

Summary

Thermosetting polymers are materials with high thermal stability because of its tridimensional crosslinked network by covalent links. Due to these characteristics, they are very useful in industry.

Dual-curing is a combination of two processes where at the end a thermoset is obtained. Both processes are different so in the first stage it is obtained a completely cured thermoplastic or thermosetting polymer and in the second stage it is obtained another thermoset similar or different from the intermediate stage polymer. Dual-curing is an alternative process that allows obtaining tailored materials and nowadays, it is studied because of its innovation.

In this project, a particular dual-curing case is studied, using mixtures of acrylates/methacrylates with epoxy resins. Epoxy resin used is Glycidyl methacrylate, a resin that also incorporates a methacrylate group. In this case, dual-curing consists in a radical chain polymerization of acrylates and methacrylates resins by photocuring and a cationic polymerization of epoxies by thermal curing.

In the first part, acrylate and methacrylate monomers which are used through the entire project are studied separately with the purpose of obtaining, by combination of them, linear or crosslinked polymers at the intermediate stage, with tailorable thermomechanical properties.

In the second part, thermal curing and kinetics are studied to simulate results in isothermal conditions. In order to ensure safe storage stability and stable properties in the intermediate stage between photocuring and thermal curing, the use of reaction stabilizers effect is studied and verified experimentally.

Finally, thermal-mechanical properties of the materials after the photocuring process and after the thermal curing process have been analyzed.



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1. Glossary

GLICMA	Glycidyl methacrylate
HEA	Hydroxyl acrylate
HEMA	Hydroxyl methacrylate
HDDA	Hexanediol diacrylate
BA	Butyl acrylate
BMA	Butyl methacrylate
DMPA	2,2-Dimethoxy-2-phenylacetophenone
N	Jeffamine D-230 Polyetheramine
S	Trimethylolpropane tris(3-mercaptopropionate)
DSC	Differential Scanning Calorimetry
DMA	Dynamomechanical Analysis
TGA	Termogravimetry Analysis
T_g	Glass transition temperature
T_{g0}	Glass transition temperature of a sample before curing
$T_{g_{gel}}$	Glass transition temperature where occurs gelification and vitrification
T_{g^∞}	Glass transition temperature of a sample completely cured
T_c	Curing temperature
TTT	Time-Transformation-Temperature
x	Conversion
x_{gel}	Conversion when occurs gelification
dx/dt	Reaction rate

β	Heating rate
k	Kinetics constant
$f(x)$	Kinetics model
R	Ideal gas constant
$g(x)$	Integration of kinetics model
E_a	Activation energy
E_x	Apparent activation energy
T_i	Temperature at a certain instant
$t_{i,x}$	Required time to achieve x conversion in temperature T_i .
Δh	Reaction heat
Δh_{UV}	Heat evolved during the photocuring stage at room temperature
Δh_{post}	Residual heat of the photocuring stage evolved during post-cured
$\Delta h_{thermal}$	Heat evolved during the thermal curing with a dynamic program
Δh_{total}	Heat evolved during the photocuring and thermal curing.
dh/dt	Heat flow
dx/dt	Reaction rate
dm/dT	Degradation rate
ε	Deformation
γ	Deformation rate
E'	Storage modulus
E''	Loss modulus
$\tan\delta$	Loss factor

2. Preface

2.1. Origin of the project

The research group at the *Thermodynamics Laboratory (Heat Engines Department)* from the ETSEIB has carried out an intense research labor in the field of thermosetting polymers for more than 25 years, and for the last 15 years in collaboration with the *Department of Analytical and Organic Chemistry* from the Universitat Rovira i Virgili (URV). Research focuses on the processing and characterization of novel thermosetting materials with optimum thermal-mechanical properties by means of calorimetric, thermomechanical, imaging and spectroscopic techniques, among others.

Throughout the years, the research group at the ETSEIB has gained a deep experience in polymeric concrete, composites for sheet molding compound (SMC) applications, powder coatings, inter-penetrated networks, unsaturated polyester and epoxy resins, among others. The group is also expert in the kinetics analysis of curing processes with the purpose of optimizing curing processes in terms of time and energy savings.

2.2. Motivation

Thermosetting polymers are usually obtained after the polymerization reaction of monomers, oligomers or mixtures of them (resins), triggered by the application of heat or UV light, and with the help of adequate initiators or catalysts. During this process, this liquid-like mixture transforms into a non-flowing crosslinked network structure with high thermal and mechanical resistance. Processing can take place in one stage (A-staging), by which the curing reaction to produce the final component takes place in one step, or in two stages (B-staging), by which the polymeric precursors are pre-cured (or pre-dried) in a first stage, and completely cured later one in a final application and curing stage. B-staging is commonly used in complex and flexible processing of components and to eliminate production bottlenecks. However, B-staging requires a tight time and temperature control to avoid overcuring in the first step or else the use of solvents that are eliminated to produce a dried uncured material before the final application.

In order to overcome the limitations of B-stage processing, dual-curing (the combination of two curing processes for the obtaining of a thermosetting material) is emerging as a promising alternative to permit flexible processing without time-temperature constraints and better control on the material properties in the intermediate stage, and without needing to use solvents in the first curing/drying stage. In the present project, a particular dual-curing system is explored, combining the radical chainwise polymerization of methacrylates/acrylates by UV light and the thermal cationic homopolymerization of epoxy groups.

3. Objectives

The objective of this work is the study of sequential dual-curing processing of mixtures of methacrylate/acrylate components, of which at least one of them bears an epoxy group. The curing is carried out sequentially in two stages: first, the acrylate/methacrylate groups are polymerized by means of UV light and the use of a suitable photoinitiator, leading to a linear or crosslinked polymer depending on the acrylate/methacrylate functionality. In the second stage, the epoxy groups are homopolymerized by means of a thermal cationic initiator. A focus is placed on the possibilities of designing the structure of the material after the first curing stage, ranging from soft, uncrosslinked thermoplastic polymers to rigid and moderately crosslinked thermosets, and on the change of structure and properties after the second curing stage, leading usually to a more densely or tightly crosslinked network structure. Another focus is placed on the latency of both curing stages, especially the second one, in order to be able to adapt to flexible processing situations with intermediate storage for a prolonged period of time before the final application.

In more specific terms, the objectives of this work are the following:

- The analysis of the curing kinetics of methacrylate/acrylate monomers for the first curing stage (radical chainwise polymerization).
- The measurement of the thermal-mechanical properties resulting from the first curing stage of the methacrylate/acrylate monomers.
- The design of formulations comprising a mixture of monomers undergoing fast and effective cure in the first stage and with tailored structure and properties.
- The measurement of the thermal-mechanical properties and thermal stability of the designed formulations after the first curing stage.
- The analysis of the curing kinetics of the second curing stage (epoxy homopolymerization) after the first curing stage.
- The measurement of the thermal-mechanical properties and thermal stability of the designed formulations after the second curing stage.
- The study of the effect of reaction stabilizers on the kinetics of the second curing stage.
- The assessment of the long term stability of the materials before the second curing stage.

4. Introduction

4.1. Thermosetting polymers

Polymers can be classified for its behavior with respect to temperature in thermoplastics and thermosets [1]. A thermoplastic material presents a rigid behavior below its glass transition temperature (T_g) and it is soft and rubber-like when temperature is above T_g , eventually becoming fluid because of the absence of permanent (covalent) crosslinking between polymer chains. In contrast, a thermoset material only softens above T_g , remaining in a rubbery state and incapable of flowing at elevated temperatures due to the presence of permanent (covalent) crosslinking. For this reason, thermosets cannot be molded when it is cured unlike a thermoplastic, which is possible to bring it from vitreous state to fluid and the other way round.

The crosslinked structure of thermosetting polymers is not altered until high temperature causes bond cleavage and degradation of the material. Polymerization of monomers with a functionality of 2 leads is necessary to the formation of linear polymers, while it is required (but not sufficient, since composition and ratio is also important [1]) to use monomers with a functionality of at least 3 to form a polymer network.

The synthesis of thermosetting polymers is illustrated in Figure 1. The process starts with a soluble phase consisting of monomers (a). Monomers are joined as reaction is advanced and polymeric chains are formed, with increasing size and degree of ramification (b). During the conversion of functional groups, there is a point when gelation phenomenon occurs and a giant macromolecule with infinite mass, percolating the entire system appears (c). This is a non-reversible transformation by which the material changes from viscous liquid (soluble) state to a non-flowing elastomer gel (insoluble) state. As the curing advances, the gel fraction increases in size and the amount of soluble phase is decreased until disappearing to create a 3-dimensional network within all the material (d)

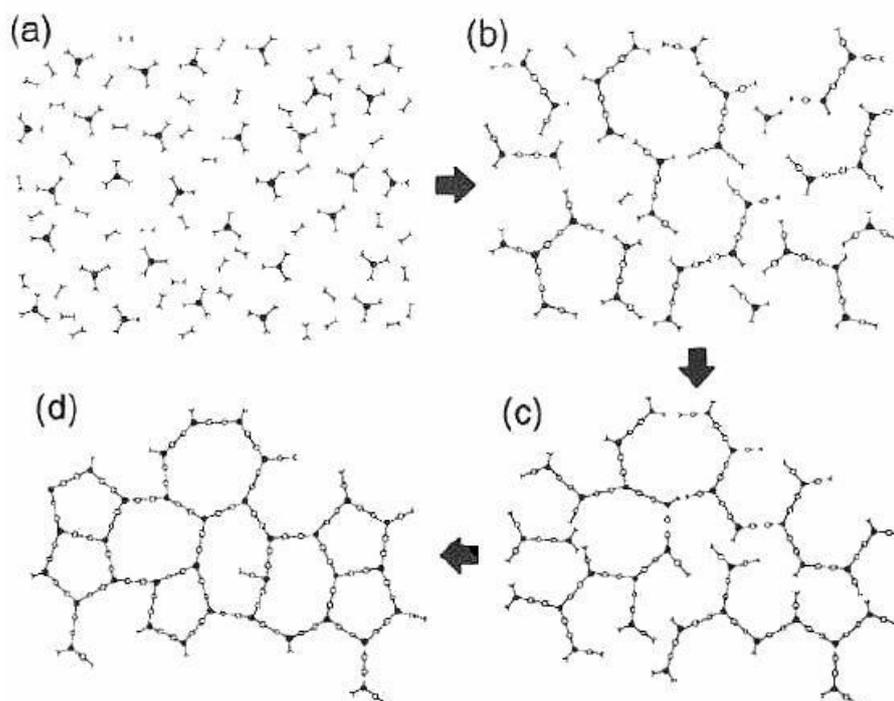


Figure 1. Formation of a thermosetting polymer network during a curing process

The glass transition temperature is a very important parameter in thermoplastic and thermosetting polymers, as it reflects the change from a rigid, glassy state with very low chain mobility ($T < T_g$) to a state where chain mobility is allowed and significant chain rearrangements can occur ($T > T_g$). Many important properties as elasticity modulus are dependent on proximity between curing temperature and glass transition temperature. Glass transition temperature is determined using techniques as differential scanning calorimetry (DSC) or dynamomechanical analysis (DMA).

