

Properties and structure of elastomeric two-stage emulsion interpenetrating networks

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Interpenetrating polymer networks (IPNs) consist of two crosslinked polymers which form a network within a network. Bulk-prepared IPNs are thermosetting and cannot be processed due to the formation of a macroscopic network. Emulsion IPNs, although thermosetting, can be processed as thermoplastic materials. This is due to a special particle-slippage flow mechanism which is practically insensitive to molecular weight. The morphology of the reported latex particles is unique in the sense that very small polystyrene domains are formed by phase-separation of polymerizing styrene added to a seeded flexible polyacrylate latex. Compression or injection moulded specimens of these crosslinked elastomeric materials show significant mechanical properties. Some properties and structural observations using a special electron microscopy technique are described in this article. This method is based on the differential radiation damage to various polymers embedded in ice and can be used as an analytical tool to determine the microstructure of certain multiphase systems.

(Keywords: interpenetrating networks; polymers; emulsions; electron microscopy; polymer composites; elastomers)

INTRODUCTION

Interpenetrating polymer networks (IPNs)¹ are synthesized by swelling a crosslinked polymer with a second monomer, also containing a crosslinking agent, and polymerizing the second monomer to yield a network within a network. Incompatibility of the two polymers may cause domain formation by phase-separation. Even when phase-separation occurs, the system can still be considered intimately mixed, containing small domains on the order of hundreds of angstroms. Bulk-prepared IPNs are thermosetting and cannot be processed due to the formation of a macroscopic network. Emulsion IPNs are different in this respect, since their thermosetting nature is limited to the size of their particles which is on the order of several hundreds to a few thousands of angstroms. In spite of their thermosetting nature emulsion IPNs can be processed as thermoplastic materials, although their flow mechanism is different from that of conventional thermoplastic materials. Emulsion IPNs are prepared by a sequential procedure, namely, the preparation of a crosslinked seed latex of the first monomer, the addition of a second monomer plus crosslinker and polymerization. The morphology of a two-stage latex particle is a complicated subject which depends on such factors as sequence and method of addition, proportion of monomers, hydrophilicity difference between the monomers, surface tensions and molecular weights²⁻⁴.

The work presented here describes elastomeric emulsion IPNs prepared by first polymerizing ethyl acrylate, butyl acrylate (or mixtures of) ethyl acrylate and butyl acrylate with ethylene glycol dimethacrylate as a crosslinking moiety. Styrene containing divinylbenzene was added dropwise to the crosslinked seed latex and polymerized. Following coagulation and drying, elastomer granules consisting of 75% polyacrylate and 25% polystyrene were usually produced. These materials

were processable by compression moulding and by using a thermoplastic screw injection moulding machine. Transmission electron microscopy observations of frozen-hydrated specimens of a diluted latex were carried out using a cold-stage technique⁵. This method utilizes observable phenomena associated with radiation damage to organic inclusions in ice⁶.

EXPERIMENTAL

Seed lattices were produced and the following seeded emulsion polymerizations were carried out using standard emulsion polymerization procedures^{2,7}. Monomers were always added continuously to the reaction vessel during the polymerization course (2-3 h).

The tensile properties were determined with an Instron machine on specimens cut from compression moulded sheets, at a crosshead speed of 10 cm min⁻¹.

Thin frozen specimens were prepared by the 'double-film' technique⁸, in which a thin, <0.5 μm, layer of a diluted latex was sandwiched between two polyimide films. The specimens were frozen in liquid nitrogen and transferred into a JEOL JEM 100CX electron microscope using a Cold Stage Transfer Module (CSTM), and a modified JEOL cooling holder. All the samples were examined with 100 kV electron beam at 95 ± 2K in the TEM mode. After finding a suitable area in the sample at low magnification a first low electron dose micrograph was taken at a magnification of typically 20 000 ×. The beam was left on, and a series of micrographs at intervals of 30 or 60 s was recorded, usually until 4-6 min had elapsed. This corresponded to electron exposures ('doses') of about 2-30 kC m⁻².

RESULTS AND DISCUSSION

Early experiments, where acrylate monomers were added

to a polystyrene seed latex yielded very poor elastomers. No significant improvements were noticed if crosslinking agents were added. Only a reversal of the sequence of monomer addition, namely adding styrene to polyacrylate seed lattices, produced elastomers having significant strength properties. A summary of these experiments is depicted in *Figure 1* where the effect of the presence of crosslinking agents can also be seen. The dramatic effect of the sequence of monomer addition as demonstrated in *Figure 1* should be attributed to different particle morphologies characterizing the two preparation methods. In fact, the authors have been able to produce some elastomers having tensile strengths greater than 10 MPa (1500 psi) by adding styrene to acrylate seed lattices. The trends shown here are in agreement with literature reports²⁻⁴, although very little information is available on the physical and mechanical behaviour of emulsion, IPN type, two-stage elastomers.

