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MICROCELLULAR OPEN-POROUS POLYSTYRENE-BASED COMPOSITES FROM EMULSIONS

MIKROCELIČNI ODPRTOPOROZNI POLISTIRENSKI KOMPOZITI IZ EMULZIJ

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Series of cross-linked polystyrene samples were prepared using an emulsion templating approach, where monomers were contained in the continuous phase of the emulsion, while the droplet aqueous phase induced primary pores, connected with a number of secondary pores. Emulsions with a high fraction of the droplet phase (HIPEs) were used and stabilised with a combination of a surfactant (sorbitan monooleate) and various types of particles (charcoal powder, copper powder and carbon nanopowder). The morphology of the resulting porous polymer depends on the type and amount of the particles added to the emulsion; however, in all the cases open-cellular morphology was formed. The size of the primary pores (cavities) ranged from 5 μm to 25 μm, while the size of the secondary interconnecting pores was from 1 μm to 5 μm. The materials were investigated using scanning electron microscopy and nitrogen adsorption/desorption.

Keywords: polyHIPE, porous polymers, nanocomposites, porosity, polystyrene

Z uporabo emulzij z visokim deležem notranje faze smo pripravili serijo zamreženih polistirenskih vzorcev. Monomeri so bili vsebovani v kontinuirni fazi emulzije, kapljice notranje vodne faze pa so povzročile poroznost materiala z vrsto primarnih por, povezanih s povezovalnimi porami. Emulzije z visokim deležem notranje faze (HIPE) smo stabilizirali z uporabo surfaktanta v kombinaciji z različnimi delci (oglje v prahu, baker v prahu in ogljikov nanoprah). Na morfologijo pripravljenih odprtoporoznih materialov sta vplivala tako vrsta kot tudi količina dodanih delcev. Velikost primarnih por je bila v območju med 5 μm in 25 μm, medtem ko je bila velikost sekundarnih povezovalnih por v območju med 1 μm in 5 μm. Materiale smo karakterizirali z uporabo vrstičnega elektronskega mikroskopa in adsorpcijo/desorpcijo dušika.

Ključne besede: poliHIPE, porozni polimeri, nanokompoziti, poroznost, polistiren

1 INTRODUCTION

As a template for the preparation of highly porous polymers, high internal-phase emulsions (HIPEs) can be used. They are defined as the emulsions, whose internal phase exceeds 74.05 % of the total volume[1] and which are formed by mixing together two immiscible liquids and a stabilizer. With a polymerisation of HIPEs, highly porous polymers, termed polyHIPEs, are produced, usually having an interconnected structure and a high porosity, up to 99 %.[2] PolyHIPEs are usually prepared in the form of monoliths; however, polyHIPE beads[3–5] or even membranes[6–8] can be produced. With their exceptional properties, such as a high porosity and surface area and a low density, they find use in various applications, such as tissue engineering[9–11], filtration[12], separation[13,14], gas storage[15], catalyst supports[16–18], etc.

HIPEs are thermodynamically unstable systems and their stability is affected by flocculation, sedimentation, coalescence, Ostwald ripening and phase inversion.[1] Their stabilization is usually done by adding an appropriate amount of a suitable surfactant, resulting, after the polymerisation, in an open and interconnected porous structure. The quantities of the surfactant can vary between less than 1 %[19,20] and 50 %.[21,22]

