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Preparation of macrocellular PU–PS interpenetrating networks

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Abstract

Macromolecular monoliths were synthesised from concentrated emulsions. Matrixes with only a polyurethane network were too soft and it was necessary to add to the formulation a rigid network such as polystyrene to obtain a material with a good dimensional stability. Either unconnected or interconnected interpenetrating networks were prepared, the later by using hydroxybutyl methacrylate as a comonomer that chemically links both networks. The modifications of the mechanical properties were evaluated by estimating the Young's modulus from compression tests.

Keywords: HIPE; Interpenetrating network; Polyurethane

1. Introduction

Highly porous systems, known in the literature for many years as polyHIPEs [1], have found an increasing number of applications. According to their name, these materials are obtained by polymerisation of a HIPE® (high internal phase emulsion), which corresponds to the dispersion of a large volume of internal phase (or dispersed phase) in a continuous phase (or monomeric phase). The volume of internal phase must be above 74% of the total volume of the emulsion for the emulsion being called a HIPE. This limiting value represents the compact stacking of rigid spheres. In fact, while increasing the volume of this phase, the formation of a HIPE corresponds to the deformation of the droplets into polyhedra, these droplets being surrounded by a thin film of continuous phase [2]. This structure has to be stabilised by one or more surfactants. Thus, the polymerisation of the continuous phase 'freezes' the structure and the removal of the dispersed phase creates voids, or cells, in the material. The main characteristic of polyHIPEs is that, during the polymerisation process, pores appear in the polymer film and permit communication between adjacent cells. Because of the structural particularities of this type of polymer materials (large interconnected cells), a lot of research was conducted on the formation of the structure [1–8]. A number of applications can take advantage of the high porosity of polyHIPEs. Among them, it can be mentioned: absorbents for liquids [9], supports for organic synthesis [10,11], scavengers [12], aerosol filtration [13,14], insulation [15]. The monomer system the most commonly used corresponds to the copolymerisation of styrene (Sty) with divinylbenzene (DVB) [8,16], leading to very rigid and relatively brittle materials (PS). Therefore, in order to improve the properties of the materials, other formulations have been considered [2,16–19].

In this paper, we report for the first time on the preparation of polyHIPEs based on a polyurethane network. Firstly, we studied the synthesis of purely polyurethane-based polyHIPEs, and then their association with a rigid network of PS. We further examined the influence of the polyurethane network over the mechanical properties of the obtained materials.

2. Experimental part

2.1. Materials

Styrene (stabilised, p.a.), tetradecane (TD, 99%) and sodium chloride (p.a.) were purchased from Acros Organics and used as received. Divinylbenzene (technical, 80% DVB

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+20% ethylstyrene, mixture of isomers), 1,12-dodecanediol (99%), 1,4-dihydroxymethyl-cyclohexane (99%, mixture of *cis* and *trans*), dibutyltin dilaurate (DBTDL, 95%), potassium persulphate (99%+, A.C.S. Reagent), hydroxybutyl methacrylate (HBM, 94%, mixture of isomers 2-hydroxybutyl methacrylate and (1-hydroxymethyl)propyl methacrylate) and sorbitan monooleate (Span®80) were purchased from Aldrich and used as supplied. 1,4-Butanediol (99%) was purchased from Avocado organics and used without further purification. Hexamethylene diisocyanate biuret (Desmodur N3400) was a gift of Bayer. Polyglycerol polyricinoleate 90 (PGPR90), was a gift of Danisco, Denmark.

2.2. Characterisation of polyHIPEs

2.2.1. Determination of macroporosity

The porosity and pore size distribution of each sample were determined by mercury intrusion porosimetry with a Micromeritics Autopore 4 instrument.

2.2.2. Surface area measurements

The specific surface area was determined by N_2 adsorption measurements performed on a Micromeritics ASAP 2010. The resulting data were subjected to the Brunauer, Emmet and Teller (BET) treatment [20].

2.2.3. Electron microscopy investigations

The morphology of the monoliths was observed by scanning electron microscopy (SEM) on a Jeol JSM 5200 microscope. The photographs were taken with several different magnifications between 1000× and 20,000×.

The samples were prepared as follow: pieces of polyHIPEs (about 0.5 cm^2), cut from the corresponding monoliths, were mounted on a copper stub, which ensured a good conductivity. A thin layer of gold was sputtered on the polyHIPE fragment prior to analysis.

2.2.4. Mechanical analysis

Compression tests were carried out at room temperature on an Instron 4460 testing machine with a static loading cell of 500 N. Cylindrical samples (diameter = 7 mm, thickness = 4 mm) were compressed at constant speed rate (5 mm min^{-1}) on their flat surfaces between metallic plates.

2.3. Emulsification system

Emulsification was performed in a laboratory-made system composed of two polyethylene syringes (50 mL) connected by a small-section tube (internal diameter = 4 mm). The components of the emulsion (about 20 mL) were put into one of the syringes and the emulsion was formed by successive passages through the tube produced by the backwards and forwards motion of the syringe plungers.

2.4. HIPE preparation and polymerisation

Typically, the continuous phase was composed of the comonomers, a surfactant (20%wt of the continuous phase) and, in some cases, a co-surfactant. The choice of the surfactants was imposed by the type of emulsion researched: Inverse. Each surfactant is characterized by its HLB value (hydrophilic–lipophilic balance) which defines the relative proportion between water-soluble and oil-soluble moieties of the surfactant and several empirical scales have been proposed [7]. Polyglycerol polyricinoleate (PGPR) and sorbitan monooleate (Span®80) have HLB values of 1 and 4.3, respectively, in the Griffin scale [21]. In order to form a reverse water-in-oil HIPE emulsion, a surfactant with a HLB value below 6 is necessary.

