Technical paper

Ring Opening Metathesis Polymerisation (ROMP) As a Tool for PolyHIPEs With Extraordinary Mechanical Properties

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Abstract

PolyHIPE materials have been prepared by Ring Opening Metathesis Polymerisation (ROMP) of dicyclopentadiene. Two characteristic features for successful stabilization of high internal phase emulsions (HIPEs) were tuned in order to achieve improvements regarding mechanical properties of polyHIPEs. Mechanical properties of the new materials were related to variations of the surfactant concentration and the volume ratio of the internal phase in HIPEs. Values for Young's moduli were about a hundred times higher than in standard polyHIPE materials with the same level of porosity, which represents a major improvement for highly porous cellular polymeric materials. Moreover, fully interconnected macroporous morphology was found for polyHIPEs, where respective HIPEs were stabilized with only 0.25 v% of surfactant.

Keywords: Emulsion templating, Ring Opening Metathesis Polymerization (ROMP), dicyclopentadiene, mechanical characteristics, polyHIPEs

1. Introduction

High Internal Phase Emulsions (HIPEs) are an interesting class of emulsion, usually characterized by an internal phase volume fraction exceeding 0.74, the critical value of the most compact arrangement of uniform, undistorted spherical droplets.[1] Consequently, the droplets of the dispersed phase are polydisperse and deformed adopting polyhedral shapes, separated from each other by a thin film of the continuous phase.[2] HIPEs are thermodynamically meta-stable dispersions in which drops of liquid are dispersed in continuous immiscible liquid phase of a different composition. The process by which emulsions can completely separate into two phases (oil and water) is generally considered to be governed by four different droplet loss mechanisms, namely creaming, flocculation, coalescence and Ostwald ripening.[3] In order to prevent phase separation, the interface between phases is stabilized by surfactants (cationic, anionic or non-ionic). Conventional surfactants have an amphiphilic molecular structure and stabilize an emulsion by taking position specifically at the oil/water interface to minimize the interfacial energy, thereby preventing phase separation of the emulsion. Generally, the quantity of surfactant required to successfully stabilize a HIPE varies between 5–50 v%,[4] yet a concentration of 20 v% has been used most frequently.[5] Recently, HIPEs stabilized with only 0.25 v% of the surfactant could successfully be obtained.[6] Polymerization of the continuous phase of the kinetically stable HIPEs and removal of the droplets of the dispersed phase used as soft template, leads to solid macroporous foams, termed as polyHIPEs (*cf.* Fig. 1).[7] The morphology of these polyHIPEs is quite original; however, as underlined recently, the terminology in that rather new and fast growing field is not yet completely established.[8] Therefore, in this paper the term 'cavity' will be used as a representative for voids, whereas interconnecting pores formed at contact points of neighboring droplets, will be termed as 'windows' (*cf.* Fig. 1).

Although the morphology of the polyHIPE materials is highly porous and interconnected (with pore volume up to 10 cm^3/g) their surface areas are naturally low due to the relatively large cavity sizes, usually situated in the microcellular range (1–100 μm). PolyHIPE materials

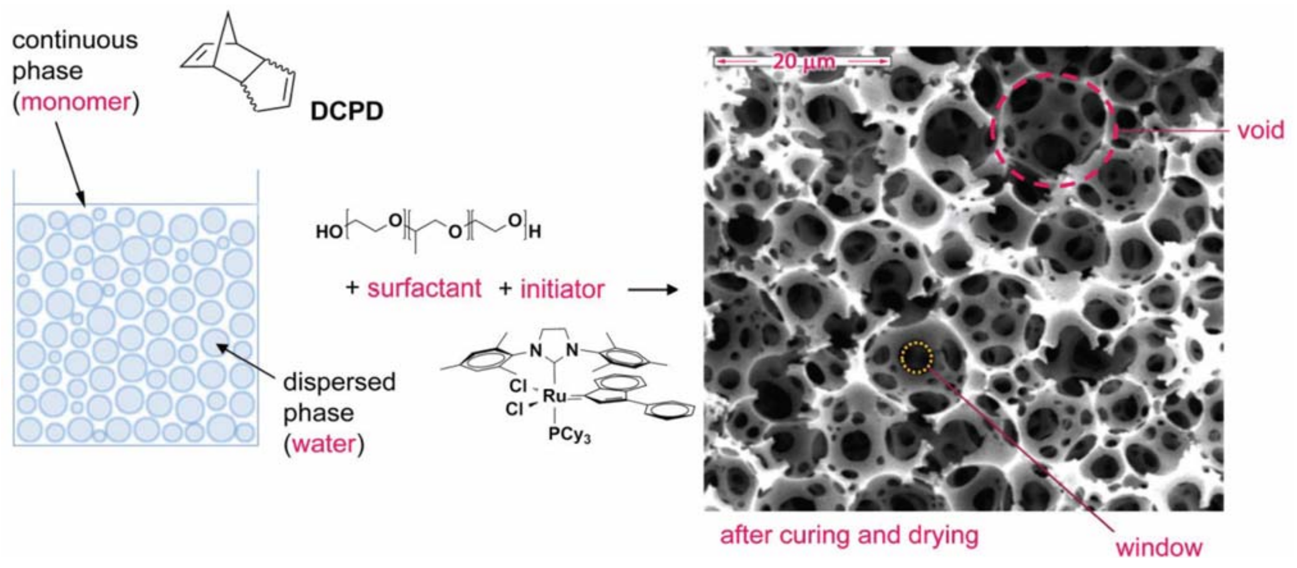

Figure 1. Sketch of the polyHIPE preparation and a scanning electron micrograph of a typical polyHIPE sample (picture courtesy of C. Slugovc)

