

POLYCARBODIIMIDE AND POLYURETHANE CROSS-LINKERS FOR LEATHER FINISHING

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ABSTRACT. This review focuses on polyurethane and carboxylic acid-carbodiimide cross-linked systems for leather finishes. Recently, these cross-links have become very popular in leather finishing. The cross-links in leather finishes improve the strength properties of the finished leather, the excess of cross-links causes brittleness. The multifunctional carbodiimide cross-linkers are useful for leather surface properties improvement. The carbodiimide groups are sensitive to hydrolysis; life time of this functional group during polymerization is enhanced. Water dispersible isocyanates, polyurethane copolymers and polyisocyanate cross-links have applications in new technologies are discussed in this review.

KEY WORDS: cross-linker, polycarbodiimide, diisocyanate, leather, polyurethane

AGENȚI DE RETICULARE PE BAZĂ DE POLICARBODIIMIDĂ ȘI POLIURETAN PENTRU FINISAREA PIELII

REZUMAT. Acest articol se concentrează asupra sistemelor de reticulare pe bază de poliuretan și acid carboxilic-carbodiimidă pentru finisarea pielii. Recent, aceste tipuri de reticulări au devenit foarte populare în finisarea pieilor. Reticularea pielii la finisare îmbunătățește proprietățile de rezistență ale pieii finite, în timp ce excesul de legături încrucișate determină fragilitate. Agenții de reticulare multifuncționali carbodiimidici sunt utili pentru îmbunătățirea proprietăților de suprafață ale pielii. Grupările carbodiimidice sunt sensibile la hidroliză; durata de viață a acestui grup funcțional în timpul polimerizării este sporită. Reticulările cu izocianatii dispersabili în apă, copolimerii poliuretani și poliizocianatii discutate în această lucrare au aplicații în tehnologii noi.

CUVINTE CHEIE: agent de reticulare, polycarbodiimidă, diizocianat, piele, poliuretan

AGENTS DE RÉTICULATION POLYCARBODIIMIDE ET POLYURÉTHANE POUR LA FINITION DU CUIR

RÉSUMÉ. Cet article met l'accent sur les systèmes de réticulation à base de polyuréthane et de l'acide carboxylique-carbodiimide pour la finition du cuir. Récemment, ces types de réticulations sont devenus très populaires dans la finition du cuir. La réticulation du cuir dans l'opération de finition améliore les propriétés de résistance du cuir fini, tandis que la réticulation excessive entraîne une fragilité. Les agents de réticulation multifonctionnels de carbodiimide sont utiles pour améliorer les propriétés de surface du cuir. Les groupes carbodiimide sont sensibles à l'hydrolyse; la durée de vie de ce groupe fonctionnel pendant la polymérisation est augmentée. Les réticulations avec des isocyanates dispersables dans l'eau, des copolymères de polyuréthane et des polyisocyanates décrits dans cet article ont des applications dans de nouvelles technologies.

MOTS CLÉS: agent de réticulation, polycarbodiimide, diisocyanate, cuir, polyuréthane

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INTRODUCTION

In leather industry majority of the finishing systems are waterborne and are most often based on aqueous polyurethane dispersions (PUDs) or acrylic as principal binders. Often these two binders are used in combination also. The PUDs are best replacement of solvent based cross-linker and exhibit high flexibility and resistance up to -65°C . Polyurethanes (PU) are good cross-linking binders, which create a bond, that is resistant to oil, fat, heat and different organic solvents [1].

PU binders are formed by the reaction of isocyanates (R-N=C=O) with hydroxyl group [2]. The benefits of polyurethane binders are improved toughness and cohesive strength

with low tack. The basic chemical products, in PU systems are diisocyanate, polyols (polyester or polyether), solvent (organic or aqueous), chain extender, viscosity modifier and catalyst (see Figure 1). Outstanding properties of PU are extensibility, elasticity, abrasion resistance combined with mirror like gloss and clarity. The PU dispersions are miscible with almost all chemicals, have good solvent resistance, excellent low temperature properties and good weather resistance. However PU dispersions are quite expensive compared to acrylics and have poor product stability (shelf life).