The aqueous phase represents between 80 and 90%wt of the total weight of the emulsion. It is constituted of distilled water, sodium chloride (2%wt) and a radical initiator (2%wt, in the case of PS–PU networks preparation). Williams and coll. [5] put in evidence that a water-soluble initiator gives materials with better mechanical properties than an oil-soluble one such as azobisisobutyronitrile (AIBN): With potassium persulfate, polyHIPEs were 50% stiffer than those prepared with AIBN. That was the reason why potassium persulfate was chosen as the radical initiator.

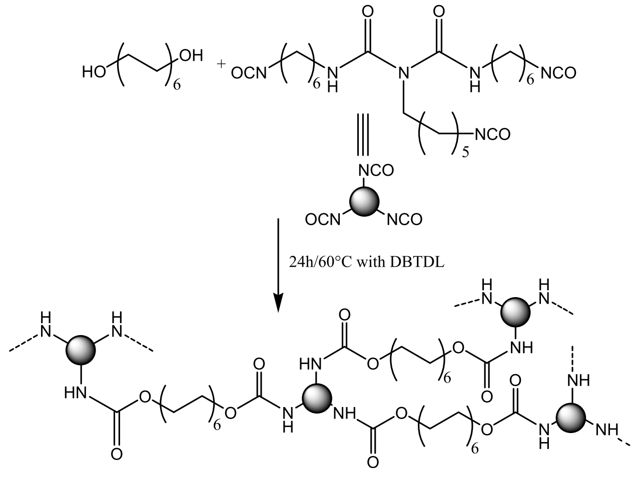
The continuous phase was first triturated in a mortar to solubilize the solid diol in others monomers to obtain a homogeneous phase. Both phases were then put into a 50 mL syringe and intimately mixed for 30 min. A polycondensation catalyst (DBTDL, 1%wt of the total weight of polycondensable monomers) was then added to the resulting concentrated emulsion. The emulsion was finally placed in a PTFE cylindrical mould (internal diameter = 15 mm; thickness = 16 mm) and was polymerized for 24 h at 60 °C in a water bath. The resulting polyHIPE monoliths were extracted by refluxing a mixture ethanol/water (50:50 v/v) in a Soxhlet apparatus (24 h) and dried in a vacuum oven (48 h, 10 mmHg) at room temperature.

3. Results and discussion

3.1. PolyHIPEs of polystyrene

Classically, monomers for polyHIPEs elaboration are styrene-derived compounds and so, the polymerisation process is a radical one. Among the monomers, styrene and divinylbenzene represent the most commonly used system and give materials with various applications [2,11, 22].

First of all, we investigated the elaboration of styrene-divinylbenzene HIPEs stabilized by sorbitan monooleate (HLB = 4,3). Radical polymerisation of emulsions with a dispersed phase fraction from 80 to 90%wt gave materials with a good dimensional stability. Mercury porosimetry and



Scheme 1. Formation of PU network.

scanning electron microscopy analyses confirm the presence of the porous structure and the controlled porosity, characteristic of polyHIPE materials. However, when manipulated, the monoliths were quite brittle and tended to disintegrate into fingers.

3.2. PolyHIPEs of polyurethane

Our objective was to prepare more resistant, porous materials presenting some flexibility. In this issue, the use of polyurethane (PU) elastomers appeared to be an interesting route, because of their properties that are more or less modulable by varying the formulation, and the nature of the monomers employed. Furthermore, this choice was reinforced by numerous papers on the synthesis and the mechanical studies on this type of materials [23–31].

From a structural point of view, the remarkable mechanical properties of PU are explained by the association of rigid segments with flexible ones. The polyisocyanate connected with small diol or diamine play the role of rigid fragments and allow the establishment of intermolecular hydrogen bonds, which act as physical crosslinks and reinforce the structure. On the other hand, the long chain diol used in this work gives PU some flexibility.

This system presents a great interest for us, not only because of the expected mechanical properties of the final material, but also because these monomers have never been used for the synthesis of polyHIPEs. However, synthesis of PU in a dispersed medium had already been studied. Thus, Cramail and coll. [32] reported the synthesis of monodispersed polyurethane microspheres, prepared from ethylene glycol and tolylene-2,4-diisocyanate, by dispersion in cyclohexane. Open-pore polyurethanes have already been developed as chromatography columns, but not from a HIPE approach [33].

In our case, we worked on the elaboration of PU networks by polyaddition of a HIPE. To form a stable reverse emulsion, it is necessary to use hydrophobic monomers. In this issue, we used a diol with a long chain, making it hydrophobic, and conferring some flexibility to the resulting PU. In order to form a network, the diol was associated with an aliphatic polyisocyanate, hexamethylene diisocyanate biuret, commercially named Desmodur N3400 (Scheme 1). This choice was dictated by the fact that this polyisocyanate has the lowest viscosity among all commercially available products. This characteristic was thought to facilitate the homogeneity of the continuous phase. In addition, PGPR90 was used because of its very low HLB value (1–2 estimated), allowing it to be a very efficient emulsifier for obtaining a stable, concentrated reverse emulsion in our case. More widely used surfactant such as sorbitan monooleate (Span®80) did not permit to obtain a stable emulsion under the same conditions.

