Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

On the Mechanical Properties of HIPE Templated Macroporous poly(Dicyclopentadiene) Prepared with Low Surfactant Amounts

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Electronic Supplementary Information

1. Experimental

Dicyclopentadien (*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 and the mixture was stirred with an overhead stirrer at 400 rpm. The corresponding amount (*cf.* Table S1) of deionised water was added drop wise under constant stirring. After addition of 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 further 1 min. Subsequently, the emulsion was transferred to the mould (polystyrene container or steel moulds or glass vial) and was 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

Table S1. Emulsion composition (80v% aqueous phase)

sample	m (**DCPD**) [g]	m (**M2**) [mg]	Surfactant	Surf. [g]	Surf. [vol. %]	$V(H_2O)$ [mL]
$_{80}$**DCPD**$_{0.25}$	8.06	8.08	Pluronic®121	0.021	0.25	33
$_{80}$**DCPD**$_{1}$	8.08	8.08	Pluronic®121	0.092	1	33
$_{80}$**DCPD**$_{3}$	8.06	8.04	Pluronic®121	0.26	3	33
$_{80}$**DCPD**$_{5}$	8.03	8.11	Pluronic®121	0.44	5	33
$_{80}$**DCPD**$_{6}$	8.02	8.12	Pluronic®121	0.52	6	33
$_{80}$**DCPD**$_{7}$	8.02	8.13	Pluronic®121	0.62	7	33
$_{80}$**DCPD**$_{8}$	8.08	8.08	Pluronic®121	0.73	8	33
$_{80}$**DCPD**$_{9}$	8.01	8.04	Pluronic®121	0.82	9	33
$_{80}$**DCPD**$_{10}$	8.06	8.08	Pluronic®121	0.91	10	33
$_{80}$**DCDP**$_{Span80}$	8.04	8.10	Span™80	0.084	1	33
$_{80}$**DCDP**$_{Span80}$	8.03	8.25	Span™80	0.25	3	33
$_{80}$**DCDP**$_{Span80}$	8.01	8.31	Span™80	0.43	5	33
$_{80}$**DCDP**$_{Brij52}$	8.06	8.08	Brij® 52	0.42	5	33

Elemental Analyses

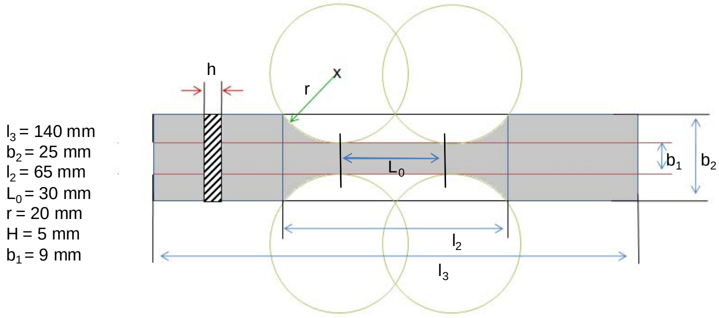
In the case of non-oxidized sample calculations from elemental analysis reveal oxygen content of the samples right after the preparation and purification (sample stored under vacuum). In each case three samples from a bigger specimen were submitted for elemental analysis and a mean value is given in 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			Un-oxidized		
	Elemental analysis			Elemental analysis		
	C[%]	H[%]	O[%]	C[%]	H[%]	O[%]
$_{80}DCDP_{0.25}$	65	7	28	90	9	1
$_{80}DCDP_{1}$	62	6.5	31.5	89.5	9	1.5
$_{80}DCDP_{3}$	63	6.5	30.5	89	9	2
$_{80}DCDP_{5}$	63	6	31	88.5	8.5	3
$_{80}DCDP_{6}$	63	6	31	89	9	2
$_{80}DCDP_{7}$	63	6	31	89.5	9	1.5
$_{80}DCDP_{8}$	63	6.5	30.5	89.5	9	1.5
$_{80}DCDP_{9}$	62	6.5	31.5	89	9	2
$_{80}DCDP_{10}$	63	6.5	30.5	89.5	9	1.5

2. Mechanical properties

2.1 Mechanical testing: 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 strain rate of 1 mm/min at ambient temperature. The Zug/Druck-Universalprüfmachine (Typ Z010, Fa. ZWICK) was equipped with a force measuring range up to 10kN. The experimental Young's modulus was determined from the initial linear slope of the stress/strain plot. The theoretical Young's modulus was calculated using Gibson´s equation and was compared with actual Young's moduli determine from the stress/strain plots.

Gibson´s equation,[1]

$$E_f = \left(\frac{d_f}{d_p}\right)^2 E_p$$

where E_p, E_f, d_p and d_f stands for polymer modulus, foam modulus, polymer density and foam density, was used to calculate the theoretical E-modulus of DCPD polyHIPEs. Polymer modulus and polymer density were taken from a database (2 GPa and 1.04 g cm^{-3}).[2] In our case, calculated values were compared with experimental values assessed from stress strain plots and % of theoretical yield strength was determined (Table S3).

