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Polymer 44 (2003) 3795–3801

polymer

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Glycolysis of epoxide-amine hardened networks. I. Diglycidylether/aliphatic amines model networks

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Received 17 October 2002; received in revised form 31 March 2003; accepted 17 April 2003

Abstract

Epoxide-amine hardened networks are high performance materials in composites, coatings and adhesives area. Solvolysis is an efficient method of polymer waste valorisation, particularly for fibre-reinforced composites, allowing recovery of inorganic parts (fibres, charges, metals), whereas the matrix yields depolymerization products which may be recycled in useful raw materials for the chemical industry.

However, the curing of epoxides with amines results from non-reversible condensation reactions, and then, the controlled depolymerization by chemical reactives seems to be impossible.

We have found that the networks from diglycidylether of bisphenol-A (DGEBA) cured with polyamine may be decomposed by glycols, in relatively mild conditions, leading to 'liquefaction' of the matrix. A solvolytic cleavage of ether linkages, originally present in the DGEBA molecular structure, has been identified. Apparently, the reaction is a transetherification one. Depolymerization products are, for a part, aromatic hydroxyl terminated low molecular weight compounds.

Keywords: Epoxy resins; Glycolysis; Transetherification

1. Introduction

Epoxy resins are widely used as adhesives, coatings, encapsulants and also in material area as matrix for high performance fibre-reinforced composites. The epoxies may be cured by several types of reactants, along them polyamines are an important class. Once fully cured, the highly cross-linked three-dimensional networks have strong adhesive and thermomechanical properties.

However, the recycling of wastes of such thermosets is very difficult, because of the inherent infusibility and insolubility of the structure. Moreover, frequently, the composite materials mostly consist in inorganic parts (reinforcing fibres, metals, fillers).

The known recycling processes [1] are not fully satisfactory: mechanical comminution leads to fillers/short fibres mixtures, with poor reinforcing properties. Efficient destruction of the organic matrix may be obtained either from thermolysis processes but with a poor value of the decomposition products or from incineration processes but with considerable non-combustible residues. In both the cases, a fibre mechanical weakening [2] is observed and a risk of toxic gaseous emission is present.

Alternatively, two streams of valuable matters could result from an efficient solvolysis process of the organic matrix: on the one hand the reinforcing fibres (and other inorganic parts) and on the other hand the depolymerization products.

Solvolysis (chemical depolymerization) consists in the breaking of cleavable bonds, present in the backbone of step-growth polymers, by solvolytic processes such as alcoholysis, glycolysis, hydrolysis and aminolysis. Solvolysis is widely used [3] for the valorisation of thermoplastic wastes. Solvolysis processes of PET bottle wastes are well known [4] and industrialized, leading back to monomers or specialty products (polyols, unsaturated polyesters, alkyds, plasticizers,…). Such solvolytic processes may be theoretically extended to three-dimensional networks. But, the feasibility for fully cured thermoset is not assured.

In our laboratory, we have found [5,6] that the ester linkages of a bisepoxide (diglycidylether of bisphenol-A (DGEBA)), cured with a diacid anhydride, are cleaved by glycolysis. Diethyleneglycol (DEG) is an efficient solvolytic

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doi:10.1016/S0032-3861(03)00324-0

reagent. When a transesterification catalyst—titanium(IV) *n*-butoxide (TBT)—is used, the resulting mixture essentially contains the monomeric species. The TBT catalysed glycolysis of 70% glass fibres/epoxide-anhydride composites allows the recovery of organic free long fibres, whereas the liquid depolymerization products may be converted to useful industrial raw materials (polyols, unsaturated polyester resins,…).

We have also treated, within the same experimental conditions, other composites with a DGEBA—aromatic diamine cured matrix. Surprisingly, despite no esters bonds are present in such structures, a destruction of the matrix occurs, leading to the release of the fibres. One of the linkages found in these network is ether type. The cleaving reaction could be a transetherification: $R_1OR_2 + R_3OH \leftrightarrows R_1OR_3 + R_2OH$. These reactions are well known, but for some particular structures: acetals and vinyl, benzyl or allyl ethers.