can be obtained using both organic and inorganic monomers, polymerized mostly by free radical or step growth mechanisms.[9] Besides free radical and step growth mechanisms, also thermally- and photo-initiated procedures, as well as radiation polymerization using γ-rays or electron beams are used to obtain porous polymers.[10] Another way to synthesize porous polymers is living polymerization, such as atom transfer radical polymerization (ATRP), nitroxide mediated polymerization and ring opening metathesis polymerization (ROMP).[11] Olefin metathesis and especially ROMP has opened up efficient synthetic routes to complex natural products, drug molecules and new polymeric materials as demonstrated by the numerous metathesis applications found in the literature during the past decade.[12] ROMP is a type of olefin metathesis yielding polymers by chain-growth polymerization mostly driven by release of ring strain in cyclic olefins.[13] Olefin metathesis is a well known chemical reaction that entails redistribution of the fragments of alkenes (olefins) upon scission and regeneration of C – C double bonds (*cf.* Fig. 2) and finds number of applications in organic synthesis, polymer and material chemistry.[14] Polymers obtained via ROMP exhibit a high potential for post – functionalization due to the high amount of the C–C double bonds in the polymer back bone and the living character of ROMP also allows for grafting of functional monomers at the chain end. ROMP is a living metal-catalyzed process, initiated mostly with the Ru- (Grubbs'),

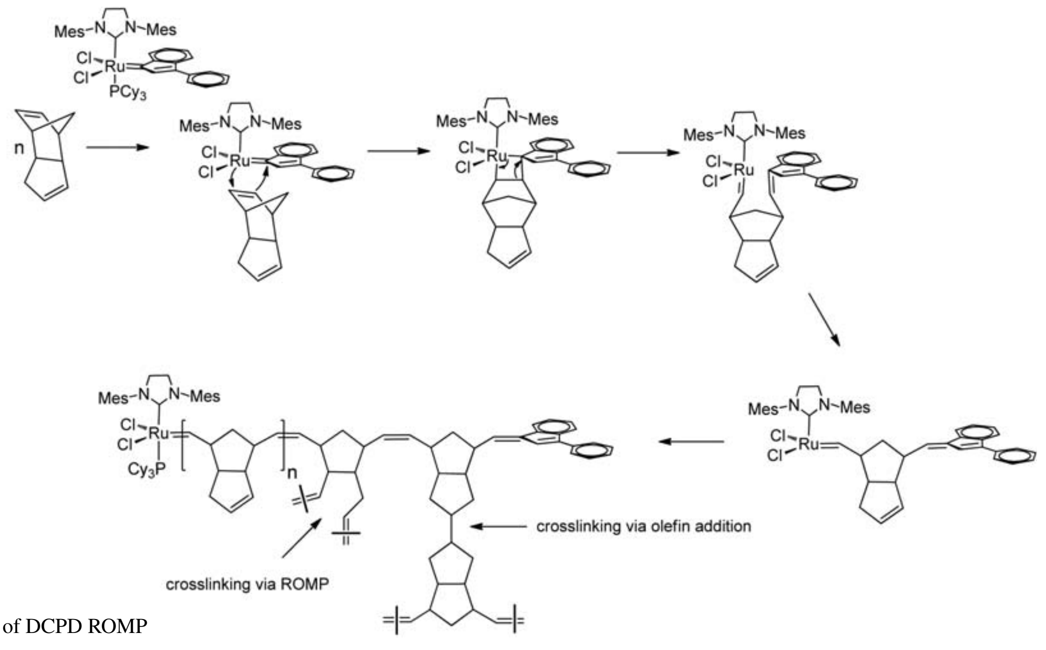

Figure 2. Mechanism of DCPD ROMP

or W- and Mo-based (Schrock's) catalysts. Ruthenium based catalysts proved to be highly water tolerant, air stabile and active at very low loadings (less than 0.0001 mol%).[15] Deleuze *et al.* used ROMP as the curing system to obtain polyHIPEs from norbornene derivatives using Grubbs catalysts.[16] Metal-carbene chain ends were shown to be still active after the polymerization thus living character of the ROMP was shown within the modification of polyHIPE using ethylvinyl ether and 5-chloromethylbicyclo[2,2,1] hep-2-en. Recently, dicyclopentadiene (DCPD) HIPEs were cured using ring opening metathesis polymerization, whereby high mechanical resilience of the resulting polyHIPEs was uncovered.[6,17,18]

Due to the polyHIPE´s highly porous and interconnected morphology their mechanical strength is naturally rather low, which represents a big drawback for real industrial applications.[19] PolyDCPD is known as an industrially important cross-linked polymer with high modulus, impact strength, high ductility, low density, chemical resistance and high operating temperature.[20] Therefore, preparation of DCPD polyHIPEs exhibiting very favorable mechanical and thermal properties increases possibilities for polyHIPEs to be industrially applied.

