

Polyurea Spray Applied Systems for Concrete Protection

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Abstract

Polyurea spray coatings technology is a recent one of the new development of the last twenty years in the polyurethanes coatings industry. The technology combines fast curing, even at very low temperatures, and water insensitivity with exceptional mechanical properties, chemical resistance and durability. The development of new raw materials and improved spray equipment has made it possible to overcome the initial problems associated with this technology such as substrate wetting, intercoat adhesion and surface finish quality.

The latest development programs focus on the extension of the application fields through the introduction of MDI-prepolymers, combining low viscosity with low NCO-content, resulting in slower reactivity and/or higher flexibility. Alternatively, prepolymers with higher NCO-content produce coatings with superior hardness.

This paper details the technology and provides an update on the latest developments in the field of raw materials, formulation and performance of polyurea spray coatings in construction applications.

0- Introduction

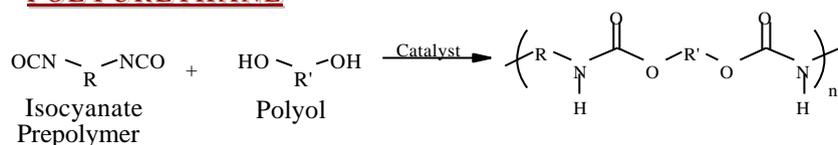
Polyurea spray coatings technology is a recent development in the polyurethane coatings industry. Polyurethane chemistry has been in existence for approximately 60 years, while elastomeric urethane coatings have been available since the 1970s. The polyurea elastomer technology was introduced some 10 years later. The two main application areas are Reaction Injection Moulding (RIM) and sprayable coatings.

Polyurea coatings combine extreme application properties such as rapid cure, even at temperatures well below 0°C, and insensitivity to humidity, with exceptional physical properties such as high hardness, flexibility, tear and tensile strength, and chemical and water resistance. This results in good weathering and abrasion resistance. The systems are 100 per cent solids, making them compliant with the strictest VOC regulations. Due to its specific curing profile and exceptional film properties, the polyurea spray coating technique has been introduced into many areas, including corrosion protection, containment, membranes, linings and caulks.

1- Definition

The term 'polyurea' has been wrongly used in the past. The urethane coatings chemistry can be divided into three sub segments: i/ polyurethane coatings, ii/ polyurea coatings, and iii/ hybrid polyurethane/polyurea coatings, all linked to different isocyanate reactions (Figure 1). Each of these segments deals with systems, which can be aromatic, aliphatic, or a blend of both aromatic and aliphatic. Pigments, fillers, solvents and/or additives can be introduced to all of them.

POLYURETHANE



POLYUREA

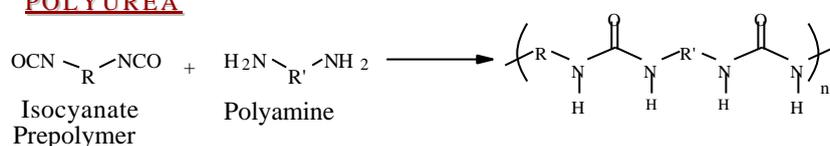


Figure 1: Isocyanate chemistry

i/ A purely **polyurethane** coating is the result of a reaction between an isocyanate component and a resin blend made with only hydroxyl-containing resins. The final coating film will contain no intentional urea groups. A polyurethane system will most probably contain one or more catalysts.

ii/ A **polyurea** coating is the result of a one-step reaction between an isocyanate component and a resin blend component. The isocyanate can be monomer based, a prepolymer, a polymer or a blend. For the prepolymer, amine- and/or hydroxyl-terminated resins can be used. On the other hand, the resin blend should only contain amine-terminated resins and/or chain extenders and not any hydroxyl reactive polymer components. All the polyurea coatings mentioned in the paper comply with this requirement.

iii/ A **polyurethane/polyurea hybrid** coating has a composition which is a combination of the above-mentioned two coating systems. The isocyanate component can be the same as the "pure" polyurea systems. The resin blend is a blend of amine-terminated and hydroxyl-terminated polymer resins and/or chain extenders. The resin blend may also contain additives, or non-primary components. To bring the reactivity of the hydroxyl-containing resins to the same level of reactivity as the amine-terminated resins, the addition of one or more catalysts is necessary.

The **water/isocyanate** reaction also produces urea-groups at the end of the process. However, this reaction should not be considered to be a polyurea reaction as the mechanism is a two-step process, which is controlled by the much slower isocyanate water reaction, and produces carbon dioxide.

