Thermal Study of Aluminum Trifluoromethyl Sulfonate as Effective Catalyst for the Polymerization of Epoxidized Linseed Oil

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Abstract It was studied the Aluminum Trifluoromethyl Sulfonate ((Al(OTf)$_3$) as a very effective catalyst to polymerize Epoxidized Linseed Oil (ELO) in bulk, in a very wide range of temperatures, from room temperature (25°C) to the peak temperature of the exothermal curve of polymerization. Those temperatures and times of polymerization were depending on the amount of catalyst, which was evaluated in a very wide range of loads, from 0.5 x10^{-3} to 70 x10^{-3} molar percent. As an instance, a 55 x10^{-3} molar percent of catalyst showed at exothermic curve from 82 to 187°C with the peak temperature at 120.3°C. This preparation allows to ELO polymerize at 25°C in 24 hrs, at 60°C in 1hr and at 80°C in 20 min and only takes 7 min to polymerize at peak temperature. The study of the opening of the epoxy ring and polymerization of ELO was made by DSC and FTIR-HART analysis. Also was evidenced by ^{1}H-NMR that no side reactions are promoted by this catalyst at least in the first minutes of reaction.

Keywords Aluminum triflate, Oxirane aperture, Epoxidized linseed oil

1. Introduction

Epoxides (oxiranes) are functional groups reactive to a wide range of nucleophiles due to their angular tension and their C-O polar bond and are often used as starting materials and intermediates. Extrapolating to the epoxy resins, they can homopolymerize under acidic or basic conditions and/or with a variety of curing agents called curing agents or crosslinkers. Cured epoxy resins typically exhibit excellent thermal, mechanical, and thermal properties with low shrinkage properties so they are widely used as protectors, adhesives, composites, among others. On the other hand, with the demand for biopolymers and resins with practical applications, vegetable oils have been considered within renewable natural sources with high availability and low cost, as an excellent alternative of high synthetic potential to produce biodegradable polymers. [1,2]. Epoxidized vegetable oils (EVO) have been prepared by the epoxidation of C=C double bonds of fatty acids using peracids. There is a lot of literature about this reaction [3-8] due the EVOs [9]

have been considered as intermediate reagents to generate other functional groups suitable [10-12] for the synthesis of polymers and they are industrially applied in the PVC industry as plasticizers. Among the most studied EVOs are epoxidized soybean oils (SBO) and epoxidized linseed oil (ELO) and are to date the only ones produced on an industrial scale. The content of oxirane groups depends on the type of vegetable oil (number of double bonds) [1] and the epoxidation method. EVOs can be polymerized by a cationic mechanism or can be used in UV curable systems efficiently at room temperature. The cationic polymerization performed at around 100°C may generate some lateral reactions [13,14]. While the Lewis acid catalyzed ring opening photo-polymerization is performed at room temperature using boron trihalides [15], superacids as fluorosulfonic acid [16,17] and strong acids [18], and salts of diaryliodonium [19]. However acids super acids and strong acids are toxics and/or corrosives and generates many side reactions as described in [16,17]. The aluminum trifluoromethanesulfonate or aluminum triflate, Al(OTf)$_3$, a Lewis acid type catalyst that has been little studied for the opening of epoxy rings by amines [20] and by alcohols [21] in simple terminal epoxides (styrene oxide), finding that nucleophilic alcohol attacked the most hindered carbon atom of the epoxy ring (regioselective reaction) at temperatures of 0°C and in amounts on the order of 0.0005% by weight of the catalyst and achieved reaction yields of up to 97% with