Herein, a new class of polyHIPE materials with extreme high mechanical properties has been prepared by using ring opening metathesis polymerization (ROMP) of dicyclopentadiene. The preparation and characterization of poly(dicyclopentadiene) HIPEs will be discussed.

2. Experimental

Dicyclopentadiene (*Sigma-Aldrich*, amounts according to Table S1) and surfactants (Pluronic®L-121 (Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol; MW = 4400 g·mol^{-1}); Brij®52 (Polyethylene glycol hexadecyl ether; MW = 330 g · mol^{-1}); Span™80 (Sorbitan monooleate; MW = 428 g · mol^{-1}) all *Sigma-Aldrich*) were placed in a three necked 250 mL flask in the corresponding amounts (*cf.* Table S1) and the mixture was stirred with an overhead stirrer at 400 rpm. The corresponding amount (*cf.* Table S1) of deionized water was added drop wise under constant stirring. After addition of the water the mixture was further stirred for 1 h until a uniform emulsion was produced. 250 μL solution of the initiator $(H_2IMes)(PCy_3)Cl_2Ru$(3-phenyl-indenylid-1-ene) (**M2**, H_2Imes = N,N-bis(mesityl) 4,5-dihydroimidazol-2-yl) (Umicore; *cf.* Table S1) in toluene was added to the emulsion and the mixture was stirred for 1 min. Subsequently, the emulsion was transferred to the mold (polystyrene container, steel mold or glass vial) and cured at 80 °C for 4 h. Resulting polymers were purified via Soxhlet extraction with acetone and dried under vacuum until constant weight was obtained. The different HIPE recipes are listed in Table S1 (*cf.* ESI). The number left of the sample name indicates surfactant concentration in v% and the number right of the sample name indicates porosity of the sample. For example: $_1$**DCDP**$_{80}$, 1 v% of the surfactant and 80% porosity.

2. 1. Morphology

Morphology was investigated by scanning electron microscopy (SEM) on a JWS-7515, JEOL Ltd. microscope. Micrographs were taken at several magnifications between 2500 X to 7000 X, at 7 mm working distance and 20 kV voltage applied. A piece of the each sample was mounted on a carbon tab for better conductivity and a thin layer of gold was sputtered on the sample's surface prior to scanning analysis.

2. 2. Mechanical Properties

The tensile properties were determined from the stress/strain plots according to a method described elsewhere.[,18] Tensile strength of the samples was tested at a rate of 1 mm/min (modulus determination) on a Zug/Druck-Universalprüfmachine Typ Z010, Fa. ZWICK. to elongation 0.2%. Resolution was 0.6 μm.

3. Results and Discussion

Poly(dicyclopentadiene) (pDCPD) prepared by ROMP is instantly cross-linked via olefin addition and/or olefin metathesis,[21] thus no additional cross-linker, usually used in polyHIPE preparation protocols, is necessary (*cf.* Fig. 2). Dicyclopentadiene was chosen as a monomer to prepare DCPD polyHIPEs since it is readily available, being a cheap by-product of steam cracking of naphta and gas oils to ethane and its ROMP has been extensively studied.[22] Dicyclopentadiene and non-ionic surfactants with a volume ratio of 0.25 to 10 v% (with respect to DCPD) were used as an oil (continuous) phase and pure deionised water as the internal (droplet) phase with a volume ratio of the internal phase ranging from 50 to 80 v% (*cf.* Table 1). For the preparation of styrene based HIPEs, an electrolyte is usually incorporated in the aqueous phase to inhibit Ostwald ripening.[23] In contrast, DCPD shows low partitioning between the phases ($log\ P_{ow}$ of DCPD = 3.60, insoluble in water at 25 °C; for comparison styrene $log\ P_{ow}$ = 2.80, solubility 0.3 g/L at 25 °C).[24] Accordingly, interactions between the DCPD phase and aqueous phase are very weak which in turn favors interactions of surfactant molecules with both phases and greatly stabilizes the HIPE without any electrolyte. After slow addition of the droplet (aqueous) phase to the continuous (dicyclopentadiene) phase under vigorous stirring, ring opening metathesis polymerization (ROMP) is triggered upon addition of the 2nd generation of Umicore initiator **M2** (dissolved in 0.5 mL of toluene). As ROMP starts as soon as **M2** gets into contact with the monomer (even at room temperature), appropriate initiator loading is crucial at that point (0.015 mol % with respect to DCPD dissolved in 0.5 mL of toluene) to be able to homogeneously incorporate initiator solution and transfer HIPEs into the appropriate molds before curing. After Soxhlet extraction and drying in a desiccator under the vacuum the preparation of the polyHIPE specimen is finished. For the morphological characterizations, specimens have to be broken, cut or grinded and therefore have to be aged in this particular case, (i.e. oxidized) so that samples become brittle. According to SEM investigations, all samples exhibit typical open porous polyHIPE architecture, with a mean cavity size of 2.0 ± 1.7 µm in case of $_{10}$DCDP$_{50}$, 4.0 ± 2.5 µm in case of $_{10}$DCPD$_{60}$, 3.6 ± 1.2 µm in case of $_{10}$DCPD$_{70}$ and 3.4 ± 1.2 µm in case of $_{10}$DCPD$_{80}$. Mean cavity sizes steadily increases with decreasing surfactant amount at 80% porosity from 3.4 ± 1.2 µm in case of $_{10}$DCPD$_{80}$ (10v% surfactant used) up to 69 ± 53 µm in case of $_{0.25}$DCPD$_{80}$, (0.25v% surfactant used). The same trend was observed with the window sizes which were determined using mercury porosimetry and revealed increasing window sizes when going from $_{10}$DCDP$_{50}$ (433 nm) to $_{10}$DCDP$_{80}$ (1.1 µm) and again steadily increase upon decreasing the surfactant amount at 80% porosity from 1.1 µm in case of $_{10}$DCDP$_{80}$ up to 24 µm in case of $_{0.25}$DCPD$_{80}$ (*cf.* Fig. 3 and Table 1).