For many high performance applications

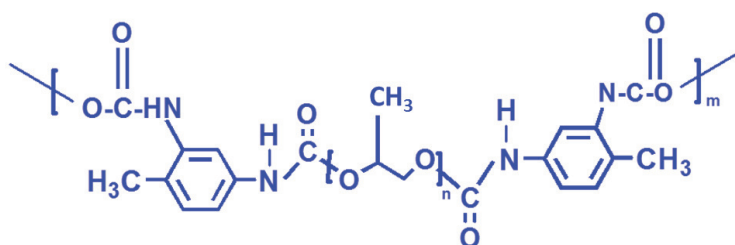


Figure 1. Polyurethane structure [3]

such as upholstery leather finishing, dress lining, cross-linking is essential and more commonly encountered cross-linkers are medium oligomeric molecular weight water dispersible isocyanates prepolymers. They are available in solvent medium at 50-60 weight % solids or as solvent free viscous liquids. Cross-linking is employed to improve performance related to water resistance, solvent (straining) of toughness to improve mechanical film properties like hardness, toughness, abrasion resistance and rose flux. In leather industry the most prevalent cross linking involves the use of dispersed oligometric isocyanates. The polymeric binders in such aqueous coatings are either polyurethane dispersion in water or acrylic latexes or two combinations [4]. The carbodiimide could act as excellent cross-linkers and provide better platform to the leather, plastic and footwear industries. This review will be useful to design new water based cross-linking applications.

CHEMISTRY OF CROSS-LINKING

Cross-linking is the process of chemically joining two or more molecules by a covalent bond and formation of three dimensional networks. The

cross-linking agents are molecules that contain two or more reaction ends capable of chemically attaching to specific functional groups like primary amine on protein or other trifunctional amines or alcohols. When combined with different sizes and types of chemical backbones (called spacer arms because they define the distance between respective reaction ends) the numbers of cross-linking compounds are enormous.

Selection of Cross-Linkers

Cross-linkers are selected on the basis of their chemical reactivity (i.e. specially for particular functional groups) and other chemical properties, that affect their behaviour in different applications (see Table 1). Chemical specificity refers to the reactive targets of the cross-linkers reactive ends. A general consideration is whether the reagent has the same or different reactive groups carbodiimide (R-N=C=N-R), isocyanates ($-\text{NCO}$) aziridine ($-\text{CH}_2\text{-NH-CH}_2$) at either end, mono or bifunctional cross-linkers have identical reaction groups, they must be used in one step reaction procedures to randomly "fix" or polymerise the molecules.

Table 1: Materials and physical properties

Materials	
Isocyanates	Carbodiimides
1) Oligomeric	Oligomeric
2) Aliphatic	Aliphatic
3) Functionality (f=>2, averages<4)	Functionality (f=>2, averages<4)
4) Avail in PMAc,* EEP#	Avail in PMAc @50%
5) Solids: 50 up to 100%	Or 40 % aq. (zero VOC)
6) Use: hotpotted or in-line	Use: hotpotted or in-line
7) Geometry: branched	Geometry: linear [2].

*PMAc: Propylene glycol methyl ether acetate, #EEP: Ethyl 3-Ethoxypropionate

These reagents allow single conjunction of molecules that have the respective target functional groups and also allow for sequential conjugations that minimise undesirable polymerisation.

TYPES OF CROSS-LINKERS

Isocyanates

The cross-linkers based on diisocyanate chemistry have high end applications in leather

finishing particularly for automotive applications. This is due to an excellent property profile with regard to processability and quality of the resulting leather. The finish does not suffer from thermally or UV induced yellowing and other severe ageing systems. The key advantage of isocyanate is its flexibility with respect to the property profile (Figure 2). This is due to the broad variety of isocyanates and polyols (see Figure 3), which are available for combination