Vitrification is a reversible transformation that occurs when the temperature of the material decreases below its glassy temperature and it is of key importance during processing of thermosetting polymers. The starting monomers have a very low glass transition temperature (T_{g0}) and, when the curing process starts, the T_g of the system increases due to increasing molecular weight and subsequent decreasing chain mobility. If the glass transition temperature approaches and overcomes the curing temperature, the system undergoes vitrification, with the subsequent decrease in chains mobility slowing down curing rate and eventually leading to a halt. Since vitrification is a reversible phenomenon, curing can be completed increasing curing temperature, as the partially cured thermoset is devitrified and the mobility of the reacting species is high enough to permit curing at a sufficient rate.

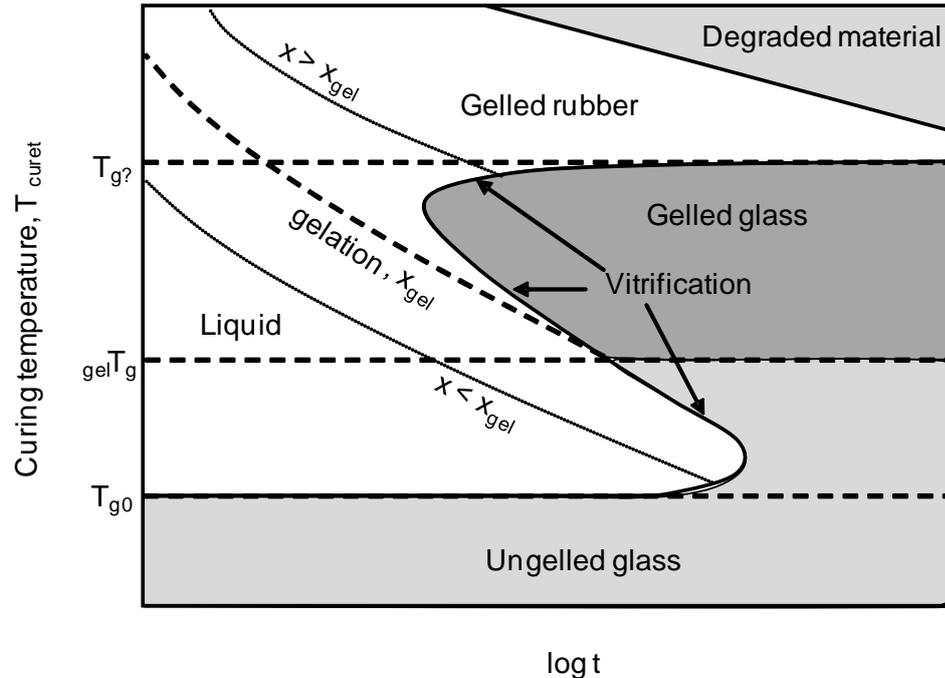


Figure 2. Diagram TTT of a thermoset system

TTT diagrams (Time-Transformation-Temperature) are used to study thermoset polymers curing [2]. Difference states through which it passes thermosets polymers during curing and its three critical temperatures are indicated in TTT diagrams.

T_{g0} = glass temperature of material before curing.

T_{ggel} = glass transition temperature where occurs gelification and vitrification.

$T_{g\infty}$ = temperature where curing is complete.

Some remarks can be made in terms of the relationship of the curing temperature T_c with these critical temperatures:

1. When $T_c < T_{g0}$, material is in the glassy state and is not be able to cure.
2. When $T_{g0} < T_c < T_{ggel}$, liquid resin can react until T_g coincide with T_c . In this point, vitrification process is initiated and, as mentioned before, reaction is controlled by diffusion processes. As material does not gel, it retains its flowing ability and it can be processed and manipulated easily. This is usually the intermediate stage during B-stage processing of thermosets.
3. When $T_{ggel} < T_c < T_{g\infty}$, the material first undergoes gelation and, as curing temperature reaches glass transition temperature, it vitrifies and, as it is incapable of flowing, some processing operations and manipulations are not further allowed.
4. When $T_c > T_{g\infty}$, material will be completely cured and will remain in rubbery state.

However, this description is only strictly applicable to simple curing processes. When more than one curing reaction is combined and the process can take place in a sequential way, such a diagram should be adapted for each one of the curing process taking place. Some of the events and states discussed above might not be present in the specific TTT diagram of each curing process depending on the state of the system between the stages (i.e. the polymer might not gel during the first curing stage, or it might already gelled before the second curing stage).

4.2. Dual-curing

Dual-curing is an alternative way of processing thermosetting materials consisting of two reactive processes that coexist in a system, which can be activated simultaneously, sequentially or with overlap. These reactions must be compatible to avoid inhibition between them. Dual-curing emerges as a way of enhancing conventional processes in terms of flexible processing and overcoming some drawbacks of the so-called B-stage processing.

The term B-stage refers to thermosetting systems that are heat- or photocured for a short period of time and then cooled to prevent complete polymerization of the resin system. At this point, it is a solid that is partially cured and it is found in a stage for convenience of an overall process. At some later point, it is heated to reactivate polymerization and complete the curing cycle [1]. One of the drawbacks of this methodology is the risk of over-curing the resin when is applied to a surface and pre-cured, losing some relevant characteristic such as adhesion that might be relevant for the application. In some cases, the use of a solvent is necessary in this process to blend epoxy resins for the reason of its high viscosity and then this solvent has to evaporate. Therefore, the term B-stage refers here to the first drying step needed to obtain the material in a convenient state or after application as coating on a substrate, for instance.

There are a high number of possible combinations of curing processes leading to dual-curing systems, only a few of them are shown and commented to illustrate their application:

- *Dual-curing of Waterborne Urethane-Acrylate Coatings by UV and Thermal Processing [3]*: The authors synthesized a water-based dual cure urethane-acrylate oligomer containing hydroxyl and protected isocyanate groups that formed stable dispersions in water due to the presence of carboxylate groups grafted on the oligomer chain. The dry films were cured mainly by a combination of UV to induce the polymerization of the acrylate double bonds, followed by a thermal cure to release blocked isocyanates that promote the polycondensation by reaction with the hydroxyl groups, thus allowing cure of the material in shadowed areas that were not accessed by the UV light.

- *Dry adhesive bonding of nanoporous inorganic membranes to microfluidic devices using the OSTE(+) dual-cure polymer* [4]: The authors combined thiol-ene (activated by UV light) and thiol-epoxy (thermal activation) curing processes for transfer bonding applications, allowing the incorporating fragile nanoporous inorganic membranes into microdevices. After the photochemical thiol-ene reaction, the material was soft and suitable for bonding, while during the thermal cure, it stiffened.
- *UV-radiation curing of acrylate/epoxide systems* [5]: Interpenetrating polymer networks (IPN's) are synthesized by light-induced cross-linking polymerization of a mixture of acrylate and epoxide monomers.
- *Two-Stage Reactive Polymer Network Forming Systems* [6]: The authors combined sequential base-catalyzed thiol-acrylate reaction (room temperature) with the radical chainwise polymerization of excess acrylate groups (UV light). Following this methodology, it was possible to synthesize a wide range of thermosetting materials with properties ranging from soft elastomers to tightly crosslinked polymers by making small changes in the composition of the curing formulation.

The number of possible combinations leading to dual-curing processing is very large. In the present case it has been chosen to study the combination of radical, chainwise polymerization of methacrylate/acrylate monomers triggered by UV light and the cationic epoxy homopolymerization of epoxides triggered by means of a latent thermal initiator. There are some close precedents to our approach such as those shown in [5] and [7]. However, the focus will be placed on the possible tailoring of the material structure after the first stage, the material properties at the end of the process and the possibility of controlling the sequential curing process by enhancing the latency of the second process.

4.3. Epoxy resins

Epoxy resins are very used for its properties and can be used as adhesives and surface coating for example [8]. Due to its high reticulation, they have a fragile behavior so it is limited in certain applications.

Epoxy groups are characterized by the presence of more an oxygen atom linked to two carbon atoms which are united together with a chemical link are contained in an epoxy group, forming a cycle with three atoms. High reactivity of this molecule is due to its own annular tension in C-O-C ring and polarity in C-O links. This fact improves the reaction with a large number of substances, so it provides a wide range of applications.

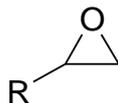


Figure 3. Epoxy group

Epoxy resins are classified as glycidyl or non-glycidyl resin. First ones are obtained through polycondensation reaction with diols (glycidyl ethers), diacids (glycidyl esters) or diamines (glycidyl amines) with epichlorhydrine (ECH). Non-glycidyl resins are synthesized by direct oxidation of olefins at high temperature, with silver catalyst or under mild conditions using oxidizing agents such as 3-chloroperbenzoic acid [9] and they can be classified in aliphatic or cyclic.

The variety and the number of available curing agents for epoxy resins is very large due to the high reactivity of the epoxy ring [1]. However, in the project the cationic ring-opening polymerization of epoxy rings will be used.

In ring-opening polymerization, the Activated Monomer Mechanism (AMM) has been proposed for the polymerization of several cyclic monomers [10],[11]. The AMM of cyclic ethers is based on the established mechanism of hydrolysis for these compounds.

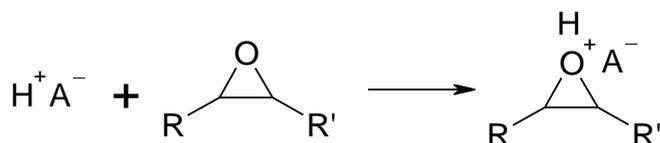


Figure 4. Cationic polymerization of epoxides (1)

If an excess of epoxy groups is present in the system, the hydrolysis shown above can be followed by several consecutive steps of alcoholysis, proceeding by the same path:

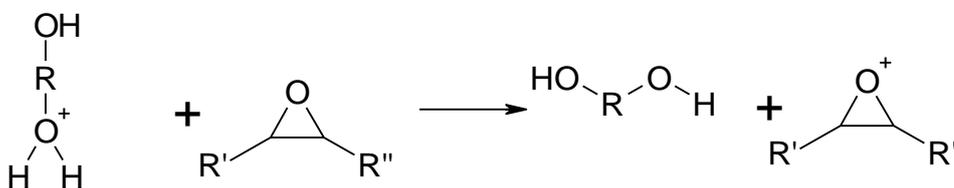


Figure 5. Cationic polymerization of epoxides (2)

Thus, propagation proceeds on the hydroxyl chain ends by addition of the protonated monomer. After each addition, a new hydroxyl group is formed.

When cyclic ether is protonated and if in the reaction mixture the hydroxyl groups are absent, the protonated cyclic ether reacts with the non-protonated giving the tertiary oxonium ion:

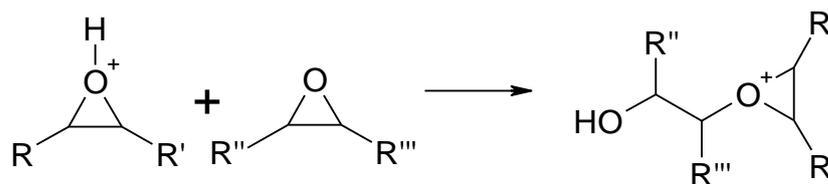


Figure 6. Cationic polymerization of epoxides (3)

Polymerization can be proceeded again as a chain process with tertiary oxonium ions as chain carriers located at the ends of the macromolecules. This mechanism is called the Active Chain End [10],[11]. The presence of hydroxyl groups at the polymer ends complicate this mechanism and Activated Monomer Mechanism and Active Chain End can coexist, both being responsible for building the polyether macromolecules. When there is sufficiently high concentration of hydroxyl groups, then the Active Monomer Mechanism may outweigh Active Chain End mechanism.

