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Structure and properties of an interpenetrating polymer network-like system consisting of polystyrene–polyethylene: 2. Electron microscopic investigation

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Polyethylene–polystyrene (PE–PS) interpenetrating polymer network-like materials with various ratios of PE/PS were prepared. A morphological study using a transmission electron microscopic technique showed that with increasing content of styrene in the system the frequency distribution of the diameter of PS particles becomes increasingly broader and a foam-like structure is formed. Contractions at polymerization and crosslinking as well as interfacial tensile forces are responsible for the IPN morphology. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polystyrene–polyethylene; interpenetrating networks; morphology of IPNs)

INTRODUCTION

In our previous paper (Part 1) concerning the preparation and characterization of an interpenetrating polymer network (IPN) consisting of polyethylene (PE) and polystyrene (PS)[1] the method of synthesis *in situ* was described. This method is a one-step process, where a grafting of styrene on polyethylene also occurs. Therefore, in this process we do not obtain the pure IPN product, which is generally characterized as a blend consisting of two or more polymer networks with no covalent bonds between the polymers of each component[2,3]. For this reason we describe these materials as an IPN-like system.

Up to now, the network density, crystallinity and dynamic mechanical properties of PE-PS IPN-like system have been investigated[1]. This paper is focused on the influence of the molar ratio of PE:PS on the supermolecular structure of the IPN system using a transmission electron microscope technique.

EXPERIMENTAL

Preparation of IPN-like samples

Polyethylene (Bralen, Slovnaft, Bratislava, RA 2-19 type with a flow index of 1.7–2.3 g/10 min) was dissolved with various molar ratios of PS to PE (*Table 1*). Di-tert-butylperoxide (DTBP) (3 wt%) was used as initiator. Divinylbenzene (DVB) (0.5 wt%) was used as a crosslinking agent in all samples. The crosslinking polymerization of S solution of PE was carried out as described elsewhere[1].

Sample preparation and electron microscopic technique

Small blocks were prepared from polymeric materials (of sizes suitable for using in an ultramicrotome). These blocks were chemically stained by application of $ClSO_3H$ and OsO_4 (usual staining procedure for PE). Using an ultramicrotome BS 490 A (from Tesla/Brno) ultra-thin sections were cut. After mounting on thin supporting films the sections were investigated in a 90 kV transmission electron microscope (BS 500 from Tesla).

Table 1 Composition and network density of the IPN samples with various ratios of PS/PE

Sample [a] no.	PS/PE (molar ratio)	ν [b] (10^{-4} mol cm^{-1})	Gel content (wt%)
1	PE alone	—	—
2	37.5:62.5	3.59	—
3	40:60	—	86.5
4	50:50	2.73	90.8
5	75:25	1.47	94.5

[a] Sample no. equals figure no.
[b] ν: Network density from ref. 1

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RESULTS AND DISCUSSION

Figure 1(a, b) shows the typical supermolecular structure of a low density PE which was used for preparation of PE-PS IPN samples. As a consequence of the selective staining the amorphous regions appear dark and the crystalline lamellae are bright. From *Figure 1(a, b)* we can distinquish spherulites with diameters up to above 10 μm with concentric rings. There are two kinds of lamellae: one in radial orientation inside the spherulites and the other in random orientation outside (or between) the spherulites. Inside the lamellae dark defect layers are visible, forming small crystalline blocks; these blocks are arranged in rows, forming the lamellae. The average thickness of lamellae (thickness of internal crystalline part of lamellae) is 7–8 nm, average length of lamellae is a few 100 nm.

The electron micrographs in *Figure 2(a, b)* show the morphology of IPN-like system of molar ratio PS/PE = 37.5:62.5. The micrographs show a two-phase structure system where the PE phase is stained and appears dark and the PS phase appears bright. Particles of PS are surrounded by the PE phase, which forms a network-like structure containing the PS particles forming the meshes of the PE network. This network-like structure is pronounced and PS particles are homogeneously distributed in the whole sample. The PS particles possess diameters between about 0.05 and 0.6 μm with average values of about 0.2 and 0.3 μm. The result of the quantitative estimation of the PS particle diameters is shown in the frequency distribution *(Figure 2c)*.

At the molar ratio of PS/PE = 40:60 of sample shown in *Figure 3(a, b)* the morphology of the IPN is very similar to the previous one *(Figure 2a, b)*, only the frequency distribution of the PS particles seems to be broader.