To prepare the HIPEs, the classical method of mechanical stirring with a D-shaped paddle was not efficient in our case because it was sometimes difficult to incorporate a large volume of water into the emulsion and the solid diol did not always dissolved well in the continuous phase. So, manual mixing in a mortar, which allowed us to facilitate the mixing of monomers and to make emulsions with water weight fraction above 80%, was then considered. However, the materials made with this emulsification method presented a large cell size distribution. Therefore, we

Table 1
Composition of emulsions for PU polyHIPE synthesis

Sample	Nature of the diol	Organic phase composition mol ($\times 10^{-3}$)			%wt H_2O	HIPE stability
		Diol	N3400	TD		
PU1	1,12-Dodecanediol	7.67	5.11	0	80	−
PU2	1,12-Dodecanediol	7.67	5.11	0	90	−
PU3	1,12-Dodecanediol	7.67	5.11	2.555	80	+
PU4	1,12-Dodecanediol	7.67	5.11	2.555	90	−
PU5	1,12-Dodecanediol	7.67	5.11	5.11	80	+
PU6	1,12-Dodecanediol	7.67	5.11	5.11	90	−
PU7	1,4-Dihydroxymethyl-cyclohexane	7.67	5.11	5.11	80	+
PU8	1,4-Dihydroxymethyl-cyclohexane	7.67	5.11	5.11	90	−
PU9	1,4-Butanediol	7.67	5.11	5.11	80	+

N3400, triisocyanate Desmodur® N3400; TD, tetradecane; −, uncompleted emulsion; +, stable emulsion.

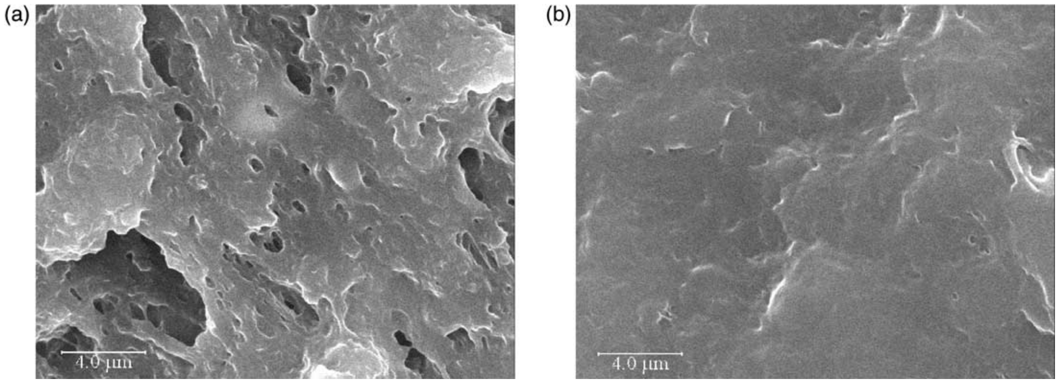


Fig. 1. SEM micrographs of PU polyHIPE networks; (a) **PU5**, (b) **PU7**.

looked for a more mechanical method that permitted to obtain a smaller cell size distribution and a better reproducibility of mixing conditions. This objective was reached with the emulsification system described in Section 2.

The compositions of the different emulsions prepared are reported in Table 1. The relative proportions between polyisocyanate and polyol were imposed by the functionality of each monomer. To achieve a maximal crosslinking, three equivalents of bifunctional alcohol for two equivalents of trifunctional isocyanate were used, giving a NCO/OH ratio of 1. The stability of the emulsions was estimated by the visual non-observation of a surnatant after 1 h at room temperature. With 1,12-dodecanediol, Desmodur N3400 and PGPR90 as the continuous phase, it was not possible to obtain a stable emulsion, whatever the aqueous phase fraction incorporated (PU1 and PU2). This behaviour can be explained by a hydrophobic character of the continuous phase not high enough. Thus, it was necessary to increase this character by adding a long chain molecule, such as tetradecane (TD), acting as a co-surfactant, as it was recently reported by Tiarks and coll. [34]. The same authors also put in evidence that the reaction of isocyanate groups with water was negligible in comparison to their reaction with the diol, for a system isophorone diisocyanate and dodecanediol. This observation was very important for us, because we worked on highly concentrated reverse emulsion, and so, with a large volume of water. Indeed, even with the co-surfactant, the maximum fraction of incorporated aqueous phase allowing a stable emulsion was limited to 80%wt (PU3 and PU5). Concerning tetradecane, in a first approach we use the lowest possible quantity to minimise its influence on the structure of the polyHIPE. As it was impossible to incorporate a 90%wt aqueous fraction under these conditions (PU4, molar equivalents tetra-decane/N3400/diol = 1/2/3), the fraction of tetradecane was increased (PU5 and PU6, molar equivalent tetradecane/N3400/diol = 2/2/3). Nevertheless, even it that case, a stable emulsion with an aqueous fraction of 90%wt was never obtained.

The obtained stable emulsions were cured at 60 °C in the presence of an organotin catalyst (DBTDL) known to be the most suitable for urethane formation between alcohols and isocyanates [35].

PolyHIPE monoliths obtained after demoulding, solvent extraction and vacuum drying did not retain the geometrical integrity of the original emulsion. Their structure seemed to be too flexible and collapsed when the water phase, which gave support to the network formation, was removed and thus, the dimensions of the final material were smaller than those of the mould. This behaviour could be provoked by a too long diol chain, which induced too much flexibility. To improve the rigidity of the network, we tried to make polyHIPEs with a hydrophobic diol having a more rigid structure (1,4-dihydroxymethylcyclohexane) but the same behaviour was observed (PU7 and PU8). In the same way, the use of a short diol, butanediol, instead of dodecanediol did not modify the resulting aspect of the material (PU9).

Because of the collapsing of the structure, the actual porosity values of the different samples, as determined by mercury intrusion porosimetry, were very low compared to the expected values (values not showed). SEM analyses confirmed the lack of porous structure of the samples, whatever the composition (Fig. 1).

