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Modified MDI-prepolymers improve the initial physical properties and reduce the 'in-service' time of aromatic polyurea coatings

MARC BROEKAERT
Huntsman Polyurethanes
Everslaan 45, B-3078 Everberg, Belgium
Tel.: +32 (0)2 758 8814

Abstract

Sprayable aromatic polyurea coatings are very reactive, building in high internal stress in the first phase of the curing process. These stresses have a negative influence on the measured physical properties and to reach its optimal properties, the coating needs time to relax from such stresses. When using specifically modified MDI-prepolymers, the relaxation during the initial curing of the film is more pronounced, resulting in less stress, no deformation, improved adhesion and superior physical properties within a shorter period of time.

Introduction

The polyurea spray elastomer technology is a new technology in the well-established European coatings landscape. Due to the specific curing and properties, polyurea coatings are developing their own application fields. [1,2]

The solvent free polyurea coatings, a development of Texaco Chemical Co. (now Huntsman Corp.), were introduced in the US in 1989 [3]. The market has grown remarkably in the US and Asia regions and now the European coatings industry is beginning to respond positively. For applications, where humidity and temperature insensitivity, cure speed, high mechanical and/or chemical demands cannot be met by the established coating chemistry, polyurea coatings can supply a solution.

The fast curing qualities of polyurea can be used in areas where storage for post-curing is impossible or too expensive. Pipes, freight ship liners, train wagon liners, industrial floors need to be put on transport or back into service as soon as possible. A high resistance to impact and/or abrasive forces of the surface is needed, preferably as soon as possible after the coating is applied.

Technology

A plural component polyurea spray coating is made of two or three components.
The first component is the isocyanate prepolymer with typical NCO values of 15 to 16%, giving the optimal compromise between viscosity and reactivity (Table 1).
The resin blend, a mixture of polyetheramines and amine functional chain extenders, is the second vital component (Table 1).
An important advantage is that no catalyst is required.

Table 1: Basic polyurea spray raw materials - typical values

A. MDI-prepolymer	%NCO	Viscosity, mPas at 25°C	Functionality
'Suprasec'® 2054	15.0	750	2.0
'Suprasec' 2058	15.5	850	2.0
'Suprasec' 2059	15.0	1750	2.1
B. Polyetheramines	Mw	Viscosity, mPas at 25°C	Functionality
'Jeffamine'® D2000	2000	250	2.0
'Jeffamine' T5000	5000	820	3.0
C. Chain extender	Mw	Viscosity, mPas at 25°C	Functionality
DETDA	178	155	2.0
D. Reactive diluent	Mw	Viscosity, mPas at 25°C	Functionality
'Jeffsol'® PC	102	2.5	1.0

The optional third component is the filler component. Due to the importance of a low viscosity for the first two reactive components, the addition of mineral fillers to the resin blend is limited. Incorporation of higher amounts of fillers like glass fibers, barite or texturing agents is possible via a third outlet that can be mounted on the spray gun.

For the application of polyurea spray coatings, adequate spraying equipment and suitable personal protective equipment is required. The systems are applied at high-pressure, between 150 and 200 bar, at high temperature, 70°C to 80°C, and with a direct impingement mixing spray gun. The spray gun is the most critical part of the application equipment. The high pressure is needed for the nebulization of the components and the pressure drop in the mixing chamber results in an efficient mixing of the components. The higher temperature gives lower viscosities for the two components, thus improving the mixing and resulting in superior final coating properties.

The first polyurea spray coatings developed using the modified pure MDI prepolymers were very fast, with gel times of about two seconds. The application of those fast systems was difficult, sometimes resulting in poor adhesion and/or poor surface quality.

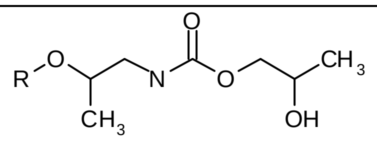

Figure 1: Carbamate

The application properties can be improved by using propylene carbonate (PC) as a reactive diluent. The choice of propylene carbonate is based on the fact that it is not considered as a VOC, and it reacts with an amine group, forming a carbamate (figure 1).

More recently, higher 2,4'-MDI isomer prepolymers proved to offer good performance results. [4] By extending the gel and tack-free times of polyurea spray coatings, the application performance of high 2,4'-MDI isomer prepolymers improves significantly.