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[1] Gibson, L. J., Ashby, M. F. *Cellular solids structure and properties*, Cambridge University Press, Cambridge, 2nd edn, **1999**.
[2]http://www.matweb.com/search/DataSheet.aspx?MatGUID=16d3d6b1e32c4c368fa1dda c6afb2b93&ckck=1

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Table S3. Characterisation of pDCPD foams prepared with different surfactant amount

sample	$_{80}$DCPD$_{0.25}$	$_{80}$DCPD$_{1}$	$_{80}$DCPD$_{3}$	$_{80}$DCPD$_{5}$	$_{80}$DCPD$_{6}$	$_{80}$DCPD$_{7}$	$_{80}$DCPD$_{8}$	$_{80}$DCPD$_{9}$	$_{80}$DCPD$_{10}$
skeletal density [g·cm^{-3}][a]	1.325	1.325	1.350	1.342	1.320	1.350	1.180	1.250	1.204
bulk density [g·cm^{-3}][a]	0.261	0.256	0.274	0.250	0.240	0.250	0.240	0.230	0.251
not oxidized									
$Rp_{0.2}$ [MPa][b]	1.5±0.3	1.3±0.2	1.8±0.2	1.5±0.3	1.0±0.2	1.5±0.2	0.2±0.07	0.2±0.01	0.1±0.03
ε @ break [%][b]	11±2	17±4	22±1	34±2	23±17	43±9	35±6	27±6	25±7
E-module [MPa][b]	94±5	94±10	105±8	97±4	94±2	88±2	18±2	16±1	12±3
E_{foam} [MPa][c]	125	121	138	115	106	115	106	98	116
$E_{exp.}/E_{teo.}$[%][d]	75	78	76	84	88	76	17	16	10
oxidized									
E-module [MPa][e]	228±14	267±15	273±10	243±2	230±18	242±2	69±1	61±10	78±25
ε @ break [%][e]	0.76±0.06	0.62±0.12	1.20±0.2	1.21±0.08	1.2±0.3	1.05±0.2	0.7±0.1	0.62±0.1	1.2±0.2

[a] determined by helium pycnometry of oxidized samples; [b] assessed from stress strain tests at constant speed rate and ambient temperature of not oxidized samples; [c] theoretical modulus estimated from Gibson´s equation; [d] % of theoretical strength; [e] determined for oxidized samples

