

Reversible/irreversible networks formation in thermally removable adhesive

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Abstract

The ability to separate adhesive bonded assemblies for structural applications without causing damage to the substrates is clearly very desirable. Thermally removable adhesive by incorporating thermally reversible furan–maleimide Diels–Alder adducts have also synthesized. They form at low temperature and dissociate at higher temperature in a low modulus epoxy adhesive formulation. The debonding mechanisms of dismantlable adhesives are mainly based on changes in the bulk properties of the adhesive, making competition between strong bonding and easy debonding by controlling the cohesiveness of the adhesive. Unwanted side reactions cause the formation of crosslinks that are not reversible in nature, thereby reducing the self-healing performance. Against this background, an epoxy-amine adhesive with thermally responsive Diels–Alder linkages has been prepared. Precisely, Bisadduct epoxy was synthesized by Diels–Alder cycloaddition from furfuryl glycidyl ether as diene and hexamethylene bismaleimide as dienophile. This last was synthesized from reaction between amino groups of hexamethyldiamine and anhydride group from maleic anhydride. Then, the physico-chemical properties of the bisadduct epoxy were performed during heating and cooling cycle by FourierTransformed Infra-Red spectrometry, differential scanning calorimetry and dynamic rheometry. Ultimately, the same methodology has been applied on the bisadduct epoxy cured with isophorone diamine. Particular attention is given to the counterbalance between reversible, irreversible chemical and physical reactions on the macromolecular dynamics in the thermoset network during the heating and cooling steps.

Key Words: furan–maleimide Diels–Alder adducts synthesis, reactive blend, reversible/irreversible networks, thermal and thermomechanical analyses

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I. Introduction

In recent years, the recyclability of adhesive bonding materials is one of the solutions to mitigate global pollution. An effective way of meeting this demand is to develop dismantlable adhesives that can be easily debonded using external stimuli.

Epoxy/amine-based adhesives possess a combination of many interesting and desirable characteristics such as excellent chemical resistance, electrical insulation properties, strong adhesion and heat resistance, as well as good mechanical properties [1]. They are chemically compatible with most substrates as metals and ceramics.

Chemical reaction between amines and epoxide groups leads to a covalently crosslinked network formation controlled by temperature. Upon curing, epoxy resins form insoluble and infusible crosslinked networks, which are very difficult or impossible to thoroughly remove without introducing damage to the substrates. To circumvent this problem, thermally or chemically degradable linkages must be incorporated into the epoxy resin structure in order to allow the degradation of the crosslinked polymer network and removal of the adhesive.

The Diels–Alder (DA) reaction is thermoreversible and provides the advantages of atom economy, functional group tolerance, and high yields ([2],[3],[4],[5],[6],[7]). At low temperatures, the diene and dienophile reactive functions ([8],[2]) react together via DA reaction to give the so-called adduct that dissociate via retro Diels–Alder (rDA) reaction at higher temperature. After dissociation, diene and dienophile are regenerated ([3],[4],[9]). In particular, Diels–Alder chemistry has been incorporated into epoxies ([4],[10],[11]).

However, unwanted side-reactions are often encountered in such combinations, particularly in the case of epoxies. Such side reactions cause the formation of crosslinks that are not reversible in nature, thereby reducing the self-healing performance ([6],[9],[12]). So, contact between maleimides and free amines should be avoided to prevent a Michael addition reaction that can occur even at room temperature [13].

In this work, the commercially available Furfurylglycidyl ether epoxy resin (FGE) was modified by synthesized Hexamethylene bismaleimide (HMBMI) to prepare a new epoxy resin called EPOBAD. IPDA amine hardener is used to obtain a polymeric network. In our case, amine/maleimide Michael reaction is a one of side encountered reaction. The contribution of this work is to show what is the impact of the kinetical competition between epoxy-amine crosslinking in one hand and Michael reaction in the other hand on the obtained material when they both proceed at the time, a situation which is not studied in the other works implying Diels-Alder and epoxy-amine chemistries.

II. Material And Methods

1.1. Chemicals

Reagents used for the synthesis of Hexamethylene bismaleimide (HMBMI) are 1,6-Diaminohexane (HMDA, CAS 124-09-4, purity>98%) purchased from Acros Organics, and Maleic anhydride (CAS 108-31-6, purity>99%), Zinc acetate ($ZnAc_2$), Triethylamine (TEA, purity $\geq 99.5\%$), Acetic anhydride (AA, purity >99%) and anhydrous Diméthylformamide (DMF, purity>99.8%), which were provided from Sigma Aldrich.

HMBMI was combined with 2,3-Epoxypropyl 2-furylmethyl ether named furfuryl glycidyl ether (FGE, CAS 5380-87-0, purity>96%) obtained from Sigma Aldrich, for the synthesis of the thermoreversible epoxy resin (Epoxyde bis adduct EPOBAD). 5-amino-1,3,3- trimethylcyclohexanemethylamine, also known as Isophorone diamine (IPDA, CAS: 2855-13-2; purity $\geq 99\%$) with a molecular weight of $170.33 \text{ g}\cdot\text{mol}^{-1}$ was purchased from Sigma Aldrich and used as hardener. Its composition, a mixture of cis (76.1%mol) and trans (23.1%mol) stereoisomers was determined by $^1\text{H-NMR}$ analysis in D_2O . All reagents were used without purification. Chemical structures of commercially available FGE and IPDA are given in following scheme (

Figure 1):

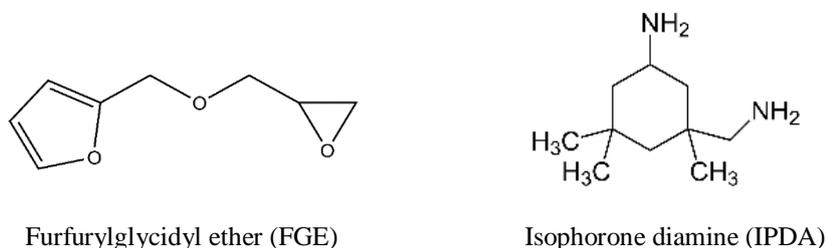


Figure 1 : Chemical structure of Furfuryl glycidyl ether (left) and Isophorone diamine (right)

1.2. Methods

1.2.1. Nuclear magnetic resonance liquid ($^1\text{H-NMR}$)

$^1\text{H-NMR}$ spectra were recorded on a Bruker Avance III spectrometer operating at frequency 400 MHz. We are in a liquid NMR setup for the entire study, so this is proton NMR. The solvent used is deuterated DMSO (d_6 -DMSO) to which we added TMS for the reference peak at $\delta = 0 \text{ ppm}$. The chemical shifts were in part per million (ppm), where (s) means singlet, (d) a doublet, (dd) a doublet of doublet, (m) a multiplet and (br) a broad signal. This method was used to verify the purities and chemical composition of our products (HMBMI and EPOBAD).

1.2.2. Fourier Transformed Infrared (FTIR)

The exact nature of the compounds formed at the different stages of the chemical reaction was investigated by Fourier Transform Infrared (FTIR) Nicolet Is50 spectrometer, in an Universal Attenuated Total Reflectance (ATR) mode equipped by heating plate. The chemical absorption spectra of samples by direct contact on the instrument diamond surface are registered in the range $4000\text{--}500 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} by registering 32 scans.

1.2.3. Differential Scanning Calorimetry (DSC)

DSC experiments were registered using TA instruments Q200® differential scanning calorimeter under a nitrogen atmosphere, with a flow at 50 ml/min as gas. These DSC analyses were firstly performed on EPOBAD prepolymer, FGE and HMBMI molecules. Then, the EPOBAD/ IPDA hardener reaction were monitored at 3°C/min. This system allowed us to follow the crosslinking and the thermoreversibility of the epoxy amine system.

1.2.4. Thermomechanical analyses

The thermomechanical properties of EPOBAD prepolymer, then EPOBAD/IPDA system during curing were performed using a stress-controlled dynamic rheometer AR2000Ex from TA Instruments equipped with cup-plate geometry, in which the diameter of upper plate is smaller (25 mm) than the diameter of the cup (40 mm) in order to prevent side effects. All the tests were carried out under air flow, under shear solicitation and in the viscoelastic linear domain, determined previously from dynamic strain sweep analyses. Frequency sweeps analyses in shear mode on EPOBAD/IPDA were also performed in cup/plate configuration.

1.3. Synthesis of chemicals

1.3.1. Synthesis of Hexamethylene bismaleimide (HMBMI)

HMBMI was synthesized from reaction between amino groups of HMDA and anhydride group from maleic anhydride. The method employed is the slightly modified two steps procedure described by Balasfalvy [1], in which author replaced classical Nickel acetate by non-toxic catalysts. To produce HMBMI, Zinc acetate was chosen as catalyst.

The synthesis proceeds in two steps. In the first step, amino groups react with anhydride ones by nucleophilic attack to give maleamic acid functions. The maleimide groups are formed in the second step by cyclic dehydration of maleamic acid functions in the presence of acetic anhydride and zinc acetate as described in Supporting Information (Figure S1).

The light brown obtained solid which synthesis is described in Supporting information was characterized by FTIR, ¹H-NMR analyses.

¹H-NMR (400MHz, DMSO-d₆) δ (ppm) presented in Supporting Information (Figure S3): 6.99 (s, -CH-C=O, H₁, 4H), 3.37 (t, N-CH₂-CH₂-, H₂, 4H), 1.46 (m, N-CH₂-CH₂-, H₃, 4H), 1.21 (m, N-CH₂-CH₂-CH₂-, H₄, 4H). FTIR (cm⁻¹), presented in Supporting Information (Figure S2): 3189-3110 (νC_{sp2}-H), 2850-2950 (νC_{sp3}-H), 1690 (νC=O), 1130 (νC-N-C), 840-700 (δC_{sp2}-H). DSC: mp= 140°C; T_{cr}=223°C.