formation of oligomers quantity that was managed to minimize to traces increasing the amount of alcohol. When they performed the reaction with butylene oxide, they obtained an isomer ratio of approximately 50:50. When they performed the reaction on non-terminal epoxides but on small molecules such as cyclohexene oxide, 0.001% catalyst was required to generate the opening product in 85% yield. However, in performing the reaction on the cyclododecane oxide, they had to increase the amount of catalyst (0.04%) by 14 times and the yield was decreased to 49% yield. They attribute it to the effects of polarity difference between cyclododecane and alcohol (methanol) the difficulty of attack. Another study [15] made on different metal (Sc, Bi, La, Cu, Al, and Zn) triflate catalysts was on the transesterification reaction of *Jatropha curcas* L. oil with many alcohols. Aluminum trimethanesulfonate was the most effective catalysts rendering conversions of 99% followed by bismuth triflate. They also observed some methoxylation depending on the methanol excess and using Aluminum trimethanesulfonate as catalyst. In a previous work [22] that catalyst was tried to use in the functionalization of ELO with propargyl alcohol, obtaining in most cases the polymerization of ELO rather than functionalization. Even though EVOs are generally polymerized in formulations with other comonomers, hardeners and / or reinforcing agents [Lozada, 2009], one characteristic of thermal homopolymerization without catalysts is that it is carried out at temperatures around 200°C because of problems inherent in its structure as its flexibility and limited reactivity due to the high steric hindrance (internal oxiranes) in relation to the low amount of epoxy groups present (for ELO is around 6). This is why in this work it was determined to use Al(OTf)$_3$ to study its effectiveness in the opening of 1,2-epoxy rings and polymerization of ELO in the absence of any external nucleophiles (amines or alcohols) in a range of amount of catalyst and temperatures below their exotherm curve. It was so effective that it becomes important to know the limit of temperature-time that we could keep the mixture once prepared in order to avoid a spontaneous polymerization below the range of temperatures observed under the exotherm curve. DSC and FTIR-HART spectroscopies allow to follow the degree of cure of reactive mixtures of ELO containing different amount of catalyst, Al(OTf)$_3$.

2. Experimental

2.1. Materials

Epoxidized linseed oil was previously prepared following the procedure described in [23]. It was characterized obtaining a 63% of epoxidation (4.0 of oxirane rings), and with a molecular weight of 873 g/mol (calculated by H^1 NMR, 23). Al(OTf)$_3$ 99.9% trace metal bases, 474.19 g/mol molecular weight was purchased from Sigma-Aldrich, Co., all analytical grade solvents (THF, Acetone, CDCl$_3$) were also purchased from Sigma-Aldrich, Co. and used as received.

A stock solution of the catalyst in acetone was prepared (0.021 M) in order to take the necessary volumes to reach the molar percentage required: 0.5, 2.5, 5.0, 1.0, 15, 25, 35, 55 and 70 x10^{-3} mol% to study the polymerization reaction of ELO. Each mixture of ELO + Al(OTf)$_3$ was prepared using 1g of ELO to which was added the required volume of the catalyst stock solution. Then it was stirred in an ultrasonic bath for one minute at 10°C. The acetone was evaporated under reduced pressure at room temperature for 2 h. Samples were characterized by FTIR spectroscopy and DSC/TGA analysis immediately after being prepared, and then kept under refrigeration at -20°C.

2.2. Methods

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis were performed on an SDT Q600 modulus from TA Instruments. Three type of analysis were made: (i) Both DSC and TGA were recorded to evaluate the thermal properties of pure ELO, Al(OTf)$_3$ (named references) and the final polymers over the range of temperature from 25 to 570°C at 20°C/min under Nitrogen atmosphere (100 mL/min). It was used a 90μL alumina DSC pan with alumina topper, an empty ceramic pan was used as reference (ii) For Isothermal experiments at temperatures lower than the respective cure curve (40 and 50°C, 60 80°C, 100 and 120°C). Experiments were performed using 5-7 mg of the reactive mixture (ELO+ Al(OTf)$_3$) for detecting the exothermic crosslinking curve and the range of temperature associated to this polymerization process. iii) For characterizing the decomposition temperature (T$_{10}$) of the products totally polymerized.

FT-IR spectroscopic measurements were performed on a FTIR Prestige 21, Shimadzu spectrometer equipped with a horizontal attenuated total reflectance (HART) crystal made of diamond. FTIR spectroscopy was useful for (i) characterizing the references ELO and Al(OTf)$_3$, and for characterizing the initial mixtures of ELO + Al(OTf)$_3$ over the range of 4000 to 560cm^{-1}. (ii) For monitoring the crosslinking reactions at temperatures at 25, 40, 50, 60, 80, 100 and 120°C from isothermal running on DSC. With this spectra was possible to quantify the degree of cure (equation 1) by normalize the spectrum to the carbonyl band (reference band) at 1740 cm^{-1} and by measure the area under the curve that form the pair of peaks centered at 821 and 798 cm^{-1} corresponding to the epoxy ring [24,25].

$$a = 1 - \frac{A_{epoxy}(t)/A_{ref}(t)}{A_{epoxy}(0)/A_{ref}(0)} \tag{1}$$

Were A(t) and A(0) corresponds to area under the bands at a time t and at the beginning of the experiment (time 0), respectively. (iii) For following the reactions in real time at 25°C. The established parameters to give a real-time follow-up to the degree of cure and for all the other studies, were continuous running of 200 scans at 4 cm^{-1} and of resolution (each run takes 4 min) in Absorbance mode.

