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Effects of morphology on mechanical properties of styrene–butadiene–styrene triblock copolymer/methyl methacrylate–styrene copolymer blends

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The morphology and mechanical properties of the moulded polymer blends of poly(styrene-*block*-butadiene-*block*-styrene) triblock copolymer (KR05) with methyl methacrylate–styrene copolymer (MS-200) were investigated. The KR05 phase of the blends exhibits lamellar morphology and phase separation from the MS-200 phase, and mechanical properties of the blends depend on the microstructural orientation and orderliness. Ductile KR05 is toughened by incorporation of brittle MS-200, and synergistic improvement of toughness is observed for the KR05-enriched blends. Under tensile stress excessive stress concentration leading to critical failure of the blends could be restrained effectively by the far-reaching morphological changes with shear yielding of KR05 lamellae, cavitation in the polybutadiene phase and debonding in the KR05/MS-200 interfacial region. The synergistic effect of toughening is much more prominent for the blends with oriented KR05 lamellae and spherical MS-200 domains than for those with crooked KR05 lamellae and wavily elongated MS-200 inclusions, since on impact the former blends could dissipate larger energy through dominant expansion of the polybutadiene lamellar spacing and delocalized debonding at smooth KR05/MS-200 interfaces. The latter blends show enhanced rigidity and heat resistance since the crooked lamellae offer more resistance against the deformation because of the close and complicated networks of the polybutadiene phase tangled with the rigid polystyrene phase, and because of more efficient interconnection of elongated MS-200 domains. Copyright © 1996 Elsevier Science Ltd.

(Keywords: styrene–butadiene–styrene; methyl methacrylate–styrene; impact strength)

INTRODUCTION

It is well known that styrenic polymer blends find general acceptance in the commodity plastics field because of their advantages such as good processability, balanced properties and cost-effectiveness. Among the blends of commercial use, blends composed of a poly(styrene-*block*-butadiene-*block*-styrene) triblock copolymer (KR05, Phillips Petroleum Co.) with a methyl methacrylate–styrene copolymer (MS-200, Nippon Steel Chemical Co.) cut a unique figure, since simple melt mixing of the two unmodified polymers can lead to a good degree of mixing of the blends without any compatibilizing agents and the injection-moulded blends show a synergistic improvement in toughness with the clearness from the parent polymers KR05 and MS-200[1]. The Izod impact strength of the injection-moulded KR05/MS-200 blends goes through a maximum between 10 and 30 wt% MS-200, reaching a value three times as high as that of injection mouldings of the two parent polymers. This toughening phenomenon is noticeable since for the KR05/MS-200 blends, brittle spherical inclusions (MS-200) toughen the ductile matrix exhibiting lamellar morphology (KR05), which completely differs from conventional rubber-toughening phenomena. When tensile stress is applied to injection mouldings of the KR05-enriched KR05/MS-200 blends, the blends form numerous microcavities in the PB (polybutadiene) phase of the KR05 lamellar matrix and in the KR05/MS-200 interfacial region[1]. Such cavitational breakdown could restrain excessive stress concentration to delay fatal crack propagation. This should lead to synergistic toughening of the KR05-enriched blends since analogous cavitation cannot be seen in the injection-moulded specimen of neat KR05 under tensile stress[2]. Some ductile polymers such as PC (polycarbonate), PBT (poly(butylene terephthalate)) and nylon-6 are also toughened by the incorporation of brittle polymeric particles[3–7]. The ductile commodity polymer PE (polyethylene) is also reactively toughened by the inclusion of brittle PMMA (poly(methyl methacrylate))[8]. However, these methods enhance toughness through cold drawing of the brittle polymeric inclusion, in a different manner from microcavitation of the KR05/MS-200 blends.

Many researchers have found that mechanical properties of styrene–butadiene block copolymers rely heavily on their phase-separated morphology. This is well exemplified by the large difference in mechanical behaviour between films cast from different solvents, one with lamellar morphology and another with cylindrical morphology, for the same styrene–butadiene block copolymers[9–12]. Mechanical properties of the copolymer also depend on orientation of the microdomain structure. A noticeable difference of mechanical properties is found between injection mouldings with oriented lamellae and compression mouldings with unoriented lamellae for the same styrene–butadiene block copolymer[13]. When oriented domain morphology of a styrene–butadiene block copolymer is formed in a specimen, significant anisotropy of mechanical properties in the specimen is often seen[2,14–16]. Therefore, it is easily inferred that for KR05-enriched KR05/MS-200 blends, lamellar orientation of the KR05 matrix could have great influence on the mechanical properties of the blends.

Orientation of MS-200 dispersed domains of the blends must also be influential on the mechanical properties since those of many polymer alloys are highly sensitive to orientation[17,18] and orientation-induced connectivity[19–21] of the dispersed domains. Mechanical properties of KR05-enriched KR05/MS-200 blends, accordingly, could depend on the two morphological factors, lamellar orientation of the PS (polystyrene) and the PB phases microphase-separated in the KR05 matrix, and domain orientation of the MS-200 phase macrophase-separated from the KR05 matrix. Note in this paper that the terms micro- and macrophase separation indicate the intra- and interpolymer phase separation, respectively[1,22,23].

In this paper, effects of oriented morphology on toughness and other mechanical properties have been examined for compression and injection mouldings of KR05/MS-200 blends. The comparison between the two mouldings is very useful to investigate the morphology–property relationship, because a large difference of shear stress induced during mould filling could cause a noticeable difference of oriented domain morphology between the two mouldings[24].

EXPERIMENTAL

Materials

The commercial star-shaped poly(styrene-*block*-butadiene-*block*-styrene) triblock copolymer (SBS) and a commercial methyl methacrylate–styrene copolymer (MS) used here are the same polymers as chosen in the author's previous study[1]. The SBS is manufactured by the Phillips Petroleum Co. under the trade name of K-Resin KR05. The number- and weight-average molecular weights (M_n and M_w), their polydispersity coefficient (M_w/M_n), and the weight fraction of PB block component for KR05 used are 5.23×10^4, 1.51×10^5, 2.89 and 0.245, respectively[1]. KR05 was melt mixed with commercial MS supplied by Nippon Steel Chemical Corp. under the trade name of MS-200. M_n, M_w, M_w/M_n and the weight fraction of styrene component for MS-200 used are 1.00×10^5, 2.30×10^5, 2.30 and 0.78, respectively[1]. The polymers were used as received.

Sample preparation

Extrusion. The extruder, conditions and designation of the resultant pellets are the same as those adopted previously[1]. KR05 was melt mixed with different weight ratios of MS-200 dried in an oven at 80°C for 4 h to avoid hydrolytic degradation. Melt mixing was carried out with a twin-screw extruder (partially intermeshing, counter-rotating, $D = 20$ mm and 25D full-flighted screw) at 200°C with a screw speed of 70 rev min^{-1}. Extruded strands were quenched in a water trough and pelletized. As-received KR05 and MS-200 were also extruded to give the same thermal history as the blends. Pellets extruded once are termed once-extruded pellets.

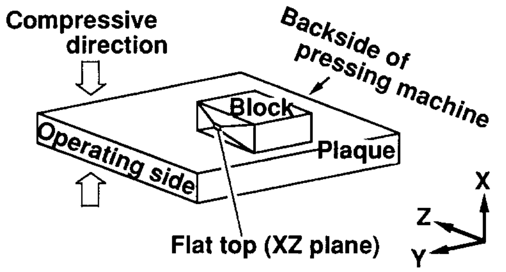

Figure 1 Diagram showing a pyramid-shaped piece cut from a compression-moulded plaque. The X axis is fixed in the compressive direction. A flat top on the piece was made for microtoming parallel to the XZ plane

Good dispersion on extrusion was not attained since the extruder used was equipped with no effective mixing sections on full-flighted screws[1]. The degree of mixing of once-extruded KR05/MS-200 blends was improved through re-extrusions, in which dried once-extruded pellets were re-extruded in the same way as mentioned above. Re-extruded pellets are termed twice-extruded pellets.

The compositions of the blends are indicated as weight percentage KR05/MS-200. For example, KR05/MS-200 (85/15) represents a blend of 85 wt% KR05 and 15 wt% MS-200.

Compression moulding. Once- and twice-extruded pellets were compression moulded at 200°C for 5 min into three types of rectangular plaques of different thickness ($150 \times 150 \times 3.0$ mm, 4.0 mm and 6.0 mm), followed by cooling in hot moulds rapidly. Cooling was carried out by running cold water through pipes in the mould clamping plates of the pressing machine in order for the mould temperature to drop down to 50°C in 3 min. The compressive direction was identical to the thickness direction of the plaques. *Figure 1* shows the geometry of a moulded plaque. For convenience the axes of coordinates are fixed on the plaque so that the X direction is identical to the compressive direction and the XZ plane is parallel to the operating side and also the back of the pressing machine used here. This directional definition on the plaque relative to the pressing machine is indispensable since the morphological information with the direction considered in this paper will be used for discussion related to mechanical anisotropy of KR05/MS-200 blends compression moulded on the pressing machine. The mechanical anisotropy should be based on the orientational anisotropy of microdomain structure of the KR05 lamellar phase of the blends[2]. This morphological anisotropy could be induced by non-uniform cooling due to unbalanced layouts of the water-cooling pipes embedded in the mould clamping plates of the pressing machine[2]. The anisotropic characteristics of the blends are not discussed in this paper, but will be dealt with in a future paper.

