Features of Reaction Amino-cyclocarbonate for Production of New Type Nonisocyanate Polyurethane Coatings

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Summary: We have studied different ways of preparing UV resistant oligomers with terminated cyclocarbonates, epoxy and amino groups. We have studied possibility of preparing HNIPU UV stable coatings. Linear and branched amino containing oligomers based on di- and tricyclocarbonates and primary diamines were investigated. It was found that oligomers should be used for curing epoxy-saturated resins, but since the residual quantity of amines this system can't be used for UV resistant coatings. The same problem was in system on the base of nonisocyanate epoxy-urethane oligomers cured by tertiary amines. Coating on the base of acrylic cyclocarbonates and oligomers with primary amines are similar to conventional polyurethane coatings on the base of acrylic hydroxyl containing oligomers and isocyanates, but mechanical properties and chemical resistance are better.

1. Introduction

Applications of polyurethane materials have significantly increased in comparison with some other thermosetting polymer materials. Conventional monolithic polyurethanes have good mechanical properties but they are porous and possess poor hydrolytic stability and insufficient permeability. The involvement of toxic components, such as isocyanates, in their fabrication process makes the production extremely toxic and dangerous.

Polyurethanes have weakness inherent to them due to their molecular composition. Within their polymer structure there are hydrolytically unstable bonds that make the material vulnerable to environmental degradation. By modifying the structure of the polymer, a new promising method of raising hydrolytic stability is introduced and readily displayed in nonisocyanate polyurethanes – a modified polyurethane material with lower permeability, increased resistance properties and safe fabrication processes.

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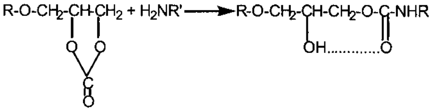
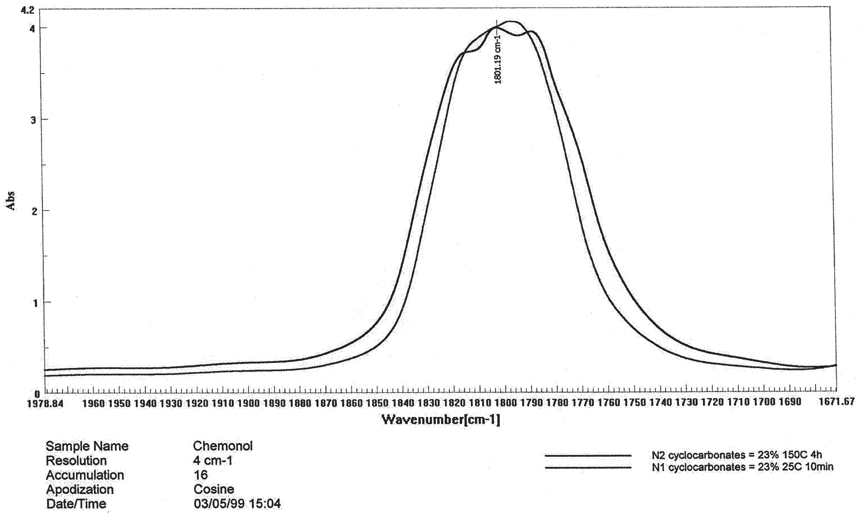
Network nonisocyanate polyurethanes are formed as a result of the reaction between cyclocarbonate oligomers and primary amine oligomers [1, 2]. This reaction forms an intra-molecular hydrogen bond through the hydroxy group at the ß-carbon atom of the polyurethane chain as illustrated below:



$$R\text{-}O\text{-}CH_2\text{-}\underset{\underset{O}{|}}{C}H\text{-}\underset{\underset{O}{|}}{C}H_2 + H_2NR' \longrightarrow R\text{-}O\text{-}CH_2\text{-}\underset{OH}{\underset{|}{C}}H\text{-}CH_2\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}NHR$$

Quantum-mechanical calculation, IR and NMR spectroscopic investigations have confirmed the stability of such a ring [2].



Sample Name	Chemonol
Resolution	4 cm-1
Accumulation	16
Apodization	Cosine
Date/Time	03/05/99 15:04

Fig 1. Reaction between cyclocarbonates and aromatic amines (Ethacure 100)

The blockage of carbonyl oxygen considerably lowers the susceptibility of the whole urethane group to hydrolysis. Moreover, materials containing intra-molecular hydrogen bonds display chemical resistance 1.5-2 times more as compared to materials of the similar chemical structure without such bonds [2].

Basic cyclocarbonate oligomers are formed by bubbling the carbon dioxide through epoxy liquid oligomers in the presence of a catalyst, and by interacting oligomeric chlorinehydrine ethers with carbonates of alkaline metals or oligomeric polyols with ester (chloride) of carbonic acid [2].

The reaction of aromatic diamines with cyclocarbonate and epoxy groups was studied by the authors, and a new method of synthesis of advanced cyclocarbonates is described below [7].

The data about the reaction between aromatic amines and cyclocarbonates are given on Fig.1.