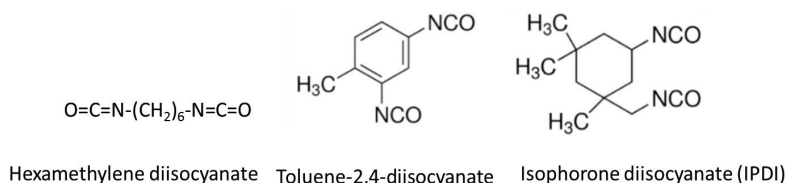


Figure 2. Different isocyanates for PU synthesis

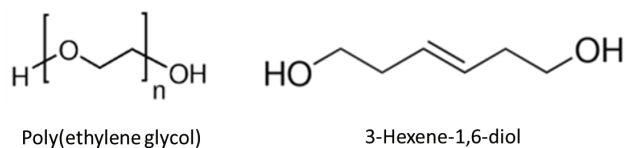


Figure 3. Different types of polyols used for polyurethane synthesis

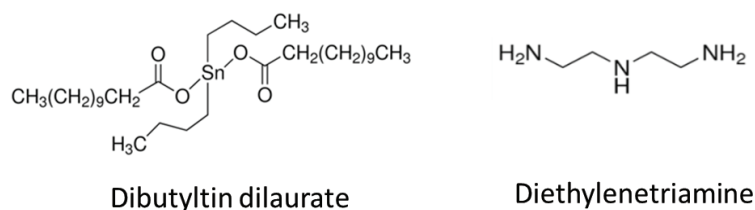


Figure 4. Different types of catalysts used for polyurethane synthesis

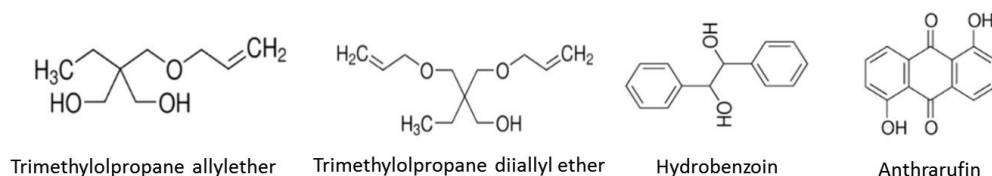


Figure 5. Different types of cross-linkers

to form polyurethanes in polyaddition reaction [5]. Different types of catalysts and cross-linkers are used for polyurethane synthesis as shown in Figures 4 and 5.

Polycarbodiimides

In leather finishing most of the prevalent cross-linking system involves the use of water dispersible oligomeric polyisocyanates. In many industrial coating applications, aqueous carboxyl acrylics act as main binders and were cured with cross-linkers at high temperature. However, it had concerns about toxicity, handling and even yellowing on ageing. Hence better way to cure carboxyl polymers in water with carbodiimide and their properties. The carbodiimide has excellent chemical resistances and very low VOC compared with other isocyanates. It can be easily reacted with $-COOH$ functional groups to provide better hardness. Unfortunately, carbodiimide will be hydrolyzed at $pH < 11$, since

it will prevent $-COOH$ from forming. Moreover, polycarbodiimide could be a suitable alternative to isocyanates for preparation of PU [6].

A dispersion containing particles of one type with carbodiimide ($-N=C=N-$), the other containing carboxylic acid groups ($-COOH$), and cross-linking occurs to form or N-acylurea in reaction-diffusion process (Figure 6), to low volatile emission during processing for the environmental protection and work hygiene [7, 8]. A hybrid of polyisocyanate (a dynamic helical polymer) and isocyanate prepolymers (a static helical polymer) is the backbone of polycarbodiimide [9].

Carbodiimides are much more stable in water than isocyanates, water borne polycarbodiimides have useful pot life of at least several days to a week or more. Polycarbodiimides can be viewed as a hybrid between the static polyisocyanate and the dynamic polyisocyanate helical polymers [10].