Crosslinking agents in the acrylate phase were found to be essential to the elastomeric properties, and their presence at suitable concentrations has reduced the tackiness of the elastomer, and greatly improved the

elastomer's tensile and rheological properties. The emulsions could usually be classified as film-forming, unless the crosslink density was too high. All these experimental facts have led to the conclusion that the systems in question (prepared by adding styrene to a seeded polyacrylate latex at a ratio of 25 styrene/75 acrylate) consist of crosslinked polyacrylate particles containing small rigid crosslinked polystyrene domains which act as an efficient reinforcing material for the elastomeric acrylate. Thus, the styrene monomer added to the seeded polyacrylate latex enters the particles, polymerizes, phase-separates and forms polystyrene domains within the soft acrylate particle, rather than forming external hard polystyrene shells. If styrene is polymerized first and the acrylate monomer second, the size of the polystyrene 'domains' is equal to the size of the latex particles. The latter is probably roughly an order of magnitude greater than the size of the polystyrene domains formed by phase-separation in a polyacrylate environment. With the PS seeded latex also IPN structures are not formed and the total PS interfacial surface area is relatively small compared with the previous domain structures. This explains the very pronounced effect of the sequence of monomer addition, in a two or multistage emulsion polymerization procedure on the mechanical properties of the resulting elastomers. The effects of the crosslinkers added, in addition to the formation of IPN structures, are also to provide sites for grafting between the two phases, to increase the tensile strength of the rubbery matrix and to preserve the shape of the primary particles in order to confer a particle flow mechanism⁹ that enables the utilization of thermoplastic processing machines. Without crosslinking agents, molecular deformation processes (highly dependent upon molecular weight) constitute the flow mechanism leading to viscosities much too high for thermoplastic processing. Thus, without crosslinking agents, tacky materials, too viscous for processing and having inferior mechanical properties are obtained. With crosslinking agents a particle-slippage process, practically independent of molecular weight, constitutes the flow mechanism and processible materials are obtained¹⁰. The precise crosslinking agent concentration is crucial, since a too high crosslink density may cause particle flocculation during the polymerization step and poor particle-particle interactions in the solid state, leading to elastomers having inferior mechanical properties.

A summary of the various possible morphologies of two-stage latex particles was given by Lee and Ishikawa³. The relevant case for the present systems is where the more hydrophilic monomer (acrylate) is used first to prepare the seed latex. The hydrophobic monomer (styrene) then added, polymerizes and phase-separates within the seed particles to form many different structures. These authors distinguish between low and highly hydrophilic seed lattices where domain structures are favoured in the former, and 'inverted' core-shell morphologies are favoured in the latter case. The exact particle structures depend both on the ratio between the monomers and the molecular weight. Domain structures are favoured by systems whose seed latex has a higher molecular weight. The present systems constitute IPN structures which are expected to yield small domains rather than inverted core-shell morphologies due to the limited chain mobility. This expectation is thoroughly

