

Polycarbodiimide crosslinkers

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Abstract

Polycarbodiimides are very efficient crosslinking agents for carboxylic group containing polymers in water, such as polyurethanes, polyacrylates and latexes. They are an environment friendly replacement for the former frequently used polyaziridines and in particular they are non-mutagenic. A great step forward in the development of crosslinkers are the polycarbodiimides containing additional functional groups which contribute to the crosslinking. At applying the polymers in water together with these polycarbodiimides an additional inter-polymer network is formed by the additional functional groups. As a result the film properties, such as the film strength, water and chemical resistance, abrasion properties, of the obtained film are enhanced.

The latest developments are solvent-free polycarbodiimide dispersions in water, which are of particular interest when solvent free systems are required.

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1. Introduction

Crosslinking is widely practiced in nearly all of the coatings industries, be the end-use application as coatings for the exterior surfaces of cars and airplanes, high-wear interior wood flooring, or for flexible substrates such as paper, textiles, and leather. In all cases where crosslinking is employed, the object of its use may be stated generally to be to improve performance. The improvement is usually one related to wear, resistance (to water, solvent, staining, etc.), toughness, to improve mechanical film properties (hardness, resistance to abrasion) or to improve integrity after repeated flexure. Crosslinking can be used in all the indicated fields of application to improve in one-way or another the performance of solvent-borne and of aqueous coatings. In the leather industry, one would be hard-pressed to identify any leather used for automotive seating or steering wheel covers where the topcoat or, less likely, base as well as topcoat are not crosslinked.

Crosslinking, especially network formation, has the potential to reduce elongation and to increase tensile strength, thus

polymer hardness, and one must therefore exercise care not to overdo crosslinking. For hard coatings on rigid substrates one can go all out with crosslinker; for soft coatings on extensible, flexible substrates such as leather, low levels may be best.

The most prevalent crosslinking system in the leather industry involves the use of water-dispersible oligomeric polyisocyanates. The polymeric binders in such aqueous coatings are either polyurethane dispersions in water, or acrylic latexes or the two used in combination. Generally, the use of polyisocyanate crosslinkers is not based on the reaction with functional groups in the coatings, but they form an interpenetrating network upon the reaction with water, accompanied by a limited pot life. Another type of crosslinker are the aziridines, which were for a long time the gold standard for property development. They cure at low-temperature and even ambient temperature, but struggle under the weight of concerns about toxicity and handling.

Water-dispersible polycarbodiimides are less used as crosslinkers, but the situation concerning polycarbodiimides in leather and artificial leather finishing is changing, because there are now not only water-dispersible polycarbodiimides available, but also fully aqueous-zero VOC-polycarbodiimides. These have decent stability in water, and exhibit much longer useful pot life than isocyanates could achieve. In addition, multifunctional water-dispersible polycarbodiimides are available that display a higher performance when used as crosslinker.

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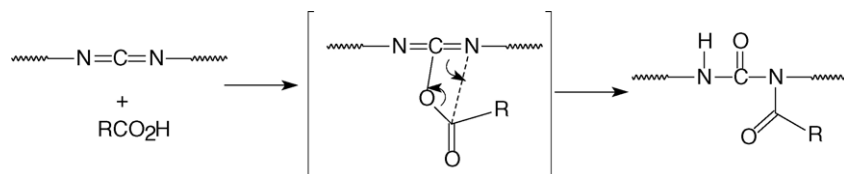


Fig. 1. Reaction of carboxylic group with carbodiimide moiety.

The chemistry of polycarbodiimide crosslinking involves mainly the reaction of carboxylic acid ($-\text{CO}_2\text{H}$) groups in acrylic latexes or in polyurethane dispersions with carbodiimide ($-\text{N}=\text{C}=\text{N}-$). As shown in Fig. 1, an *O*-acyl urea is formed as an intermediate and it rearranges to an *N*-acyl urea [1–3]. The *O*-acyl urea is a reactive species in its own right, and it can react with other functionalities as well, though most of these do not apply because these other functionalities may not be present. Since the polycarbodiimide contains several $-\text{N}=\text{C}=\text{N}-$ groups, one polycarbodiimide molecule can react with carboxylic groups on different polymer chains tying them together via the reaction, forming a crosslink. Reaction of carboxylic acid with carbodiimide can be quite fast under ambient or mild thermal cure conditions.

