



## **New Advances in Polymeric MDI Variants**

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### **ABSTRACT**

Polymeric MDI and its variants are commonly used in coating and adhesive applications. One component systems are formed by reacting polyols and a polymeric MDI variant. Very often the compatibility between the raw materials is limited and results in hazy products, which tend to phase separate, therefore limiting the shelf life of the products. Polymeric MDI variants are also used as crosslinkers in two component systems. Here, the reactivity between the two raw materials is highly important to ensure workability.

New polymeric MDI variants with high miscibility and their effect within one and two component systems will be discussed. The study focuses on compatibility, reactivity differences and long term stability of model prepolymers and two component systems.

### **0- INTRODUCTION**

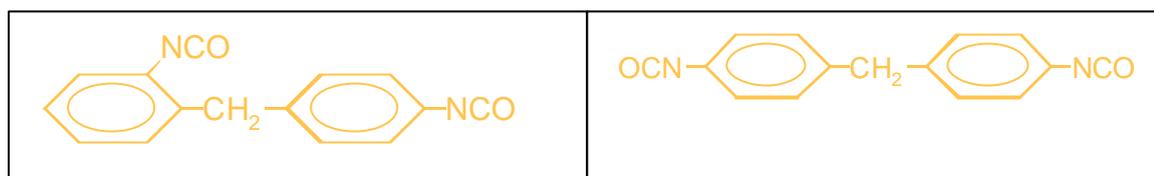
Polymeric MDI and its variants are important raw materials for coatings and adhesives. It has been recognised for over 40 years and is considered as a commodity product. Often it is believed that the performance of polymeric MDI cannot be changed or altered. The aim of this paper is to demonstrate the versatility of polymeric MDI in combination with other main MDI streams, making them the products of choice for one and two component systems.

To understand the complexity of polymeric MDI it is necessary to review its chemistry.

## 1- CHEMISTRY

The production of diphenylmethane diisocyanate (MDI) and its homologue is a complex process. MDI is produced from a reaction between aniline and formaldehyde, using hydrochloric acid as a catalyst. This reaction produces a complex mixture of polyamines which are phosgenated to obtain a polyisocyanate mixture. Afterwards, this mixture is split into polymeric MDI and pure MDI.

Pure MDI consists mainly of two isomers: 2,4'-MDI and 4,4'-MDI. (figure 1)



2,4'- MDI

4,4'- MDI

Figure 1: MDI isomers

The main effect of the isocyanate groups (NCO) in the 2 and 4 positions is on reactivity. The isocyanate group in 2 (ortho) - position is three times less reactive than the isocyanate group in 4 (para) - position. Pure 4,4' - MDI is solid at room temperature, melts at 38°C and is a major raw material for adhesive and coating applications where high reactivity and linearity is required. The 2,4' - MDI isomer is not readily available in 100 per cent purity. Concentrations of up to 50 per cent are commercially available. The so-called mixed isomer 50 (MI 50), with a melting point of 18°C, exhibits a good compromise between lower reactivity and liquidity.

Above their melting point, both isomers and their mixtures have very low viscosities, typically below 10 mPa.s.

A common modification of MDI, especially pure MDI, is the condensation reaction of the isocyanate groups, forming carbodiimide and reversible uretonimine (Figure 2). Uretonimine modified MDI typically is a liquid at room temperature with a viscosity at 25°C of approximately 50 mPa.s and a functionality of 2.15. Materials of that kind crystallise at temperatures of about 15°C.

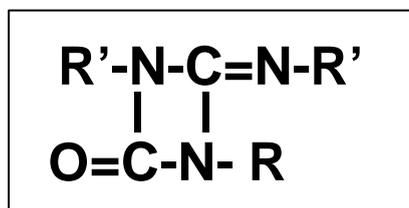


Figure 2: Uretonimine structure

Polymeric MDI is a complex mixture of pure MDI and higher homologue (figure 3). The letter n ranges from 1 to higher numbers, meaning that in polymeric MDI, polyisocyanates with functionalities of 3 and higher are present.

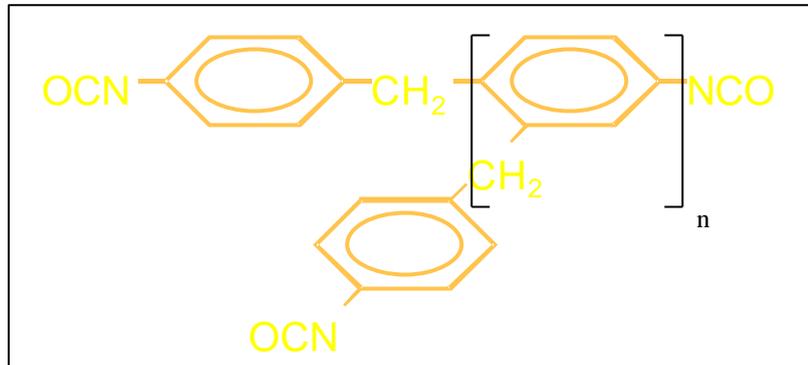


Figure 3: Polymeric MDI structure

A typical polymeric MDI consists of approximately 50 per cent pure MDI, 30 per cent tri-isocyanate, 10 per cent tetra-isocyanate, 5 per cent penta-isocyanate and 5 per cent higher homologue. The average functionality of a standard polymeric MDI is about 2.7 with a typical viscosity of approximately 200 mPa.s at 25°C. Standard polymeric MDI is storage stable as no crystallisation takes place down to temperatures of 0°C.