Exchange reactions are obtained by treating allylic or benzylic ethers in monoalcohols as reactive solvents (MeOH, EtOH, iPrOH). Yields higher than 90% were obtained in the presence of cerium ammonium nitrate as catalyst [7]. Catalysis with Fe^{3+} salts [8] or p-toluenesulfonic acid (PTSA) [9,10] was also reported.

Recently, polyethers were obtained [11] by PTSA catalysed melt polycondensation of diols and difunctional monomers having methyl benzyl ether end groups, with methanol elimination. The reverse reaction occurs, by reacting the polymer with excess of methanol. Apparently, when monomers contain φ-OCH_3 structure, transetherification of the methylphenylether does not occur under the polymerization conditions (185 °C; PTSA catalysis).

Another system of decomposition of epoxy materials, printed wiring boards, was reported [12]. In these products bromobisphenols are used in the resin synthesis for fire retardancy effect. The solvolytic system associates a polar solvent, preferably *N*-methyl-2-pyrrolidone, and an alkali metal salt (preferably KOH). A cleavage of ether linkage is mentioned, but without experimental evidence. Clearly, the reaction is made easier by the presence of the electron-withdrawing Br substituents on the phenyl nuclei.

But, in our case, no particular structure where the carbocation could be stabilized is observed.

To understand the mechanism and to improve the yield of the depolymerization, we have decided to study the glycolysis of polyamine—DGEBA hardened model matrix. Triethylenetetramine (TETA, hexafunctional) and methylenedianiline (MDA, tetrafunctional) were chosen as aliphatic and aromatic polyamines.

We describe in this part I the results obtained from the depolymerization of the TETA/DGEBA model matrix by the DEG/TBTsystem. The solvolysis of the aromatic amine-cured matrix and of the composite materials will be described later in part II.

2. Experimental part

2.1. Materials

The epoxy resin is a diglycidylether of bisphenol-A (named DGEBA, diepoxide) with a low degree of polymerization (DP ≈ 0.15; $M = 374$ g/mol), supplied by Aldrich.

TETA (hexafunctional) DEG (diol) and TBT (catalyst) were used without purification. Tetrabutylammonium hydroxyde (TBAH) was a 40 wt% aqueous solution.

2.2. Synthesis of a model matrix

DGEBA (200.4 g, 1.07 mol epoxide) and TETA (28 g, 1.15 mol N–H) were mixed at room temperature. The mixture was cast to 3 mm plate. Curing reaction was conducted at room temperature during seven days, and post-curing at 200 °C for 2 h [13,14]. Disappearance of the epoxide functions was checked by FTIR (971, 916, and 775 cm^{-1}). Tg of the cured material was determined as 129 °C, from a differential scanning analysis at a heating rate of 5 °C/min.

2.3. Depolymerization of the model matrix (glycolysis)

Pieces (about $4 \times 4 \times 0.3$ cm) of the model matrix (49.9 g), DEG (250.1 g) and catalyst TBT (0.25 g) were introduced in a three-neck reactor equipped with a reflux condenser and a mechanical stirring. The system was kept, in an inert atmosphere, under reflux of the DEG (245 °C) for 14 h. Excess of DEG was then distilled under vacuum.

2.4. Post-solvolysis of PET and polyurethane foams synthesis

A glycolysat was prepared, as described above, from the model matrix and DEG. Free DEG was not distilled. The OH value (OHV) was 847 mg KOH/g.

176.5 g of PET granulate was added to 200 g of the glycolysat and the mixture was heated to reflux temperature under nitrogen atmosphere. Solid phase disappearance occurred within less than one hour, and heating was maintained during two more hours. The OHV of the resulting polyol was 503 mg KOH/g.

57.6 g of the polyol was mixed with 0.56 g of water, 0.42 g of dimethylcyclohexylamine (catalyst), 1.13 g of Polyurax SR 242 (surfactant, foam stabiliser) and 11.2 g of 1,1dichloro-1-fluoroethane (HCFC 141b, foaming agent). To this blend was added, in 10% molar excess, 85.8 g of a polymeric dicyanatodiphenylmethane (isocyanate, NCO: 31%, average functionality: 2.5) and the mixture was immediately mixed with a high-speed mixer. The mixture was poured into a box and allowed to expand freely. Characteristic foaming times were: cream time: 53 s; gel time: 83 s; tack free time: 95 s. After 3 days cure, the foam density was 38 kg/m^3 with a fine, closed cell structure.