The influence of functionality on the final film properties [5] indicated that the higher functionality prepolymers have higher viscosities, resulting in shortened gel and tack-free times. The improved chemical resistance and higher hardness expected from the final film properties were not obtained due to the insufficient mixing of the two components and loss of crosslink efficiency.

The high reactivity, sprayable aromatic polyurea coatings build in high internal stress during the first phase of the curing process, resulting in a negative influence on the measured physical properties. To obtain its optimal physical properties, the coating needs some time to relax those stresses. When using specifically modified MDI-prepolymers, the relaxation during the initial curing of the film is more pronounced, resulting in less stress, no deformation, improved adhesion and superior physical properties within a shorter time. This paper describes the evolution of the mechanical properties in function of time.

Experimental program

1. Products

The MDI-prepolymers used for this program are two commercially available products with high 2,4'-isomer content 'Suprasec' 2058 and 'Suprasec' 2059, both diluted with 5% of propylene carbonate, and a new development product, EID 9346, designed to obtain higher mechanical strength in the initial phase of the curing.

The resin blend used for the test program is a blend of 'Jeffamine' T5000, 'Jeffamine' D2000 and DETDA in a mixing ratio of 62/10/28.

2. Spray application

All systems were applied with a Gusmer H3500E plural-component, high-pressure metering unit and a Gusmer GX7-400 plural-component, high-pressure spray gun with module 453. The products were preheated at 80°C and applied with 160 bar pressure. The volume mixing ratio was kept at 1:1 for an index of approx. 1.05.
To obtain good mixing of the two components, the viscosity of the products at the application temperature should be below 100 mPas and as close as possible for the two components. Table 2 indicates the viscosity of the components in function of the temperature.

Table 2: Viscosity = f(temperature)

Product	Viscosity, mPas	
	25°C	80°C
'Suprasec' 2058/'Jeffsol' PC	540	44
'Suprasec' 2059/'Jeffsol' PC	868	79
EID 9346	1040	87
B-component (resin blend)	916	62

3. Conditioning

The samples were produced on a stainless steel panel, pre-treated with release agent. The samples for the cold impact test were 12 mm thick. The samples for physical testing and abrasion varied between 600 and 1500 microns. During the test program the samples were conditioned at 23 ± 2ºC and 55 ± 5% relative humidity.
An overview of the tests executed on the samples is shown in table 3. The tests were repeated the day of the application and after 1, 4, 7 and 14 days. On the first day, the cold impact test at -20°C was performed within the hour after the application of the film.

Table 3: Test methods

Reactivity	Manual test
Aspect of the film, applicability	Visual evaluation
Izod cold impact with notch	ISO 180
Tensile	DIN 53504
AngleTear	DIN 53515
Trouser tear	DIN 53507
Elongation at break	DIN 53504
Taber Abraser	ASTM D 4060-90 1000 cycles, H-18 wheels, 1000g load

Results and discussion

1. Reactivity, applicability, visual aspect

The systems are too reactive to be tested on reactivity with existing equipment and the gel and tack free times are measured by the applicator. The gel time is the time a shot of sprayed material continues to run down on a vertical surface, while tack free time is determined by touch.

The goal of this study is to shorten the time before putting the coated surface in-service, and this without compromising the application properties and the surface quality. The gel time is the same for the three tested systems. And although the gel times are fast, all systems applied very well, giving smooth, defect-free films.

Table 4: Reactivity

System	A-component	B-component (wt %)	Gel time	Tack free time
1	'Suprasec' 2058/'Jeffsol' PC	'Jeffamine' T5000 (62)	3 seconds	6 seconds
2	'Suprasec' 2059/'Jeffsol' PC	'Jeffamine' D2000 (10)	3 seconds	5 seconds
3	EID 9346	DETDA (28)	3 seconds	5 seconds