4.4. Acrylate resins

Acrylate monomers are based on the structure of acrylic acid, which consists of a vinyl group and a carboxylic acid terminus. They are known for their transparency, resistance to breakage and elasticity, used in many applications [12], and highly versatile monomers as they can form linear or crosslinked polymers easily by the radical chainwise polymerization of the double bond(s) present in their structure.

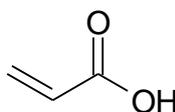


Figure 7. Acrylic acid

Acrylates and methacrylates are typically polymerized by radical chainwise mechanism [11] consisting in a sequence of three steps: initiation, propagation and termination. Initiation step involves two reactions. The first is the production of free radicals by dissociation of an initiator species I to yield a pair of radicals $R\cdot$.

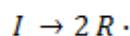


Figure 8. Radical chain polymerization (1)

The second part involves the addition of this radical to the first monomer molecule M to produce the chain initiating radical $M_1\cdot$.

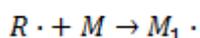


Figure 9. Radical chain polymerization (2)

Propagation consists of the growth of $M_1 \cdot$ by the successive additions of large numbers of monomer molecules. Each addition creates a new radical that has the same identity as the one previously, except that it is larger by one monomer unit.

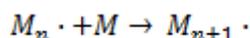


Figure 10. Radical chain polymerization (3)

Finally, termination occurs when the propagation polymer chain stops growing by bimolecular reaction between radicals. There are two types of reaction: by combination (coupling) or by disproportionation which results the formation of two polymer molecules, one saturated and one unsaturated. Termination can also occur by a combination of them. The two different modes of termination can be represented in general terms by:

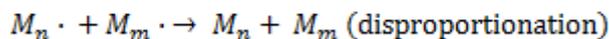
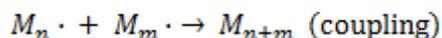


Figure 11. Radical chain polymerization (4)

Photochemical polymerization occurs when radicals are produced by ultraviolet and visible light irradiation in a reaction system. Some compound in the system undergoes excitation by energy absorption and subsequent radicals decompose.

The initiation rates can be very fast and are controlled by a combination of the source of radicals, light intensity and temperature. Photochemical offers several advantages: can be spatially directed and turned on and off by turning the light source off and on or, can use solvent-free systems and offer economic and environmental considerations.

4.5. Reaction stabilizers and latency concept

When an initiator is added, reaction can take place within several days at environmental conditions. To prevent premature thermal curing different additives can be used. Stabilizing agents may be used to prevent the occurrence of side reactions such as oxidation, chain scission, cross-linking and uncontrolled reactions caused by heat and ultraviolet light. For example, heat stabilizers are mainly used for products made of polyvinyl chloride and light stabilizers for polypropylene and polyethylene.

Latency period refers to the stability of a sample without reacting for a period time. To increase this period and allow safe shelf storage of the prepared formulations, different additives may be used.

Concerning the present project, acrylates and methacrylates usually contain an inhibitor such as hydroquinone, a radical trapping agent, to prevent premature polymerization of the double bonds. Furthermore, the initiator used is activated upon irradiation with UV light, and therefore the acrylate/methacrylate polymerization should not occur as long as the sample is protected from the light. In order to control the curing sequence, the use of a photoinitiator for the epoxy resin is prevented as irradiation of the sample would lead to the simultaneous polymerization of double bonds and epoxy groups [5]. For that purpose, a latent thermal initiator has been used but some additives should be used to prevent its slow decomposition and release of the active species leading to premature polymerization.

One possibility is the addition of thiol compounds that can participate in the radical polymerization of acrylates/methacrylates. Polymerization of compounds with thiols groups are begun by photochemical curing, originating initiating free radicals. These primary radicals can react with the thiol group, producing a thiyl radical. Then, the thiyl radical reacts with the double bond of the unsaturated monomer, in this project with the double bond of the acrylate or methacrylate group, to generate a secondary free radical. This secondary radical can continue the polymerization by double bond or reacts with another thiol group. When thiols are exhausted, principal reaction is radical chain wise polymerization of double bond.

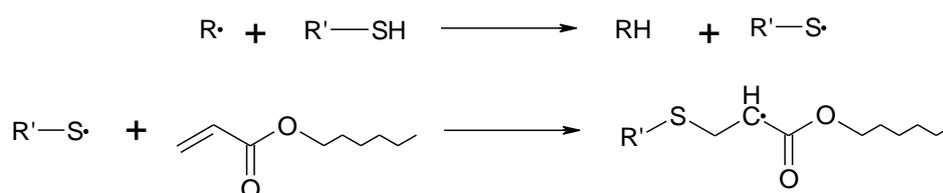


Figure 12. Scheme of polymerization of compounds with thiols groups (1)

The presence of thio-ether groups in the medium has been described to affect the cationic epoxy homopolymerization of epoxides [13],[14]. Sulfur is a nucleophile, so it has free electron pairs which can react with oxonium cations that propagate epoxy polymerization.

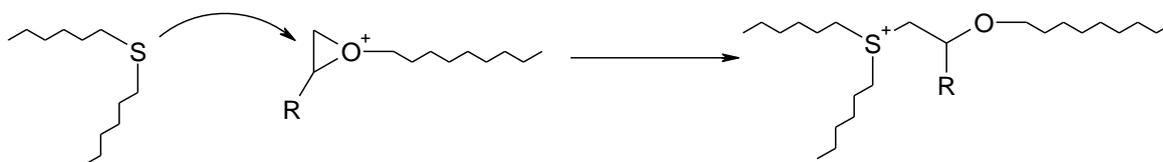


Figure 13. Scheme of polymerization of compounds with thiols groups (2)

It is formed a trialkylsulfonium cation that is inactive at low and moderate temperatures but when temperature increases, it decomposes and propagation reaction is reactivated [14]. This mechanism based on cationic reaction initiators is complex [15].

Another tentative agent that can be used is an amine. In the case of primary or secondary amines, condensation of epoxy and amine groups can take place [1]. Amine also has free electron pairs, so nucleophile attack occurs and it can be at room temperature when it is an aliphatic amine. A secondary amine is produced when a primary amine reacts and a tertiary amine is given when a secondary amine reacts.

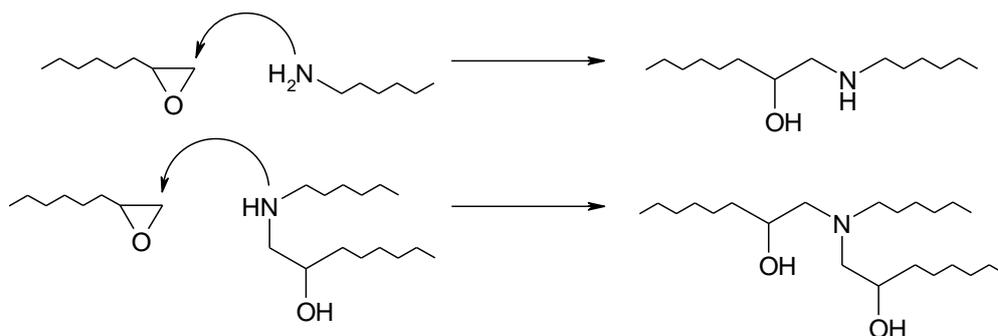


Figure 14. Scheme of polymerization of compounds with amine groups

Tertiary amines are used, with small amounts, to stabilize systems which can have cationic polymerization [16]. The mechanism by which it takes place is not well known, but it can be hypothesized that quaternary ammonium salts can be produced when tertiary amines interact, due to their free electron pairs, by analogy with sulphur compounds, as shown above. Different quaternary ammonium salts are known to act as latent thermal initiators [17].

The advantage of using thiol or primary/secondary amine compounds is that these two kinds of reaction stabilizers are linked to the material structure, so completely cured materials have a lesser amount of volatile or soluble compounds.

5. Kinetics analysis

The reaction rate of these samples during a curing process can be described, from a phenomenological point of view, depending on k and $f(x)$. k is kinetics constant, it relies on temperature, and $f(x)$ is function which relies on conversion.

$$\frac{dx}{dt} = k \cdot f(x) \quad (1)$$

Kinetics constant k can also be expressed with Arrhenius equation and previous equation is expressed as:

$$k = k_0 \cdot e^{-\frac{E}{RT}} \cdot f(x) \quad (2)$$

$$\frac{dx}{dt} = k_0 \cdot e^{-\frac{E}{RT}} \cdot f(x) \quad (3)$$

Every kinetics process is totally characterized when E , k_0 and $f(x)$ are known. This equation is appropriate for single-step as for multi-step. The term multi-step refers to the coexistence of different physics and chemical processes. It's considered two kinds of kinetics analysis:

- Isoconversional method or model-free: the key parameter is the apparent activation energy during a process at every instant without knowing the kinetics model and independently of the thermal process.
- Model-fitting method: approximation of the experimental data to kinetics models is searched and E , k_0 and $f(x)$ kinetics parameters are calculated.

Isothermal and dynamic integral methods [19] are described below.

5.1. Isothermal integral method

Integration of kinetic differential equation is as follows:

$$g(x) = \int_0^x \frac{dx}{f(x)} = \int_0^t k_0 \cdot e^{-\frac{E}{RT}} \cdot dt \quad (5)$$

Reaction mechanism is represented with $g(x)$ as integral function. In isothermal conditions, $g(x)$ is:

$$g(x) = \int_0^x \frac{dx}{f(x)} = k_0 \cdot e^{-\frac{E}{RT}} \cdot t \quad (6)$$

Considering k_0 and E are constant in conversion interval $0-x$, in other words, from time 0 to time t , previous equation can be expressed as:

$$\ln(t_{i,x}) = \ln\left(\frac{g(x)}{k_{0,x}}\right) + \frac{E_x}{RT_i} \quad (7)$$

Where $t_{i,x}$ is required time to achieve x conversion in temperature T_i .

$\ln(t_{i,x})$ representation respect $1/(RT_i)$ results in a line with E_x as slope. With E_x and $\ln(g(x)/k_{0,x})$ for each conversion, isothermal curves can be simulated at any temperature.

5.2. Dynamic integral method.

This method is applied to processes with constant heating rate β . Temperature is not constant, therefore it is necessary changing variable $dt = dT/\beta$ and considering that to $T=0$ is not possible to have any reaction, integral expression results in:

$$g(x) = \frac{k_0}{\beta} \cdot \int_0^T e^{-\frac{E}{RT}} \cdot dT \quad (8)$$

This integral has no analytical solution and solution can be approximated or integral has to be numerically solved. Kissinger-Akahira-Sunose method expression (KAS) is used to approximate this integral and it is supposed that $E \gg 2RT$ and is constant in throughout the interval:

$$\ln\left(\frac{\beta_i}{T_{i,x}^2}\right) = \ln\left(\frac{k_{0,x}R}{g(x) \cdot E_x}\right) - \frac{E_x}{R \cdot T_{i,x}} \quad (9)$$

Activation energy E_x is obtained from the slope of the representation of $\ln\left(\frac{\beta_i}{T_{i,x}^2}\right)$ respect $-\frac{1}{R \cdot T_{i,x}}$. It is deduced from origin ordinate the parameter $\ln\left(\frac{g(x)}{k_{0,x}}\right)$ when activation energy E_x and isothermal cured can be simulated form both dates to any temperature.

