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Towards a Process for the Reduction of Monomer Content in MDI-Based Prepolymers

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Abstract:

The selective removal of methylene diphenylene diisocyanate (MDI) monomers from commercially important MDI-based prepolymers by means of fractionation through a semipermeable polymeric solvent-resistant nanofiltration (SRNF) membrane is demonstrated at laboratory scale.

Introduction

Isocyanate-ended (NCO-ended) prepolymers containing urethane groups are important intermediates for the production of many types of polyurethane products. They are typically formed by reacting diisocyanates with substoichiometric amounts of difunctional polyethers or polyesters to produce a mixture of the NCO-ended reaction product in the excess isocyanate (Figure 1).[1]

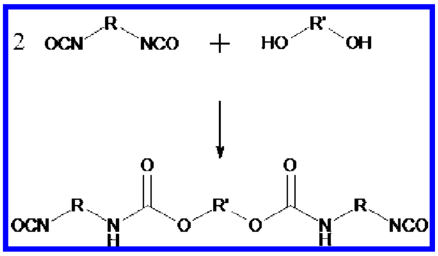

Figure 1. **Reaction scheme of the ‘prepolymer’ formation.**

Amongst the aromatic diisocyanates, 4,4′-methylene diphenylene diisocyanate (hereafter MDI) is most frequently used, although prepolymers employing mixtures of 4,4′-MDI and 2,4′-MDI are also produced (Figures 2 and 3, respectively).

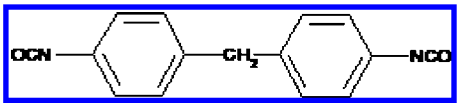

Figure 2. **4,4-MDI.**

Despite the presence of excess MDI, some of the formed MDI−polyol−MDI product, with an A−B−A structure, inevitably reacts further with polyol and MDI to produce decreasing amounts of higher-molecular weight (MW) oligomers of the form ABABA, ABABABA, etc. The formation of such oligomeric species is undesirable since they are not the targeted reaction products, and thus, their presence can have a negative effect on the properties of the final polyurethane product.[2] In addition, the viscosity of the prepolymer itself generally increases with the extra degree of polymerisation which can have a deleterious effect on its processing.

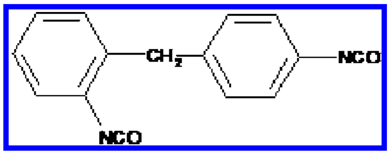

Figure 3. **2,4-MDI.**

The amount of higher oligomer formation can be minimised by increasing the excess of MDI. However, in such an approach, the amount of unreacted MDI then needs to be decreased. This is typically accomplished via fractional distillation, requiring relatively high temperatures and low pressures because of the low volatility of MDI, a process step which itself causes viscosity increase in the prepolymer product by the creation of carbodiimide linkages between isocyanate-ended species. These may be carbodiimides formed in any of the various reaction permutations, for example, MDI + MDI, prepolymer + prepolymer, or MDI + prepolymer (Figure 4).

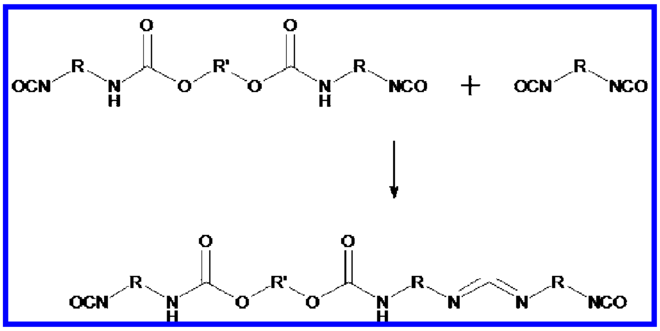

Figure 4. **Carbodiimide formation between isocyanate-end species.**

Carbodiimides can react further with isocyanates to form uretonimines of even greater MW. Therefore, the use of semipermeable solvent-resistant nanofiltration (SRNF) membranes in a novel, easy to operate, relatively low-temperature and low-energy fractionation process to decrease the amount of free MDI in MDI-based prepolymers as a sustainable alternative to distillation has been investigated.