2. Physical testing

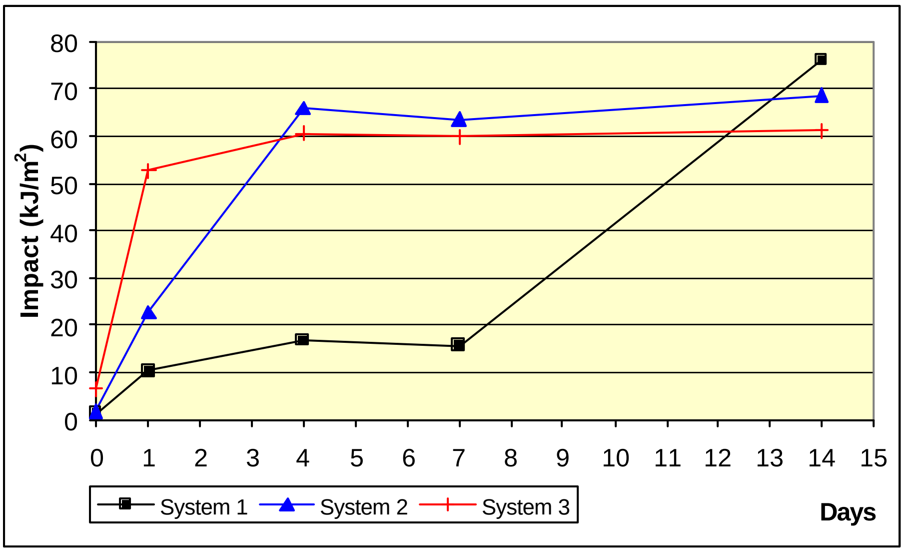

Figure 2: Cold impact strength development at -20ºC as a function of time

Physical properties are measured in function of time, from the day of application during fourteen days. The purpose of this series of tests is to confirm that the initial mechanical properties can be improved, and that the final mechanical properties are not negatively influenced by the modification of the system.

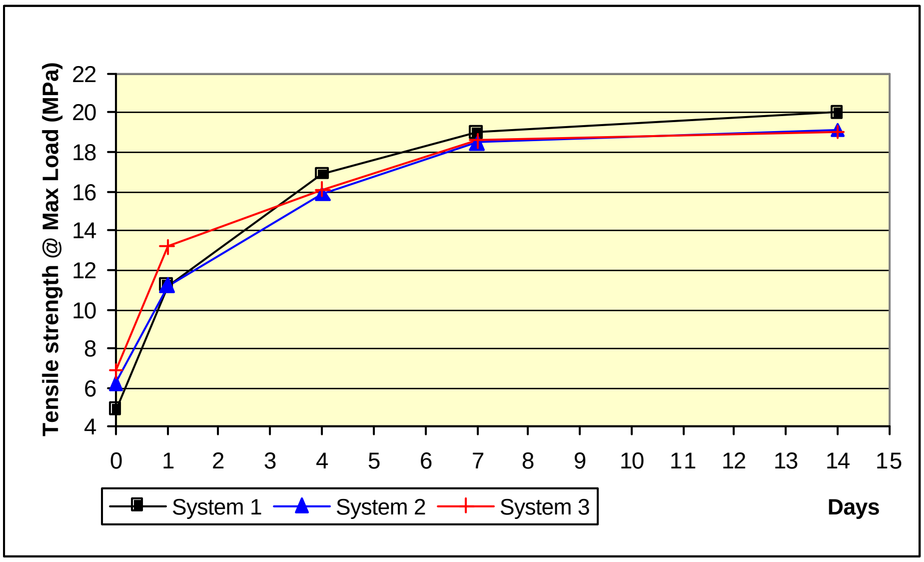

Figure 3: Tensile strength development as a function of time

The best indication for a fast development of the mechanical strength is obtained from the Izod cold notch impact test. The first day the impact test was performed within the hour after the application of a 12 mm thick sample. The samples are cut on a size of 10 by 80 mm. A notch is cut into the impact surface, leaving a material thickness of 10 mm behind the notch.

The cold impact test results for system 1 in figure 2 show clearly that the standard polyurea spray coatings only develop mechanical strength after more than seven days of post-curing. 'Suprasec' 2059 (system 2) obtains already 30% of its maximal mechanical strength after one day and full strength within four days. The experimental product EID 9346 reaches 90% of the final strength within the first 24 hours.