FTIR spectrum of HMBMI displayed the characteristic maleimide C=O stretching and C_{sp2}-H bending absorption bands at respectively 1690 cm⁻¹ and 840 and 695 cm⁻¹. No remaining absorption band that could be assigned to maleic anhydride C=O symmetric and asymmetric stretching vibration at around 1780 cm⁻¹ was observed suggesting the success of the anhydride ring opening.

In ¹H-NMR spectrum, the appearance of the peak at 7 ppm corresponding to H₁ proved the presence of maleimide functions. Furthermore, no peak at around 1 ppm corresponding to protons of amino functions of HMDA was observed, meaning that no HMDA remains. As there is no peak indicating the presence of maleamic acidic functions, it is possible to conclude that cyclic dehydration was complete. Then, the functionality of HMBMI controlled by ¹H-NMR is 2, and its molecular weight is 277.43g.mol⁻¹.

1.3.2. Synthesis of DA bisadduct (EPOBAD)

Bisadduct EPOBAD was synthesized by Diels-Alder cycloaddition from FGE as diene and HMBMI as dienophile as explained in Supporting Information (Figure S4).

A slight excess of diene in regards to equifunctionality between diene and dienophile functions was employed in order to achieve the total consumption of maleimide functions. The reaction was conducted in bulk by first mixing reactants at high temperature then cooling to room temperature, and led to a dark brown viscous oil. The synthesis protocol is described in Supporting information.

¹H-NMR (400MHz, DMSO-d₆) δ (ppm) presented in Supporting Information (Figure S6): 6.54-6.49 (m, -HC=, H_{5,6exo}, 4H_{exo}), 6.43-6.32 (m, -HC=, H_{5,6endo}, 4H_{endo}), 5.26 (m, -HC-CO, H_{7endo}, 2H_{endo}), 5.09 (d, -HC-CO, H_{7exo}, 2H_{exo}), 3.14 (m, -CH-, H_{8,9endo}, 4H_{endo}), 3.03-2.90 (dd, -CH-, H_{8,9exo}, 4H_{exo}), 3.10 (m, -CH₂-CH-CH₂, H₂, 2H), 2.71-2.54 (m, -CH₂-O-, H₁, 4H), 1.40 (m, -CH₂-, H₁₁, 4H), 1.17 (m, -CH₂-, H₁₂, 4H). FTIR (cm⁻¹), presented in Supporting Information (Figure S5): 2850-2950 (νC_{sp3}-H), 1696 and 1776 (νC=O), 1400 (νC-N-C), 1185(νC-Oadduct), 915 (νC-Oepoxyde)

The appearance in FTIR spectrum of the specific C=O and C-O absorption bands of DA adduct at respectively 1776 and 1185 cm⁻¹ and the disappearance of C-H absorption bands at 840 and 695

cm⁻¹ from HMBMI proved that the reaction was achieved. ¹H-NMR spectrum confirmed the absence of protons of maleimide ring at 7ppm and exhibited characteristic peaks of adduct in particular at 6.6-6.3 ppm due to signals of protons H_{5,6} belonging to the cycle. The two endo and exo forms of DA adduct are well identified and the proportion determined from NMR data (SI). Thus, the adduct is a mixture containing 18,8%mol and 81,2% mol of endo and exo form respectively. Moreover, as expected, the protons signal of FGE introduced in stoichiometric excess (15%mol) are present in the spectrum.

The average epoxy functionality of EPOBAD determined taking account of the monofunctional FGE presence in the mixture was 1,9. Data are given in Supporting Information.

III. Results and discussion

3.1. Study of the thermal behaviour of the thermoreversible epoxy resin (EPOBAD)

3.1.1. DSC characterization of the thermoreversible epoxy resin

DSC thermogram of EPOBAD prepolymer, performed at a temperature ramp of 3°C/min from 25°C to 240°C is shown in Figure 2.

The slight endothermic signature between 25°C and 100°C may be explained by several phenomena. The first one is the evaporation of FGE present in excess - 15% molar - to guarantee the consumption of the whole maleimide functions during its synthesis (Figure S6). The Figure 2 also represents the endothermic peak of evaporation of FGE monomers.

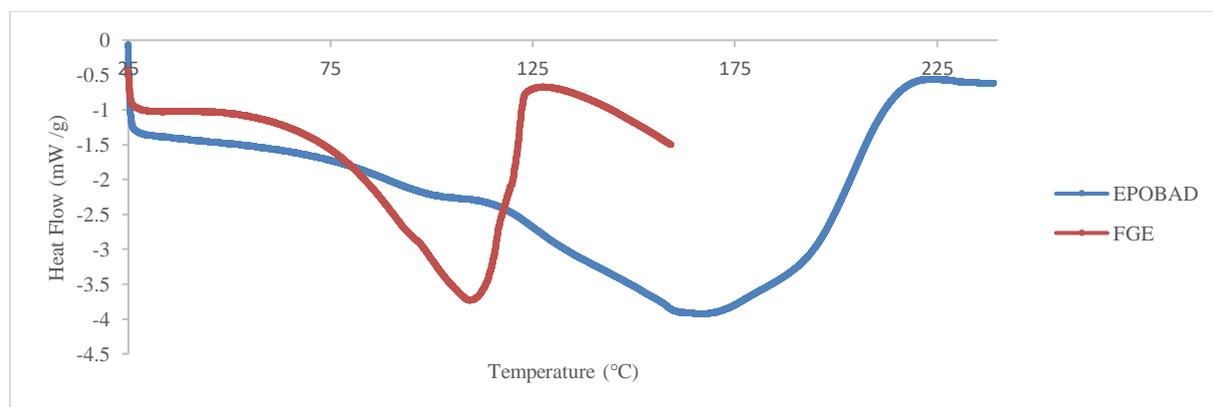


Figure 2: DSC Thermograms of EPOBAD (blue) and FGE (red), 3°C/min from 25 to 160°C, nitrogen

FGE evaporation begins around 40°C to have a maximum kinetics rate around 80°C with a maximum endothermic evaporation peak close to 110°C and ends around 125°C. The gap of evaporation temperature clearly matches the first slightly endothermic phenomenon between 40°C and 100°C observed on the thermal behavior of EPOBAD prepolymer. From 100°C, the first endothermic phenomenon testifies to an rDA reaction of the 18,8% adducts of "endo" conformation, less stable in temperature than adducts of "exo" conformation [14]. The following exothermic phenomenon (peak around 120° C) shows that the "endo" adducts separated by rDA reform directly into adducts of "exo" form. Then, the reactive products (HMBMI and FGE) are regenerated as all of the adducts of "exo" adducts separate between 130 and 140°C by rDA reaction leading [15]. Moreover, this last endothermic phenomenon can be partially attributed to the highly endothermic fusion of the HMBMI molecules trapped in the mixture until then and regenerated from the adducts during the rDA reaction (Figure 3).

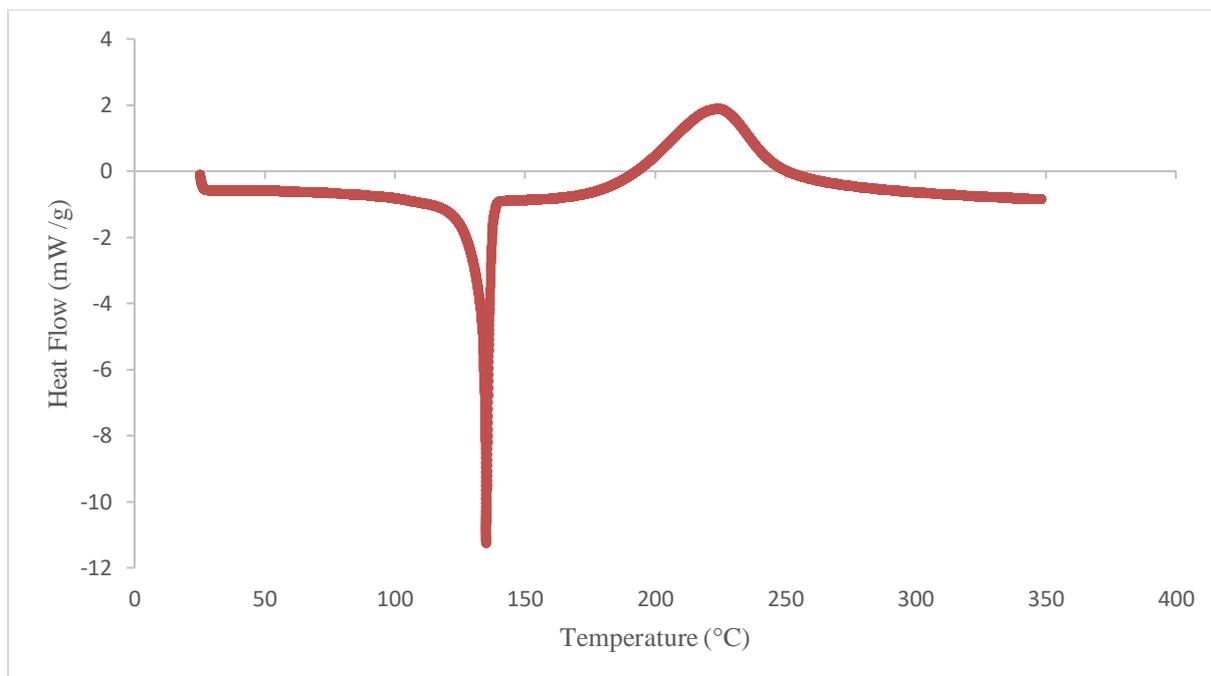


Figure 3: DSC thermogram: Hexamethylene Bismaleimide (HMBMI), 3°C/min from 25°C to 350°C, nitrogen

Indeed, the melting peak of the HMBMI molecules occurs around 140°C, which roughly corresponds to the rDA reaction of the “exo” adducts. The final endothermic peak is reached around 160°C (Figure 2). Finally, the exothermic rise above 160°C may be due to the end of evaporation of FGE, but also to an exothermic homopolymerization of the maleimide functions present in the mixture [16], at least partially (Figure 3).