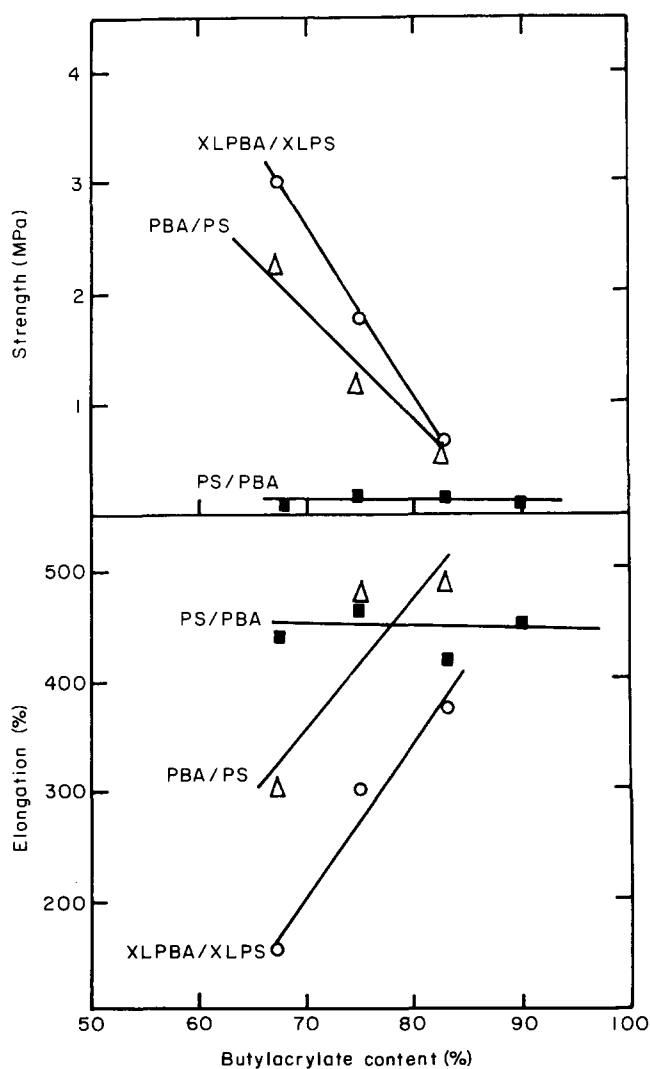


Figure 1 Tensile properties of two-stage emulsion elastomers as a function of monomer sequence of addition, butyl acrylate/styrene ratio and crosslinking. PS/PBA – butyl acrylate added to polystyrene seed latex; PBA/PS – styrene added to poly(butylacrylate) seed latex; XLPBA/XLPS – styrene containing some divinyl benzene added to crosslinked polybutyl acrylate seed latex

supported by the electron microscopy studies. Min *et al.*⁴ also report that the emulsion polymerization of styrene in the presence of polybutyl acrylate seed particles proceeds in the seed. These authors have also suggested several structural morphologies in core-shell latex particles.

Direct images of the microstructure of two-stage latex particles were recorded by cold-stage electron microscopy of frozen hydrated (undried) samples of the latex system. Whether the morphology was of a core-shell type was determined by the behaviour of the sample under the electron beam.

Polymers subjected to ionizing radiation, such as γ -rays or high energy electrons, undergo chain scission and crosslinking. In some polymers, e.g., poly(methyl methacrylate) (PMMA), the former process is predominant, while in others, such as polystyrene (PS), the latter predominates¹¹. Recently Talmon⁶ has shown that this behaviour is more complicated when the electron irradiated particles are embedded in an ice matrix. A detailed description and explanation of these phenomena are given in the original work⁶; we describe them here in brief as they are essential for the present work.

Figure 2 shows PS and smaller PMMA particles embedded in hexagonal ice. The same specimen area is shown after increasing exposures to the electron beam. At first (Figure 2a and 2b) no change is observed in or around the PS spheres. After exposure of 14 kC m^{-2} cavities begin to form around the PS particles (Figure 2c). These cavities increase in diameter under additional irradiation, and eventually a small decrease in the PS particles diameter is also observed (Figure 2f). The behaviour of the PMMA spheres is quite different. Even the relatively small electron dose needed to focus and to expose the first plate (Figure 2a) is sufficient to cause mass loss in the PMMA

particles and to give them cellular appearance. Additional irradiation causes the particles to lose more mass, to swell, and in the case of neighbouring particles to fuse together; this is seen clearly by following the appearance of the group of particles in the lower left-hand side of Figures 2a-2f.

The etching of ice and PS is the result of formation of free radicals in both species. PS tends to crosslink under free-radical attack, and hence is rather stable, whereas the ice is etched more rapidly. When the gap between the ice surface and the PS becomes large enough the mutual attack of free-radicals from both species is no longer possible, and the rate of etching decreases, and follows the pattern of radiolysis exhibited by each species alone. (This is illustrated below in the explanation to Figure 6).

PMMA undergoes mostly scission under the free-radical attack; this explains the massive mass loss observed in the PMMA particles. These free-radicals come both from the polymer and the ice matrix. Some of the short-chain free radicals diffuse outwards and repolymerize, thus filling the cavity formed by the etched ice. Etching and repolymerization take place simultaneously, hence no cavities are seen in the ice. Repolymerization also explains the 'fusion' of neighbouring particles. The newly formed polymer may include molecular fragments from the ice. It is a stable crosslinked polymer and eventually causes termination of swelling or etching of the ice matrix.