Emulsions can also be stabilized by incorporating solid particles instead of a surfactant and such systems are termed the Pickering or Ramsden emulsions.[23,24] The stability of emulsions in such cases depends on the particle size and shape, while the interactions between the particles and the wetting ability can be improved by modifying the particle surfaces.[25] The Pickering HIPEs have similar properties as the surfactant-stabilized emulsions and are used for the applications where the surfactants are difficult to remove or have a negative influence on the final product, for example, the irritancy. When polymerised, the Pickering emulsions usually tend to have a closed porous structure, but they possess other interesting futures such as electrical conductivity, magnetic properties, better mechanical properties, etc.[26,27] Preparations of polymer materials from the Pickering HIPEs were reported for several applications and, without a surfactant, they usually result in a closed-cellular porous morphology.[25,28,29] On the other hand, the Pickering emulsions, in combination with surfactants, can give open-porous materials.[30,31] Particles and nanoparticles are added to a polymer matrix for several reasons like to influence the mechanical properties or surface area by inducing additional pores, introduce novel properties to a

matrix polymer material, such as magnetic, electrical or optical properties. However, in the case of porous polymers, an addition of particles can significantly influence the resulting morphology. It is, therefore, worth investigating the influence of added particles on the morphology of porous composite materials.

In this paper we report on the preparation of highly porous polyHIPEs based on styrene and divinylbenzene and with added particles, namely, the charcoal powder, copper powder and carbon nanopowder.

2 EXPERIMENTAL SECTION

2.1 Materials

A monomer styrene (Sigma Aldrich) and divinylbenzene (DVB, Sigma Aldrich) were passed through a layer of basic alumina (Al_2O_3, Fluka) to remove the inhibitors. The initiator potassium persulfate (KPS, Fluka), the surfactant sorbitan monooleate (Span 80, HLB (hidrophilicity-lipophilicity balance) = 4.3, Fluka), calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$, Merck), ethanol (Merck), charcoal powder (Sigma Aldrich, 10–40 μm), copper powder (Sigma Aldrich, < 10 μm), and carbon nanopowder (Sigma Aldrich, < 50 nm (BET)) were used as received without any further purification. In all the experiments deionized water was used.

2.2 PolyHIPE preparation

PolyHIPEs were prepared by slowly adding the internal phase to the continuous phase under constant stirring. The continuous phase consisted of styrene and DVB monomers, surfactant Span 80 and an appropriate amount of the particles (**Table 1**). It was placed in a 250 mL three-necked reactor, fitted with an overhead stirrer. The aqueous phase was prepared separately by dissolving $CaCl_2 \cdot 6H_2O$ and the initiator KPS in degassed and deionised water and was added dropwise to the continuous phase under constant stirring at 300 r/min. After a completed addition of the appropriate amount of the aqueous phase, stirring was continued for another 60 min to produce a stable emulsion. The emulsions were transferred into polypropylene tubes and exposed to 60 °C for 24 h. The resulting monoliths were being extracted in a Soxhlet apparatus using water for 24 h and ethanol for another 24 h and then dried in a vacuum at 40 °C for 24 h. A series of 16 emulsions of varying solid-particle concentrations were prepared (**Table 1**).

Table 1: HIPE formulations and morphological features of polyHIPEs
Tabela 1: Formulacije HIPE-ov in morfološke lastnosti poliHIPE-ov

Sample	Particle type	Amount (%)	Cavity diameter (μm)	Interconnecting pore diameter (μm)
S0	/	/	/	/
C1	charcoal powder	0.5	25	5
C2	charcoal powder	1.5	20	5
C3	charcoal powder	2	12	2.5
Cu1	copper powder	0.5	14	4
Cu2	copper powder	1	/	/
Cu3	copper powder	1.5	5	1
Cu4	copper powder	2	/	/
CNP1	carbon nanopowder	0.1	/	/
CNP2	carbon nanopowder	0.35	20	5
CNP3	carbon nanopowder	1	/	/
CNP4	carbon nanopowder	3	5	2
CNP5	carbon nanopowder	5	9	1.5
CNP6	carbon nanopowder	7	/	/
CNP7	carbon nanopowder	10	/	/
CNP8	carbon nanopowder	15	9	2

*all emulsions consisted of volume fractions 70 % styrene, 30 % DVB, 20 % Span80 – oil phase (20 %) and KPS, $CaCl_2 \cdot 6H_2O$ and deionized water – water phase (80 %)

2.3 Characterisation

Typical polyHIPE morphology was determined using a scanning electron microscope (SEM), Quanta 200 3D (FEI Company). Samples were mounted on a sample holder using a graphite tape and sputter coated with a layer of gold. Nitrogen adsorption/desorption measurements were done on a Micromeritics TriStar II 3020 porosimeter using a BET model for the surface-area evaluation.