2.5. Characterization

- Size exclusion chromatography (SEC) analyses were carried out with a Knauer SDV 100 (5 μm) column, with tetrahydrofuran elution at 0.5 ml/min and 254 nm absorbance detection. Molecular weight calibration was carried out with DGEBA samples with various polymerization degrees.
- Infra-red (FTIR) spectra were recorded on a Perkin Elmer, spectrum one, spectrometer equipped with an attenuated total reflectance crystal.
- Ultra-violet (UV) spectra were recorded on a Varian CARY 300 spectrophotometer. Spectra were obtained in a dual-beam technique with solvent (THF/ethanol, 1/2 v/v) in the reference compartment and with an optical path of 0.021 cm. In order to determine the concentration of the formed phenol group, a slight excess of TBAH was added to the solution to analyse. In such conditions, the signal of phenol shifts to about 300 nm. Then the concentration of phenol group was calculated from the difference of absorbance with and without TBAH, at 300 nm. The molar extinction coefficient (ε) was experimentally calculated from a known solution of bisphenol-A (BPA).
- NMR spectra were recorded, on a Brücker AC 200 operating at 200 MHz for ^{1}H NMR. The analyses were carried out in D_2O/DMSO d_6.
- Titrations of amines: the depolymerization products were first dissolved in tetrahydrofuran and then, diluted with ethanol. The basic substances, in THF/ethanol/-water mixture (50/95/5), were potentiometrically titrated with ethanolic hydrochloric acid (0.22 M).
- Gas chromatography: the chromatograph was equipped with a SE30 column and FID detector. DEG and BPA were esterified in acetic anhydride–pyridine mixture containing appropriate amount of internal standard and analysed as their acetate derivatives.

3. Results and discussion

3.1. Glycolysis of the model matrix

The epoxy-amine cured plate was broken into pieces of about 40 × 40 × 3 mm. The reaction was carried out under reflux conditions (245 °C) in the initial weight proportion: 500 parts DEG (to cover the pieces of matrix); 100 parts polymer; 0.5 part catalyst (TBT). After 8 h of reaction, total disappearance of the solid pieces was observed. Heating was again maintained for 6 h. Two experiments, conducted with identical compositions, gave similar results. Molecular weight distribution was investigated by SEC.

The final reaction product was called 'glycolysat'. Most of the free DEG excess was then distilled under vacuum, giving two fractions: distilled DEG and 'glycolysis product (GP)' (Scheme 1). Two different pressures were tested: 2 mm Hg (exp 2, Table 1) and 3.5 mm Hg (exp 1, Table 1). The boiler temperature was nearly constant (typically 115–120 °) during the major part of the distillation, but increased sharply at the end. The heating was stopped when the boiler temperature reached 170 °C.

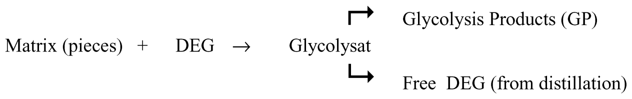
GC analysis showed that the distillate was pure DEG, whereas the GPs still contained some free DEG. The distillation performances are summed up in Table 1.

The GPs were also characterized by SEC, with UV detection, for the two experiments. Thus, only molecules containing aromatic moieties are detected. Molecular weight distribution is broad, but with a low proportion of molecular weight higher than about 2000 g/mol (exclusion volume). From the comparison of chromatograms, before and after the distillation (see Fig. 1), it is obvious that the main molecular weight is higher after the distillation step. These results seem to indicate that condensation reactions occur within the free glycol-stripping step. Although not encountered for the epoxy/anhydride glycolysis [6], the same feature is observed during the catalysed glycolysis of PET [15,16]. In this latter case, free glycol elimination within reactive conditions (high temperature, transesterification catalyst) implied polycondensation reactions until the concentrations of the different species become in accordance with the equilibria constants.