3.1.2. Thermomechanical analyses of EPOBAD prepolymer

To go further in the identification of phenomena during the heating of the EPOBAD, its viscoelastic properties were measured as a function of temperature in dynamic mode at 1 Hz frequency and at 1% strain applied. Figure 4 presents the data registered between 25°C and 180°C with a heating rate of 3°C/min. Firstly, it should be noted that the torque sensors are no longer operational and sensitive from viscoelastic moduli as the values are lower than 0,01 Pa.

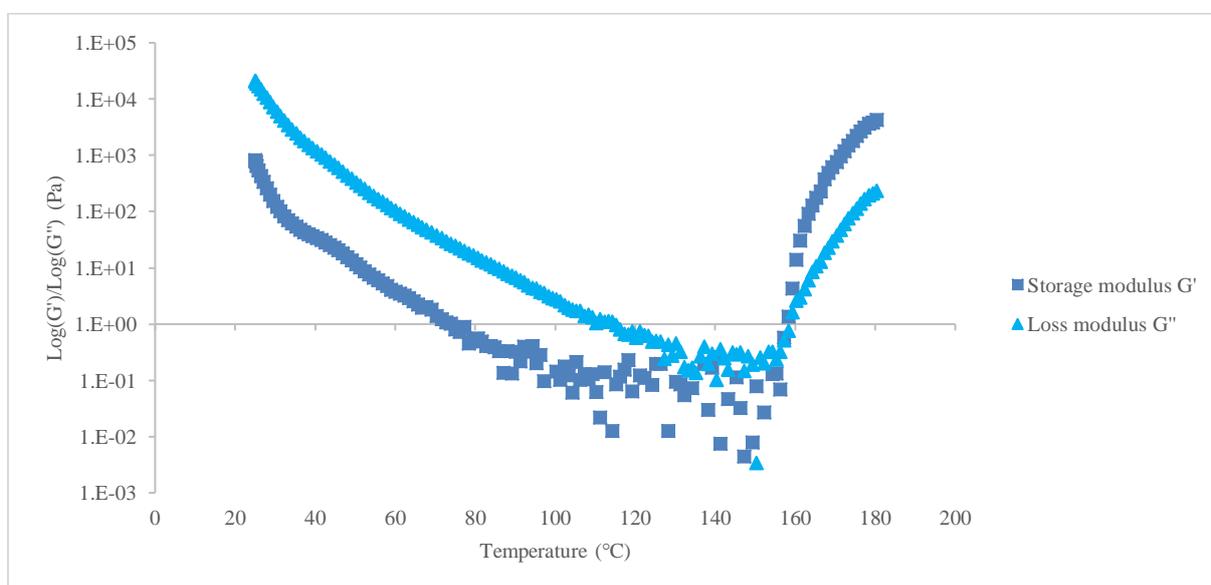


Figure 4: Thermomechanical analysis of EPOBAD prepolymer as a function of temperature, 3°C/min from 25°C to 180°C, $f = 1$ Hz, $\gamma = 1\%$, air

The EPOBAD is characterised by low values of G' and G'' and the viscous character is predominant ($G'' > G'$) until 130°C with a first strong decrease as temperature increases due to thermal mobility. Then the noisy signal followed by the signal loss on elastic and viscous moduli are related to the separation of the “endo” adducts separated by rDA reformed directly into adducts of “exo” form. After that, the whole adducts of “exo” adducts separate up to 140/150°C in accordance with the DSC behavior (Figure 2).

Finally, at high temperature between 160°C and 180°C (Figure 4), G' and G'' strongly increase with $G' > G''$. This behavior also occurs under nitrogen (Figure S7). It could be due to the homopolymerisation of epoxy groups and homopolymerisation of maleimide as suggested by the exothermic peak on maleimide thermogram (Figure 3).

To understand the chemical transformation of the EPOBAD during thermal loadings, FTIR analyses were performed in the following section.

3.1.3. FTIR characterisation of the EPOBAD in temperature

Firstly, the FTIR spectrum of EPOBAD reported Figure S5 in supporting information shows the presence of the ether groups of the Diels-Alder adducts at 1185 cm^{-1} . The ketone groups of the maleimides and the ethers of the epoxy rings are also present at 1654 cm^{-1} and 915 cm^{-1} respectively. It is important to note that the C-H stretching vibrations of the maleimide ring does not appear at 695 cm^{-1} , ensuring the full consumption of maleimide functions.

The evolution of the chemical composition of the EPOBAD prepolymer during heating is performed by IRTF in ATR mode. The sample are set on a temperature-controlled plate and spectra are registered at different temperatures during heating at 3°C/min from 25 to 180°C. Figure 5 gathers the spectra at 25°C, 70°C, 90°C, 110°C, 130°C, 145°C, 160°C and 180°C. It focuses on the band corresponding to C-H stretching vibrations of the maleimide ring [17] (Figure 5). The increase of the band amplitude at 695 cm^{-1} is related to the rDA reaction which allows the regeneration of maleimide functions from 110°C. This result confirms that the G' decrease is due to the retro Diels-Alder reaction (Figure 4).

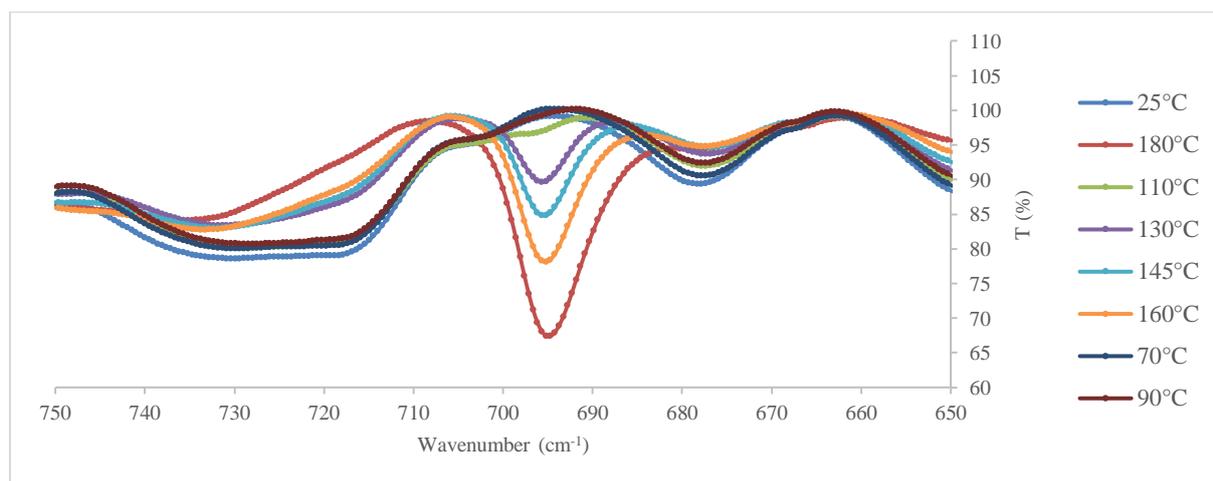


Figure 5: FTIR: C-H stretching vibrations of the maleimide ring of EPOBAD during heating, 3°C/min from 25°C to 180°C, air

Furthermore, a sharp broadening of the band around 3500 cm^{-1} assigned to the stretching vibration of OH bonds (Figure 6) appears at 180 °C [18]. The appearance of that band at higher temperature than 160°C confirms the homopolymerization of the epoxy functions present after rDA ([19], [20], [21]).

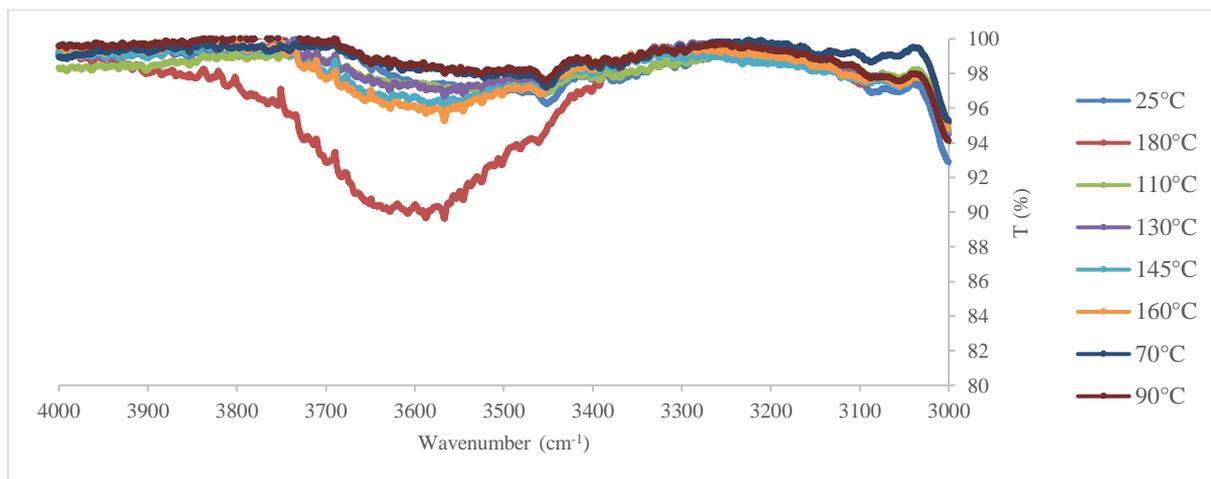


Figure 6: OH bonds bands of EPOBAD, 3°C/min from 25°C to 180°C, air

3.2. Study of the reaction between EPOBAD prepolymer and IPDA hardener

As explained in introductory part, the main objective is to qualify and quantify the different chemical and physical phenomena which could appear during the heating reaction between EPOBAD and IPDA amine. The experimental approach has combined thermal and chemical analyses. Then, thermomechanical responses of EPOBAD/IPDA system during cure reaction and in frequency dynamic responses after curing have been performed.

