

SPRING ELEMENTS FOR REWOD ENERGY HARVESTERS: PRINTING EMULSION TEMPLATES TO MANUFACTURE MACROPOROUS POLYMERS

Angelika Menner¹, Qixiang Jiang¹ and Alexander Bismarck^{1,2}

¹ Institute of Material Chemistry and Research, University Vienna, Währinger Straße 42, 1090 Vienna, Austria

Email: angelika.menner@univie.ac.at, Web Page: <http://www.univie.ac.at>

²Polymer and Composite Engineering Group, Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW72AZ, United Kingdom

Keywords: energy harvesting, emulsion templating, printing, macroporous polymer spring

Abstract

We aim to develop an energy harvesting device that allows charging a battery of e.g. a smart phone while jogging simply by converting mechanical energy into electrical energy using the “REWOD” (Reverse-Electrowetting-On-Dielectric) effect. A vital part of such an energy harvester are highly interconnected and flexible macroporous polymer springs which are required to improve the harvesting efficiency. We use emulsion templates as inks and syringe print them on the harvester’s dielectric in any desired shape and dimension (e.g. cages having dimensions ranging from 2mm ×2mm down to 0.5mm×0.5mm which are up to 400 μm high). UV-polymerisation of the polyurethane diacrylate/ethylhexyl acrylate based continuous phase of the emulsion templates and subsequent removal of the internal phase yields in highly flexible macroporous polymer springs: cyclic compression tests confirmed that they can repeatedly be compressed by 70% without experiencing permanent plastic deformation. Furthermore, we will present a REWOD energy harvesting prototype achieving a capacity change of up to 1000pF upon mechanical deformation.

1. Introduction

There is an increasing demand for sustainable and cheap energy sources. People are using more and more mobile devices like smart phones and MP3 players, which currently need to be charged after a few hours of use. In order to gain independence of mobile devices from external energy source we develop an energy harvester, which will convert mechanical energy into electrical by deformation of a flexible electrode using the REWOD effect; this energy will be stored in a battery. In order to improve the harvesting efficiency highly interconnected, macroporous, polymeric spring elements are required. We aim to manufacture such materials by a technique called emulsion templating[1, 2]. Thereby, high and medium internal phase emulsions (HIPEs and MIPEs) consisting of a continuous monomer phase and an internal droplet phase, which is usually an aqueous electrolyte, are utilised as templates to produce macroporous polymers. The polymerisation of such emulsion templates and the subsequent removal of the internal phase leads to macroporous polymers called polyHIPEs and polyMIPEs, respectively. Their pore structure is a replica of the droplet structure of the emulsion at the gel point of the polymerisation[1]. The pore sizes, interconnectivity, porosity and morphology of emulsion templated macroporous polymers can be tailored simply by tuning the physical properties of the emulsion templates; typically this is realised by adjusting the formulation (e.g. internal phase level, type and concentration of the emulsifier and) and process parameters such as agitation type, speed and

time. However, other materials properties of polyH/MIPes such as their mechanical performance, thermal and electrical properties and multi-functionality can be adjusted by cleverly choosing monomers[3-6] and addition of (multifunctional) reinforcements[12-18] as well as post-synthesis chemical modification[7-9] and thermal treatment[10, 11].

This makes emulsion templating a versatile tool to manufacture macroporous polymers with the requirements of specific applications, including scaffolds for cell cultural and tissue engineering[19, 20], supports for catalyst[8, 21], medium for separation[9, 22, 23], adsorbents and release control agents[24, 25]. Another advantage of emulsion templating is the liquid nature of the emulsions; the emulsions can be shaped by moulding, casting and redispersing, allowing the production of macroporous polymers into monoliths, films[22, 26] and beads[27]. Emulsion templates have also been used as inks in stereo-lithography. [28, 29]

Here we used polyurethane acrylate and ethylhexyl acrylate based emulsion templates as inks and syringe print them in to cage patterns and UV polymerised; cages with macroporous polymer walls of defined height and width were produced. Furthermore, we will provide evidence that our macroporous polymer cages are efficient spring elements in a REWOD energy harvester; a capacity change of up to 1000pF upon mechanical deformation was observed.

2. Experimental Section

Materials

Ethylhexyl acrylate (EHA), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ were purchased from Sigma Aldrich (Gillingham, UK). Polyurethane diacrylate (PUDA, Ebecryl 8402) was kindly supplied by Cytec (Belgium). Darocur 1173 was purchased from Ciba (Basel, Switzerland). Hypermer B246 was kindly supplied by Croda (East Yorkshire, UK).

Emulsion preparation

A reaction vessel equipped with a glass paddle rod connected to an overhead stirrer was used for the preparation of the emulsion templates. To prepare the continuous phase, the crosslinker PUDA, the diluting monomer EHA, the surfactant Hypermer B246 and initiator Darocur 1173 were mixed in the vessel. Afterwards, varying volumes of internal phase (65-75 vol.-%), which was an aqueous solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ with a concentration of 10g/L, was added dropwise while stirring at a speed of 400 rpm. After the entire internal phase was added, the emulsions were stirred for further 3 min at rates between 600 rpm and 2000 rpm for homogenisation.