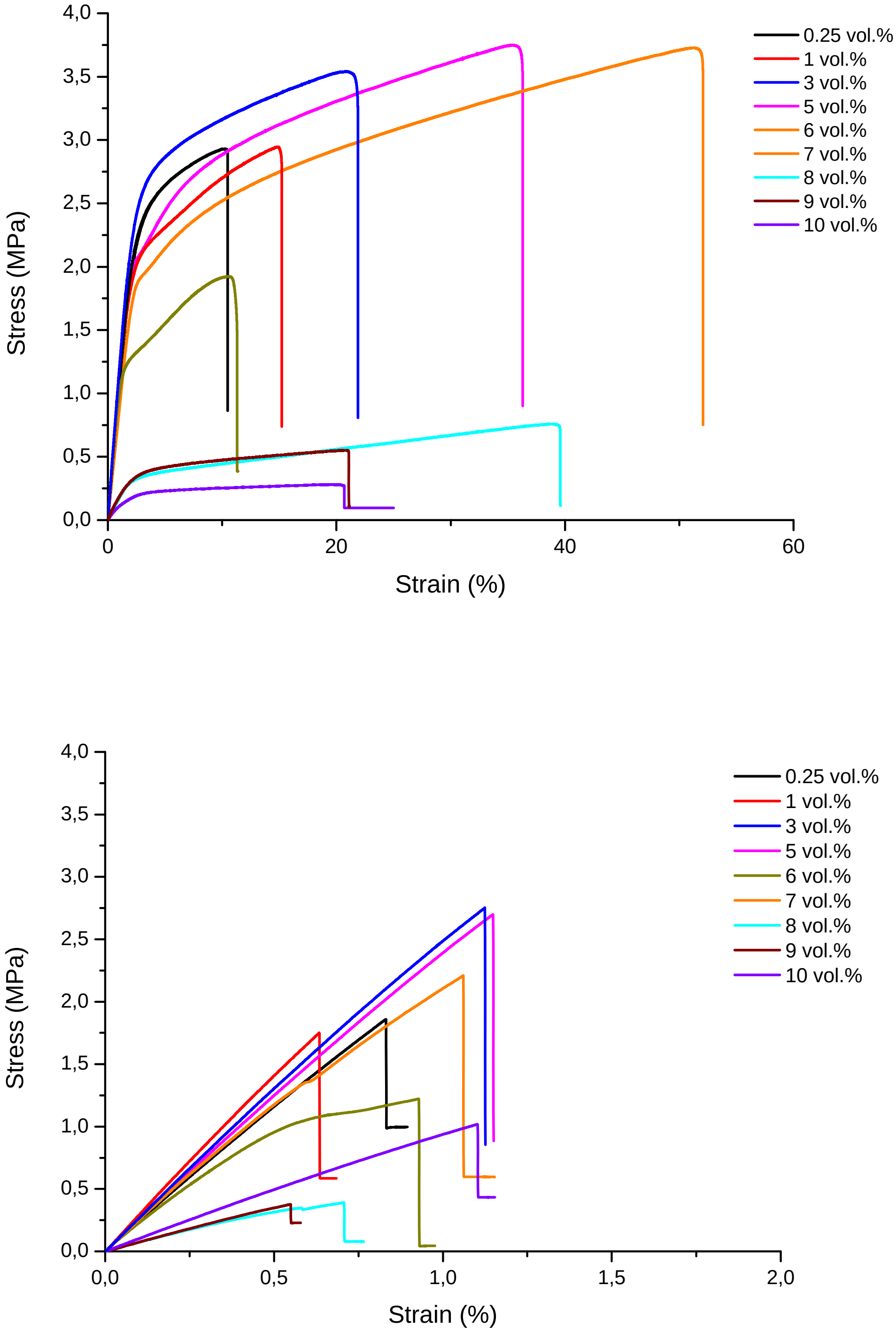


Figure S1. Strain-stress curves for not oxidized (above) and oxidized (below) $\mathbf{pDCPD_{80}}$ at different surfactant loadings

2.2 Mechanical strength vs. surfactant system

High internal phase emulsions with 5 vol. % of the surfactant used were prepared as described above. Changes made was chemistries of the surfactant used, which were in this particular case Span™80 and Brij® 52 in spite of Pluronic®121. Afterwards, HIPEs were transferred into the special stainless steel templates and samples for mechanical testing were prepared as described above.

Table S5. Characterisation of $_{80}$**DCPD**$_{Span80}$ and $_{80}$**DCDP**$_{Brij52}$ foams

sample	$_{80}$DCDP$_{Span80}$	$_{80}$DCDP$_{Brij52}$
$Rp_{0.2}$ [MPa]	0.7±0.1	1±0.2
ε @ break [%]	13±0.2	9.9±0.4
E-module [MPa]	75±3	50±2

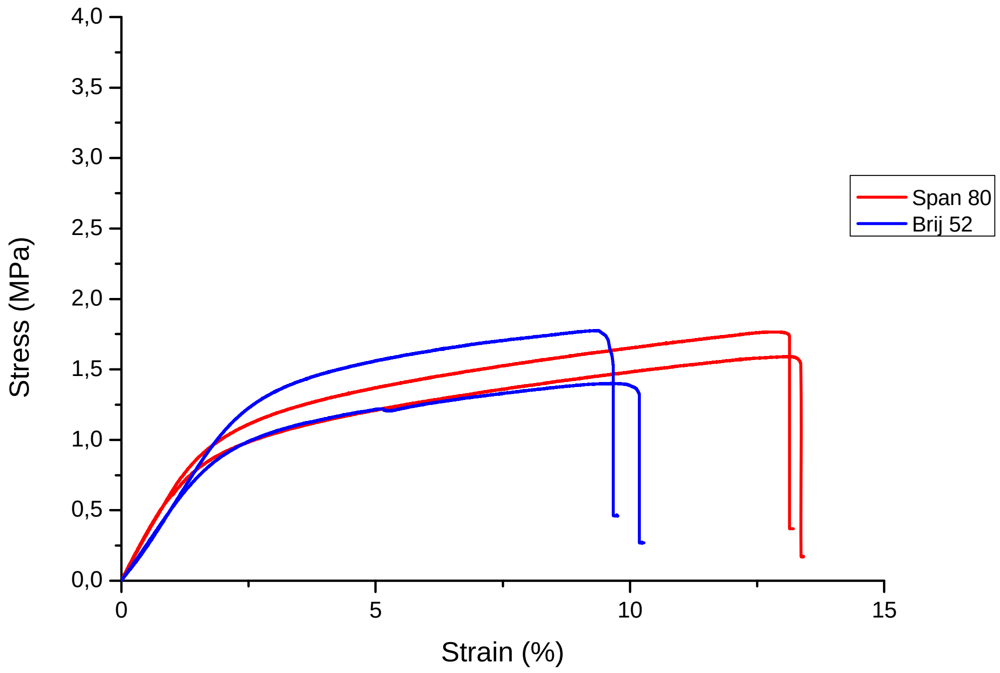


Figure S2. Strain-stress curves for un-oxidized **p$_{80}$DCPD$_3$** with 5v% of Span™80 and Brij®52 in the HIPE system

2.3 Mechanical strength vs. porosity

Table S6. Characterisation of $_{\mathbf{p}}$**DCPD** foams prepared at 3 vol. % of the surfactant (Pluronic L121) used with porosities of 50, 60 and 70 (marked with subscripts on the left side of the abbreviation)

sample	$_{p50}$**DCPD**	$_{p60}$**DCPD**	$_{p70}$**DCPD**
$Rp_{0.2}$ [MPa]	5.6±0.9	3.6±0.2	2.45±0.2
ε @ break [%]	24±10	23±11	20±6
E-module [MPa]	405±15	269±9	175±6

