Particle entrapping by crazes in HIPS

C. Maestrini, L. Castellani, M. Merlotti and M. Vighi
Enichem Polimeri, Mantova Research Centre, Via Taliercio 14, 46100 Mantova, Italy
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Plastic deformation in two high impact polystyrenes containing mainly small particles (average size $<1\ \mu m$) with different internal structures (core–shell, salami) has been investigated by means of transmission electron microscopy of crazed films produced using a modified procedure derived from the copper grid technique first introduced by Lauterwasser and Kramer. General evidence of the small particles being entrapped inside the crazes is presented.

(Keywords: high impact polystyrene; rubber particles; crazing; transmission electron microscopy)

Introduction

It was recognized long ago that the tensile yielding of polystyrene (PS) goes through the formation of crazes[1]. The increase in toughness of high impact polystyrene (HIPS), with respect to the PS homopolymer, is related to the effects of the rubber particles on the crazing mechanisms. It is generally agreed that the rubber particles act as craze initiators, promoting the nucleation of several crazes[2]; some authors also propose that the particles can function as craze terminators, avoiding the changeover of crazes into cracks[2]. Additionally it has been noted that below a critical particle size ($\sim 1\ \mu m$) improvement in material toughness is negligible[3]; submicrometre rubber particles seem to be ineffective either in initiating[4] or terminating crazes[5].

In this communication evidence of the interaction, different from nucleation or termination, between crazes and small rubber particles is reported in deformed thin films of HIPS observed by transmission electron microscopy (TEM).

Results and discussion

We chose to analyse two different HIPSs containing small particles: the first, (HIPS-1) contains polybutadienic core–shell particles whose number average diameter is $\sim 0.2\ \mu m$, while in the second (HIPS-2) small polybutadienic salami particles with number average diameter of $\sim 0.25\ \mu m$ are present. Both materials were diluted in a single screw extruder with PS homopolymer in order to obtain a constant level of rubbery phase ($\sim 5\%$) measured as the insoluble weight fraction (*Figure 1*). *Table 1* displays the main molecular and morphological data for the two materials.

Lauterwasser and Kramer[6] introduced a technique in which PS films cast or drawn from solutions are bonded to annealed copper grids. Deforming the grids no microtoming after the deformation procedure is needed and the observation of fresh and undamaged crazes is possible. The copper grid technique has been used in many studies[7,8] and provides a means of understanding the microscopic and molecular aspects of crazing in PS and several other polymers[9–13].

Donald and Kramer[4,13] used this approach to study the deformation mechanism of HIPS, but in this case the fact that the films were obtained from solutions introduced some difficulties. Systems like HIPS are only partially soluble: the crosslinked rubber particles do not dissolve and the original structure is hard to reproduce from casting or drawing. The distribution in space of particles, in general, is not completely homogeneous, depending on the procedure of film preparation and the real rubbery phase content in the samples is hard to calculate. Again, if not removed, the presence of excess solvent in the film can lead to the rubber particles remaining in a swollen state, thus changing their properties.

Nevertheless the idea of deforming samples already suitable for TEM observation is still appealing and we tried to apply it to our samples of HIPS with small particles using two ways of preparing films: by compression moulding and microtoming.

Films ($\sim 5\ \mu m$ thick) suitable for optical microscopy are easily obtained from standard compression moulding machines, but for TEM the film thickness should be $\leqslant 1\ \mu m$, if the accelerating voltage is <100 kV. In order to produce films as thin as possible we cut fragments using a microtome: the fragments had an approximate thickness of 20–30 μm and a surface area of ~ 0.5–$1\ mm^2$. These fragments were inserted between two glass slides. The glass slides were then introduced in a compression moulding machine and heated to 200°C without load for 15 min, then a load of ~ 2000 kg was applied for 20 min. The compression chamber was rapidly cooled and the glass slides removed: in this way a film with a thickness of $<1\ \mu m$ was obtained.

Using the techniques of microtoming and cryomicrotoming it is possible to obtain films $<0.1\ \mu m$ thick. Increasing the film thickness it is possible to also increase the surface area of the slice cut. We observed that the optimum between film thickness and usable surface was achieved with films $\sim 0.5\ \mu m$ thick and surface area of 0.5–1 mm^2.

