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Efficient microencapsulation of a liquid isocyanate with \textit{in situ} shell functionalization

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ABSTRACT: We report on a one-pot, facile approach for the encapsulation of the liquid hexamethylene diisocyanate isocyanurate trimer in polyurea microcapsules formed via the oil-in-water interfacial reaction of an uretonimine-modified diphenyl methane diisocyanate trimer with triaminopyrimidine, with \textit{in situ} shell functionalization/modification using different types of hydrophobic agents. Remarkably, the use of hexamethylenedisilazane resulted in microcapsules of about 70 µm in diameter, with a smooth outer surface and a high isocyanate core content up to 85 wt% as determined by quantitative online FT-IR analysis of the extracted core. On the other hand, the use of an alkylamine, fluorinated aromatic amine and/or perfluoride amine provided microcapsules of approximately 100 to 150 µm in diameter containing around 65-75 wt% of the isocyanate core content, with the outer shell surface bearing pendant hydrophobic groups as confirmed by SEM-EDX. The effects of the functionalizing compound on the microcapsule properties such as shell morphology, size distribution and stability were assessed. After one day immersion in water, the initial isocyanate content of the microcapsules with a non-functionalized shell dropped rapidly from 49 to 15 wt%, whereas the ones with the modified shell structure maintained their core content, suggesting a significantly enhanced microcapsule stability.
KEYWORDS. Microencapsulation, multi-isocyanate, polyurea, shell functionalization

INTRODUCTION

The wide applications of polymeric microcapsules in many areas such as cosmetics, food and printing technologies, catalysis and drug delivery have attracted increasing research on the synthesis as well as functionalization of different types of capsules. A remarkable application of microcapsules, having received great interest in the last decade, is their use in self-healing materials where damage-induced cracking is the healing trigger. Liquid healing agents are encapsulated in microcapsules embedded in polymeric matrices. Upon rupture of microcapsules in the damaged area, the healing agents are released and undergo chemical reactions to repair the affected region. Commonly used are dual microcapsule systems, in which a catalyst and a healing agent that can polymerize, or two healing agents that can react with each other, are encapsulated in separate microcapsules. Examples include dicyclopentadiene/Grubbs’ catalyst, 5-ethylidene-2-norbornene/Grubbs’ catalyst, thiol/epoxy, vinyl-functionalized PDMS/PDMS crosslinker and azide/alkyne healing systems. On the other hand, single microcapsule healing systems have been used, with the catalyst, initiator or healing agent dispersed in the matrix and the other healing component sequestered in capsules. However, this is only applicable to specific materials, depending on the stability and compatibility of the dispersed agent with the matrix.

The development of different microcapsule systems consisting of various shell materials and self-healing core liquids has accompanied progress in autonomous self-healing polymers. Examples of microencapsulated self-healing agents include dicyclopentadiene, epoxy resins, poly(dimethylsiloxane) and multi-maleimide reagents covered by poly(urea-formaldehyde) (PUF) shells, aksosilanes covered by PU, polythiols covered by poly(melamine-formaldehyde), norbornene in melamine-urea-formaldehyde
microcapsules, solvents in PUF or polyurethane (PU)/PUF microcapsules for use in solvent-promoted self-healing systems, and amines in polyurea microcapsules.

Lately, the use of encapsulated liquid diisocyanates as healing agents to react with water for one-part, catalyst-free self-healing coatings to prevent corrosion in an aqueous or humid environment has been proposed by Sottos and coworkers, and later preliminarily tested by the group of Yang. Isocyanates are highly reactive toward many functional groups, such as an amine, alcohol or thiol, and hence are also potential healing agents for other various robust healing chemistries.

Nevertheless, as a result of the high reactivity of isocyanates with water, the difficulty of microcapsule synthesis and the low shelf-life of encapsulated isocyanates can challenge the wide application of isocyanate chemistry in self-healing materials. Thus, the solid state or blocked form of isocyanates has been utilized to facilitate the encapsulation. However, for healing cracks formed in samples, heat is required either to initiate flow of solid isocyanates or to generate the free isocyanate functionality.

Sottos and coworkers reported for the first time the microencapsulation of liquid-phase isophorone diisocyanate (IPDI) in linear polyurethane microcapsules via the interfacial polymerization of an in-house synthesized toluene diisocyanate-based urethane prepolymer with 1,4-butanediol in an oil-in-water emulsion. A maximum liquid core content of 70 wt%, comprising 60 wt% of IPDI and 10 wt% of chlorobenzene, was obtained for microcapsules of an average diameter of 100 µm, which could be stored in a sealed glass vial with only 10 wt% loss of IPDI after six months. The use of toxic chlorobenzene was necessary to dissolve the shell-forming prepolymer. However, the release of chlorobenzene in self-healing materials upon microcapsule disruption may cause matrix softening and a toxicity problem via leakage to the environment.