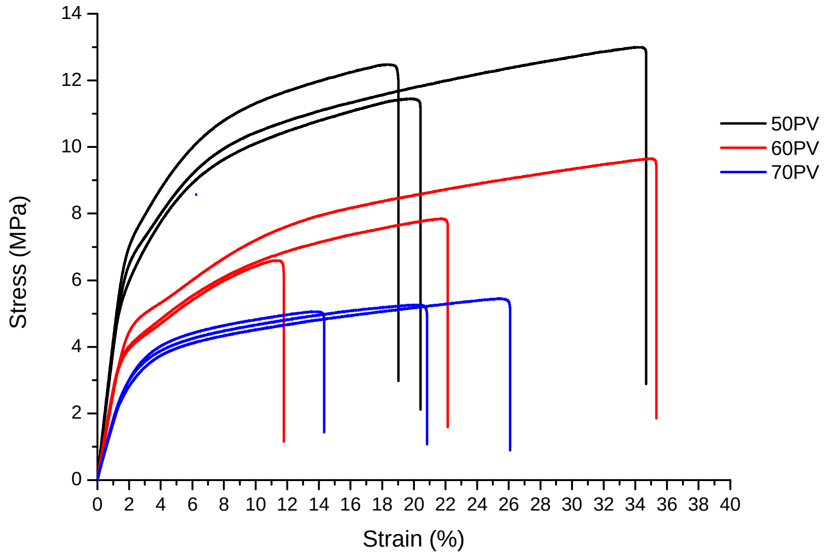
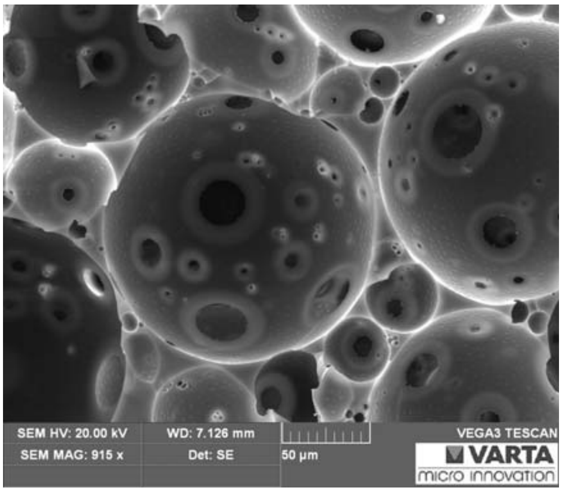
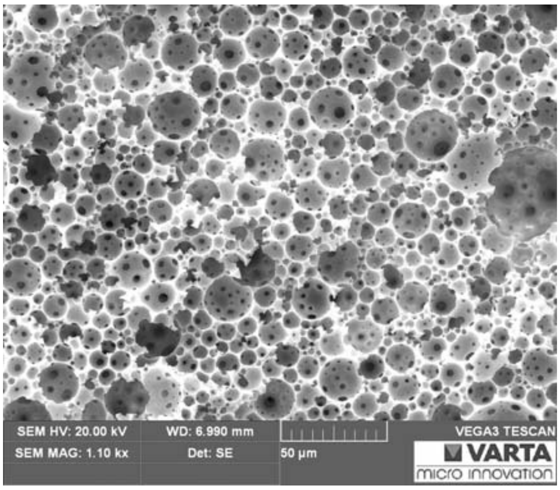


Figure S3. Strain-stress curves for un-oxidized **pDCPD$_3$** with different porosities at 3v% of Pluronic L121 used.

3 *Scanning Electron Microscopy (SEM) investigation*

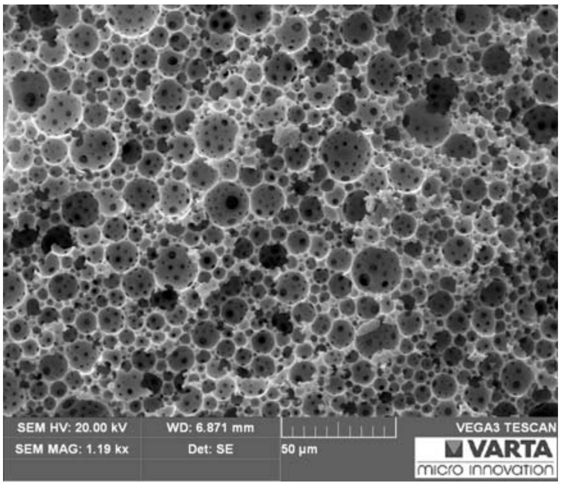
3.1 *SEM images of p_{80}DCPD with different surfactant concentrations*

