

Electronic Supplementary Information (ESI)

Solvent stable polymeric membranes via UV depth-curing

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1. Experimental section

Table 1 presents an overview of the photoinitiators used for the investigation of the influence of photoinitiator type and concentration on the UV curing efficiency.

Table 2 illustrates the cross-linkers applied to study the change in UV curing efficiency upon addition of a cross-linker with different functionality.

Table 3 shows the absorbance peak of the photoinitiators and the co-initiator used in this research.

Table 4 gives the composition of the membranes used to explore the effect of different type and concentration of the photoinitiator on the C=C conversion (Results and discussion section, paragraph 1), while Table 5 shows the composition of the membranes applied for studying the influence of the cross-linker functionality on the C=C conversion (Results and discussion section, paragraph 2). In further paragraphs, the membrane 3M5^{TPO} (Table 5) was used.

The SRNF filtrations were carried out using a high-throughput dead-end filtration module (HTML, Belgium) with 8 filtration cells and an active membrane surface area of $1.54 \cdot 10^{-4} \text{ m}^2$ mechanically stirred at 300 rpm. A solution of $17.5 \text{ }\mu\text{M}$ of Rose Bengal B (RB, $M_w = 1017 \text{ Da}$) in IPA was used as a feed. Separation was performed under various pressures ranging from 5 to 20 bar, depending on the membrane. The permeance was calculated as a ratio of collected permeate (V , l) to the active surface area of the membrane (A , m^2), collection time (t , h) and applied pressure (p , bar), as in eq. 1:

$$\text{Permeance} = \frac{V}{A \cdot t \cdot p}, \quad (\text{l m}^{-2} \text{h}^{-1} \text{bar}^{-1}) \quad (1)$$

The rejection was determined based on eq. 2:

$$R = \left(1 - \frac{C_P}{C_F}\right) * 100, \quad (\%) \quad (2)$$

where C_P and C_F are concentration of RB in the permeate and in the feed solution, respectively ($\mu\text{mol/l}$). The concentration of the RB in the permeate was determined by means of UV/Vis spectrophotometry at $\lambda_{\text{max}} = 555 \text{ nm}$ (Perkin - Elmer, Lambda 12 spectrophotometer).

2. Results and discussion section

Fig. 1a is an example of the way of choosing a photoinitiator based on the conversion of the C=C bond of SR399LV cross-linker for the membrane with various concentrations of the TPO photoinitiator. ATR-FTIR analysis of the conversion of the C=C bond (of SR399LV) for various types of PhIn systems and various PhIn concentrations (from 1 up to 7 wt%) (see Manuscript, Fig. 1), indicated TPO and IR819 as the most efficient photoinitiators. Because there was no spectacular increase of the conversion of the C=C bond upon addition of higher concentrations of TPO or IR819, a concentration of 3 wt% was chosen for further studies. As for the photoinitiator, TPO was selected mainly because of the yellowing effect of IR819 when applied in coatings and also because membranes loaded with IR819 exhibited worse adhesion to the non-woven support.

Table 6 contains the Hansen solubility parameters for PSU, cross-linkers, and photoinitiator. The solubility parameters (δ) of the cross-linkers and the photoinitiators were calculated based on the group contribution method of Hoftyzer and Van Krevelen [1] (eqs 3 – 6), and the interactions between compound (i) and (j) ($j = \text{DMF, H}_2\text{O or PSU}$) according to eq. 7.

$$\delta_{d,i} = \frac{\Sigma F_{d,i}}{V_i} \quad (3)$$

$$\delta_{p,i} = \frac{\sqrt{\Sigma F_{p,i}^2}}{V_i} \quad (4)$$

$$\delta_{h,i} = \sqrt{\frac{\Sigma E_{h,i}}{V_i}} \quad (5)$$

$$\sqrt{\delta_{t,i}^2} = \sqrt{\delta_{d,i}^2 + \delta_{p,i}^2 + \delta_{h,i}^2} \quad (6)$$

$$\Delta\delta_{t,j/i} = |\delta_{t,j} - \delta_{t,i}| \quad (7)$$

where:

$\delta_{d,i}$, $\delta_{p,i}$, and $\delta_{h,i}$ are the partial (Hansen) solubility parameters attributed to dispersive forces, polar forces, and hydrogen bonding, respectively;

$F_{d,i}$, $F_{p,i}$, and $E_{h,i}$ are group contributions to dispersive forces, polar forces, and to hydrogen bonding, respectively;

$\delta_{t,j}$, $\delta_{t,i}$ and $\Delta\delta_{t,j/i}$ are total solubility parameter of a component j and i and the difference between the total solubility parameter of the component j and i, respectively;

and V_i is the molar volume of the component (i).