2- The polyurethane landscape

The choice between the different polyurethane (PU) technologies is based upon different parameters (Figure 2). Polyurethane presents the best compromise between cost and quality, but is limited by the application performance. The polyurethane system is susceptible to blistering when the substrate contains more than five per cent humidity. This is due to competition between hydroxyl-polyols and water for the reaction with an isocyanate group. The humidity content of the environment and the application temperature are limiting factors for polyurethanes and other chemically reacting systems.

Hybrid systems already have a larger scope for application conditions, but the presence of catalysts in hybrids makes them more sensitive to humidity than “pure” polyurea systems. Moreover, because the catalysed polyol/isocyanate reaction behaves differently from the amine/isocyanate reaction to changing application temperatures, the system becomes less robust.

Polyurea can be used in extreme conditions. When it is used on substrates almost saturated with water, polyurea will not provoke blistering nor will blistering occur when the air contains high amounts of humidity. Even at very low temperatures (as low as minus 20°C) the polyurea coating will still cure. Polyurea coatings combine high flexibility with hardness. They are the most suitable coatings when the following is required:

- high curing speed,
- application under high humidity and/or at low temperatures,
- extreme abrasion resistance,
- impermeable membranes,
- high thickness build up,
- chemical resistance.

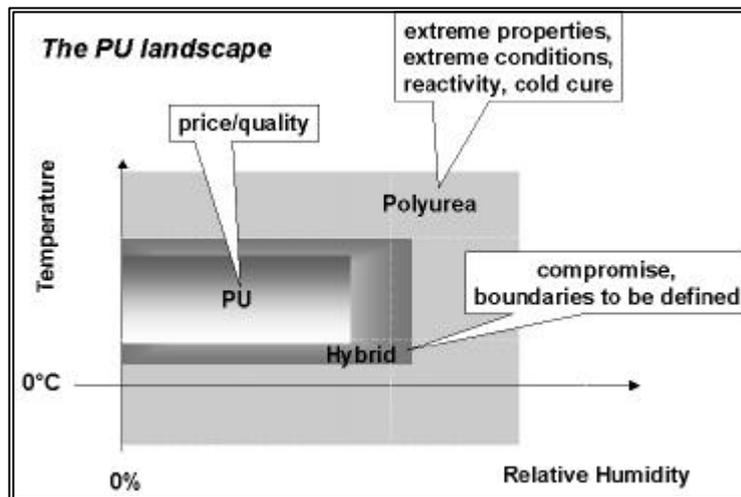


Figure 2: Applicability of the different PU chemistries

3- The applications for polyurea coatings

A good understanding of the properties of polyurea spray coatings is required to specify the right application. Table 1 provides a general overview of the physical and chemical properties that can be expected of polyurea spray products. Polyurea systems are known to be very tough. They combine high elasticity with high surface hardness, resulting in very good abrasion resistance.

Table 1: Typical physical properties of polyurea and their specifications

Property	Unit	Specification	Results
Reactivity			
Gel time	seconds	Manual	1 - 20
Tack free time	seconds	Manual	3 - 120
Physical properties			
Shore A	-	DIN 53505	50 - 100
Shore D	-	DIN 53505	10 - 75
Tensile	N/mm ²	DIN 53504	10 - 30
Elongation	%	DIN 53504	20 - 800
Angle tear	N/mm	DIN 53515	50 - 125
Trouser tear	N/mm	DIN 53507	20 - 60
Abrasion	mg	ASTM D 4060-90	150 - 500
Cold impact resistance	kJ/m ²	ISO 180	50 - 100 at -20°C
Flexural bending modulus	N/mm ²	ASTM D790	50 - 600

The market development started in the US, followed by Asia, with very strong growth during the second half of the 1990s. In a first stage of development, polyurea was used as a protective layer over polyurethane insulation foam for roofing applications. In Europe, the polyurea spray coatings market only started to develop in the last few years.

The broad window of application conditions, with a high tolerance for humidity, both from the environment and from the substrate and temperature, makes polyurea a very suitable coating for concrete in construction applications such as roof repair, containment liners, membranes, car park decks, bridges and offshore. The high abrasion resistance leads to its application in liners for truck, bulk transport wagons, freight ships and conveyor belts. Tables 2a and 2b represent an overview of the application fields where polyurea is chosen based on one or more of the unique application and/or film properties.