Compression-moulded plaques were machined along the Y and the Z directions with metal templates into impact (4.0 mm in thickness), tensile (3.0 mm) and flexural (6.0 mm) test bars. The longitudinal directions of the bars were normal to the compressive direction. The flexural test bars were also used for measurement of deflection temperature under flexural load (DTUL). All test bars were cut from the inner regions far from the sides of these plaques so that one could ignore the end effect of microdomain structure on mechanical properties. This effect is based on the disturbance of microdomain structure due to melt flow complexity near the plaque sides during compression moulding.

Materials were not injection moulded since this paper reproduces experimental data taken from a previous study on mechanical properties and morphology of injection-moulded KR05/MS-200 blends[1]. When once- and twice-extruded pellets were injection moulded into impact (6.35 mm in thickness), tensile (3.2 mm), flexural (6.35 mm) and DTUL (6.35 mm) test bars, barrel temperature, mould temperature and injection rate were set at 210°C, 40°C and 40 cm^3 s^{-1}, respectively.

Mechanical tests

The notched Izod impact strength was measured at 23°C according to ASTM D256 using a pendulum-type tester. Tensile and three-point loading flexural tests were performed on a conventional Instron testing machine at 23°C according to ASTM D638 and ASTM D790, respectively. The DTUL was measured under a maximum fibre stress of 1820 kPa according to ASTM D648. To compensate the mechanical anisotropy, two sets of test bars were machined from compression-moulded plaques in the two respective directions which meet each other at right angles, namely, in the Y and the Z directions. The resultant mechanical data for both directions were averaged.

For comparison with the mechanical data of compression mouldings, those of injection mouldings are reproduced from a previous paper[1].

Examinations of morphology

Morphology of compression-moulded blends of KR05/MS-200 was observed by transmission electron microscopy (TEM). Pyramid-shaped pieces were cut from the inner regions of compression-moulded plaques (4.0 mm thick) as shown in *Figure 1*. Apexes of the pieces were machined from regions close to the geometrical centres of the plaques and were cut off to expose surfaces of the XZ plane on the resultant flat tops. The microscopic surfaces for morphological observation were always made at fixed positions close to the geometrical centres of the plaques, and on the specified plane (the XZ plane of the plaques). When comparison was made of the morphology viewed on such surfaces, effects of morphological anisotropy as mentioned above could be ignored since these surfaces were subjected to

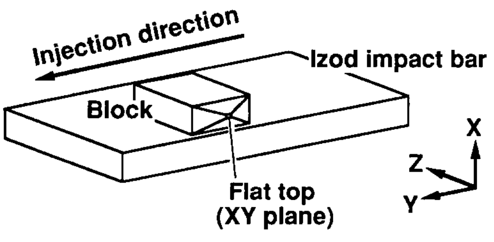

Figure 2 Diagram showing a pyramid-shaped piece cut from an injection-moulded impact bar. A flat top on the piece was made for microtoming parallel to both the thickness (X) and the injection (Y) directions

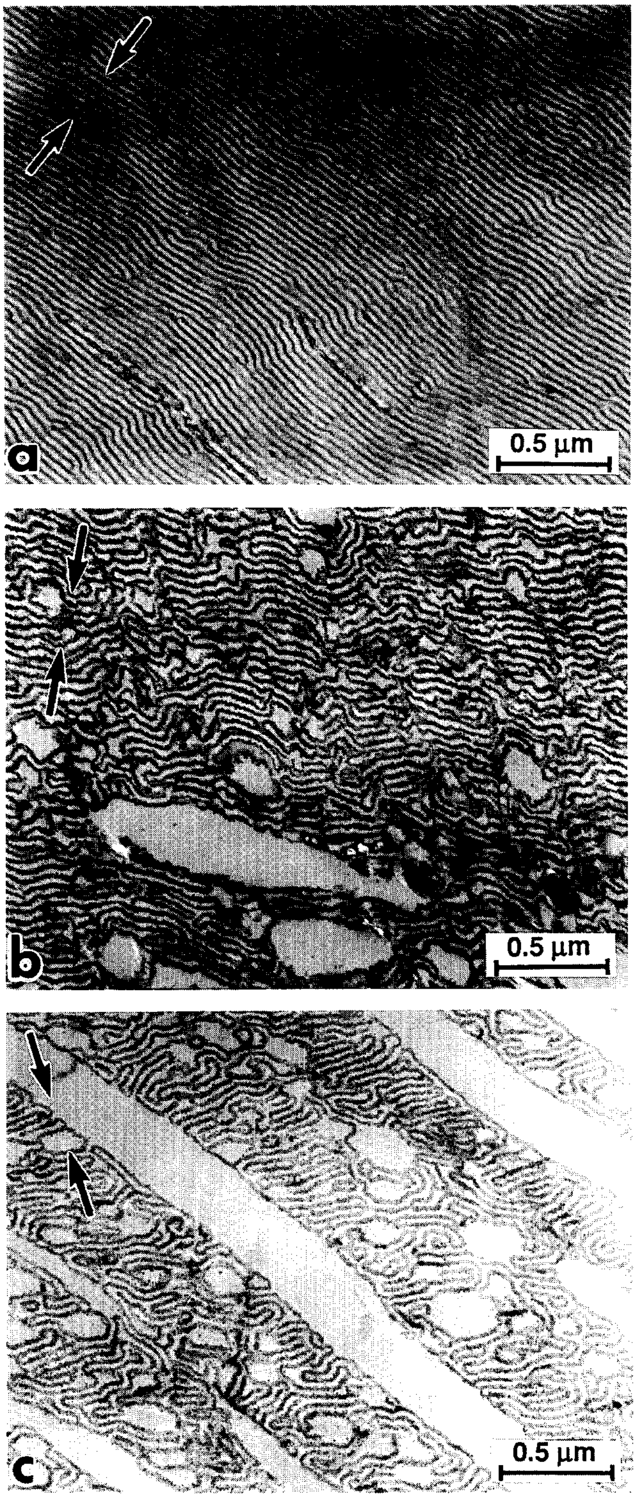

Figure 3 Transmission electron micrographs of compression mouldings of once-extruded KR05/MS-200 blends: (a) (100/0); (b) (85/15); (c) (70/30). The morphology was viewed on sections microtomed on the XZ plane (see *Figure 1*). The arrows on micrographs show the compressive directions

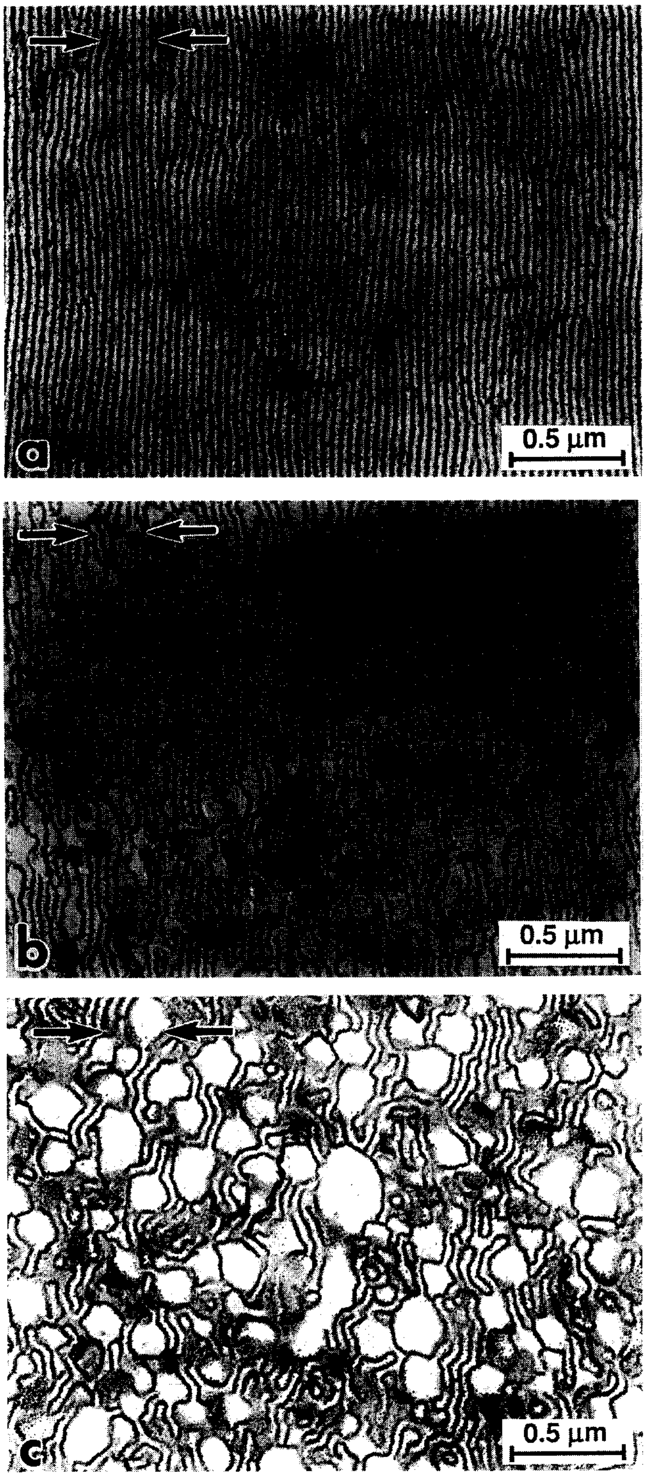

Figure 4 Transmission electron micrographs of compression mouldings of twice-extruded KR05/MS-200 blends: (a) (100/0); (b) (85/15); (c) (70/30). The morphology was viewed on sections microtomed on the *XZ* plane (see *Figure 1*). The arrows on micrographs show the compressive directions

much the same cooling history during cooling the plaques on the pressing machine used here. They were at the same geometrical position relative to the layouts of water-cooling pipes embedded in mould clamping plates of the machine.