^{1}H-NMR spectra were recorder using a Varian 300 spectrometer using $CDCl_3$ as solvent and TMS as a standard and 40°C in case of real time polymerization of the mixture of ELO + Al(OTf)$_3$ at 36×10^{-3} % mol of catalyst. This evaluation was the evidence of oxirane aperture.

3. Results and Discussion

3.1. Characterization of References by DSC/TGA Analysis

The characterization of both references: ELO and the catalyst were performed by DSC/ TGA. Figures 1 and 2 show the respective analysis. As it could be appreciate, DSC thermogram for pure ELO only shows the exothermic peak centered at 200°C and a highest exothermic peak corresponding at the decomposition process in the range of 350-425°C. Also ELO has a decomposition temperature, T_{10} at 389.6°C.
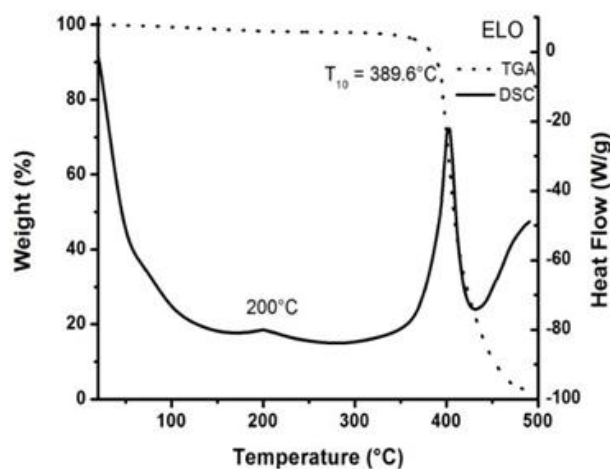

Figure 1. Thermograms DSC and TGA for Epoxidized Linseed Oil (ELO)
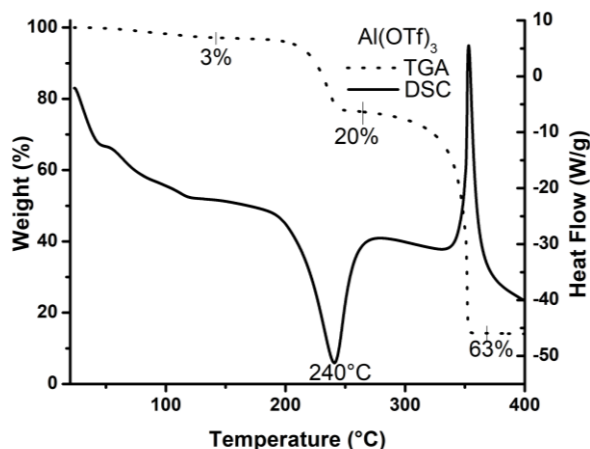

Figure 2. Thermograms DSC and TGA for Aluminium Triflate

On the other hand, the pure catalyst shows 3% weight lost in their TGA thermogram: a small one of 3% in the range of 30-100°C due to moisture. After there is a loss of 20%

corresponding to a molecule of sulfur trioxide. The biggest loss of 63% corresponds to the loss of the other two sulfur trioxide gas molecules and a residual trifluoromethyl anion. As would be explained latter, the decomposition of the catalyst will have repercussions on the thermal stability of the polymers obtained using this catalyst.