The network structure of the sample PS/PE = 50:50 is still pronounced, with network walls being thin. The maximum diameter of particles is larger than in previous cases *(Figure 4c)* and adjacent PS-particles starting to obtain a foam-like structure[4].

The sample with the highest content of PS (PS/PE = 75:75) has very large PS particles (in addition of very small ones) *(Figure 5a, c)* all surrounded by the PE network as before. The maximum diameter of PS particles is larger than 10 μm. In particular the higher magnification *(Figure 5b)* reveals the small PS particles, which are space filling polyhedra. Polyhedra are separated by both crosslinked and grafted polyethylene membrane[4]. In *Figure 5* a section through a foam-like structure where cells meet in threes to minimize interfacial area is seen. Angles of 120°C are generated by surface tension forces during the sample preparation of IPN-like systems. We assume that this effect is also caused by contraction of the PE network during crosslinking since the PS particles are interpenetrated by PE chains and vice versa. On the other hand, the very broad frequency distribution of the diameters of PS particles at high content of PS in IPN samples is probably due to the lower network density of the PS particles. Under these conditions the structure responsible for small-cell structure is not thermodynamically stable and where this structure breaks down large particles form. Therefore, they agglomerate during crosslinking of the whole IPN system. With increasing content of styrene in the IPN

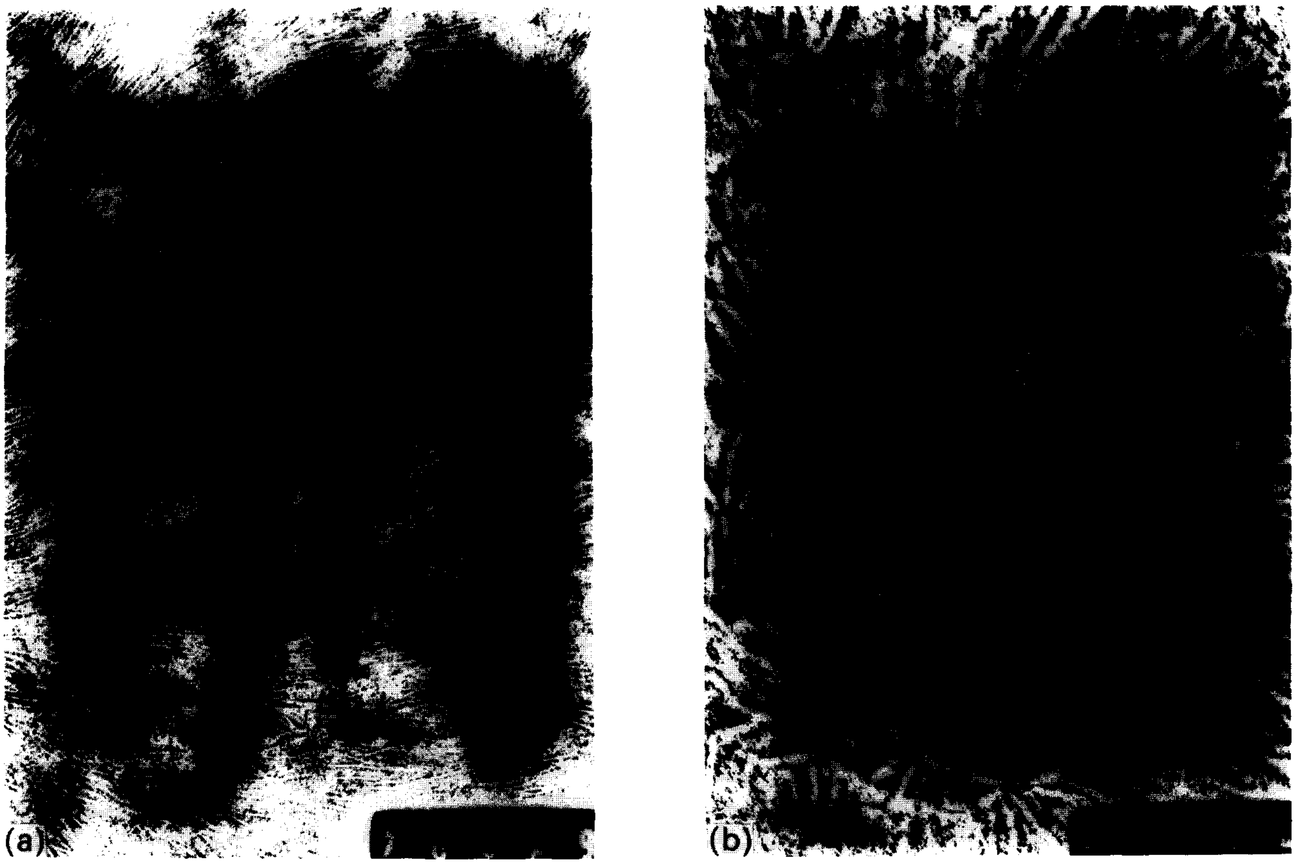
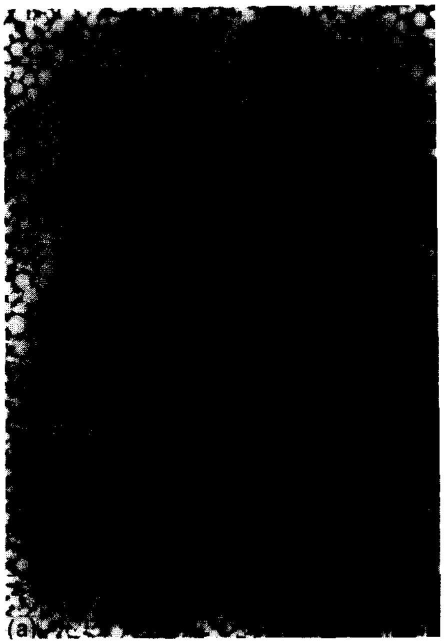
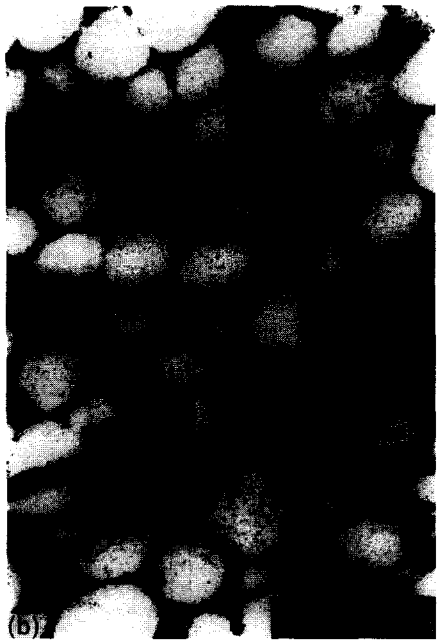