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Table 1. **Commercial membranes tested for stability in MDI**

commercial membranes	manufacturer
Solsep 010206	Solsep
Solsep 030306F	Solsep
Solsep 030305	Solsep
Solsep 010207	Solsep
Solsep 010306	Solsep
Starmem 228	Membrane Extraction Technology
Starmem 240	Membrane Extraction Technology
MPF-50	Koch Membrane Systems

SRNF is a pressure-driven membrane process with operating pressures typically between 10 and 40 bar and molecular weight cutoffs (MWCO) between 200 and 1000 Da.[3] It has already been applied successfully in an industrial plant (ExxonMobil's lube oil dewaxing plant in the United States (USA)), and it also has potential applications in a variety of industries (chemical, petrochemical, pharmaceuticals, food applications, among others). Lately, it has received enhanced attention, motivated by increased environmental concerns and the search for cleaner and more energy-efficient technologies, and is also favored by the recent developments and improvements of the stability of polymeric membranes in harsh solvents.[4,5] This leads to the possibility of applying SRNF in the process described, this being the first time that membrane technology has been considered as a separation technique for this application. A wide set of commercially available and laboratory-made membranes was selected for investigating in this context.

Experimental Section

Prepolymer Solutions. Two prepolymer solutions based on mixed diisocyanate isomers (MIs) were used in this work so as to keep any separated diisocyanate liquid at room temperature, thus avoiding the additional complexity at this stage of maintaining the temperature of the whole setup above the melting point of any 4,4′-MDI-rich compositions.

The first prepolymer (PP-1) was based on 90 wt % of a commercially available MI-30 product (i.e. ~70:30 mass ratio of 4,4′-MDI to 30% 2,4′-MDI) reacted with 10 wt % of mixed tripropylene glycol (TPG) isomers, whilst the second prepolymer (PP-2) had the same proportions of MDI to TPG, but was based on an MI-50 (i.e. ~50:50 mass ratio of 4,4′-MDI to 50% 2,4′-MDI). Both PP-1 and PP-2 were analysed by GPC which gave a ratio of 0.34 and 0.31 for the diisocyanates to the higher-molecular weight polymers respectively. Some tests were carried out with the prepolymers diluted 50:50 with monochlorobenzene (MCB, Acros Organics, Belgium) in order to maintain a low viscosity of the MDI-reduced retentate and to keep membrane fluxes reasonable.

Commercial Membranes. Solsep membranes were supplied by Solsep (The Netherlands), Starmem membranes were acquired from Membrane Extraction Technology (UK), and membrane MPF-50 was purchased from Koch Membrane Systems (USA). The commercial membranes considered for screening are listed in Table 1.

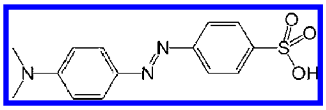

Figure 5. **Methyl orange.**

Membrane Polymers. In addition to the screening of commercial membranes, it was the intention to test laboratory-prepared membranes as well. Before starting the actual membrane synthesis, a selection of possible membrane polymers was first screened to verify the material's stability against the isocyanate mixture. For each case, 1 g of polymer was exposed to 5 g of prepolymer solution. A list of these materials with the corresponding specifications and suppliers is provided in Table 2.

Preparation of P84-Based SRNF Membranes. SRNF-membranes were prepared *via* the phase inversion technique.[6] P84 polyimide (Evonik Fibres, Austria) was dissolved in *N*-methylpyrrolidone (NMP, Acros, Belgium) up to 25 wt % of polymer. A film of this casting solution was deposited on a polypropylene nonwoven support (Novatex 2471, Freudenberg, Germany) by using an automatic film applicator (Braive Instruments, Belgium). After 30 s, the films were immersed in a water coagulation bath at room temperature for 15 min to solidify the polymer. The resulting membranes were kept in isopropyl alcohol (IPA, WVR, Belgium) for 3 h and transferred to another bath of IPA/glycerol (Acros, Belgium) (60:40) for at least 3 days. All solvents used were of analytical grade. One of these membranes was included in the testing described below.