3.2. Characterization by DSC and FTIR-HART Techniques of the Reactive Mixtures: ELO + Al(OTf)$_3$

DSC characterization of the initial mixtures and pure ELO is shown in Figure 3. Those thermograms were run at a heat rate of 20°/min. As could be seen, pure ELO (0% of catalyst) shows a lightly exotherm centered in 200°C (curve in green). As load of catalyst increases, that exotherm is shifted at lower temperatures. It is possible to appreciate three regions, the first defined by the peak temperature around 165°C (curves in blue) which corresponds to the lowest amount of catalyst (0.5 and 1×10^{-3} % mol). For the second region (curves in red) the peak temperatures are around the 120°C. These temperatures are for the mixtures with 2.5, 5, 11 and 16×10^{-3} % mol of catalyst. And finally the region with the lowest peak temperatures (in grey color) around 77°C for the highest amount of catalyst, 27, 35, 55 and 70×10^{-3} % mol. It is evident that cure temperature is diminished as the amount of catalyst is increased. From 200°C that requires the ELO without catalyst to approximately 77°C there is 100°C of difference. However, the curves for the third region are very small and for some compositions the exotherm is not longer visible. This fact is attributed to some oxirane aperture during the preparation, and even under refrigeration at -20°C. For mixture with 70×10^{-3} % mol of catalyst there is no exotherm. These evidences were supported by FTIR, in Figure 4. Something that is sure is that at room temperature (23-25°C) they polymerize in around 30min. In fact for the mixture with 16×10^{-3} % mol resulted difficult to made a following of the cure process due to even in refrigeration each 12 h there was some degree of reaction as evidenced by FTIR and DSC. Due to the difficult to work with the compositions of the third region and with 16×10^{-3} % mol, we decided not to study them. All the other compositions were stables under refrigeration for long periods of time (weeks).

By perform FT-IR analysis, was also possible to quantify the cure by measure the decrements of the pair of peaks centered at 821 and 798 cm^{-1}, the signal that corresponds to the epoxy ring vibration. In Figure 4 are the spectra corresponding to pure ELO (0% of catalyst) and some reactive mixtures containing high content of catalyst: 16, 55 and 70×10^{-3} mol%. The spectrum of pure ELO and the mixtures containing until 10×10^{-3} % mol of catalyst are practically the same but for mixtures from 16×10^{-3} and higher amount of catalyst some decrement on the epoxy signal area and increasing the band corresponding to the hydroxyl groups formed during the aperture of epoxy rings are observed practically immediately of being prepared. For

the mixture with 55 x10^{-3} mol% of catalyst the area under the curve of the band of epoxy group has decreased almost in 50%. These results confirm those obtained by DSC about of the extremely reactivity of the epoxy rings in the linseed oil under the presence of the catalyst at that loads. In less than 30 min those reactive mixtures were cured at room temperature (23-25°C).
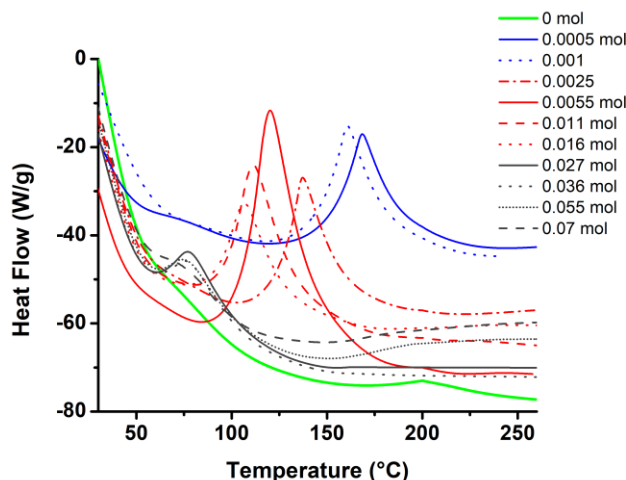

Figure 3. Exhotherms from DCS curves of pure ELO and the mixtures respect to the mol percentage of catalyst
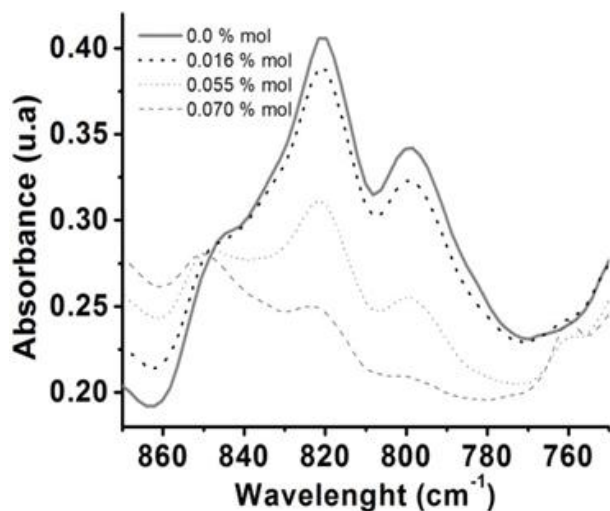

Figure 4. Normalized FTIR-HART spectra in the range of the corresponding epoxy signal of ELO and the mixtures containing 16, 55 and 70 x 10^{-3} mol% of catalyst

3.3. Cure under Isothermal Experiments by DSC

The propose of this type of analysis was to detect a low temperature below the exothermic peak (Figure 1), at which is possible to cure and monitoring the reactive mixtures with different amount of catalyst.