Later, using a similar polyurethane-based microcapsule synthesis protocol, the group of Yang systematically investigated the effects of microencapsulation parameters on the
core content and size of polyurethane microcapsules containing the liquid hexamethylene diisocyanate (HDI). The shell was formed by the reaction of a commercial methylene diphenyl diisocyanate (MDI) based prepolymer and 1,4-butanediol. The MDI-prepolymer could be dissolved in HDI to form an oil phase, thus avoiding the use of a solvent. Nevertheless, the resulting microcapsules (90 µm) had a maximum HDI core content of 60 wt%, which dropped to 45 wt% upon microcapsule storage in an open air environment for a month, and quickly to below 20 wt% upon immersion of the microcapsules in water for 24 hours.

Recently, Wang et al.\(^3\) reported the microencapsulation of IPDI by PUF embedding pre-treated carbon nanotubes to improve the micromechanical properties of microcapsule shells. Quantification of the IPDI core content was not performed, and distinction was not possible between the IR isocyanate signal ascribed to the core material on the one hand and the pendant isocyanate groups attached to the solid shell on the other hand.

The main objective of this paper is to present a facile approach for the efficient synthesis of crosslinked polyurea microcapsules containing a liquid tri-isocyanate monomer, with the shell being functionalized with various hydrophobic groups. \textit{In situ} surface modification and functionalization of the shell employing various reagents, including hexamethyldisilazane (HMDS) and primary amines bearing hydrophobic groups, were performed with the aim not only to impart more hydrophobicity to the shell and thereby enhance the shelf-life of the encapsulated tri-isocyanate, but also to increase the core content. The effect of functionalization reagents on the microcapsule stability as well as on the shell morphology will be described in detail. The shell functionalization presented in this work is useful for providing microcapsules with a high isocyanate core content, i.e. above 80 wt%, and can also in general serve as a pathway to introduce desired functional groups to the shell for tuning the shell surface properties.
EXPERIMENTAL SECTION

Materials. 2,4,6-Triaminopyrimidine (TAP, 97%), 2-ethylhexylamine (EHA, 98%), hexamethyldisilazane (HMDS, 99.9%), 3,4-difluorobenzylamine (DFBA, 98%), N,N-dimethylformamide (DMF, 99.8%) and gum arabic from acacia tree were purchased from Sigma-Aldrich. 1H,1H,2H,2H-Perfluorodecylamine (99%) was purchased from Acros. Hexamethylene diisocyanate isocyanurate trimer (HDI-trimer, Tolonate™ HDT-LV) was provided by Perstorp. Uretonimine-modified methylene diphenyl diisocyanate (MDI-trimer, Suprasec® 2020) was provided by Huntsman. All chemicals were used as received. Deionized water was used in all experiments.

Synthesis of microcapsules. All microcapsules with and without shell modification were synthesized at the same emulsification rate and shell-to-core feeding mass ratio. Typical procedure: 40 g of Tolonate™ HDT-LV was mixed well with 19 g of Suprasec® 2020 and the mixture was emulsified in 150 mL of a 13 wt% gum arabic aqueous solution by a Ultra-Turrax T 18 basic (IKA, Germany) homogenizer at 3500 rpm for 3 minutes. The emulsion was transferred to a double-walled cylindrical glass reactor (250 mL, Radleys) equipped with an external circulating heating bath (Julabo F-12 unit), and a three-bladed teflon overhead turbine stirrer (Cowie Ltd.) fitted at approximately 2 cm from the bottom of the reactor vessel and stirred at 600 rpm at 20 °C. 4.44 g (0.0355 mol) of TAP, previously dissolved in 130 mL of deionized water, was added dropwise, subsequently followed by the dropwise addition of 3.81 g (0.0267 mol) of 3,4-difluorobenzylamine mixed with 10 mL of tetrahydrofuran. The total dropwise addition time was 9 minutes. The reaction was then left at 20 °C for 5 minutes, after which it was heated to 76 °C in 20 minutes (see Figure S1 for the temperature profile). Microcapsule samples were collected after every five minutes during the heating process to determine the shortest reaction time to give well-dispersed stable microcapsules (see Table S1 for the optimal reaction time). After stopping the reaction, the microcapsules were filtered, washed several times with distilled water and air-
dried at room temperature for 48 hours before further analysis. Model capsule shells for HR-MAS NMR and DVS measurements were made using a similar procedure, replacing the hexamethylene diisocyanate isocyanurate trimer (HDI-trimer) by butyl acetate as the core liquid.