After treatment with a 2% aqueous solution of osmium tetroxide, ultrathin sections (500 to 900 Å in thickness) were microtomed on flat tops of the pieces using an LKB microtome with a diamond knife. Sections were observed by using a Hitachi H700 transmission electron microscope at an accelerating voltage of 100 kV, and routine magnifications of 15 000 ×, 30 000 × and 100 000 × were used.

The morphology of compression-moulded bars after stress application was examined in the same way as reported previously[2].

The morphology of injection-moulded blends of KR05/MS-200 was not observed here. Their transmission electron micrographs were taken in the previous study[1], and therefore some of them were put to use here for morphological comparison with the corresponding compression-moulded blends. In order to examine morphology of injection mouldings, pyramid-shaped pieces with flat tops were cut out of injection-moulded impact test bars (6.35 mm in thickness) as shown in *Figure 2*[1]. Their morphology was observed at core regions of the bars on the plane parallel to both the thickness and the injection directions.

RESULTS AND DISCUSSION

Morphology of compression mouldings

Morphologies of compression mouldings of once- and twice-extruded pellets are shown in *Figures 3* and *4*, respectively, for neat KR05, KR05-enriched blends of KR05/MS-200 (85/15) and (70/30). They were observed on sections microtomed parallel to the compressive direction on the *XZ* plane at the core region of a 4.0 mm thick plaque (see *Figure 1*). The compressive directions are shown by the arrows on the figures. The island-matrix morphologies have three distinct phases: the unstained MS-200 dispersed phase macrophase-separated from the KR05 matrix, and the PS and the PB phases microphase-separated in KR05. A noticeable difference in MS-200 domain morphology is seen between compression mouldings of once- and twice-extruded blends with identical blending ratio. Once-extruded blends show poor dispersion of MS-200 domains, which are more diverse in size and shape than those seen in twice-extruded blends. Some MS-200 domains in once-extruded blends are comparatively large. This morphological difference reflects a difference in degree of mixing between once- and twice-extruded pellets from which examined plaques were compression moulded. As reported previously, MS-200 particles were full of size variety and showed poor dispersion in once-extruded pellets of KR05-enriched blends, but fairly good degree of mixing of MS-200 particles with narrower size distribution was observed in the corresponding twice-extruded pellets[1]. Rough sketches of the morphological features in the respective extruded pellets are kept in the compression mouldings since it seems that degree of mixing in the extruded pellets scarcely changes during compression moulding of the pellets. Comparison between MS-200 domain morphologies before and after compression moulding has suggested that the blends were neither mixed further nor demixed perceptibly during compression moulding. Degree of mixing in the pellets could not be enhanced under the compression moulding condition employed since the squeezing flow which was brought about for the first few seconds on hot pressing merely induced very low shear stress with no

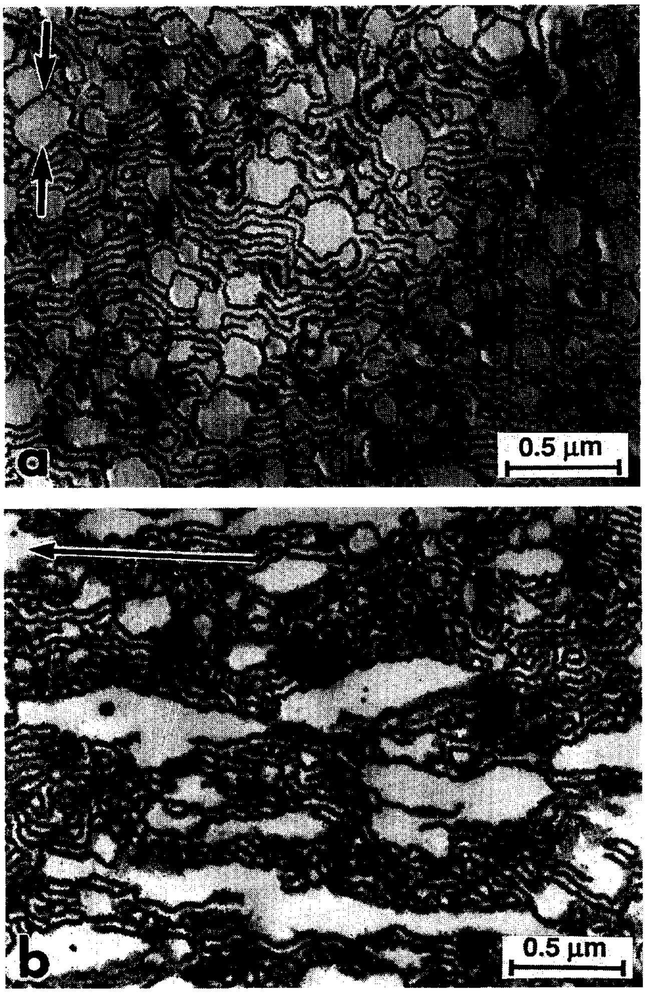

Figure 5 Transmission electron micrographs of (a) compression and (b) injection mouldings of twice-extruded KR05/MS-200 (70/30) blends. Micrograph (b) was taken in the previous study[1]. Micrographs (a) and (b) were viewed on cross-sections parallel to the XZ plane of a compression-moulded plaque (see *Figure 1*) and the XY plane of an injection-moulded bar (see *Figure 2*), respectively. Arrows on micrographs (a) and (b) show the compressive and injection directions, respectively

potential for further mixing. Significant demixing, namely, coarsening of macrophase-separated structure consequent on coalescence of MS-200 domains, also did not occur although blends were subjected to 5 min static hot pressing. This long pseudo-stagnant period at the high temperature, however, allowed the majority of elongated MS-200 domains to be transformed towards the spherical shape. This is caused by the retracting force due to interfacial tension of MS-200 to KR05. MS-200 domains of the size far above the average (several micrometres or more) seen in once-extruded pellets are hardly retracted since the extraordinarily large domains cannot be relaxed without large-scale rearrangement of polymer chains in the domains, and therefore retraction could progress very slowly.

In *Figure 5* morphology of compression mouldings of twice-extruded KR05/MS-200 (70/30) is compared with that of the corresponding injection mouldings, which was viewed in the previous study[1]. The compressive and the injection directions are shown by arrows on (a) and (b), respectively. MS-200 domains of the former are roughly spherical whereas those of the latter are elongated in the injection direction. A significant difference in the thermal history and the kinetic field on moulding between the two moulding processes should be responsible for the morphological difference between the two resultant mouldings. At the melt temperature of 200–210°C adopted, KR05/MS-200 blends should be macrophase-separated in the molten state, and on moulding the memory of the separation would not be lost and only reorientation and relaxation with the above-mentioned retraction of the MS-200 domains could occur[1]. When compression moulded, highly elongated MS-200 domains formed on the preceding extrusion[1] could be largely relaxed on 5 min hot pressing and subsequent gradual cooling in the mould (the mould temperature dropped down to 50°C in 3 min). However, when injection-moulded, MS-200 domains could be reoriented and re-elongated by intense shear flow on mould filling, and could not be relaxed well on subsequent cooling since the melt rapidly became more viscous and soon solidified in a thermodynamic disequilibrium state as the resin temperature fell rapidly in the cold mould.

One can compare detailed morphologies of compression and injection mouldings of twice-extruded pellets with higher magnification micrographs shown in *Figures 6–8*, for compression- and injection-moulded KR05s (*Figures 6a* and *b*, respectively), a compression-moulded KR05/MS-200 (85/15) blend (*Figure 7*), and compression- and injection-moulded KR05/MS-200 (70/30) blends (*Figures 8a* and *b*, respectively). Arrows on micrographs show the compressive and the injection directions for the compression and the injection mouldings, respectively. Micrographs of the injection mouldings were taken in the previous study[1]. Whether compression or injection moulded, the KR05 phase is microphase-separated, and both the stained PB phase and the bright PS phase form alternating lamellae ranging from 150 to 200 Å and from 200 to 250 Å in thickness, respectively. However, lamellar orientation and orderliness differ between the two mouldings, which is more noticeable for neat KR05 (*Figures 6a* and *b*). Lamellae of compression-moulded KR05 show ordered stratification although KR05 before compression moulding shows chaotically corrugated lamellae[1], whereas those of injection-moulded KR05 remain wavy (see *Figures 6a* and *b*). This difference of lamellar formation could be due to differences of the thermal and kinetic history on moulding between the two moulding processes. At the melt temperature of 200–210°C employed KR05 should be microphase-separated in the melt state, and the memory of the lamellar morphology would not be initiated and only reorientation and lattice ordering of the lamellae could occur[2]. When compression moulded, orientation and lattice ordering of the KR05 lamellae could be developed very well before complete solidification. The molten lamellae could be relaxed well on 5 min hot pressing and on subsequent gradual cooling in the mould. However, when injection moulded, KR05 lamellae could undulate further by intense shear flow on mould filling, and could not be relaxed well on subsequent rapid cooling.