3 RESULTS AND DISCUSSION

In order to examine the effect of different particle additions to the emulsion on the morphology of the resulting polymers, polyHIPE samples from styrene and divinylbenzene (DVB) with added particles were prepared (**Table 1**). To avoid a misinterpretation of the influences on the morphology, the basic matrix always consisted of a high internal-phase emulsion with styrene and DVB (volume fractions 70 % styrene and 30 % DVB). The continuous phase of all the emulsions consisted of monomers and surfactant Span 80 (the volume fraction 20 % of the monomer content). The internal aqueous-phase volume was kept at 80 % in all the cases consisting of deionized water, $CaCl_2$ and the initiator (potassium persulfate). A sample without any added particles was also prepared (S0) as a reference for comparison. For the other experiments three different types of particles were used: charcoal powder, copper powder and carbon nanopowder.

Charcoal powder was first tried as an additive to the monomer containing the continuous phase of the emulsion. As predicted, the addition of solid particles to the oil phase showed a significant effect on the resulting polyHIPEs morphology. By increasing the amount of the charcoal powder from 0.5 % to 2 %, the cavity diameter decreased from 25 μm to 12 μm and the interconnecting pore diameter from 5 μm to 2.5 μm, which suggests an increased stability of the particle-stabilized emulsions caused by the Pickering effect. No visible particle agglo-

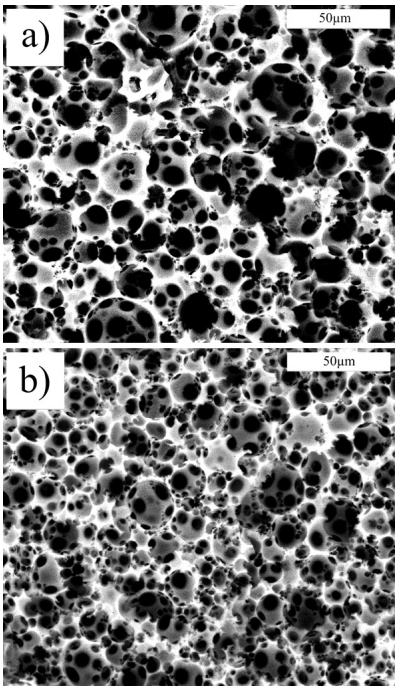

Figure 1: SEM images of: a) 1.5 % charcoal and b) 2 % charcoal polyHIPEs
Slika 1: SEM-posnetka poliHIPE-a z: a) 1,5 % oglja in b) 2 % oglja

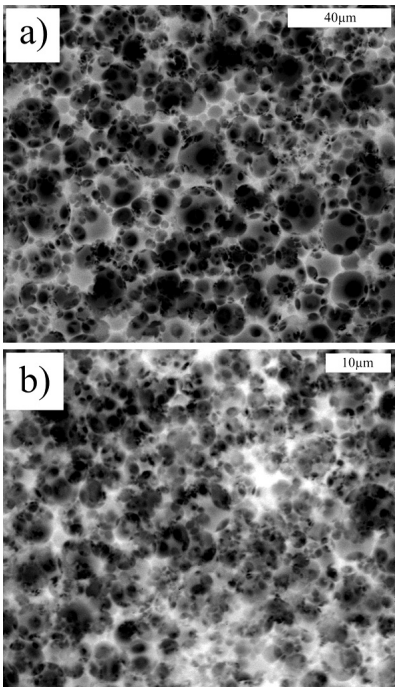

Figure 2: SEM images of: a) 0.5 % copper and b) 1.5 % copper polyHIPEs
Slika 2: SEM-posnetka poliHIPE-a z: a) 0,5 % bakra in b) 1,5 % bakra