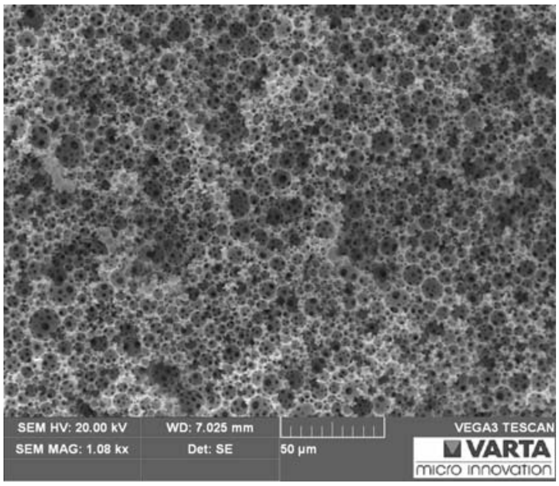




$_{80}$DCDP$_{0.25}$

$_{80}$DCDP$_{1}$





$_{80}$DCDP$_{3}$

$_{80}$DCDP$_{5}$

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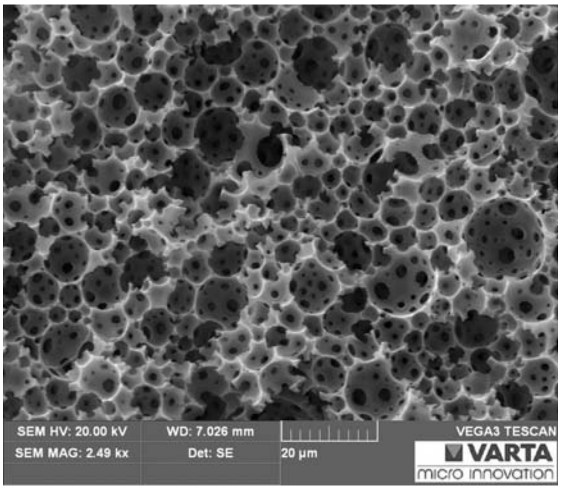
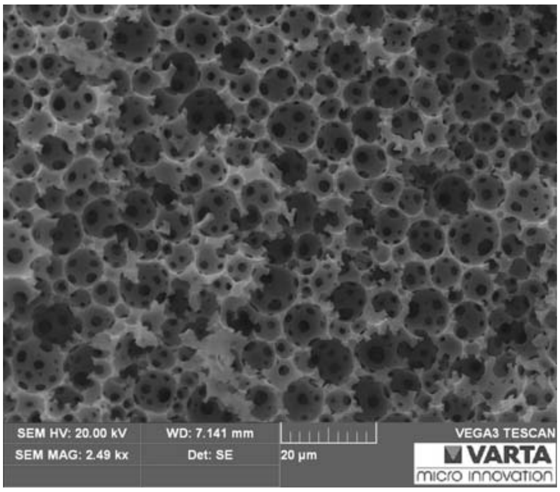
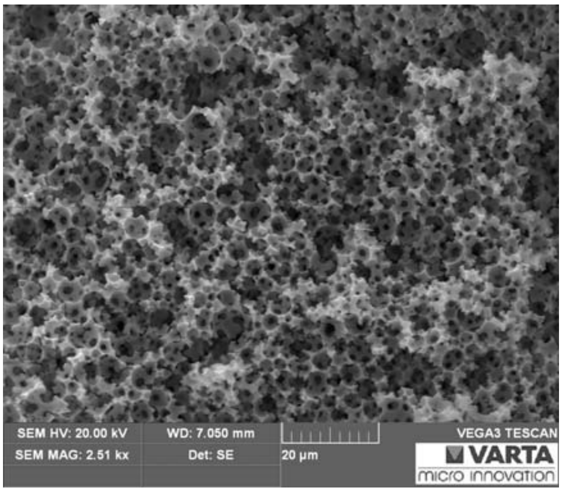