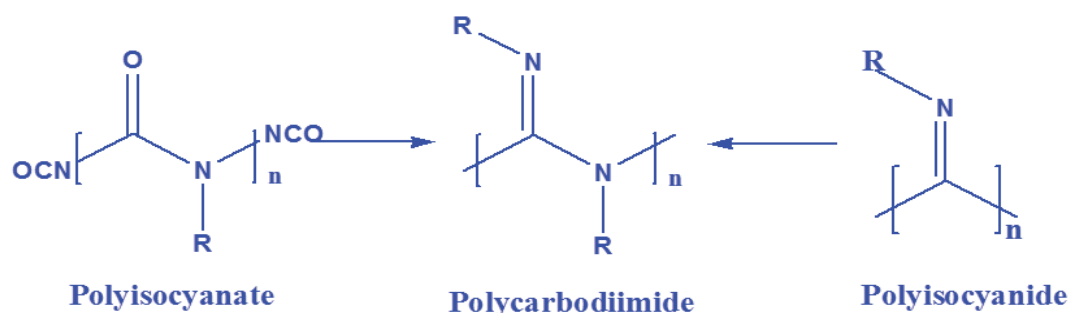


Figure 6. Structure of various cross-linkers

High performance multifunctional polycarbodiimides offer maximum resistance in wet abrasion, hydrolysis, sweat, chemical resistance and UV durability. The advantage of aqueous polycarbodiimide can be used in line, top coats (7-10 weight %) to achieve better performances. Polycarbodiimide and polyisocyanate cross-linkers can be used together to achieve high reactivity of the polycarbodiimide

and carboxylic acid promotes an early and fast curing. The better performance originates from the formation of a continuous network, which may be formed by reaction of cross-linkers with the binder. For the latter route reactive groups on the polymer chain are needed [9]. One of the most profile properties of polycarbodiimides is their asymmetric back bone which allows the formation of excess helical sense and/

or chiral polycarbodiimides. EDC (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide) hydrochloride cross-linking reactions must be performed in conditions devoid of extraneous carboxyl and amines (see Figure 7). Acidic (pH of 4.5 to 5.8) MES (2-[morpholino]ethanesulfonic acid) buffer is most effective. Polycarbodiimide

can be effective, environmentally friendly, long pot-life cross-linking agents. MES buffer solution is most suitable for carbodiimide reaction system. MES (other non-amine or non-carboxylate buffer) can be used at neutral pH to increase their efficiency.

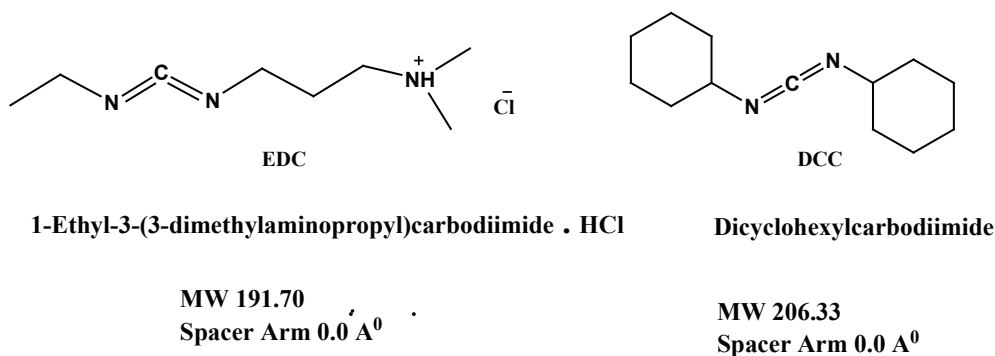


Figure 7. Carboxyl reactive cross-linker

Though carbodiimides react with carboxylic acids, it is not the only path freely available to carbodiimide for most ambient curing aqueous coating chemistry. High performance multifunctional water dispersible polycarbodiimides have also come out in the systems.

CROSS-LINKING SYSTEM IN CARBODIIMIDES

Carboxyl reactive chemicals in biomolecular probes for labelling and cross-linking carboxylic

acids to primary amines include carbodiimides compounds EDC and N,N'-dicyclohexyl carbodiimide (DCC) (see Table 1). Very few types of groups are known to provide specific conjugation to carboxylic acids (-COOH) such as in proteins and various other biomolecules. Carbodiimides work through activating carboxyl groups for direct reaction along with primary amines via amide bond formation [7].

