Soft matrix fracture surface as a means to reveal the morphology of multi-phase polymer systems

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To disclose the interior phase structure of soft polymeric materials, a classical procedure exploits the hardening of a material on freezing, usually, in liquid nitrogen. However, there exist some polymer systems, for which the application of the procedure is not suitable due to low differences in the toughness of the individual components in the frozen state. A new procedure of the fracture surface preparation is described, based on a specific property of polymer materials, namely up to a three-decade difference in the Young modulus below and above the glass transition temperature. According the the procedure, the fracture surface is prepared at a temperature at which the matrix is soft (sufficiently high above the glass transition temperature) and the inclusions are hard (below the glass transition temperature) at the same time. Especially at a low volume fraction of the hard dispersed phase a relatively smooth and distinct fracture surface is obtained, the interpretation of which presents no problems. The method has been successfully tested for several systems, such as, silicon rubber/hard methacrylate copolymer, EPDM rubber/inorganic filler, EPDM rubber/polypropylene, liquid rubber/epoxy, and ABS/inorganic filler.

1. Introduction

It is very well known that polymer material properties strongly depend on its supermolecular structure (morphology) [1, 2]. It is then obvious that to interpret and predict the behaviour of a given material, one has to gather information on its supermolecular structure by morphology investigations.

There exist a number of experimental techniques to reveal the polymer morphology (cf. [1]). Among them, microscopic methods are the most frequently used. To picture the tiny structural units in the minority phases of multi-phase polymer systems, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) with appropriate preparation techniques serve as very useful tools [3].

SEM is very often preferred to TEM mainly because of the easiness in both the preparation and observation steps. As polymers are metal-coated for the SEM observations, only topographical contrast is obtained. As a result, only structurally developed surfaces can be observed.

Fracture surfaces are very popular for disclosing the interior structure of bulk polymer samples. They are easy to obtain, very often being a product of previous mechanical tests. However, the preparation of fracture surfaces always involves sample deformation, also in the case of a brittle fracture. Thus, the fracture surface morphology reflects both the interior structure of the sample and the deformation processes preceding the

fracture. To obtain information on the entire sample morphology, the two influences have to be separated.

The aim of this article is to propose a new method for fracture surface preparation developed to disclose the bulk morphology, namely, fracturing above the glass transition temperature of the sample matrix. The method is based on traditional fracture surface investigations and on the correlation of fracture surface morphologies obtained under varied fracturing conditions. Several examples illustrate the method.

2. Experimental details

Fracture surfaces were produced on samples similar to those used in impact testing. Samples were provided with a notch on the shortest side of their cross section and were fractured in bending (hard materials) and extension (soft materials) at various temperatures.

Fracture surfaces were sputter-coated with a gold layer about 10 nm thick or vacuum-evaporated with a C/Ag layer and observed in a scanning electron microscope.