The four product streams described above are often mixed together to produce customised polymeric MDI variants.

## 2- TWO COMPONENT SYSTEMS

In general, two component systems consist of polyol or polyol mixtures and an isocyanate crosslinker. The two components are mixed together at the application site in various ratios and, after mixing, applied onto the substrate to be bound or coated. Two component systems have the advantage of fast reaction time, or cure speed, in comparison to typical one component systems, which will be discussed later in the paper. The main curing mechanism of two component systems is the formation of urethane linkages, resulting from the reaction of the isocyanate with the hydroxyl function of the polyol.

Two component systems are commonly used in applications for the building industry, for example in floor coating, panel laminating adhesives and sealant applications. The individual components are quite often stored in unconditioned warehouses or even on the construction site. Therefore both components need to be storage stable, yielding no change in morphology, for a prolonged time. Typical polyols, like polyethers, are resistant to cold temperatures, until and even below the freezing point. Isocyanates very often tend to crystallise during cold storage. To melt a crystallised isocyanate, temperatures of approximately 80°C are required. Since such heating is very often not present on the construction site, it is necessary to develop isocyanates which can be stored under cold conditions. In this study all isocyanates were stored at 5°C for 28 days to determine the resistance against crystallisation.

Another important parameter for two component systems is the cure behaviour. The ideal system should present long enough working times and then cure almost instantaneously. However a system of that kind does not exist and compromises have to be made. In this study the cure profile of the two component systems was determined by monitoring their viscosity increase over time. The polyol used in all trials was castor oil.

## 2.1- Experimental principle:

Figure 4 shows the cure profile of SUPRASEC<sup>®</sup>5025, a standard polymeric MDI.

From the graph shown in figure 4, the following main values can be determined:

- The time when the reaction mixture reaches 10 Pa.s corresponds to the **working time**, the time at which the application of the reaction mixture is easy
- The time when the reaction mixture reaches 100 Pa.s corresponds to the **open time**, i.e. the maximum viscosity at which a coating exhibits flow and self levelling properties, whereas in adhesives, the mixture loses its ability to bond different substrates
- The time when the reaction mixture reaches 1000 Pa.s corresponds to the **set time**, which is especially of interest for adhesives. It is typically the time at which the adhesive has sufficient strength to allow handling of the laminate.

Furthermore the cross over point between the elastic modulus ( $G'$ ) and the loss modulus ( $G''$ ) was determined. Theoretically this point is the change over from viscous to elastic behaviour, meaning that the material is no longer able to flow. This value represents the minimum time after which the coating or adhesive presents resistance against stresses.