Due to the highly unsaturated polymer network of polyDCPD, functionalization should be easily feasible. On the other hand, DCPD polyHIPE is also very prone to the oxidation. This side reaction contributes to the favorable mechanical properties of the material but at the same time the material loses its ductility and becomes very fragile.

The mechanical characteristics of DCPD polyHIPEs were determined by tensile stress/strain tests with unoxidized (*i.e.* not aged) and oxidized (*i.e.* aged) samples (elemental analysis given in the *ESI*). Two parameters were changed during HIPE preparation to gain insights the mechanical behavior of DCPD polyHIPEs. Surfactant concentration was changed from 0.25 v% up to 10 v% at constant volume ratio of internal (droplet) phase being 0.8 and secondly surfactant concentration was kept constant at 10 v% whereby volume ratio of internal (droplet) phase was changed from 0.5 up to 0.8 (Table 1). Therefore, the E-modulus of unoxidized specimens was found to increase with decreasing the porosity at the same surfactant concentration from 23 MPa for $_{10}$DCPD$_{80}$ up to 330 ± 20 MPa for $_{10}$DCDP$_{50}$. Decreasing the surfactant concentration at constant volume ratio of internal phase also raises the E-modulus. When going from 10 v% down to 0.25 v% of surfactant the E-moduli are 10 ± 3 MPa for $_{10}$DCPD$_{80}$ up to 97 ± 5 MPa for $_{0.25}$DCPD$_{80}$ sample (*cf.* Fig. 4 and Table 1). The E-moduli found for oxidized pDCPD polyHIPEs are extremely high. By decreasing the porosity of the samples, E-modulus starts to increase, being 85 ± 25 MPa for $_{10}$DCPD$_{80}$ sample, 430 ± 30 MPa for $_{10}$DCPD$_{70}$ sample and 770 ± 30 MPa for $_{10}$DCPD$_{60}$ sample. Surprisingly, the E-modulus of oxidized $_{10}$DCDP$_{50}$ was only 370 ± 10 MPa and did not change significantly compared to the un-oxidized sample with 330 ± 20 MPa (*cf.* Fig. 4 and Table 1). Also when the surfactant concentration is decreased within the HIPE at constant volume ratio of the internal phase, oxidized pDCPD improves the E-modulus (85 ± 25MPa for $_{10}$DCPD$_{80}$ sample, up to 228 ± 14MPa for $_{0.25}$DCPD$_{80}$ sample (*cf.* Fig. 4 and Table 1)). Upon oxida-