Table 2a: Polyurea applications in construction

<ul style="list-style-type: none"> Roof coatings Flat roof repair Waterproofing membranes Secondary containment Car park decks Bridges Offshore
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Table 2b: Other polyurea applications

<ul style="list-style-type: none"> Pipe protection Inner pipe repair Tank coatings Truck bed liners Freight ship liners Bulk transport wagon liners Conveyer belts

4- Raw materials

A polyurea spray coating formulation consists of five different elements:

1. isocyanate component;
2. (reactive) diluent;
3. polyetheramines;
4. chain extenders;
5. additives, fillers and pigments.

4.1- On the isocyanate side

1. Isocyanate

Since the most commonly used isocyanate is diphenylmethane diisocyanate (MDI), this paper focuses on MDI-based products. Aliphatic systems can be used where UV-stability is an issue.

Standard polyurea spray coatings use MDI-prepolymers with a NCO-content of 15 to 16 per cent. In this NCO-range, a good compromise between viscosity of the material and the reactivity of the system is obtained. Lower NCO-prepolymers have a higher viscosity, but give higher elasticity and slower reactivity. Higher NCO-prepolymers are lower in viscosity, which provides an effective mixture of the two components. However, they become much more reactive, with the risk of building up more internal stress. Higher NCO-prepolymers will be used if higher surface hardness is needed. Table 3 provides an overview of the main properties of the MDI-prepolymers used for polyurea spray coatings in Europe.

Table 3: Properties of the MDI-prepolymers used in Europe for polyurea spray coatings

MDI prepolymers	% NCO	2,4'-MDI content	Viscosity, typical value at 20°C, mPa.s
SUPRASEC® 2049	10.2	Low	2830
SUPRASEC 2054	15.0	Low	750
SUPRASEC 2058	15.5	High	850
SUPRASEC 2059	15.0	High	1750
EID 6468*	19.3	Medium	620
SUPRASEC 2069	19.0	Low	1660

*EID = Experimental Isocyanate Development product

2. Diluent

JEFFSOL® PC or propylene carbonate is a reactive diluent for polyurea. Propylene carbonate has a high flash point, low toxicity and should not be considered as a volatile organic compound (VOC).

The main advantages of using propylene carbonate are:

- improved shelf life of the isocyanate-prepolymer;
- a compatibiliser for the mixing of the two components in the mixing chamber of the spray gun;
- a viscosity reducer for isocyanate-prepolymers;
- improved levelling of the applied film.

Propylene carbonate reacts with an amine to give a carbamate structure containing a secondary hydroxyl group. Due to the quick reaction between isocyanate and amine,

the secondary hydroxyl does not have the opportunity to react with an isocyanate group. The propylene carbonate molecule should, therefore, be considered as a mono-functional molecule (Figure 3).

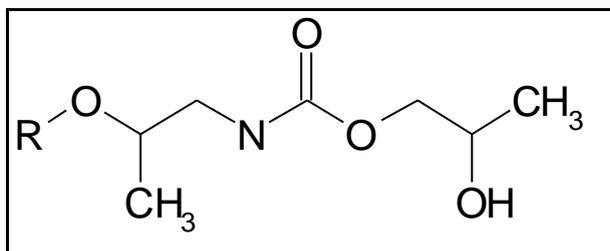


Figure 3: Carbamate structure

In applications where contact with water cannot be avoided, the use of propylene carbonate should also be limited, as propylene carbonate is completely miscible with water and unreacted propylene carbonate could be extracted, increasing the water permeability of the film.

Huntsman Petrochemical Corporation owns certain patents relating to the use of propylene carbonate in polyurea elastomers.

Other solvents or viscosity reducers can be used if they are compatible with the isocyanate component. They may be considered as a VOC. However, they will increase the shrinkage effect.

4.2- On the resin blend or amine blend side

The amine blend used in polyurea spray coatings is a mixture of polyetheramines and chain extenders.

1. Polyetheramines

The main component of the resin blend is a mixture of amine terminated ethylene oxide and/or propylene oxide polyether with molecular weights varying from 200 to 5000 g/mole. The primary amine groups provide a very fast and reliable reaction with the NCO-groups of the isocyanate component. Table 4 represents the properties of the polyetheramines commonly used in polyurea.

Table 4: Polyetheramines

Polyetheramines	Molecular Weight	Functionality	Viscosity, 25°C, mPa.s
JEFFAMINE® T5000	5000	3	820
JEFFAMINE D2000	2000	2	250
JEFFAMINE D400	400	2	21
JEFFAMINE D230	230	2	9

2. Chain extenders

Diethyl-toluenediamine or DETDA is the standard chain extender used in aromatic polyurea spray coatings. DETDA contributes to the hard block and improves the heat resistance of the cured film. It is the most reactive amine in the resin blend but, because of the phase separation during the curing, it controls the reaction mechanism and makes it possible to spray a polyurea film.