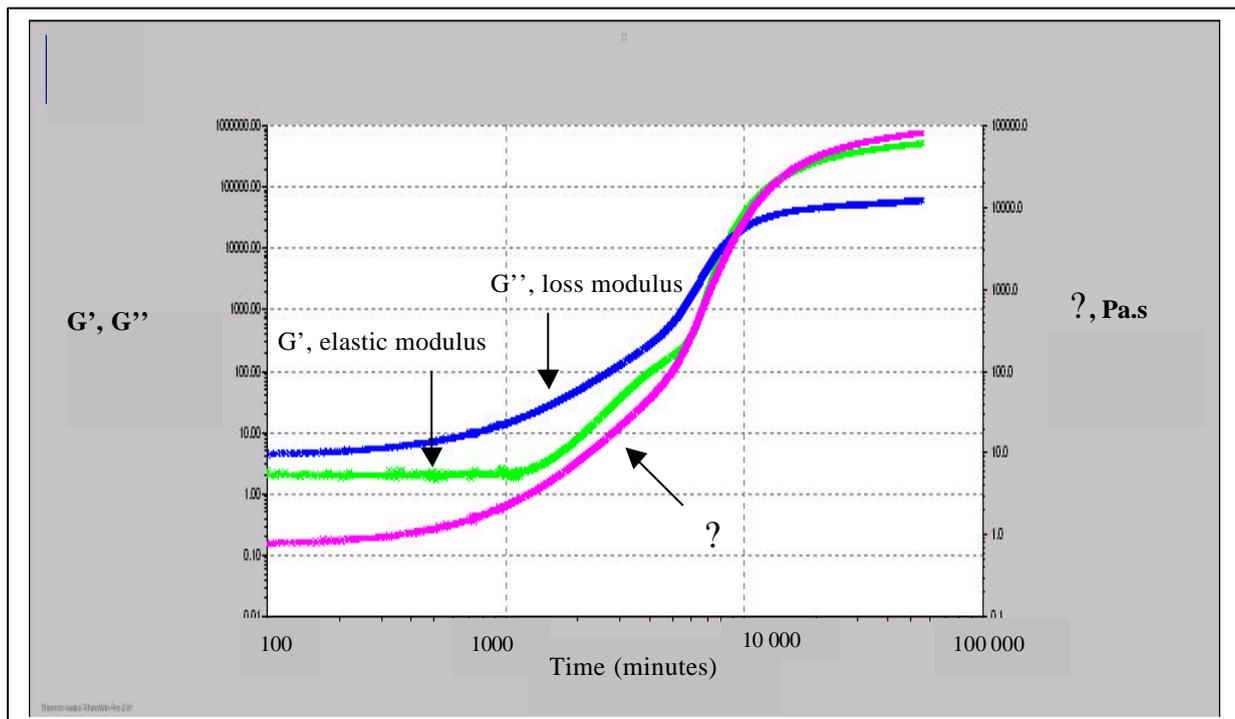


Figure 4: Cure profile of SUPRASEC 5025, a standard polymeric MDI

For practical reasons the cure was monitored at 40°C. The ability to repeat the achieved results is very high with an approximate failure rate of 2 per cent. Naturally, at lower temperatures the cure time is prolonged, whereas at higher temperatures the reaction will be faster.

The values determined for SUPRASEC 5025 alone are:

10 Pa.s Working time	100 Pa.s Open time	1000 Pa.s Set time	Cross Over point
38 minutes	85 minutes	120 minutes	145 minutes

Several mixtures were produced based on the polymeric MDI SUPRASEC 5025, and varied amounts of 4,4'-, 2,4'-MDI, as well as uretonimines. The effect of the varied compositions on the resulting product cold stability and cure behaviour was investigated.

## 2.2- Series 1: Mixtures of polymeric MDI and pure MDI

In the first series SUPRASEC 1306 (pure 4,4'-MDI ) was mixed with SUPRASEC 5025 at levels of 0, 20, 40, 60, 80 and 100 per cent.

- **Cold stability:** the mixtures with 60 per cent of SUPRASEC 1306 and higher do not give storage stable materials at 5°C. Crystallisation occurred in these samples.
- **Cure behaviour:** see figure 5;  
The addition of SUPRASEC 1306 has only a marginal influence on the cure speed of the resulting system. The test of 100 per cent SUPRASEC 1306 has not been performed, since the material itself has a melting point of 38°C. Handling and storage of this material are too complex for it to be useful as a crosslinker in two component systems.

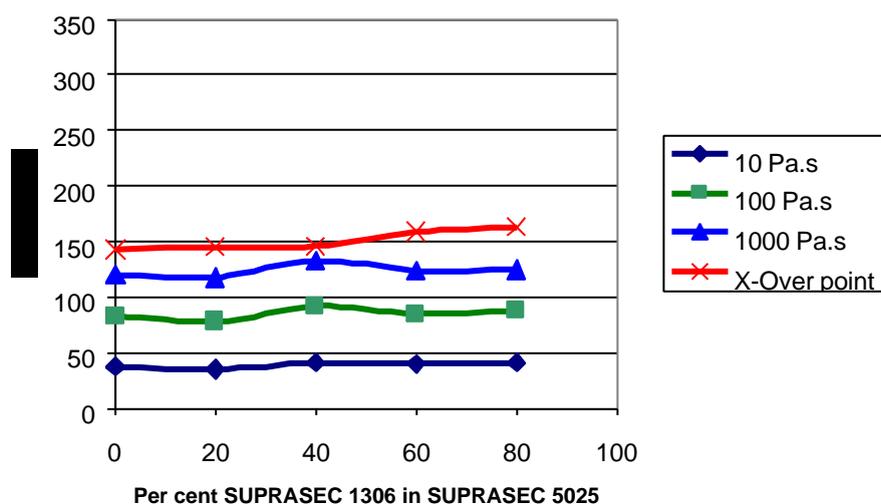


Figure 5: Cure behaviour of mixtures of pure MDI in polymeric MDI

### 2.3 - Series 2: Mixtures of mixed isomer MDI, MI 30 type, and polymeric MDI

In the second series SUPRASEC 1004 (70 per cent 4,4'-MDI and 30 per cent 2,4'-MDI isomer mixture) was mixed with SUPRASEC 5025 at levels of 0, 20, 40, 60, 80 and 100 per cent.

