

Polycarbodiimides as classification-free and easy to use crosslinkers for water-based coatings

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Polycarbodiimides (CDI) selectively react with carboxylic acid ($-\text{COOH}$) groups in polymer chains. This type of crosslinking reaction results in a classic 3D polymer-crosslinker network. Compared to polyisocyanates, polycarbodiimides are much less sensitive to the presence of water and are able to achieve long pot lives in water-based systems. Due to the high reactivity, curing with CDI type crosslinkers can be done under room temperature or in typical oven conditions used for applied coatings. Furthermore, a new family of VOC-free polycarbodiimides, in aqueous delivery form, have been introduced, which demonstrate even longer pot lives with equivalent properties.

Introduction

Crosslinking is widely employed in the coatings industry as a way to improve surface performance. These improvements include wear, abrasion, chemical resistance and toughness^[1]. The improved performance originates from the formation of a continuous three-dimensional network, which may be formed by the crosslinker alone, or by reaction of the crosslinker with the resin or binder^[2].

Crosslinkers, with their reactive groups, can be harmful, irritant or sensitising depending on the type of reactive groups, the molecular weight of the crosslinker molecules and the ease of penetrating living cells. Polycarbodiimides contain the carbodiimide reactive group, sometimes combined with other functional reactive groups. However, importantly, CDI are neither irritant nor sensitising, as determined in toxicological studies^[3]. CDI products do not carry a classification unless another harmful component is present, such as a solvent. As a consequence, CDIs are a safe crosslinker choice. For clarification, in this article, polycarbodiimides are considered to be oligomers or polymers containing on average two or more carbodiimide groups, and not polymers derived from carbodiimide monomers^[4].

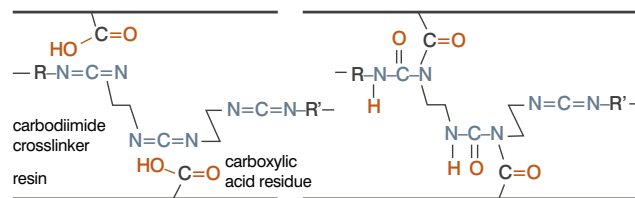
Crosslinking can reduce elongation and increase the tensile strength and hardness of a polymer. A high level of crosslinking may be acceptable for hard coatings on rigid substrates, but lower levels may be more suitable for soft coatings on flexible substrates, like leather or rubber. An important crosslinking system for aqueous resins involves the use of water-dispersible oligomeric polyisocyanates. The polymeric binders in such aqueous coatings are either polyurethane dispersions, acrylic resins or a combination of both. In general, the use of such polyisocyanate crosslinkers is not based on a reaction with functional groups in the coating, rather they form an interpenetrating network on the reaction with water. The main drawbacks of polyisocyanate crosslinkers are moisture sensitivity and limited pot life. Aziridine is another crosslinker family which, for many years, was the reference in terms of the properties imparted in

polymer-based coating formulations. However, the use of aziridines is falling due to concerns about toxicity and handling.

The use of polycarbodiimides in coatings based on aqueous resins is growing and new water-based and VOC-free types have been introduced in recent years. These new CDIs are easy to use and exhibit a much longer useful pot life than isocyanates can achieve in water-based systems. In addition, "multifunctional" water-dispersible CDIs are also available that display a high crosslinking performance.

The chemistry of polycarbodiimide crosslinking involves mainly the reaction of carboxylic acid ($-\text{COOH}$) residues in acrylic resins or in polyurethane dispersions with carbodiimide ($-\text{N}=\text{C}=\text{N}-$) groups of the crosslinker. After the formation of an unstable intermediate, a stable N-acylurea is formed as shown in *Graph 1*^[5-8]. Since the CDI contains several $-\text{N}=\text{C}=\text{N}-$ groups, one CDI molecule can react with carboxylic acid residues on different polymer chains, tying them together to form a three-dimensional network. The reaction of carboxylic acid with carbodiimide can be quite fast under ambient or mild thermal curing conditions.