Table 2: Properties of EDC [11]

Molecular formula	$C_8H_{17}N_3 \cdot HCl$
Molecular weight	191.7 kDA
Storage conditions	-20 °C, protect from moisture, use only fresh solutions
Reactive group	Carbodiimide
Column of property	Carboxyl-reactive at pH 4.7-6.0, intermediate then reacts with amines

EDC Reaction Chemistry

EDC is most common used carbodiimide and it has water soluble materials. The toxicity of carbodiimide can be low, when EDC transformed into non-toxic urea derivatives in the coupling reactions. EDC reacts with carboxylic acid groups to form an active o-acylic urea intermediate that is easily displaced by nucleophilic attack to form primary amino groups, in the reaction process (see Figure 8). The primary amine forms an amide

bond with the carboxylic group and an EDC by product released as a soluble urea derivative. The o-cyclic urea intermediate is unstable in aqueous solutions, failure to react with an amine results in hydrolysis of the intermediary, regeneration of the carboxylic group and the release of an unsubstituted urea.

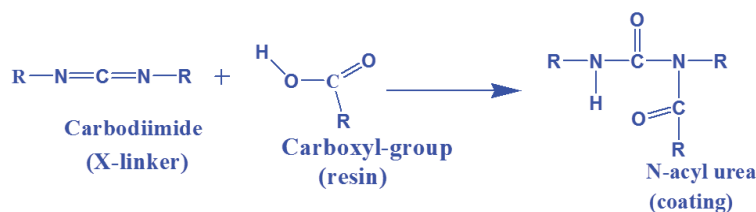


Figure 8. Carbodiimide cross linking mechanism [12]

EDC cross-linking is most effective in acidic (pH 4.5) conditions and must be performed in buffers, devoid of extraneous carboxyl and amines. MES is a suitable buffer, phosphate buffers and neutral (up to pH 7.5) conditions are

compatible. Polycarbodiimides are very effective cross-linking agents for carboxylic group containing polymers in water such as acrylic acid containing polymers, polyacrylates latexes (see Figures 7, 9).

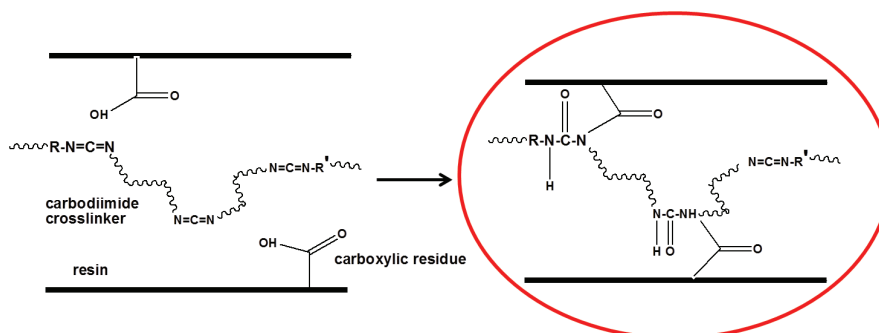


Figure 9. Generic carbodiimide cross-linking reaction [12]

Polymers with carbodiimide groups form additional interpenetrating networks (IPN). The network formation has the potential to reduce elongation and to increase tensile strength and hardness. The water dispersibility of carbodiimide is achieved by incorporating some hydrophilic components into the cross-linkers [13]. This was done by adding an external surfactant or by having an internal surfactant (polyethylene oxides PEO or salts) built into carbodiimide itself [14]. In most leather finishes there is no significant amount of hydroxyl or other reactive functionality accomplished of reacting with isocyanates (see Figure 10). The polyisocyanates and polycarbodiimide are used in leather finishing based on aliphatic back bones. Both types of the cross-linkers have an average functionality per cross-linker molecule of greater than 2.

These cross-linkers can be mixed into aqueous finishing before being applied. The cross linking will generally reduce ultimate % of elongation at break [6].

APPLICATIONS OF CARBODIIMIDES

Carbodiimide mediated inter or intra molecular cross-link of protein is highly useful [15-21]. The availability of functional groups, such as carboxyl, amino, thiol and imidazols in protein and enzymes allow interaction with carbodiimides [22-25]. The reaction of carbodiimide alone with a protein can lead to deactivation, but since o-acylureas are liable to hydrolysis reaction occurs in presence of water. Intramolecular cross-linking is often used to study the folding of proteins. Film forming carbodiimide homo and copolymers are used in amino encapsulation techniques for pressure sensitive adhesives. In dyeing, treatment of wool or hair with carbodiimide improves the wash fastness of applied dyes. A variety of carbodiimides are commonly used (see Figure 7). However EDAC or EDC as it is known is particularly useful in aqueous reactions [7].