Preparation of polyHIPE and polyMIPE films and cages

In order to produce macroporous polymer films suitable for characterisation the emulsions were casted on a substrates, on which two stripes of tapes were stacked to define the height of the film (350 μm), using the blade.

The syringe printer was home-assembled from an EFD Ultimius 4 dispenser (Nordson, Germany) and a Stepcraft 420 3D system (STEP-CRAFT, Germany). The emulsions were transferred in a 5 ml syringe; the syringe was connected to the EFD dispenser and fixed onto the movable head of the Stepcraft 420. A straight needle with outer diameter of 750 μm was attached to the syringe for printing. The substrate was a polypropylene projector film. The distance between the end of the needle and the substrate (d) was set to be the outer diameter (OD) of the needle. The cage patterns were an array of cells (10 \times 10) which have a size of 2 \times 2 mm², 1 \times 1 mm² and 0.6 \times 0.6 mm². The volume of the emulsions for one pattern can be calculated; the printing speeds were set to be 5mm/s, 10mm and the dispensing rate was 1.44 $\mu\text{L/s}$.

After casting and printing, respectively, the emulsions were placed in a water bath and UV-polymerised using a UV lamp (UVP-100 (wavelength of 365 nm), UVP, UK) for 2 min. The polyH(M)IPE films were dried in air at room temperature before characterisation.

Characterisation

The morphology of the polyHIPEs and polyMIPes (the disks and the cages) were investigated using scanning electron microscopy (JCM-6000, JEOL GmbH, Echting, Germany). The fracture surface of the samples were gold coated using JFC-1200 (JEOL GmbH, Echting, Germany). The pore and pore

throat sizes were analysed using ImageJ. *The skeleton densities* ρ_s were measured using Accucyc 1330 (Micrometrics Ltd, Dunstable, UK). *The foam densities* were calculated according to equation 1:

$$\rho_f = m/(a \cdot b \cdot c) \quad (1)$$

where ρ_f is the foam density, m the weight of the specimen and a , b and c are the dimensions of the specimen, which were determined using a calliper. *The porosity* P of the samples was calculated using equation 2:

$$P = (1 - (\rho_f / \rho_s)) \cdot 100\% \quad (2)$$

In order to evaluate *the mechanical performance* cyclic compression tests were carried out using an Instron 5969, (Instron GmbH, Buckinghamshire, UK) equipped with a 1 kN load cell on cubic samples with dimensions of 7mm x 15mm x 15mm. Therefore, the samples were 500 times deformed by 70% and released at a rate of 5 mm/min. The elastic modulus and crush strength were determined from the first loading curve.

3. Results and Discussion

Since it is our aim to produce highly flexible and durable macroporous polymer springs we employed PUDA, which is commonly used as flexible and scratch resistant coating, as property defining crosslinker within the continuous phase of our emulsion templates. However, PUDA is highly viscous and has to be diluted by EHA (which also serves as co-monomer) in order to allow for the formation of stable emulsions. In order to investigate the influence of processing parameters such as internal phase level and homogenising speed on the morphology and the mechanical performance of the resulting polymer foams several HIPEs (75% internal phase) and MIPEs (65% internal phase), which were homogenised at varying speeds, were prepared, casted into films and UV polymerised.

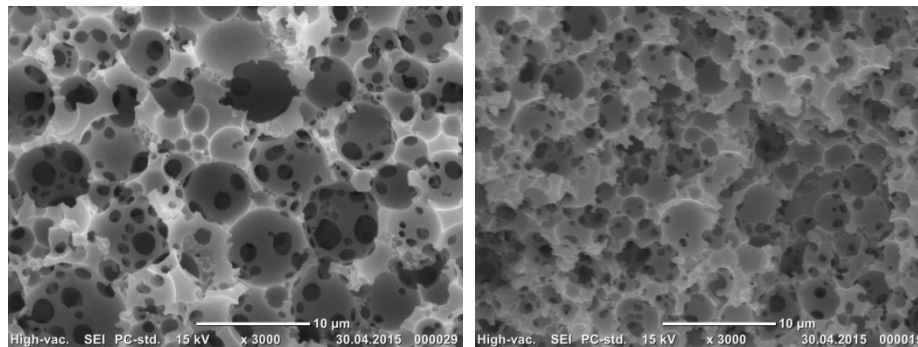


Figure 1. SEM images of a representative PUDA based polyHIPE (left) and polyMIPE (right), respectively.