merates can be seen on the SEM images (**Figure 1**). As it is known from the previous studies that a stabilization of high internal-phase emulsions with particles only usually results in a polyHIPE material with a closed-cellular morphology,[28,29] the combination of the surfactant and the particle-stabilized emulsion, in our case, leads to an open-cellular morphology. The role of the particles as emulsion stabilizers is different from the role of the surfactant; the latter causes a thinning of the polymer film during the phase separation and gelation, having, therefore, a detrimental effect on the mechanical properties.

A similar effect on the morphology was also found when incorporating copper powder and carbon nanopowder into the oil phase of a HIP emulsion. In the case of copper powder, by increasing its mass fraction amount from 0.5 % to 1.5 %, the cavity diameter changed from 14 μm to 5 μm and the interconnecting pore diameter changed from 4 μm to 1 μm. An agglomerate is seen on the SEM images (**Figure 2b**) where the concentration of the incorporated copper powder is 1.5 %.

The mass fraction amount of the carbon nanopowder used for the investigation of the effect on the morphology was changed from 0.35 % to 15 %. However, an addition of more than 3 % of carbon nanopowder caused agglomerates in the polyHIPE matrix (**Figure 3**) and had a slight reverse effect on the cavity and interconnecting-pore diameters (**Table 1**). By varying the amount of the carbon nanopowder used (from 0.35 % to 3 %), the average cavity diameter of polyHIPE changed from 20 μm to 5 μm and the interconnecting-pore diameter changed from 5 μm to 1.5 μm. At lower particle concen-

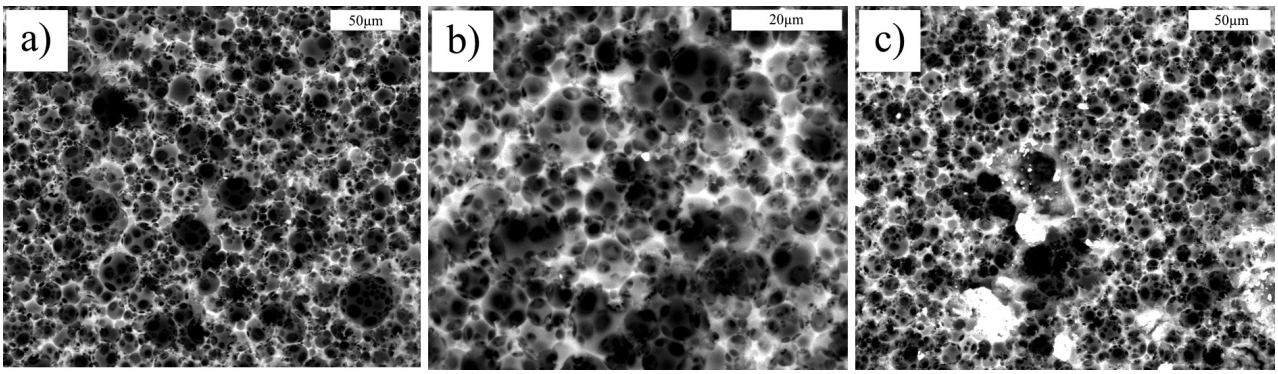

Figure 3: SEM images of: a) 0.35 % carbon nanopowder, b) 3 % carbon nanopowder and c) 15 % carbon-nanopowder polyHIPEs
Slika 3: SEM-posnetki poliHIPE-a z: a) 0,35 % , b) 3 % in c) 15 % ogljikovega nanoprahu