3.2. Characterization of the depolymerization products

Knowing the idealised structure of the polymer matrix (Scheme 2), different ways of cleavage of the polymer chains may be considered. A hypothesis of the cleavage of the C–N bond can be proposed. However, the percentage of nitrogen (elementary analysis) of the GP was consistent with no loss of nitrogen during the reaction. This implies that no volatile nitrogenous compounds (such as N_2 or NH_3) are produced during the depolymerization. An acid–base potentiometric titration of the GPs showed a complex curve, but similar to that of the TETA used for the synthesis. Although a precise determination of the basic nitrogenous moieties concentration was not possible, it appears unlikely that C–N linkage may be cleaved during the depolymerization.

The cleavage of the ether linkages (C–O–C) then becomes as the most envisageable reaction. This reaction between an ether function and an alcohol, giving another ether and another alcohol is known as alcoholysis of ether or transetherification.



Scheme 1. Glycolysis of the epoxy matrix.

Table 1
Distillation of the DEG excess after depolymerization

Exp	Distillation conditions	Results			
	p (mm Hg)	GP (g)	Distilled DEG (g)	GP appearance at 25 °C	Free DEG (%) (GC analysis)
1	3.5	161	439	Red viscous liquid	30.1
2	2	125	475	Solid	14.6

100 g epoxy matrix + 500 g DEG + 0.5 g TBT; 14 h reaction at 245 °C GP: Glycolysis products.

Moreover, as the ether is not symmetrical, two different cleavage ways should be envisaged (Scheme 3). A phenolic derivative is formed within the first way, whereas an alkylarylether is obtained within the second way.

The infra-red analysis of the two GPs did not enable us to conclude about the presence or not of phenol groups. Characteristic peaks of 2,2-bis(4-oxyphenyl)propane moieties (1600, 1580, 1515, 1390, 1250, 1180, 1040 and 830 cm^{-1}) and DEG moieties (1460, 1350, 1130, 930 and 900 cm^{-1}) are well present. We notice significant differences of the relative peak intensities in the oxyphenyl [17] absorbance zone (1050–1200 cm^{-1}) between our GP and unambiguously alkylarylether structures (original network or the GP of a DGEBA—anhydride hardened matrix). However, IR attribution to $-\Phi-\mathrm{OH}$ or $-\Phi-\mathrm{O}-\mathrm{C}-$ structure appears hazardous.

On the other hand, if phenolic groups are formed, UV analysis should show their presence. Phenolic groups are known to show a bathochrom and hyperchrom shift by adjunction of TBAH according to phenate ion formation. This property was used to identify and quantify them [18]. The UV spectrum of GP is shown in Fig. 2. The presence of phenol group is undoubted. The concentration of phenol group can be calculated by the relation $C_{\Phi-\mathrm{OH}} = \Delta A/\varepsilon l$ with ΔA the difference of absorbance at 300 nm, with and without TBAH. ε was determined by standardization from pure BPA solutions. The results are shown in Table 2. In the two cases, the calculations give the yields of formation of phenol group higher than 75%. The first way, presented in Scheme 3, seems then favoured.

To confirm and also quantify the formation of a phenolic structure, NMR analyses of the GP were carried out (Fig. 3, Table 3). The aromatic area of the spectrum shows the presences of the two types of aromatic protons: $\varphi-\mathrm{O}-\mathrm{C}-$ and $\varphi-\mathrm{OH}$. Indeed, by comparison between this spectrum and the spectra of model compounds (BPA and DGEBA) (Table 4) we may identify each signal. The calculations from the integration curves of each signal give a yield of 45% of formation of phenol groups, much lower than estimated from the UV results. We think that NMR analyses are more reliable than the UV one, because they are not dependent of standardization with a similar but not identical compound.

