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Functionalization of a multiepoxy resin by methacrylic compounds and study of its thermal properties

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Summary : Methacrylation of triglycidyl triphenyl methane (via methacrylic acid) has been done using three catalysts: dimethyl dodecyl amine (DMDA), tetrabutyl ammonium bromide (TBAB) and chromium (III) diisopropyl salicylate (Cr Dips). The reaction has been followed by epoxy colorimetric titration, CPG and ^{1}H NMR.

This study has shown the superiority of chromium catalysis because of its rapidity and ease of process.

Then, these cured products (TACTIX and methacrylated TACTIX) show homogeneous Tg values which are higher than 200°C.

INTRODUCTION

Composite matrices are very diverse, but epoxy resins are widely used, as different thermal behaviours can be obtained depending on their nature (1,2). So, with diglycidylether of bisphenol A, we obtain materials which resist about 150°C heating continuously and with tetraglycidyl methylene dianiline, performances reach 200°C. However, these resins, cross-linked by diamines, are fastidious to manipulate and control (long thermal cycle, problem of toxicity) (3).

Other matrices have been used, like acrylic resins in which cross-linking is obtained by radical or photochemical initiation (4), and recently, new composite materials have been cross-linked with Electron Beams going more deeply inside (5). Nevertheless, in this case, Tg values of these materials are too low (about 100°C).

So, our research aimed in obtaining resins which are cross-linked by radical route (such as UV or electron Beam) easier than by chemical way (using diamines as hardeners), and having high Tg values.

We attempted methacrylation of epoxy resins having high Tg to obtain this kind of materials. The reaction has already been realized on epoxy resins (DGEBA) (6), silicon resins (7) and polyurethannes (8). Also our team, expert in telomers (9), has prepared multiacrylic telomers by this route (10,11).

The epoxy-acid reaction need the use of catalysts: amines and ammonium salts (12), other bases than amines (13) and metal derivatives: tin (14), iron (15) and above all chromium (16).

These catalysts not only accelerate the reaction, but they also modify the ratio of secundary compounds: α and β additions, etherification, esterification, hydrolysis, and so on... (17).

Remarkable sudies on reaction mechanisms have been carried out (18), but it's not the purpose of our study.

We present here an example of triglycidyl triphenyl methane (or TACTIX) methacrylation and we compare the final product properties with those of products directly obtained with diamines.

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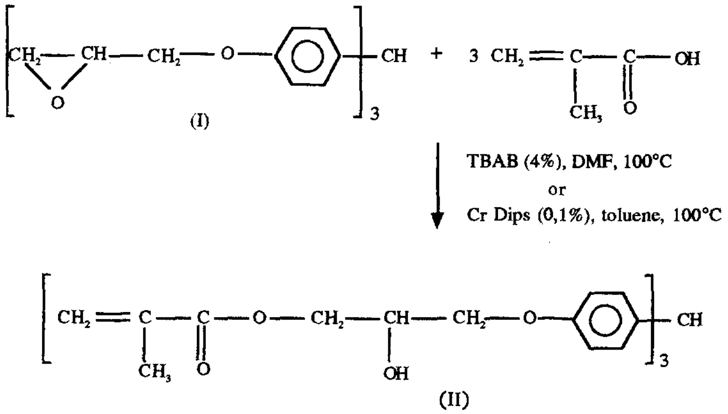
RESULTS AND DISCUSSION

The reaction is the following:



Three catalysts have been used:

-dimethyl dodecyl amine DMDA
-chromium (III) diisopropylsalicate (Cr Dips)
-tetrabutylammonium bromide (TBAB)

Experiments have been carried out in an inactinic vessel with hydroquinone (200 ppm) to inhibit photochemical and thermal polymerisations.

The reaction pathway has been analysed by different technics:

- first : titration of epoxy functions by colorimetry
- second : following the disappearence of product (I) and appearence of product (II) by GPC
- and third : following the evolution of CH_2 group of epoxy by ^{1}H NMR.