For isothermal analysis made using the DSC and temperatures of 40, 50, 60 and 80°C and in some mixtures 100 and 120°C, the range of programed time was from 5 min to several days. After cooling at 25°C, the same sample was reheated from 25 to 270°C in order to detect some residual curing. If would be one, a new sample of the same mixture

was submitted at the same conditions but at longer times until confirm the nonexistence of residual curing. The same procedure was made for the other temperatures and for all the mixtures. The respective kinetics is showed in Figure 5.
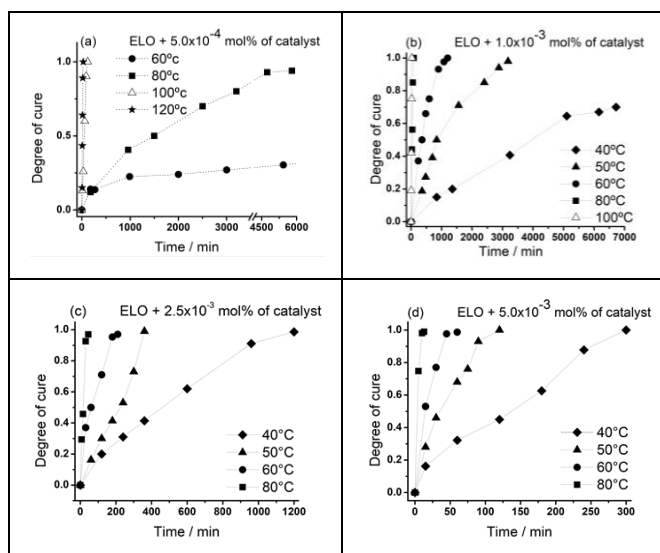

Figure 5. Following of the Degree of cure from isothermal experiments for (a) 5.0 x 10^{-4}, (b) 1.0 x 10^{-3}, (c) 2.5 x 10^{-3}, and 5.0 x 10^{-3} mol% of Al(OTf)$_3$

For the last two mixtures (2.5 and 5.0 x 10^{-3} mol%) the cure ocurrs in less than 1500 min (25 hrs) at any temperature, even at 40°C, and the percent of cure is above 97%. However, for 1.0 x 10^{-3} mol%, at 50 maximum curing takes 3000 min (50hrs) but for 40°C reaches a maximun percent of cure of 70% between 4980 min (83 hrs) and 6600 min (110 hrs). For the minimus load of catalyst (5 x10^{-4} mol%) there was a radical change in the behaviour of the curing process. For 120°C and 100°C the cure takes place in some hours but for temperatures lower than 80°C it was necessary several days.

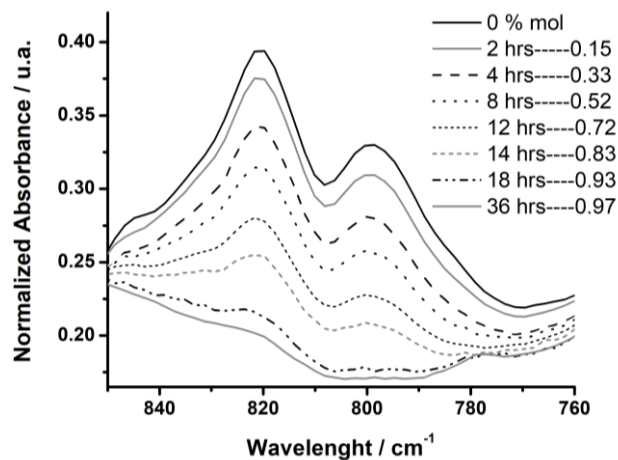### 3.4. Cure at 25°C Monitoring *in situ* by FTIR-HART Spectroscopy

