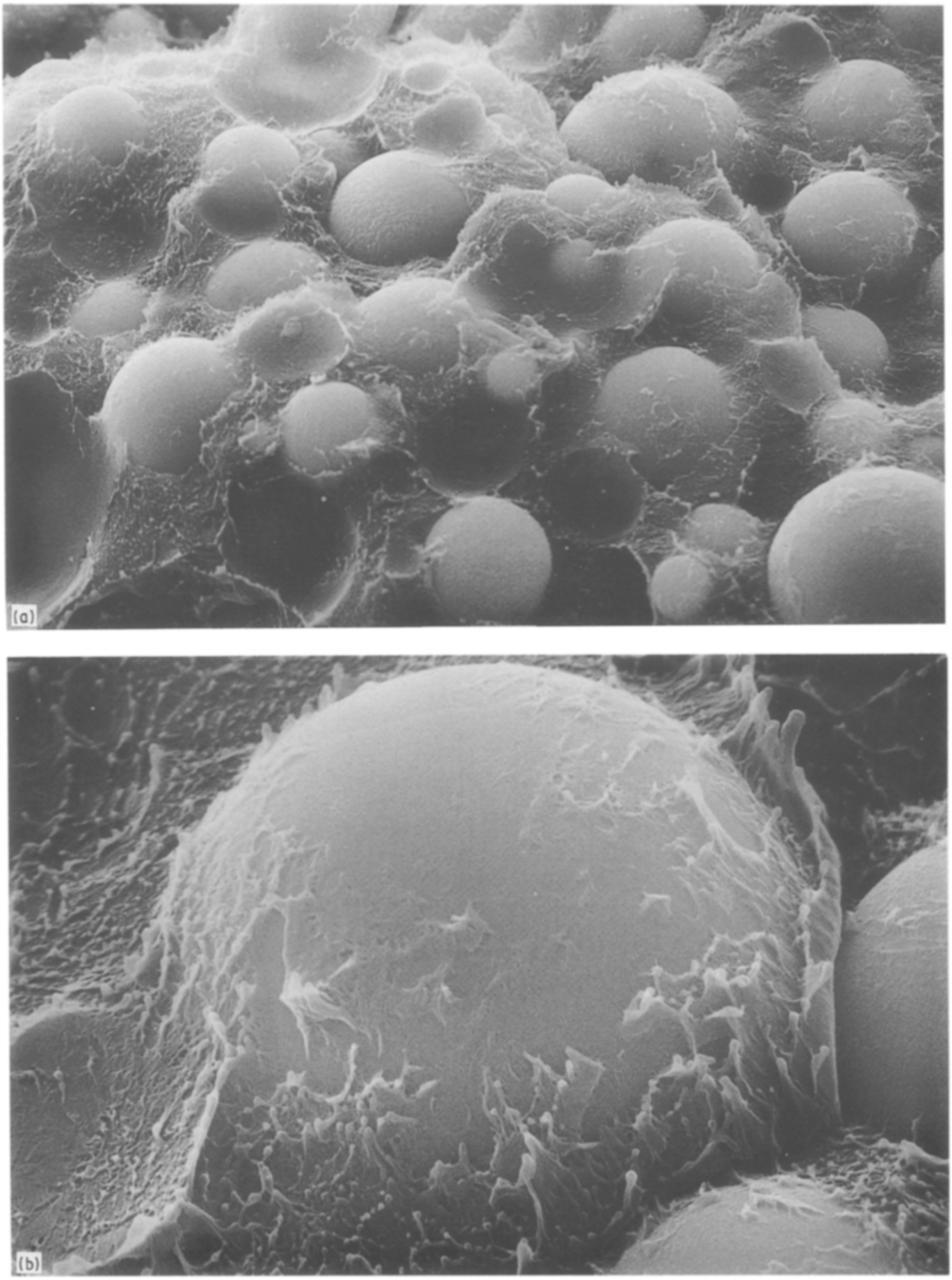

*Figure 11* Scanning electron micrographs of glass/polyethylene composite fracture surface with 50 vol % glass modified by 20 equivalent molecular layers of azido-functional silane at magnifications of (a) × 3000 and (b) × 12 500.

that, when the milling process creates greater mixing efficiency at high volume fraction of glass, the resulting modified interfacial layer is presumably larger but not bound to the glass surface. Therefore, it does not remain at the glass surface on fracture and has a lesser influence on the properties of the composite [6, 10]. These results explain the observations that the use of silane coupling agents is less effective in injection-moulded composites where there is high shear, than in compression-moulded composites.

Fig. 12 demonstrates that the mechanism for bonding polyethylene to glass is through the azide functionality rather than by way of interpenetration with the polysiloxane network or some other physical interaction.