Figure 1 Electron micrographs of LDPE: (a) magnification 64 000×; (b) magnification 200 000×





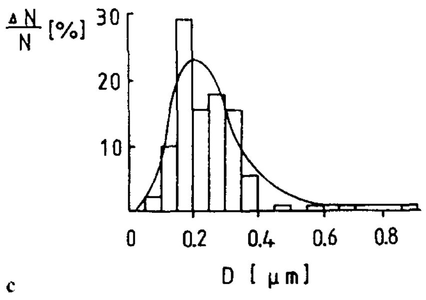
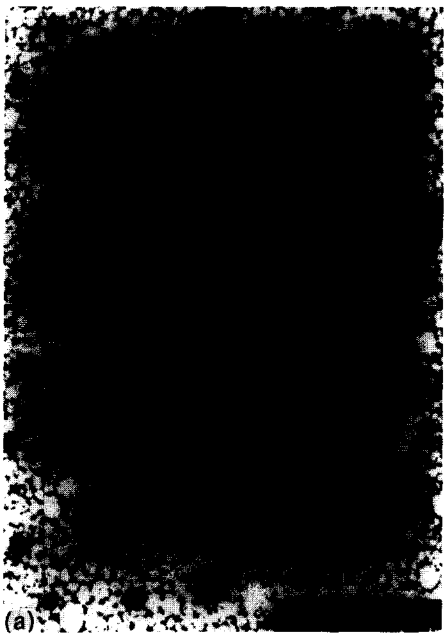


Figure 2 Electron micrographs of IPN with the PE/PS ratio of 62.5:37.5: (a) magnification 12000×; (b) magnification 64000×; (c) frequency distribution of the diagrams of PS particles