The above described difference in behaviour under the electron beam can be used to determine whether the two component particle is structured as core-and-shell, or consists of a domain interpenetrating network. In the latter case the particle should behave similarly to a PMMA particle; the PMMA part of the network should

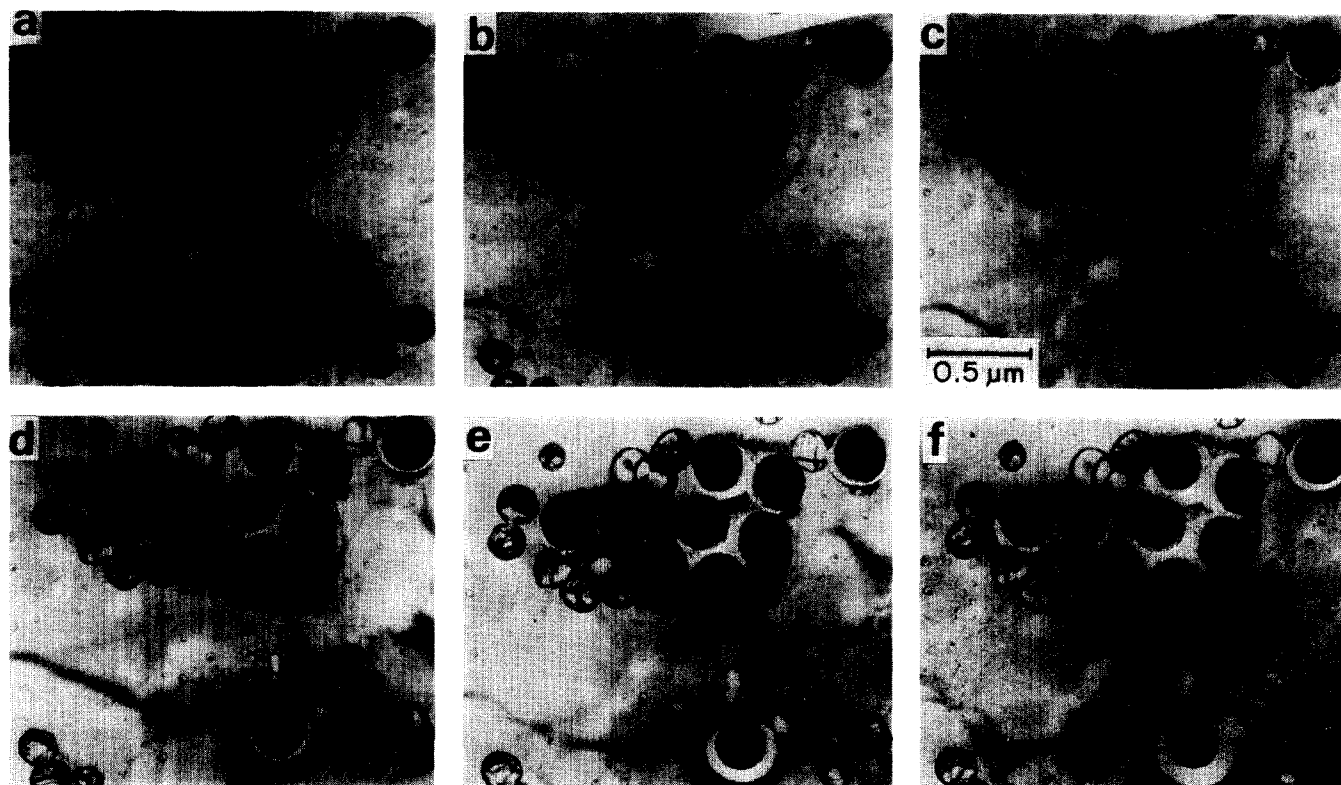


Figure 2 Transmission electron micrographs of a frozen specimen (95 K) of mixed lattices of PS (large spheres) and PMMA (smaller spheres) after increasing exposures to a 100 kV electron beam (a) after electron exposure of 1 kC m^{-2} ; (b) 7 kC m^{-2} ; (c) 14 kC m^{-2} ; (d) 28 kC m^{-2} ; (e) 42 kC m^{-2} ; (f) 56 kC m^{-2} . Note the rapid swelling and loss of mass from the PMMA particles, and formation of cavities in the ice around the PS spheres