3.2.1. Study of the thermal behaviour of the crosslinked adhesive by DSC

The study of the EPOBAD-IPDA system is first performed by anisothermal tests. A stoichiometric amount of IPDA with respect to the oxirane functions was added in EPOBAD prepolymer and stirred at ambient temperature. Figure 7 shows the corresponding DSC thermogram, performed under nitrogen at 3°C/min from 25°C to 300°C.

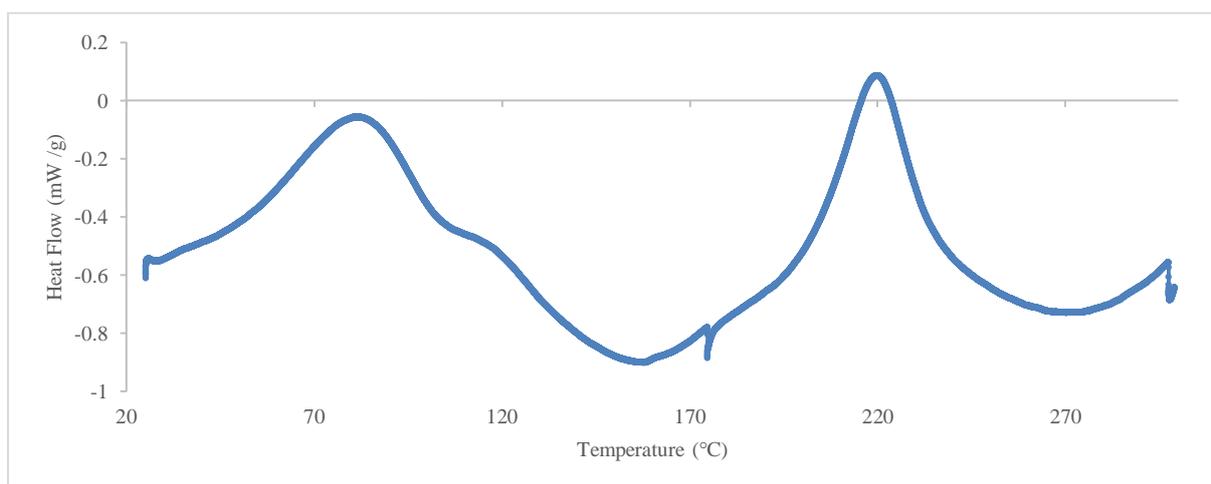


Figure 7: DSC thermogram: EPOBAD/IPDA blend crosslinking, 3°C/min from 25°C to 300°C, nitrogen

The first exothermic signal detected from room temperature is the signature of the EPOBAD-IPDA crosslinking's reaction. The thermal flow which begins at the beginning of the thermal load at ambient temperature and reaches a maximum around 80°C, then goes down because of the three following phenomena previously detailed: i) the endothermic retro-Diels-Alder, ii) the endothermic evaporation of FGE excess, iii) the melting temperature of regenerated HMBMI molecules by the rDA reaction.

Simultaneously, the Michael reaction (Figure 8) can take place between amine functions of IPDA which have not yet reacted kinetically with the oxirane rings of EPOBAD and the regenerated maleimides functions after retro-Diels-Alder reaction [22]. The occurrence of Michael reaction was verified by performing a DSC analysis at 3°C/min from 25°C to 80°C (Figure 9). The exothermic peak of Michael reaction in a HMDMI-

IPDA mixture is observable below 40°C. Clearly, a competition between the chemical epoxy/amine crosslinking and maleimide/amine reaction exists.

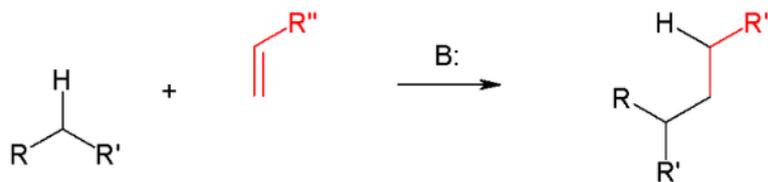


Figure 8: Michael Reaction [23]

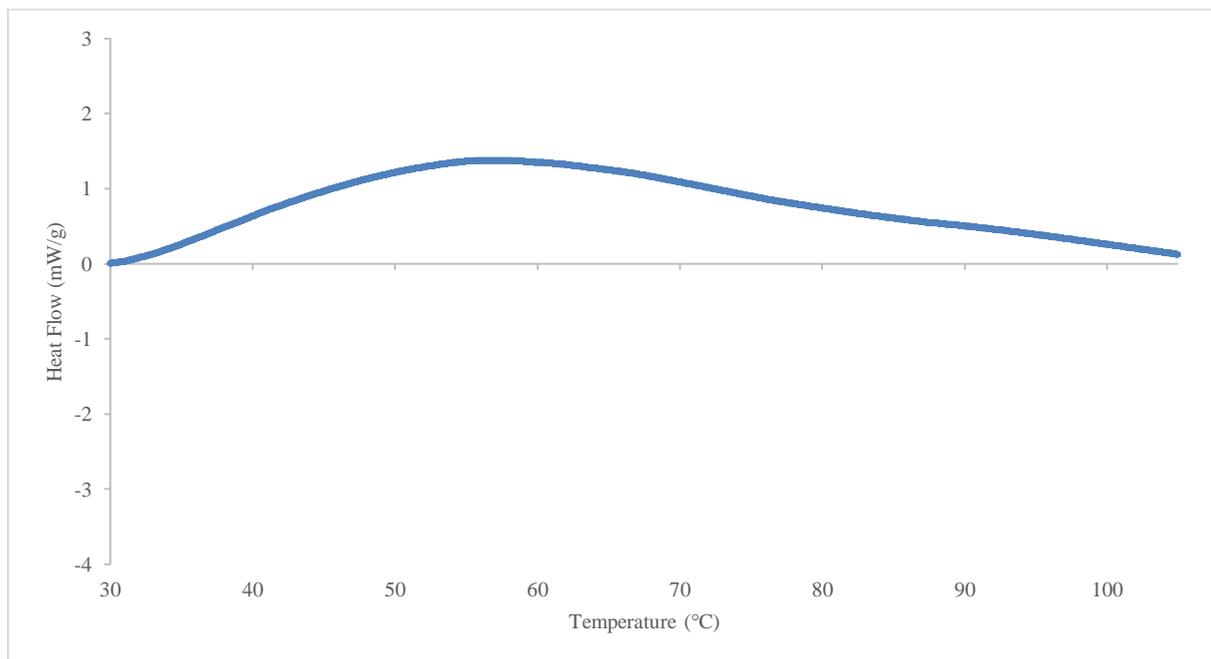


Figure 9: DSC thermogram: Michael reaction between HMBMI and IPDA, 3°C/min from 25 to 240°C, nitrogen

Moreover, a new exothermic peak occurs above 160°C on the EPOBAD thermogram (Figure 2). It would be due not only to the epoxy homopolymerization on the EPOBAD but also to the homopolymerization of regenerated HMDMI functions.

To analyze the thermoreversibility, EPOBAD-IPDA blend was cured in DSC at 3°C/min and cooled at 2°C/min. Then several temperature looping performed with four heating rate at 7°C/min and four cooling rate at 2°C/min have been carried out on the cured EPOBAD-IPDA blend. Despite irreversible Michael's reaction, the shape of the thermal signature of DA/rDA reactions during heating steps seems unchanged after some temperature loops as expected by the literature (Figure 10) [24], between 30°C and 160°C.