Table 7 gives the solvent stability results for the reference and UV cured PSU membranes. The stability in the various solvents at room temperature was defined by visual inspection.

Table 1. List of photoinitiators (PhIns), their name and structure.

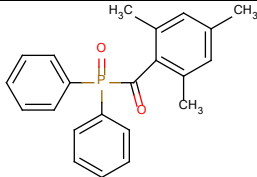
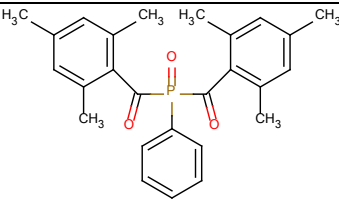
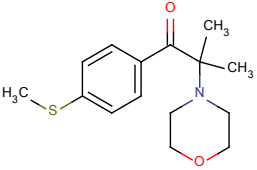
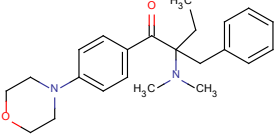
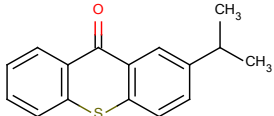
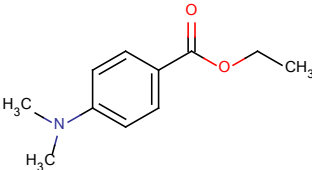
Photoinitiator	Name	Structure
TPO	2,4,6-trimethylbenzoyl-diphenylphosphineoxide (Darocur TM TPO)	
IR819	bis (2,4,6- trimethylbenzoyl)-phenylphosphineoxide (Irgacure TM 819)	
IR907	2-methyl-1-[4-(methylthio) phenyl]-2-(4-morpholinyl)-1-propanone (Irgacure [®] 907)	
IR369	2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone (Irgacure [®] 369)	
ITX	isopropylthioxanthone (Darocur [®] ITX)	
EDB (co-initiator)	ethyl 4-(dimethylamino) benzoate (Darocur [®] EDB)	

Table 2. List of cross-linkers, their name and structure.

Cross-linker	Name	Structure
EGDA	ethylene glycol diacrylate (EGDA)	
SR351	trimethylolpropane triacrylate (Sartomer™ SR351)	
SR295	pentaerythritol tetraacrylate (Sartomer™ SR295)	
SR399LV	dipentaerythritol pentaacrylate (Sartomer™ SR399LV)	
M600	dipentaerythritol hexaacrylate (Miramer™ M600)	

Table 3. Absorbance peaks in DMF of the photoinitiators and the co-initiator.

Photoinitiator	Absorbance peak (nm)
TPO	280, 360, 380, 400
IR819	290, 365, 395
IR907	230, 305
IR369	232, 325
ITX	270, 380
EDB (co-initiator)	230, 310

Table 4. Composition of the UV curable membranes with various PhIns before NIPS.

Membrane code	PSU (wt%)	PhIn system	PhIn (wt%)	Cross-linker (SR399LV) (wt%)	DMF (wt%)	THF (wt%)
M0	21	-	-	-	67,11	11,89
XM5 ^{TPO}	21	TPO	1-7	5	56,96÷ 62,05	10,05 ÷10,9 5
XM5 ^{IR819}		IR819				
XM5 ^{I+IR907}		ITX + IR907 (1:1)				
XM5 ^{I+IR369}		ITX + IR369 (1:1)				
XM5 ^{I+EDB}		ITX + EDB (1:1)				

XY^z: X – PhIn concentration, x = 1, 3, 5 or 7 wt%; Y – cross-linker type; z – PhIn type

Table 5. Composition of the UV curable membranes with various cross-linkers before NIPS.