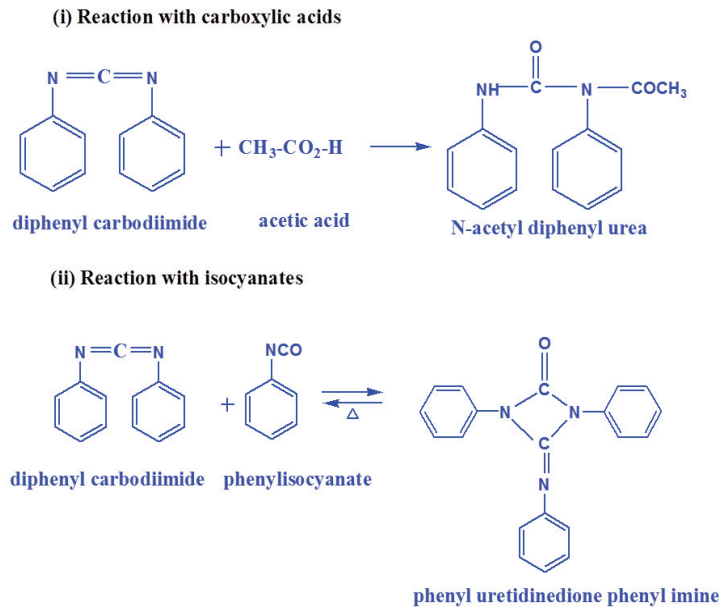
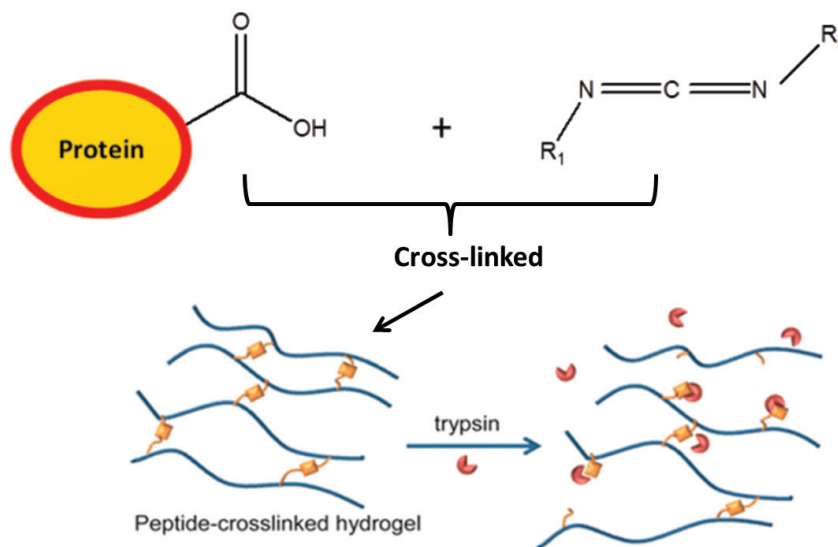


Figure 10. Carbodiimides and isocyanates reactions [6]

Pot-life

The carbodiimide cross-linkers [26-33] exhibit good pot-life in aqueous systems. Multifunctional water dispersible polycarbodiimides display a higher performance, when used as a cross-linker. Water dispersibility of carbodiimide is obtained with some hydrophilic components in the cross-linker, by the addition of an external surfactant or internal surfactant. The cross-linking capability in leather finish can be tested by Veslic tests [8, 34] differential scanning calorimetry (DSC) and dynamic mechanical

analysis (DMA). In DMA the $\tan \delta$ peak value can be identified as a glass transition temperature, can be useful for identifying the processing of the cross-linking applications [8]. The carbodiimide cross-linking is calculated based on the amount of carbodiimide required for polymeric acid. The less stoichiometric carbodiimide is used to react with all of the carboxylic acid present. There is a possibility that in some instances rapid loss of carbodiimide functionality in excess may be due to self-condensation, similar in the case of polyisocyanates [35].