Filtration Experiments. Filtrations were carried out in a laboratory-made stainless steel dead-end pressure cell sealed with Kalrez O-rings. Circular membrane coupons were used with an active filtration area of 12.56 cm^2. The feed solution (20 mL) was introduced in the cell, stirred at 700 rpm, and pressurized with nitrogen gas. Permeate samples were collected for designated periods of time during the experiments and placed into closed vials. Experiments carried out at higher temperatures required the use of a tailor-made heating cylindrical block incorporating a temperature sensor, which was adapted around the filtration cell. Before filtrations, both the laboratory-made and the commercial membranes were kept for at least 20 min in chlorobenzene. Subsequently, chlorobenzene was filtrated through the membrane at 15 bar for at least 30 min to wash out possible traces of conditioning agent present in the membrane pores and to keep it in a solvent medium compatible with the MDI-based samples. Permeabilities, expressed in ($\mathrm{l \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}}$), were calculated by weighing the collected permeates. Retention was calculated as $(1 - C_p/C_f) \times 100$, where C_f and C_p denote the solute concentration in the initial feed and in the permeate, respectively.

Prior to carrying out fractionation tests with MDI-based prepolymers, experiments were undertaken with a 70 μM solution of methyl orange (Fluka, Germany) (Figure 5) of

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Table 2. **Polymers tested for stability in MDI**[a]

possible polymers for laboratory-made membranes	specifications	form	company
polyimide Matrimid (PI)	Matrimid 9725 US	powder	Huntsman
polyimide P84 (P84)	P84 Powder SG	powder	Evonik Fibres
polysulfone (PSf)	UDEL P1835	powder	Solvay Advanced Polymers
polyethersulfone (PES)	RADEL A 13000	powder	Solvay Advanced Polymers
polyphenylsulfone (PPh)	RADEL R 5000	powder	Solvay Advanced Polymers
polyacrylonitrile (PAN)	M_w 150000	powder	Scientific Polymer Products Inc.
polydivinylfluoride (PVDF)	SOLEF 6010	powder	Solvay Advanced Polymers
poly(2,6-dimethyl-1,4-phenylene oxide (PPO)	M_w 50000	powder	Scientific Polymer Products Inc.
polydimethylsiloxane (PDMS)	RTV 615	resin	General Electric

[a] Tests performed with 1 g of polymer in 5 g of prepolymer solution.

Table 3. **Fractionation experiments of prepolymer solutions**[a]

entry	membrane	prepolymer solution	dilution in MCB	temperature (°C)	pressure (bar)
1	Solsep 030305	PP2	yes	r.t.	10
2	Solsep 030305	PP2	no	66	40
3	Solsep 030305	PP1	no	66	40
4	P84M	PP2	yes	r.t.	30
5	P84M	PP2	no	66	40
6	P84M	PP1	no	66	30

[a] Dead end mode, membrane area 12.56 cm^2); r.t. indicates room temperature.

Table 4. **Membrane performance in filtrations of methyl orange in IPA**

membrane	retention (%)	permeability ($l \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)
Solsep 030306F	8	0.7
Solsep 030305	55	1.0
Solsep 010207	13	0.4
Solsep 010306	11	1.9
P84M	16	20.3

molecular weight similar to that of MDI (MW of 327 g/mol, compared to 250 g/mol for MDI) in IPA, in order to assess the separative properties of the membranes quickly. Dye concentrations in these permeates were determined with a Perkin-Elmer Lambda 12 UV−vis spectrophotometer at 415 nm.

Prepolymer fractionation tests were carried out either with pure prepolymer solutions or diluted with monochlorobenzene for ∼100 min at constant pressure (details for each experiment are summarized in Table 3). Some tests took place at room temperature, and others at 66 °C, depending on the viscosity of the feed solutions. Pressure was adapted for each filtration in order to obtain reasonable times for permeate collection for each membrane/feed combination.

Samples of the feed, the permeate, and the retentate were analysed by gel permeation chromatography (GPC) using a GPC from the 1050 series of Hewlett-Packard with UV detection at 254 nm.