3.3. PolyHIPEs of PU–PS IPNs

The synthesis of pure polyurethane polyHIPEs was not possible because the porous structure collapsed during the drying step, due to the too important flexibility of the polyurethane network. On the other hand, physical and chemical associations between different types of polymers constitute a commonly used route to improve the properties of materials. Thus, PS networks are known to be very rigid and brittle and can be toughened by incorporation of an elastomeric material like PU. Thus, we considered the association of a rigid network of PS with a PU network in an interpenetrating network (IPN) structure, these IPNs being interconnected or not.

3.4. Unconnected PU–PS IPNs

3.4.1. Synthesis of polyHIPEs

PU–PS association by unconnected IPNs has already been developed in the literature [36–38], but not in

Table 2
Composition of the HIPE for unconnected PU–PS IPNs polyHIPE synthesis

Sample	Molar equivalents (mol)				%mol Sty + DVB	%wt H_2O (expected porosity)	Measured porosity (%)	PolyHIPE aspect
	PU network		PS network					
	N3400	Diol	Sty	DVB				
IPN1	2.00	3.00	1.25	1.25	33	80	12	−
IPN2	2.00	3.00	1.67	1.67	40	80	13	−
IPN3	2.00	3.00	2.50	2.50	50	80	36	±
IPN4	2.00	3.00	3.75	3.75	60	80	79	+
IPN5	2.00	3.00	10.00	10.00	80	80	78	++
IPN6	2.00	3.00	10.00	10.00	80	90	90	+

PolyHIPE aspect: −, collapsed; ±, partially collapsed; +, soft; ++, rigid.

polyHIPEs applications. The synthesis of IPNs is generally based on a two-step approach, combining polyaddition and radical polymerisation [39–41]. However, several researches have been carried out to develop a one-pot synthesis, and an interesting work relates the elaboration of polymer hybrid particles in an aqueous dispersed medium [42]. We prepared concentrated emulsions (HIPEs) containing a mixture of styrene, divinylbenzene, dodecanediol and Desmodur N3400 as the organic phase to generate simultaneously a PS network and a PU network. The two components required for the PU network were added in stoichiometrical proportions (NCO/OH ratio = 1) to obtain a completely crosslinked network. Styrene and divinylbenzene were added in a 1/1 molar ratio. The surfactant used was PGPR 90. The molar proportion of Sty + DVB in the organic phase was varied from 33 to 80%. Potassium persulphate was introduced in the aqueous phase as the radical initiator of the styrenic network, while DBTDL was added to the final emulsion as the polyaddition catalyst of the PU network. Aqueous phase amount was varied from 80 to 90%wt. The compositions of the different HIPEs prepared are reported in Table 2. In all cases, stable emulsions were obtained without the need of tetradecane: Obviously, addition of styrene and DVB allowed the continuous phase to be hydrophobic enough. The obtained HIPEs were converted into polyHIPEs by heating at 60 °C.

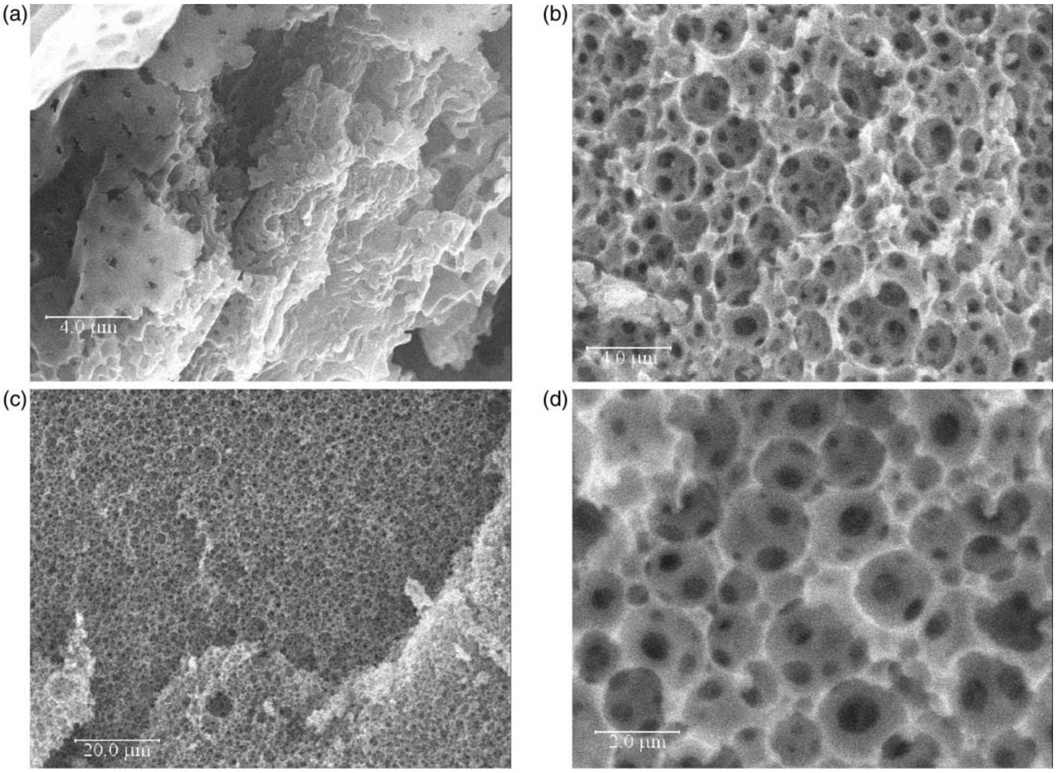


Fig. 2. SEM micrographs of PU–PS unconnected IPNs; (a) **IPN3**, (b) **IPN4**, (c)–(d) **IPN5**.