Other chain extenders like dimethylthio-toluenediamine (DMTDA), N,N'-di(sec.butyl)-amino-biphenyl methane (DBMDA) or 4,4'-methylenebis-(3-chloro, 2,6-diethyl)-aniline (MCDEA) slow down the reaction significantly. Table 5 lists various chain extenders and their characteristics.

Significantly slowing down the reaction also means that the competition with the water reaction becomes more important and precautions need to be taken.

Table 5: Chain extenders

Chain Extenders	Molecular weight	Functionality	Viscosity, typical value, mPa.s
DETDA	178	2	280 at 20°C
DMTDA	214	2	691 at 20°C
DBMDA	310	2	8 at 38°C
MCDEA	379	2	Solid at 20°C

3. Additives, fillers, pigments

Depending on the application, solvents, additives, pigments and/or fillers are introduced to the formulation. Adhesion promoters like silanes are used to enhance the adhesion on steel and concrete. UV absorbers are used to slow down the yellowing effect of aromatic polyurea systems. Fillers are added to lower the raw material cost and/or improve the physical properties of the coating. The addition of pigment and/or fillers is limited because the viscosity of the two components at the application temperature has to be kept under control. Higher amounts of fillers and reinforcement fillers can be added to the system as a third component.

5- Product application specifics

The most important element of handling polyurea coatings is the mixing. Good mixing will be obtained in a suitable mixing module by impingement with mechanical purge. The operational pressure and temperature of the products will also help to optimise the mixing efficiency.

Due to the high cure speed of polyurea and the short mixing time, the products are mixed by impingement at high pressure. Indeed, for field applications, it is preferable to formulate the products on a fixed 1:1 volume-mixing ratio. The pressure used in the field will vary between 150 and 250 bar. The viscosity of the products at application temperature ideally needs to be lower than 100 mPa.s and the viscosity of the two components needs to be at the same level. The properties of these prepolymers can be found in Table 3.

The viscosity of the resin blend at 25°C is approximately 900 mPa.s, dropping below 100 mPa.s at application temperature.

Experiments prove that polyurea films produced at 65°C, 70°C and 80°C have different properties and these properties improve with increasing temperatures. The new spray equipment allows different temperature settings for the two components, ensuring an optimum mixing in the spray head.

The spraying equipment has improved significantly. New features are:

- separate temperature settings for both components;
- easier variable ratio settings;
- easy output control;
- easy monitoring of application parameters.

The index of a polyurea system is typically kept at a slight over-index of the isocyanate in the range of 1.05-1.10. As the isocyanate-group reacts to humidity, the excess isocyanate compensates for the 'loss' of isocyanate-groups during storage and/or application. The film properties of the 1:1 volume ratio sprayed system were measured for an index variation between 0.90 and 1.15. The test results indicate that the film performs best at an index of 1.05 and higher. Below an index of 1.05 the results can vary significantly and become unpredictable, even for small index shifts.

In the following chapter, the correlation between index and film properties will be discussed in detail.

6- Important aspects of the spray polyurea technology

The application of polyurea has known some problems during the initial start-up phase, which are at the origin of the misconception still existing about polyurea technology. These problems can be attributed partly to the lack of experience at the time of the introduction of the technology, partly to the lack of adequate application equipment, and partly to the fact that this new technology could not be applied in the same way as the current coatings systems.

At first, polyurea spray coatings simply looked almost too easy to apply. Polyurea is very fast, the coating can be put into service immediately after the application and the final properties of the coating are obtained only a few hours afterwards. Polyurea is not water or temperature sensitive, and is easy to formulate and produce.

The first systems on the market were indeed very fast with a gel time of less than two seconds, and initially a number of problems were linked to the reactivity of the systems.

A first problem mentioned was substrate wetting. This was a problem linked to the development phase of polyurea with the use of extremely fast spray systems. Development programs focusing on adhesion on concrete, with polyurea systems presenting gel times of three to four seconds, resulted in cohesive adhesion failure in the concrete. In practice, to limit the risks under variable field conditions, a multi-layer system is applied, made of a primer and a topcoat.

A second remark from the market was the lack of intercoat adhesion. Lab tests with times between coats of several weeks have shown that intercoat adhesion is very good. When problems occur with intercoat adhesion, most of the time they can be related back to problems with the raw materials, the manufacturing of the systems or the spray equipment. Spray equipment problems or a disturbance of the feeding of one or both components towards the mixing module can cause poor mixing. Adapting the machine settings of the spray can solve this.