Graph 1: Reaction of carboxylic acid residue from a resin with a polycarbodiimide crosslinker



Types of polycarbodiimides

Solvent-based CDIs can be readily used as a crosslinker in aqueous polyurethane or polyacrylate dispersions. A special family are the so-called multifunctional polycarbodiimides. These solvent-based CDIs contain additional functional groups, which have a reactivity towards functional groups in the resin or towards corresponding groups, i.e. by self-condensation or self-addition. This results in an increased crosslinking capacity, since both the carbodiimide and the additional reactive functional group contribute to the crosslinking^[9]. Multifunctional CDIs are now also available co-solvent-free, an important improvement over the first generation of multifunctional CDIs^[10]. Indeed, stable aqueous CDIs have become available^[11-13]. This is remarkable as a carbodiimide can react with water to form a urea, so the formulation parameters have to be selected wisely to be able to achieve stable aqueous CDIs. This selection ultimately influences the stability of the CDI, its pot life in aqueous resins and its reactivity as a crosslinker.



Hence, multiple types of aqueous CDIs are available. The main advantages of such CDIs supplied in water are:

- Ease of use, can be readily mixed into aqueous systems
- Zero VOC
- Non-irritant
- Long pot life

In a typical aqueous latex resin, which has no hydroxyl or other isocyanate-reactive groups, the amount of polyisocyanate crosslinker has no relation to the functional groups of the resin. On the contrary, CDI crosslinkers function by reacting with carboxylic groups of the resin. A stoichiometric ratio between the amount of CDI crosslinker to be used and the number of carboxylic groups in the resin exists. However, it appears that for optimal performance a higher or a lower level than the stoichiometric amount can be required. Running a dosage ladder will determine the optimum crosslinker level. In many applications, typical use levels are often below the theoretical stoichiometric level.

2. Testing, properties

Several polycarbodiimide crosslinkers^[14] were tested in combination with different acrylic and polyurethane resins:

- CL-A, a hydrophilic aqueous CDI (40% solids)
- CL-B, a hydrophobic aqueous CDI (40% solids)
- CL-C, a multifunctional solvent-based CDI (50% solids)
- CL-D, a VOC-free multifunctional CDI (100% solids)

Dosage ladder

The acid number of an acrylic resin can be taken into account when predicting an optimum amount of a polycarbodiimide crosslinker, since the optimum reaction mechanism favours a one-to-one ratio between carbodiimide groups and carboxylic groups. However, the acid number of a resin is not always available and diffusion and mobility constraints during curing may lead to a different ratio than the theoretically calculated one designed for optimal crosslinking performance. Therefore, it is important to run a dosage ladder to determine the optimum ratio between resin and polycarbodiimide crosslinker. Such a dosage ladder has been determined for a typical acrylic resin in combination with the zero-VOC multifunctional polycarbodiimide CL-D. Chemical resistance was determined as a function of the crosslinker amount (*Table 1*). Testing is performed on cured

Table 1: Results* from dosage ladder determination for combination of acrylic resin RA and zero-VOC 'multifunctional' polycarbodiimide crosslinker CL-D

	50% ethanol (16 h)*	10% ammonia (1 h)*	Acetone (16 h)*	Handcream (16 h @ 50°C)*
RA, no XL	4-5	3	4	5
RA + 1% CL-D	4-5	3	5	5
RA + 2% CL-D	5	5	5	5
RA + 3% CL-D	5	3	5	5
RA + 4% CL-D	3-4	2	5	5
RA + 5% CL-D	4	2	5	5

*Rating on a 1 to 5 scale: 1 is the worst and 5 is the best.

Graph 2: Reduction in water uptake as a function of the percentage of CL-A added, shown for three different types of polyurethane film

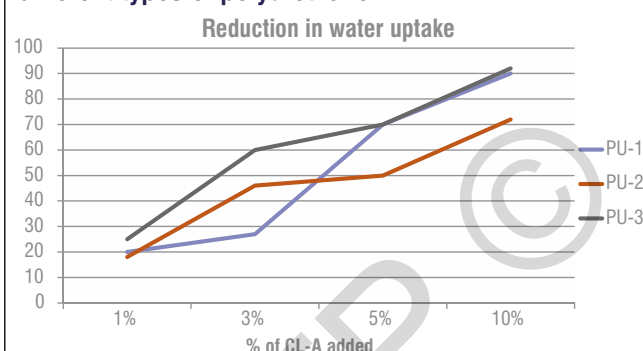


Table 2: Reduction in water uptake as a function of the percentage of CL-A added, shown for three different types of polyurethane film