**Online FT-IR for core content analysis.** A weighed amount of microcapsules was stirred in a known volume of DMF, while a silicon attenuated total reflectance (ATR) probe (SiComp, optical range 4400–650 cm⁻¹, React-IR 4000 Instrument, Mettler Toledo AutoChem ReactIR) was dipped in the mixture to online record FT-IR spectra every minute as a function of stirring time. The solvent spectrum was recorded in advance and subtracted to enhance the signal of the reaction species. From the maximum measured IR intensity of the isocyanate peak at 2270 cm⁻¹ and the intensity-concentration Lambert-Beer's law calibration plots of HDI-trimer and MDI-trimer, and the MDI-trimer to HDI-trimer molar ratio as determined by ¹H NMR analysis of the extracted core in acetone-d₆, the mass of the extracted isocyanate core was determined. The core content in wt% was calculated as the mass ratio of the reactive isocyanate core and the microcapsule weight.

**¹H NMR.** Microcapsules were sonicated in acetone-d₆ for 3 hours, followed by filtering off the solid shell. Then, the solvent containing the extracted core was submitted to ¹H NMR analysis. ¹H NMR spectra were recorded on a Bruker Avance 300 at 300 MHz. For the HR-MAS NMR measurements, the solid shell powder was placed in a 4 mm rotor (50 µL) and DMF-d₇ was added to swell the network. ¹H NMR spectra were recorded on a Bruker Avance II 700 at 700 MHz with an HR-MAS probe. Samples were rotated at a frequency of 6 kHz.

**Scanning electron microscope (SEM).** SEM images were performed on a TM-3000 Hitachi table top microscope, using Leit adhesive Carbon Tabs 12 mm from Agar Scientific.
Scanning electron microscope-Energy Dispersive X-Ray (SEM-EDX) analysis. SEM-EDX were recorded with a Quanta 200 FEG FEI scanning electron microscope operated at an acceleration voltage of 5 kV, equipped with the EDX-system Genesis 4000. 

Particle sizer. Average particle sizes and dispersities of the microcapsules were measured by laser diffraction particle size analysis using the Beckman Coulter LS 200. 

Dynamic vapor sorption (DVS). DVS measurements were performed on a DVSA-STD Dynamic Vapor Sorption Advantage (Surface Measurement Systems) instrument equipped with an active control of the relative humidity (RH) and organic vapors, sample pre-heating and a Cahn-D200 ultra-microbalance allowing gravimetric analysis up to 0.05 µg of resolution. To prevent the influence of any humidity present on the pans, compressed dry air at a 200 mPa pressure was flown over the two closed chambers for approximately 10 minutes. The sample was pre-equilibrated at 0% RH in a continuous flow of dry air at 200 mPa before the sample was ramped to the desired %RH. The temperature was set constant at 25°C. The sample was then exposed to 80% RH with dm/dt (change in mass/time) mode. The instrument maintained the sample at a constant RH until the rate of change in mass (dm/dt) was less than 0.02% min$^{-1}$. 

RESULTS AND DISCUSSION 

Synthesis of polyurea microcapsules. Hexamethylene diisocyanate isocyanurate trimer (HDI-trimer) was selected as the encapsulated material because of its high isocyanate functionality and very low vapor pressure (0.6 $10^{-6}$ Pa at 20 °C) compared to other common diisocyanate monomers, such as HDI (vapor pressure of 0.7 Pa at 20 °C) and IPDI (vapor pressure of 0.04 Pa at 20 °C), making it a useful healing agent. Uretonimine-modified methylene diphenyl diisocyanate (MDI-trimer) was mixed with HDI-trimer in an oil phase. Because of the higher reactivity of MDI-trimer compared to HDI-
trimer, at the oil-water interface, MDI-trimer reacted primarily with the triaminopyrimidine (TAP) tri-amine, soluble in the water phase, to form a stable polyurea shell wall. The reaction was accelerated by heating the emulsion from 20 to 75 °C within 20 min, following a specific temperature profile (Figure S1). Nevertheless, on account of the hardly avoidable reaction between isocyanate groups and water and the low reactivity of the TAP primary amine groups due to resonance effects, the formation of the crosslinked polyurea shell plausibly occurred via both reactions of the MDI-trimer isocyanate groups with TAP amine groups and with water (1-3, Scheme 1). Indeed, carbon dioxide evolution, indicated by bubble formation at elevated temperature, and the presence of unreacted TAP upon reaction completion, indicated by the yellowish color of the water phase, were observed. Note that the reaction was stopped right after raising the temperature to 70-75 °C, since the opening of the MDI-trimer uretonimine ring, leading to carbodiimide and isocyanate, starts at 80 °C.