Due to the high reactivity of the systems, the surface quality of the sprayed film was initially very poor. The fine-tuning the spraying equipment was a first step improvement towards solving to the problem. The use of non-VOC, reactive diluents and the development of new MDI-prepolymers with higher 2,4'-isomer content resulted in perfect surface quality without compromising on working time.

The cost of the polyurea spray coatings technology is seen as a barrier to entry. "Pure" polyurea systems are more expensive, when considering raw materials cost alone, but can be applied in areas where all other systems will fail or where they are not suitable. Also the initial investment in equipment is rather costly.

But, when estimating the capital for a project, polyurea is even more competitive when both the processing time and the waiting period before the coated substrate is put back into service are included.

As highlighted above, the success of the project is very equipment and applicator dependent and we believe that the high entry barrier can only guarantee quality services from specialised and skilled operators.

7- Construction related aspects

7.1- General considerations

As polyurea chemistry is very fast, does not experience negative side effects caused by the presence of humidity and also cures at temperatures below 0°C, polyurea spray coatings can be used under difficult weather conditions. However, when using polyurea coatings, a number of precautions still have to be taken.

At the development phase of the product for an application:

- The formulation needs to meet the performance requirements related to the application.
- A suitable “system” needs to be fine-tuned for the application.
- The developed system needs to be evaluated in real life conditions.

At the surface preparation phase:

- A good surface preparation is mandatory in order to guarantee a good adhesion and a good finish. In all cases the surface must always be sound, dry and clean.
- The surface quality needs to be examined.
- The consistency of the surface quality for the complete project needs to be evaluated.

At the application phase:

- Although humidity in the substrate or in the air does not disturb the curing performance of the coating, it is still better to respect the dew point rules. The presence of water on the surface to be coated will always have a negative effect on the adhesion performance of the coating.
- When the preheated products are applied on a cold surface, the increase of the viscosity will have a greater impact on the wetting of the substrate than the slowing down of the reactivity at those lower temperatures. If cold substrates need to be coated, the necessary precautions need to be taken.

If primers are considered, a good approach is to start with the evaluation of existing primers with known performance on the substrate. It is important to determine the adhesion performance of the polyurea coating on the primers and to check whether the application conditions of the primer and the re-coating conditions for the primer still work for a system with polyurea as a finish.

7.2- Concrete surface defects and surface preparation

The low cost, high strength and structural properties of concrete make it the material of choice for the construction industry. Some of the typical properties of concrete like the limited chemical resistance, dust release and porosity or permeability make it necessary to put a protective and/or decorative layer onto the surface.

The preparation of the surface is extremely important. Depending on the surface quality of the concrete, one or more of the following actions needs to be taken:

- water jet and/or solvent cleaning
- grit blasting
- bughole and crack filling
- repair layer of concrete
- priming.

7.3- Steel surface defects and surface preparation

The life cycle of steel construction coatings depend largely upon the protective system put in place. The life of the protective coating itself is strongly depending on the surface condition prior to the application of the coating. The protection of the substrate is mainly obtained by ensuring a good adhesion. Two adhesion mechanisms are possible:

- molecular attraction of the interfacial forces from both the coating and the substrate,
- mechanical bonding or anchoring of the coating on the substrate

Depending on the condition of the surface, one or more of the following pre-treatments will be necessary:

- cleaning and degreasing with solvents, water jet or detergents
- hand tool or power tool cleaning,
- grit blasting.

On freshly grit-blasted, dust-free steel with a surface roughness SA 2½ to SA 2 according to the specification ISO 8501-1, very high adhesion values can be obtained for polyurea, even without the use of primers.

