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Synthesis of (6-isocyanato *n*-hexyl)carbamoyloxyethylmethacrylate and its uses as sizing-agent for carbon fiber composite materials cured by electron beam

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Summary : Bifunctional acrylic and isocyanate compound, the (6-isocyanato n-hexyl)-carbamoyloxyethylmethacrylate has been synthetized with a good degree of purity (94% mol/mol) by the reaction of hydroxyethylmethacrylate with hexamethylenediisocyanate (HDI) in equal molar ratios. This acrylic-isocyanate compound has been used as sizing agent of carbon fiber, acting as a coupling agent between the fiber and the matrix. Substantial improvement of interfacial adhesion of the carbon/acrylic composite cured by electron beam has been obtained and mechanical properties are quite competitive with thermal process generally used.

INTRODUCTION

Nowadays, bifunctional compounds with both polymerizable unsaturated and isocyanate groups are more and more used in the field of polymers and in particular for urethane coatings and adhesives (fig.1).

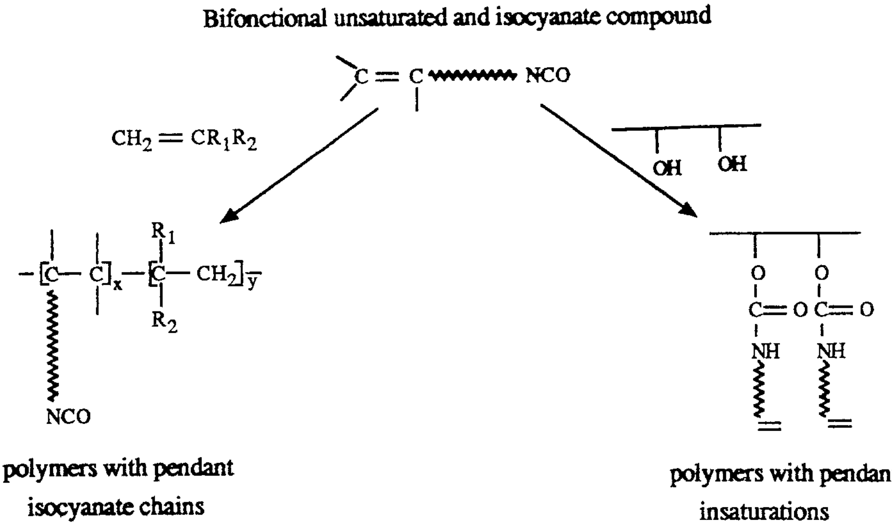

Figure 1 : Applications of bifunctional unsaturated and isocyanate compounds

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Two compounds, the isocyanatoethylmethacrylate (IEM) (1-3) and the m-isopropenyl α,α dimethylbenzylisocyanate (m-TMI) (4) are currently used today and are commercially available. Nevertheless allylisocyanate (5,6), vinylisocyanate (7,8), 3-vinylphenylisocyanate (9,10) and methacryloylisocyanate (11) for which acylisocyanate group is very reactive, have been prepared and can also be used. However, preparations of these compounds from relatively dangerous reagents like phosgene are sometimes long and difficult.

Bifunctional unsaturated and isocyanate compounds can also be prepared in an undirect way by the reaction of the hydroxyl group of an unsaturated-hydroxy compound, such as hydroxyethylmethacrylate (HEMA), with only one of the two isocyanate groups of a diisocyanate, such as 2,4 toluylenediisocyanate (TDI) (12-15) or hexamethylenediisocyanate (HDI) (15). All the difficulty of that reaction is to avoid or at least to limit the preparation of diadduct which results from the reaction of both of the isocyanate groups with the unsaturated-hydroxy compound.

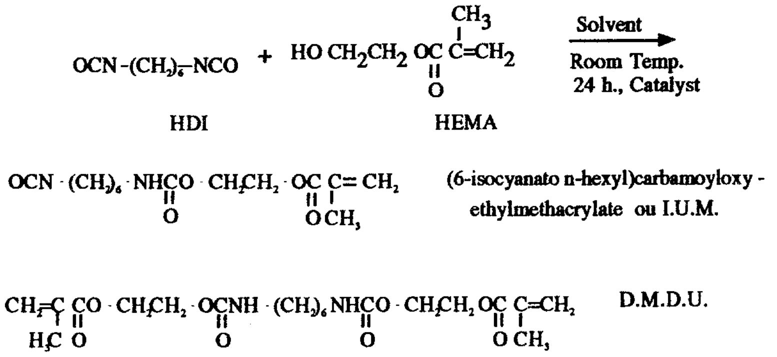
Some synthesis procedures have been carried out in an homogeneous phase (12,13) or in an heterogeneous phase (14,15,16) but there is no real comment about what is different between them. Besides, no analytical method is known until now, which permits to distinguish and quantify the reaction products (monoadduct, diadduct, unreacted diisocyanate).