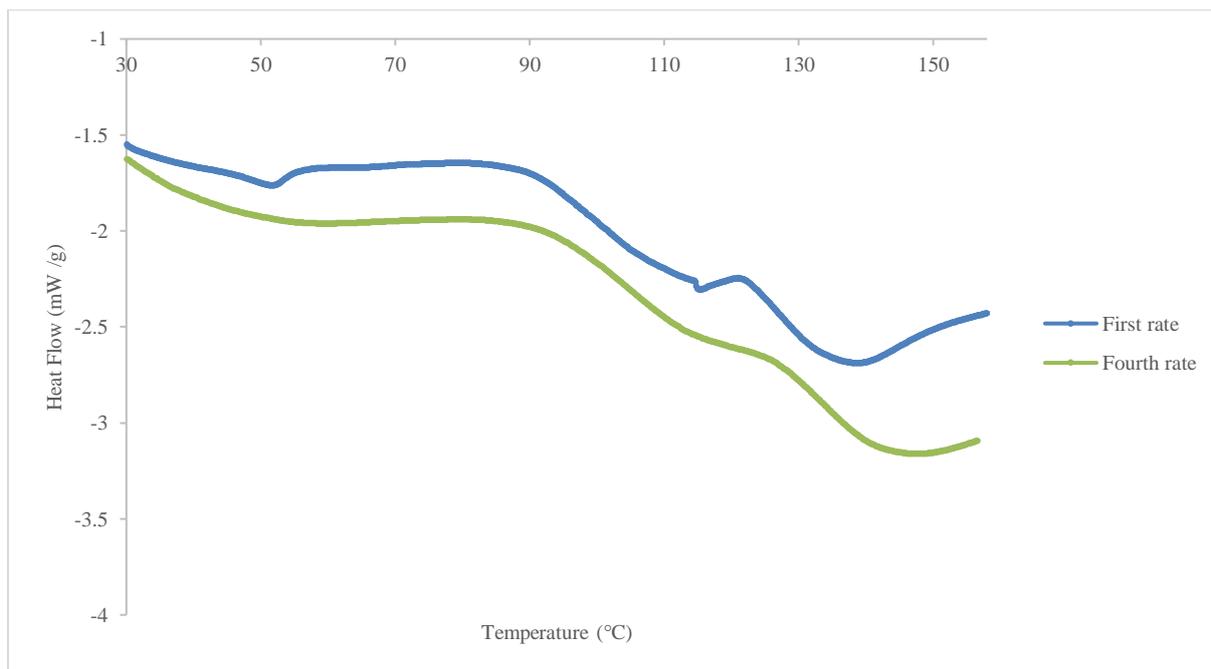


Figure 10: Reversibility of the adhesive after crosslinking, 7°C/min for each rate of heating between 30°C and 160°C, cooling: 2°C/min, nitrogen

So, to better quantify the competition between EPOBAD-IPDA crosslinking's and the Michael addition's reaction between amine and maleimide, FTIR analyses were performed. It has to be mentioned that the oxirane band cannot be used for the study because of the initial excess of FGE in the blend. The most relevant parameters to study are the primary amines peak and the maleimide peak respectively centred at 1560 and 695 cm^{-1} .

3.2.2. Study of the thermal behaviour of the crosslinked adhesive by FTIR

The evolution of the chemical composition of the EPOBAD-IPDA system during heating, then cooling is performed by FTIR in ATR mode. The sample are set on a temperature-controlled plate and spectra are registered at different temperatures during heating, then cooling at 3°C/min respectively from 25 to 160°C and from 160°C to 25°C.

During heating step, the FTIR spectra of the EPOBAD/IPDA blend taken at different temperatures (25°C, 70°C, 80°C, 90°C, 100°C, 110°C, 120°C, 130 and 160°C) and centred around 1560 and 695 cm^{-1} are gathered on Figure 11a and Figure 11b.

At 110°C, the maleimide peak is present while primary amines are not consumed yet completely by epoxy-amine crosslinking begun at room temperature. Then this last reaction is partial before the rDA reaction occurs and Michael reaction is activated as proved Figure 9. Exactly, the rDA reaction gets started between 100 et 110°C since the maleimide band appears from 110°C to increase with temperature up to 160°C. Then the strong decrease of primary amine band is both due to Michael reaction and epoxy-amine crosslinking creating a double chemical network. Moreover, the strongest kinetics of decrease in the height of the bands at 1560 cm^{-1} from the appearance of the Michael reaction would prove a reaction kinetics faster than that of epoxy-amine crosslinking.

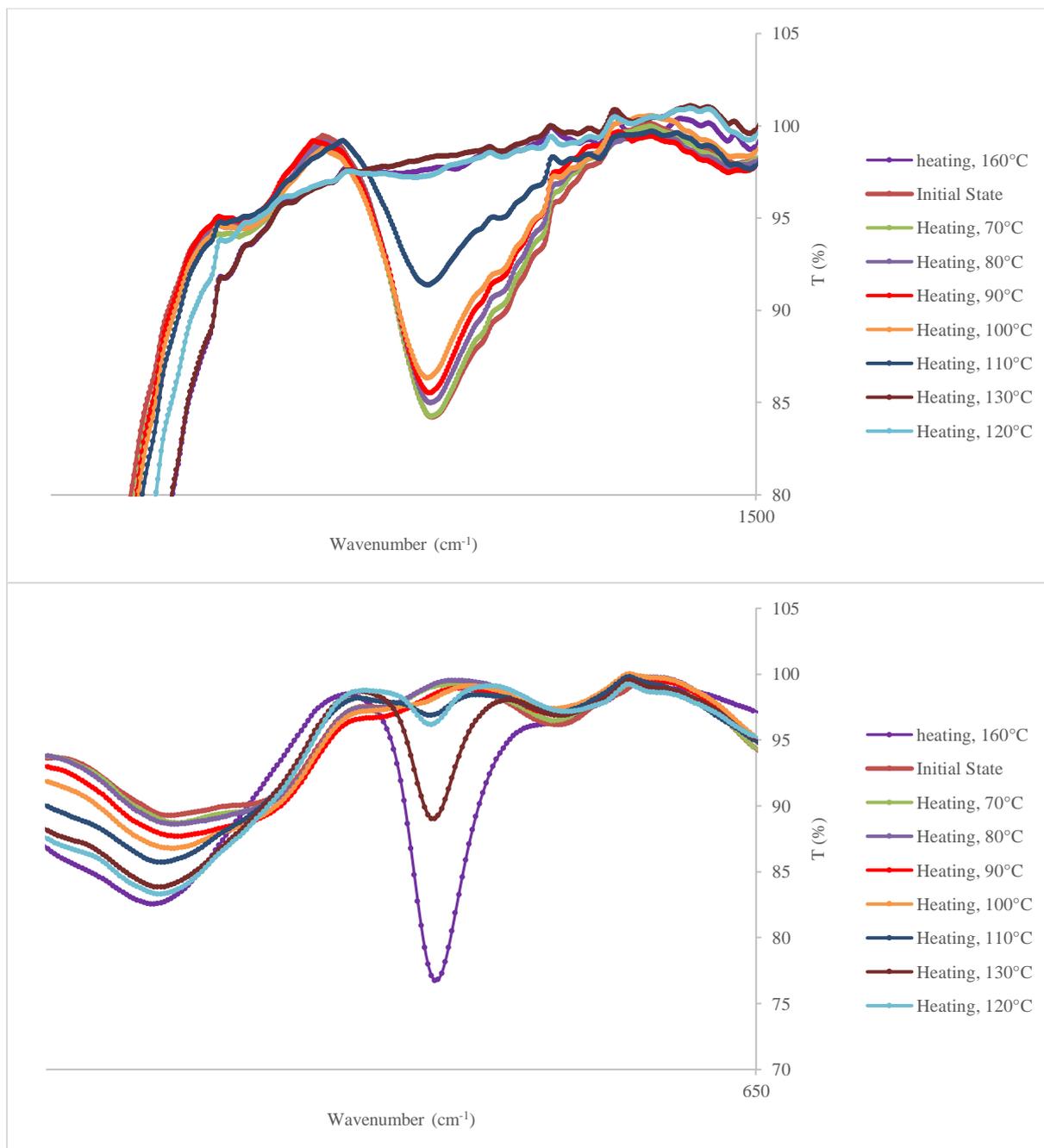


Figure 11: FTIR: Primary amine band (a) and maleimide band (b) at different temperatures during heating between 25°C and 160°C at 3°C/min, air

It has to be mentioned that the chemical reversibility of Diels-Alder chemistry cannot be the one expected because of the Michael reaction also takes place. Secondly, the conversion ratios of epoxy-amine and Michael are unknown because of their competition at high temperatures. To quantify the consequences on the macromolecular dynamics, thermomechanical analyses on the uncured EPOBAD/IPDA blend have been performed during curing and cooling.

3.2.3. Thermomechanical analyses of the crosslinked adhesive by rheology

Thermomechanical dynamic analyses in a cup /plate configuration are performed (Figure 12), applying a first heating at 3°C/min from 25°C to 160°C followed by a cooling at the same thermal rate.

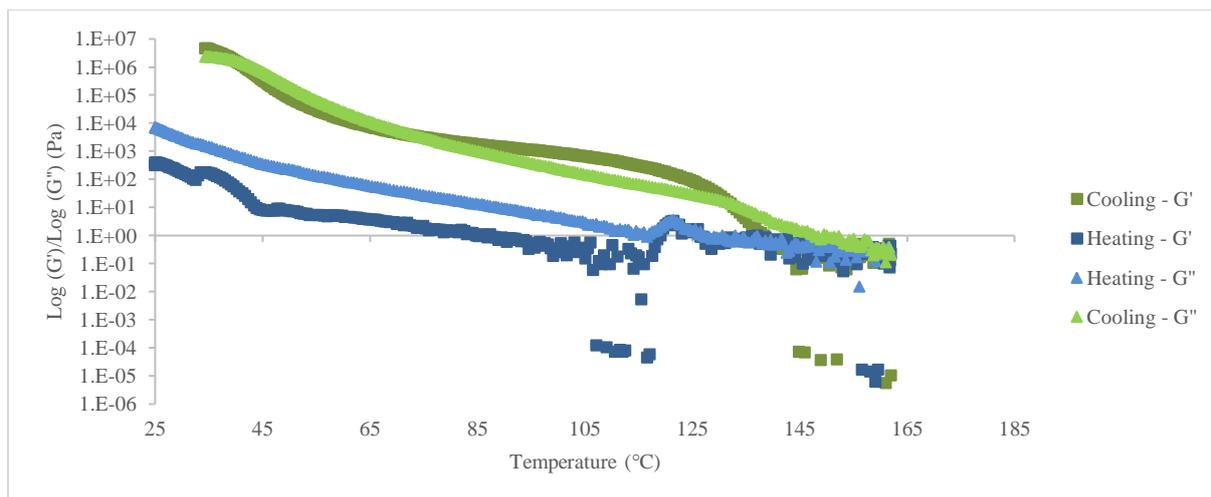


Figure 12: Thermomechanical analyses of initially uncured EPOBAD/IPDA blend: heating step(green) and cooling step (grey) at 3°C/min between 25 and 160°C, $f = 1\text{Hz}$, $\gamma = 1\%$, air