Results and Discussion

Membrane and Materials Stability Screening. The underlying stability of the most common polymers used for membrane preparation was tested in relation to this potential application by soaking either a piece of a preformed membrane or a small amount of the parent polymer in a polymeric MDI mixture at room temperature in a closed bottle. Both short-term (4 days) and long-term (60 days) immersion experiments were carried out. The polymers and commercial membranes considered are listed in Tables 1 and 2. Although at first most of the polymers seemed to be resistant and no signs of degradation could be detected (observations after 4 days), eventually only polyimide P84 and the commercial Solsep membranes still appeared unchanged after 60 days. In all the other cases, the polymers were dissolved in the polymeric MDI mixture, as for the case of the nonresistant commercial membranes.

Preliminary Assessment of Membrane Performance. The results of the fast membrane screening with a dye solution are shown in Table 4. Since membrane performance depends not only on the intrinsic properties of the membrane but also on the particular system (solute and solvent), the absolute retentions and permeabilities for the prepolymer sample fractionations will be different, although the trend between the membranes is expected to be the same. Indeed, even though performed in another type of solvent and with another solute, useful information for the final MDI fractionation could be obtained. The four different Solsep membranes tested here clearly have the potential to provide different fractionation patterns, as reflected in the different retention values. However, only the 030305 membrane provided any significant retention of the methyl orange, i.e. demonstrated a nanofiltration behaviour that would potentially be suitable for application in the fractionation of MDI-based prepolymers. The molecular weight cutoff (95% retention) of this membrane is quoted by the manufacturer as being between 300 and 1000 g/mol, depending on the solute and solvent, which is consistent with these results.

Solsep 030305 membrane was thus selected for further testing with MDI, because it showed the highest retention for methyl orange of the four membranes and also combined this with a reasonable permeability. P84M membrane was selected among other laboratory-made membranes because it showed certain methyl orange retention and a relatively high permeability which made it suitable for this application.

MDI-Based Prepolymer Fractionation Tests. The ratio of the total MDI diisocyanates to higher MW species was determined by GPC for the initial feed, permeate, and retentate samples.

For the fractionation of the diluted PP2 sample with the Solsep 030305 membrane after 100 min at 10 bar and room temperature (entry 1, Table 3), these ratios for the initial feed and the permeate were 0.31 and 0.93 respectively, showing clearly that the diisocyanates had selectively passed through the membrane. The same ratio in the retentate was 0.28.

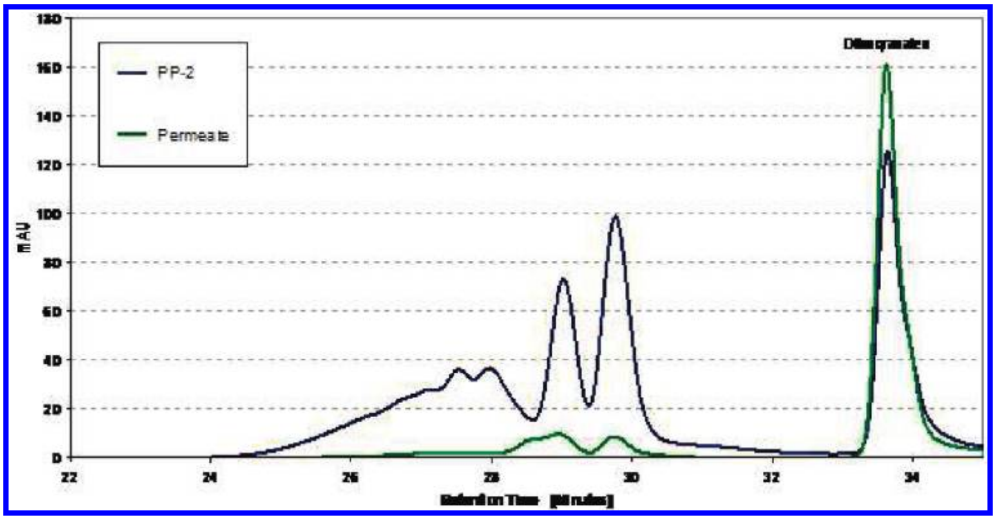

Figure 6. **GPC comparison of the PPI prepolymer and the permeate fractionated from it.**