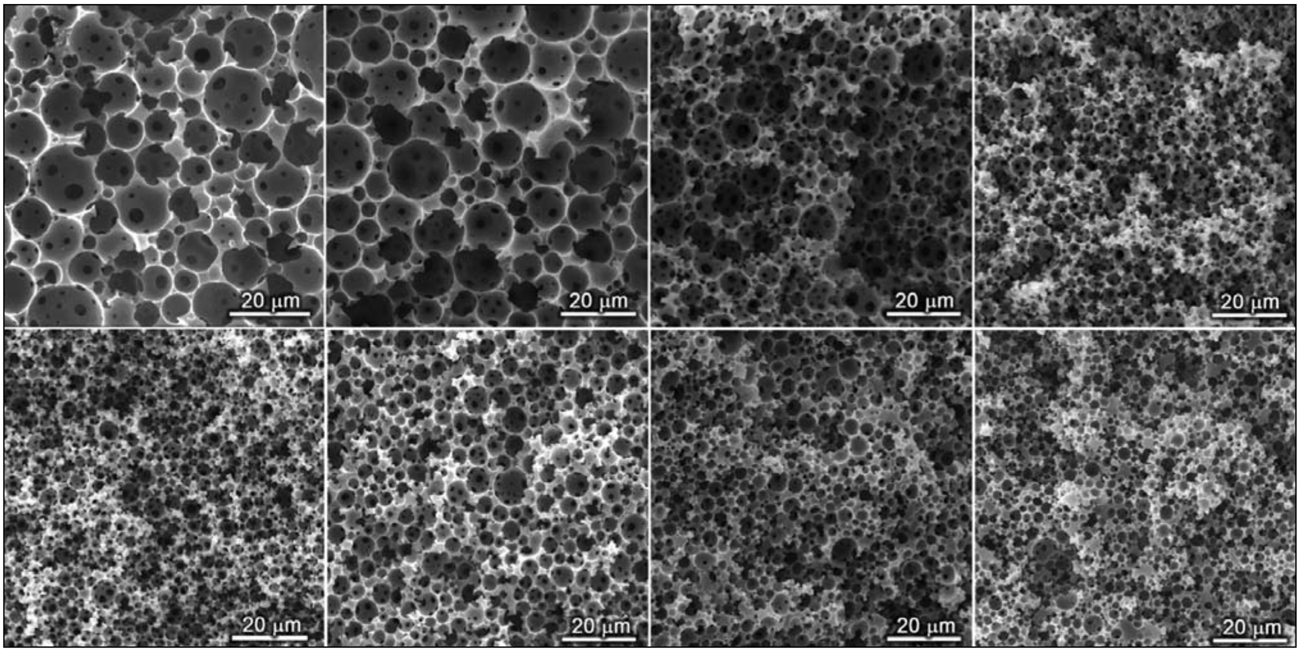

Figure 3. First row from left to right: SEM pictures of **$_1$DCDP$_{80}$**, **$_3$DCDP$_{80}$**, **$_5$DCDP$_{80}$** and **$_8$DCDP$_{80}$**; second row from right to left: SEM pictures of **$_{10}$DCPD$_{80}$**, **$_{10}$DCPD$_{70}$**, **$_{10}$DCPD$_{60}$** and **$_{10}$DCPD$_{50}$**

Table 1. Characterisation of **pDCPD** foams

Sample	ϕ_{exp} (%)^a	Av. window size [μm]^a	Av. cavity size [μm]^b	Young's mod. [MPa]^c	$Rp_{0.2\%}$ [MPa]^c	Elongation at break [%]^c	Young's mod. [MPa]^d
$_{0.25}$**DCPD**$_{80}$	80	24	69 ± 53	97 ± 5	1.7 ± 0.3	11 ± 2	228 ± 14
$_{1}$**DCPD**$_{80}$	81	8.4	35 ± 23	94 ± 10	1.5 ± 0.2	17 ± 4	272 ± 15
$_{3}$**DCPD**$_{80}$	80	2.7	7.4 ± 5.5	105 ± 8	1.9 ± 0.2	22 ± 1	277 ± 10
$_{5}$**DCPD**$_{80}$	81	1.7	6.7 ± 2.6	97 ± 4	1.9 ± 0.3	34 ± 2	243 ± 2
$_{7}$**DCPD**$_{80}$	82	1.3	4.2 ± 2.4	88 ± 2	1.5 ± 0.2	43 ± 9	242 ± 2
$_{8}$**DCPD**$_{80}$	81	1.1	4.6 ± 2.3	18 ± 2	0.23 ± 0.07	35 ± 6	69 ± 1
$_{9}$**DCPD**$_{80}$	80	1.3	3.9 ± 2.1	16 ± 1	0.22 ± 0.01	27 ± 6	60 ± 10
$_{10}$**DCPD**$_{80}$	79	1.1	3.4 ± 1.2	10 ± 3	0.27 ± 0.10	25 ± 7	85 ± 25
$_{10}$**DCPD**$_{70}$	70	0.7	3.6 ± 1.2	60 ± 10	0.94 ± 0.11	18 ± 7	430 ± 30
$_{10}$**DCPD**$_{60}$	59	0.5	4.0 ± 2.5	170 ± 10	2.9 ± 0.2	27 ± 7	770 ± 30
$_{10}$**DCPD**$_{50}$	55	0.4	2.0 ± 1.7	330 ± 20	3.9 ± 0.3	27 ± 10	370 ± 10

[a] assessed from mercury porosimetry data of oxidized samples; [b] Estimated from SEM images; [c] Young's modulus determined for unoxidizes samples by tensile testing of at least 3 specimens; [d] determined for oxidized samples

tion, all samples lose their plastic behavior and become brittle with maximal elongations of only 0.2–1.6% before break (various porosities) and from 0.6–1.3% (various surfactant concentrations) (*cf.* Fig. 4).

The yield strength at 0.2% offset strain ($Rp_{0.2\%}$) increased with decreasing porosity, from 0.27 ± 0.1 MPa (for sample with 80% porosity) up to 3.9 ± 0.3 MPa (for sample with 50% porosity). Surprisingly, we encountered the yield strength to increase up to 1.9 ± 0.2 MPa when decreasing the surfactant concentration at 80% porosity, meaning that the material can withstand almost 8 times higher stress at the same porosity before plastic deformation begins due to a different surfactant concentration during HIPE stabilization (*cf.* Fig. 4). At the same time the material remains ductile until stress at break of 3.3 ± 0.2 MPa resulting in a 22 ± 1% elongation at break (*cf.* Fig. 4).