3. Results and discussion

3.1. Fracture surfaces of homogeneous materials

Homogeneous amorphous polymers do not possess any interior supermolecular structure. Fracture surfaces of such materials, however, show some features given by the state in which they were fractured depending on a
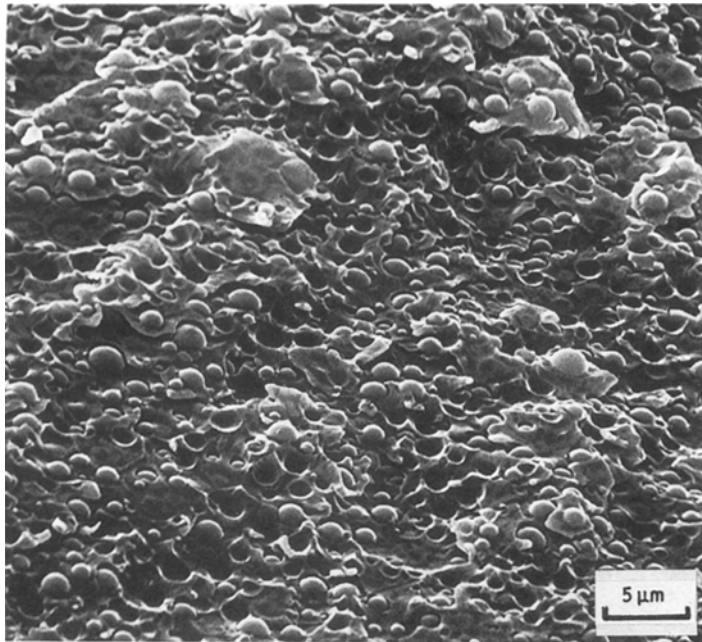
Figure 1 Fracture surface of an epoxy with rubber particles: low interfacial adhesion.
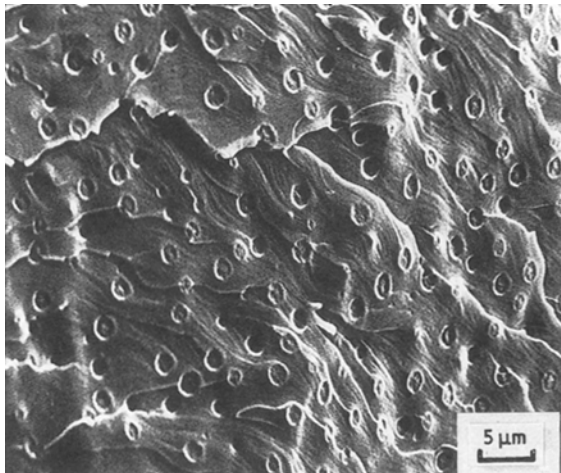

Figure 2 Fracture surface of an epoxy with rubber particles: higher interfacial adhesion.
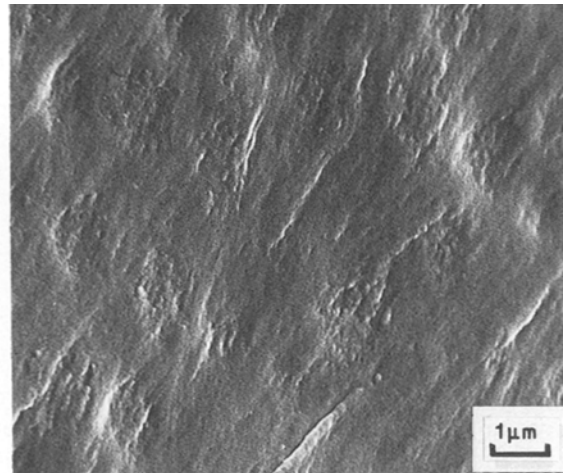

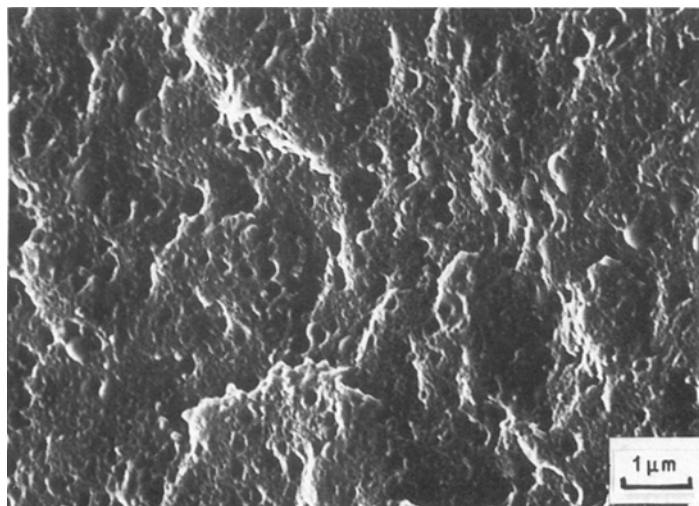*Figure 3* Fracture surface of an epoxy with a liquid rubber: rubber partially dissolved in epoxy matrix.