Figure 6. Cure monitoring by FT-IR *in situ* at 25°C for ELO + 5.0 x 10^{-3} % mol of Al(OTf)$_3$
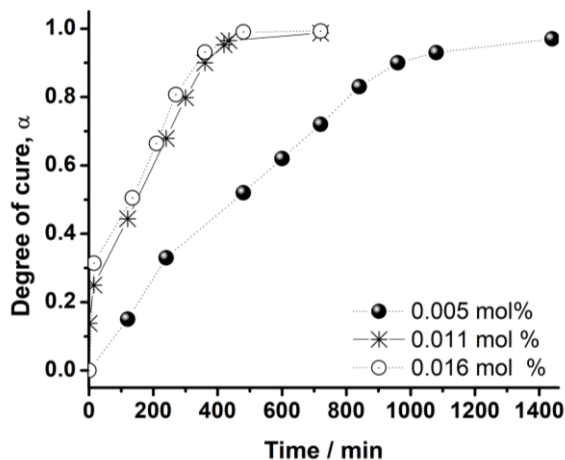
Figure 7. Cure monitoring by *in situ* FT-IR at 25°C for ELO + 5.0 x 10^{-3} % mol of Al(OTf)$_3$

The analysis was performed directly on the liquid sample holder of the HART device in which 0.2 mg of sample was deposited. The spectrometer was programmed to generate a spectrum every 200 sweeps, at 4 cm^{-1} resolution in absorbance mode. Each sweep takes 4 min and all the time the sample is being irradiated by IR radiation during the experiment, keeping constant the temperature of the sample at 25°C. The experiment was stopped when the signal corresponding to the vibration of the epoxy ring vanished. Only the complete cured samples (confirmed first by FT-IR) were analyzed by DSC. An illustration of how this analysis was performed is exemplified in Figure 6 for the mixture ELO + 5.0x10^{-3} mol% of catalyst. It is possible to appreciate the degree of cure with the time.

Figure 7 shows the following of the cure for three mixtures only: 5, 10 and 16 mol% due the feasibility to polymerize in less than 1440 min (24 hrs). Higher loads of catalyst are not stable and polymerize very fast, while lower loads the curing process at room temperature resulted very slow in order to keep in use the FTIR. It is seen the catalytic effect of the triflate in the curing of ELO. As the load of catalyst increases the time for the maximum curing increases at the same temperature. For the same load of catalyst, but a higher temperature the cure reaction appears to proceed faster, and this time decreases as the temperature increases. With 5x10^{-3} mol% of catalyst, the system is very stable at room temperature, but it was possible to decrease at a half the temperature of curing of pure ELO. For both 5x10^{-4} and 1.x10^{-3} mol% of catalyst this could be not enough to fully catalyze the system at lows temperatures (50 and 40°C, respectively) due they did not reach a percent of cure higher than 90%. In all the followings the final product resulted in an insoluble polymer.

In situ ^{1}H-RMN experiment was performed for the mixture of ELO + Al(OTf)$_3$ at 36x10^{-3} mol% of catalyst in order to follow the structural changes during polymerization. As mentioned before, it was made at 40°C. A medium load of initiator and a low temperature were chosen to prevent the system from gelling rapidly that avoids to visualize the changes in the signals during the curing reaction. As could be appreciate in Figure 8, there are plotted 6 spectra, the first one corresponds to the initial mixture at 26°C; the others were taken at 40°C at 3, 7, 10, 15 and 22 min. The range that is showed is from 2.2 to 4.6 ppm. After and before this range there was not any changes in the spectra.
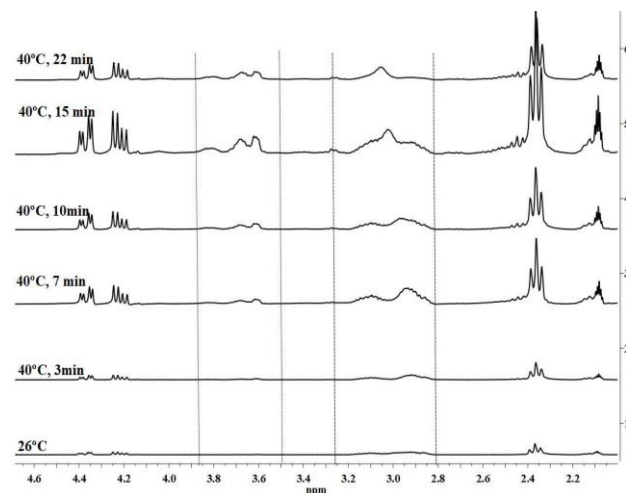

Figure 8. Cure following by *in situ* 1H-NMR at 40°C for ELO + 36 x 10^{-3} % mol of Al(OTf)$_3$