Such an improvement in mechanical strength can be explained in two ways. First, polyDCPD bears a large number of C–C double bonds with two tertiary carbon atoms in α-position per repeating unit. These positions are very prone to react with oxygen, thereby initiating an artificial aging process which leads finally to a complete loss of the thermoplastic properties with extraordinary high E-moduli. Second, the surfactant concentration used during HIPE stabilization significantly affects the material´s mechanical properties. Samples greatly improved their E-modulus and also became more ductile exhibiting a pronounced plastic behavior with elongations until break of 35 ± 6%. At low surfactant concentrations the surfactant is mainly located at the HIPE´s interface between DCPD and water and can be easily removed from polyHIPEs upon extraction together with the water. In contrast, at higher concentrations (> 5 v%), excess surfactant moves from the interface into the DCPD phase during HIPE preparation, and thus additional pores and cracks are formed in the polymer phase upon curing and extraction. By using Atomic Force Microscopy (AFM), cracks in the polymer phase were found as a consequence of different surfactant concentrations (*cf.* ESI) which most probably influencing the less favorable mechanical properties of the material.

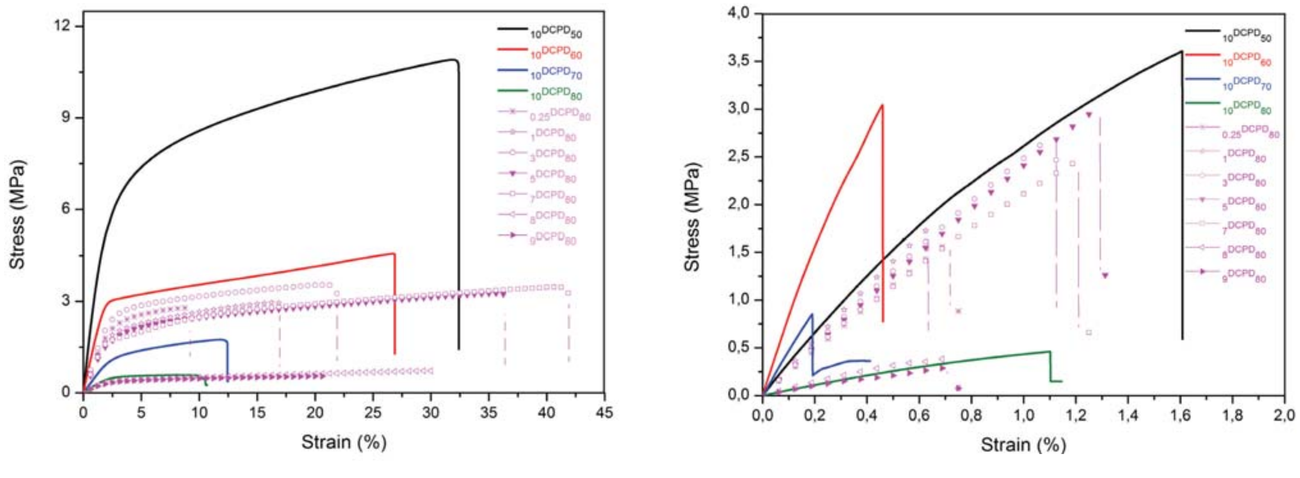

Figure 4. Strain-stress curves for un-oxidized (above) and oxidized (below) samples