- **Cold stability:** Mixtures with 80 per cent or higher levels of SUPRASEC 1004 yield crystalline products at storage temperatures of 5°C.
- **Cure behaviour:** see figure 6;  
The lower reactivity of the ortho-isocyanate group in the 2,4'-MDI isomer influences the cure speed. The working time improves gradually from 38 minutes for the 100 per cent SUPRASEC 5025 system to almost 50 minutes for the 80 per cent system. The set time is enhanced by 25 minutes from originally 85 to 110 minutes. The cross-over point is delayed by 90 minutes (235 minutes instead of 145 minutes). Higher amounts of the 2,4'-MDI isomer result in crosslinkers with improved working time, but prolonged cure times. The enhanced cure time will be reflected by the fact that the coating or adhesive will have more time to relax and absorb possible stresses.

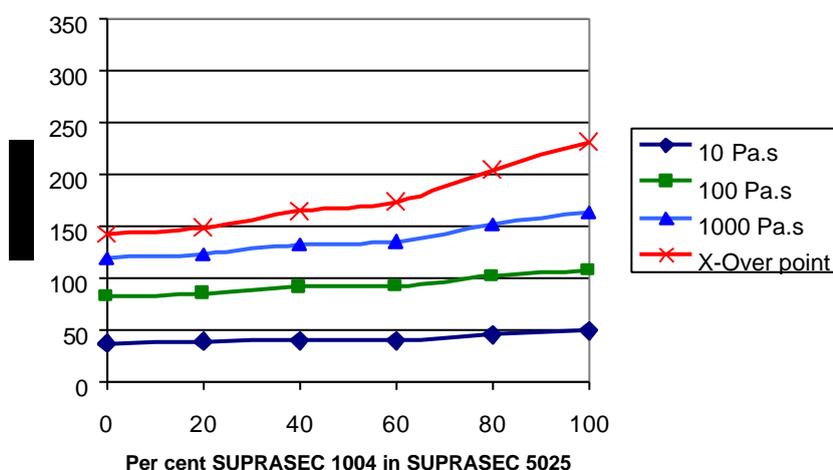


Figure 6: Cure behaviour of mixtures of mixed isomers, MI 30 type, in polymeric MDI

### 2.4- Series 3: Mixtures of mixed isomer, MI 50 type, and polymeric MDI

The third series describes the effect of mixtures between SUPRASEC 5025 and SUPRASEC 3051. SUPRASEC 3051 contains approximately 50 per cent of the 2,4'-MDI isomer.

- **Cold stability:** The typical 0 to 100 per cent mixtures have been tested for their cold stability. Only the 100 per cent SUPRASEC 3051 material crystallised at 5°C. All other mixtures were storage stable.

- **Cure behaviour:** see figure 7;

Also here, the lower reactivity of the ortho-isocyanate group in the 2,4'-MDI isomer influences the cure behaviour of the system. The change is more pronounced than in the SUPRASEC 1004 mixtures. The working time improves gradually from 38 minutes for the 100 per cent SUPRASEC 5025 system to almost 60 minutes for the 80 per cent system. The set time is enhanced by 50 minutes from originally 85 to 135 minutes. The cross-over point is delayed by almost 200 minutes (340 instead of 145 minutes).

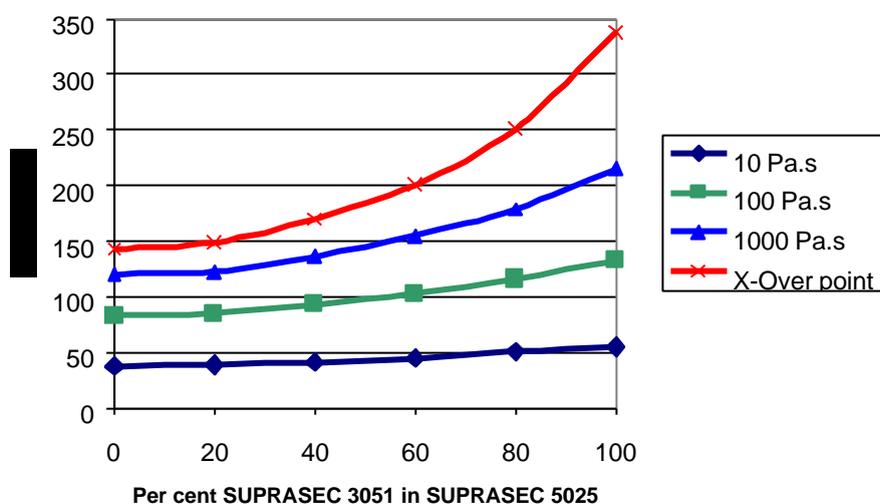


Figure 7: Cure behaviour of mixtures of mixed isomers, MI 50 type, in polymeric MDI

## 2.5- Series 4: Mixture of uretonimine modified MDI and polymeric MDI

As described in the chemistry section, difunctional MDI is used as a raw material in the uretonimine process. The formation of carbodiimides and uretonimines effectively destroys the crystallinity of pure 4,4'-MDI. The uretonimine modified product, SUPRASEC 2020, was mixed with SUPRASEC 5025 at levels of 0, 20, 40, 60, 80 and 100 per cent.