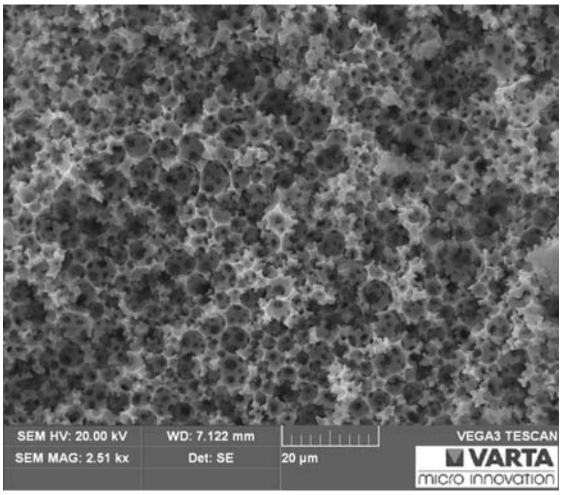
${}_{80}$DCDP$_6$



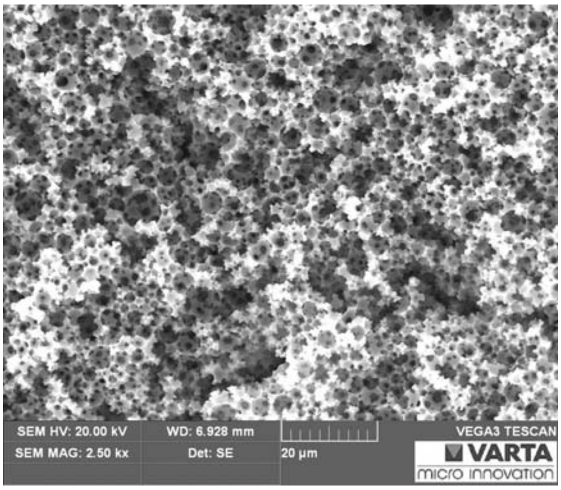
${}_{80}$DCDP$_7$



${}_{80}$DCDP$_8$



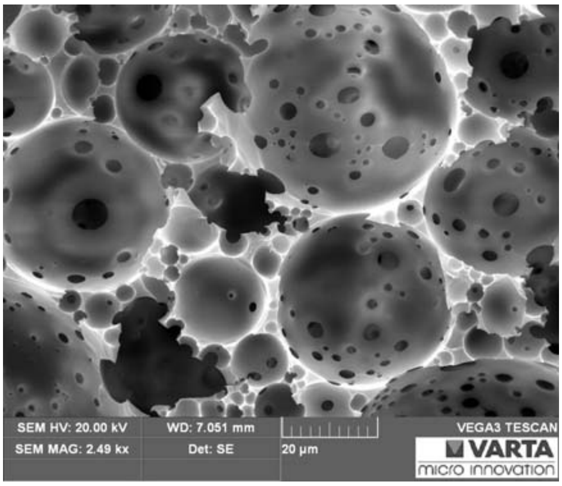
${}_{80}$DCDP$_9$



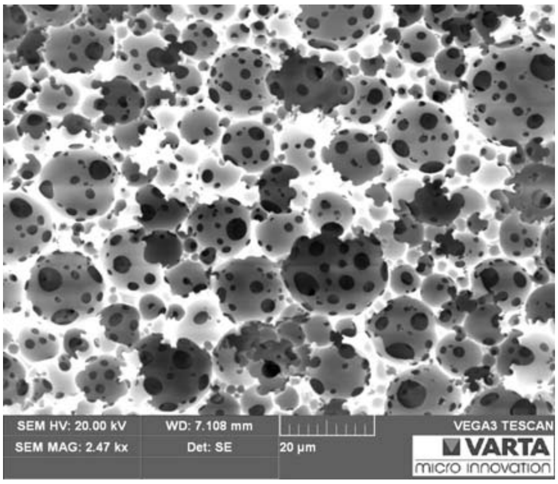
$_{80}$DCDP$_{10}$

Figure S4. SEM images of **p$_{80}$DCDP** at different surfactant (Pluronic L121) concentrations (marked with subscripts 0.25. 1, 3, 5, 6, 7, 8, 9, and 10 on the right side of the abbreviation)

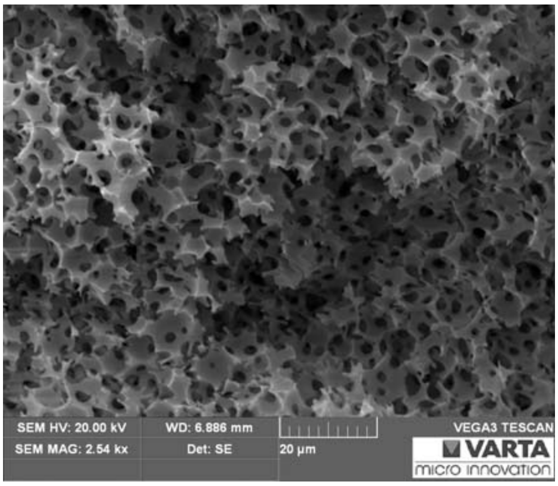
3.2 SEM images of p$_{80}$DCPD prepared with Brij®52 or Span™80