Films prepared according to the two procedures were then deposited on pretreated copper grids (as described by Lauterwasser and Kramer[6]). In order to promote

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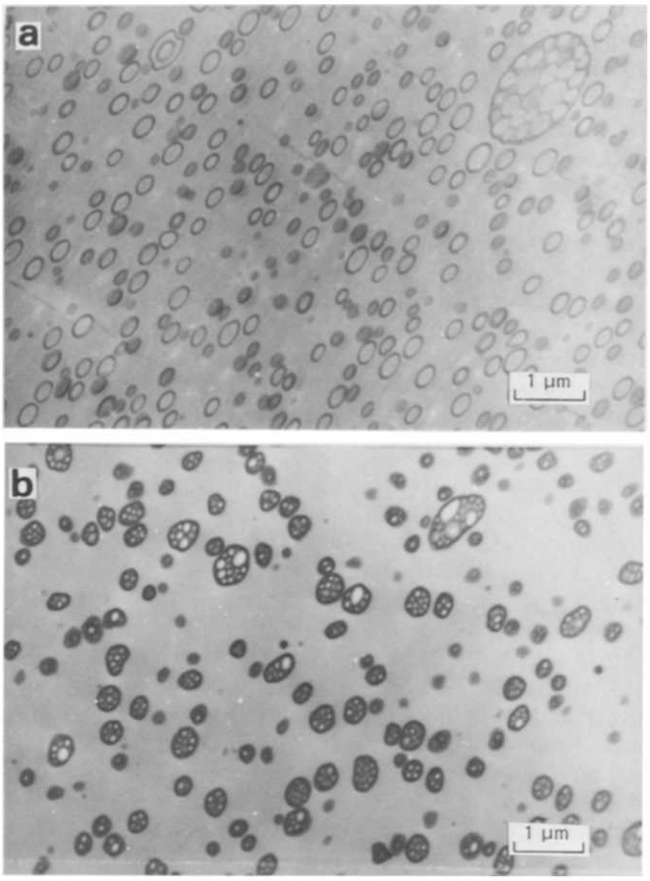

Figure 1 TEM micrographs of (a) HIPS-1 and (b) HIPS-2

Table 1 Characteristics of the HIPS samples

	PS phase		Rubbery phase	
Material	M_w[a] ($\times 10^{-3}$)	M_w/M_n[a]	Total amount (%)	Particle diameter (μm)
HIPS-1	170	~2	5	~0.2
HIPS-2	190	~2	5	~0.25

[a] M_w, weight average molecular weight; M_n, number average molecular weight

adhesion between the films and the coated grids, they were put in an oven at 110°C overnight: a temperature higher than the glass transition temperature of PS assured the adhesion between PS molecules in the HIPS films and those on the grids. Films and grids were, at last, strained uniaxially at room temperature with a strain rate of $\sim 10^{-4}\,\mathrm{s}^{-1}$ up to a deformation for which visible crazing took place inside the samples. Grid portions were cut and observed by TEM at an accelerating voltage of 100 kV. If necessary the films were stained using OsO_4 according to Kato[14]; the staining procedure followed the deformation.

In the case of the relatively thick films obtained by compression moulding, we estimate that the craze structure should be very similar to that in a bulk sample. In the case of films obtained from microtoming, it is perhaps questionable that the extreme thinness of the slices and the possible presence of sectioned particles could modify the stress field during the deformation and, consequently, the features of the formed crazes. However, observations of several samples obtained by both techniques and the impressive equivalence of the examined phenomena indicate that the results are not simply artifacts due to the preparation procedure.

In HIPS-1 an extensive study of the films did not show any craze nucleation due to the small particles: the crazes originated at the surface of dust particles or around big rubber particles that were present, in a small percentage, in the material. In HIPS-2 it is impossible to exclude the fact that the small particles had produced a contribution to the craze nucleation: it was hard to separate particles giving rise to new crazes at their borders from those which interacted with existing crazes. However, the different craze initiation capability of the two materials, that can be ascribed either to the different particle size, particle size distribution and/or to the different internal structure of the particles themselves, is not directly related to the main topic of this communication and we will not discuss it further.

What is unambiguous is that in both materials analysis of significant regions of the deformed films did not reveal any evidence for the termination of crazes induced by the small particles. *Figures 2* and *3* show crazes in HIPS-1 and HIPS-2, respectively. It is possible to recognize the presence of rubber particles inside the crazes.

We propose at this point some qualitative conjectures for the plastic deformation of HIPS with small particles. After the nucleation the craze grows in thickness by drawing fresh material into existing fibrils[6] and in area