- **Cold stability:** Due to the introduction of uretonimine/carbodiimide all mixtures containing up to 80 per cent SUPRASEC 2020 are storage stable at 5°C.
- **Cure behaviour:** SUPRASEC 2020 has almost no effect on the cure performance in mixtures with polymeric MDI. See figure 8.

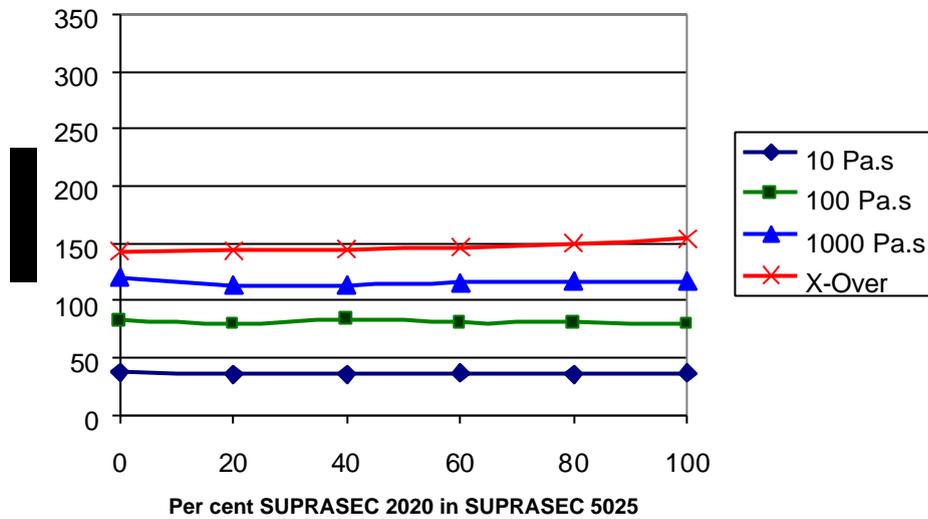


Figure 8: Mixture of uretonimine modified MDI and polymeric MDI

## 2.6- Conclusion: Polymeric MDI mixtures in two component systems

Various raw material streams are available to adjust the performances of the MDI isocyanate in two component systems. Besides cold stability and cure behaviour other important properties will be affected by mixing these various streams:

### - *Effect on the viscosity of the raw material:*

The addition of diisocyanates effectively reduces the viscosity of the isocyanate mixture. A reduction of viscosity improves the mixing of the individual components even at lower temperatures. It allows higher filler loading and a better initial flow of the freshly mixed material (figure 9).

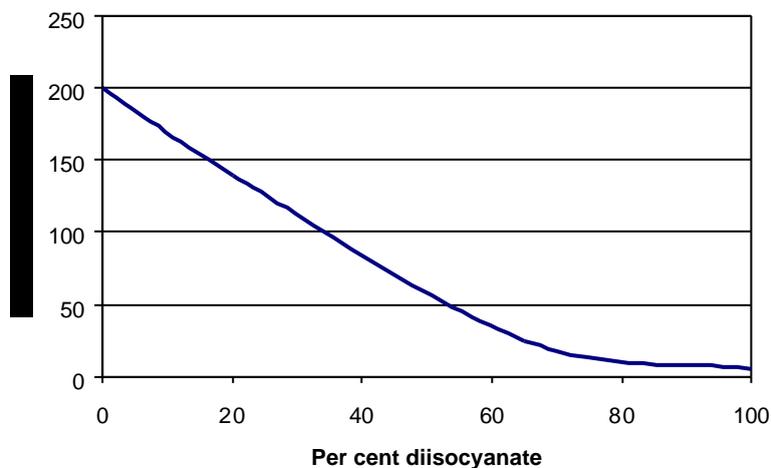


Figure 9: Viscosity of polymeric MDI mixtures

- **Reduction of functionality:**

By adding di-functional species in SUPRASEC 5025, which has an average functionality of 2.7, the overall crosslinking of the resulting films will be reduced. Therefore its elasticity increases. Surprisingly though, a reduction of the functionality of the mixture did not alter the tensile strength of the films, typically at 3.2 MPa.