8- Latest developments

8.1- Mixing efficiency

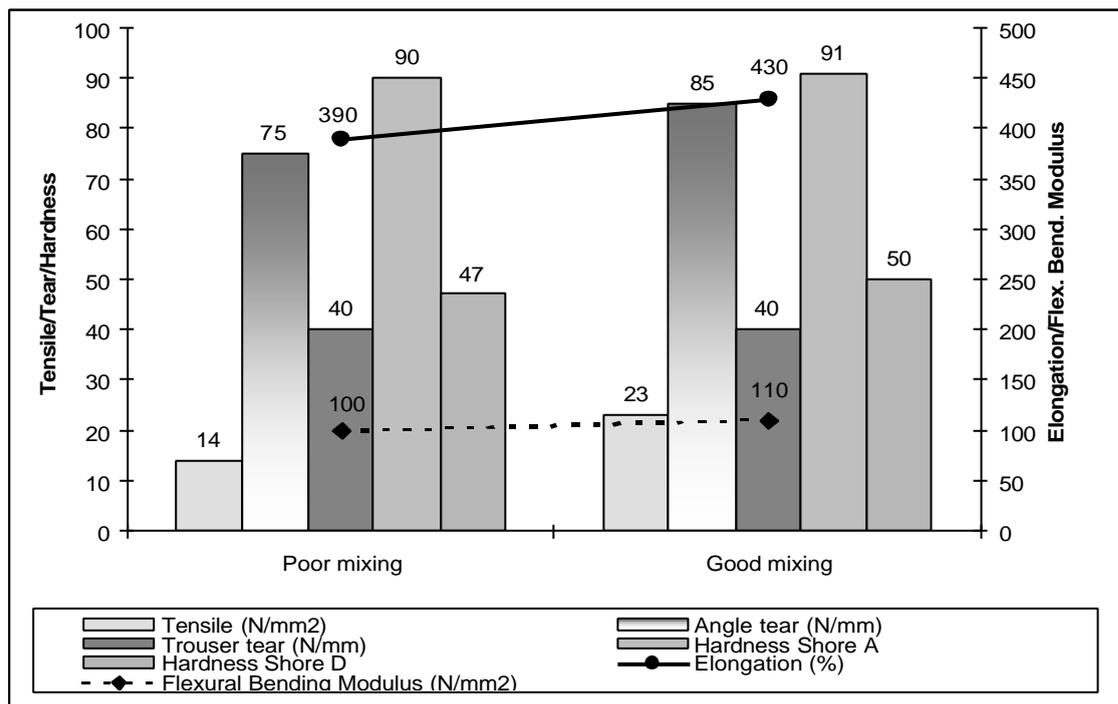


Figure 4: Influence of the mixing efficiency on the physical properties of a polyurea coating system

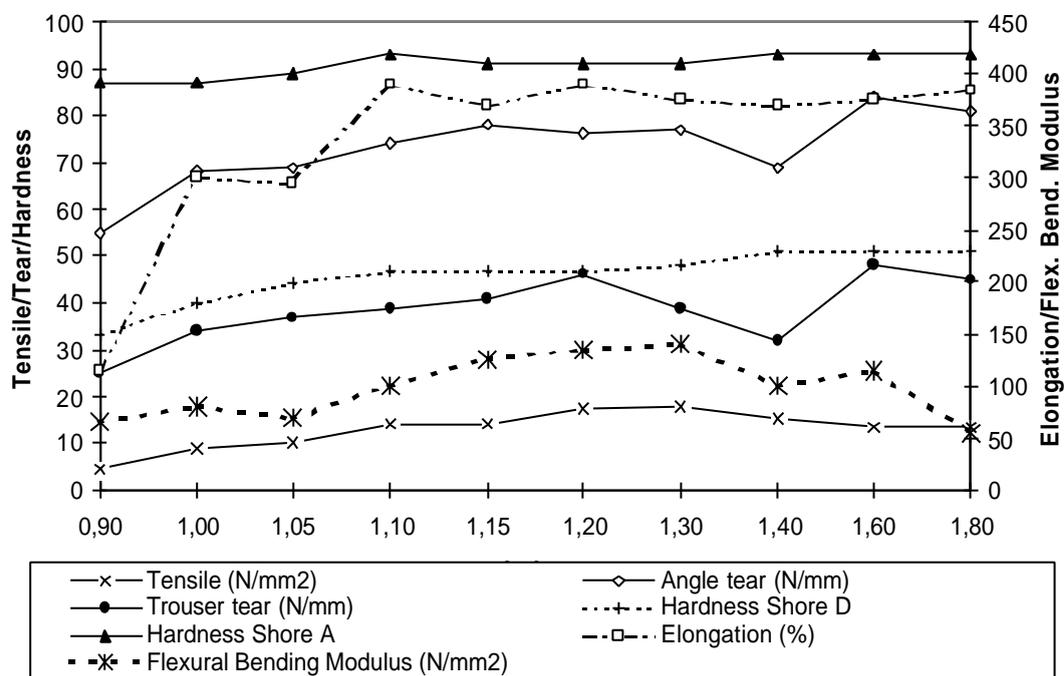
The mixing efficiency of the application equipment is of vital importance. When formulating a system or modifying an existing system, it is necessary to verify the mixing efficiency constantly. Figure 4 shows the influence of changing the mixing on the physical properties of a formulated product. The tensile strength almost doubles from 14 N/mm² to 23 N/mm², the angle tear increases from 75 N/mm to 85 N/mm and the

elongation increases from 390 to 430 per cent. In this case, the influence on the other physical properties is limited.