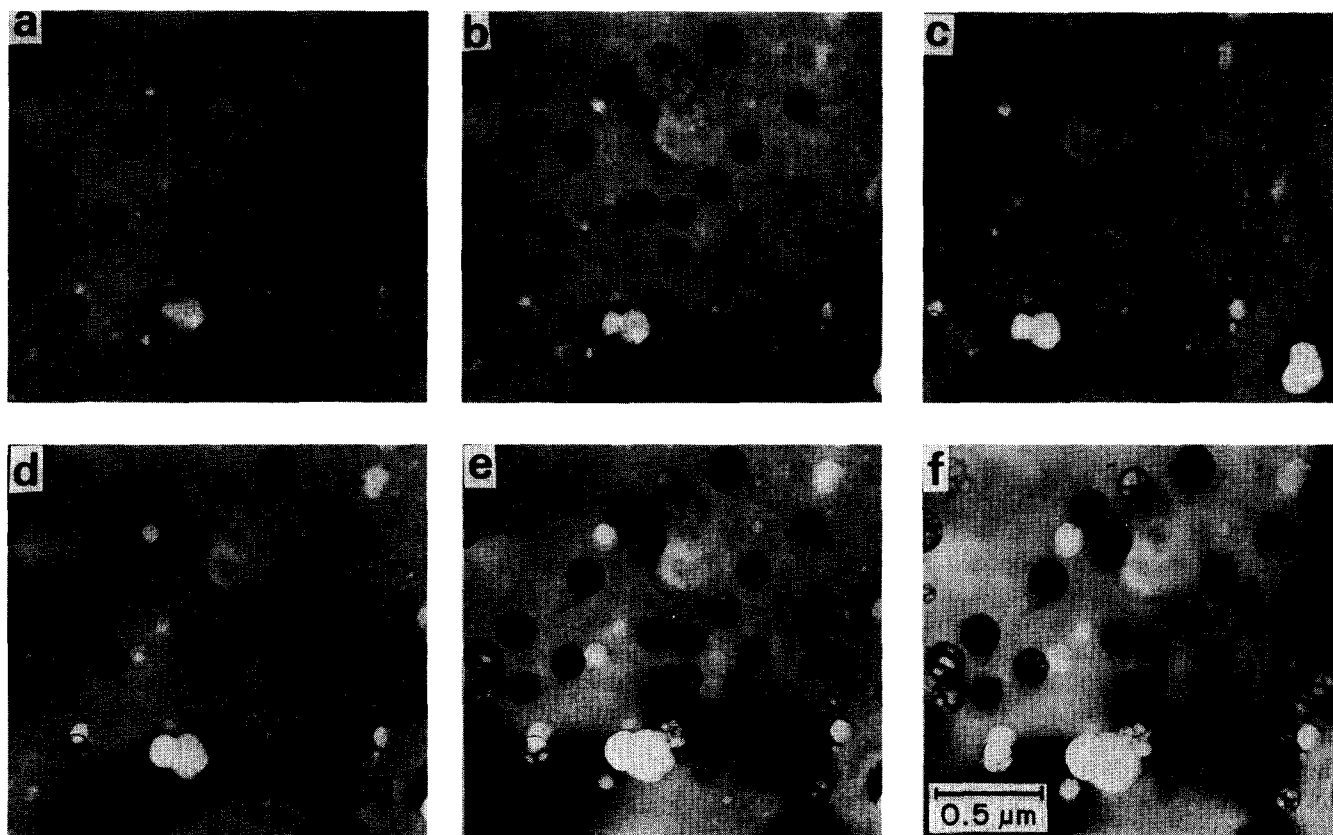


Figure 3 Transmission electron micrographs of a frozen specimen (95 K) of a polyacrylate latex made of 70% ethylacrylate and 30% butylacrylate, (a) after electron exposure of 1 kC m^{-2} ; (b) after 7 kC m^{-2} ; (c) 14 kC m^{-2} ; (d) 28 kC m^{-2} ; (e) 42 kC m^{-2} ; (f) 56 kC m^{-2}

swell and lose mass, while the PS microdomains should lend the particle some stability. A particle with a PS crust should behave as a PS particle, since the ice matrix is in contact with PS only. In this case we expect to see cavities in the ice around the electron-irradiated particles.

Figure 3 shows latex spheres of a copolymer made of 70% ethylacrylate and 30% butylacrylate (PEBA). As expected this polymer behaves under the beam very similarly to PMMA. Figure 4 shows a similar experiment,

this time with particles prepared by adding styrene (25%) to a seed polyacrylate latex (75%). The behaviour of this latex is similar to that of Figure 3, suggesting that no PS crust was formed around the PEBA cores. Comparison of the latex particles after the same electron exposure (Figure 5) reveals that less swelling and mass-loss took place in the PEBA/PS latex. This too suggests that the PS has formed an interpenetrating network, where small crosslinked PS domains in the latex particle give it additional resistance