This paper deals on the synthesis and the characterization of (6-isocyanato n-hexyl)-carbamoyloxyethylmethacrylate obtained from hexamethylenediisocyanate and hydroxyethyl-methacrylate. In the case of carbon / acrylic composite materials cured by electron-beam (17)), the bifunctional acrylic and isocyanate compound has been used as sizing-agent of carbon fiber in order to promote adhesion between the fiber and the matrix (18) : indeed, that coupling agent is able to react with the hydroxy groups onto the surface of the fibers, and with the acrylic matrix.

RESULTS AND DISCUSSION

1) Synthesis, characterization and purification.

The synthesis of (6-isocyanato n-hexyl)carbamoyloxyethylmethacrylate has been performed by the reaction of hydroxyethylmethacrylate (HEMA) and hexamethylene-diisocyanate (HDI) in equal molar ratios. Since the two NCO groups of HDI are equivalent in reactivity, the crude products will also contain DiMethacrylateDiUrethane (DMDU) and some unreacted diisocyanate in addition to the IsocyanatoUrethaneMethacrylate (IUM) (eq.1) . So as to compare with the literature, this reaction has been carried out both in an homogeneous phase or in an heterogeneous phase, respectively in toluene and in hexane. In this last solvent, reaction products (IUM, DMDU) precipitated as they appeared.



$$OCN-(CH_2)_6-NCO + HO\,CH_2CH_2\,O\underset{\underset{O}{\|}}{C}\,\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{Room Temp. 24 h., Catalyst}]{\text{Solvent}}$$

HDI HEMA

$$OCN-(CH_2)_6-NH\underset{\underset{O}{\|}}{C}O-CH_2CH_2-O\underset{\underset{O}{\|}}{C}\,\underset{\underset{CH_3}{|}}{C}=CH_2$$

(6-isocyanato n-hexyl)carbamoyloxy - ethylmethacrylate ou I.U.M.

$$CH_2=\underset{\underset{H_3C}{|}}{C}\,\underset{\underset{O}{\|}}{C}O-CH_2CH_2-O\underset{\underset{O}{\|}}{C}NH-(CH_2)_6NH\underset{\underset{O}{\|}}{C}O-CH_2CH_2O\underset{\underset{O}{\|}}{C}\,\underset{\underset{CH_3}{|}}{C}=CH_2$$

D.M.D.U.

Identification and separation of IUM, DMDU and unreacted HDI were performed by high-performance liquid chromatography (HPLC), after the isocyanate groups had been blocked by an excess of di-n-butylamine. An octadecylsilyl phase column has been employed, with a solvent program of methanol/water and with a light diffusion detector. Figure 2 shows the chromatogram of the products, as well as the external standard : diurethane obtained by the reaction of an excess of butanol with hexamethylenediisocyanate.

In the two studied reactions, the concentration of each species, determined by HPLC as a function of time, shows that if the final yield in IUM is always about 60% mol/mol, the kinetic of the reaction is three times faster in hexane than in toluene (respectively 2h30 against 8 hours) (fig.3). The higher reactivity in hexane may be due to the non solubility of IUM and DMDU in that solvent.

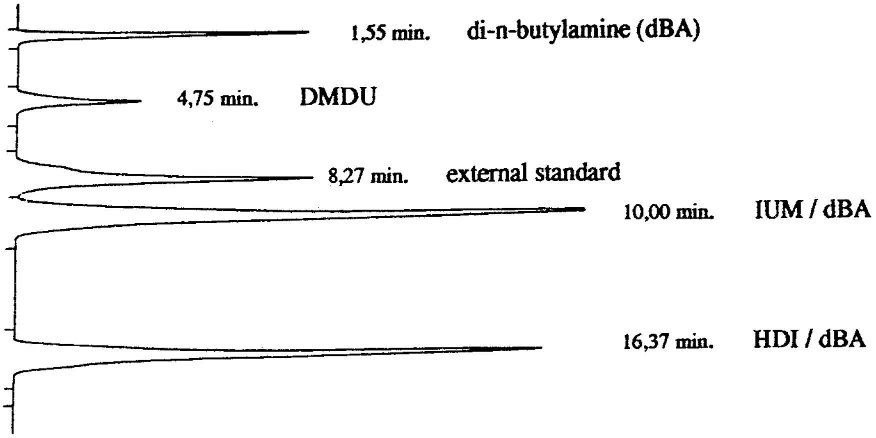


Figure 2 : HPLC chromatogram of reaction mixture blocked by di-n-butylamine (dBA)