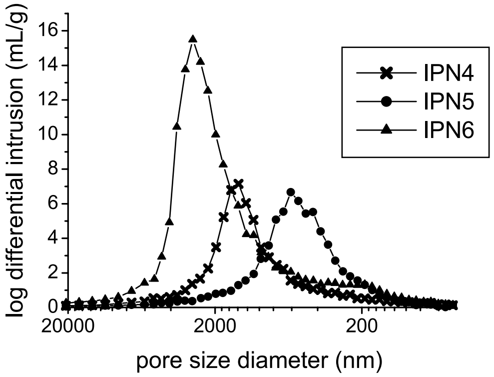


Fig. 3. Pore size distribution of unconnected PU–PS IPNs.

3.4.2. Structural characterisations of unconnected PU–PS IPNs polyHIPEs

PolyHIPE monoliths were obtained after polymerisation/polyaddition, solvent treatment and vacuum drying. Results of the structural analyses of the resulting unconnected PU–PS IPN polyHIPEs are reported in Table 2. For compositions **IPN1** and **IPN2**, the samples collapsed during the vacuum drying step. Consequently, the quantity of PS network appeared to be insufficient to give support to a polyHIPE structure. The rigid PS domains were too small so the flexible character of PU was prevalent. This visible observation was confirmed by SEM analysis where no typical porous polyHIPE morphology was observed. Mercury intrusion porosimetry, which allows to determine the effective porosity of the samples, also put in evidence the very low porosity of the samples (~10–15% compared to 80% expected) and so the absence of any polyHIPE structure.

When the molar ratio of Sty+DVB was enhanced to 50%mol (**IPN3**), the polyHIPE was still compacted but in a proportion lower than for previous samples, which seems to indicate that there was a reinforcement of the structure, but still not sufficient (porosity = 36% for 80% expected). SEM observations confirmed the presence of a low porosity. Furthermore, this porosity was not homogeneously distributed on the sample surface and no polyHIPE structure was observed (Fig. 2(a)).

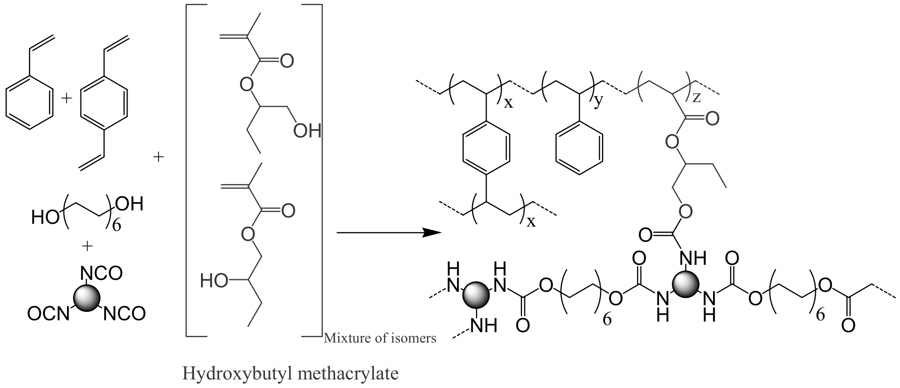
The samples **IPN4** and **IPN5** containing 60 and 80% of PS network did not collapse and conserved the shape of the mould because of a structure reinforced by the rigid PS network. This strengthening was confirmed by the observation of a polyHIPE structure by SEM (Fig. 2(b)–(d)) and by the porosity measurements, which were in accordance with the expected value (Table 2). Structural analysis also put in evidence a decrease of the peak maximum when the amount of PS in the formulation was increased: 1.44 and 0.61 μm for 60 and 80% of PS, respectively (Fig. 3). This observation supports the hypothesis concerning the formation of the pores. The mechanism of this formation is not really known but it is commonly assumed that, during the polymerisation process, some polymer contraction occurs [5,6]. This contraction would produce pores by film tearing where the polymer film is the thinnest, i.e. where water droplets are the closest. When increasing the amount of PS, the rigidity of the film increases, which could limit the film tearing and so, the pore formation. Concerning the case of **IPN6**, the greater volume of dispersed phase resulted in a thinner film, compared to **IPN5**. Consequently, this film was less resistant than that for **IPN5**, and so, the pore size increased (Fig. 3, maximum pore size at 2.83 μm).

The specific surface areas determined by N_2 adsorption were roughly equal for all the compositions studied (about 10 m^2/g) and were analogous to the value of surface area for a network composed of 100% of PS [8]. The incorporation of polyurethane network did not modify the surface area of the resulting materials.

3.5. Interconnected PU–PS IPNs polyHIPEs

3.5.1. Synthesis

PS and PU are non-compatible, immiscible networks, because of differences in polarity (PU has a polar nature and PS a non-polar one) and in their solubility parameters [43]. Therefore, in the case of IPNs with these polymers, it may appear separated domains by phase separation, which will reduce the mechanical properties of the resulting materials [44]. A solution to this problem could be to link chemically both networks, giving access to interconnected PU–PS



Scheme 2. Formation of interconnected PU–PS IPNs.

Table 3
Formulation of interconnected PU–PS IPNs polyHIPEs

Sample	Molar equivalents (mol)					Grafting density	%mol Sty + DVB	Measured porosity (%)	PolyHIPE aspect
	N3400	Diol	HBM	Sty	DVB				
IPNc2	12.00	16.50	3.00	6.50	9.50	1/12	40	16	−
IPNc4	12.00	16.50	3.00	18.375	21.375	1/12	60	56	±
IPNc7	12.00	12.00	12.00	6.00	18.00	1/3	60	73	++
IPNc5	12.00	16.50	3.00	54.00	57.00	1/12	80	79	++
IPNc8	12.00	12.00	12.00	36.00	48.00	1/3	80	79	++

PolyHIPE aspect: −, collapsed; ±, partially collapsed; +, soft; ++, rigid.