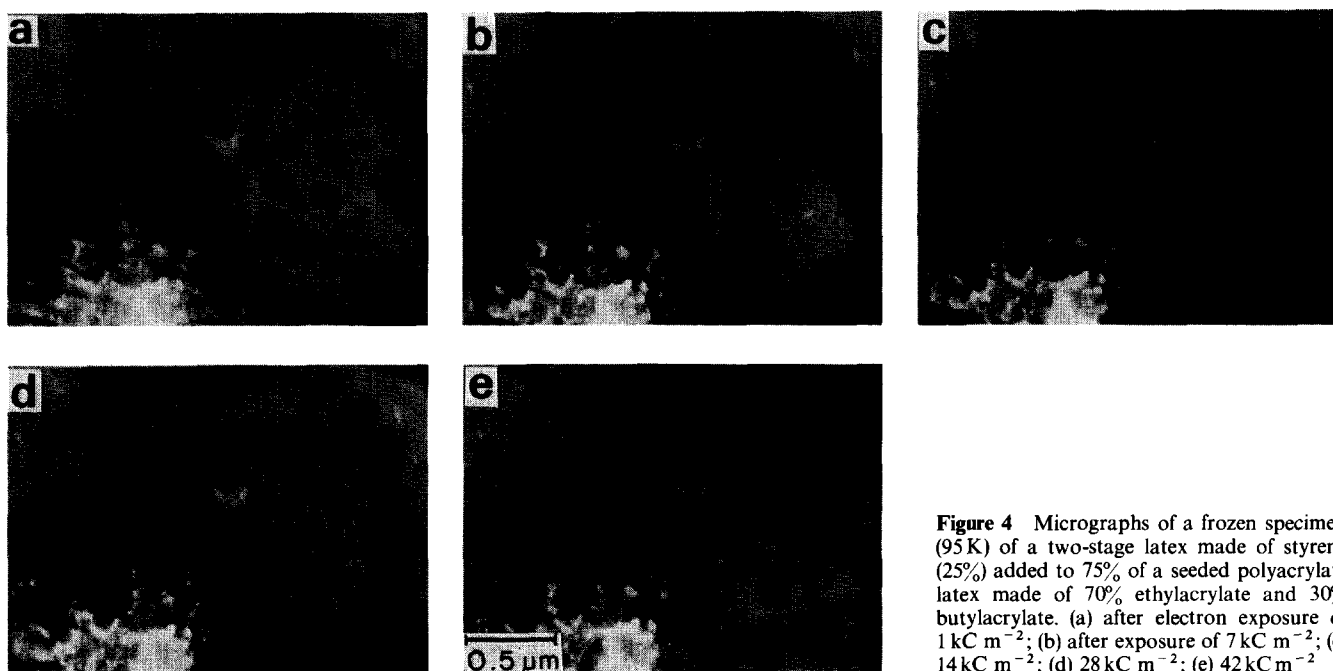


Figure 4 Micrographs of a frozen specimen (95 K) of a two-stage latex made of styrene (25%) added to 75% of a seeded polyacrylate latex made of 70% ethylacrylate and 30% butylacrylate. (a) after electron exposure of 1 kC m^{-2} ; (b) after exposure of 7 kC m^{-2} ; (c) 14 kC m^{-2} ; (d) 28 kC m^{-2} ; (e) 42 kC m^{-2}

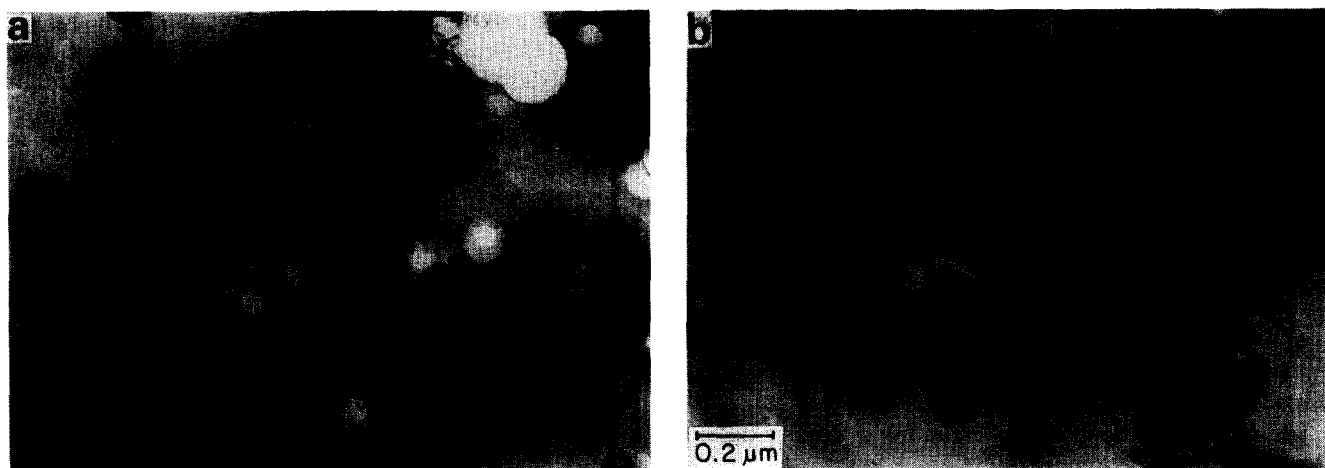


Figure 5 (a) Comparison between the latex particles of *Figure 3* and (b) those of *Figure 4* after the same exposure to the electron beam (42 kC m^{-2}). Note the more pronounced swelling and mass-loss in the polyacrylate latex as compared to the two-stage polyacrylate/PS latex