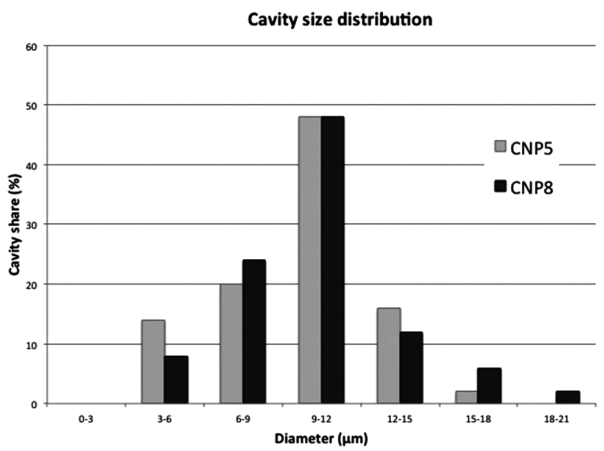

Figure 4: Cavity-size distribution of CNP5 and CNP8 samples
Slika 4: Porazdelitev velikosti por v vzorcih CNP5 in CNP8

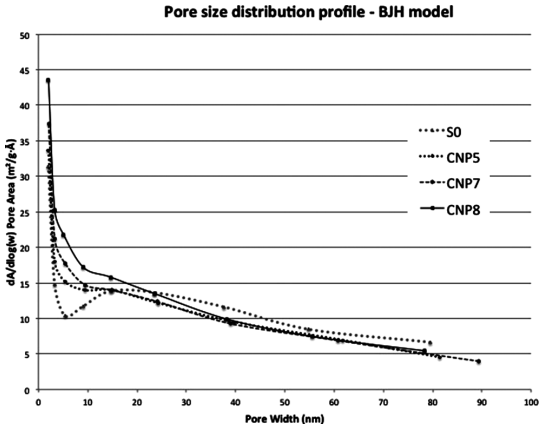

Figure 5: Pore-size-distribution profile (r < 100 nm) of S0, CNP5, CNP7 and CNP8 samples
Slika 5: Porazdelitev velikosti por (r < 100 nm) v vzorcih S0, CNP5, CNP7 in CNP8

trations the effect of an agglomeration is not as evident as in the case of higher amounts of the incorporated particles, which is mainly the result of high specific-surface area of the particles. After reaching the concentration maximum, the added particles do not have a stabilising effect but tend to form agglomerates (**Figure 4**).

Additionally, nitrogen adsorption/desorption experiments were carried out to determine the surface area and pore-size distribution of the prepared polyHIPEs. A BET model was used for the surface-area determination while a BJH model was applied for the pore-size-distribution profile. As shown in **Table 2**, the surface area of the polyHIPEs stabilized using a combination of the surfactant and solid particles (samples CNP5, CNP7 and CNP8) is between 23.6 m^2/g and 29.2 m^2/g, which is similar to the surface area of the styrene-based polyHIPEs stabilized with the surfactant only (22 m^2/g, sample S1). This is surprising because we predicted that, due to the high specific-surface area of the incorporated particles, the surface area would increase with the increasing amount of solid particles. Obviously, the addition of the particles did not produce any additional pores within the meso or micro range of the pore size (below 50 nm; **Figure 5**) that would significantly increase the surface area of polyHIPEs.

Table 2: Surface areas of polyHIPEs with different carbon-nanopowder amounts
Tabela 2: Površina poliHIPE-ov z različno vsebnostjo ogljikovega nanoprahu

Sample	Particle amount	*BET*/(m^2/g)
S0	0 %	22.03
CNP5	5 % C	23.58
CNP7	10 % C	25.84
CNP8	15 % C	29.22

4 CONCLUSIONS

We have demonstrated that it is possible to prepare styrene-based polyHIPEs stabilized with a combination of a surfactant and various solid particles. Their interconnecting open-porous morphology can be successfully controlled by changing the amount of the incorporated solid particles until they start to agglomerate. We have also shown that the amount of solid particles has no significant effect on the polyHIPE specific-surface area. The ability of controlling the morphology by changing the concentration of the particles is important with respect to the applicability of polyHIPE materials. Further experiments are needed to determine the effect of incorporated particles on the mechanical properties of the obtained polyHIPEs.

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