We have compared three catalysis methods:

* with DMDA (10% molar with regard to epoxy) (19); the reaction is realised at 60°C in THF. Determinations at 10, 20, 40 and 80 hours show the presence of epoxy groups.

* with TBAB (4% molar with regard to acid) (20); the reaction is realized in DMF at 100°C during 70 hours. After this time, all epoxide has reacted.

* with Cr Dips prepared according to Le BLainveaux (21) (0,1% weight of total reagents). The reaction is realized in toluene where reagents and catalysts are both soluble. The evolution of the reaction at 100°C is shown on figure 1.

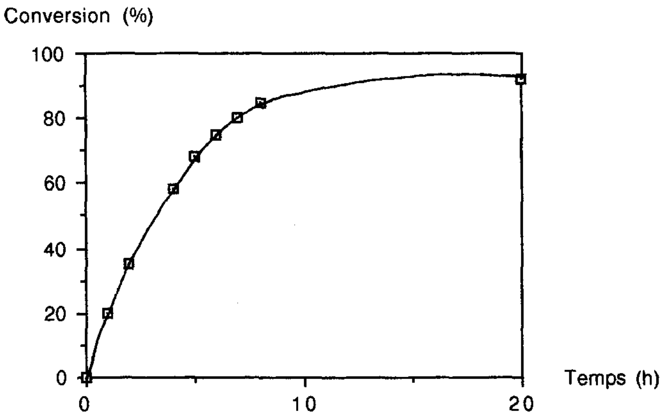


Figure 1: Time dependance of TACTIX methacrylation, catalysed by Cr Dips

Accordingly, after ten hours, 85% of epoxy has reacted.

These experiments show the superiority of Cr Dips catalysis, but also the efficiency of TBAB.

However, the purification of the reaction products obtained with Cr Dips being easier, we have prefered this catalysis.

It is interesting to compare by ^1H NRM the two spectra of product (I) (figure 2) and methacrylated product (II) (figure 3).

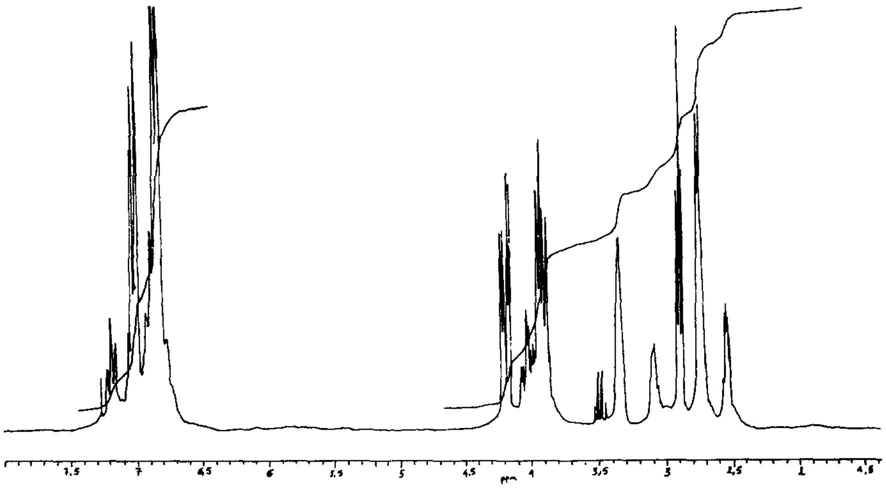


Figure 2: NMR 1H spectra 250 MHz of product (I)