In order to functionalize or modify the shell properties, 20 mol% of the primary amine groups of TAP was replaced by either amines bearing different hydrophobic groups or hexamethyldisilazane (HMDS), which were involved in reactions with isocyanate groups throughout the shell formation (vide infra). For a facile comparison, all microcapsules with and without shell modification were synthesized at the same emulsification rate and shell-to-core feeding mass ratio to aim at microcapsules with similar sizes of approximately 100 µm.

It is worthwhile to note that increasing reaction temperature and time strengthened the shell structure, but, nevertheless, reduced the core fraction as a result of water diffusing through the shell wall and reacting with the isocyanate core. Thus, for the preparation of each type of microcapsules, the reaction was stopped as soon as strong and well-separated microcapsules were obtained (see experimental part). We observed that for all samples, after reaching the optimal reaction time (corresponding to 70–75 °C), a further
extension of the reaction time for another 5 min dropped the core content by 10 to 20 wt% (Table S1).

Scheme 1. Schematic depiction of used compounds and possible reactions to form functionalized polyurea shells using various hydrophobic agents.
**Core analysis.** The liquid HDI-trimer core of the microcapsules was separated from the polyurea shell wall by adding acetone-d$_6$ and sonication of microcapsules in this solvent for 3 hours, followed by filtering off the solid phase and analysis of the liquid phase by $^1$H NMR. The result (Figure 1) indicated that the core comprised of HDI-trimer and a trace of MDI-trimer. The content of MDI-trimer varied between 0 to 9 wt% of the total core, decreasing with the reaction time and temperature, which varied for each type of microcapsule preparation.

![Figure 1](image.png)

**Figure 1.** $^1$H NMR spectra of HDI-trimer in chloroform-$d$ (A), MDI-trimer in acetone-$d_6$ (B) and the extracted core in acetone-$d_6$ of polyurea microcapsules (entry 3, Table 1) (C).
To quantify the core fraction, the liquid core was extracted by vigorous stirring microcapsules in dimethylformamide (DMF). This highly polar solvent swells the shell significantly, releasing the encapsulated core into the solvent. Simultaneously, an ATR FT-IR probe was dipped in the mixture, recording online FT-IR spectra of the soluble phase. A sufficient amount of solvent was necessary to assure that the solid microcapsules and shell materials do not come in contact with the FT-IR probe. Vigorous stirring not only facilitated the extraction and diffusion of the core but also maintained a homogeneous concentration in the liquid phase. In other words, despite the fact that the ATR FT-IR probe only measures an in-contact thin layer of the liquid, quantification of the concentration of a vibrational group can be obtained via its IR intensity.

The viability of the encapsulated core was indicated by the appearance of the N=C=O stretch vibration at 2270 cm$^{-1}$ (Figure 2), the intensity of which reflects the concentration of the isocyanate groups according to the Lambert-Beer’s law. In addition to the Lambert-Beer’s law plots calibrated for the HDI-trimer and MDI-trimer in DMF (Figure 2, S2 and S3) and the HDI-trimer to MDI-trimer molar ratio of the extracted core as determined by $^1$H NMR, the maximum intensity of the NCO vibration allowed for an estimation of the microcapsule core content (Table 1).
Figure 2. (a) FT-IR spectra (after solvent signal subtraction) of MDI-trimer in DMF, HDI-trimer in DMF and polyurea microcapsules in DMF. (b) Illustrated online FT-IR waterfall plot for microcapsules vigorously stirred in DMF as a function of immersion time.

Table 1. Core content and size of the non-functionalized and shell-modified microcapsules using various hydrophobic agents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Functionalizing compound</th>
<th>Core content (wt%)</th>
<th>Microcapsule size(a) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HDI-trimer</td>
<td>MDI-trimer</td>
</tr>
<tr>
<td>1</td>
<td>non-functionalized</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2-ethylhexylamine</td>
<td>67</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>3,4-difluorobenzylamine</td>
<td>66</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>perfluorodecylamine + 2-ethylhexylamine</td>
<td>71</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>3,4-difluorobenzylamine + 2-ethylhexylamine</td>
<td>66</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>HMDS</td>
<td>76</td>
<td>7</td>
</tr>
</tbody>
</table>