6. Experimental

6.1. Materials

All the methacrylate and acrylate monomers have been supplied by Sigma-Aldrich. Photoinitiator 2,2-Dimethoxy-2-phenylacetophenone (DMPA) has been supplied by Sigma-Aldrich. Thermal cationic initiator CXC-1612 (described as a quaternary ammonium salt) has been supplied by King Industries. Trimethylolpropane tris(3-mercaptopropionate) has been supplied by Sigma-Aldrich. Polyetheramine Jeffamine D-230 has been supplied by Huntsman. All the reagents have been used without further purification and kept in a fridge to protect them from high temperatures and sunlight.

The following table shows some characteristic properties of the acrylate and methacrylate monomers used and their acronyms. Their structure appears in the scheme below. GLICMA has been used as a compound that is polymerized in the first process but can also undergo homopolymerization of the epoxy group in the second stage. HEMA and HEA are hydrophilic compounds that are used in specific applications other than thermosetting formulations: poly(2-hydroxyethyl methacrylate)(pHEMA) was first used as an optical implant, as a suitable material for contact lenses for their functions as a hydrogel. Polyhydroxyethyl acrylate can be used to materials and coatings for medical devices. However, in the present project they have been chosen for their reactivity in the first curing process. As mentioned in the introduction section, the epoxy homopolymerization process is greatly influenced by the presence of compounds bearing hydroxyl groups. HDDA has been used as crosslinking agents for the first curing stage as it is a tetra-functional monomer (each double bond is bifunctional in chainwise polymerization process) that lead to the formation of a crosslinked network. BA and BMA have been selected to reduce the hydrophilicity of the materials. The choice of both methacrylate and acrylate monomers enables to tune the glass transition temperature of the materials after the first curing stage, as poly(methacrylates) are known to have a lower mobility than poly(acrylates).

Table 1: Characteristics of the acrylate and methacrylate monomers and the acronyms used in this work.

Resins	Acronym	Molecular weight (g/mol)	Nº epoxy groups	Nº Acrylate and methacrylate groups
Glycidyl methacrylate	GLICMA	142,15	1	1
2-Hydroxyethyl methacrylate	HEMA	130,14	-	1
2-Hydroxyethyl acrylate	HEA	116,12	-	1
1,6-Hexanediol diacrylate	HDDA	226,27	-	2
Butyl acrylate	BA	128,17	-	1
Butyl methacrylate	BMA	142,20	-	1

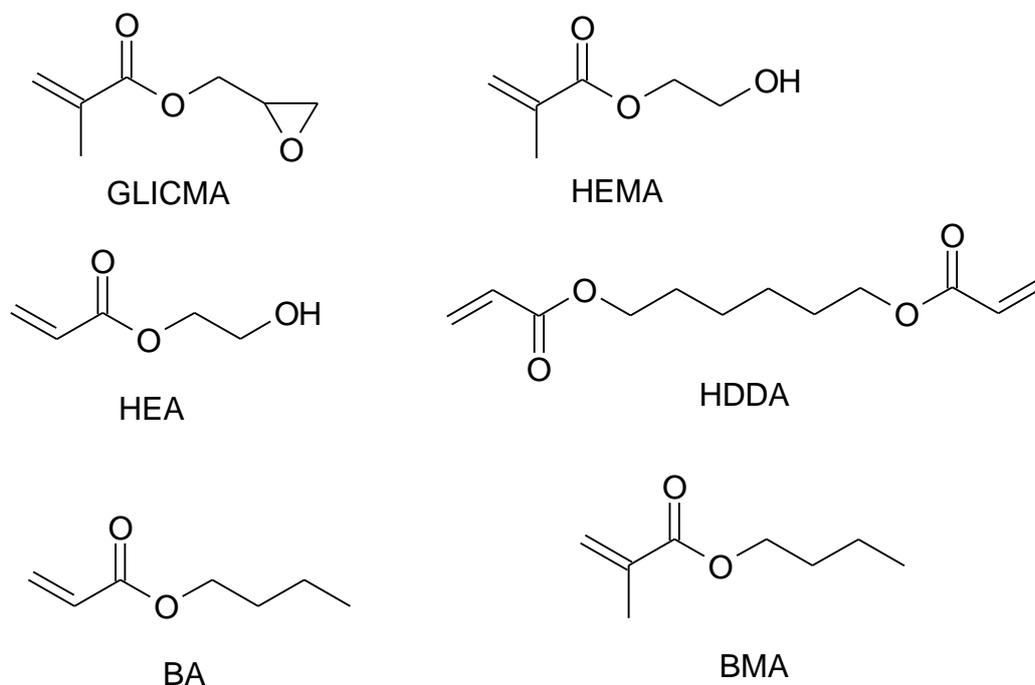


Figure 15 Structure of the different acrylate and methacrylate monomers

The following table shows the initiator and stabilizing agents used in this work, their acronym and their use. Their structure (where available) is shown in the figure below.

Table 2: Initiators and stabilizing agents. *The structure of CXC-1612 is not known.

Materials	Acronym	Type
2,2-Dimethoxy-2-phenylacetophenone	DMPA	Photochemical initiator
CXC-1612 quaternary ammonium salt*	CXC	Thermal cationic initiator
Trimethylolpropane tris(3-mercaptopropionate)	S	Reaction stabilizer
Jeffamine D-230 Polyetheramine	N	Reaction stabilizer

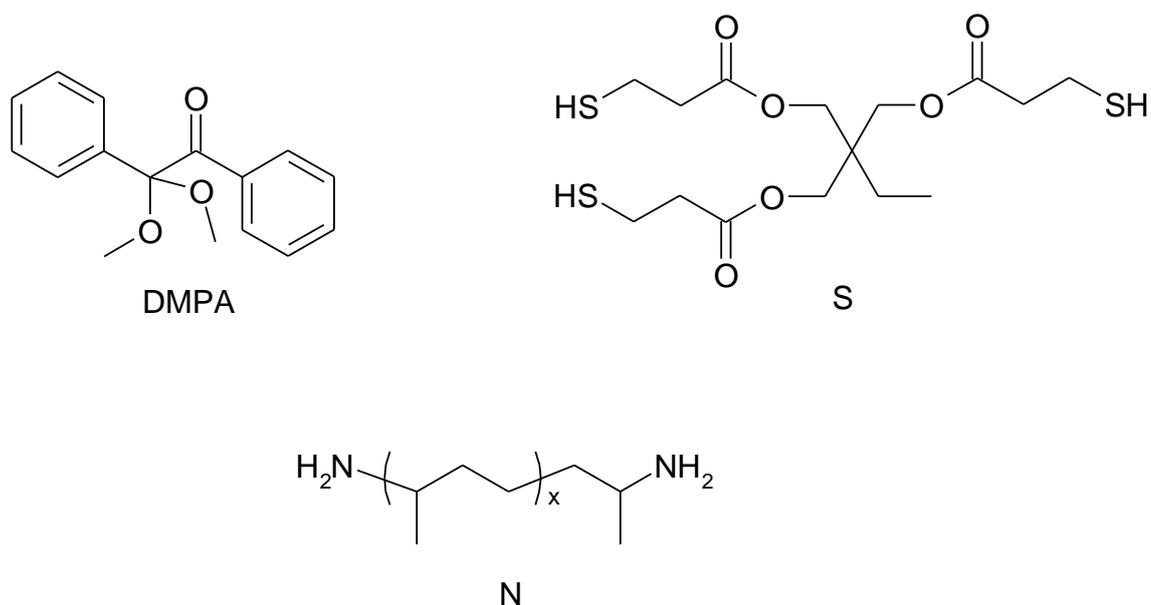


Figure 15. Structure of the photochemical initiator DMPA and the stabilizing agents for the epoxy homopolymerization process.

6.2. Preparation of the samples

All of the formulations are prepared in a 5 mL vial. First of all, it is introduced initiators with a spatula and resins are added with a syringe.

The mixture is homogenized by mechanical stirring with a spatula and the vial is closed, sealed with paraffin wax and stored in a freezer to prevent premature polymerization.

Formulations containing the single acrylate/methacrylate monomers and mixtures of them with different weight proportions and 3 phr (parts per hundred) of DMPA were prepared in order to study the first curing process and the properties of the intermediate materials. For the study of the second curing process, selected formulations with 3 phr of DMPA and 1 phr of CXC were prepared. In addition, in order to study the effect of the different stabilizing agents, 1 phr S or 0,1 phr N were also added.

Prismatic rectangular shape samples were prepared for the different analyses. A Teflon mould covered with glass slides on both sides to permit irradiation was used. The glass slides were previously coated with silicone mould release agent and the assembly was fixed with metal clips. To fill the mould with sample a syringe was used. The samples were cured with a transilluminator UV and later on heat-cured in a thermal oven.

Other sets of samples were prepared for the study of the effect on the latency of the different stabilizing agents. Aluminum pans were filled with a small amount of formulation sample, photocured, subsequently sealed and placed in glass tubes. The glass tubes were placed in a thermostatic bath at a controlled temperature and removed after different periods of time for their posterior analysis.

6.3. Instrumentation

6.3.1. Differential Scanning Calorimetry (DSC)

It is used the calorimeter Mettler DSC822e, equipped with a TSO801RO robotic arm and refrigerated using liquid nitrogen. It is possible to make the process inert because there is a nitrogen gas entrance. Approximately 5 mg of the sample is introduced in an aluminum pans and it is added a cover with a hole to allow volatiles components exit.

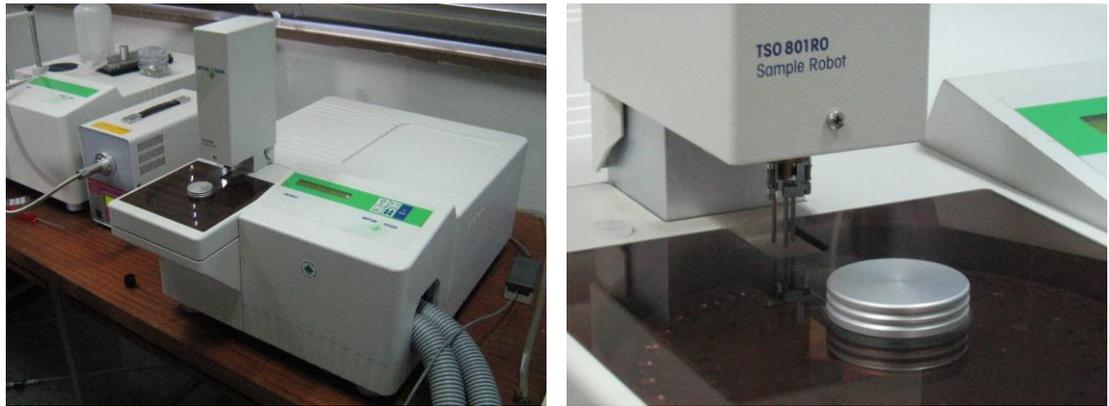


Figure 16. Calorimeter DSC822e with a TSO801RO robotic arm

Calorimetry is useful to know thermal properties as T_g , heat capacity, reaction enthalpy, etc. using the variation in the sample and the reference sample. When the sample is suffered by some thermal transformation as fusion or glass transition, it is noticed a temperature variation between both samples and it is proportional to transition of the sample. But in compensated power systems, equipment is capable of measuring or applying the necessary heat in order that the sample and the reference sample follow the same thermal program, directly proportional to the heat absorbed or evolved.