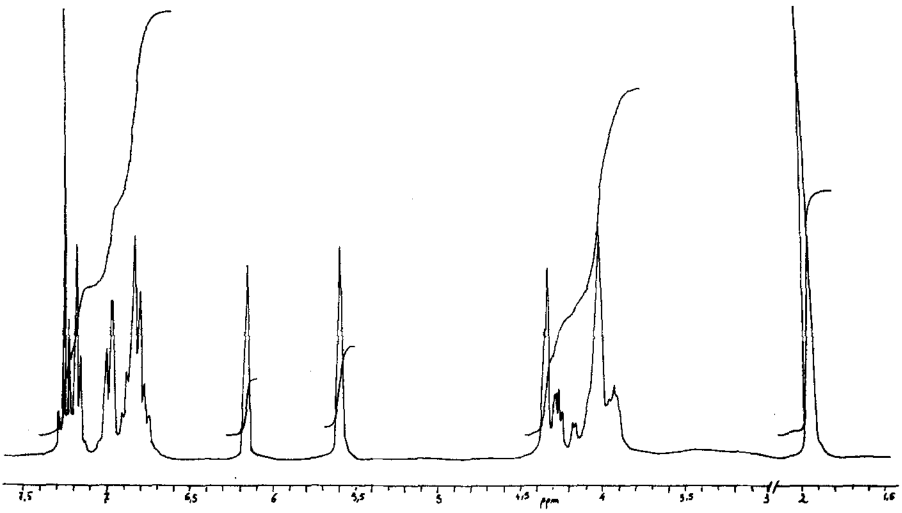
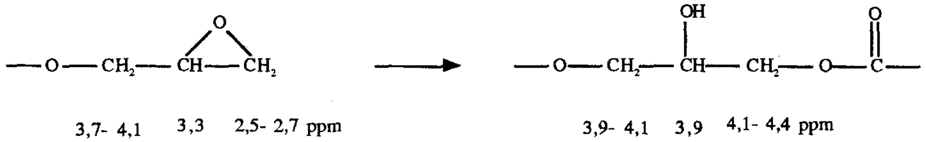


Figure 3: NMR 1H spectra 250 MHz of product (II)

Characteristic peaks of the methacrylic part appear (CH_3 at 2 ppm and two singlets at 5,5 and 6 ppm). Supplementary, we can perfectly follow the evolution of glycidyl group into glyceric group



The total disappearence of peaks at 3 ppm shows obviously that the epoxy groups have disappeared.

Curing of TACTIX (I) is realized with diamino diphenyl sulfone (DDS) or with diethyl toluene diamine (DETDA) according to the thermal cycle: one night at 80°C, one hour at 150°C, two hours at 175°C, two hours at 200°C and two hours at 225°C.

Curing of methacrylic compound (II) is realized with Trigonox C (tertio butyl peroxy benzoate) (2,5% weight), and with reactive diluent to modify the resin viscosity.

Two diluents were used: N-vinyl pyrrolidone (NVP) and hydroxy methyl methacrylate (HEMA).

A simplified thermal cycle was chosen: 14 hours at 65°C, 4 hours at 80°C and 12 hours at 130°C.

For the methacrylic resins, we have also tested cross-linking with UV irradiation (with 2-hydroxy-2-methyl-1-phenyl propane ' one = DAROCUR 1173) and with electron beam (15 Mrads) without catalyst. In both cases, NVP is used as reactive diluent.

After cross-linking, we obtain an orange colored material, and we have studied its thermal properties with DMA. Tg are given in following table:

Cross-linking	Analysis method	ducissor or reactive diluent	Tg (°C)
Curing of (I)	TMA	DDS	205
with amines	TMA	DETDA	260
Curing of (II)	DMA	NVP	210
with trigonox C	DMA	HEMA	225
EB of (II)	TMA		210
	DMA		180

Tableau 1: Tg of the materials cross-linked by diverse routes

TMA = thermo mechanical analysis
DMA = dynamic mechanical analysis

Moreover, we notice that thermal degradation of all samples occurs between 390°C and 400°C.

In UV, the samples which are spread on aluminium sheet present a bad adhesion on metal, but they have a very good resistance to methyl ethyl ketone and a great hardness.

In conclusion, we can state that the introduction of a methacrylic group doesn't reduce thermal properties of these resins.

Moreover, this group offers a very wide flexibility of use and a lot of methods of cross-linking to lead to matrices used in composites.

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