8.2- Influence of the system index on the final film properties

Earlier experiments reveal that a polyurea coating needs to be formulated at an index above 1.00, meaning with a slightly higher amount of isocyanate-groups than amine-groups. At an index of 1.00 or lower, the physical properties of the coating become unreliable. Figure 5 demonstrates that most properties obtain very good values at indexes 1.10 to 1.30. Above an index of 1.30 the performance tends to drop again. Taking into account that, in practice, slight variations might occur in the application parameters, related to the precision of the spray equipment and variations in application conditions, it is safer to work at a minimum index of 1.10 to 1.15.

Figure 5: Variation of the physical properties at varying system index



8.3- Influence of fillers on the physical properties

Adding fillers to a polyurea system can be useful for different reasons such as a reduction in the raw material cost or improvement in physical properties. Inorganic fillers have a different hardness and some will abrade parts of the spray equipment more than others. The most sensitive parts are the mixing chamber and the nozzle of the spray gun. The filled systems need to be carefully filtered before packaging.

Depending on the performance of the spray installation, the dosing of filler can vary. We added up to 40 per cent of filler to the resin blend. The main limiting factor for the processing will be the increase in viscosity of the filled component. This can result in:

- difficulties with the pumping unit,
- poor mixing due to big differences in viscosity for both components.

Adding fillers improves the surface hardness, the angle tear and flexural bending modulus but has a negative influence on the elongation and the tear propagation or trouser tear (Figure 6).