During the first heating a slow but steady decline in the value of the G' and G'' moduli measured during the thermomechanical analysis is observed. Therefore, the thermal mobility of the molecules responsible for the decrease in the moduli up to 95°C is stronger than the epoxy/amine's curing reaction visible by the increase in the viscoelastic response. The conversion rate of the cure reaction should be low, in this first heating step. Several phenomena explain the evolution of the viscoelastic response between 95 °C and 160 °C. Indeed, the first drop of the elastic and viscous moduli is related to the reaction of retro-DIELS-ALDER of the adducts of "endo" form present in the system. In this state, the network contains oligomers behaving as a viscoelastic liquid. Then the maleimide functions of the HMBMI which induced "endo" adducts are therefore regenerated. The increase of moduli between 120 °C and 155 °C is explained by the DIELS-ALDER reaction which directly follows the retro-DIELS-ALDER reaction of the "endo" adducts to form adducts of "exo" conformation, more stable in temperature. A second retro-DIELS-ALDER reaction again loosens all the adducts just after. In addition to DA/rDA events between 120 and 160°C, the competition between epoxy-amine crosslinking and Michael reaction takes place as well, and they both are mechanically opposite to the rDA reaction (Figure 11). This opposition explains the seeming stability of the moduli and would lead to the creation of a viscoelastic gel as evidenced by the equality between the storage and loss moduli. Whatever, the weak values of loss and elastic moduli, respectively around 1 and 0,1 Pa confirm the weak conversion rate of the crosslinking reaction. During the cooling step, before 130°C, the polymer behaves as a viscoelastic liquid. Then, the elastic modulus becomes greater than the viscous modulus as temperature decreases to return in a viscoelastic liquid state towards 70°C up to 40°C. Finally, the polymer behaves as a viscoelastic solid when the temperature is lower than 40°C.

As the evolution of the chemical composition of the EPOBAD-IPDA system during heating previously presented, cooling is performed by IRTF in ATR mode.

Figure 13 focuses on the evolution of the maleimide peak during the cooling step. The FTIR spectra of the system are taken at different temperatures: 25°C, 60°C, 80°C, 90°C, 100°C, 110°C, 130°C and 140°C during a thermal ramp of 3°C/min from 160°C to 25°C. The intensity loss of the 695 cm^{-1} peak at 130°C attests to the reformation of the adducts as the cooling progresses inducing a solid viscoelastic behavior. Nevertheless, the FTIR peak does not disappear and its height stabilizes between 80°C and 70°C. The residual quantity of HMBMI would be due to the evaporation of the FGE possible from 45°C limiting the quantity of reformed adducts.

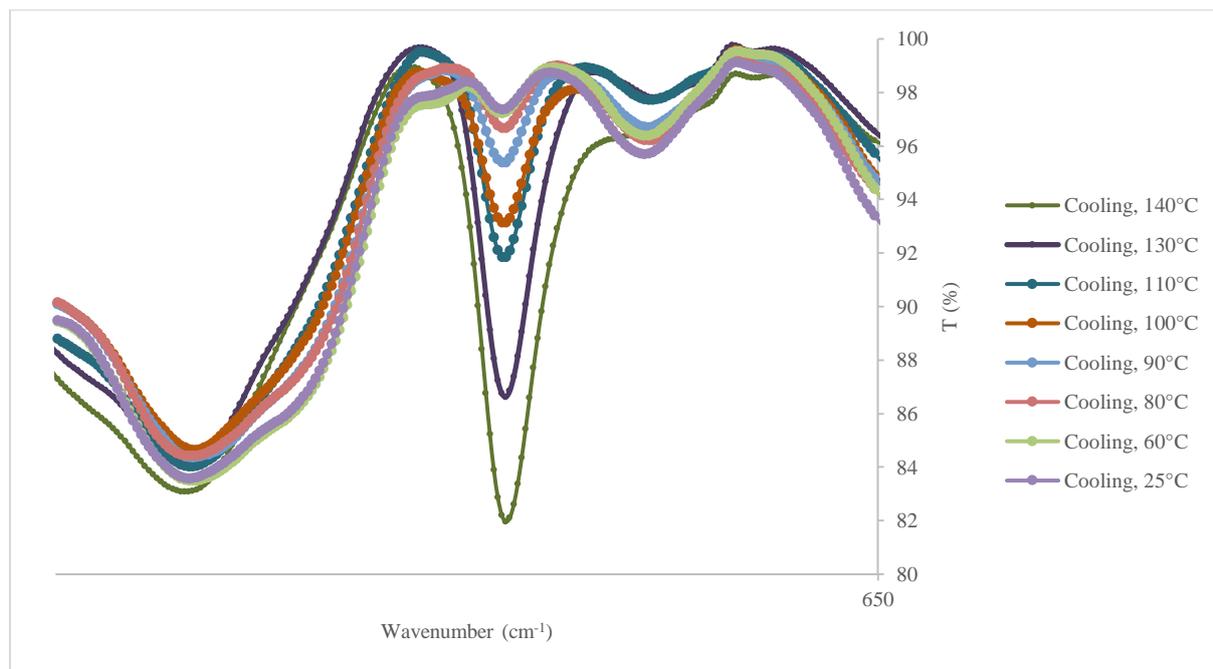


Figure 13: FTIR: C-H Maleimide at 160°C (red), 140°C (grey), 130°C (brown), 110°C (blue) and 100°C (green), 90°C (clear blue), 80°C (orange), 60°C (clear grey) and 25°C (yellow) during cooling between 25°C and 160°C at 3°C/min, air

During this cooling step, the Michael reaction and the crosslinking reaction between epoxy and amine groups cannot be achieved without amine monomers fully consumed at 120°C during the heating step according to FTIR analyses (Figure 11a). However the Michael reaction which takes place between maleimide and amine functions forms bonds of amide type ([25], [26]), and the crosslinking reaction between epoxy and amine functions forms bonds of alcohol type ([27], [28]). In presence of these two resulting chemical functions amides and alcohols, a formation of weak bonds of the hydrogen type or OH bridge occurs ([29], [30], [22]), creating a physical network partly responsible for the increase in moduli in addition to the loss of mobility due to the decrease in temperature.

At 70°C, the inversion of moduli values during the crossover would suggest an unlikely viscoelastic liquid behaviour since the adhesive behaves as viscoelastic solid at higher temperatures and since the reaction of retro-DIELS-ALDER is impossible during cooling.

To explain this temperature behaviour of the mixture, frequency sweep analyses from 0.1 to 100 rad/s (0,031 Hz to 32 Hz) at 1% strain were performed at different temperatures between 50 °C and 80 °C during cooling step and Figure 14 gathers the curves for 60 and 80°C.

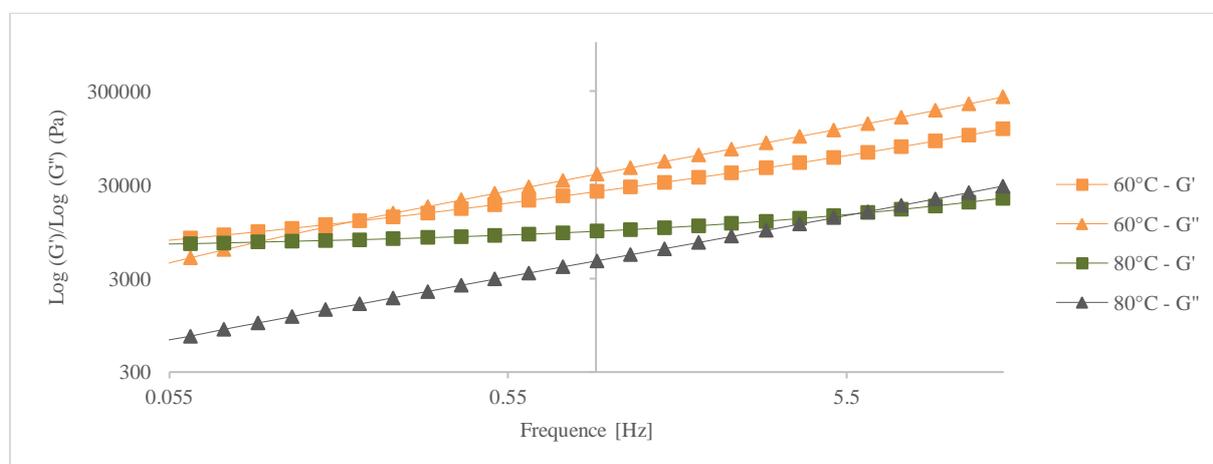


Figure 14: Frequency sweep analyses on EPOBAD/IPDA adhesive after crosslinking and cooling at 3°C/min, from 0,1 to 100 rad/s, $\gamma = 1\%$, air

Crossover between G' and G'' occurs for the two isotherm temperatures. As expected the crossover corresponding to $G' > G''$ shifts towards higher frequency with temperature. Then this temperature/frequency superposition explains why, at 1 hertz (marked at vertical axis) corresponding to imposed frequency applied on Figure 13, the adhesive apparently behaves as a viscoelastic liquid at 60°C while its state is like a viscoelastic solid at higher temperature (80°C).