	No XR	XR-5350	CL-A	CL-B	CL-C	CL-D
Dosage (% of total top coat)	0	10	5	5	5	3
Wet Rubs 1000	4	5	4	5	5	5
Sweat rubs 300	3	5	4	4/5-5	5	5
Flex 100,000	1	5	5	5	4	5
Cold-18°C Flex 15,000	1	5	5	5	4	5

*Rating on a 1 to 5 scale: 1 is the worst and 5 is the best.

films of each formulation in the left-hand column. The conclusion from the data is that 2% of CL-D is the optimum amount for crosslinking the acrylic resin RA (i.e.: highest score for ethanol, ammonia, acetone and hand cream resistance). It can also be observed in the data that increasing the amount of crosslinker beyond the optimum amount results in a drop in properties, notably in ethanol and ammonia resistance.

Water uptake tests on polyurethane films

The water uptake of films made from three types of water-based polyurethanes crosslinked with CL-A was measured as a function of the amount of crosslinker. The results show that even a small amount of CL-A reduces the water uptake by about 20% (*Graph 2*). Higher amounts of CL-A lead to higher reductions in water uptake, with up to 90% of reduction of the water uptake when 10% of CL-A has been added. The water uptake was measured after 24 hours of soaking in water.

Testing on leather

The capabilities of various polycarbodiimide crosslinkers were evaluated on leather in a typical automotive top coat system using an isocyanate crosslinker as reference. The reference, isocyanate crosslinker (XR-5350), was added in a typical amount of 10%, whereas most of the polycarbodiimides were added in a 5% amount compared to the total top coat formulation. Only CL-D was added in a smaller dosage to compensate for its higher solids content. The leather pieces were subjected to various tests. The results are summarised in *Table 2*. The top coat was sprayed twice in 2.5g per square feet on leather that was already base coated, and this base coat contained 3% of CL-A as crosslinker. The leather pieces were cured for five minutes at



70°C in an oven. Testing was performed after 24 hours.

Test methods:

- Bally flex, 100,000 bends
- Cold (Bally) Flex, -18°C, 15,000 bends
- Wet rubs, 1000 cycles Veslic test, felt soaked in distilled water, 500g weight on samples with 10% extension.

When no crosslinker was added, a fair rating was obtained in the wet rubs and the sweat rubs tests however the results obtained in the flex test and the cold flex test were very poor. Clearly, the addition of a crosslinker improves the performance significantly. All CDI crosslinkers tested gave a good to satisfactory outcome in the 100,000 flex tests and the cold flex tests, since only the leather with CL-C showed some minor damage after 100,000 flexes. It is likely the crosslinking was too strong here due to the multifunctionality of the CL-C, as described in the introduction. Both “multifunctional” polycarbodiimides (CL-C and CL-D) gave an excellent performance in the wet rub and the sweat rub tests. The aqueous polycarbodiimide CL-A showed some minor damage after the wet rub and the sweat rub tests (all rating 4). The other aqueous product, CL-B, yielded a better outcome in the wet rub and the sweat rub tests (5 or 4.5-5 rating). Only the reference isocyanate crosslinker scored a 5 in all tests, whereas each particular polycarbodiimide scored some 5 ratings. However, not one scored a 5 rating in all tests.

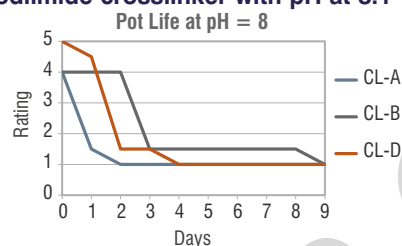
The results demonstrate that both aqueous and “multifunctional” polycarbodiimide crosslinkers are able to boost the performance of the coating on leather, making them a feasible alternative for a polyisocyanate crosslinker. Although the CDIs did not score the highest rating in all the tests, they have other advantages over an isocyanate crosslinker, such as a friendlier classification, greater ease of use and a much longer pot life. One should consider all these properties when selecting which crosslinker to employ in leather finishing.