Figure 4 Fracture surface of an ABS copolymer at liquid nitrogen temperature.

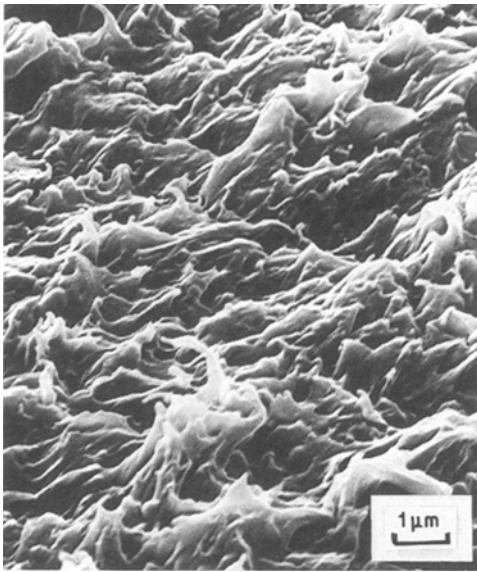Figure 6 Fracture surface of an epoxy/liquid rubber system after the phase inversion.

Figure 5 Fracture surface of an ABS copolymer at room temperature.

number of parameters, e.g. molar mass (degree of crosslinking), glass transition temperature, deformation rate, etc. Brittle materials like poly(methylmethacrylate) and polystyrene, in which plastic deformation occurs prior to fracturing (crazing), show a pronounced formation of fracture curves [4]. The curves on the fracture surfaces are not a consequence of any structure feature, they are only a product of the crack spreading through the breaking sample (though in their centres they can reveal sporadic fracture precursors). Extremely brittle materials like crosslinked epoxies [5] and hard organic glasses [4] show fracture curves in the form of lines oriented in the direction of the spreading crack. Fracture curves can be found on fracture surfaces, if the sample is fractured in the glassy state, i.e. well below its glass transition temperature.

A marked difference is observed when examining notched fracture surfaces of amorphous polymers well above the glass transition temperature, i.e., in the state of rubber elasti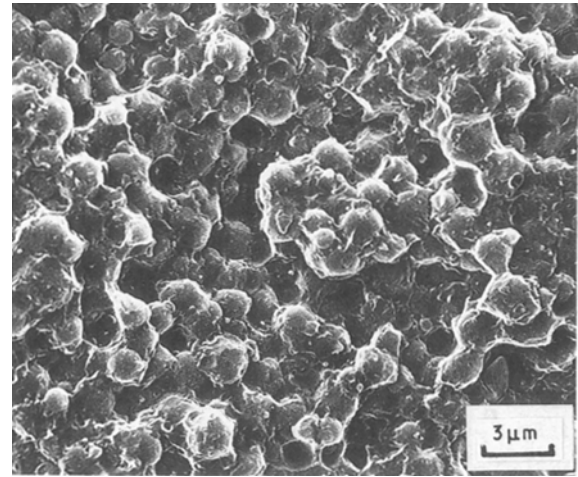city. Fracture surfaces are usually flat and smooth with hardly any trace of a spreading crack. The fact will be used to improve the visibility of particles in polymer composites (Section 3.3).

3.2. Fracture surfaces of particulate composites with a hard homogeneous matrix

Simple composites of a hard homogeneous amorphous matrix with evenly distributed soft rubber particles show differences depending on the interfacial adhesion of both components. In the systems with low interfacial adhesion we obtain a clear-cut fracture surface picture (Fig. 1).

Fracture paths follow the interface between the matrix and the rubber particles, and the particles can be traced (distinguished) without difficulties. Both spherical particles and the dimples remain after the particles are observed on the fracture surfaces.