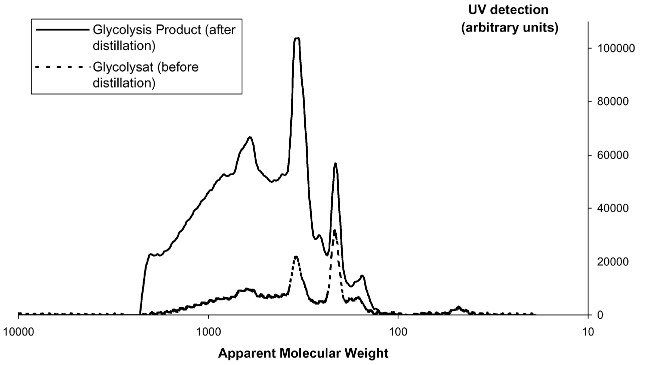


Fig. 1. SEC of glycolysat and GP (UV detection).

3.3. Separation of phenols from the glycolysis product

A separation of the phenolic compounds was then carried out by liquid–liquid extraction. Simple phenols are extracted with organic solvents from neutral or acidic aqueous phase (molecular form), but not from basic phases (ionised phenate form). For this, the GP of the experiment 2 was dissolved in dichloromethane and then extracted with aqueous solutions of sodium hydroxide. Next, the aqueous phases were acidified with hydrochloric acid. Finally, a last extraction, with dichloromethane, of the turbid resulting solution enabled to obtain, after solvent evaporation, a crystalline material, but in very low amount (0.3 g for 6 g treated). This product was found to be BPA: IR spectra identical to authentic BPA and melting point 146–148 °C (compared to MP = 149–151 °C for BPA).

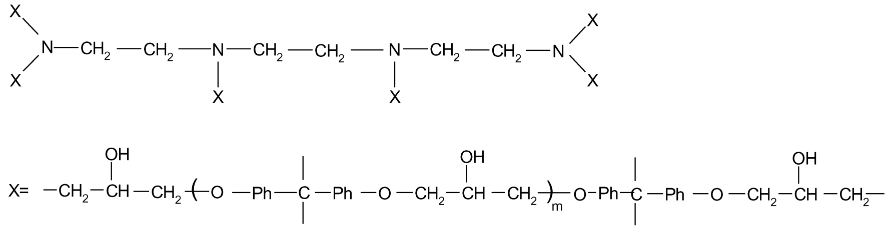
A direct GC analysis of BPA in GP from experiment 1 gave similar results: BPA = 2.8 ± 0.8 w/w%.

Thus, BPA is formed, but in low amount. The fact that only a low amount of nearly pure BPA was obtained from the extraction procedure would show that the major part of phenolic groups belongs to the phenols substituted with a long chain (only one cleavage of the BPA radical) and then, not extractable in basic aqueous solution.

Table 2
Concentration of phenol group in GPs

Exp	$C_{\Phi-\mathrm{OH,\ th}}$ [a] (mmol Φ–OH/g of GP)	$C_{\Phi-\mathrm{OH,\ exp}} = \Delta A/\varepsilon l$ (mmol Φ–OH/g of GP)	Apparent yield (%)
1	3.27	2.9	88
2	4.2	3.26	77

[a] Calculated value for quantitative way 1 reaction.



Scheme 2. Molecular structure encountered in a DGEBA/TETA cured network ($m \approx 0.15$).

3.4. Valorisation of the glycolysat

The GP, as obtained after the free glycol distillation step, is a solid or very viscous liquid material. It contains phenolic end groups, but the yield of valuable BPA is very low. It contains also aliphatic hydroxyls and, thus, it could be used as polyol in polyurethane fabrication. But the physicochemical properties are unfavourable.

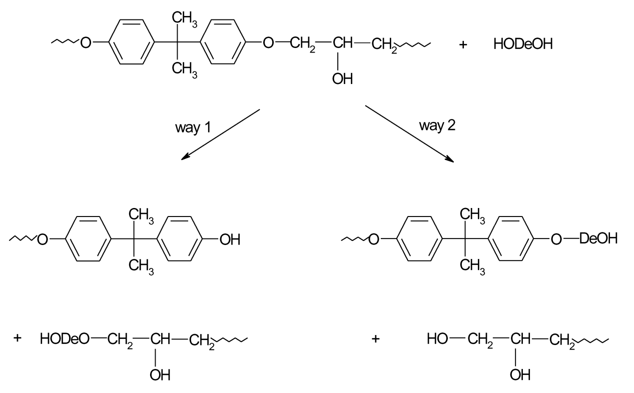
Most of the end groups in the glycolysat (i.e. before free glycol distillation step) are alcoholic hydroxyls but, mainly composed by free DEG, the hydroxyl value is much too high for polyurethane synthesis.