It is assumed that during the curing process in DSC, heat evolved is proportional to the degree of conversion x , and the rate of reaction dx/dt is proportional to the heat flow released dh/dt .

$$\frac{dx}{dt} = \frac{\left(\frac{dh}{dt}\right)_t}{\Delta h_{total}} \quad (10)$$

$$x = \frac{\Delta h_t}{\Delta h_{total}} \quad (11)$$

Where $(dh/dt)_t$ and Δh_t are heat flow released in an instant t and released heat until an instant t , and Δh_{total} is reaction heat total.

Dynamic and isothermal experiments are possible with DSC. T_g , residual heat and thermal process heat are determined with a dynamic program of $\beta = 10^\circ\text{C}/\text{min}$. Residual heat and heat thermal process are found by integrating the curve between T_1 and T_2 .

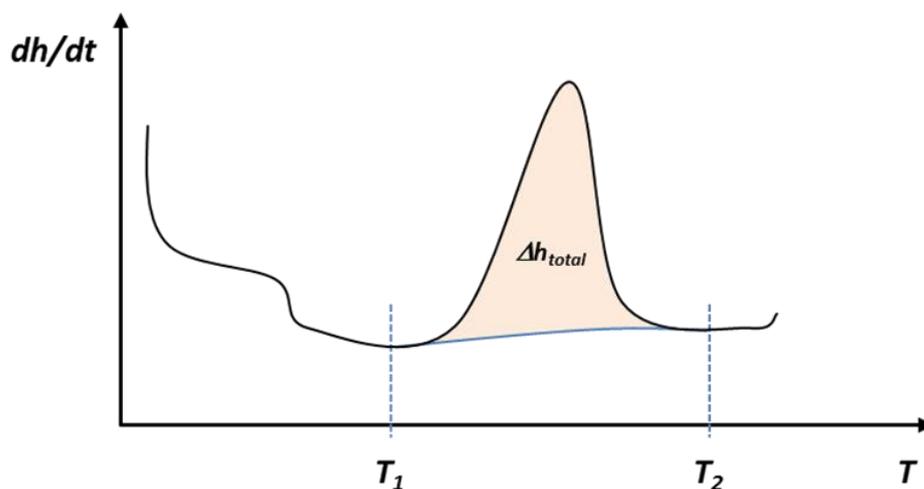


Figure 17. Curve obtained with DSC during a dynamic process

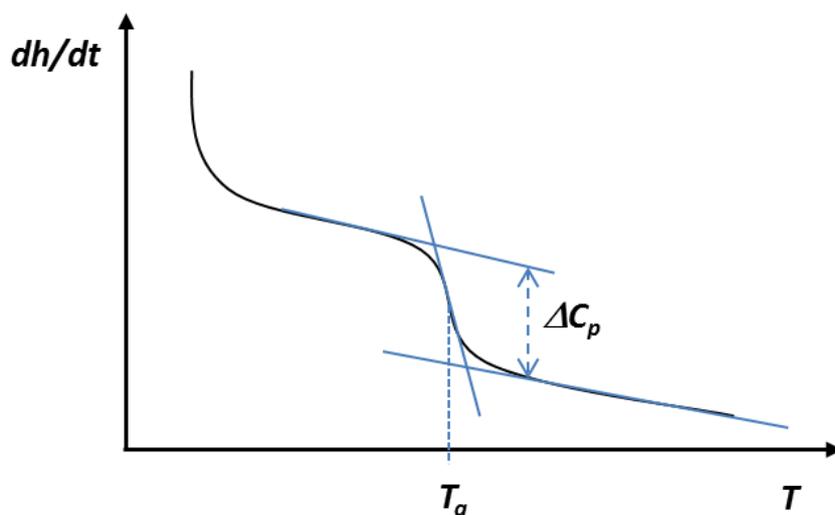


Figure 18. Theoretical curve to calculate Tg

Kinetics is studied with different β : 20, 10, 5 and 2,5 °C/min for each formulation. It is possible to extract a conversion-temperature curve and conversion is calculated as:

$$x = \frac{\Delta h_T}{\Delta h_{total}} \tag{12}$$

Δh_{total} is the total reaction heat and Δh_T is heat released to a temperature T.

With isoconversional integral method KAS and the application of the isothermal method it is possible to simulate isothermal curves at any temperature and the hypothetical latency at low temperature.

6.3.2. Photo-DSC

This technique is used to analyze the heat of photocuring reaction in each sample. Samples are photocured with a Mettler DSC-821e calorimeter appropriately modified to permit irradiation with a Hamamatsu Lightningcure LC5 (Hg-Xe lamp) with two beams, one for the sample side and the other for the reference side. Samples weighing approximately 5 mg are cured in open aluminum pans in a nitrogen atmosphere. Two scans were performed on each sample to subtract the thermal effect of the UV irradiation from the photocuring experiment. Samples are photocured at 30°C and program consists of 2 min of temperature conditioning, 6 min of irradiation and finally, 2 min more without UV light, and at intensity of $\sim 60 \text{ mW/cm}^2$.

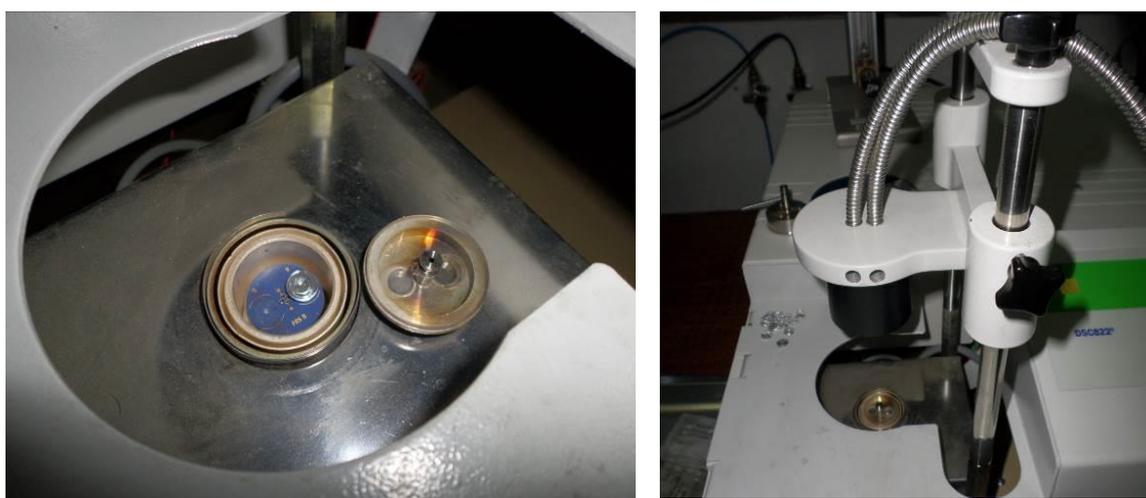


Figure 19. Mettler DSC-821e calorimeter with a Hg-Xe lamp

6.3.3. Thermogravimetry Analysis (TGA)

Mass loss experienced by a sample in an isothermal or dynamic program is able to measure with thermogravimetry analysis. This technique makes possible studying polymer degradation and knowing decomposition temperature. Thermal resistance of the sample is shown and it is associated with its intern structure.

The model used is thermobalance Mettler-Toledo TGA/SDTA 851e/LF/1100 with a gas controller GC200.



Figure 20. Thermobalance Mettler-Toledo TGA/SDTA 851 e/LF/1100

For each cured sample, it is cut approximately a piece around 10 mg and is collocated in a crucible of silicon oxide with a perforated cover. Sample is inserted on the balance into the heating chamber, and it is subject to a thermal program. Mass loss is registered while temperature increases and volatile elements are released. During the whole process, chamber is inert with N_2 . Finally, it is possible to obtain loss mass curves depending on temperature.

A dynamic process is programmed to make thermogravimetry analysis from 30°C to 800°C with $\beta=10^\circ\text{C}/\text{min}$ as heating rate and a flux of 50 mL of N_2 .

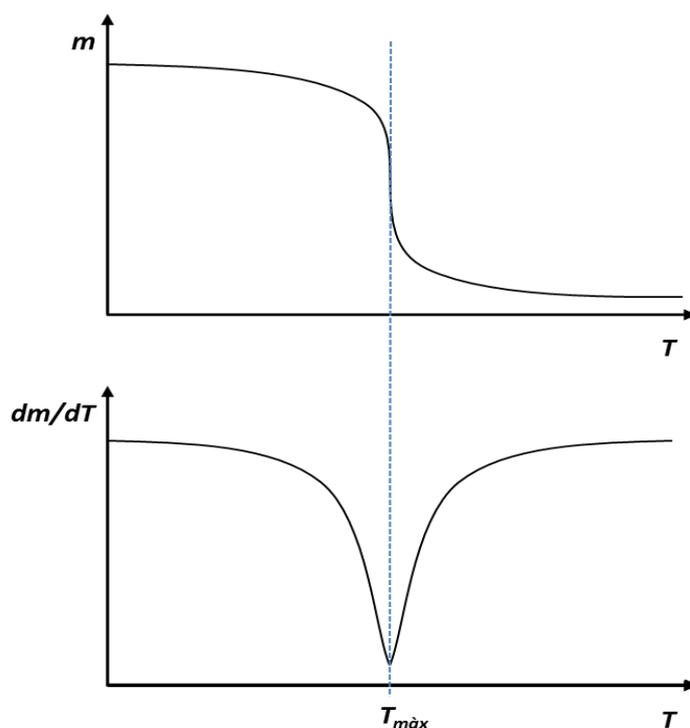


Figure 21 TGA curves. Mass loss and decompose rate

6.3.4. Dynamic Mechanical Analysis (DMA)

A TA Instrument DMA Q800 model with air cooling is used.



Figure 22. TA Instrument DMA Q800

Dynamomechanical analysis is based on the viscoelastic nature of polymers. Hooke's law is followed by elastic materials and they show a deformation ϵ proportional to applied stress σ (0° phase angle), while deformation is proportional to the speed of deformation $-\dot{\gamma}$ (90° phase angle) when materials are viscous. Polymers have a viscoelastic nature, so presents an intermediate behavior. Samples are analyzed following a sinusoidal deformation program and, as a consequence of the viscoelastic behavior, there is a phase lag between the deformation and the stress applied to the samples. A complex stress modulus E^* can be measured by the ratio of amplitudes between stress and deformation. Three parameters can be calculated with dynamomechanical analysis:

$E' = |E^*| \cdot \cos\delta$: component with phase difference which is proportional to elastic behavior.
Storage modulus.

$E'' = |E^*| \cdot \sin\delta$: component with phase difference which is proportional to viscous behavior.
Loss modulus.

$\tan \delta = E''/E'$: ratio between both modulus. Phase difference between stress and deformation waves. Loss factor.

Depending on the temperature and the frequency of the measurement, the material can behave like a rigid elastic solid (high modulus, negligible loss factor), a soft elastic material (low modulus, negligible loss factor) or else have a significant viscous component (high loss factor) resulting in significant mechanical energy dissipation. Relevant structural relaxations of polymeric materials such as glass transition (α relaxation) or local mobility relaxations below glass transition temperature T_g (β relaxation) can be detected as drops in the elastic component of the modulus or peaks in the loss factor, as shown in the figure below.