When a similar system (epoxy/liquid rubber) but with higher interfacial adhesion of the two phases is fractured at room temperature, the fracture crack proceeds through the rubber particles. Particles mark the fracture surface so that it is possible to follow their
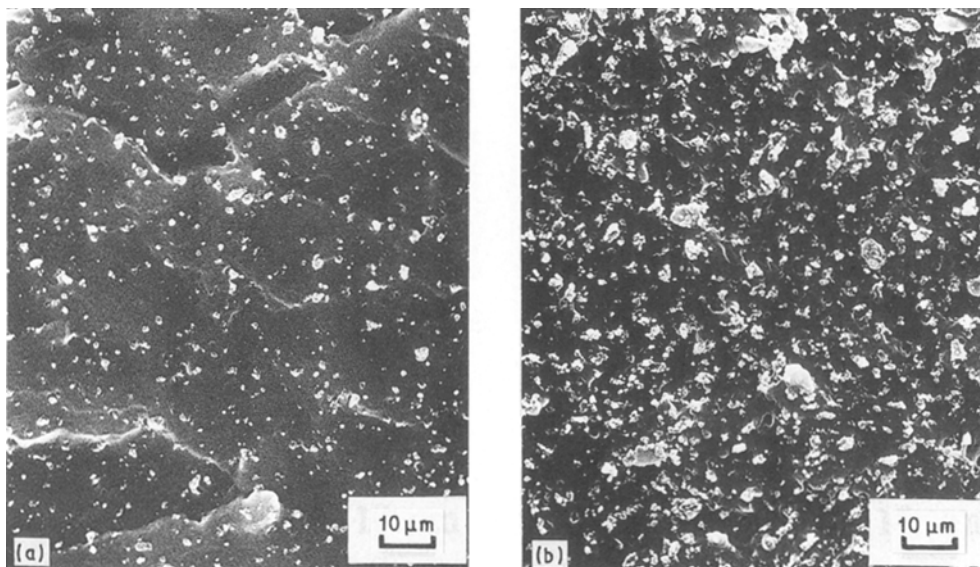

Figure 7 Fracture surface of a system silicon rubber/hard methacrylate copolymer, (a) lower and (b) higher copolymer content.
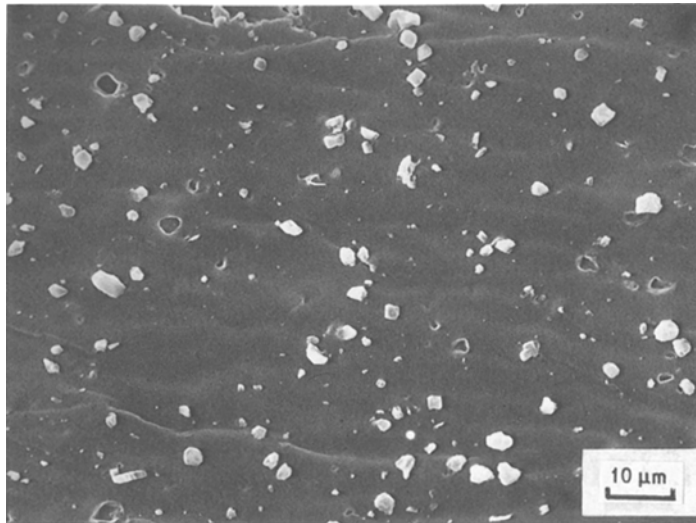
size and position in the matrix, but no true particles can be observed directly (Fig. 2). In a system with an even higher interfacial adhesion, in which the rubber phase was partially dissolved in the epoxy matrix, the marking of the fracture surface by the domains is still less pronounced: only waving of the fracture surface in the place of softer domains can be observed (Fig. 3).

High and nearly equal moduli of the matrix and the particles in the glassy state (well below the glass transition temperatures of both constituents) are the reason why the fracture surface is mainly modified due to the fact that there exist differences in the shrinkage of the individual phases when the sample is cooled to the fracture temperature. Rubber particles of an ABS copolymer can be revealed in this way (although with some difficulties) by fracturing at the liquid nitrogen temperature (Fig. 4).