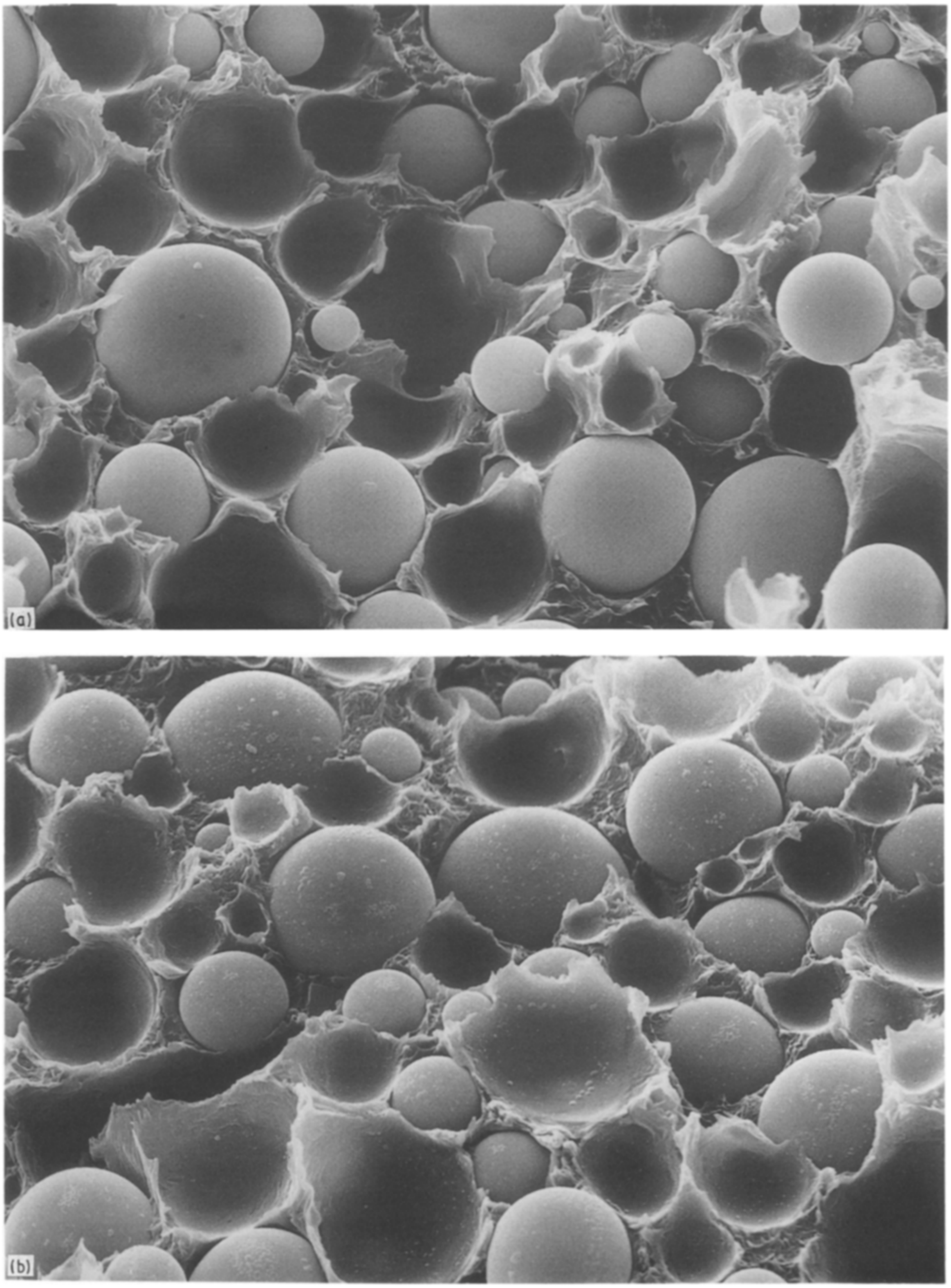

*Figure 12* Scanning electron micrographs of glass/polyethylene composite fracture surface with 50 vol % glass modified by 7.5 equivalent molecular layers of azido-functional silane (a) before reaction and (b) after reaction.

It can be predicted theoretically that under conditions of no interfacial modification, the equator of the glass spheres should fall in the plane of fracture. When there is adhesion at the interface and a layer of sufficiently modified matrix surrounding the glass spheres, the fracture plane should move to the poles of the spheres. Both these predicted phenomena are experimentally observed in Figs 1 and 6. Fig. 14 plots the experimentally observed locus of failure taken visually from the micrographs as a function of the level of surface modification.

