Center odličnosti PoliMaT

Polimerni Materiali in Tehnologije

1st International Workshop of CoE PoliMaT

Contributions to the Working Session with the International Scientific Council

Ljubljana, 1st-2nd December 2011

CONFIDENTIAL!

PREPARATION OF BIOCOMPATIBLE POROUS POLYMERS FROM MULTIFUNCTIONAL ACRYLATES

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1. Introduction

An alternative method for the preparation of highly porous monolithic polymer material is polymerisation of the continuous phase of a high internal phase emulsion (HIPE). [1] Typically, the yielding polymer has an open cellular structure with interconnects, which is the result of the internal phase being trapped inside the continuous phase during the polymerisation. After the extraction of internal phase, the porous structure remains. Such monolithic polymers, termed Poly HIPE [2] were initially prepared as styrene/divinylbenzene copolymers and applied as precursors for reactive species [3], as biocatalysts supports [4] and as supports for filtration [5]. With the addition of 4-vinylbenzyl chloride as a monomer, a reactive PolyHIPE monolith was produced, functionalized and utilized as a scavenger in a flow through mode [6].

HIP emulsions are known for a very long time and Lissant first defined them. [7] HIP emulsions are useful in various fields of science, among other in the field of tissue engineering. [8] Two types of emulsions are widely used:

- Oil in water emulsions (o/w),
- Water in oil emulsions (w/o). [9]

Emulsions are compound from internal and continuous phase. High internal phase emulsion (HIPE) is emulsion where the volume of internal phase exceeds 74.04 % of total volume. [7] HIP emulsions are commonly used in the field of material science. The polymers formed from high internal phase emulsions are called polyHIPEs. Such type of monolithic polymers can be prepared from different monomers. [10]

The initiators play an important role in the polymerisation reactions.

2. Results and discussion

Biocompatible poly(trimethylolpropane triacrylate) monolithic supports were prepared by the polymerisation of the continuous phase of water in oil high internal phase emulsions. Different photoinitiators and thermal initiators were used. The influence of initiators on porous structure was studied. The combination of different surfactants was used and the influence of surfactants on porous structure was investigated. Morphology of monolithic materials was studied by scanning electron microscopy.

Different photo and thermal initiators were used to prepare biocompatible poly (trimethylolpropane triacrylate) porous monolithic supports. Three different photoinitiators were used: Darocure 1173, Irgacure 819 and K69:

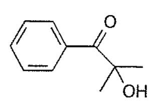

Figure 1: Darocur 1173

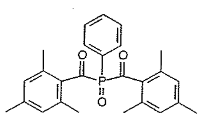

Figure 2: Irgacure 819

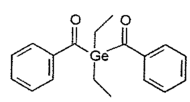

Figure 3: K69 [11]

Different combinations of surfactants were used to find the polyHIPE structures of prepared samples. Surfactants play an important role in preparing a stable emulsion. Surfactants can be anionic, cationic, amphotermal and non-ionic. [12]
Surfactant decrease surface tensile between two immiscible phases and stabilize the emulsion. Different volume percent of surfactants and thermal initiator potassium peroxodisulfate (PPS) were used (Table 1).

ID Sample	Surfactant	Surfactant [%]	HLB value	Initiator
MS30	PEL 121	20	0,5	PPS
MS33	PEL 121	25	0,5	PPS
MS32	PEL 121	30	0,5	PPS
MS31	PEL 121	40	0,5	PPS

Table 1: Compositions of emulsions used for polyHIPE preparation.

A combination of two surfactants was also used (Table 2).

SAMPLE	SURFACTANT	SURFACTANT [%]	HLB VALUE	INICIATOR
MS42	PEL 121, Span 85	30	0,5	AIBN
MS55	PEL 121, Span 85	30	0,7	AIBN
MS51	PEL 121, Span 85	30	1,0	AIBN
MS56	PEL 121, Span 85	30	1,2	AIBN
MS57	PEL 121, Span 85	30	1,4	AIBN
MS58	PEL 121, Span 85	30	1,6	AIBN
MS68	PEL 121, Span 85	30	1,8	AIBN

Table 2: Compositions of emulsions with a combination of surfactants

For initiation, three different photoinititators were used (Table 3).

SAMPLE ID	PHOTOINITIATOR
MS83	Darocur 1173
MS88	Irgacure 819
MS107	K 69

Table 3: Different photoinitiators

We investigated the influence of different surfactants and initiators on porous structure. We have found out that the best porous structure was prepared by using photoinitiators.

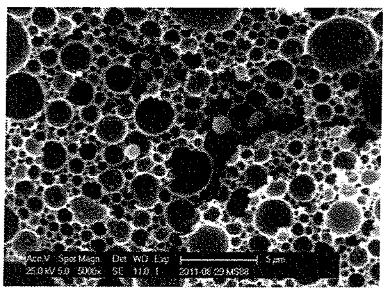

Figure 4: SEM of sample MS88

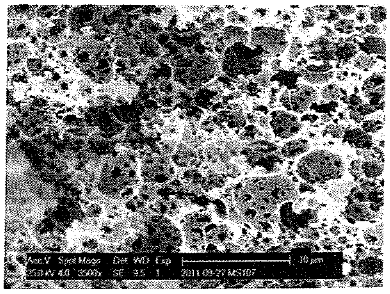

Figure 5: SEM of sample MS107

3. Conclusions and possible applications

We have shown that highly porous structures can be prepared by using different types of surfactants and initiator. Such structures will be potentially used for tissue engineering.

Acknowledgement

The financial support of the Ministry of Science, Higher Education and Technology of the Republic of Slovenia (Center of Excellence PoliMaT, contract No. 3211-10-000057) is gratefully acknowledged. Slovene Human Resources Development and Scholarship Fund is acknowledged for scholarship to Maja Sušec.

References

[1] F. Švec, T.B. Tennikova, Z. Deyl, Monolithic Materials: Preparation, Properties, and Applications, *Elsevier*, Amsterdam, **2003**, p. 173.
[2] D. Barby, Z. Haq, Eur. Pat. 0060138, **1982**.
[3] N.R. Cameron, D.C. Sherrington, I. Ando, H.J. Kurosu, *Mater.Chem.* 6, **1996,** 719.
[4] H.F.M. Schoo, G. Challa, B. Rowatt, D.C. Sherrington, *React. Polym.* 16, **1992**, 125.
[5] D.C. Walsh, J.I.T. Stenhouse, L.P. Kingsbury, E.J.J. Webster, *Aerosol. Sci.* 27 (Suppl. 1), **1996,** S629.
[6] P. Krajnc, J.F. Brown, N.R. Cameron, *Org. Lett.* 4, **2002**, 2497.
[7] Lissant, K. J. J. *Colloid Interface Sci*, **1966**, 22, 462-468.
[8] Lissant, K.J. (Ed.). Emulsions and emulsion technology. New York: Marcel Dekker Inc.; **1974**.
[9] Xu, J. H.; Li, S. W.; Tan, J.; Wang, Y. J.; Luo, G. S. *Langmuir*, **2006**, 22, 7943.
[10] N. R. Cameron. *Polymer*, **2005**, 46 1439-1449.
[11] Ganster, B.; Fischer, U.; Moszner, N.; Liska, R. *Macromolecules*, 7, **2008**, 41; S. 2394 - 2400.
[12] Philip Haw, The HLB System, *Presentation to the Midwest chapter of the Society of Cosmetic Chemists*, **2004**.