It would seem that a substantial difference in the moduli of the individual constituents is a sufficient condition for obtaining a suitable fracture surface to analyse the phase structure. However, this is not true in some cases, e.g. when crazing occurs in the matrix, as in ABS copolymers fractured at room temperature (Fig. 5). Deformation structures then overwhelm the fracture surface morphology and no conclusions can

be drawn on the phase structure of the material under investigation.

3.3. Fracture surfaces of particulate composites with a soft homogeneous matrix

3.3.1 Conventional route

In contrast to the fracture surface of a notched sample of an amorphous polymer well above its glass transition temperature, hard particles immersed in a soft matrix yield a fracture surface which is marked almost exclusively by the particles themselves. Particles are sometimes covered with remnants of the matrix as in the case of an epoxy/liquid rubber system after phase inversion [7] (Fig. 6), but very often they are revealed as such, perhaps because of low interfacial adhesion, and the percentage of particles on the fracture surface corresponds to their amount in bulk [8] (Fig. 7).

Similar conditions are met both in a system of an EPDM rubber and an inorganic filler (Fig. 8) and in the same matrix with a low concentration of harder polypropylene particles (Fig. 9), which simultaneously shows that crystalline polyproplene (which is only slightly harder than the matrix), when fractured, shows the same effect as the relatively very hard inorganic filler.
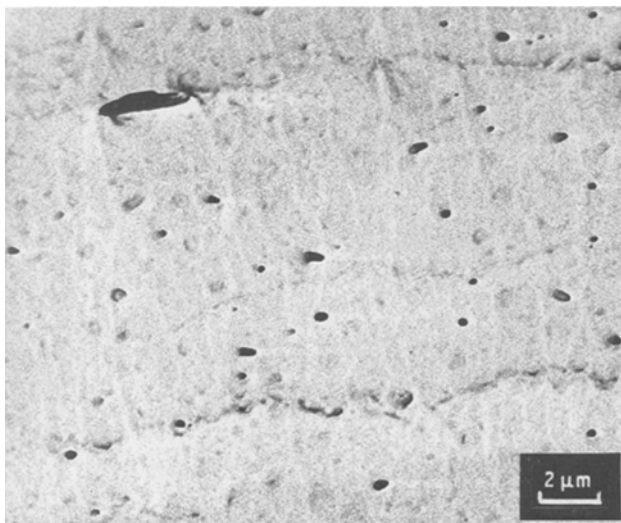
3.3.2. Non-conventional route

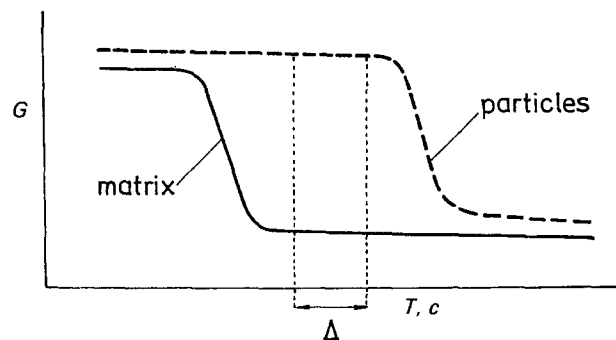It is obvious that the results described above can be generalized to develop a new method for revealing the

Figure 9 Fracture surface of a EPDM rubber with a low content of polypropylene.