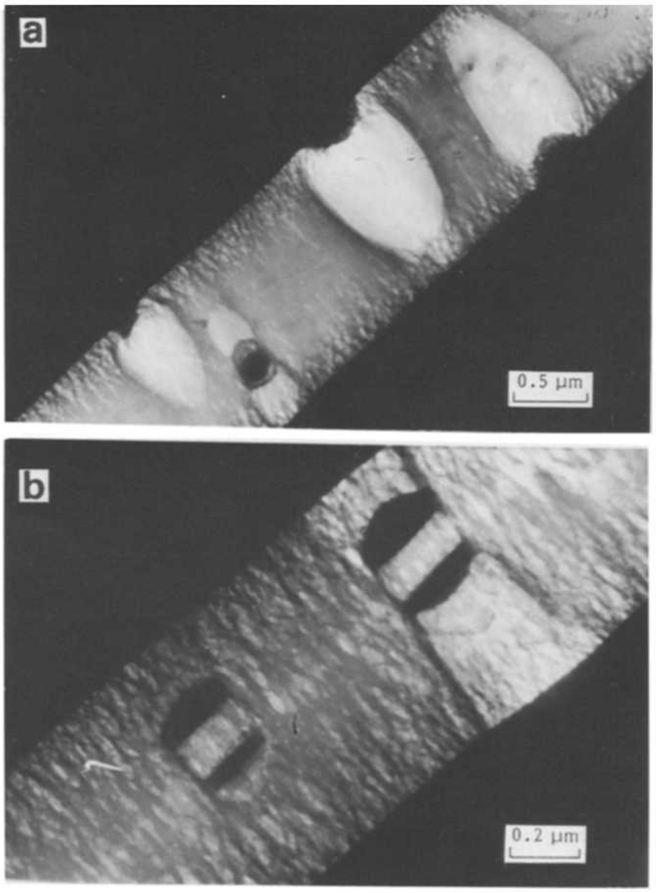

Figure 2 TEM micrograph of a craze in a film of HIPS-1. The film is microtomed from a bulk sample according to the described procedure and has a thickness of <1 μm. In (a) entrapped particles and regions of local fibril break-down are visible. In (b) entrapped and broken particles lying on the midrib zone of the craze are visible

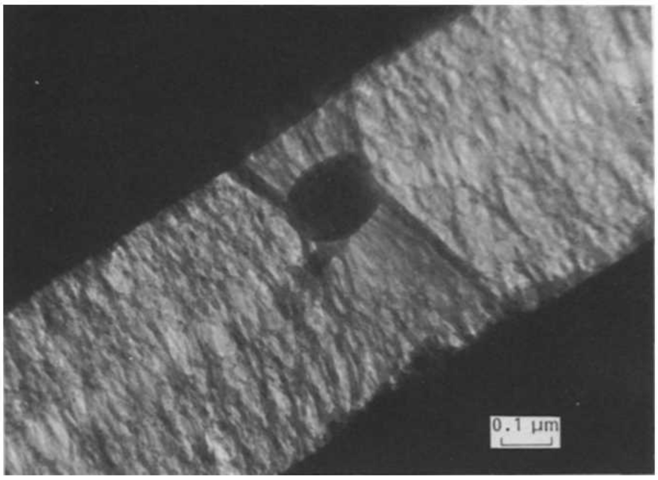

Figure 3 TEM micrograph of a craze in a film of HIPS-2. The film is microtomed from a bulk sample according to the described procedure and has a thickness of <1 µm. An entrapped particle is visible

as the craze tip advances and the expansion of the craze periphery generates new fibrils. The rubber particles can then come in to contact either with the craze–bulk interface, during the drawing mechanism, or with the advancing craze tip.

In the first case, when the particles cross the active layer at the border of the craze–bulk interface[15], we can imagine that, if they are small enough not to stop the drawing process, they could be driven inside the craze by the same forces that control the growth of the fibrils. For HIPS-1 some local fibril break-down has been observed corresponding to the large number of entrapped particles, testifying that fibril growth has been temporarily stopped during the crossover at the interface, while in HIPS-2 the percentage of entrapped particles connected to unbroken fibrils is higher. Furthermore a distortion in the structure of the fibrils is visible around many entrapped particles.

On the other hand, when the particle is on the path of the craze tip, it experiences an extremely large deformation: in general the extension ratio at the craze tip can double that of the fibrils[6,16]. It is possible then that the high deformation could be enough to cause the fracture of the rubber shell. The broken, dark shells that are visible in *Figure 2b* lie, in fact, on the midrib zone of the craze and this means that they have been in contact with the craze tip[7]. An appreciable number of broken shells inside the crazes is visible in the deformed films of HIPS-1 and they all settle on the midrib zone or in its vicinity, confirming our above suggestion. In HIPS-2 no broken particles on the midrib are observable: the particles are intact, nonetheless their deformation at the midrib, roughly judged by the picture contrast, seems greater than elsewhere. The case of HIPS-2 is complicated by the fact that it is not clear if the particles lying on the midrib are entrapped or if they are the nucleating agents from which the craze itself developed.

Conclusions

The plastic deformation in two HIPSs containing rubber particles having average size below 1 µm and different structures (core–shell, salami) has been observed by means of a modification of the copper grid technique first introduced by Lauterwasser and Kramer[6].

Our observations confirmed the views asserting that small particles are poorly effective in nucleating and stopping crazes. However, we observed that they can interact with the growing and widening of the crazes: the small particles are completely entrapped in the fibrillar texture. The features of the entrapping process were briefly discussed.

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