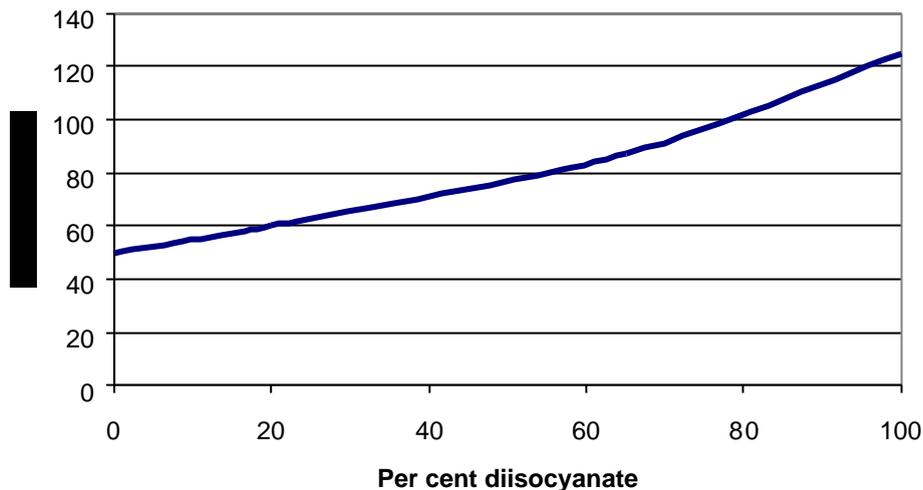


Figure 10: Per cent elongation of films made of mixtures of isocyanates

As discussed above, mixtures of isocyanates can effectively change the performance of a two component system. Typically, the polyol component alone, in two component systems, is modified to meet specific needs. We demonstrated above that by varying the overall composition of the isocyanate, the formulator of coatings and adhesives has even more tools to modify and customise his products.

### 3- ONE COMPONENT SYSTEMS

One component systems are very often preferred to two component systems for logistical reasons: the material transport is less cumbersome and possible mixing errors are avoided. Applications for one component systems are numerous and the performances required are multiple.

Polymeric MDI or mixtures of polymeric MDI with other isocyanate streams are rarely used for one component coating or adhesive applications. The isocyanate content (or NCO value) of those materials is typically in the range of 30 to 33 per cent. The curing mechanism of one component polyurethane is the reaction between humidity/water, and the isocyanate, resulting in the formation of urea groups under decarboxilation. Since the isocyanate content of the system is very high, considerable carbon dioxide develops and the coating or adhesive can foam. In many applications, foaming is not wanted as the presence of gas bubbles destroys the performance, and/or the appearance of a coating/adhesive.

Moreover, the viscosity of a straight polymeric or a mixture of polymeric isocyanate with diisocyanates is very low. The material lacks inner cohesion which makes film forming very difficult.

The most preferred method to improve both the issue of high NCO content and low viscosity is to react isocyanates with a polyol to a so-called prepolymer. Typical prepolymers have isocyanate contents ranging from 2 to 16 per cent and present viscosities of 1500 to 25000 mPa.s at ambient temperature.

In this study, the influence of the amount of diisocyanates in polymeric MDI as raw materials for the prepolymer production was evaluated. The polyol used was polypropylene glycol (PPG) with a molecular weight of 2000. The prepolymers were not further formulated with fillers, catalysts or other methods. The viscosity, drying characteristics under normal climate conditions (23°C, 50% relative humidity), and miscibility of the obtained prepolymers were tested.

### 3.1- Chemistry and experimental principle

The prepolymers used are reaction products of isocyanates and polyol, carrying hydroxyl functions.

The reaction of isocyanates, NCO, with hydroxyl, OH functions is depicted in figure 11 as well as the reaction of isocyanates with water/humidity. The urethane groups, resulting from the reaction of NCO with OH groups, can form hydrogen bonds among themselves. Therefore physical forces interact between individual prepolymer chains. The more isocyanate groups are converted into urethane groups, the more interaction between the individual polyurethane chains and the higher the resulting viscosities. Prepolymers with low isocyanate content typically have higher viscosities.

Prepolymers with high amounts of NCO groups form more carbon dioxide when they are in the presence of moisture, which could lead to bubble formation or foaming.

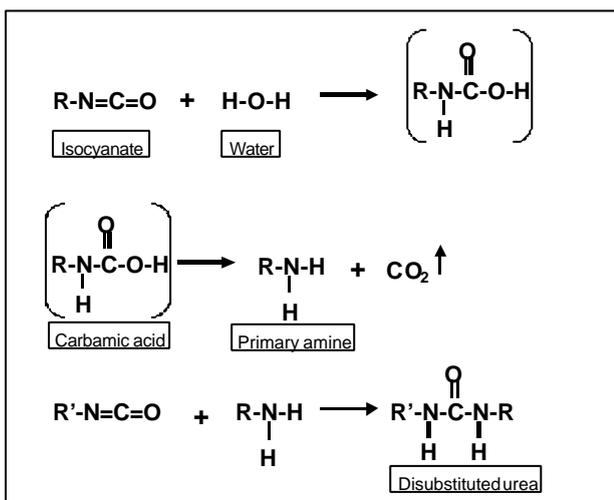


Figure 11: The isocyanate reactions

This paper focuses on materials with an isocyanate content of approximately 10 per cent, typical content for raw materials for the manufacturing of construction adhesives and one component floor coatings.

SUPRASEC 5025, polymeric MDI, was mixed with either pure MDI (SUPRASEC 1306) or SUPRASEC 3051, the high 2,4'-MDI containing diisocyanate, in different ratios. Each mixture was then reacted with PPG 2000 to an isocyanate content of 10 per cent.