It was found out that up to 150^0C there was no reaction between cyclocarbonate group and aromatic amine group.

Nonisocyanate polyurethanes have superior properties over conventional polyurethanes. Their tensile strength and deformation are similar to those of conventional isocyanate polyurethane materials, but they display chemical resistance properties 30-50% higher, and have significantly reduced permeability: three to five times less than conventional isocyanate polyurethane materials [2]. Due to their unique molecular composition nonisocyanate polyurethanes have transformed into the material with practically no pores being insensitive to the moisture on the surfaces or on the fillers upon formation. As a result, nonisocyanate polyurethane materials exhibit superior resistance to degradation, making them optimum for their applications in crack resistant composite materials, chemically resistant coatings, sealants, glues, etc.

As nonisocyanate polyurethanes do not contain a highly toxic isocyanate, the material synthesis can be carried out in a safe and nontoxic process. Furthermore, nonisocyanate polyurethanes can be employed for the material hardening at room temperature [2].

Due to their superior structure and excellent resistance to degradation, NIPU is optimum for the numerous applications including crack resistant composite materials, chemically resistant coatings, sealants, glues, etc. Their outstanding properties are beneficial to many different industries [4,6]. Siloxane-polyurethane sealants fabricated from siloxane pentacyclocarbonate oligomers displayed the same high adhesion, elasticity and strength properties as conventional polyurethane sealants. However, their thermal stability and heat resistance properties proved to be twice as great [2].

Data about mechanical properties of filled nonisocyanate polyurethanes are given in table 1.

Due to the "data" it is possible to produce materials with different properties from elastic to rigid.

The coatings produced from nonisocyanate polyurethanes have excellent water-resistance properties equivalent to the conventional polyurethanes and epoxy coatings combined [2]. On addition of inorganic powdered substances during the fabrication process the chemical resistance of NIPU can be increased. These substances interact selectively with water and the aggressive medium, i.e., acids, alkalis, and salts transforming the system of high-strength hydrate complexes into durable inorganic adhesive cements. Since the substances interact with the medium, hydrate complexes (crystalhydrates) are always formed in the defects, i.e., micropores, microcracks of the material. This process eliminates the defects of the material and increases its strength.

Crystalhydrates form the volume and the contact-specific surface of an active additive that expands into a constant volume of the polymeric matrix. Due to the increased specific surface of the active filler and the material with viscous features formation, adhesion on the polymer-crystal boundary becomes stronger [5].Till now it was not investigated perspective way for synthesis of UV-stable nonisocyanate PU for coatings.

Table 1. Mechanical properties of filled nonisocyanate polyurethanes

Types of cyclocarbonate Oligomers	Functionality of cyclocarbonate Oligomer	*σt/εp by applying primary amines				
		III				IV
		Functionality				
		2.92	3.47	4.31	5.08	2
I	~2	1.9/710	2.7/565	4.9/325	5.3/108	------------
	~3	8.8/220	13.7/114	15.3/90.5	15.4/63.5	26.6/88.5
	~5	21.3/72	21.8/50	18.7/31	17.2/22	20.3/48.5
II	2.45	8.2/315	17.3/98	23.9/47	2.6/19.6	30.8/20.5
	3.10	19.3/88	22.7/62	23.8/37	18.2/18.8	33.9/19.2
	3.95	19.9/82	26.1/42	25.4/28	17.1/14.3	34.2/18.3
	4.70	16.9/73	13.7/30.5	12.7/24.5	10.6/13.6	27.1/16.9

*σt- tensile strength, MPa; εp- elongation, %

I- aliphatic cyclocarbonate oligomer
II- aromatic cyclocarbonate oligomer
III- aliphatic polyamine
IV- Adduct of BPA epoxy resin and DETA

2. Results and Discussions

Cyclocarbonate olygomers were used for production adducts with polyamine olygomers. The following materials have been employed:

Laprolate 803-aliphatic cyclocarbonate oligomer (functionality~3) with polyoxypropylene chain (Russia);

Eponex 1510 (diglycidyl ether of hydrogenated BPA) Shell;
Polypox R-14 (neopentyl glycol diglycidyl ether);
Polypox R-19 (polypropylene glycol diglycidyl ether;)
Polypox R-20 (trimethylol propane triglycidyl ether);
UPPC (Germany)
and acrylic epoxy resin Setalux 17-1433 (Akzo Nobel, The Netherlands).

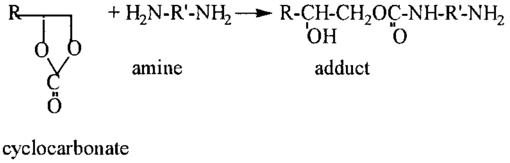
It were prepared different CC-carbonates by bubbling CO2 with catalyst (tetrabutylammonium bromide) and their adducts with diamines:

Pentamethylenediamine (Du Pont)
Trimethylhexamethylenediamine
(Degussa)
Jeffamine EDR-148 (Huntsman)
Isophorondiamine (BASF)

3. Adducts Formation

Adducts have been manufactured by mixing cyclocarbonates with aliphatic and cycloalyphatic amines for 2-4 hours at 60-120^{0}C. Synthesis of adducts is safe and easy: the control was provided by IR spectroscopy. When cyclocarbonate groups had disappeared, the reaction was finished.