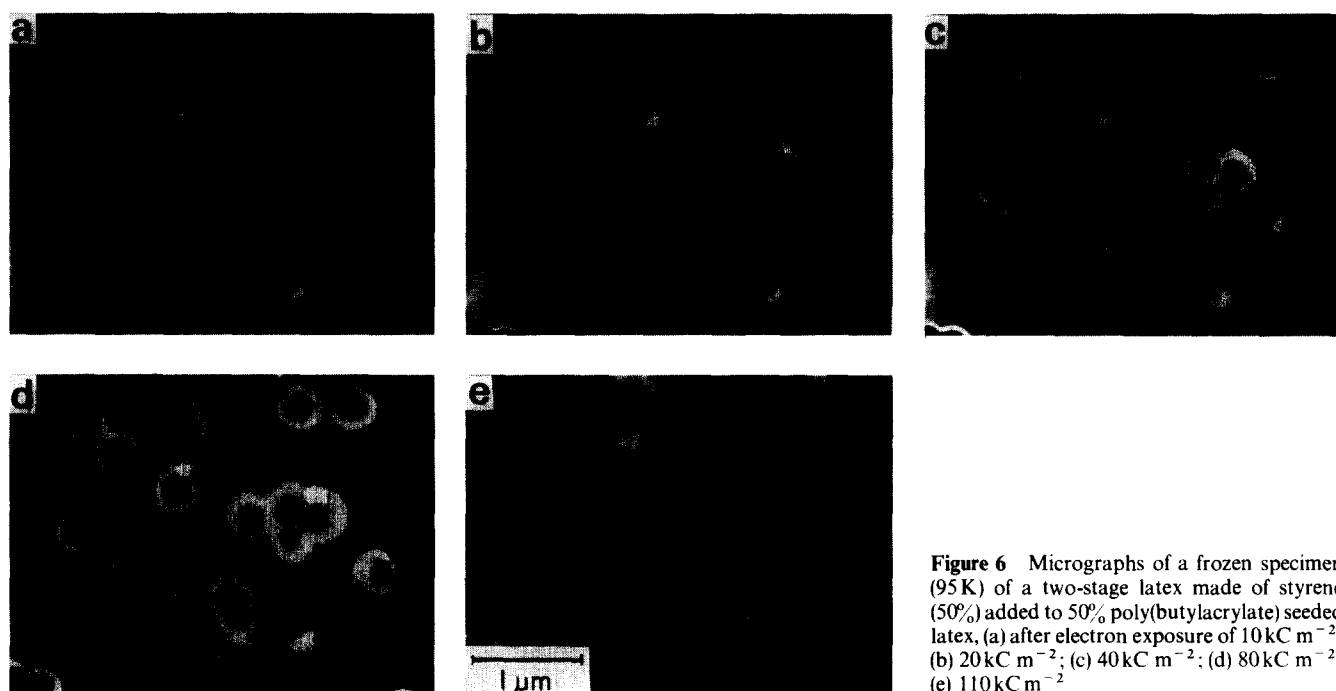


Figure 6 Micrographs of a frozen specimen (95 K) of a two-stage latex made of styrene (50%) added to 50% poly(butylacrylate) seeded latex, (a) after electron exposure of 10 kC m^{-2} ; (b) 20 kC m^{-2} ; (c) 40 kC m^{-2} ; (d) 80 kC m^{-2} ; (e) 110 kC m^{-2}