(a) based on volume
(b) size with the highest frequency
(c) two-peak distribution
(d) coefficient of variation
Figure 3. SEM and SEM/EDX images of HDI-trimer containing polyurea microcapsules without shell functionalization (A) and with shell modification using HMDS (B), 2-ethylhexylamine (C), a 50:50 molar mixture of perfluorodecylamine and 2-ethylhexylamine (D), 3,4-difluorobenzylamine (E), a 50:50 molar mixture of 3,4-difluorobenzylamine and 2-...
ethylhexylamine (G), and 3,4-difluorobenzylamine with the HDI-trimer/methyl benzoate feeding mass ratio of 6/4 (H). Image C’ is a crushed microcapsule with 2-ethylhexylamine-functionalized shell while image E’ presents a ruptured microcapsule with 3,4-difluorobenzyl-functionalized shell after core removal and a zoom-in showing the shell thickness.

**Microcapsules with non-functionalized shell.** Without the addition of any functionalizing agent, stable and well separated microcapsules were obtained with a maximum achievable core fraction of about 50 wt% and a relatively rough shell surface (Figure 3A). In an effort to increase the core content, either increasing the core-to-shell feeding mass ratio or lowering the reaction time and temperature failed to produce non-agglomerated microcapsules, which was similarly observed for the previously reported preparation of polyurethane microcapsules containing HDI and IPDI.26, 27

**Microcapsules with HMDS-modified shell.** HMDS was used with the aim to induce reactions between isocyanate groups to partially form polyisocyanates and other urea derivatives as crosslinked components resulting in a reinforcement of the polyurea network shell. Scheme 1 shows numerous parallel competing reactions involving HMDS and isocyanate groups. These reactions were postulated to occur simultaneously with the other isocyanate-amine and isocyanate-water reactions (1-3, Scheme 1). Although HMDS can react with water at the HMDS droplet interface (5, Scheme 1), these oil droplets might simultaneously tend to go to isocyanate droplets and react with isocyanate moieties. It has indeed been reported that already at 20 °C, the reactions between silazanes and isocyanate groups can take place.35 The Si–N bond of HMDS cleaves and the silyl group (CH₃)₃Si adds to the nitrogen of the isocyanate group to form silylurea derivatives, which could easily hydrolyze with the formation of ureas (6 and 7, Scheme 1). Nevertheless, more
likely at an isocyanate to HMDS molar ratio far above unity and at elevated temperatures (i.e. up to 70-75 °C), the migration of the trimethylsilyl group of the resulted urea derivatives to the isocyanate nitrogen might lead to the formation of silyl-biurets and silyl-polyisocyanates, which could be transformed to the corresponding biurets and polyisocyanates via hydrolysis of the Si-N bonds (8-11, Scheme 1). Although not likely occurring at this temperature, the degradation of silylureas to silyamines, which further react with isocyanate moieties to form isocyanurate linkages (12-14, Scheme 1), might not be excluded. On the other hand, ammonia and trimethylsilanol as the hydrolysis products of HMDS, as well as trimethylsilyl isocyanate (TMSNCO) as a degradation product of silyureas, could respectively react with isocyanate and amine functions (15-18, Scheme 1).

Interestingly, high-quality microcapsules were obtained, being well-separated and containing a high core fraction up to about 85 wt% (Figure 3B and Table 1). In addition, these microcapsules had a smooth shell outer surface, which was quite different from that of the other HDI-trimer encapsulated microcapsules prepared in the absence of HMDS (Figure 3A-E). The EDX analysis of the outer shell surface showed no evidence for the presence of the silicon, indicating an inconsiderable amount of attached silyl groups (Figure 3B).

This fact suggests the occurrence of HMDS-induced isocyanate oligomerization reactions and the hydrolysis of HMDS. In fact, the oligomerization process can be considered as additional crosslinking of the isocyanates by HMDS with loss of trimethylsilyl compounds due to the presence of water. The structure of polyisocyanates and isocyanate derivatives can contribute greatly to the thermal stability and modulus of the network.
Hence, the hypothetical reactions between the isocyanate groups of MDI-trimer, mostly at the oil-water interface upon contact with HMDS droplets added to the emulsion, were expected to result in a densely-packed network, interpenetrated by the polyurea one. As a consequence, a relatively thin but sufficiently strong shell was promptly formed.

In conclusion, the use of HMDS as an additional reactant in the isocyanate reactions results in two clear advantages. On the one hand, the crosslinking density of the shell network could be increased and on the other hand water diffusion to the oil droplets containing HDI-trimer could be limited during the encapsulation. Indeed, a lower reaction time and thereby lower temperature was required in this case as compared to other shell-functionalized microcapsules.