In a second experiment (entry 2, Table 3), after fractionation of this undiluted prepolymer through the Solsep 030305 membrane at 40 bar and 66 °C for 100 min, the ratios of the total MDI diisocyanates to higher MW species of samples of the initial feed and the permeate as determined by GPC analyses were 0.31 and 2.82, respectively. The analysis of a retentate sample showed again that the fractionation had decreased the ratio of diisocyanates to higher MW species, in this particular case to 0.29.

The same trend was found in the experiments with the PP1 sample. This undiluted prepolymer was fractionated through the Solsep 030305 membrane at 40 bar pressure at 66 °C for 100 min (entry 3, Table 3). The ratio obtained for the permeate was 3.99. A comparison of the GPCs is given in Figure 6, which clearly shows that the permeate is significantly enriched in MDI compared to the original feed composition and that the highest-molecular weight species have not passed through the membrane.

Fractionation experiments with the P84-based membrane also showed promising results. A 50 wt % solution of the prepolymer in MCB was fractionated with the P84-based membrane at 30 bar pressure (entry 4, Table 3). The ratio of diisocyanates to higher-molecular weight isocyanates in the retentate was 0.25, showing clearly that the diisocyanate content of the retentate was reduced compared to that in the initial feed composition (0.32). It was noted that the colour of the permeate was lighter than the color of both the initial feed material and the retentate.

Regarding the membrane permeabilities, there is a clear difference in the permeability for the different undiluted feed solutions (entries 2 and 3, Table 5) due to their differences in viscosity and intrinsic properties. Also, the permeability of the Solsep 030305 membrane is lower compared to that of the laboratory-made P84 membrane, as seen from experiments with the same feed solution at equal temperature (comparison of entries 1 and 4, entries 3 and 6, and entries 2 and 5 in Table 5). In view of these results, it is possible to conclude that the laboratory-made membrane presents a better overall performance than the commercial one (better selectivity and permeability), although it is still necessary to optimize the membrane further in order to improve its performance and make it more attractive for its application in the process at industrial scale. Additionally, the amount of product processed in the present study (20 mL) as well as the permeate volumes are still far from the conditions envisaged at the industrial plant. Nevertheless, the most interesting fraction for application purposes is the retentate, which ideally should contain the minimum possible MDI content. The purpose of the experiments presented in this article is only to prove that SRNF can be applied to separate MDI from these prepolymer mixtures. Further work is ongoing in order to investigate and mimic the most appropriate laboratory conditions comparable to a real industrial-scale application.

Table 5. **Membrane performance in polymer fractionation experiments**[a]

	ratio MDI/higher oligomers				
entry	feed	permeate	retentate	permeability ($l \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)	total volume permeated (mL)
1	0.31	0.93	0.28	0.036	0.75
2	0.31	2.82	0.29	0.015	1.25
3	0.34	3.99	0.31	0.013	1.08
4	0.32	0.49	0.25	0.093	5.8
5	0.32	n.a.	n.a.	0.018	1.5
6	0.34	n.a.	0.23	0.045	2.8

[a] n.a. = non-available, samples could not be analyzed.

Conclusions

SRNF could be a suitable process to remove MDI selectively from MDI-based prepolymers. It is the first time that such a fractionation has been demonstrated, with positive results for both commercially available NF-membranes (Solsep) and a laboratory-made P84-based membrane. The MDI-depleted retentate could, in principle, be used in a variety of applications where the decreased MDI content (in comparison to the content of the parent prepolymer) offers advantages, whilst the MDI-rich permeate could be processed further, used as a product in its own right, or reused as the starting material for the manufacture of more prepolymer by reaction with additional polyol or a different polyol. Scale-up to a commercial manufacturing process based on this SRNF-effect still requires significant development in order to obtain sufficient data on which to assess the future process viability, e.g. by investigating different equipment and process configurations, but the results documented here prove at laboratory scale the basis of the concept.

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