Figure 10 A sketch of moduli (G) conditions appropriate for the method using the soft-matrix fracture: region Δ in the temperature (T) or concentration (c) dependence can be exploited.
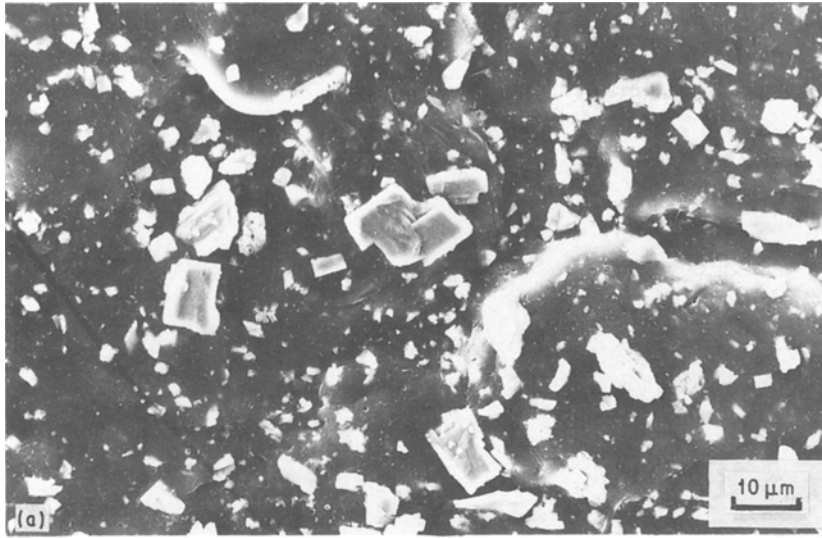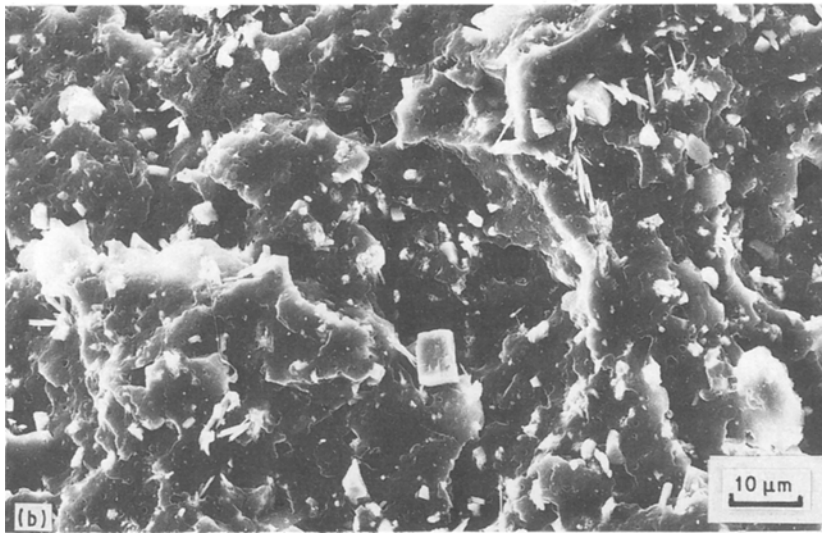
morphology of composite systems, based on an examination of the fracture surfaces of systems with a soft matrix. The fracture surface has to be obtained in such a state of the material when the matrix has a low modulus and the inclusions are of high modulus (Fig. 10, region Δ). The difference in the moduli can be obtained by varying the sample temperature or any other parameter defining its state, e.g. the concentration of low molecular weight components.

Polymer composites deformed and fractured at a temperature close to the melting point of the matrix may serve as a good example of the method. In contrast to the room temperature fracture or low temperature fracture, when the deformation structures prevail, the high temperature fracture (with a softened matrix) yields filler particles distributed on the fracture surface (Fig. 11). Polypropylene, being a crystallizable polymer, contains a high amount of the
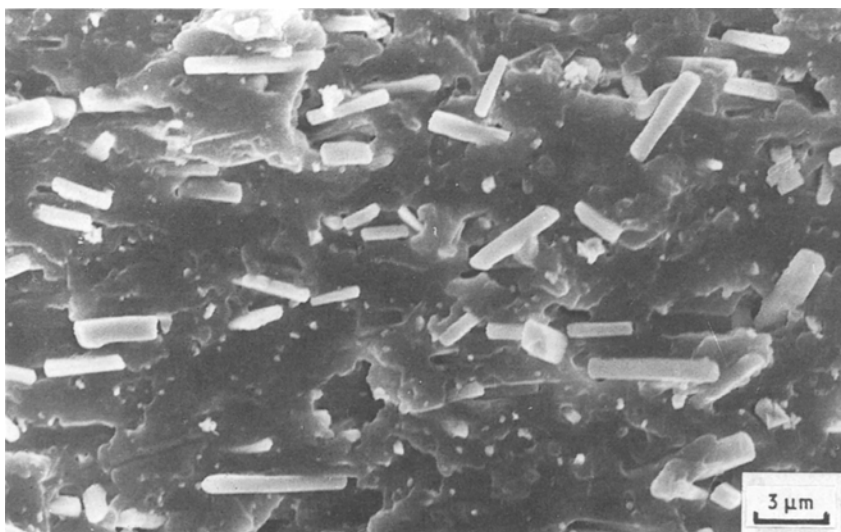