For KR05-enriched KR05/MS-200 blends, one does not perceive at a glance a conspicuous distinction of KR05 lamellar orderliness between the compression and the injection mouldings (see *Figures 8a* and *b*). However,

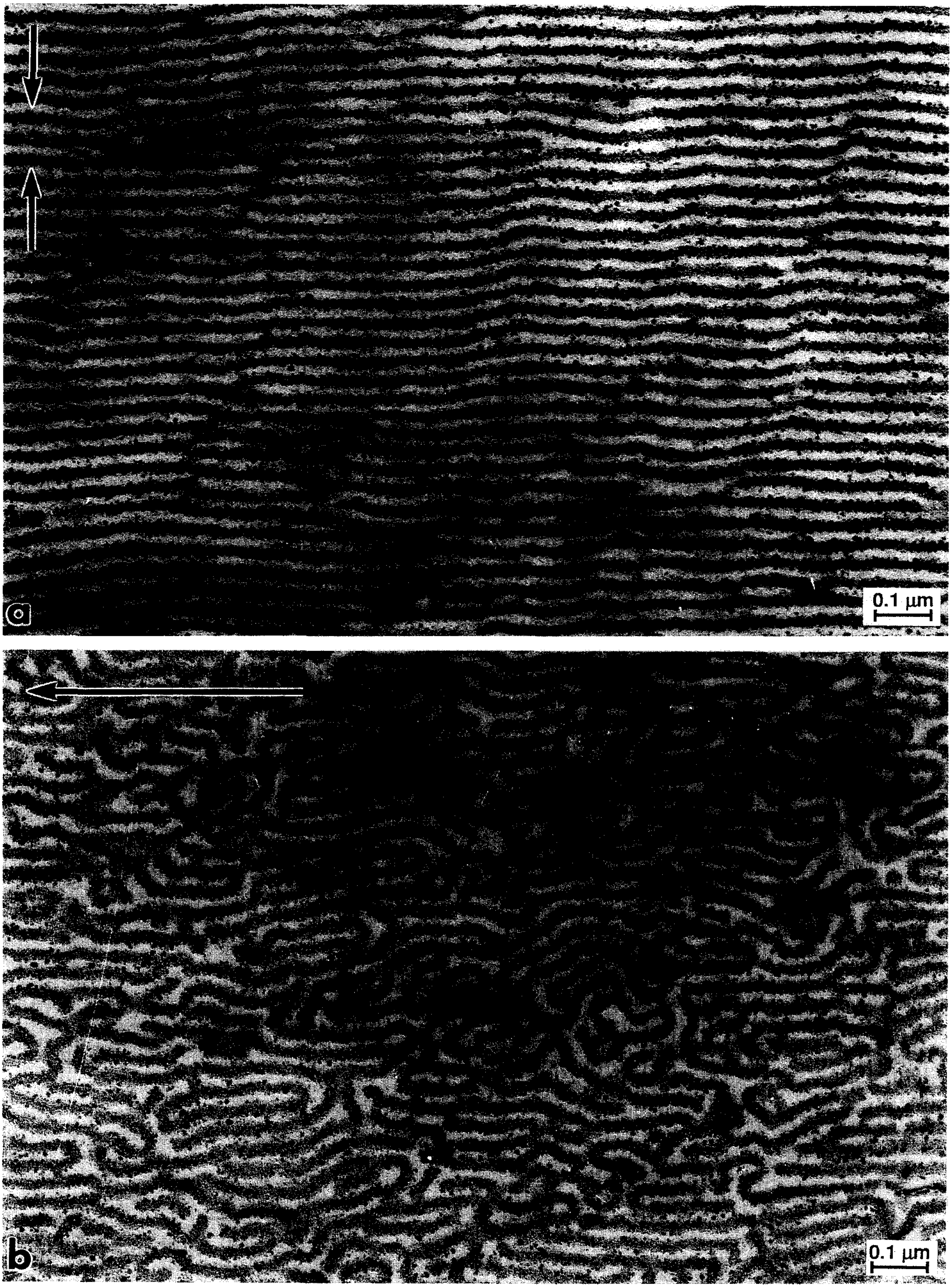

Figure 6 Highly magnified transmission electron micrographs of (a) compression and (b) injection mouldings of the twice-extruded KR05. Morphology of the compression-moulded KR05 was viewed on the *XZ* plane (see *Figure 1*) and the compressive direction is shown by a pair of arrows on the micrograph. Morphology of the injection-moulded KR05 was viewed on a cross-section parallel to the *XY* plane (see *Figure 2*), in the previous study[1]. The injection direction is shown by an arrow on the micrograph

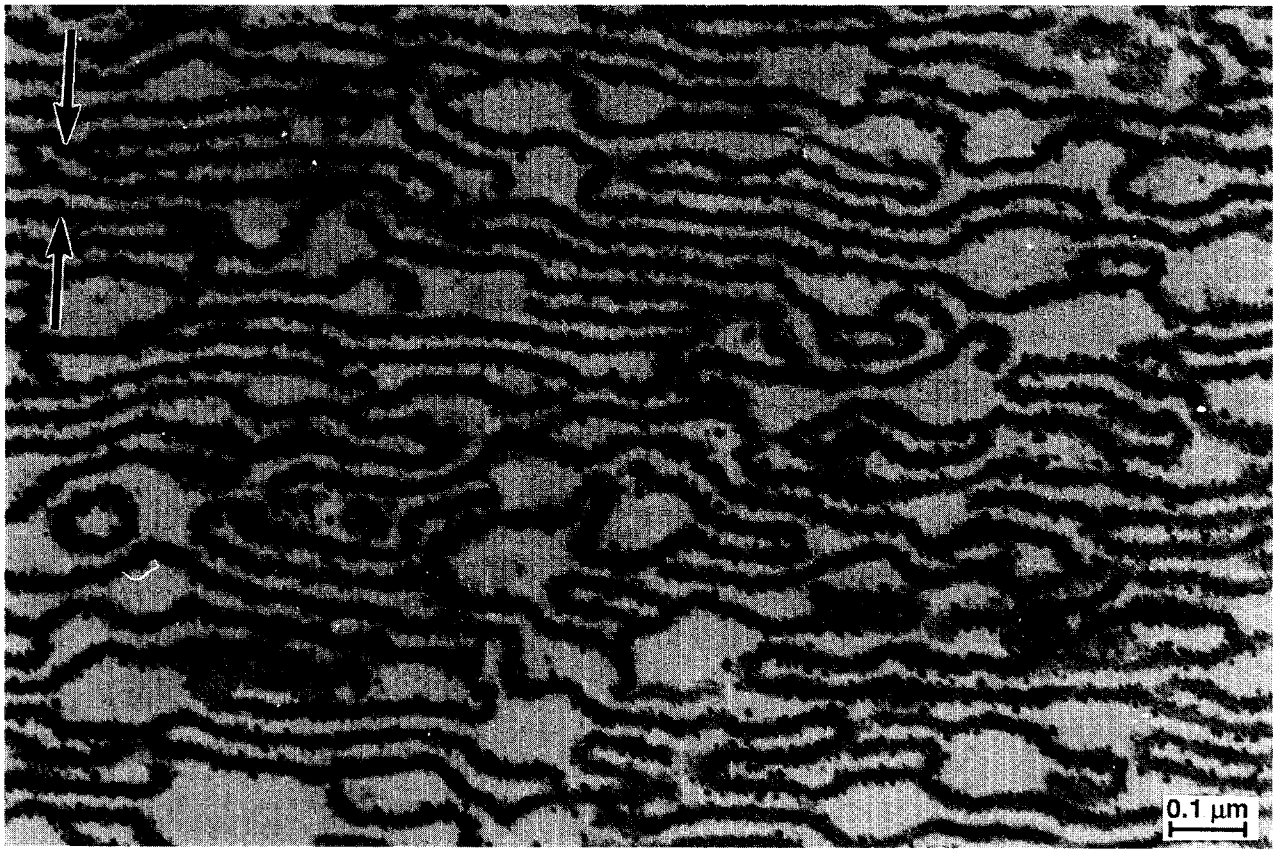

Figure 7 A highly magnified transmission electron micrograph of the compression moulding of the twice-extruded (85/15) blend. Morphology was viewed on the *XZ* plane (see *Figure 1*) and the compressive direction is shown by a pair of arrows on the micrograph