Pot life

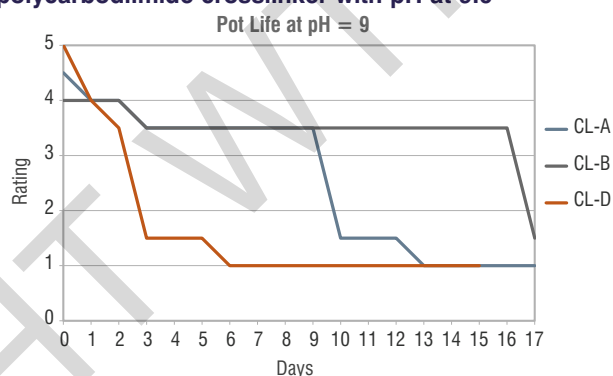
The pot life of a coating application mixture is an important parameter, since a short pot life is difficult to work with and will likely result in more waste due to incomplete consumption of the coating mixture. Polycarbodiimides react with available carboxylic groups ($-\text{COOH}$) in the aqueous resins. However, amines are usually employed to neutralise the carboxylic acid groups so that, above a pH of 9, almost all carboxylic acid groups are deactivated since they have been transformed into an inactive carboxylate anion ($-\text{COO}^-$). As a consequence, above a pH of 9, the amine effectively blocks the reaction between the carbodiimide groups and the carboxylic acid groups of the resin. Upon drying, the amine evaporates, releasing the carboxylic acid groups, decreasing the pH and activating the carboxylic acid groups again for a reaction with the carbodiimide groups. This is the crosslinking mechanism.

It is worth noting that polycarbodiimide crosslinkers are stable as provided, including the aqueous versions, but they will start to hydrolyse when they have been added to aqueous resins. A high pH of the mixture of resin and polycarbodiimide slows the rate of hydrolysis and prevents carboxylic groups from being formed. The effect of the pH on the pot life of a mixture of resin and polycarbodiimide crosslinker has been studied for an aqueous polyurethane and three types of CDIs. The mixtures were prepared and set

Graph 3: Ethanol resistance (50% ethanol, one hour), according to DIN12720 using a polyurethane dispersion as resin, as a function of the age of the mixture resin & polycarbodiimide crosslinker with pH at 8.1



Graph 4: Ethanol resistance (50% ethanol, 1 hour), according to DIN12720 using polyurethane dispersion as resin, as a function of the age of the mixture resin & polycarbodiimide crosslinker with pH at 9.0



at a pH value of either 8.1 or 9.0 and the ethanol resistance of dried films was determined as a function of the life of the resin-polycarbodiimide mixture, calculated from the moment that the films were made from the aged mixture. The results are shown in *Graph 3 and Graph 4*.

At a pH of 8.1 the pot life of the mixture of the polyurethane resin with the three polycarbodiimides varied between a few hours and three days, with the hydrophobic aqueous polycarbodiimide CL-B displaying the longest pot life of three days. However, at a pH of 9.0 the pot lives were much longer. At pH 9.0 the pot lives varied between two days for the multifunctional 100% solids polycarbodiimide, CL-D, to 16 days for the hydrophobic aqueous polycarbodiimide, CL-B. This demonstrates that the pH is a very important parameter for the pot life duration of mixtures of an aqueous resin and polycarbodiimides. Furthermore, aqueous polycarbodiimides CL-A and CL-B are more resistant to hydrolysis due to their chemical composition, which is reflected in a long pot life when the pH of the coating mixture is high enough. The actual pot life that can be obtained with the aqueous CDI crosslinkers in a coating mixture is also dependent on temperature (lower temperatures are better) and the resin types that are contained in the mixture.

3. Conclusions

Polycarbodiimide crosslinkers are an excellent alternative to the more hazardous isocyanate and aziridine crosslinkers for crosslinking aqueous polyurethane and acrylic-based coatings on leather. Polycarbodiimides themselves have no label classification and they can be readily mixed into aqueous resin mixtures. Curing of the coatings can be done at ambient or low thermal conditions. Some polycarbodiimide crosslinkers do not contain VOC, which helps to reduce the



overall VOC content of the complete coating mixture. It is advisable to perform a dosage ladder study to determine the optimum ratio between the resin and the polycarbodiimide crosslinker to achieve the desired properties of the cured coating. Long pot lives of mixtures of aqueous polycarbodiimides and aqueous resins, up to weeks, can be achieved when the pH of the mixture of crosslinker and resin is 9.0 or higher. These advantages make polycarbodiimides a safe choice as a crosslinker for aqueous polyurethane or polyacrylate coating systems. They are therefore a very suitable building block for coating mixtures.

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