## 5. Conclusion

Scanning electron micrographs of the fracture surfaces

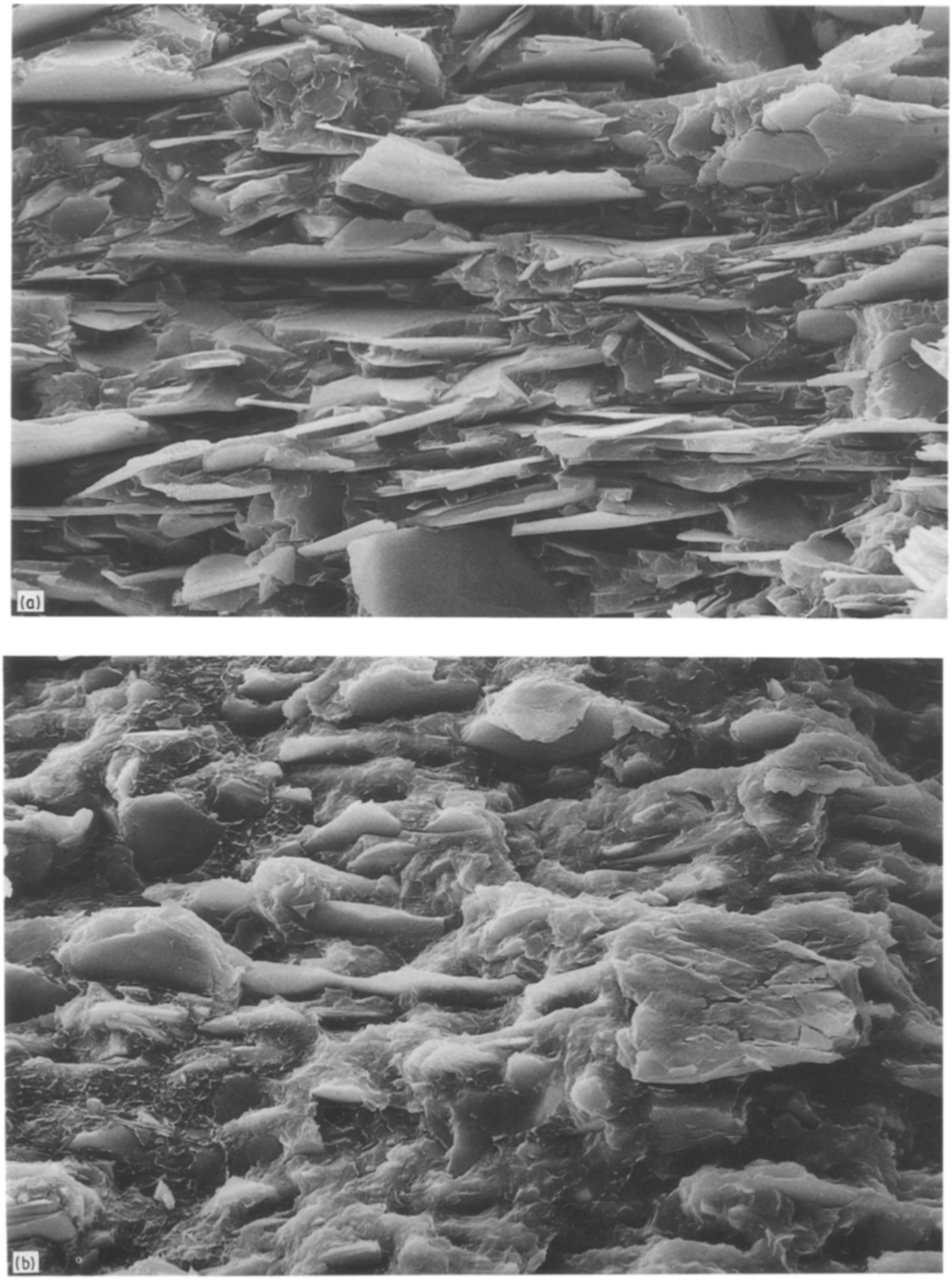

*Figure 13* Scanning electron micrographs of glass/polyethylene composite fracture surface with (a) 20 vol % unmodified mica and (b) 20 vol % mica modified with 1 equivalent molecular layer of azido-functional silane.

of interfacially modified composites show two distinct types of polyethylene bound to the glass surface. The type of bonding and the morphology at the interface can be tailored by controlling the chemistry at the interface. The interfacial modifications have large effects on the locus of fracture failure, amount of bound polyethylene, and the composite properties.

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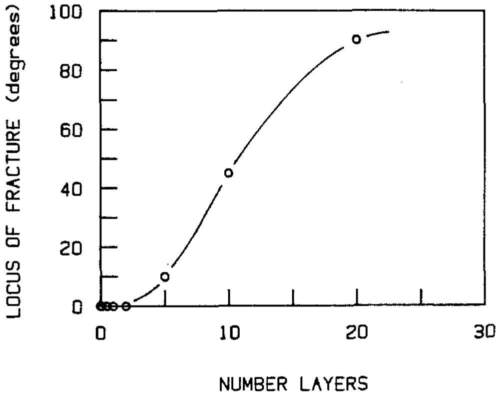

*Figure 14* Locus of the plane of fracture failure measured in degrees from equator of the glass sphere as a function of the level of surface modification by the azido-functional silane.

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