once the lamellar morphology is viewed carefully on a scale of a few tenths of a micrometre, looking at small regions as depicted with rectangular frames on *Figures 8a* and *b*, one can definitely see that KR05 lamellae of the compression-moulded blend form a more orderly layered structure in the frames than those of the injection-moulded blend. In the former the formation of long-range orderliness over the size of the frames could be disturbed by MS-200 domains scattered among the KR05 lamellae. The intermittent lamellar corrugation could be reasonable in view of the following relaxation behaviour of the lamellae on mould cooling. At the melt temperature adopted KR05/MS-200 blends should be both micro- and macrophase separated in the molten state, and on moulding the memory of both separations would not be lost and only reorientation and relaxation of the KR05 lamellae and the MS-200 domains could occur[1]. When compression moulded, the disordered phase structure formed on the preceding extrusion[1] could be significantly relaxed on hot pressing and subsequent gradual cooling, and therefore orientation and lattice ordering of the KR05 lamellae could be developed before solidification. However, MS-200 domains, which could intervene among KR05 lamellae on a submicrometre scale even in the melt, presumably disturbed long-range ordering of KR05 lamellae as temperature fell toward the glass transition temperatures (T_gs) of the PS phase of KR05 and the MS-200 phase (both T_gs are near 95°C). This could explain the formation of intermittent lamellar corrugation on a scale similar to MS-200 domain size. Injection-moulded blends show wavy KR05 lamellae even on a submicrometre scale since lamellae in the KR05 matrix phase of the molten blends were solidified in the non-equilibrium state with intense shear flow on mould filling and a steep temperature gradient on subsequent rapid cooling. Since it is most likely that thermal diffusivity of styrenic KR05/MS-200 blends is nearly identical to that of conventional styrenic polymers ($\sim 8 \times 10^{-4}\,\mathrm{cm^2\,s^{-1}}$ over T_g of PS)[25], the cooling rate of the blends after mould filling can be computed. It is estimated at ~ 60 s to cool core regions of the injection-moulded 6.35 mm thick bars taken for morphological examination, from the melt temperature on injection moulding (~ 210°C) down to T_g of PS (~ 95°C)[26,27]. This means that injection-moulded KR05 lamellae of the blends could be relaxed only for a short period of less than 60 s, even in the core regions of the bars, and is in contrast to the case of the compression mouldings, which could have enough time to anneal KR05 lamellae on long hot pressing (200°C for 5 min) and on subsequent gradual cooling (mould temperature dropped down to 50°C in 3 min). Even if the blends were injection moulded with the same cooling rate as the corresponding compression mouldings, KR05 lamellae in the former mouldings could be more undulate than those in the latter because of the very large shear stress imposed on the melt during injection moulding. The difference of degree of orientation and orderliness of KR05 lamellae between the injection- and compression-moulded blends could account for their toughness difference, which will be discussed in the next section.

In *Figures 9* and *10* one can see morphological changes

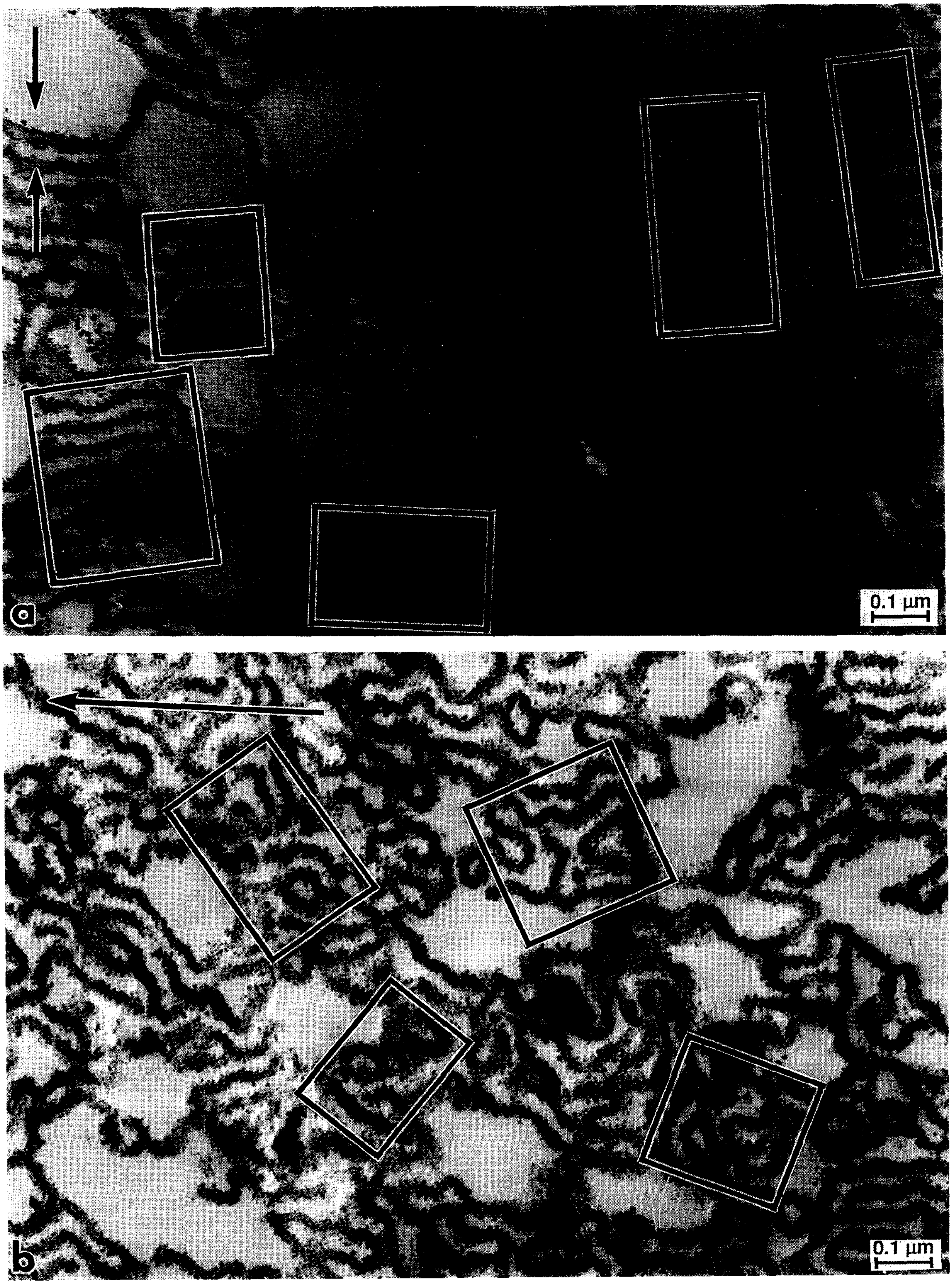

Figure 8 Highly magnified transmission electron micrographs of (a) compression and (b) injection mouldings of the twice-extruded KR05/MS-200 (70/30) blends. Morphology of the compression moulding was viewed on the *XZ* plane (see *Figure 1*) and the compressive direction is shown by a pair of arrows on the micrograph. Morphology of the injection moulding was viewed on a cross-section parallel to the *XY plane (see Figure 2)*, in the previous study[1]. The injection direction is shown by an arrow on the micrograph. Rectangular frames drawn on micrographs help one to find significant difference of KR05 lamellar orderliness between the two mouldings

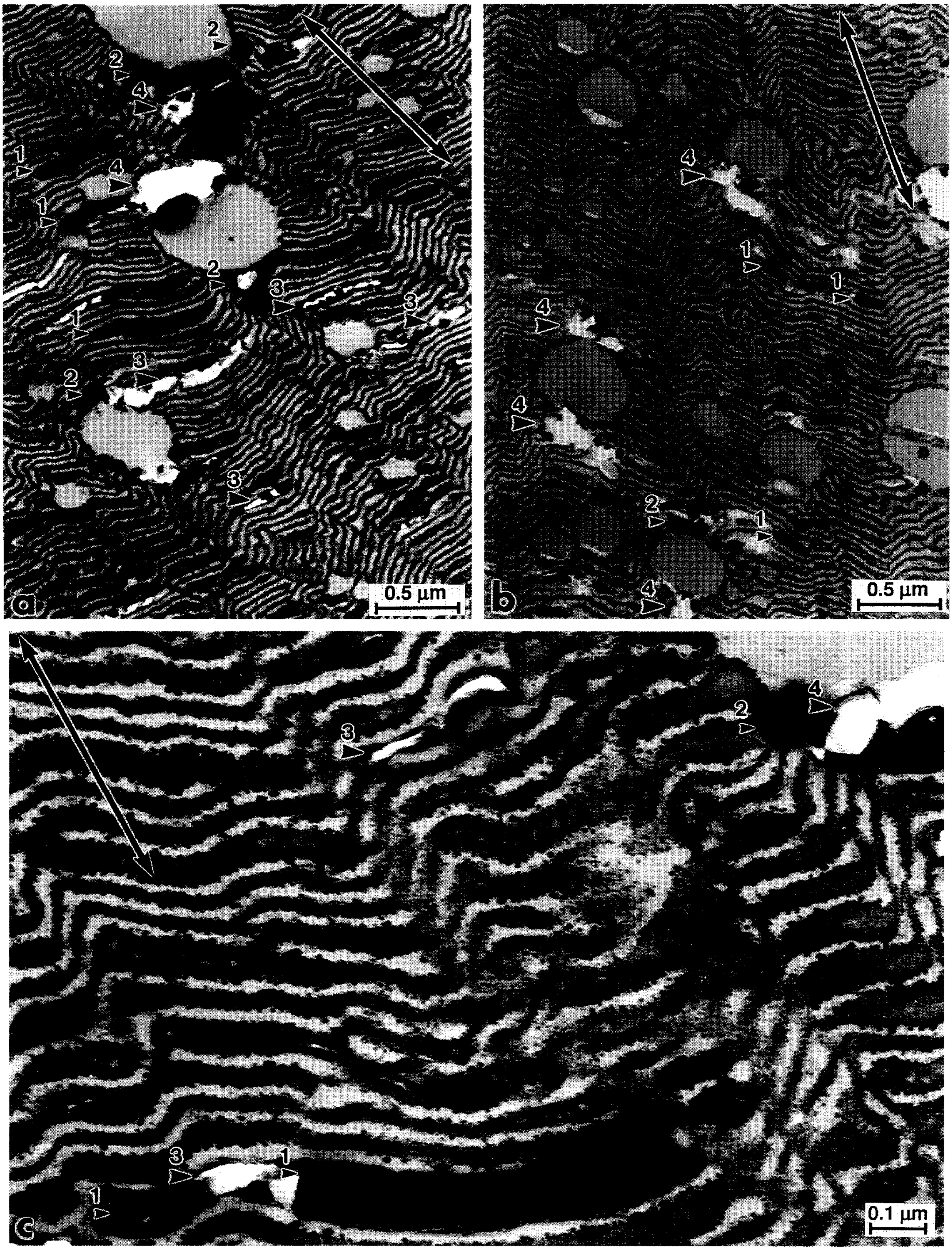

Figure 9 Transmission electron micrographs of a compression-moulded specimen of the twice-extruded KR05/MS-200 (85/15) blend after fracture under tensile stress. Morphological changes were observed on cross-sections just below the fracture surface. Tensile directions are shown by double arrows on the micrographs. Micrographs (a) and (b) were taken several micrometres away from each other on the same cross-section. Micrograph (c) is a higher magnification view of (a)