The main ^{1}H-NMR signals for ELO are at 3.1 ppm and 2.9 ppm that correspond to methylene hydrogens between two epoxy rings and to hydrogens of the carbons of epoxy rings, respectively [23,25,26]. It is evident that this pair of signals changes in form and their integral diminishes during the curing process. Also, in the region from 3.6 to 3.9 ppm a pair of signals begin to appear from the first three minutes of having started the heating at 40°C. These signals correspond to carbons that support a hydroxyl group due the aperture of the epoxy ring [26], confirmed the signals observed in FTIR at 3300 cm^{-1} (not showed region). These hydroxyl groups could be formed at the beginning of the reaction and once formed they start to react with epoxy groups in order to promote the crosslinking of ELO. Something important to notice is that there was a retention of peaks of the backbone glycerol structure (5.2-5.3 and 4.1.4.4 ppm) in ring opened resins, meaning no reactions on the ester groups is promoted by this catalyst.

Finally, the decomposition temperature (T$_{10}$) of cured products was evaluated respect to the load of catalyst and the temperature of cure. The T$_{10}$ was always diminished respect load of catalyst. It was observed in Figure 9 a first important decreasing of 34°C (10%) with the addition of the lower load of catalyst (5 x 10^{-4} mol%) and then T$_{10}$ continues decreasing as the amount of catalyst increases. For a composition of 5x10^{-3} mol%, the decomposition temperature has decreasing 63°C (18.2%), respect to the polymerized ELO without catalyst. Pure ELO was polymerized at 220°C for 2.5 hrs. An explanation could due to the presence of the catalyst into de matrix polymer so that it started to interact with the functional groups of the polymer matrix promoting braking reactions and an early decomposition of the whole resin.

Respect to temperature of cure, the T_{10} decreases as the temperature of cure diminishes. As an example, for mixture 2.5×10^{-3} mol, T_{10} at 40, 50, 60 and 80°C are, respectively: 289, 291, 293 and 294°C. This could be due to low temperatures the degree of cure usually doesn't reach more than 97%, at 40°C the most of the mixtures reach only a 60-97%. At higher temperatures enough energy is given to the mixture and the problems of diffusion during the gelling are overpassed and it reaches practically the 100% of cure, rendering a more resistant polymer network.
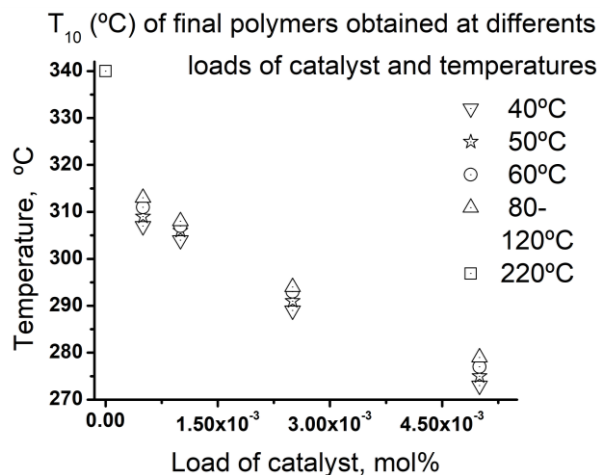

Figure 9. Degradation temperature (T_{10}) of the final polymers respect to the load of catalyst: 5.0×10^{-4}, 1.0×10^{-3}, 2.5×10^{-3}, and 5.0×10^{-3} mol% of Al(OTf)$_3$ and the differents curing temperatures

4. Conclusions

The important of this thermal following is that aluminum triflate resulted in a very effective catalyst for directly polymerization of ELO from very low loads, 5×10^{-4} mol% to 5×10^{-3} mol% for a very controlled process through a very range of temperatures from 25 to 100-120°C very much below their exothermal curve and to the cure temperature of pure ELO. Also, the reaction time was variable according to the temperature and load catalyst, but they ranged from 7 min for temperatures near to the exothermal curve and many days for temperatures of 40 and 50°C. Also, the T_{10} was also affected (diminished) more by the catalyst load than by the cure temperature. The results here showed could be useful for study profoundly the kinetic of some particular system of ELO + Al(OTf)$_3$ with or without the presence of some crosslinker agent. DSC and HART-FTIR spectroscopies used for following the cure process had a very good agreement in the determination of the percent of cure of the studied mixtures.

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