The obtained polyHIPEs and polyMIPEs consisted of a highly interconnected network of pores (Fig.1). Their pore sizes and pore throat sizes decrease from approx. 8 μm to 3 μm and 1.9 μm to 0.9 μm , respectively, due to the reduction of the internal phase level from 75% to 65% within the emulsion templates they originate from and the increase of the homogenising speed from 600 rpm to 2000 rpm. The porosity of the polyHIPEs and polyMIPEs is with approx. 74% and 63%, respectively, similar to the internal phase level of the former emulsion templates.

Cyclic compression tests revealed the elastic moduli and crush strengths of the polyMIPEs are with 0.62 ± 0.03 MPa and 0.043 ± 0.002 MPa, respectively, considerably larger than that of the polyHIPEs (0.26 ± 0.01 MPa and 0.016 ± 0.001 MPa, respectively). This is simply a result of the larger foam density and lower porosity of polyMIPEs compared to polyHIPEs; the influence of the varied processing parameters is negligible.

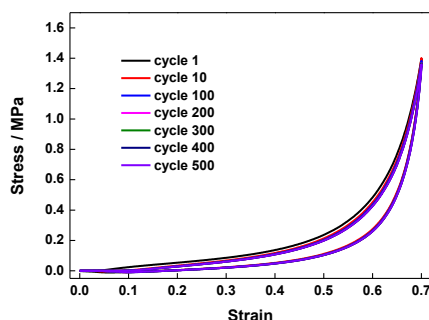


Figure 2. Stress vs. strain curve showing the results of a cyclic compression test on a PUDA based polyMIPE (representative for all samples produced).

More importantly, however, these cyclic tests did not only prove the flexibility but also the durability of our PUDA based macroporous polyHIPEs as all samples could be repeatedly and reversibly compressed (Fig.2). This is a crucial property in order to use our materials as spring element in our REWOD energy harvester.

In the next step we utilised the HIPEs and MIPEs as inks during syringe printing in order to create highly flexible, macroporous polymer cages; the size of the cages ranged from 0.6x0.6 mm² to 2x2 mm² with a wall height of about 680 µm (Fig. 3), which is similar to the outer diameter of the needle (700 µm) used during printing. Our macroporous polymer cages possess an highly interconnected internal pore structure and an open porous surface, which is vital for the harvester's spring element as it has to be easily compressed and has to recover quickly (within the time frame of one step).

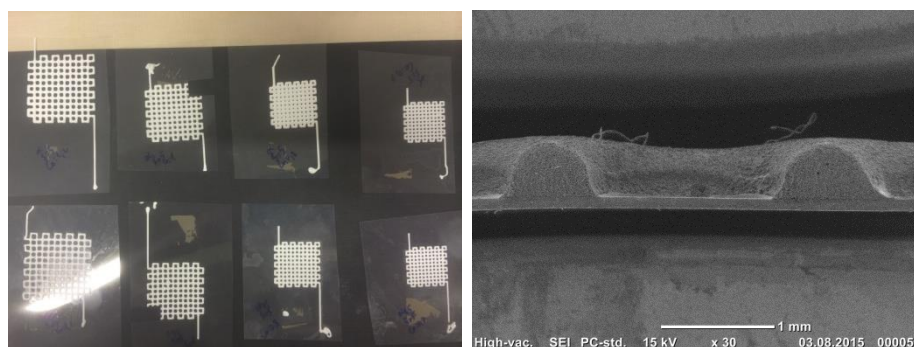


Figure 3. Photo of macroporous polymer cages on PP substrates (left) and SEM image of the cross section of a macroporous polymer cage (right).

In a final experiment we put our spring element to a test. Therefore, a polyMIPE cage pattern was applied onto a Mylar® dielectric coated copper plate, 16 cages were filled with one Hg droplet each (active area of 1 cm², Fig. 4) and covered by a copper electrode. The capacitance change was measured with the help of a Voltcraft VC940 while the device was compressed by a weight, which equals a force of 10N/cm². This is the average stepping force of a person. We observed a capacitance increase of up to 1000 pF due to the increase of contact area between the Hg droplets, which act in the device as deformable electrode, and the dielectric upon loading. The original capacity was regained after the weight was removed and the spring and, therefore, the Hg droplets recovered their original shape. This represents the proof of the harvesting concept.



Figure 4. Macroporous polymer cages on a Mylar® dielectric coated copper plate filled with Hg droplets.

4. Conclusions

We demonstrated that HIEs and MIEs can be used as inks in printing processes to create complex shapes. Since PUDA was employed as property defining ingredient of the formulation highly flexible and interconnected macroporous polymer cages were manufactured: cyclic compression tests confirmed that they can repeatedly be compressed by 70% without experiencing permanent plastic deformation. Furthermore, a simple REWOD energy harvesting device was build with which a capacity change of up to 1000pF upon mechanical deformation was achieved.

Acknowledgments

We would like to thank the European Union for the funding provided within the EU FP7 for our MATFLEXEND project. We acknowledge for the project partner Fraunhofer IZM (Berlin, Germany) for supplying the Mylar® dielectric coated copper plate.

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