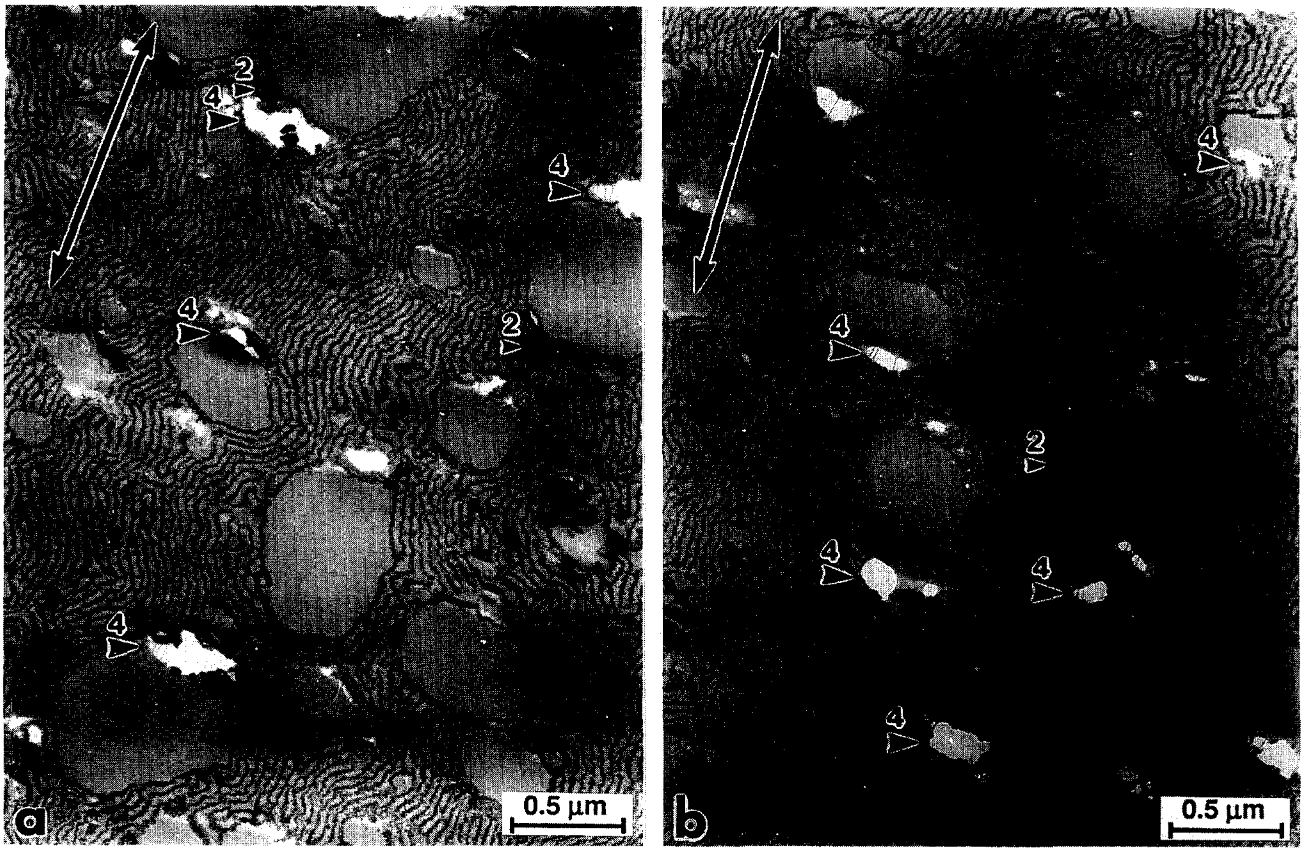

Figure 10 Transmission electron micrographs of a compression-moulded specimen of the twice-extruded KR05/MS-200 (70/30) blend after fracture under tensile stress. Morphological changes were observed on cross-sections just below the fracture surface. Tensile directions are shown by double arrows on the micrographs. Micrographs (a) and (b) were taken several micrometres away from each other on the same cross-section

which resulted from tensile stress application to the compression-moulded specimens of twice-extruded KR05/MS-200 (85/15) and (70/30) blends, respectively. The deformation structure was observed in the region just below the fracture surface after stretching in the direction shown by the arrows at 50 mm min^{-1} up to the point of break. Stretching was done normal to the compressive direction of the specimens. For each figure respective viewpoints taken for (a) and (b) were a little distance (only a few micrometres) from each other on the same cross-section. For *Figure 9a* higher magnification view (c) is added to see the deformation of KR05 lamellae clearly.

One notices a significant difference in MS-200 domain size and its distribution between identically magnified transmission electron micrographs of compression-moulded blends with the same blending ratio: *Figure 4b* and *Figures 9a* and *b* for (85/15) blend; *Figure 4c* and *Figures 10a* and *b* for (70/30) blend. This difference never occurred as a result of stretching but could result from heterogeneity of degree of mixing which is still left in twice-extruded pellets after the second extrusion. On all the micrographs taken after stretching, a larger size and size distribution of MS-200 domains were seen in the regions closer to the fracture surface. Supposing that in specimens of the blends regions with MS-200 domains over a certain size could be fractured more easily on stretching than those with smaller domains, then this could explain the coarser MS-200 domain morphology close to the fracture surface of the specimens. Toughening of KR05 by incorporation of MS-200 is considered in the next section. Effects of MS-200 domain size on the toughening will be discussed in a future paper.

Stretching of compression mouldings of twice-extruded KR05/MS-200 blend changed their KR05 lamellar structure considerably as recognized by comparison of the lamellar morphology between unstretched and stretched specimens (*Figure 4b* and *Figures 9a* and *b* for (85/15), and *Figure 4c* and *Figure 10c* for (70/30), respectively). When tensile stress was applied to the KR05/MS-200 (85/15) blend, oriented lamellae of the KR05 phase were deformed regularly in zigzags by predominant shear yielding, in much the same way as for the deformation mechanism of KR05 compression mouldings[2]. When the KR05/MS-200 (70/30) blend was under stress, however, its KR05 lamellae did not show large deformation. In the stretched (70/30) blend, herringbone-like shear bands as viewed in the stretched (85/15) blend are not clearly seen and instead a small undulation is observed (see *Figure 10*). On stretching the (70/30) blend, large lamellar motion could be restricted by the morphology crowded with MS-200 domains, which are scattered more densely in the KR05 matrix than those of the (85/15) blend.

Lamellar orderliness of the KR05 matrix of compression-moulded KR05/MS-200 blends allows one-sided expansion of lamellar spacing of the rubbery PB phase on stretching as viewed in stretched specimens (*Figures 9* and *10*), because the unstretched lamellae (*Figures 4b* and *c*) do not show networks of the PB phase tangled with the

PS rigid phase as seen in the injection-moulded blends. Such networks must be effective to restrain large deformation of the PB phase.

Black specks seen on the stretched morphology (*Figures 9* and *10*) suggest that early stages of cavitational breakdown in the PB phase and debonding in the interfacial region between the KR05 matrix and dispersed MS-200 domains resulted in preferential fixing by subsequent osmium tetroxide treatment[28]. Smaller arrowheads 1 and 2 on the micrographs point at some of the black specks in the PB phase and in the interfacial region, respectively. The PB phase could be cavitated on stretching at places where large dilational stress was concentrated. Voids seen in the same micrographs should result from the growth of cavitation and debonding. Larger arrowheads 3 and 4 point to some of the voids in the PB phase and in the interfacial region, respectively. These microcavities (specks and voids) account for whitening (opacity) in the region near the fracture surface.

Many microcavities originated around the pole positions of certain MS-200 domains for the stretching direction, which could be due to large tensile stresses induced around the pole positions of the domains. On stretching of polymer blends composed of a ductile matrix with smaller modulus and larger Poisson's ratio than those of brittle inclusions, theoretical principal stresses can be calculated with the modified Eshelby equation. Tensile stresses are induced around pole positions whereas compressive stresses are induced around equatorial positions for the stretching direction[4,5]. KR05-enriched KR05/MS-200 blends could deform in such a stress field on stretching, since the KR05 matrix shows a smaller modulus than the MS-200 particles (tensile moduli of the compression-moulded specimens of twice-extruded KR05 and MS-200 are 796 MPa and 2481 MPa, respectively) and could have larger Poisson's ratio than the MS-200 because of the rubbery PB inclusion of KR05. A very large difference of modulus between the KR05 matrix and the MS-200 particles should induce large tensile stress around the pole position of the particles, leading to debonding there in spite of possible formation of a strong interface between KR05 and MS-200[1].