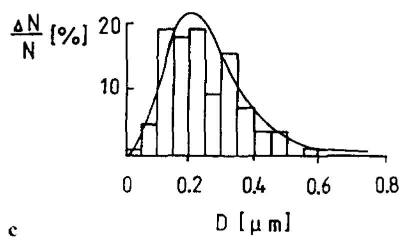


Figure 3 Electron micrographs of IPN with the PE/PS ratio 60:40: (a) magnification 12000×, (b) magnification 64000×; (c) frequency distribution of the diameters of PS particles

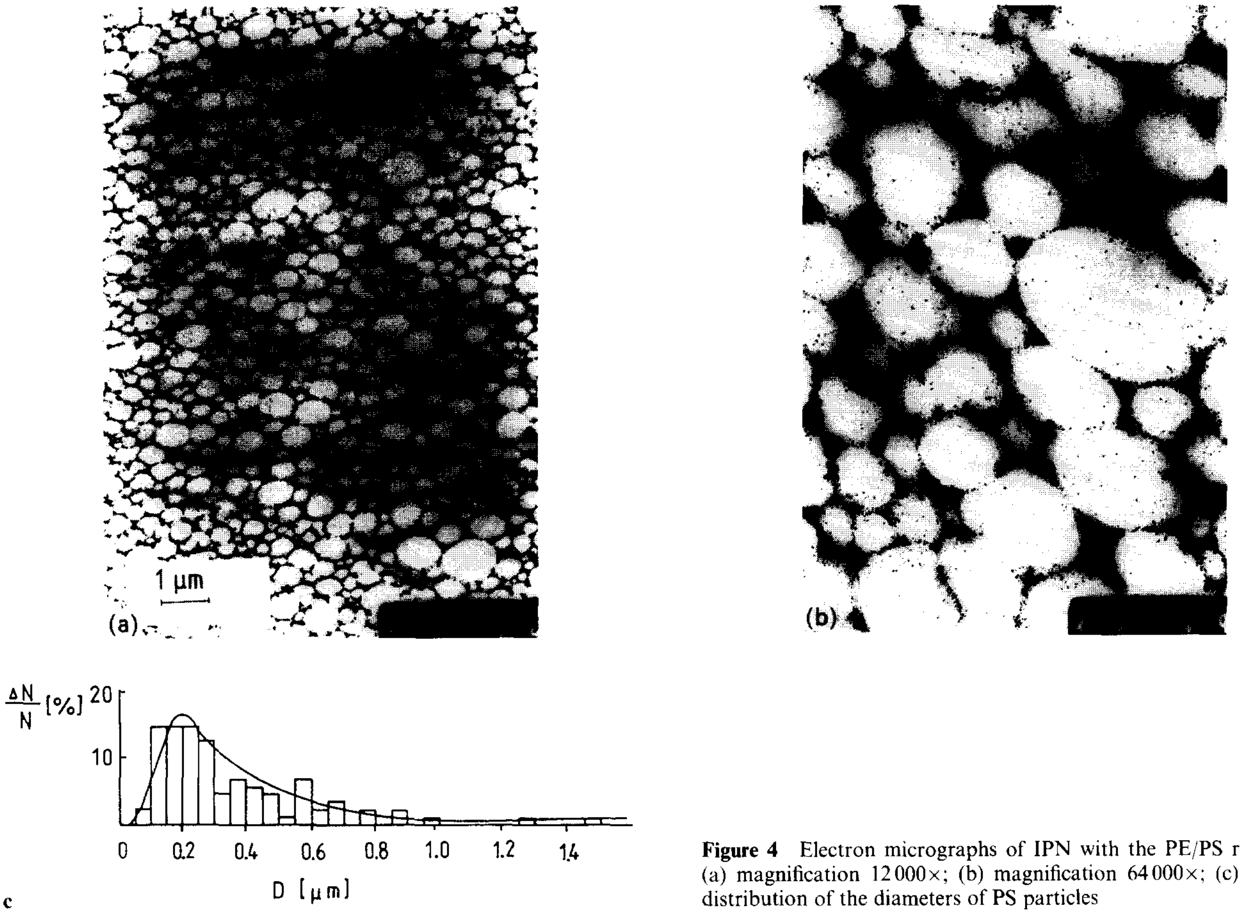


Figure 4 Electron micrographs of IPN with the PE/PS ratio 50:50: (a) magnification 12000×; (b) magnification 64000×; (c) frequency distribution of the diameters of PS particles