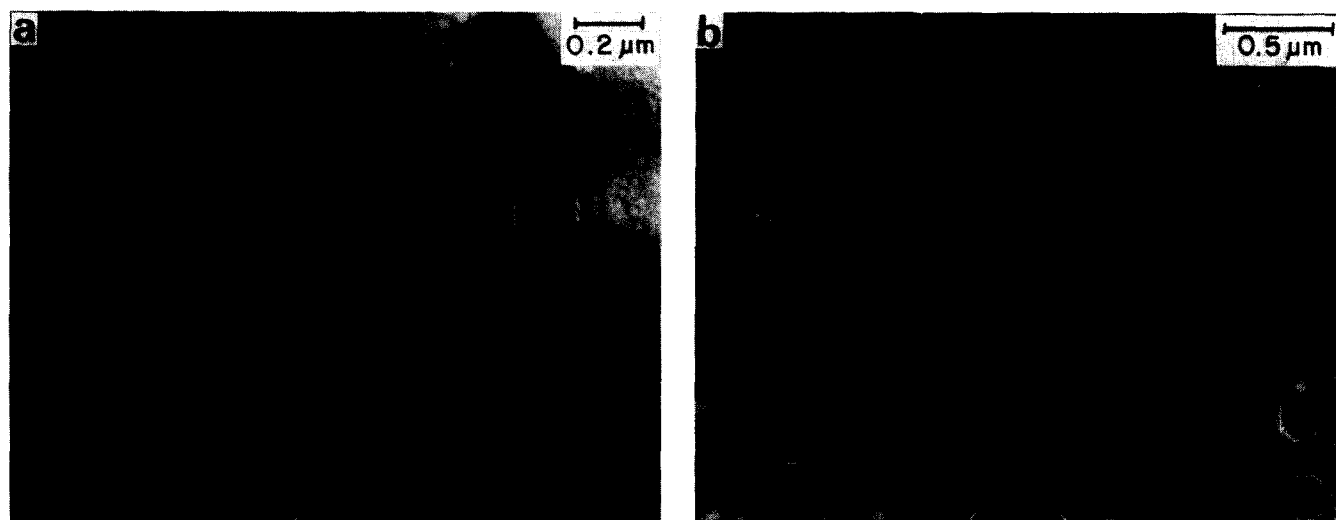


Figure 7 Frozen hydrated samples of a latex prepared by adding 75% butyl acrylate to 25% seeded PS latex; (a) latex spheres after electron exposure of about 40 kC m^{-2} . Note radiation damage to the acrylate layer; (b) an area showing latex particle as in (a), smaller PBA particles (note typical radiation damage) and larger PS spheres without acrylate layers

to radiolysis. Winnik¹², by using fluorescence techniques, has recently suggested a similar microdomain structure, rather than a core/shell structure, for his PMMA/polyisobutylene particles prepared in non-aqueous dispersions.

Micrographs such as *Figures 3* and *4* also provide information about the quality of the latex. The size distributions of the lattices were very narrow and no polystyrene particles were formed by adding styrene to the seed acrylate lattices. Such PS particles would have been distinguished by the formation of cavities around them and by the lack of swelling. Polybutylacrylate (PBA) latex and PBA/ST latex (styrene to acrylate ratio of 25:75) gave results similar to those of *Figures 3–5*.

The situation was quite different for a system with styrene-to-acrylate-ratio of 50:50. *Figure 6* shows that in this case the behaviour of the particles is similar to that of the PS latex. This suggests that at such a high styrene-to-acrylate ratio either some of the styrene forms a PS crust around the acrylate core or the formation of an external PS-rich layer which behaves similarly to PS under the electron beam. It can be seen that as long as the gap between the PS layer and the ice is small, the etching of ice around the polymer particles takes place without preferential orientation, *Figures 6a–c*. But as the gap widens etching continues along certain crystallographic planes of the crystalline (hexagonal) ice. This is manifested by the formation of hexagonal cavities around the polymer particles, *Figures 6d* and *e*. All these hexagons have parallel sides and are similar to hexagons formed in ice without the presence of polymer particles (lower right hand side of *Figures 6d, 6e*).

Finally, *Figure 7* demonstrates the behaviour of a latex prepared by adding acrylate to a seeded PS latex. Recall that such lattices yielded elastomers having only poor tensile properties (*Figure 1*). *Figure 7a* shows core-shell structures rather than domains morphology, consisting of PS cores surrounded by radiation-damaged polyacrylate shells. A core-shell model consisting of 25/75 ratio of styrene to acrylate should form a shell thickness of about 40% of the total radius which is roughly true for the particles shown in *Figure 7a*. Inspection of many particle

groups belonging to the present latex has shown that the latex was less uniform in size (compared to styrene added to a polyacrylate seed latex), that some new polyacrylate particles were formed, and that some polystyrene particles remained intact, namely, uncovered with polyacrylate, as shown in *Figure 7b*.

In summary, the reported emulsion IPNs, in spite of their thermosetting nature, are processable as thermoplastic materials, and show significant tensile properties. A latex particle, constituting the flow unit, is structured as a rubber continuum and a dispersion of small glassy domains mixed together as an IPN. Non-IPN core-shell structures can also be produced, for example, by reversing the sequence of monomer addition, however they show very poor tensile properties.

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