Macroscopic deformation of compression mouldings of KR05-enriched blends could occur through shear yielding of the KR05 matrix, and through cavitation in the PB phase and debonding in the KR05/MS-200 interfacial region. It appears that this is much the same as that of injection mouldings of the corresponding blends[1]. After sufficient yielding development, final fracture could occur through the growth of microcavities into local microcracks and further macrocrack propagation. However, it should be stressed that there is great morphological difference of shear-yielded KR05 lamellae between compression and injection mouldings. For the former, PS lamellae of the KR05 matrix are not fragmented and the continuity of the lamellae is not lost even in the region close to the fracture surface, whereas for the latter PS lamellae are deformed and fragmented destructively, leading to separate PS domains dispersed in PB lamellae[1,2].

Mechanical properties

Figure 11 shows the notched Izod impact strength of compression mouldings of once- and twice-extruded KR05/MS-200 blends, together with that of injection mouldings of once- and twice-extruded blends. Impact data for the injection-moulded blends are reproduced from the previous paper[1]. Superiority of the compression-moulded KR05/MS-200 blends in toughness is revealed. The compression mouldings are much more toughened than the corresponding injection mouldings. Whether compression and injection moulded, the impact strength exhibits synergistic improvement by incorporation of MS-200 into KR05, and goes through a maximum between 10 and 30 wt% MS-200, where the blends are composed of the ductile matrix. The synergy effect is more remarkable for compression-moulded blends than for injection mouldings.

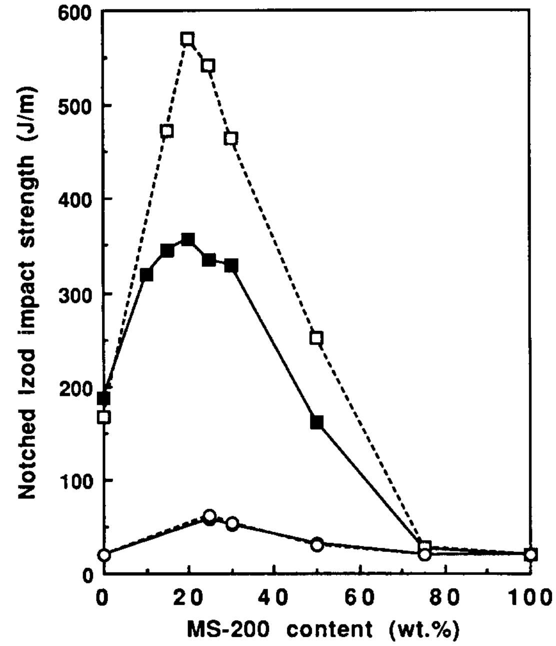

Figure 11 Notched Izod impact strength of KR05/MS-200 blends plotted as a function of MS-200 content. Filled and open squares represent the data for compression mouldings of once- and twice-extruded pellets, respectively. The data for injection mouldings of once- and twice-extruded pellets are reproduced from the previous paper[1], shown by filled and open circles, respectively

Significant difference of toughness and its synergy effect between the two mouldings could arise predominantly from their morphological difference, principally, differences of microstructural orientation and orderliness on a scale from a few tenths to a few micrometres, as mentioned in the previous section. The injection-moulded blends with KR05-enriched composition could possess the morphology responsible for toughening[1]. This is also true of the compression-moulded blends because of an analogy of deformation mechanism. When impact stress is applied to either mouldings, excessive stress concentration which may generate destructive microcracks could be avoided by extensive morphological changes with shear yielding of the lamellar KR05 matrix, cavitation in the PB phase and debonding in the KR05/MS-200 interfacial region. Larger impact energy dissipation of the compression-moulded blends is conceivably due to oriented KR05 lamellae and spherical MS-200 particles of the blends. KR05 lamellae in the compression-moulded blends look

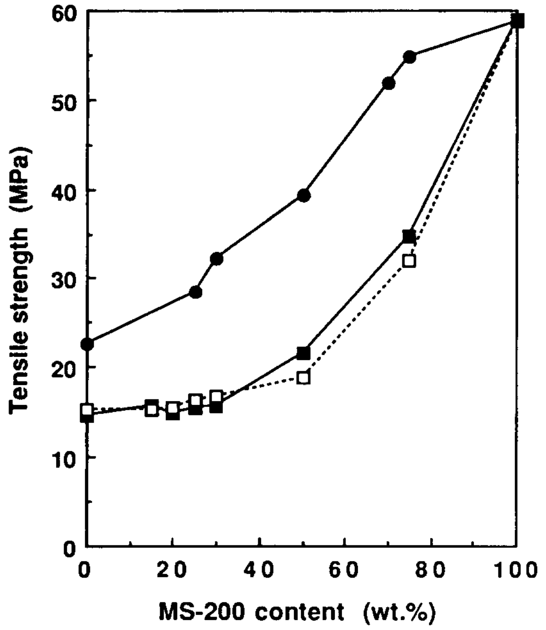

Figure 12 Tensile strength of KR05/MS-200 blends plotted as a function of MS-200 content. Filled and open squares represent the data for compression mouldings of once- and twice-extruded pellets, respectively. The data for injection mouldings of once-extruded pellets are reproduced from the previous paper[1], shown by filled circles

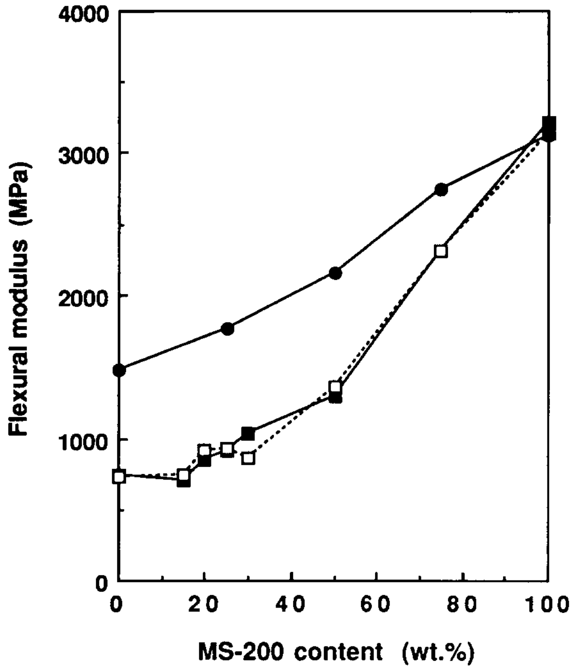

Figure 13 Flexural modulus of KR05/MS-200 blends plotted as a function of MS-200 content. Filled and open squares represent the data for compression mouldings of once- and twice-extruded pellets, respectively. The data for injection mouldings of once-extruded pellets are reproduced from the previous paper[1], shown by filled circles

roughly corrugated over a micrometre scale, but once viewed on a scale of a few tenths of a micrometre, intermittent orientation and orderliness of the lamellae, among which MS-200 particles intervene, can be seen (see *Figure 7* and *Figure 8a*). The PB rubbery phase in the oriented lamellae could be deformed more easily than the crooked one tangled with the rigid PS phase in the injection-moulded blends. The large deformation of the PB phase could facilitate extensive shear band development and dominant expansion of the PB lamellar spacing, which should play an important part in easing stress concentration on impact. Moreover, MS-200 particles in the compression-moulded blends are round in shape and their interfaces to KR05 matrices are smooth with fewer undulations. On impact, extreme stress localization at the interfaces could be avoided and more extensive debonding around MS-200 particles conceivably results without destructive microstructural change. On the contrary, fatal stress concentration may arise at some concave-shaped sites in KR05/MS-200 interfacial regions of the injection-moulded blends under tension, and therefore, could easily trigger microcracking around there. Rupturing large cracks would favour the earlier formation and propagation of macrocracks. hastening the ultimate fracture of the specimens.

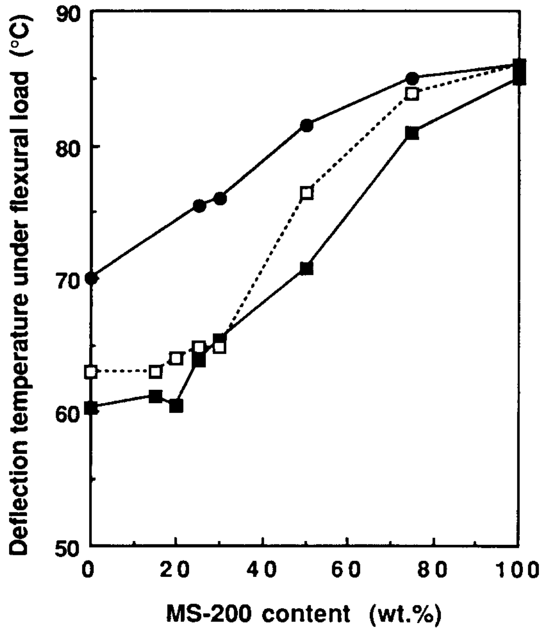

Figure 14 Deflection temperature of KR05/MS-200 blends under flexural load plotted as a function of MS-200 content. Filled and open squares represent the data for compression mouldings of once- and twice-extruded pellets, respectively. The data for injection mouldings of once-extruded pellets are reproduced from the previous paper[1], shown by filled circles

The extensive debonding in the KR05/MS-200 interface should be more responsible for synergistic toughening of the compression-moulded blends than shear yielding and cavitation in the KR05 lamellae since shear yielding and cavitation can also be seen in deformed compression-moulded specimens of neat KR05[2]. Another reason for this is that the presumably strong interface between KR05 and MS-200[1] could absorb a large amount of energy on debonding.