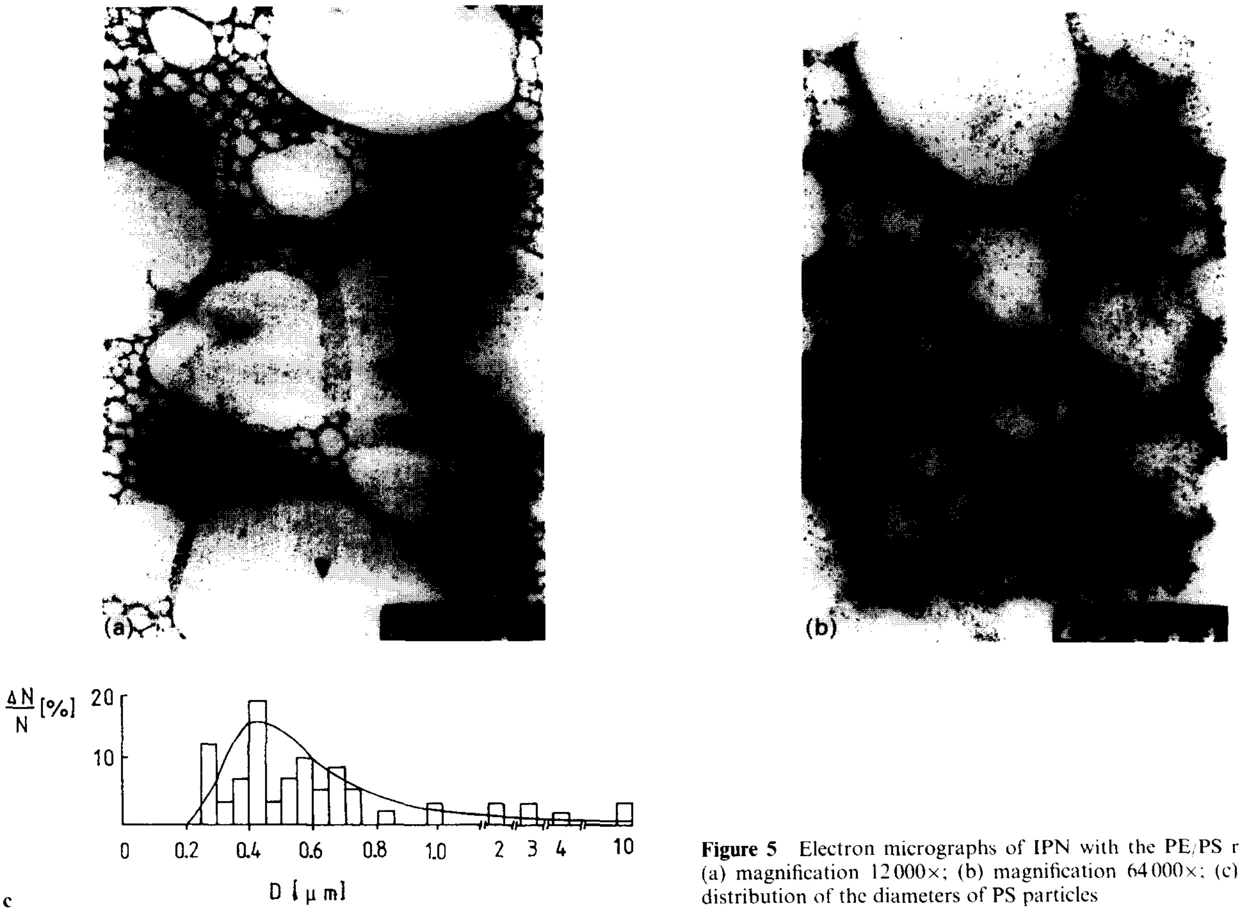


Figure 5 Electron micrographs of IPN with the PE/PS ratio 25:75: (a) magnification 12000×; (b) magnification 64000×; (c) frequency distribution of the diameters of PS particles

system the relative concentration of crosslinker (divinylbenzene) to styrene decreases (*Table 1*).

The morphology of PE-PS IPN-like systems observed differs from the morphology of PE-PS blends prepared by mechanical mixing, mainly at high PS content in the polymer blend. While in IPN only PS domains were dispersed in PE matrix at PS content as high as 85 wt% (at PS/PE = 75:25, *Table 1*), in mechanical PE-PS blend at about 56 wt% of PS a phase inversion was observed (PS becomes a continuous phase[5]).

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