IPNs. This connection requires the use of monomers presenting at the same time functional groups that are compatible with the generation of both networks. Previous works using a grafting agent for PU–PS IPNs synthesis was described in the literature [45].

We used as inter-network grafting agent, a product with one vinyl and one hydroxyl function: Hydroxybutyl methacrylate (HBM). Formulation of the emulsions was similar to that for unconnected IPNs, except that part of the styrene was replaced by HBM in such a manner that the molar ratio (Sty + HBM)/DVB was equal to 1/1 (Scheme 2). As for unconnected IPNs, in order to form a completely crosslinked PU network, the proportions of NCO and OH groups needed to be equal. However, in the present case, HBM presents a hydroxyl function that can react with NCO functions. Therefore, two considerations were taken into account for determining the stoichiometry between the different monomers:

- molar ratio (Sty + HBM)/DVB = 1/1
- number of OH_{diol} + number of OH_{HBM} = number of NCO_{N3400} ⇔ that is to say (in molar equivalents): $2n_{diol}+n_{HBM}=3n_{N3400}$.

Different formulations were considered in order to study the influence of PU content and of the proportion of grafting between the two networks on structural and mechanical properties of the resulting materials (Table 3). The grafting density corresponds to the proportion of –NCO groups of the triisocyanate that are linked to PS network by HBM molecule (i.e. $n_{HBM}/3n_{N3400}$). The aqueous phase proportion (%wt H_2O, i.e. expected porosity) was fixed at 80%wt.

Table 4
Elemental analysis of interconnected IPNs

Sample	Elements (wt%)			
	C	H	N	O
IPNc2				
Calculated	74	10	4	12
Experimental	63	10	6	18
IPNc4				
Calculated	80	9	3	8
Experimental	62	8	5	16
IPNc7				
Calculated	75	9	4	13
Experimental	60	8	5	16
IPNc5				
Calculated	86	9	2	4
Experimental	73	9	3	11
IPNc8				
Calculated	83	9	2	6
Experimental	66	8	3	13

3.5.2. Structural characterisations of interconnected PU–PS IPNs polyHIPEs

Stable emulsions were obtained for all formulations considered. The proportion of PS rigid network played an important role in the structure integrity, to prevent its collapse. The results of mercury intrusion porosimetry analyses are given in Table 3. Unlike unconnected IPNs, the introduction of 60%mol of (Sty + DVB) was not sufficient to maintain the geometrical integrity of the monolith. Samples with a grafting density between PU and PS networks of 1/12 (**IPNc4**) looked partially compacted and presented a low porosity (56%). However, when the grafting density was increased (**IPNc7**), the material did not collapse at all. This can be easily explained by the increasing of links between PU and PS networks, which produces an increase in the homogeneity of the material, reinforces the structure and so prevents the structure from collapsing. As it was already observed for unconnected IPNs, samples made from emulsions with 80%mol of (Sty + DVB), (**IPNc5** and **IPNc8**) did not collapse and kept the mould shape. The measured porosity of such monoliths was in accordance with the expected values.

The elemental analysis of interconnected IPNs is given in Table 4. The presence of oxygen and nitrogen confirms the presence of the polyurethane network in the structure of our materials. However, the experimental nitrogen contents were a little bit higher than the expected values, whereas the carbon contents were lower than the theoretical values, whatever the composition of the emulsion was. These results seem to indicate a higher proportion of PU network compared to the PS one. This can be explained by kinetic studies previously reported in the literature which put in evidence that, for simultaneous polymerizations, the PU network formation was faster than the PS network elaboration [36,46]. Futhermore, it was observed that, when the first network was elaborated, radicals could be trapped into the PU network structure, which limits the