IV. Conclusion

In this paper, the aim is to better assess the thermal and mechanical responses of a laboratory made thermally removable epoxy / amine structural adhesive that exhibits functions based on the chemistry of DIELS-ALDER (DA). The epoxy resin issued from the chemical reaction between hexamethylene bismaleimide (HMBMI) as dienophile synthesized in the laboratory and commercial furfuryl glycidyl ether (FGE) as diene. The amine hardener is the Isophorone Diamine - IPDA. Through a gradual scientific approach, several elements were shown. The functionality of HMBMI controlled by $^1\text{H-NMR}$ is 2 as wished, and its molecular weight is $277.43\text{g}\cdot\text{mol}^{-1}$. Thanks to a slight excess of diene in regards to equifunctionality between diene and dienophile functions, the consumption of maleimide functions is total during EPOBAD bisadduct formation. The average epoxy functionality of EPOBAD is 1,9 and the bisadduct contains 18,8% mol and 81,2% mol of endo and exo form respectively. EBOPAD reversibility characteristics is investigated to find the temperature ranges of DA and rDA reactions between HMBMI and FGE. To give the exact temperature ranges, calorimetric analysis alone is insufficient because of competition between the enthalpies responses of DA/rDA reaction, evaporation of the FGE and melting of the HMBMI once regenerated by the rDA. So, these temperature ranges were determined by thermomechanical dynamic approach by measuring the evolution of the shear storage modulus of the mixture G' , and its loss modulus, G'' . Then, the chemical reaction of this epoxy formulation with IPDA as hardener was investigated by FTIR analyses in temperature, anisotherm DSC studies associated to thermomechanical studies in dynamic shear mode at several frequencies. During the DA/rDA transition, a new chemical network related to a Michael reaction between released maleimides and free amines appears and is competing with epoxy / amine crosslinking during heating. Moreover, neither the Michael reaction during heating step nor the Diels-Alder reaction during cooling consumed all the maleimide functions. The thermoreversibility will then inevitably attenuate. Further curing isothermal cycles will be performed to better achieve the crosslinking reaction of epoxy-amine before the rDA, so the Michael reaction occurrence. A second investigation will deal with the study of influence of bisadduct/hardener ratios and blend of EPOBAD with epoxy systems without thermally reversible chemical functions.

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Supporting Informations

I. Synthesis of Hexamethylene Bismaleimide (HMBMI)

The molecule of hexamethylene bismaleimide, the first reactant involved in the creation of the epoxy resin, is synthesized in solution in the solvent dimethylformamide, DMF, from hexamethylene diamine and maleic anhydride according to a method described by Ferenc (Figure S2). The reaction scheme is as follows:

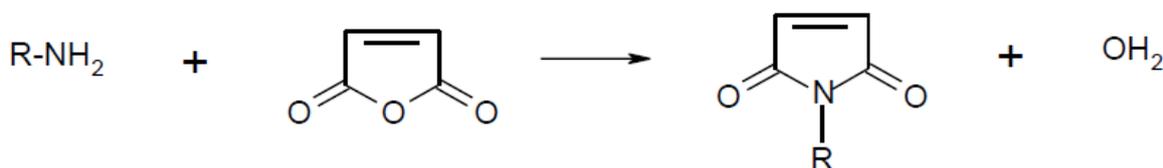


Figure S2 : Synthesis reaction of obtaining maleimide functions

The reagents used are hexamethylene diamine (98%) from Acros Organics, maleic anhydride, zinc acetate and triethylamine as well as anhydrous DMF solvent from Sigma Aldrich. All reagents were used without purification.

First, in a 250 mL three-necked round bottom flask equipped with a thermometer, Maleic anhydride (49g, 0.50mol) was dissolved in 75mL of anhydrous DMF at room temperature and under magnetic stirring. Then, the flask was introduced in a bath of iced water and 1,6- Diaminohexane (29g, 0.25mol) previously dissolved in 75mL of anhydrous DMF was slowly added. The temperature rose to 80°C and the mixture color turned to yellow. The mixture was let under stirring and when temperature reached about 40°C, the white precipitate of Hexamethylene bismaleamic acid appeared.

Then, the reaction mixture was heated under stirring and refluxing at 65°C for 30 minutes before Acetic anhydride (100g), Zinc acetate (3g) and Triethylamine (10 g) were added. The color changed rapidly to brown and the temperature was kept at 60°C for one hour. Then, the solution was cooled to 50°C, poured in iced water, and the obtained solid was subjected to several cycles of washing/filtration with a large excess of cold water. Finally, the obtained solid was dried in a vacuum oven at 80°C for 36h. The yield was about 75%.

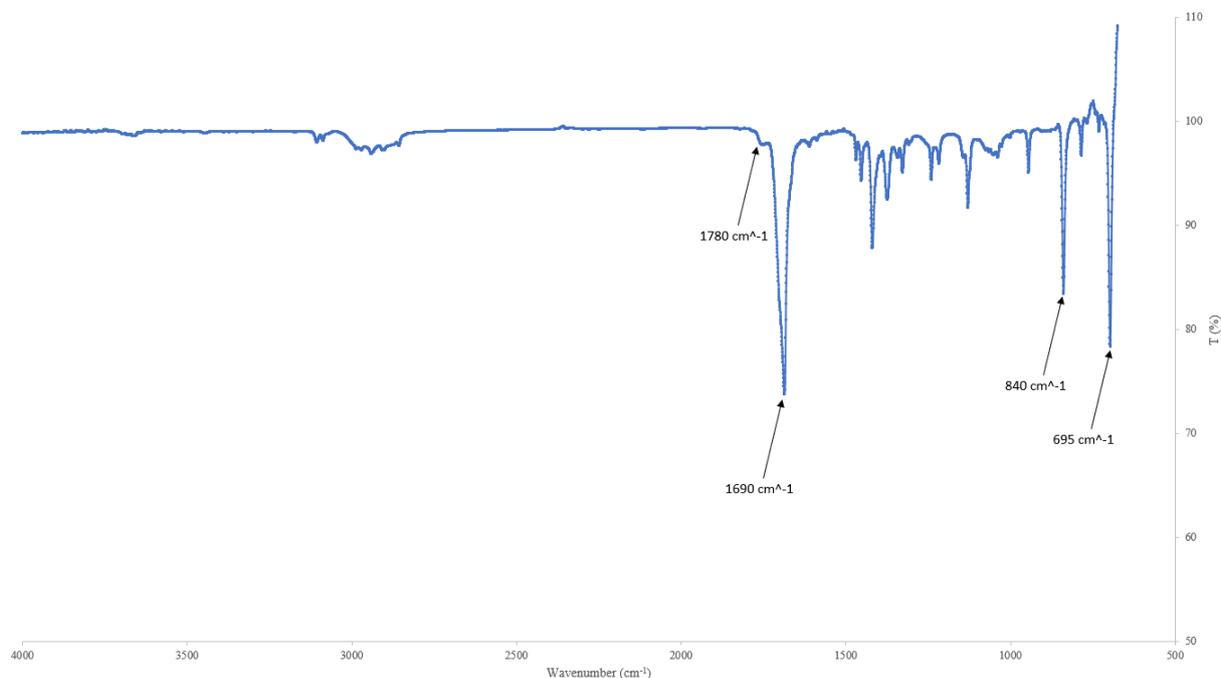


Figure S3 : FTIR-ATR spectrum of HMBMI (air)

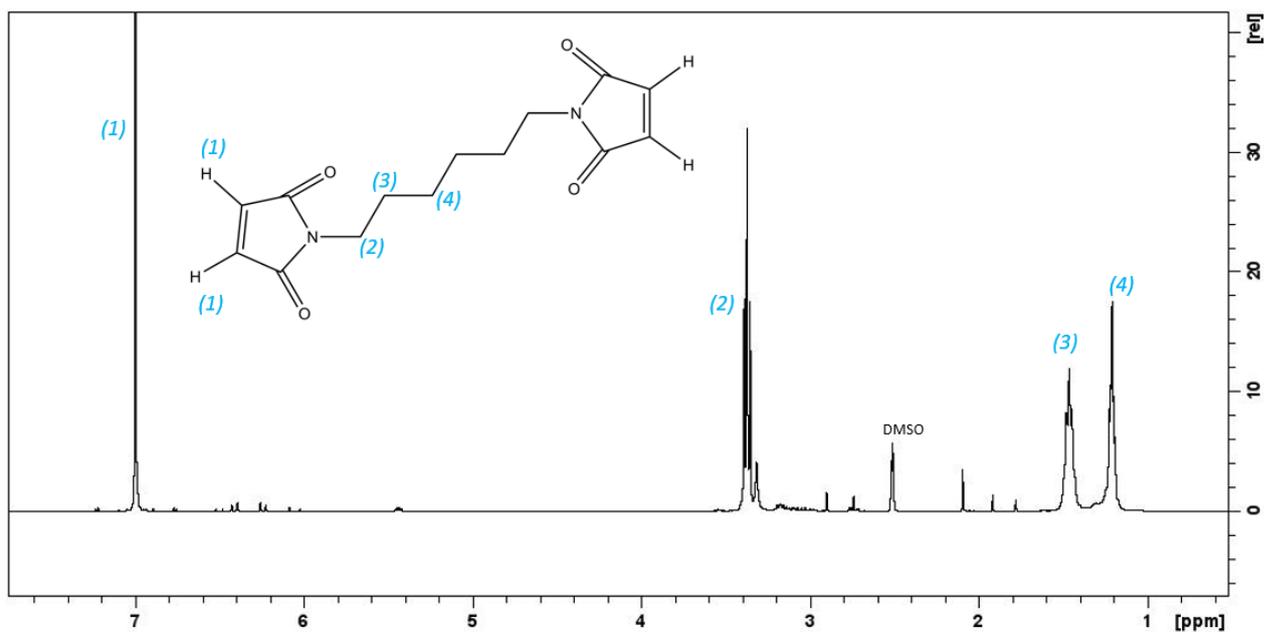


Figure S4 : $^1\text{H-NMR}$ spectrum of Hexamethylene Bismaleimide (DMSO- d_6 , 25°C)

The maleimide peak is represented at 695 cm^{-1} in FTIR (Figure S3), and the ketones peak at 1690 cm^{-1} . It can be observed better the global structure of HMBMI in $^1\text{H-NMR}$ (Figure S4).