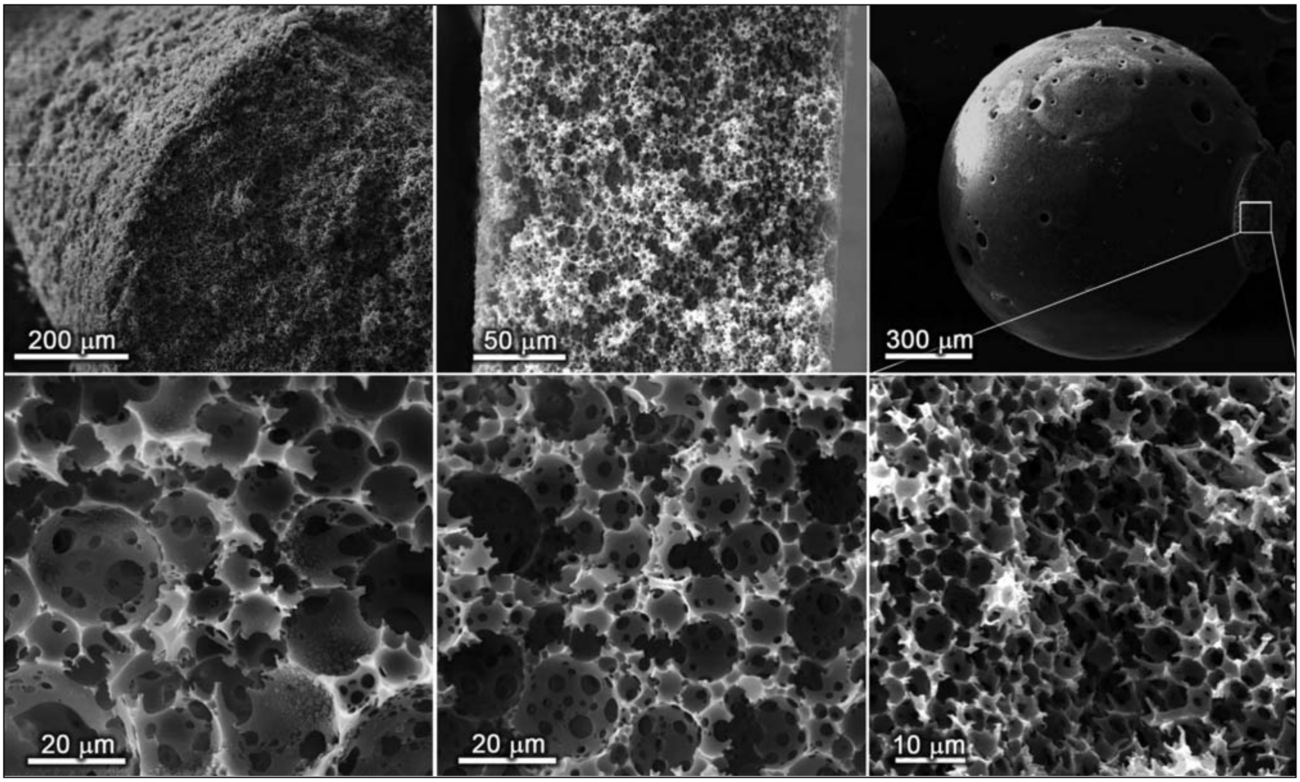

Figure 5. First row from left to right: SEM pictures of DCPD polyHIPE wire, membrane and bead; second row from left to right: SEM pictures of DCPD polyHIPE stabilized with Brij52,Span80 and interior of polyHIPE bead

The formulation Pluronic®L-121, DCPD (50–10 v%) and water (50–90 v%) turns out to be a very stable HIPE, and curing of different shapes of polyHIPEs, like membranes,[25] beads or wires is easily feasible (*cf.* Fig. 5). Not only the loading but also the chemistry of the surfactant used in HIPE preparation is very important for the quality of the polyHIPE, therefore, the choice of an appropriate surfactant is the key point in HIPE manufacturing.[26] To demonstrate the versatility of the system, DCPD HIPEs were stabilized also using other commercial available surfactants with different chemistries, e.g. Brij®52 or Span™80. Again, we were able to obtain highly interconnected open-pore structured foams with similar morphologies and mechanical properties than those obtained from Pluronic®L-121 (*cf.* Fig. 5 and ESI).

5. Conclusions

A simple formulation of a stable DCPD high internal phase emulsion which upon curing yields highly open-porous monolithic polyHIPE material was presented. High porosity of the monoliths is important for numerous applications however usually results in poor mechanical properties. Here we present dicyclopentadiene (DCPD) polyHIPEs made by Ring Opening Metathesis Polymerization (ROMP) featuring the highest mechanical resilience of a polyHIPE material disclosed so far. This represents a very important improvement in the development of highly porous cellular polymeric materials. Therefore, ring opening metathesis polymerization with the combination of high internal phase emulsion templating has proven to be a very useful method producing highly porous materials with remarkable mechanical properties.

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Povzetek

Za pripravo poliHIPE materialov smo uporabili polimerizacijo pri kateri smo polimerizirali ciklične monomerje (diciklopentadien) z metodo odpiranjem obroča (ROMP). PoliHIPE materiali polimerizirani s ROMP mehanizmom so se izkazali z izjemnimi mehanskimi lastnostmi, saj so meritve mehanske jakosti pokazale sto krat višje vrednosti v primerjavi s poliHIPE materiali polimeriziranimi z navadno radikalsko polimerizacijo. ROMP v kombinaciji s HIPE templatiranjem se je izkazal kot izredno dobra kombinacija za proizvodnjo visoko poroznih polimernih materialov z izjemnimi mehanskimi lastnostmi.

Electronic Supplementary Information

Ring Opening Metathesis Polymerisation (ROMP) As a Tool for PolyHIPEs With Extraordinary Mechanical Properties

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Table S1. Emulsion compositions

sample	m (DCPD) [g]	m (M2) [mg]	Surfactant	Surf. [g]	Surf. [vol. %]	$V(H_2O)$ [mL]
$_{0.25}\mathrm{DCPD}_{80}$	8.06	8.08	Pluronic®121	0.021	0.25	33
$_{1}\mathrm{DCPD}_{80}$	8.08	8.08	Pluronic®121	0.092	1	33
$_{3}\mathrm{DCPD}_{80}$	8.06	8.04	Pluronic®121	0.26	3	33
$_{5}\mathrm{DCPD}_{80}$	8.03	8.11	Pluronic®121	0.44	5	33
$_{7}\mathrm{DCPD}_{80}$	8.02	8.12	Pluronic®121	0.52	7	33
$_{8}\mathrm{DCPD}_{80}$	8.02	8.13	Pluronic®121	0.62	8	33
$_{9}\mathrm{DCPD}_{80}$	8.08	8.08	Pluronic®121	0.73	9	33
$_{10}\mathrm{DCPD}_{80}$	8.01	8.04	Pluronic®121	0.82	10	33
$_{10}\mathrm{DCPD}_{70}$	8.06	8.08	Pluronic®121	0.91	10	19
$_{10}\mathrm{DCPD}_{60}$	8.06	3.85	Pluronic®121	0.26	10	12
$_{10}\mathrm{DCPD}_{50}$	8.06	1.90	Pluronic®121	0.26	10	8.1
$\mathrm{DCDP}_{\mathrm{Span80}}$	8.01	8.31	Span™80	0.43	5	33
$\mathrm{DCDP}_{\mathrm{Brij52}}$	8.06	8.08	Brij®52	0.42	5	33