Microcapsules with hydrophobic group functionalized shell. In another pathway, with the aim to render the microcapsule shell surface hydrophobic, a small fraction, i.e. 20 molar percent of the MDI-trimer isocyanate groups, of primary amines bearing hydrophobic groups were added to the emulsion. These amines are highly reactive toward the isocyanate function leading to pendant hydrophobic groups on the shell surface (4, Scheme 1). The degree of crosslinking and the distribution of the functions over the shell could not be quantified (outside the scope of this paper). Nevertheless, despite the replacement of the tri-amine by a small amount of primary amines, the formation of a strongly crosslinked shell could still be ensured.

A visible consequence of the addition of hydrophobic amines to the encapsulation procedure was the significant enhancement of the isocyanate core content. This effect is assigned to the presence of hydrophobic moieties attached to the cross-linked shell during its formation, resulting in less water diffusion at the interface and thus more preservation of the isocyanate core. For the hydrophobic amines used in this study (Scheme 1), the isocyanate core content was 18 to 27 wt% higher than achieved for microcapsules with a
non-functionalized shell (Table 1). Different types of capsules were made in order to find the optimal conditions.

**Microcapsules with 2-ethylhexylamine (EHA)-functionalized shell.** Well-separated spherical microcapsules with the shell morphology similar to the non-functionalized shell were obtained (Figure 3C). However, the core content was enhanced to 67 wt%.

**Microcapsules with perfluorodecylamine and EHA-functionalized shell.** To further increase the shell surface hydrophobicity, a mixture of 1H,1H,2H,2H-perfluoro-decylamine and EHA (1:1 molar ratio) was added to the emulsion. Spherical microcapsules with a high core content of 76 wt% were obtained. The SEM image of the shell surface showed a relatively rough morphology similar to that of the non-functionalized shell, but with the presence of tiny flocks randomly distributed on top of the shell surface (Figure 3D). The EDX area analysis of the shell surface showed the presence of fluorine, strongly suggesting that the perfluorodecyl groups were incorporated to the shell. However, the EDX analysis of the flocks showed even higher intensities of the fluorine signal, indicating that these flocks consisted of agglomerates of perfluorodecylamine. As a result of its both oil-repellent and water-repellent character, an insufficiently slow addition of the perfluoro compound to the water phase might give rise to its poorly uniform distribution.

**Microcapsules with 3,4-difluorobenzylamine (DFBA)-functionalized shell.** Applying the same approach but with the addition of DFBA resulted in well-separated microcapsules with a high core content of 73 wt%. SEM analysis of the microcapsule shell surface and EDX analysis of many different spots on the surface indicated a homogeneous shell structure bearing uniformly distributed fluoro-moieties (Figure 3E). As 3,4-difluorobenzylamine is much less oil-repellent as well as water-repellent than perfluorinated compounds, it was readily well-dispersed to the surface of isocyanate droplets.

To confirm the results of core extraction in combination with FT-IR analysis, indicating a substantial isocyanate core fraction, the microcapsules were immersed in acetone and
subsequently washed extensively with acetone to remove all soluble core. This resulted in
the formation of hollow microcapsules with a shrunk but intact shell, suggesting a well-
crosslinked shell structure. As shown in Figure 3E’, the SEM image of an acetone-washed
microcapsule after being freeze-cut strongly proves the liquid core–solid shell structure of
the synthesized microcapsules.

We noticed that the microcapsules had a less rough outer shell wall, but a distinctive
“wrinkled” appearance, which did not occur under identical capsule formation conditions
using the EHA and perfluorodecylamine functionalizing agents. From this observation, we
believe that the formation of the wrinkled morphology is related to the fast reaction kinetics
of the highly reactive fluorinated aromatic amine compound. Indeed, the combination of
inhomogeneous reaction kinetics, fluid-induced shear forces, and shell-determined elastic
forces may cause wrinkles on microcapsules.39, 40 In fact, the wrinkled shell morphology
could possibly serve as an advantage in promoting the bonding of microcapsules to a
polymer matrix (not investigated).

**Microcapsules with DFBA and EHA-functionalized shell and partial methyl benzoate core.** To further manipulate the microcapsule shell morphology, we prepared microcapsules
under identical conditions, except for the fact that half of the molar number of DFBA was
replaced by EHA and that a small amount of methyl benzoate (25 wt% of the feeding HDI-
trimer) was mixed with the feeding isocyanates. As a result of both the use of less DFBA
and the plasticizing effect of methyl benzoate, microcapsules with a similar HDI-trimer core
content and considerably less wrinkled shell surface were produced (Figure 3G). EDX
analysis of the outer wall of these microcapsules showed a uniform distribution of the
fluorinated compound. It also indicated the presence of less fluoride, which is in a good
agreement with the use of lower amounts of DFBA.