Figure 11. EDC cross-linker with protein. Reprinted with permission from [36], Knipe *et al.*, *Biomacromolecules*; 16, 962 (2015), © 2015, American Chemical Society

Polycarbodiimides have practical application advantage in base coat level of 2-4% as it improves stacking due to low tack. On top coat to achieve desired wear properties, carbodiimides provide an "economical way to achieve performance inputs" [34]. Carbodiimide compounds provide the most popular and versatile method for labelling or cross-linking to carboxylic acids. Xiaoyan and Zhiwen [37] have

synthesized a new cross-linker for microcapsule by interfacial polymerization using hydrophobic carbodiimide cross-linker (Figure 11) for high tensile strength [35]. The reaction between $-COOH$ and $-NCN-$ groups forms an N-acylurea which is less polar as shown in Figure 12. Both carboxylated latex and carbodiimide containing latex films rate of diffusion was much slower than the cross-linked latex [38].

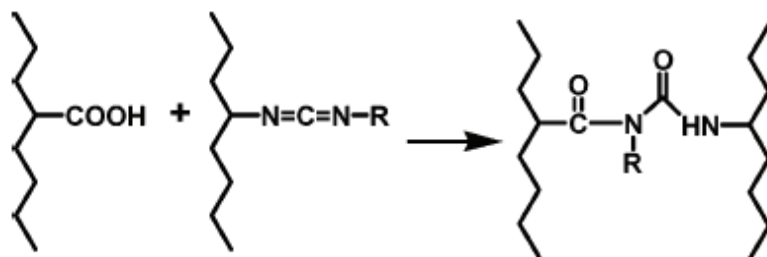


Figure 12. Chart for $-COOH$, $-NCN-$ contains latex films. Reprinted with permission from [38], Pham, *et al.*, *Macromolecules*, 39, 4, 1425 (2006). © 2006, American Chemical Society.

Benefits Offered by Carbodiimides

- i. Low VOC, zero alcohol non-polluting properties, fast drying in line.
- ii. Low odour, non-flammability, no toxicity.
- iii. Clarity of water when dry.
- iv. Significant rub, mark and block resistance.
- v. Grease, alcohol, alkali and improved moisture resistance.
- vi. Use of carbodiimides can impart greater strength and flexibility, heat resistance, increased hardness and rub resistance, upgrade adhesion.
- vii. Shift in application technology "hot pot" mixing to "in line" activation which implies, automatically controlled, ideally continuous mixing of the coating components.

CROSS-LINKED POLYURETHANE FOR LEATHER PROCESSING

To improve the leather properties [39-44], photoactive agent such as benzophenone and rose bengal were mixed into polyurethane matrix [45-47]. These mixed polyurethane solutions were applied on leather surface by painting method for effective anti-microbial leather coating [48]. Moreover, polyurethanes

are interesting block copolymers, mostly it exists in hard and soft segments. Both these segmentation is responsible for the better mechanical properties. However, the hard segment built from diisocyanate, short chain diol such as butane diol, and ethylene diols. The soft segments are developed from polypropylene glycol (PPG), polycarbonate and polytetrahydrofuran [15].

Xu *et al.* stated that water borne polyurethane cross linked acrylate composite was synthesized via *in-situ* method using different cross-link agents. The obtained composite materials could have been used in coatings, leather finishing, adhesives, sealants and also plastic coatings [16, 17]. Keywani [18] reported that acrylic resin based water borne polyurethanes [19] could enhance water resistance, chemical resistance also used in coating, print, ink and leather adhesive [49-51]. We developed polyurethane emulsion, dispersion for leather applications [2, 5].

CONCLUSIONS

This review describes that carbodiimide cross-linking and polyurethane latexes dispersions with improved properties of cross-linked films. The aqueous cross-linkers are environmentally friendly because they reduce VOC emission, are easy to handle and have

longer pot-life. The carbodiimides are effective cross-linking agents providing better chemical resistance, higher hardness and more density to coating. The carbodiimide is an alternative to other cross-linking agents with right combination of resin and cross-linkers can be used. The high reactivity with carboxylic acid promotes an early cure enhancing property development. The dosage of carbodiimide is important and can contribute to additional property development, like mechanical film performances and they can build properties upwards from base coat.

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