1. Elemental Analyses

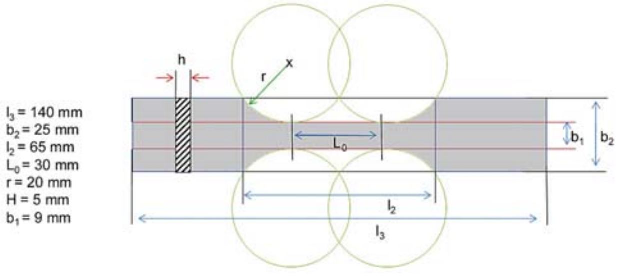
In the case of non-oxidized sample calculations from elemental analysis reveal oxygen content of the samples right after the preparation and purification (sample stored under vacuum). In each case three samples from a bigger specimen were submitted for elemental analysis and a mean value is given in the table. In the case of oxidized samples calculations from elemental analysis reveal an oxygen content (calculated according to: O[%] = 100–C[%]-H[%]) of the samples after four weeks of air exposure (Table S2).

Table S2. Elemental analysis data

sample	Oxidized Elemental analysis			Un-oxidized Elemental analysis		
	C[%]	H[%]	O[%]	C[%]	H[%]	O[%]
$_{0.25}\mathrm{DCPD}_{80}$	65	7	28	90	9	1
$_{1}\mathrm{DCPD}_{80}$	62	6.5	31.5	89.5	9	1.5
$_{3}\mathrm{DCPD}_{80}$	63	6.5	30.5	89	9	2
$_{5}\mathrm{DCPD}_{80}$	63	6	31	88.5	8.5	3
$_{7}\mathrm{DCPD}_{80}$	63	6	31	89	9	2
$_{8}\mathrm{DCPD}_{80}$	63	6.5	30.5	89.5	9	1.5
$_{9}\mathrm{DCPD}_{80}$	62	6.5	31.5	89	9	2
$_{10}\mathrm{DCPD}_{80}$	63	6.5	30.5	89.5	9	1.5
$_{10}\mathrm{DCPD}_{70}$	58	6	36	89	9	2
$_{10}\mathrm{DCPD}_{60}$	59	6	35	89	9	2
$_{10}\mathrm{DCPD}_{50}$	61	7	32	90	9	1

2. Mechanical Properties

High internal phase emulsions were prepared as written in Experimental and HIPEs were transferred into the special stainless steel templates with following dimensions:



Samples were tested at a rate of 1 mm/min (modulus determination) to elongation 0.2%. Resolution was 0.6

µm. The machine Zug/Druck-Universalprüfmachine (Typ Z010, Fa. ZWICK) was equipped with a force measuring range up to 10kN. The experimental elastic modulus was determined from the initial linear slope of the stress/strain plot.

3. Atomic Force Microscopy (AFM)

The resin embedded specimens were mounted in special holders which at the same time fit the microtome and are suitable for the examination of the block face by AFM. Ultrathin sections (10–50 nm) were obtained using a Leica Ultracut E microtome (Leica, Austria) equipped with a diamond knife (Diatome, Switzerland).

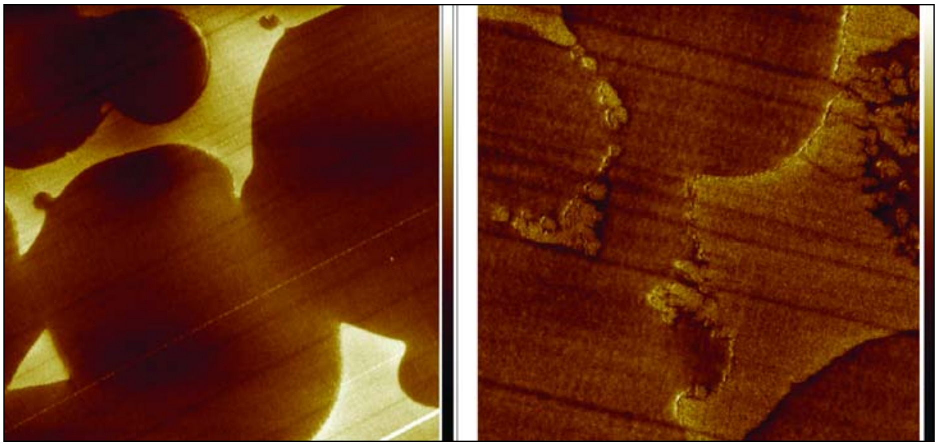


Figure 5. AFM pictures of epoxy-filled $_5$**DCDP**$_{80}$ (left) and $_8$**DCDP**$_{80}$ (right)