Membrane code	PSU (wt%)	PhIn (3 wt%)	Cross-linker (5 wt%)	DMF (wt%)	THF (wt%)
M0	21	-	-	67,11	11,89
3M2 ^{TPO}	21	TPO	EGDA	60,35	10,65
3M3 ^{TPO}			SR351		
3M4 ^{TPO}			SR295		
3M5 ^{TPO}			SR399LV		
3M6 ^{TPO}			M600		

XY^z: X – PhIn concentration, x = 3; Y – cross-linker type; z – PhIn type

Table 6. Hansen solubility parameters and $\Delta\delta_t$ for PhIns, cross-linkers, PSU, H₂O and DMF.

Compound (i)	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	δ_t (MPa ^{1/2})	$\Delta\delta_t$ H ₂ O/i (MPa ^{1/2})	$\Delta\delta_t$ DMF/i (MPa ^{1/2})	$\Delta\delta_t$ PSU/i (MPa ^{1/2})
TPO	19,7	2,9	2,7	20,1	27,7	4,7	2,8
BAPO	19,4	3,4	3,5	20,0	27,8	4,8	2,9
I907	19,8	5,1	6,6	21,4	26,4	3,4	1,5
I369	19,5	4,6	6,9	21,2	26,6	3,6	1,7
ITX	20,8	4,0	3,2	21,5	26,3	3,3	1,4
EDB	19,1	5,4	6,8	21,0	26,8	3,8	1,9
M2	14,8	4,6	9,6	18,3	29,5	6,5	4,6
M3	15,5	3,3	9,0	18,2	29,6	6,6	4,7
M4	15,6	3,4	9,9	18,8	29,0	6,0	4,1
M5	16,4	3,1	12,0	20,6	27,2	4,2	2,3

M6	16,0	2,8	10,0	19,1	28,7	5,7	3,8
DMF [2]	17,4	13,7	11,3	24,8	23,0	-	1,9
H ₂ O [2]	15,5	16	42,3	47,8	-	23,0	24,9
PSU [2]	19,7	8,3	8,3	22,9	24,9	1,9	-

[1] J. Brandrup et al., Polymer handbook, 4th edition, 1999

[2] Ch. M. Hansen, Hansen solubility parameters, A User's Handbook, 2nd edition, 2007

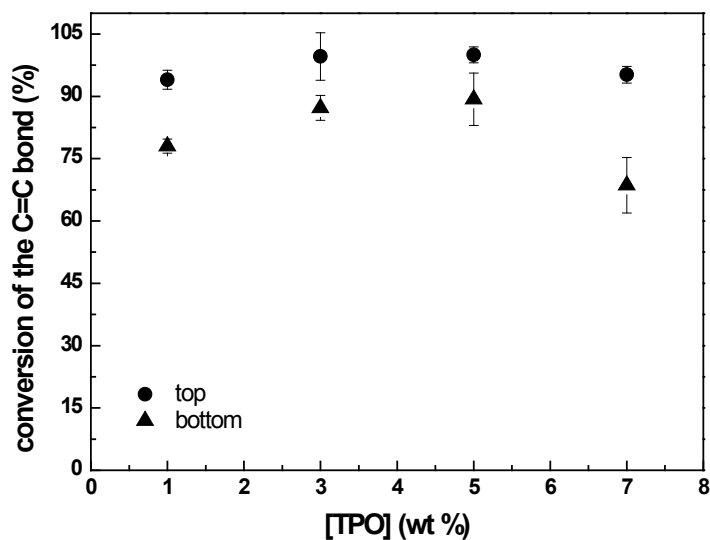


Fig. 1a. Influence of the TPO concentration on the conversion of the C=C bond (of the SR399LV cross-linker) on top and bottom side of the membrane (150 μ m wet thickness).

Table 7. Solvent stability results for the reference and UV cross-linked PSU membranes.

Solvent	PSU membrane	
	Reference	UV cured
IPA	0	0
Acetone	x	0
Ethyl acetate	1	0
THF	1	x

0-stable, x-swelling, 1-dissolution