**Microcapsules with DFBA-functionalized shell and partial methyl benzoate core.** On the
other hand, without changing the amount of DFBA but replacing 40 wt% of the initial
feeding HDI-trimer by methyl benzoate (i.e. HDI-trimer/ methyl benzoate mass ratio of 6/4) resulted in the formation of microcapsules with a remarkable smooth outer surface (Figure 3H). Moreover, as indicated by EDX analysis, the amount of fluoride appeared to be less, although still uniformly distributed over the shell outer surface. As a result of the lower HDI-trimer feeding, an HDI-trimer core fraction of 51 wt% was encapsulated together with 9 wt% of methyl benzoate. It was also noticed that only less than a third of the fed methyl benzoate was encapsulated, which is assigned to the considerable solubility of methyl benzoate in the water phase.

In order to further confirm the chemical structure of the shell, HR-MAS NMR measurements were performed. Therefore, four batches of polyurea model microcapsules (non-functionalized and functionalized with HMDS, EHA and DFBA) were synthesized with butyl acetate as the core liquid. The solvent core was then removed by crushing the capsules and performing a Soxhlet extraction for one day, in order to be able to analyze only the shell material. An overlay of the HR-MAS NMR spectra is shown in Figure 4. Full conversion of the TAP amine functional groups into polyurea bonds (polyurea NH signal at 8.4-8.9 ppm in spectrum A, B, C and D) is demonstrated by the disappearance of the TAP amine signals at 5.3-5.8 ppm. Incorporation of the MDI-trimer into the shell network is indicated by broadening and slight shifting of the MDI-trimer signals. More importantly, the incorporation of EHA (B) and DFBA (C) could be seen by the presence of signals at 3.2 ppm (EHA CH$_2$-NH), 0.7-1.5 ppm (EHA aliphatic) and 4.4 ppm (DFBA CH$_2$-NH). In these samples, a double urea NH signal is also visible, which could be attributed to the reaction of the hydrophobic amine with the MDI-trimer. Furthermore, no signal of trimethylsilyl compounds could be seen around 0 ppm in spectrum D, indicating that these were not covalently bound to the polyurea shell.
Figure 4. HR-MAS NMR spectra of triaminopyrimidine (TAP), MDI-trimer, the non-functionalized polyurea shell (A) and the polyurea shells functionalized with EHA (B), DFBA (C) and HMDS (D).

**Effect of the functionalizing compound on microcapsule size distribution**

As observed by SEM (Figure 3), the microcapsules with functionalized shells had thin shell structures, with the thickness varying with microcapsule diameter and core content. Approximately, for microcapsules with an average diameter of about 100 µm, the shell wall thickness was between 2.2 to 3.1 µm.
In addition, the *in situ* functionalization of the microcapsule shell surface with hydrophobic groups not only increased significantly the encapsulated HDI-trimer core fraction, but also greatly influenced the microcapsule size distribution. The microcapsules with non-functionalized shell showed a double distribution of the microcapsule size, with average dimensions of around 110 and 210 µm respectively (Figure 5). The fraction of the larger size microcapsules is attributed to the agglomeration and coalescence of the dispersed multi-isocyanate droplets. On the other hand, by attachment of hydrophobic groups to the shell surface, the microcapsule size distribution became more narrow. Apparently, the presence of hydrophobic moieties at the oil-water interface had a positive effect in stabilizing oil droplets as it prevented water diffusion to the inside of the oil droplets as well as isocyanate diffusion to the water phase.

Thus, a decrease in size dispersity, in accordance with a slight decrease in the mean size and an increase of the maximum encapsulated isocyanate core content, was observed in the following order of the used functionalizing agents: EHA, DFBA, the 50:50 molar mixture of 1H,1H,2H,2H-perfluorodecylamine and EHA, and HMDS (Table 1).

![Size distributions of microcapsules without and with shell functionalization using hydrophobic agents.](image-url)
For the shell functionalization using the mixture of DFBA and EHA, the co-encapsulation of a small quantity of methyl benzoate reduced considerably the viscosity of the oil phase, thereby leading to a relatively narrow size distribution and a smaller microcapsule average diameter of 61 µm (entry 5, Table 1).