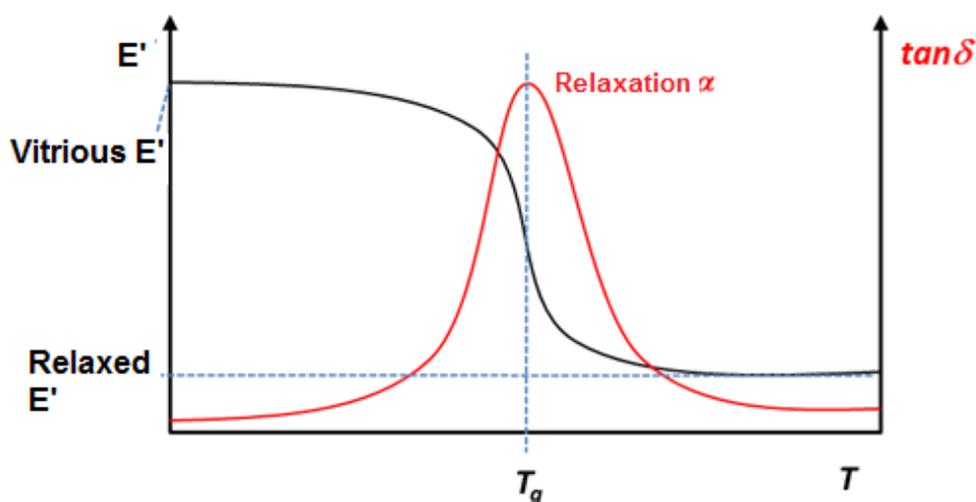


Figure 23. DMA curve. It is shown storage modulus and $\tan \delta$ with respect to temperature

Photochemically or thermally cured samples ($10 \times 10 \times 1 \text{ mm}^3$ approximately) were analyzed on single-cantilever bending, subjected to a temperature ramp starting at $30 \text{ }^\circ\text{C}$, at a heating rate of $3 \text{ }^\circ\text{C}/\text{min}$, at a frequency of 1 Hz and a deformation amplitude of 10 microns .

6.3.5. Transilluminator UV

It is used a transilluminator Bio-Link BLX of brand VilberLourmat with 365 nm as wavelength to photochemical curing of samples. Molds are collocated inside the device and one side is irradiated with $4 \text{ J}/\text{cm}^2$ and then mold is turned to irradiate the other side.



Figure 24. Transilluminator Bio-Link BLX of brand VilberLourmat

6.3.6. Thermal oven

To residual curing or thermal curing, it is used a universal laboratory thermal oven of brand Memmert. Samples were placed between two glass slides and are fastened to the ends with metal clips. For the samples containing only photoinitiator, samples were placed in the oven for 1 hour at temperature of 100°C to ensure complete reaction of double bonds. For the samples containing also thermal initiator, they were placed in the oven for 2 hours at temperature of 130°C to ensure complete curing of epoxy groups.



Figure 25. Thermal oven of brand Memmert

7. Results and discussion

7.1. Preliminary study:

The behavior of each acrylate/methacrylate during the photocuring process is analyzed in a preliminary study. The key parameters to be analyzed are the glass transition temperature (T_g) of the homopolymer and its reaction heat. As mentioned before, samples are made from 1 g of resin and 3 phr of DMPA. Results are as follows:

Table 3. Calorimetric analysis of the photocuring and postcuring of the acrylate/methacrylate monomers.

Composition	Δh_{UV} (J/g)	Δh_{post} (J/g)	Δh_{link} (kJ/mol)	T_g (°C)
GLICMA	351,5	8,8	52,8	62
HEMA	371,6	17,0	52,1	90
HEA	601,2	-	71,9	-1
HDDA	518,4	5,4	61,0	78
90:10 HEA-HDDA	604,0	-	72,0	6
80:20 HEA-HDDA	601,5	-	79,7	12

For HDDA, T_g is measured from two blends with HEA, because the high crosslinking density achieved during polymerization prevents complete curing and proper measurement of the T_g by calorimetry. It is used Fox law to calculate it:

$$\frac{1}{T_g} = \sum \frac{w_i}{T_{gi}} \quad (12)$$

The total reaction heat of polymerization of GLICMA and HEMA (including photopolymerization and postcuring) is about 52 kJ/mol, in good agreement with commonly reported values for methacrylates [21]. The reaction heat for acrylates is generally higher, about 70 kJ/mol. It should be noted that the value for HDDA is lower probably because of incomplete reaction of acrylate groups.

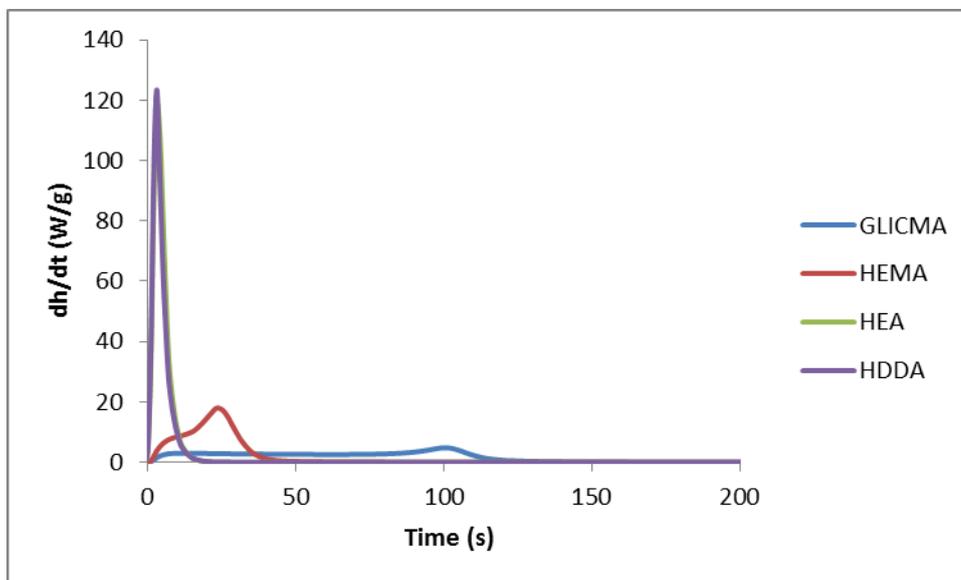


Figure 26. UV curing of acrylates and methacrylates monomers

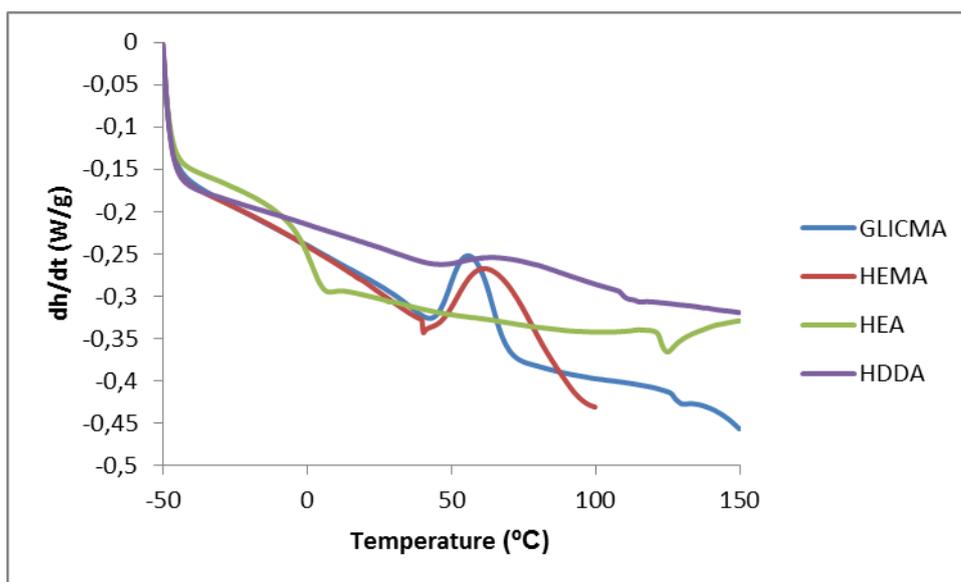


Figure 27. Residual heat flow of acrylates and methacrylates monomers

It is shown in Figure 27 how all of resins react quickly during the photopolymerization process. In addition, it can be almost considered completely reacted in this first stage because residual heat is very small compared with photochemical reaction heat. The reaction rate is substantially higher in the case of acrylates in all the results.

With these results and having Fox law as base, the objective is to prepare two linear polymers after the photocuring stage, one with glassy temperature lower than room temperature and one with a glassy temperature higher, and in the same way with two crosslinked polymers after the photocuring stage. Formulations are as follows:

Table 4. Design of linear and crosslinked polymers at different glass transition temperature

Polymer	$T_g < T_{room}$	$T_g > T_{room}$
Linear	20:80 GLICMA-HEA	20:80 GLICMA-HEMA
Crosslinked	15:70:15 GLICMA-HEA-HDDA	15:70:15 GLICMA-HEMA-HDDA

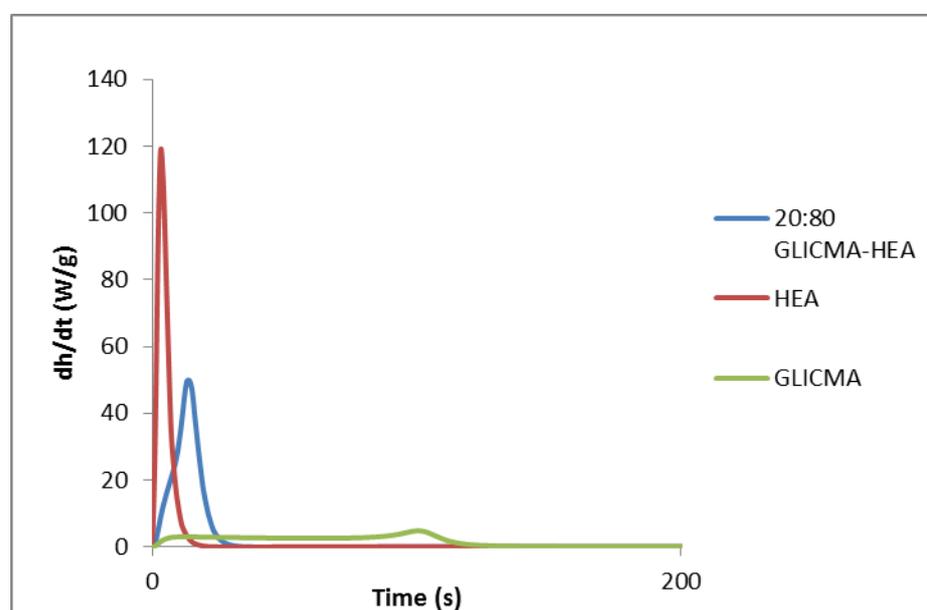


Figure 28 Comparison of UV cured 20:80 GLICMA-HEA

In this example, it is seen how mixture heat is a blend of both resins heat and a quick reaction with ultraviolet light is given. In spite of the clearly different reaction rate of the GLICMA and HEA homopolymers, the resulting photocuring process has an intermediate velocity, indicating that there is a more or less random copolymerization process (no separate reaction of HEA and GLICMA). Results of mixtures are as follows:

Table 5. Reaction heat and T_g results of formulations. T_g theoretical is calculated with Fox law.