In an alternative approach, the glycolysat may be considered as modified DEG. So, it can be used to solvolyse PET wastes giving a polyol, ready to use for polyurethane manufacture.

Polyols from direct glycolysis of PET suffer from some disadvantages [19]:

- partial solidification at room temperature leading to a paste.
- polyol functionality equal to 2.0 leading to semi-rigid foams with limited dimensional stability.

The post-solvolysis of PET occurs readily (see experimental), with no appearance of solid phase in the resulting polyol after the room temperature storage. The obtained polyurethane foams are very rigid. Probably, some multi-functional hydroxylic molecules are present in the polyol mixture, arising from the TETA moiety.



Scheme 3. Two different cleavages of the ether linkage (De = $-CH_2CH_2OCH_2CH_2-$).

Thus, the epoxy derived structural moieties compensate the shortcomings arising from the PET derived moieties and vice versa.

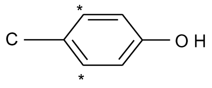
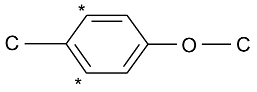
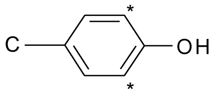
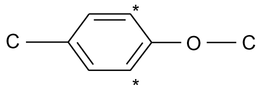
4. Conclusion

We have shown that a glycolysis of an epoxide-amine cured network is possible, leading to depolymerization products, soluble in the excess of solvent. This fact is rather surprising, even if a depolymerization of epoxy materials by 'polar solvents' was reported in a patent [20].

The cleavable linkage seems to be the alkylarylether originally present in the DGEBA molecular structure. Phenolic groups are formed. The ether group appears sufficiently reactive to enable a transetherification reaction with DEG at boiling temperature (245 °C).

Useful polyols result from glycolysis of mixed wastes of

Table 3
Attribution of the ^1H NMR spectrum (200 MHz) of GP

Peak	δ (ppm)	Attribution
a	1.5	$-C(CH_3)_2-$
b	2.4	$-CH_2-N<$
c	2.5	Moving peak
d	2.64	DMSO
e	3.44	DEG linked
f	3.85	$-CH_2-CH(OH)-CH_2-$
g	4.6	$-OH$
h	4.8	H_2O (DMSO)
I	6.61 6.65	
j	6.78 6.82	
k	6.95 6.99	
l	7 7.12	
m	9.3	$-OH$ (BPA)

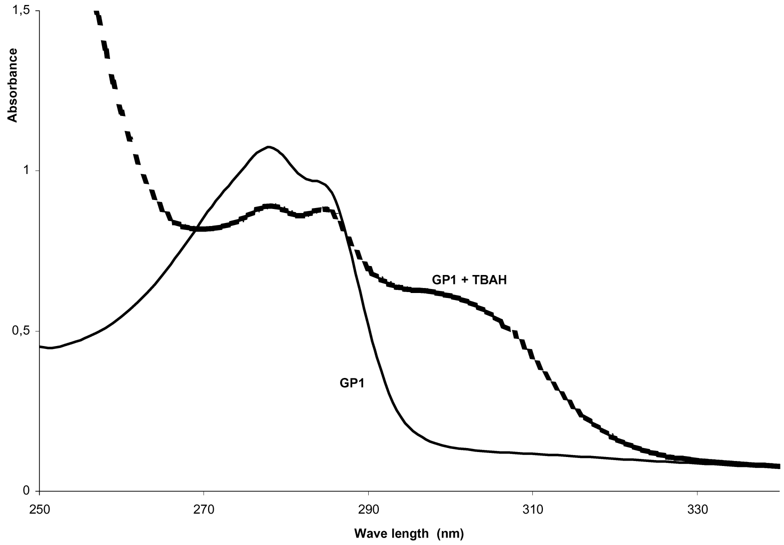
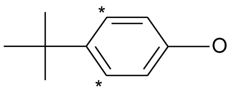
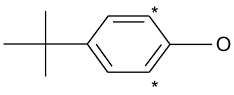


Fig. 2. UV spectra of GP1 with and without addition of TBAH (solvent = THF/ethanol, $C = 10.1$ g/l and 1 = 0.021 cm).