A noticeable difference of impact strength is seen between the compression mouldings of once- and twice-extruded KR05/MS-200 blends. Twice-extruded blends are superior to once-extruded blends of the identical blending ratio in impact strength. This could result from the enhanced degree of mixing of twice-extruded blends as mentioned above with micrographs.

Figure 12 shows the tensile strength of compression mouldings of once- and twice-extruded KR05/MS-200

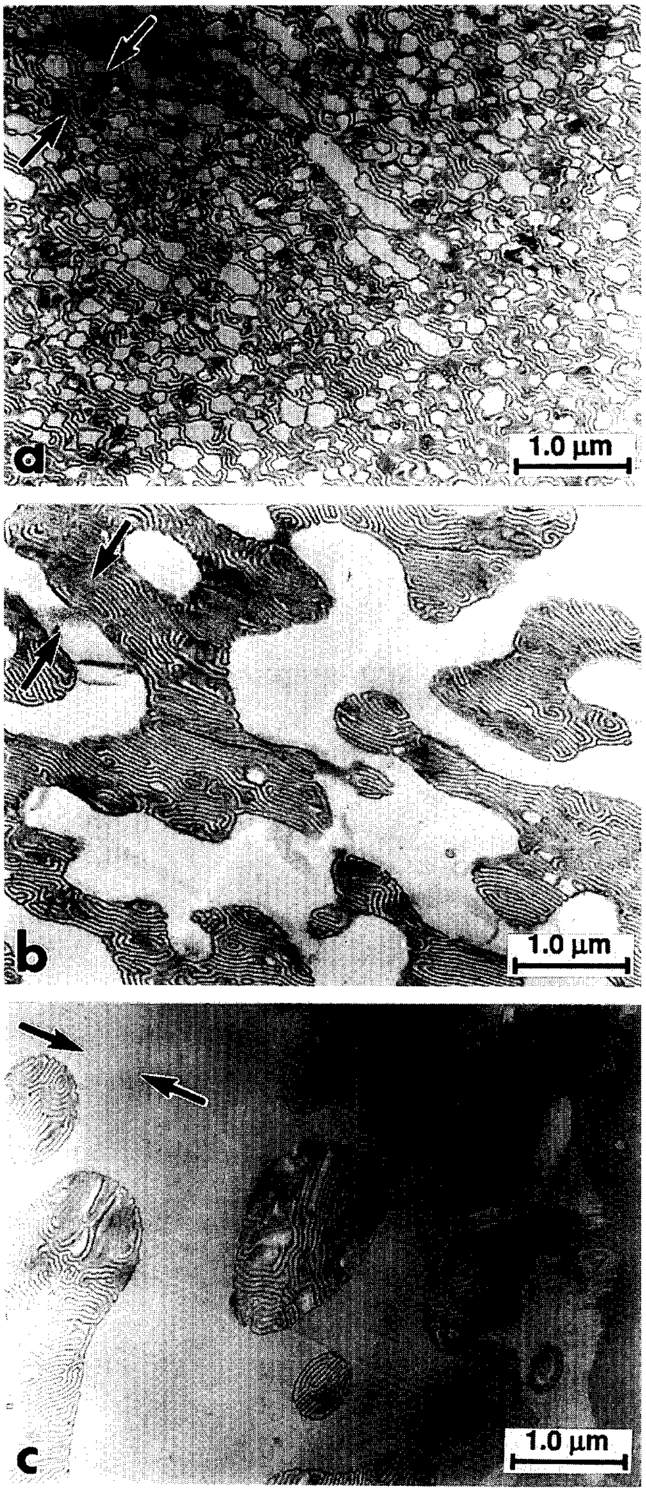

Figure 15 Transmission electron micrographs of compression mouldings of twice-extruded KR05/MS-200 blends: (a) (70/30); (b) (50/50); (c) (25/75). The morphology was viewed on sections microtomed on the *XZ* plane (see *Figure 1*). The arrows on the micrographs show the compressive directions

blends, together with that of injection mouldings of once-extruded blends. The flexural modulus of those mouldings is shown in *Figure 13*. Deflection temperature of those mouldings under flexural load (DTUL) is compared in *Figure 14*. The data for injection-moulded blends are reproduced from the previous paper[1]. The compression-moulded blends cannot match the corresponding injection mouldings for these rigidity-related properties. One reason could be the large rigidity difference of the KR05 phase between the two, since wavy and entangled lamellae of injection-moulded KR05 are significantly more rigid than oriented lamellae of compression-moulded KR05[2]. Injection-moulded KR05 is roughly twice as stiff as compression-moulded KR05 in the tensile strength and the flexural modulus, and shows higher DTUL than the compression mouldings by 14°C. Another reason could be the more efficient interconnection of elongated MS-200 domains for the injection-moulded blends than that of the spherical domains for compression mouldings, which is discussed below.

The tensile strength, the flexural modulus and DTUL of compression-moulded KR05/MS-200 blends show inflections in the plots of blends with around 30 wt% MS-200. These properties scarcely vary from the respective properties of compression-moulded KR05 below ca. 25 wt% MS-200, but begin increasing with the blending ratio over 30 wt% MS-200 (*Figures 12–14*). Such behaviour can be correlated with the microstructural change of the blends by using classical percolation theory[21,29]. For a simple binary composite composed of a polymer matrix with dispersed inclusion (e.g. polymeric domains and mineral fillers) percolative effects on its bulk properties, such as electrical conductivity[30–37] and modulus[20,21], are often found. At low MS-200 fraction of KR05/MS-200 blends, MS-200 domains are not connected and therefore, the tensile strength, the flexural modulus and DTUL of the blends could be dominated by the continuous KR05 phase. As the MS-200 fraction increases, MS-200 domains could get closer and begin to interconnect with one another, and finally form macroscopic continuity throughout the blends. The MS-200 fraction at which a macroscopic continuous chain of MS-200 domains first appears is called the percolation threshold. Above the percolation threshold the MS-200 phase should become very influential on the tensile strength, the flexural modulus and DTUL of the blends. *Figure 15* shows the morphology of compression mouldings of three twice-extruded KR05/MS-200 blends: KR05-enriched (70/30), evenly incorporated (50/50) and MS-200-enriched (25/75). The compressive directions are shown by arrows on the figures. Addition of MS-200 to KR05 induces morphological transitions from the morphology with the KR05 matrix to that with co-continuous phases and, after phase inversion is completed, to that with the MS-200 matrix. The MS-200 fraction at which a macroscopic continuity of MS-200 domains first appears as the fraction increases could be less than 50 wt%, since co-continuity of the phases is well developed in KR05/MS-200 (50/50). For compression-moulded KR05/MS-200 blends the percolation thresholds of the properties are seen near 30 wt% of MS-200 in the plots according to *Figures 12–14*, which is consistent with the microstructural change as viewed in *Figure 15*. These properties for the injection-moulded blends seemingly change linearly with the weight fraction of MS-200 and their percolation thresholds are not discernible because the number of blending ratios taken for the injection mouldings is not enough to make sure of the existence of percolation thresholds.

The effect of the shape of dispersed domains in binary blends on percolation efficiency was evaluated previously[20]. A blend with spherical domains shows a higher percolation threshold than that with elongated domains. In other words, as the fraction of dispersed domains in the two blends increases, spherical domains in the former blend interconnect with one another significantly later than elongated domains in the latter blend, but both enhance macroscopic continuity rapidly after they begin to percolate. This could be responsible for there being little change of rigidity-related properties of compression-moulded KR05/MS-200 blends below 25wt% MS-200 and their steep increase with increasing the MS-200 fraction over 30wt% MS-200. A similar effect was found previously in comparison between injection and compression mouldings of polymer blends composed of a ductile matrix with brittle inclusion[20,21].

CONCLUSIONS

In the moulded KR05/MS-200 blends KR05 exhibits lamellar morphology and phase separation from MS-200. The mechanical properties of the blends depend on the microstructural orientation and orderliness. Ductile KR05 is toughened by incorporation of brittle MS-200, and synergistic improvement of toughness is observed for the blends composed of KR05 matrix with MS-200 inclusion since under tensile stress excessive stress concentration could be restrained effectively by shear yielding of the lamellar KR05 matrix, cavitation in the PB phase and debonding in the KR05/MS-200 interfacial region. However, this synergistic effect is much more prominent for the blends with oriented KR05 lamellae and spherical MS-200 domains than for those with crooked KR05 lamellae and wavily elongated MS-200 inclusions, since on impact the former could dissipate more energy through dominant expansion of the PB lamellar spacing and delocalized debonding at smooth KR05/MS-200 interfaces. The latter shows enhanced rigidity and heat resistance since the crooked lamellae offer more resistance against deformation because of the close and complicated networks of the PB phase with the rigid PS phase, and because of more efficient interconnection of elongated MS-200 domains.

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