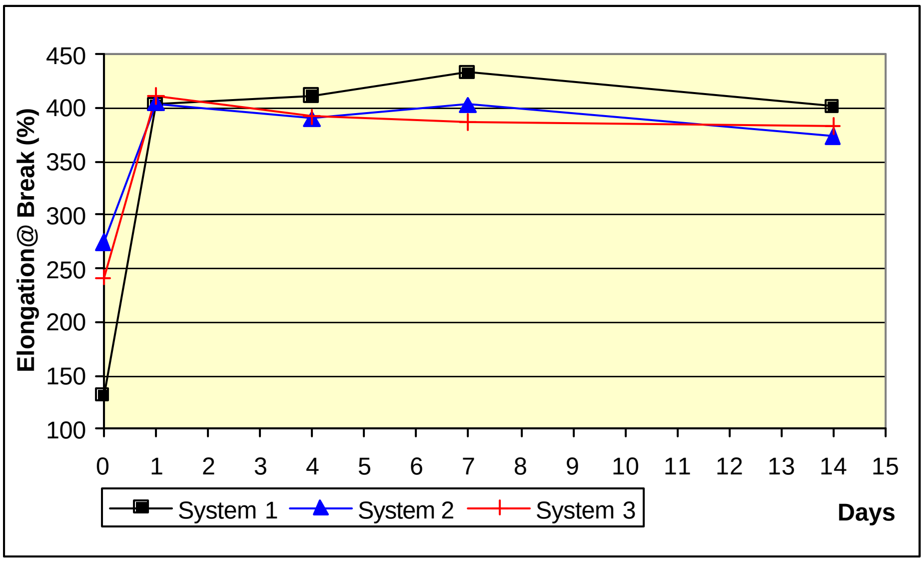

Figure 4: Elongation development as a function of time

Compared to a standard, high 2,4'-containing prepolymer (system 1), already the first day the tensile strength (figure 3) of the second system is 20% higher and for the modified prepolymer used in system 3 the tensile strength is even 40% higher. Only after four days system 1 reaches the same values as the two other systems.

When we look at the development of the elongation in function of time (figure 4), we see that this physical property develops fast for every system. After one day the maximum values are reached for every system, but again we see higher values for systems 2 and 3 when tested the day of the application.