2. Synthesis and types of polycarbodiimides

Polycarbodiimides are generally synthesized through a catalytic cycle from isocyanate compounds [4–7] (see Fig. 2). In this catalytic cycle, a phospholene catalyst first reacts with an isocyanate, upon which a rearrangement occurs and carbon dioxide is liberated. This intermediate species can subsequently react with another isocyanate group after which the phospholene catalyst is regenerated and a carbodiimide moiety is formed. When multifunctional isocyanates are used, the newly formed carbodiimide-containing molecule can again undergo the carbodiimide forming reaction and products can be made with multiple carbodiimide moieties.

The first polycarbodiimides that appeared on the scene were solvent-based ones, followed soon by solvent-based ones that were dispersible in water. A great step forward in the development of polycarbodiimides as crosslinkers were multifunctional polycarbodiimides. These solvent-based polycarbodiimides contain additional functional groups, and this combination of carbodiimide and other functional groups in the

crosslinker result in an increased crosslinker capacity, since both the carbodiimide and the additional reactive functional group contribute to the crosslinking [8] (see Fig. 3). The additional reactive functional group can be any functional group with reactivity towards functional groups in an aqueous polymer dispersion, emulsion or solution, or towards corresponding groups, for instance by self-condensation or self-addition. Examples are, amongst others: dialkylacetal, imine, alkoxy silane, aziridine, epoxide, azetidine, oxazoline or imidazoline. These agents are coupled to the polycarbodiimide chains by means of another functionality that is reactive towards either the isocyanate or the carbodiimide group.

The additional functional groups contribute, depending on the type, in a different manner to the crosslinking.

- By reactions with reactive groups in the polymer. Azirine and azetidine rings react with carboxylic moieties in polymer systems in aqueous systems. Alkoxy silanes give, after hydrolysis, a condensation reaction with silane functions, which may be present in polymers on an aqueous basis.
- By self-condensation reactions, in which the additional functional groups may be alkoxy silanes. While the carbodiimide function reacts with the carboxylic groups in the polymer system on aqueous basis, the alkoxy silane functions from the same molecule will react, after hydrolysis, with the alkoxy silane functions from neighboring molecules.
- By self-addition reactions, in which the additional functional groups may be aziridine rings. With the reactions of the aziridine ring there is a competition between the addition to the carboxylic group in water-borne polymers and a self-addition. Through this a network of coupled ethyleneamine functions may arise.

Since very recently, polycarbodiimides can also be supplied in water and they can be manufactured with zero VOC [9,10]

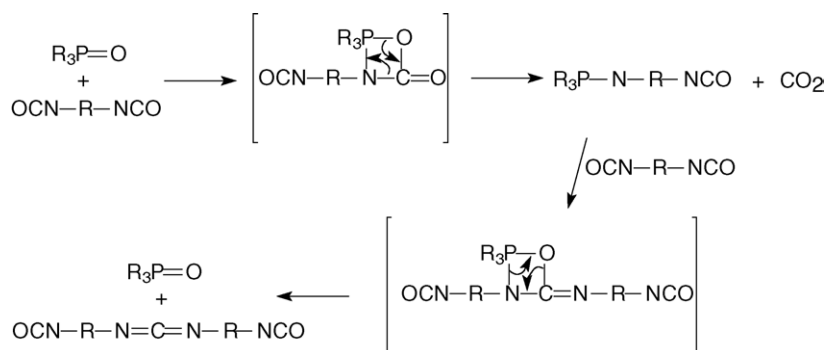


Fig. 2. Synthesis of (poly)carbodiimides.

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