II. Synthesis of the epoxy resin

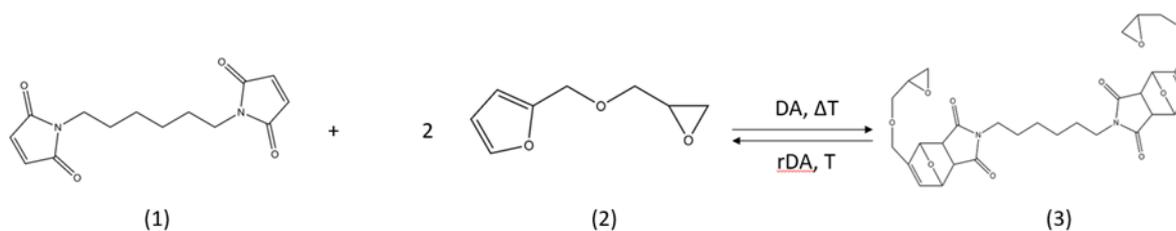


Figure S4: Reaction scheme of the reaction of DA between HMBMI and FGE to form the thermoreversible epoxy resin

First, 9.733 g (0.0631mol) of Furfuryl glycidyl ether and 7.982g (0.0287mol) of HMBMI were mixed together and introduced in an oil bath at 110°C for 15 min. Then, the mixture was slowly cooled to room temperature. The dark brown viscous oil is obtained with a yield of 100%.

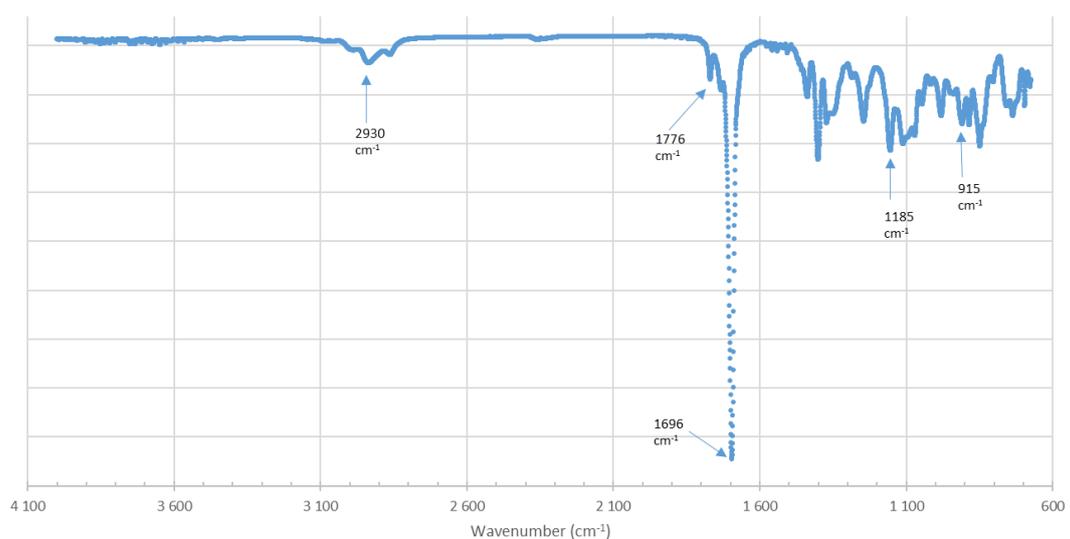


Figure S5: FTIR spectrum of EPOBAD

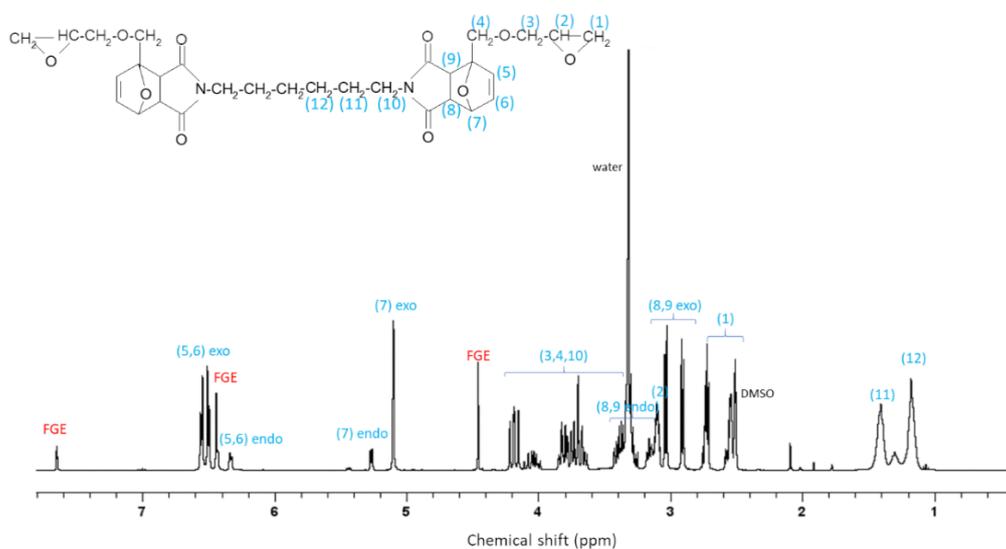


Figure S6: ¹H-NMR spectrum of EPOBAD in DMSO-d₆

The average epoxy functionality was calculated according to the following equation:

$$f_m = \frac{r_1 * f_1^2 + r_2 * f_2^2}{r_1 * f_1 + r_2 * f_2}$$

where r_1 and r_2 are the ratio of FGE and EPOBAD respectively, and f_1 and f_2 are their epoxy functionality.

With $r_1 = 0.15$, $r_2 = 0.85$, $f_1 = 1$ and $f_2 = 2$, the average functionality f_m is 1,9 and the resulting epoxy index is 3,5 mol.kg⁻¹.

III. Rheological phenomena of degradation of the epoxy resin

The same phenomenon of epoxy and maleimide homopolymerizations are observed on the epoxy at high temperature under nitrogen (**Error! Reference source not found.**).

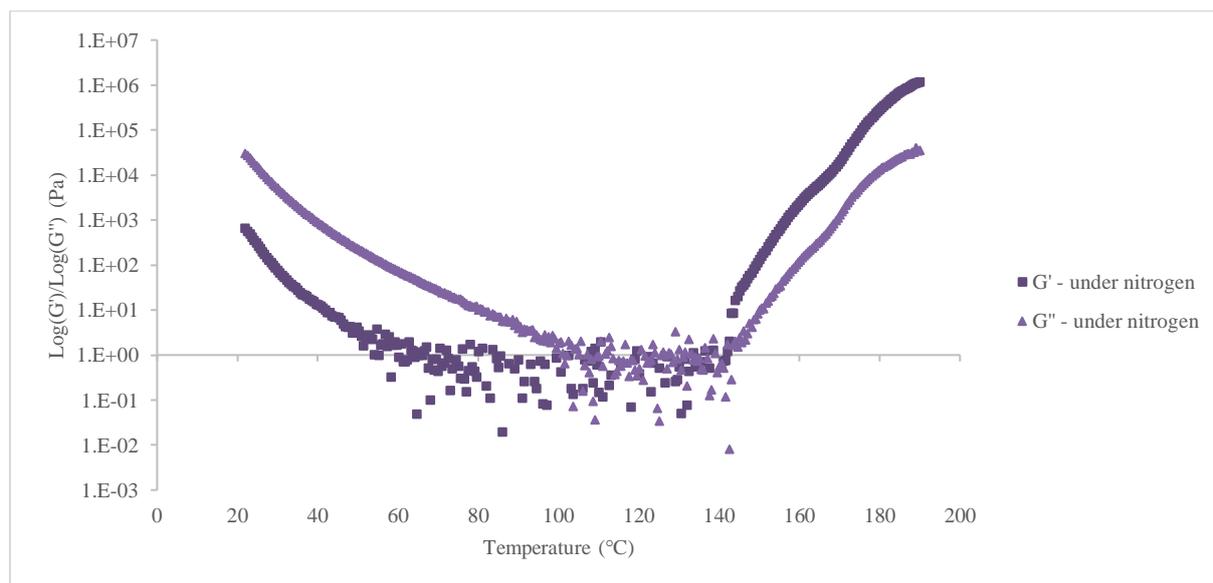


Figure S7: Thermomechanical analysis of EPOBAD prepolymer as a function of temperature, 3°C/min from 25°C to 180°C, f = 1 Hz, γ = 1% under nitrogen