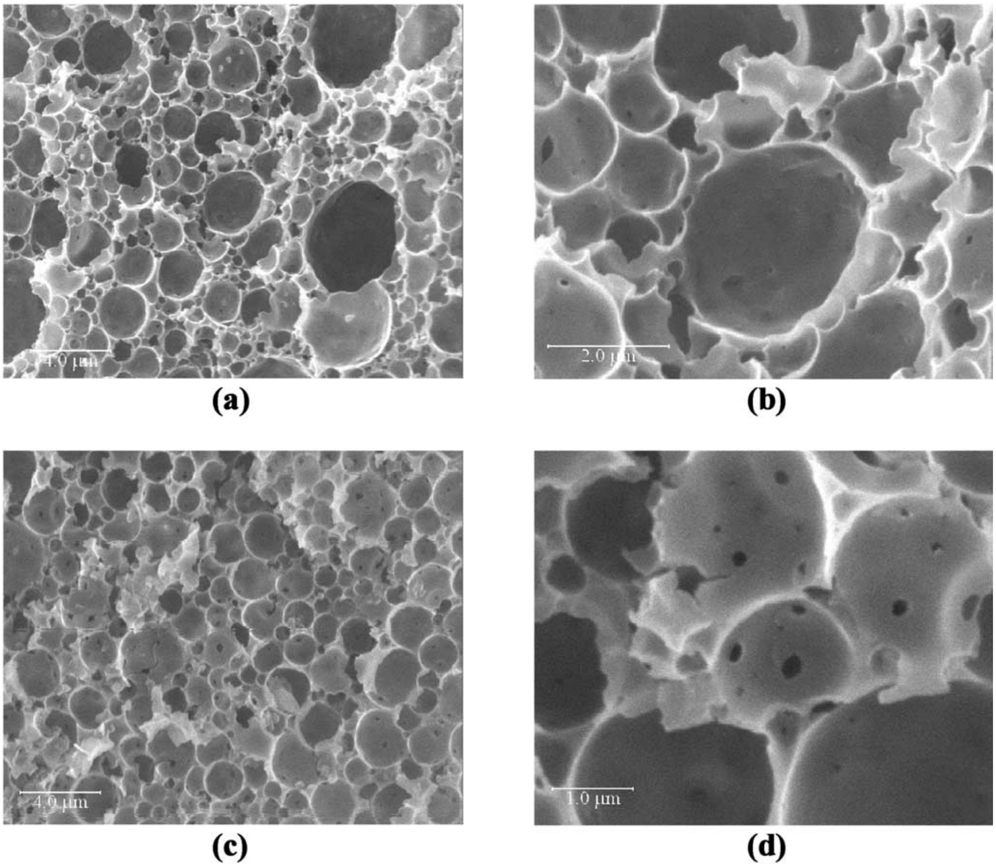


Fig. 4. SEM micrographs of PU–PS interconnected IPNs; (a)–(b) **IPNc7**, (c)–(d) **IPNc8**.

conversion of vinylic compounds [47,48]. The high experimental content of oxygen, compared to the expected value, could result from this explanation, and also from the hygroscopic character of our materials.

For materials having an acceptable porosity (**IPNc5-8**), SEM analysis permitted to investigate the presence of characteristic polyHIPE morphology (Figs. 4 and 5). For each sample, we observed a structure composed of interconnected spherical cells. In addition, the amount of interconnections varied when the composition of the emulsion was varied. Thus, when the grafting density between PU and PS networks increased, the proportion of pores decreased, even with 80% of PS: pore size ranges were 0.10–1.42 and 0.09–1.10 μm for **IPNc5** and **IPNc8** respectively. The peak maximum was 0.24 μm for **IPNc5** and 0.12 μm for **IPNc8** (Fig. 6). This result can be explained by the mechanism already developed in the paragraph concerning the unconnected IPNs. In that case, increasing the grafting density between the two networks increased the rigidity, which could limit the film tearing and so, the pore formation. Still, as for unconnected IPNs, no modification of the specific surface area was observed, whatever the composition: the measured values were around 10 $m^2\ g^{-1}$.

In spite of the fact that for some samples the proportion of pores was limited, the observed structures were similar to those of polyHIPEs already reported [3–6]. The best formulation was with 80%mol of (Sty+DVB) and a ratio of NCO groups connected to the rigid network of 1/12 (**IPNc5**, Fig. 5). The cell size diameter range for **IPNc5** was estimated to be ~2±1 μm by image analysis.

3.6. Mechanical characterisations

The influence of the proportion of PU introduced in the IPNs and of the grafting density between PU- and PS-networks on the mechanical properties of the polyHIPEs was investigated at room temperature. A study by dynamic mechanical analysis (DMA), which examines the material behaviour in function of the temperature, could not be used in our case, because the crosslinking degree of each network was too important and so, no thermal transition could be observed.

We realized mechanical characterisations at room temperature by compression tests. The deformation δ and the force F opposing to this deformation were recorded (the deformation of the device was neglected). From these experimental data, the nominal stress σ and the nominal strain ε, were calculated using, respectively, the following Eqs. (1) and (2) [49]:

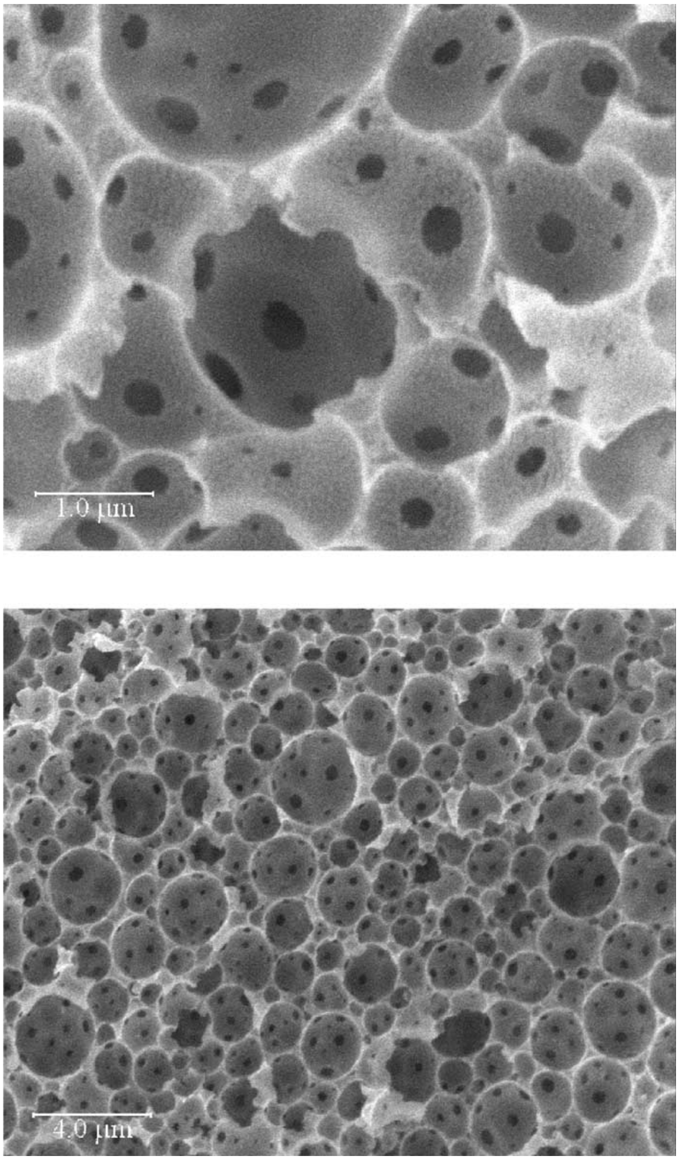


Fig. 5. SEM micrographs of PU–PS interconnected IPN **IPNc5**.