For the study on one component systems, different physico-chemical parameters were observed:

- Viscosity at 25°C - determined via Brookfield viscosimeter Spindle 28
- Cure behaviour at norm climate (23°C, 50% humidity) via BK dryer
- Miscibility of the prepolymer with the original isocyanate mixture

### 3.2- Results

- *Influence of the prepolymer functionality on its viscosity* – Figure 12 –

By mixing a di-functional isocyanate, e.g. SUPRASEC 1306, with a polymeric isocyanate, SUPRASEC 5025 with a functionality of 2.7, different functionalities can be achieved. The functionality corresponds directly with reactive branching, meaning that each individual branch carries a polyol-reactive isocyanate group. The viscosity of the prepolymer based on high functional isocyanates is much higher than that of the prepolymers using isocyanates with lower functionality. The main reason for this behaviour can be explained by chain extension of the polyol. Chain extension is the reaction of at least one isocyanate with at least two polyols, resulting in high molecular weight species. These high molecular weight species yield higher viscosities. Furthermore it is possible that higher functional isocyanates (with functionality of 3 or higher) are causing the chain extension. The molecular weight of the resulting material is a minimum of three times that of the original polyol. The higher the functionality of the original isocyanate mixture, the higher the viscosity. The immediate effect can be seen in figure 12.

The viscosity of the SUPRASEC 3051 mixtures (mixed isomer based) is slightly higher than the prepolymers based on pure MDI, SUPRASEC 1306. Occurrence of chain extension in these mixtures is higher, since the material contains more reactive groups than the mixtures based on pure MDI.

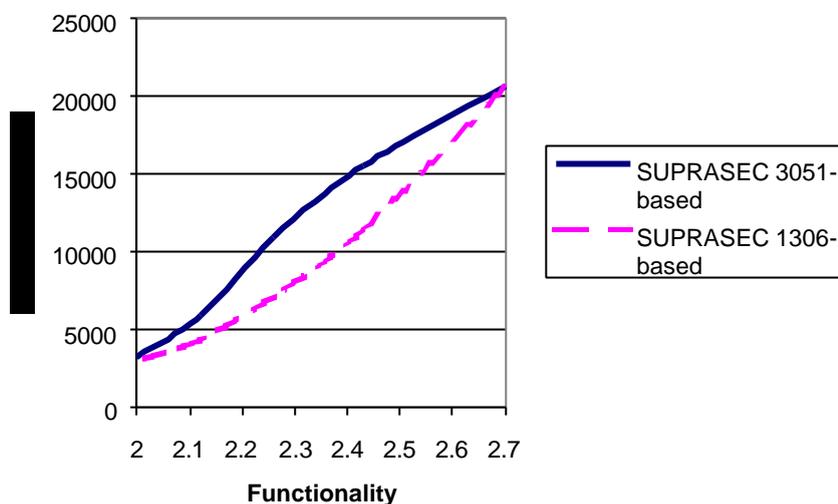


Figure 12: Viscosity of prepolymers as a function of their functionality

- *Effect of the prepolymer functionality on the cure behaviour of the one component system: Gel time* – Figure 13 –

Two main results can be determined via BK Dryer, the gel time and the cure time. The gel time defines the time at which the adhesive or coating loses its ability to flow. At this time an adhesive is no longer tacky. Therefore the lamination of the second substrate needs to occur before the gel time, when the laminate has sufficient handling strength. In a coatings application the prepolymer will no longer flow, for example, self levelling ends. Nevertheless the bond line or the coating could be deformed by mechanical stresses.

Prepolymers based on SUPRASEC 3051 require more time for gelification at lower functionalities. In these mixtures the amount of the slower reacting 2,4'-MDI isomer is higher and will extend the gel time. This effect could be highly beneficial, yielding to, for example, one component floor coatings with extended self levelling properties. On the other hand prepolymers based on pure MDI, SUPRASEC 1306, have a high reactivity against humidity and gel fast. The increased reaction speed of the 4,4'-MDI isomer dominates the system. In adhesive applications, a fast gel time is preferred as the compound can be handled much earlier; it corresponds to the adhesive's green strength.

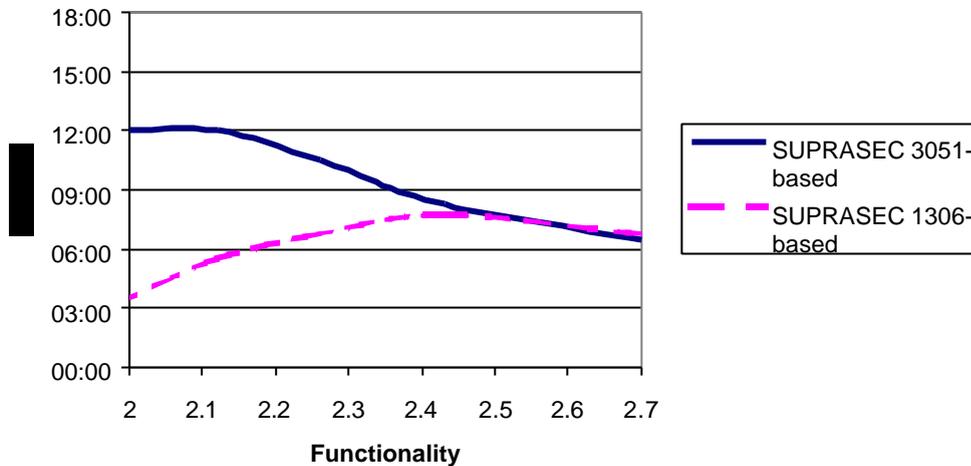


Figure 13: Gel time of the prepolymers as a function of their functionality

- *Effect of the prepolymer functionality on the cure behaviour of the one component system: Cure time* – Figure 14 –