Composition	Δh_{total} (J/g)	Δh_{link} (kJ/mol)	T_g theoretical (°C)	T_g measured (°C)
20:80 GLICMA-HEA	552,6	76,0	10	-3
20:80 GLICMA-HEMA	381,1	52,0	84	86
15:70:15 GLICMA-HEA- HDDA	606,7	74,3	17	8
15:70:15 GLICMA-HEMA- HDDA	350,2	46,5	84	85

It can be tested how the glass transition temperature measured of HEA compounds are very different from T_g theoretical. This difference may be caused by humidity taken by the sample in space of time between photo curing and post-curing or non-ideal behavior of the resulting copolymer. HEA is a hydrophilic polymer and these samples have a glass transition temperature lower than room temperature so they are not in the glassy state and it makes them prone to take up ambient humidity.

For this reason, it was tried to work with hydrophobic monomers: butyl acrylate (BA) and butyl methacrylate (BMA). Preliminary study of these resins is as follows:

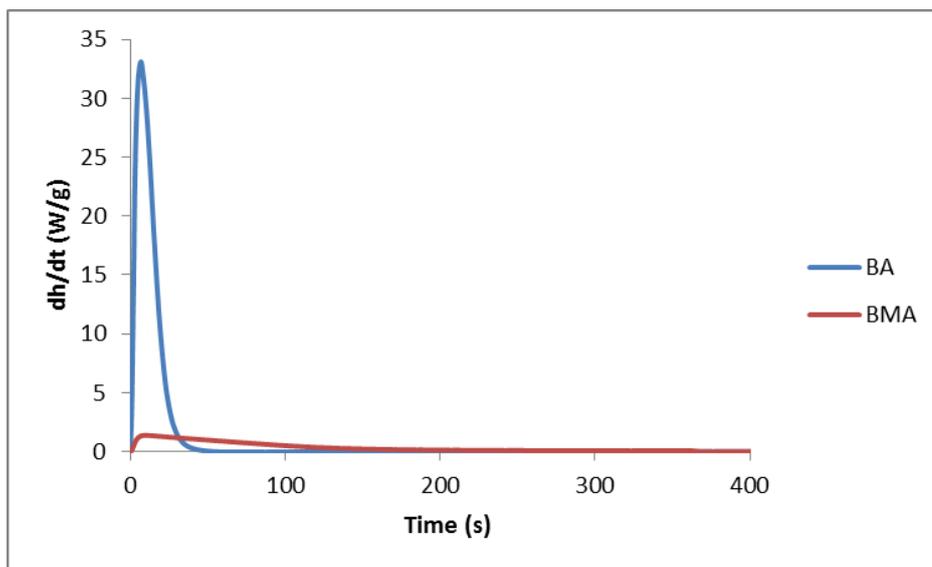


Figure 29. UV curing of BA and BMA monomers

It is observed that butyl methacrylate reacts slowly when it is irradiated with UV light. Even so, following formulations were studied: 30:70 GLICMA-BA and 30:70 GLICMA-BMA. In photocuring, they did not react completely even under high radiation intensity conditions.

Table 6. UV heat of formulations with BA and BMA

Composition	Δh_{UV} (J/g)	Δh_{ink} (kJ/mol)
30:70 GLICMA-BA	187,9	25,6
30-70 GLICMA-BMA	118,6	27,5

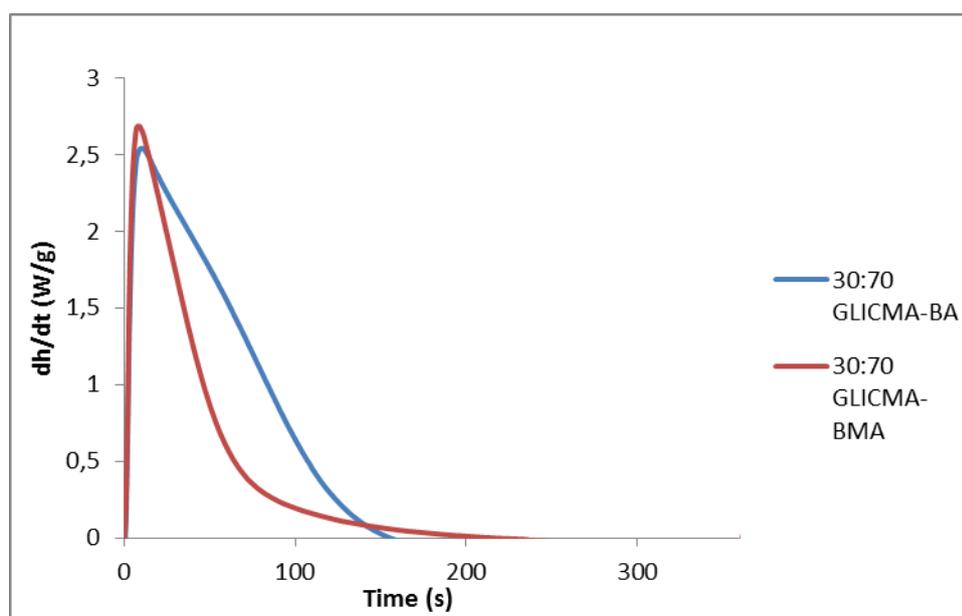


Figure 30. UV curing of formulations with BA and BMA

Given that there might be some reactivity problems between GLICMA and these monomers, it is decided to continue working with HEA-HEMA system. In order to prevent issues associated with the humidity absorption, the study on the thermal curing process will be carried out in formulations with HEMA, because it has glass transition temperature higher than room temperature, its state is more rigid and it doesn't take humidity so easily (glass transition temperature doesn't differ as it does samples with HEA in preliminary study). Results obtained with compounds with HEMA are extrapolated to HEA systems because these monomers are very similar.

7.2. Thermal process study

Thermal process study is worked with formulations of Table 4 adding a thermal initiator, in this case it is CXC-1612. Final polymer will be crosslinking due to GLICMA reticulation. Photocuring is the same as preliminary study and thermal curing of these formulation give the following results:

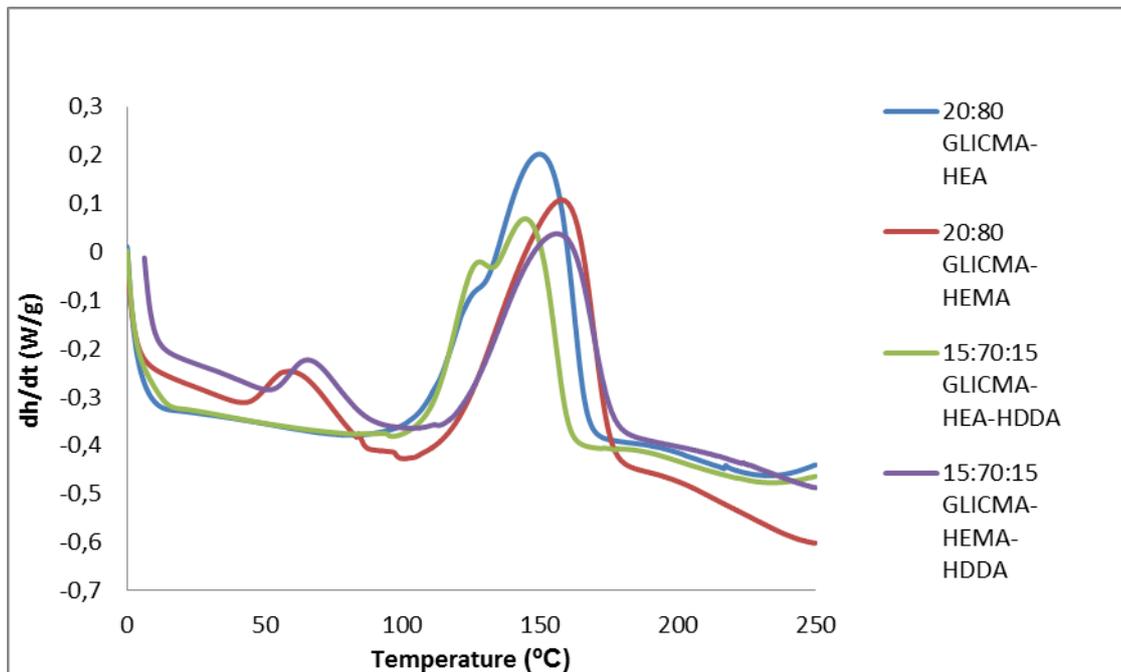


Figure 31. Thermal curing of formulations

It is observed thermal reaction takes place but it cannot be known if it is complete, because at the end of the curve it cannot be seen if reaction is finished. Also, it is shown a first small peak in formulations with HEMA that it is residual heat of the photocuring process but not in formulations with HEA, because HEMA vitrifies during photocuring but HEA doesn't.

Table 7. Comparison of thermal curing heat of formulations

Composition	$\Delta h_{\text{thermal}}$ (J/g)	Δh_{link} (kJ/mol)
20:80 GLICMA-HEA	147,0	108,7
20:80 GLICMA-HEMA	129,8	95,9
15:70:15 GLICMA-HEA- HDDA	111,7	110,0
15:70:15 GLICMA-HEMA- HDDA	105,3	103,6

It is observed how reaction heats are similar for GLICMA quantity they have and therefore reaction takes place correctly in all cases. Even though the dispersion of the results, values are close to 100 kJ/mol. Thermal peaks are small, therefore integration has errors due to uncertainty in determination of base line.

7.3. Kinetic Analysis Results

Kinetic analysis is done with systems which contain HEMA and these data are extrapolated to formulations with HEA, because of its capacity to take humidity, results can be wrong. Proportions are the same in HEMA and HEA, so at first there is no problem to extrapolate. Later, extrapolation is tested if it is correct or not.

Firstly, a dynamic analysis with different heating rate is made with 4 samples of formulation 20:80 GLICMA-HEMA: 20, 10, 5, and 2,5 °C/min, from 0 to 250°C.