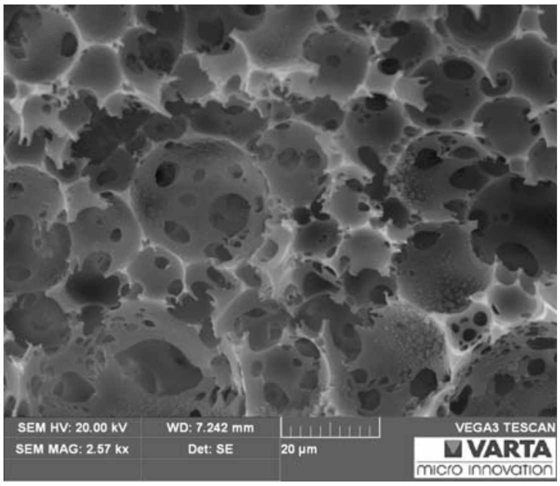
$_{80}$**DCDP**$_{Span80\_1}$



$_{80}$**DCDP**$_{Span80\_3}$



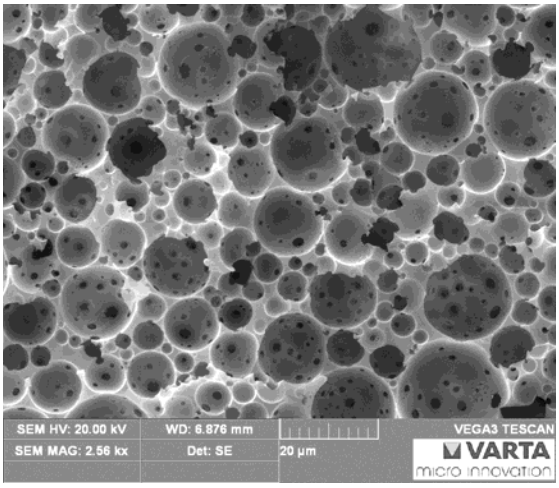
$_{80}$**DCDP**$_{Span80\_5}$



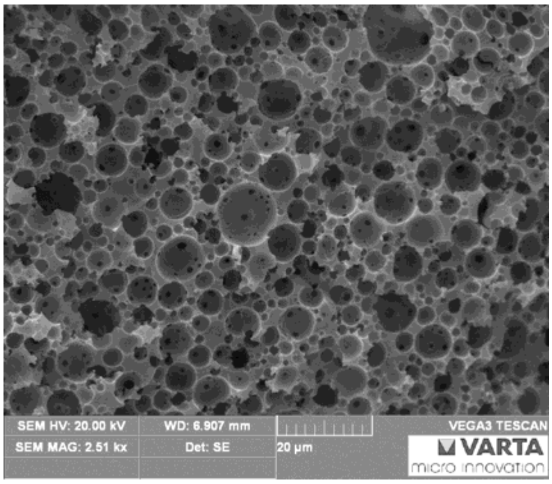
$_{80}$**DCDP**$_{Brij52\_5}$

Figure S5. SEM images of **p$_{80}$DCDP** with Span 80 in the HIPE system at different surfactant concentration (marked with subscripts 1, 3 and 5 on the right side of the abbreviation) and SEM image of **p$_{80}$DCDP** with 5v% of Brij®52 used in the HIPE system

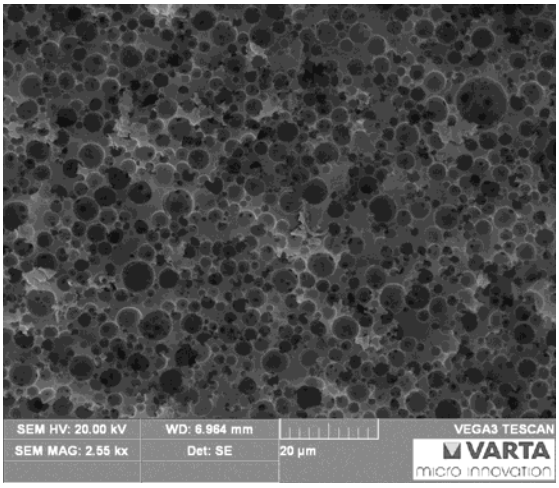
3.3 ***SEM images of pDCPD prepared with different porosities***



$_{70}$**DCDP$_3$**



$_{60}$**DCDP$_3$**

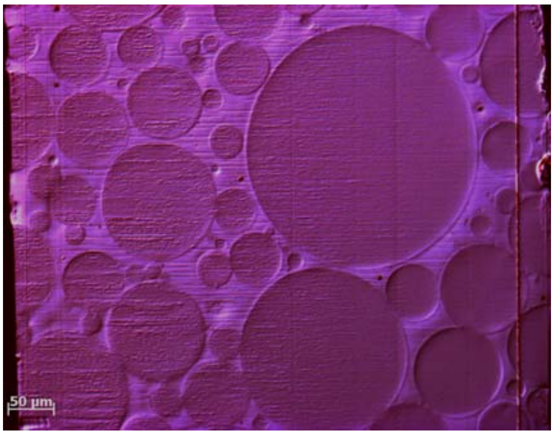


$_{50}$**DCDP$_3$**

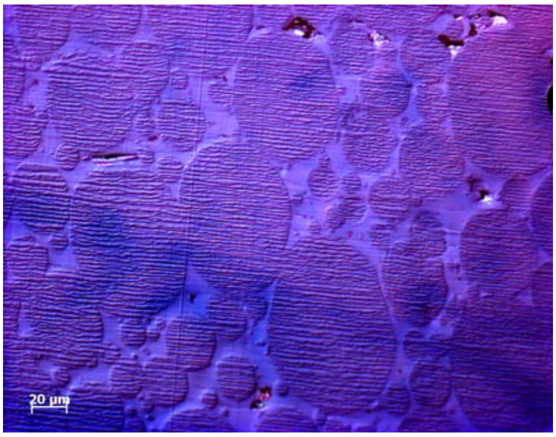
Figure S6. SEM images of **pDCDP** with different porosities (marked with subscripts as 70, 60 or 50 on the left side of the abbreviation) at 3 v% of Pluronic L121 used

4. ***Light Microscopy (LM) investigation***

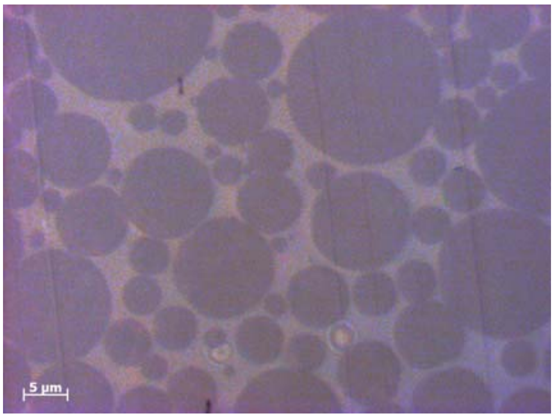
An average voids sizes were determined from LM micrographs analysis. Therefore, the mean and the standard deviation were drawn by manual measurements of diameters from a population of at least 40 voids. From SEM image analysis, it is difficult to give a correct evaluation of the void size because the voids are inside the material and during sample breaking the voids which appear are at random distance from the centre. To get a better estimation of the real void diameter by using the statistical factor $2/3^{1/2}$, void size evaluation was performed from epoxy-filled samples which were subsequently cut.