Adducts formation process:



$$\text{cyclocarbonate} + H_2N\text{-}R'\text{-}NH_2 \rightarrow R\text{-}\underset{OH}{CH}\text{-}CH_2O\underset{\overset{\|}{O}}{C}\text{-}NH\text{-}R'\text{-}NH_2$$

These adducts were used for hybrid nonisocyanate polyurethanes (HNIPU) formation.

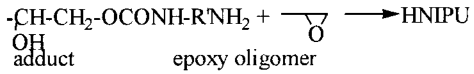
4. Analysis of Paint Properties

Linear and branched amino containing oligomers based on di- and tricyclocarbonates and primary diamines were investigated. It was found that oligomers should be used for curing epoxy-saturated resins, but since the residual quantity of amines this system can't be used for UV resistant coatings (yellowing). The same problem was in system on the base of nonisocyanate epoxy-urethane oligomers cured by tertiary amines.

It is possible to prepare only coatings with restricted UV stability by using adducts on the base of saturated cyclocarbonates and amines and saturated epoxy resins (Eponex 1510 and Polypox 14,16,18,19,20)

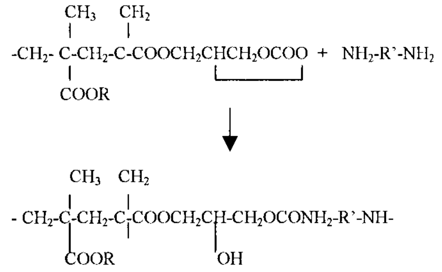
High light stability of acrylic resins is well known. We have synthesized cyclocarbonate on the base of acrylic epoxy resin Setalux 17-1433. The cyclocarbonate-terminated oligomers were synthesized by bubbling CO_2, in presence of catalyst at 140^{0}C, 10 bar.

Process of HNIPU curing:



$$-\underset{OH}{C}H-CH_2-OCONH-R'NH_2 + \underset{O}{\triangledown} \longrightarrow HNIPU$$

Process of acrylic NIPU curing:



$$-CH_2-\underset{COOR}{\overset{CH_3}{C}}-CH_2-\overset{CH_2}{C}-COOCH_2CHCH_2OCOO + NH_2-R'-NH_2$$

$$\downarrow$$

$$-CH_2-\underset{COOR}{\overset{CH_3}{C}}-CH_2-\overset{CH_2}{C}-COOCH_2\underset{OH}{C}H-CH_2OCONH_2-R'-NH-$$

WHERE: R'- ALKYL, CYCLOALKYL

The main properties of the Epoxy based paint and the HNIPU and acrylic NIPU paint are listed in Tab. 2. According to the data, modification of epoxy materials leads to production materials with high mechanical properties (impact and abrasion resistance, elasticity, adhesion, etc).

On the base of saturated epoxy resin after 100hours UV test coatings slight yellow (Baroness 160, 70 w UV, 150 w IR)

Acrylic HNIPU coatings are much more light stable.

After 200hrs UV test coatings were very slight yellow.

By using of UV absorbers and HAL S it is possible to increase UV stability.

NIPU on the base of acrylic cyclocarbonate oligomer and aliphatic diamines were prepared by adding amines to acrylic cyclocarbonate. Curing at 110^0C during 2 hours. At RT it was impossible to prepare coating with advanced properties.

Coatings on the base of acrylic cyclocarbonates and primary amines with UV -absorber are similar to conventional polyurethane coatings on the base of acrylic hydroxyl containing oligomers and isocyanates, but mechanical properties and chemical resistance are better.

Typical properties of UV stable HNIPU coatings are given in the Table 2.

Table 2. Main properties of coatings

Properties	**Aliphatic-Cycloaliphatic HNIPU**	**Acrylic HNIPU**
NV, %	95-100	70-75
Pot life (doubling initial viscosity), hours	0.5-2	0.5-2
Drying time at 23^0C, hours	2-13	-
Curing time at 80^0C, days	> 0.5	-
Curing time at 23^0C, days	3-7	2hours @ 110^0C
Film appearance	clear smooth	clear smooth
Pencil hardness	2H	H
Elasticity, mm	1-3	1
Impact, kg cm	40-50	50
Adhesion mark ASTM D3359 mark	4B	4B
chemical resistance: H_2SO_4, 10% at 25^0C, days	> 20	>20
NaCl, 3% at at 25^0C, days	> 10	> 10
Abrasive resistance after 440 revolutions	0.3-0.4	-

5. Conclusions

Hybrid nonisocyanate oligomers based on saturated and primary amino containing oligomers epoxy resins can be used for manufacturing coatings with restricted UV stability. Nonisocyanate polyurethanes coatings on the base of acrylic cyclocarbonates and primary amines are similar to conventional polyurethane coatings but mechanical properties and chemical resistance are better.

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