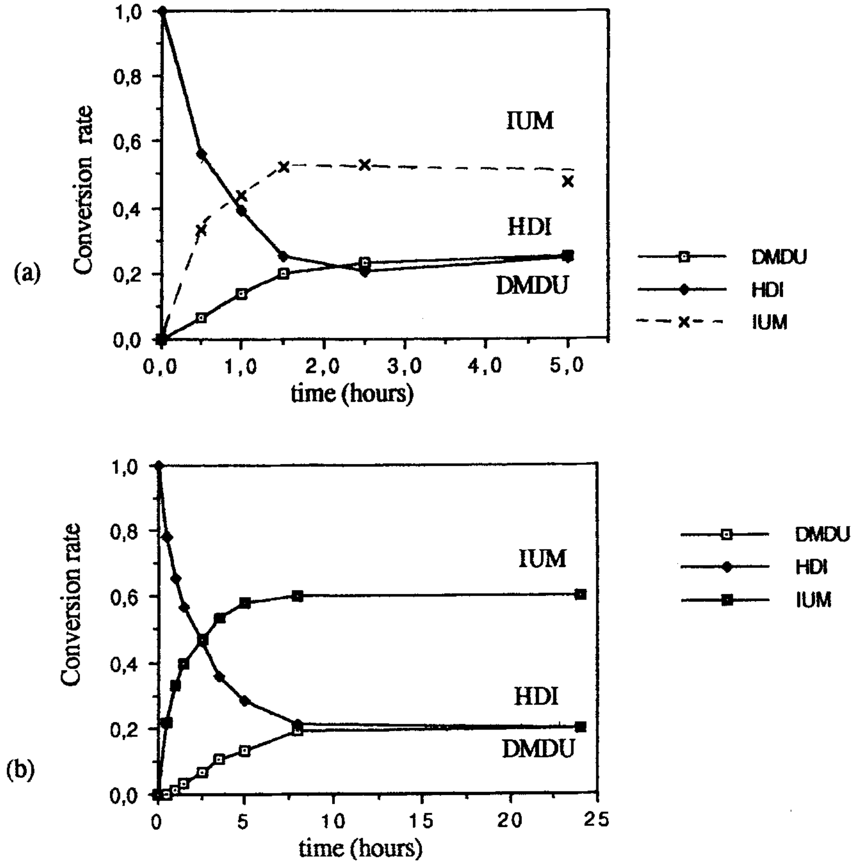


Figure 3 : Kinetics of the reactions : (a) in toluene, (b) in hexane

The purification of IUM depends on the solvent which is used :

* with hexane, the white precipitate is washed several times with small portions of hexane in order to remove unreacted HDI without removing IUM partially soluble in that solvent. This purification procedure provides a mean of preparing easily and quickly IUM with 71 % mol/mol of purity (DMDU 21%, HDI 8%).

* with toluene, even if the reaction mixture is soluble in that solvent at room temperature, DMDU precipitates at -18°C and then is removed by filtration. After distilation of toluene from the filtrate under vacuum , the residue, set at -18°C, is washed many times with hexane in order to remove the unreacted HDI. Further removal of hexane yields a white wax which is mainly the desired IUM (purity 94% mol/mol).

2) Applications

Since carbon fiber is a brittle material, fibers are often subjected to sizing treatment to improve their handleability. However, the compatibility between matrix and sizing agent is also required. Indeed, within our participation in the development of a new process for polymerizing carbon fiber/acrylic matrix composite materials cured by electron beam, the use of an intermediate modulus fiber (IM7G, ***Hercules INC.***) sized with an epoxy compound lead to a relatively low interlaminar shear strengh : that means that this epoxy sizing agent affects unfavourably composite properties. In order to improve the interfacial adhesion, the synthetized compound - (6-isocyanato n-hexyl)carbamoyloxyethylmethacrylate - has been used as sizing agent : compatible with acrylic matrix and electron beam curing process, it is further more able to react with functional groups on the surface of the fibers.

First, sizing treatment has been carried out by immersion of an unsized IM7 fiber in a bath containing a 0,75% solution of the sizing agent in methylenechloride, and a catalyst of the alcohol/isocyanate reaction (dibutyltin dilaurate). Then, fiber went through a 50°C oven before being wound again. Sizing rate measured by soxhlet extraction or pyrolysis (NFT 25-104) under N_2 atmosphere at 450°C were equivalent to industrial sized fibers (between 0,5 to 1 %).

After impregnation of sized fiber by the acrylic resin, composite materials were made by filament winding, then cured by electron beam.

Interlaminar shear strength test using the 3 points flexion procedure (ASTM 2344-7)

Fiber/Matrix	Sizing treatment			Composite	
	Catalysis in the sizing solution	temperature of the oven	Drying time in the oven	Interlaminar shear strength (MPa)	process of polymerization
IM7 / M_1 IM7G / M_1				26 ± 2 32 ± 0,5	electron beam
IM7 with synthetized-sizing-agent (IUM) / M_1	yes no	50°C	17,5s	50 ± 2 43 ± 1,5	electron beam
	yes	220°C	70s	60 ± 2	electron beam
	yes	50°C	17,5s	49 ± 2	Thermal
IM7G / M_2				62 ± 3	Thermal

with M_1 : acrylic-urethane resin and M_2 : epoxy resin ; "G" : epoxy sizing-agent

Table 1: Mechanical composites properties

was selected to evaluate adhesion at the fiber-matrix interphase, as a function of different parameters of the sizing treatment (table. 1).

The level of interlaminar shear strength (ILSS) is far higher when using fiber sized with our acrylic-isocyanate compound, compared to unsized fiber (IM7) or epoxy sized fiber (IM7G). An increase in temperature and in the drying time in the oven, during sizing treatment, enabled us to optimize mechanical composites properties. Finally, the best improvement was obtained in the case where the catalysis of the alcohol/isocyanate reaction is added in the sizing solution; this result may be due to the chemical bond formation between fiber and matrix, promoting increased fiber-matrix adhesion.

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