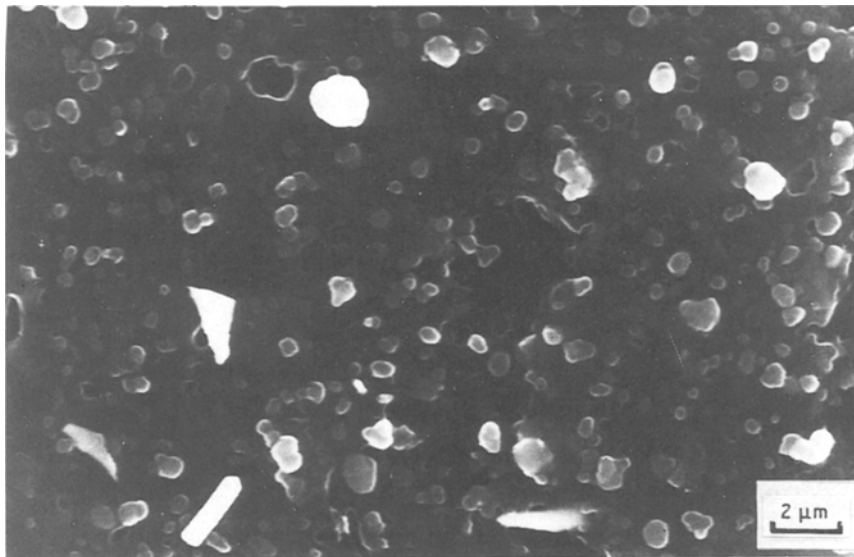*Figure 12* Soft matrix fracture of a flame-retardant ABS polymer (fracture surface prepared at 115° C, SEM).

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crystalline phase above the glass transition and below the melting temperature, which prevents the material from being as soft as amorphous polymers in the corresponding state. Successful results can therefore be obtained only after the crystallites have melted, i.e. at temperatures close to the melting point.

Additional examples are a flame retardant ABS polymer after fracturing at 115° C which shows clearly the shape and size of particles (Fig. 12), and a carbon black modified rubber fractured at 150°C (Fig. 13).

Another example was presented earlier [9]. In an ABS copolymer, soft rubber particles were hardened by osmium tetroxide treatment and the sample was then notched and fractured at 130°C. This temperature is well above the glass transition temperature of the styrene–acrylonitrile matrix, but the stained particles remain hard, so that the conditions for the relation of the moduli (Fig. 10) are fulfilled.

4. Conclusions

1. While homogeneous hard materials yield fracture surfaces marked by fracture curves, fracture surfaces of homogeneous soft materials are smooth.

2. Composites of a soft matrix with particulate hard fillers yield fracture surfaces which reveal the particles, and the particle distribution corresponds to their content in the sample.

3. Soft matrix fracture surface is convenient for studying the morphology of polymer composites.

4. By varying temperature (or some other state parameters), a sample state can be reached in which the matrix is rubber-like while the particles are hard. Fracturing under that condition may be helpful particularly in those cases when other morphological methods fail.

5. With crystalline polymer matrices, softening occurs only at a temperature close to the melting point.

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