Table 4
^{1}H NMR shift of aromatic protons of DGEBA and BPA

δ (ppm)		
DGEBA (φ–O–C)	6.78; 6.81	7.1; 7.12
BPA (φ–O–H)	6.6; 6.65	6.95; 6.99

the epoxy material and PET. Unlike to the polyols arising from the sole PET glycolysis, they have good storage stability (no deposition of solid fractions) and they lead to very rigid polyurethane foams with conventional foaming procedures.

Unlike classical procedures of aromatic ether cleavage (hot concentrated hydrohalogenated acids; very strong bases), the process operates in relative mild conditions (DEG at boiling temperature). Thus, in a composite treatment, the glass fibres should not be damaged. Moreover, this procedure of ether cleavage by glycolysis opens a

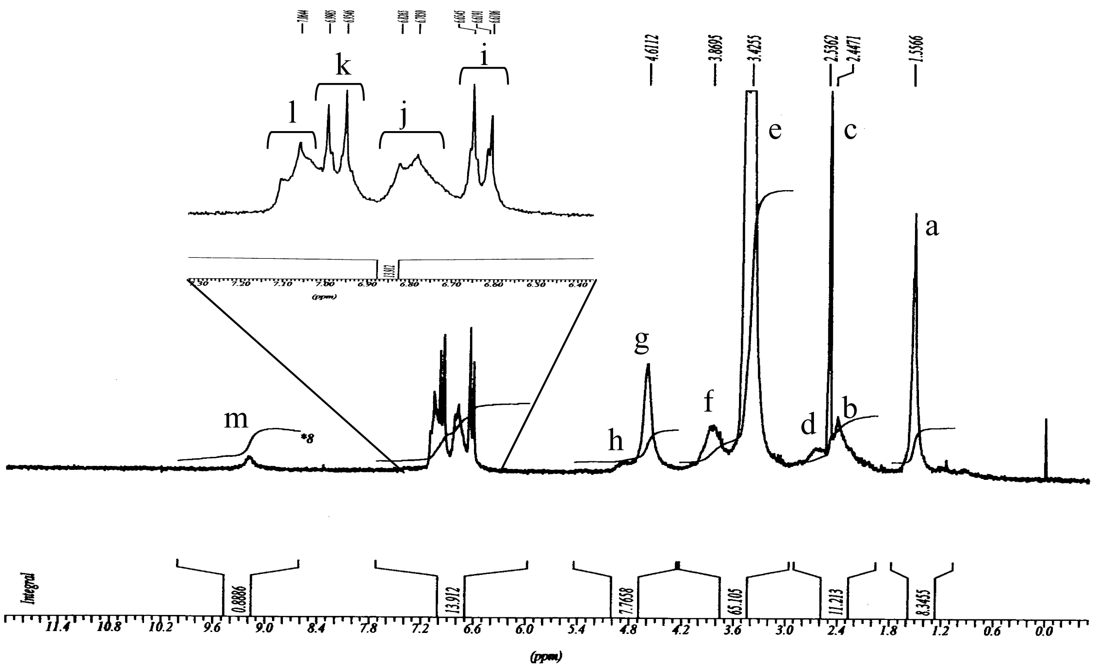


Fig. 3. ^{1}H NMR spectrum (200 MHz) of GP (Solvent: DMSO d_6 + TMS).

way for the recycling of all epoxy materials made from glycidylethers whatever the curing agent used.

For better understanding and control of the reaction, we are now working with non-macromolecular model compounds.

Acknowledgements

The presented results are a part of the doctoral thesis of Khalid El Gersifi, which was carried out in concertation and with financial support of Electricité de France (Centre National d'Equipement et de Production d'Electricité) and the Agence de l'Environnement et de la Maîtrise de l'Energie.

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