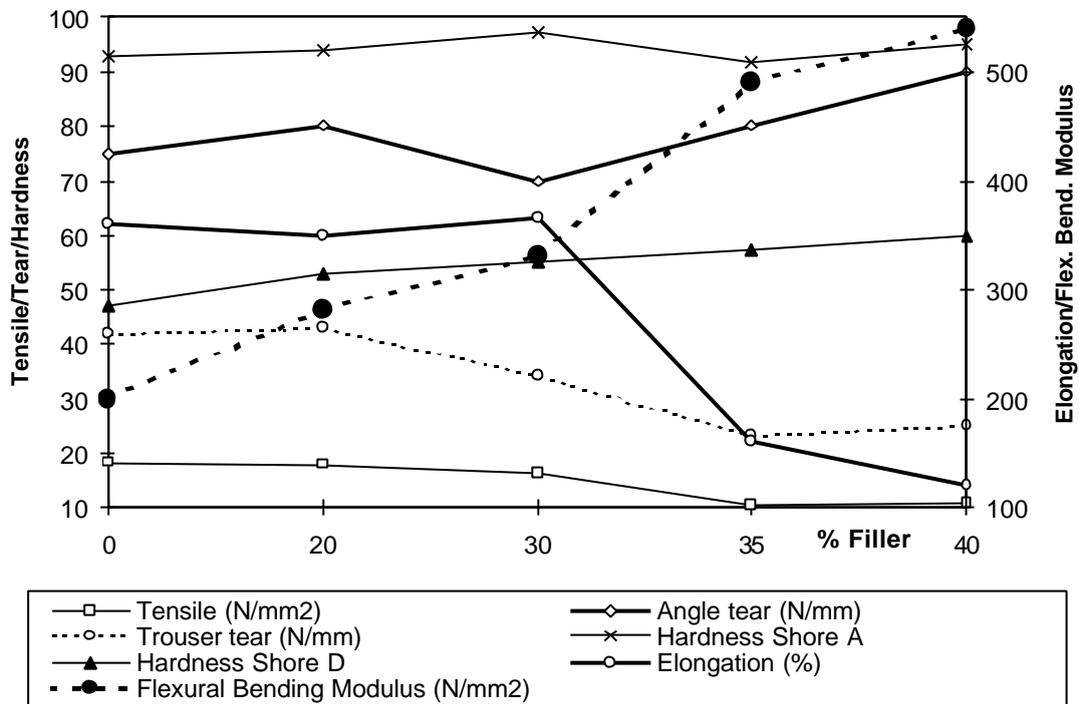


Figure 6: Physical property development as a function of filler content

8.4- Water absorption

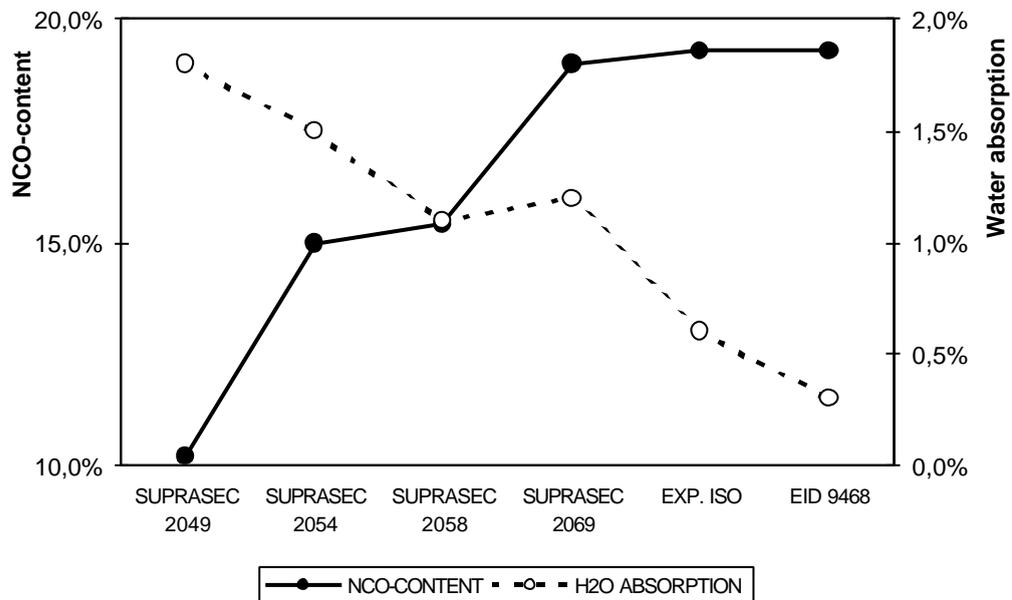


Figure 7: Water absorption for different SUPRASEC prepolymers

For corrosion protection, the main contributing property to a good performance is adhesion to the substrate. Further testing proved that, even with very good adhesion, the resistance to cathodic disbondment for some systems fails. Since cathodic

disbondment is a longer term and certainly not a simple test method, we measured the water absorption over a period of 10 days at 80°C and added 3 per cent of sodium chloride to the water.

As can be seen in Figure 7, the unmodified standard polyurea spray coatings give only a limited protection against corrosion. The water absorption drops significantly with increasing the NCO-content for the prepolymer. Further fine-tuning of the pre-polymer resulted in water absorption being well below 0.5 per cent after 10 days. Cathodic disbondment testing on this system gave very satisfying test results.

8.5- Antiskid performance

Flooring, car parks and sports floors are key applications for polyurea due to its high abrasion resistance, good mechanical properties and insensitivity to blistering during the curing process in humid conditions.

One example is the outdoor, impact absorbing playground flooring. The system tested is based on SUPRASEC 2049, formulated to be applied in a 1 to 1 volume ratio. The film properties are 70 Shore A hardness, 600 per cent elongation and 13 N/mm² tensile strength. The results in Table 6 show that it is perfectly possible to formulate a system, which complies with the antiskid needs of a flooring system, in this case for a flexible substrate.

Table 6: Antiskid test result for flooring applications

		Specification	Dry surface	Wet surface	
Reference	Sports multi-surface	BS 7044 (hard foot)	60 – 140	60 - 140	
	Impact absorbing playground	BS 7188 (soft foot)	> 40	> 40	
	Substrate, no coating	BS 7188 (soft foot)	95	55	
Test results	Substrate + polyurea	Smooth	BS 7188 (soft foot)	110	26
		Textured	BS 7188 (soft foot)	115	40
		Smooth, antiskid addit.	BS 7188 (soft foot)	110	88
		Textured, antiskid addit.	BS 7188 (soft foot)	110	90

9- Conclusions

Polyurea spray coating technology is different from other coating chemistries and can expand the application range of coatings to areas and conditions where other coating systems will fail.

Polyurea spray coatings are very suitable for applications in construction applications. The fast curing makes it possible to use it when only very short disturbance periods are allowed. The fact that the isocyanate/water reaction is not affecting the physical properties of the applied film, expands the use of polyurea to high relative humidity conditions and does not set such stringent limits on the water content of substrates like concrete. Although they slow down at colder temperatures, polyurea coatings still cure at temperatures where other chemistries fail.

The formulation of polyurea spray coatings has to be approached in a very similar way as any other coating system. Careful selection of raw materials for the fine-tuning of the formulation and the evaluation of the system, in the sometimes difficult conditions where the coating is to be applied, is still necessary.

Polyurea spray coating technology means handling reactive chemicals. While handling the chemicals during their manufacturing, packaging and application, the correct protective clothing should be worn at all times.

10- Acknowledgements

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