The difference in the shell functionalization of the synthesized microcapsules could be observed by the difference in the dynamic water vapour sorption (DVS) measurements of these microcapsules after core removal. Under our conditions, insignificant loss of the isocyanate core content was observed after exposure of the shell-functionalized microcapsules to air at room temperature for one month (Table S1). Although shell-functionalization considerably enhances the stability of the encapsulated isocyanate core, compared to similar systems previously reported,27 water diffusion through the shell still occurred upon immersion of capsules in water for many days (vide infra). It should be noted that this experiment is quite harsh and does not represent the behaviour of such capsules in an epoxy resin for example.

Hence, to avoid the isocyanate-water reaction during the DVS measurements, the four batches of polyurea microcapsules, synthesized for HR-MAS NMR spectroscopy, with butyl acetate as the core liquid were used. Again, the solvent core was removed by crushing the capsules and performing a soxhlet extraction for one day. DVS analysis showed small water uptake, i.e. 1 to 2.4 wt% at 80% relative humidity (RH). A decreasing water uptake was observed in the following order of microcapsules: non-functionalized (2.4 wt%), functionalized with HMDS (2.3 wt%), with DFBA (1.9 wt%) and with EHA (1 wt%) (Figure 6). This demonstrates that the functionalization has a significant effect on the water permeability of the microcapsules and that especially the hydrophobicity of DFBA and EHA significantly lowers the water uptake. In all cases, a small mass loss (< 1wt%) at 80% RH was also noticed over time. This was attributed to the reaction of water with residual isocyanate groups in the shell, releasing CO₂ in the process.
Effect of the functionalizing compound on the stability of encapsulated HDI-trimer

The shelf-life of the encapsulated multi-isocyanate exposed to open air is dependent on the humidity and temperature, varying with the conditions. Thus, the stability of the encapsulated isocyanate core of different microcapsules was better compared by evaluation of their core contents (by the online FT-IR method, vide supra) after immersion in water for different periods of time. To a certain extent, the stability of microcapsules in water reflected indirectly their shelf-life in a humid environment. In our conditions, the isocyanate core content after one month microcapsule storage in open air under ambient conditions was close to that after one day immersion of the microcapsules in water. Once embedded in a matrix, it is expected that the core content would be stable for much longer periods.

As revealed by Figure 7, the microcapsules with non-functionalized shell showed a considerable drop by 70% of the initial core fraction after one day immersion in water, and to almost zero after two day immersion. In contrast, the microcapsules with the shell
bearing pendant hydrophobic groups (EHA or fluoro-compounds) or with an increased crosslinking density (HMDS) maintained their initial isocyanate core fraction after one day immersion, owing to the low affinity of water towards the hydrophobic shell or the decreased diffusion through the denser crosslinked shell.

Figure 7. Isocyanate core contents of microcapsules without and with shell functionalization using various hydrophobic agents after immersion in water for different periods of time.

The loss of the reactive isocyanate core after one day immersion in water occurred rapidly for the microcapsules with shell modification using HMDS and EHA, while it proceeded gradually for the other microcapsules with fluoride functionalized shells possessing a more water repellent surface.

In summary, via shell modification by either HMDS or hydrophobic amines, a significant enhancement in both the multi-isocyanate core content and its stability under wet conditions was obtained.
CONCLUSIONS

In conclusion, a one-pot, simple and efficient approach for the synthesis of polyurea microcapsules with a high content of encapsulated reactive liquid tri-isocyanate core and a shell bearing hydrophobic groups has been successfully developed. By the choice of the hydrophobic agents comprising HMDS, alkylamine, fluorinated aromatic amine and perfluoride amine compounds, both the core content and the stability of the encapsulated core as well as the shell morphology, varying from smooth, rough to wrinkled exterior surface, could be tuned. In principle, a fraction of other specific functional groups, besides the hydrophobic moieties, could also be introduced to the shell surface using corresponding functional amines. This approach not only meets the challenges of microencapsulation of liquid isocyanates, which includes the design of capsules with a high core content and enhanced shelf-life, but also provides the possibility of making microcapsules with on-demand shell properties, depending on the type of polymer matrix and the application requirements.

ASSOCIATED CONTENT

Supporting Information. Temperature profile applied in the synthesis of microcapsules, Lambert-Beer's law calibration plots of HDI-trimer and MDI-trimer, and optical microscopic images of microcapsules in the wet state.

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REFERENCES

A one-pot, simple approach for the encapsulation of a liquid tri-isocyanate in polyurea microcapsules, with in situ shell functionalization/modification using different types of hydrophobic agents is presented.
Graphical Abstract

A one-pot, simple approach for the encapsulation of a liquid tri-isocyanate in polyurea microcapsules, with *in situ* shell functionalization/modification using different types of hydrophobic agents is presented.