The second parameter determined via the BK Dryer method describes the cure time as the time at which the system is almost fully cured and is sufficiently resistant for the final use. The results of the cure time reveal that the final cure is not affected by the amount of the 2,4'-MDI isomer in the system.

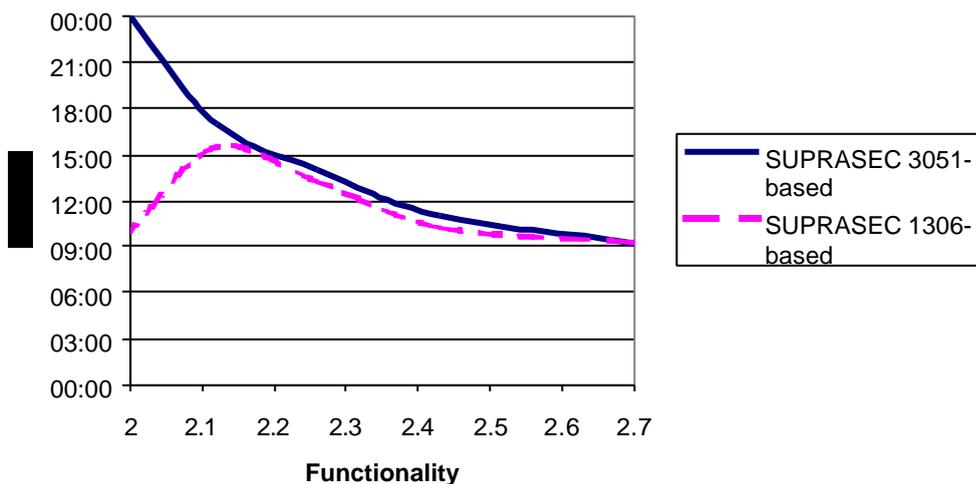


Figure 14: Cure time of prepolymers as a function of their functionality

Polymeric MDI, SUPRASEC 5025, has the most influence on the final cure. The higher the amount of polymeric MDI the faster the final cure.



- *Prepolymer miscibility for one component system NCO content adjustments*

During prepolymer production it is often necessary to adjust the final isocyanate content. If the isocyanate content is too high, polyol needs to be added. If the isocyanate content is too low, the addition of isocyanate is required.

The addition of polyol normally does not cause a problem. The polyol will react with the isocyanate and as a result will be built into the prepolymer matrix.

Adjusting the final isocyanate content with polymeric MDI or a mixture thereof is more difficult and often yields hazy final products. It has been found that the higher homologue of polymeric MDI, tetra-, penta- and higher, are not miscible with the prepolymer matrix. Even one per cent can cause a milky appearance.

Therefore, it is common practice to use diisocyanates to adjust the final NCO- content. Depending on the required amount the performance of the prepolymer can change. Furthermore, additional logistic efforts such as the storage of another isocyanate are needed and often not desirable.

Newly developed polymeric MDI variants with extremely high miscibility have been tested. One example is EID 9401, a development product with a functionality of 2.3 and a viscosity at 25°C of 80 mPa.s. The material has been prepolymerized to an NCO value of 10 per cent and then backblended to NCO- levels of 13, 16, 20 and 23 per cent. The properties of the material are comparable to the ones of a standard SUPRASEC 5025/SUPRASEC 3051 mixture with functionality of 2.3. However, the backblended prepolymers based on SUPRASEC EID 9401 are all clear products, whereas materials based on the SUPRASEC 5025/SUPRASEC 3051 mixture are all hazy.

#### **4- CONCLUSIONS**

Polymeric MDI and its variants have a strong influence on the final performance of an adhesive and coating. Parameters like cure behaviour, viscosity and miscibility are directly related to the used polymeric MDI variant. They are very versatile raw materials for the production of one and two component systems.

Straight mixtures of polymeric MDI with modified or plain diisocyanate streams have been known for many years and are common in the industry. These materials have major deficiencies in miscibility, particularly in backblending processes.

EID 9401 is a good example of the modification of a known technology. The material still shows the versatility of a polymeric MDI without the drawback of insufficient miscibility.

Choosing the right isocyanate can be highly beneficial for the producers of coatings and adhesives, as it provides more versatility for the production of customised products.

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