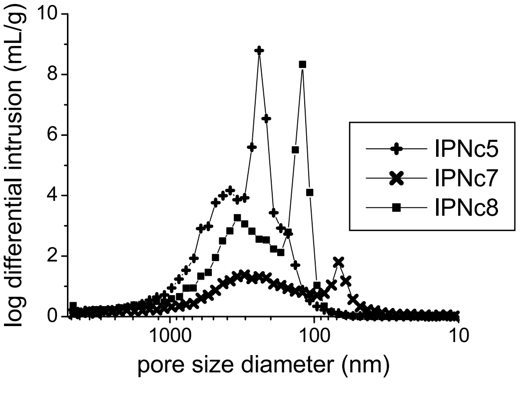


Fig. 6. Pore size distribution of interconnected PU–PS IPNs.

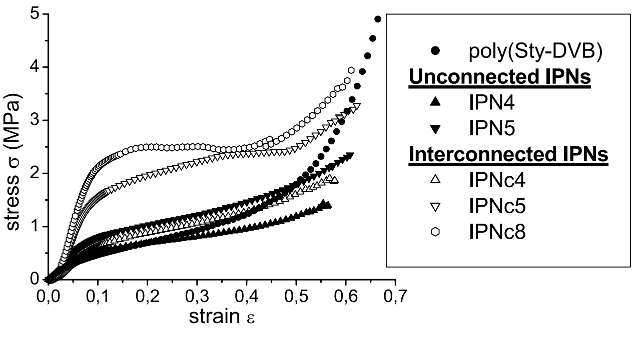


Fig. 7. Stress–strain curves of PU–PS IPNs at room temperature.

Table 5
Young's modulus of PU–PS IPNs

Type of network	PS network	Unconnected IPN		Interconnected IPN		
Sample	PS	**IPN4**	**IPN5**	**IPNc4**	**IPNc5**	**IPNc8**
E_{polyHIPE} (MPa)	9.0	7.5	14.5	9.7	29.6	38.4

$$\sigma(N) = \frac{F(\text{Pa})}{S_0(\text{m}^2)}$$

(S_0 corresponds to the surface on which the deformation is applied) (1)

$$\varepsilon = \frac{\delta(\text{mm})}{L_0(\text{mm})}$$

(L_0 is the initial length of the sample, along which the compression is applied) (2)

The stress–strain diagram $\sigma = f(\varepsilon)$ (Fig. 7) presents, for the majority of the cases, a linear relationship between σ and ε in the elastic region, which corresponds to the early stage of the curve. At small deformations, when the stress is suppressed, the sample 'relaxes' and recovers its initial shape. The slope of this linear part of the curve is defined by the Hooke's Law (3).

$$\sigma = E\varepsilon \quad (3)$$

Where the proportionality constant E corresponds to the elastic modulus or Young's modulus, and is characteristic of the rigidity of the sample. So, for the most interesting samples, we plotted $\sigma = f(\varepsilon)$ on Fig. 7 and determined their Young's modulus (Table 5), pure PS polyHIPE material being chosen as reference material.

It is observed that the incorporation of PU into a PS rigid network modifies the mechanical properties of the material. Thus, as expected, the incorporation of an elastomeric network causes a decrease of E and so the polyHIPE material becomes more flexible. This observation is valid for unconnected and interconnected network: **IPN4** (40% of PU) has a Young's modulus lower than that of the pure PS network. However, with a lower proportion of PU, polyHIPEs seems to be more rigid. The introduction of 20% of PU (**IPN5**) generates an increase in the Young's modulus, compared to PS network. This behaviour could be explained by an increase in the proportion of crosslinks [50]. This hypothesis was confirmed by mechanical studies on interconnected PU–PS IPNs. The introduction of inter-network links provoked an increase in the rigidity of the material: E increased from 14.5 to 29.6 MPa (**IPN5** and **IPNc5**). Futhermore, the higher the proportion of links, the higher the rigidity (**IPNc5** and **IPNc8**). Thus, the efficiency of inter-network crosslinking was easily put in evidence by comparing the E values for PS and interconnected IPNs polyHIPEs: The presence of chemical links between PS and PU networks improved the rigidity of the material.

4. Conclusions

In this work, we have demonstrated the possibility to synthesize polyHIPE monoliths with a polyurethane formulation. The use of a hydrophobic diol and a commercially available trifunctional isocyanate allows the preparation of a reverse concentrated emulsion. However, its curing with dibutyltin dilaurate proceeded with a high level of shrinkage. Matrixes with only a polyurethane network were too soft and it was necessary to add to the formulation a rigid network in order to obtain materials with a good dimensional stability. The addition to the emulsion of a rather high level of styrene and divinylbenzene allows the preparation of rigid microcellular interpenetrating networks. These PU–PS IPNs could be connected using a difunctional comonomer such as hydroxybutyl methacrylate, and polyHIPE materials with cell size diameter ≤ 3 μm and pore size diameter ~ 0.2 μm have been obtained. Mechanical properties modifications were evaluated by estimating the Young's modulus E from compression experiments. E appears to be three time higher for an interconnected PU–PS polyHIPE than for a simple PS polyHIPE.

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