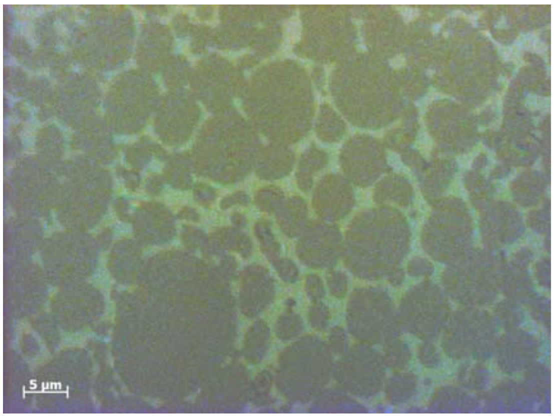
${}_{80}$**DCDP**$_{0.25}$



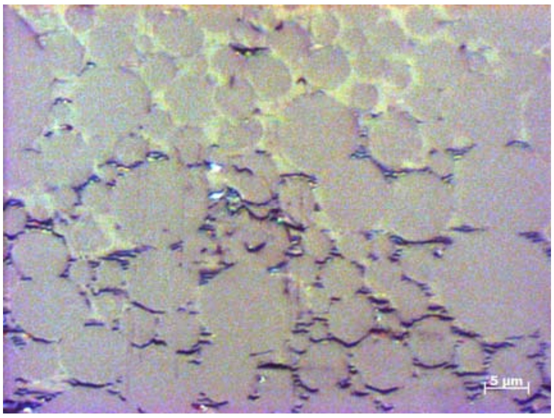
${}_{80}$**DCDP**$_{1}$



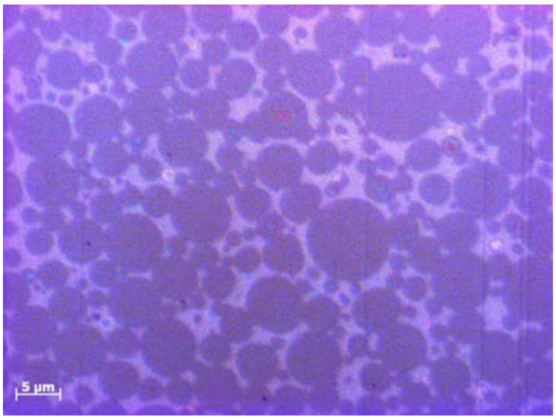
${}_{80}$**DCDP**$_{3}$



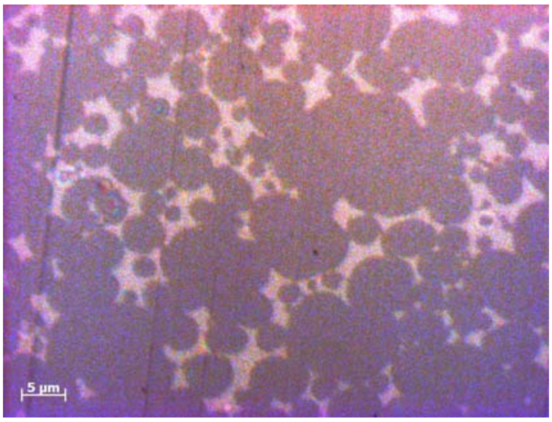
${}_{80}$**DCDP**$_{5}$



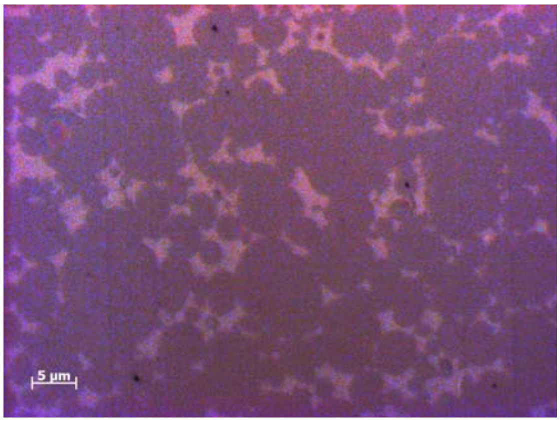
$_{80}$DCDP$_{6}$



$_{80}$DCDP$_{7}$



$_{80}$DCDP$_{8}$



$_{80}$DCDP$_{9}$

$_{80}$DCDP$_{10}$

Figure S7. LM images of **p$_{80}$DCDP** at different surfactant (Pluronic L121) concentrations (marked with subscripts 0.25. 1, 3, 5, 6, 7, 8, 9, and 10 on the right side of the abbreviation)