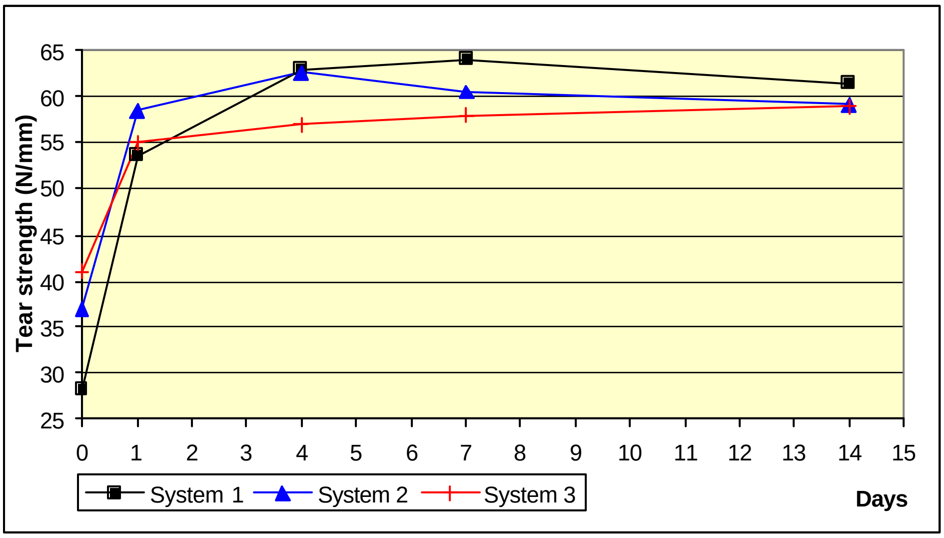

Figure 5: Angle tear strength development as a function of time

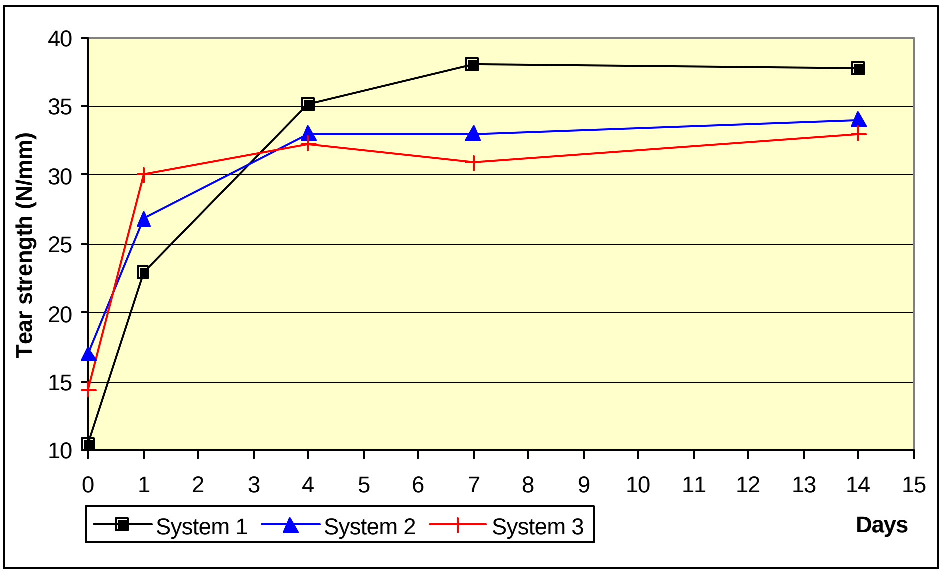

Figure 6: Trouser tear strength as a function of time

Angle tear strength (figure 5) and Trouser tear strength (figure 6) develop faster during the first 24 hours. Trouser tear or tear propagation is known to be a weak point for polyurea spray coatings, particularly during the first days of the curing process. This is due to the high stress in the coating as a result of the extremely high reactivity.

Looking at the measurements for the angle tear the day of the application, we see that system 2 is 30 % higher and system 3 even 50% higher than reference system 1. After 24 hours the three systems are close to the maximum value.

For the tear propagation, the differences after the first day are even bigger. The first day systems 2 and 3 are respectively 50% and 70% higher the reference system 1. Only after four days do the systems 1 and 2 move closer to their maximum values, where system 3 already does so after one day.

The evolution of the abrasion resistance as a function of time (figure 7) confirms the faster development of the mechanical properties for the systems 2 and 3. However, where system 2 loses abrasion resistance performance, higher weight loss after full cure, does the new development prepolymer also perform very well for the abrasion test.

In the Taber Abraser test system 2 and 3 show about 35% less weight loss the day of the application. System 2 performs less effectively after full cure with still 400mg of weight loss, where systems 1 and 3 perform comparatively with approx. 280mg of weight loss.

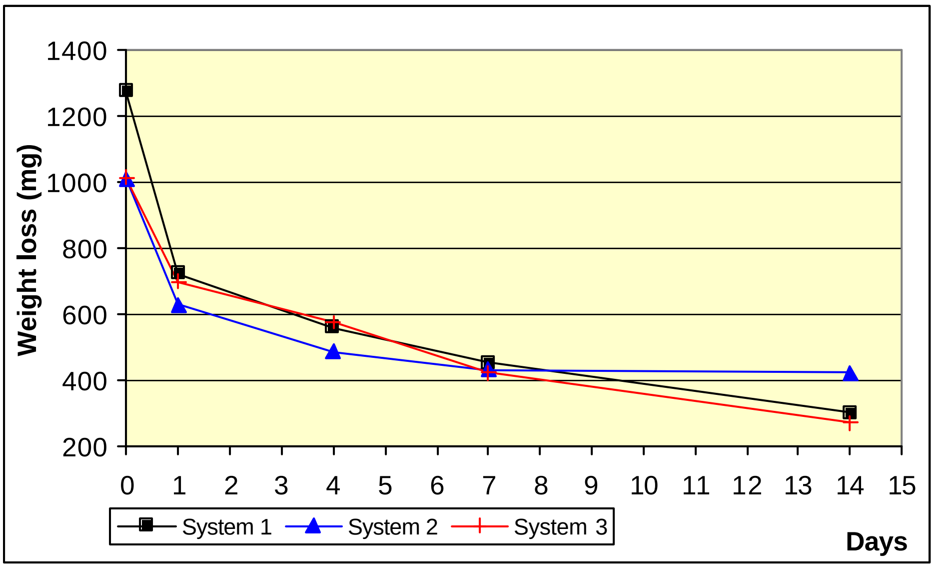

Figure 7: Abrasion resistance as a function of time

Conclusions

Aromatic polyurea coatings cure extremely fast, and can be handled or walked on almost instantly. Experience teaches us that the maximum values for the mechanical properties are only obtained after seven to ten days of curing. This can be explained by the fact that during the fast initial curing high internal stress is built up, while during the seven to ten days of post curing most of this stress disappears.

The system based on the modified prepolymer EID 9346 obtains similar overall physical properties compared to the reference high 2,4'-containing prepolymer.

Although the gel and tack free times are short, all the systems still apply very well without surface defects.

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The system based on the modified prepolymer EID 9346 reaches maximum physical properties after one day. In comparison, standard systems need about seven days to reach that optimal behavior.

The high values for the cold impact test combined with the fast abrasion resistance development make it possible to put the coated surfaces in-service much faster without risks for damage.

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