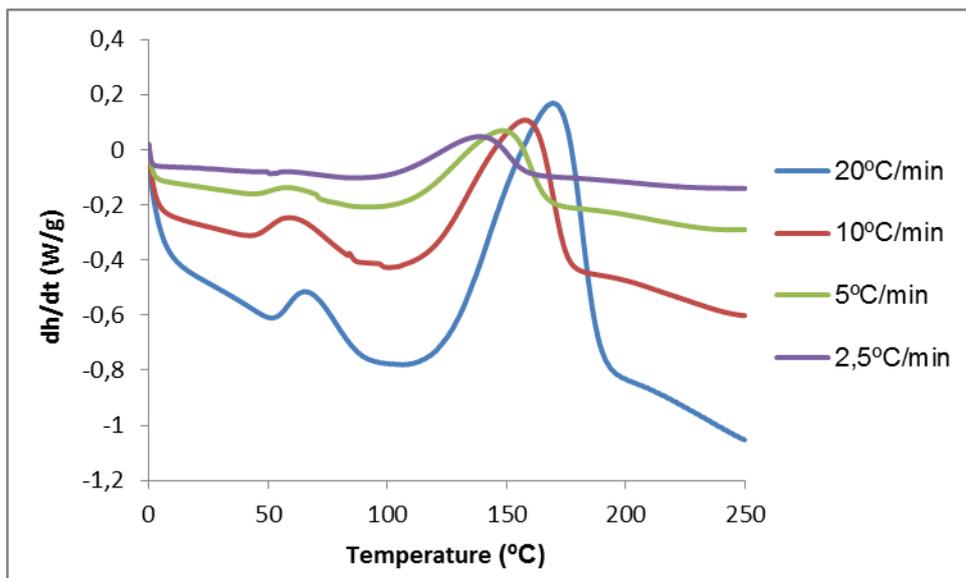


Figure 32. 20:80 GLICMA-HEMA dynamic thermal curves at different heating rate

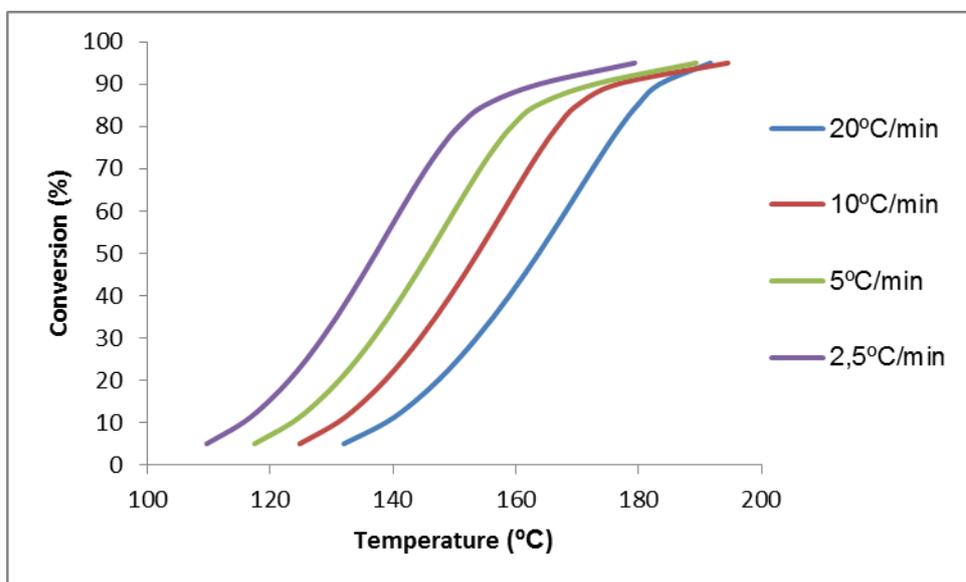


Figure 33. Conversion-temperature curves of 20:80 GLICMA-HEMA at different heating rate

Table 8. Thermal curing heat of 20:80 GLICMA-HEMA at different heating rate

Heating rate (°C/min)	dh/dt (J/g)
20	128,8
10	129,8
5	129,7
2,5	130,0

The higher is heating rate, the more pronounced is the peak because reaction takes place faster. Also, the bigger is this curve, the more moved is reaction curve to the right, because reaction needs certain time to take place. In Table 8, it can be tested how reaction heats are practically the same so these 4 samples are reacted with the same conversion grade. It should be mentioned that separation between curves are well defined and all the thermal cured heat are similar, therefore isoconversional method can be used.

The process is the same to formulation 15:70:15 GLICMA-HEMA-HDDA, giving coherent results as the previous case:

Table 9. Thermal curing heat of 15:70:15 GLICMA-HEMA-HDDA at different heating rate

Heating rate (°C/min)	dh/dt (J/g)
20	98,5
10	105,3
5	100,4
2,5	101,7

It is tried to make a kinetic analysis to formulation 20:80 GLICMA-HEA but, as expected, conversion-temperature curves are not well defined or separated because of time between photo curing and thermal curing. This time means that formulation take certain humidity.

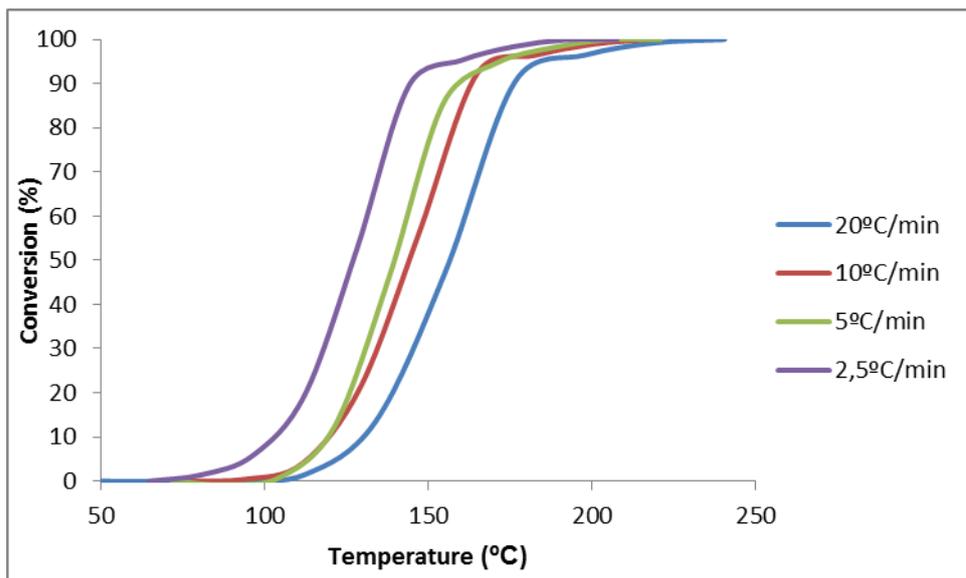


Figure 34. Conversion-temperature curves of 20:80 GLICMA-HEA at different heating rate

Using KAS method, it is obtained activation energy of formulation 20:80 GLICMA-HEMA:

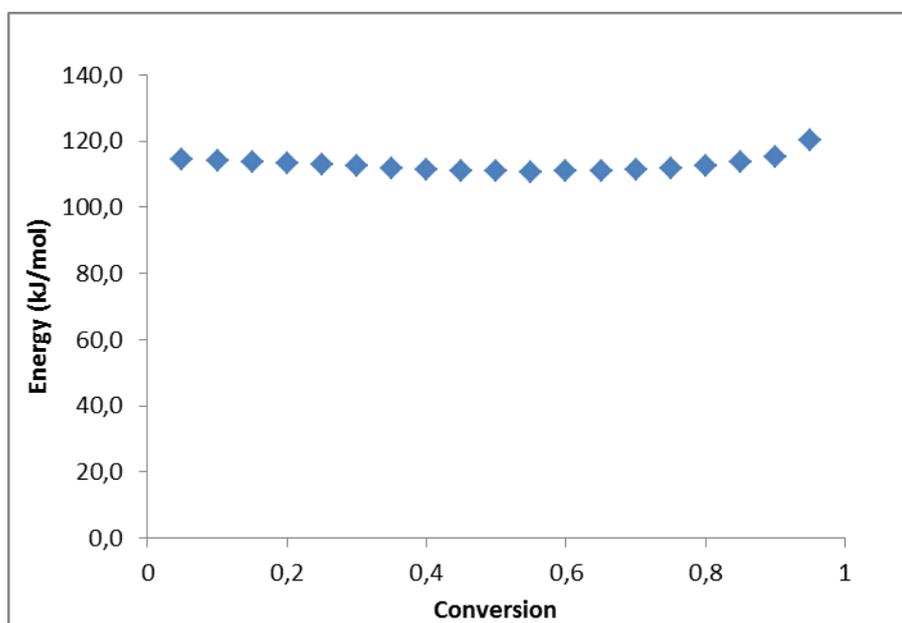


Figure 35. Activation energy of 20:80 GLICMA-HEMA

Activation energy remains constant and this is a sign that reaction takes place in a single step, and it is approximately 112,8 kJ/mol. Parameters of equation (9) are shown in the following table:

Table 10. Parameters of equation (9).

Conversion	Ex	ln[g(x)/k]	r²
0,05	114,4	-34,5	0,9915
0,1	114,1	-33,8	0,9954
0,15	113,7	-33,4	0,9967
0,2	113,3	-32,9	0,9974
0,25	112,9	-32,5	0,9978
0,3	112,3	-32,1	0,9981
0,35	111,9	-31,7	0,9984
0,4	111,4	-31,4	0,9986
0,45	111,0	-31,1	0,9988
0,5	110,8	-30,8	0,9990
0,55	110,8	-30,6	0,9992
0,6	110,8	-30,4	0,9993
0,65	111,0	-30,3	0,9994
0,7	111,3	-30,2	0,9995
0,75	111,7	-30,2	0,9995
0,8	112,5	-30,2	0,9994
0,85	113,5	-30,3	0,9991
0,9	115,4	-30,5	0,9984
0,95	120,3	-31,5	0,9940

More than 0,99 as correlation is had data and they are considered correct. Data from the beginning and the end of reaction are the most differed because of device limitations.

Isothermal curves can be simulated with these data and later is studied latency with them. Next, it is shown simulated and experimental conversion-time curves from formulation 20:80 GLICMA-HEMA at temperature of 130°C.

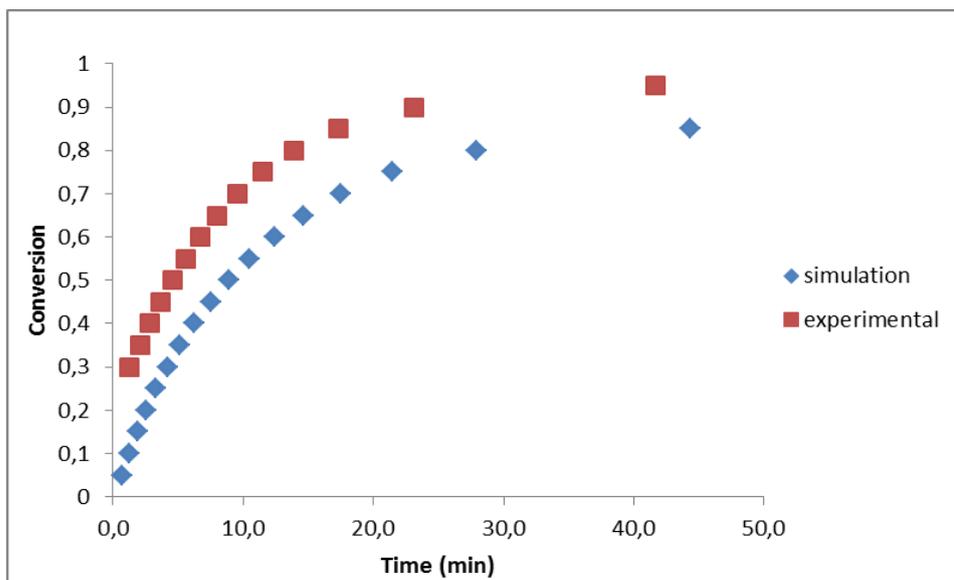


Figure 36. Simulation and experimental conversion-time curves of 20:80 GLICMA-HEMA at 130°C

Curves are very similar and difference between them is because it is difficult to measure first and final instants of a reaction, as explained before.

The same process is made to formulation 15:70:15 GLICMA-HEMA-HDDA. Conversion-time curves are as follows:

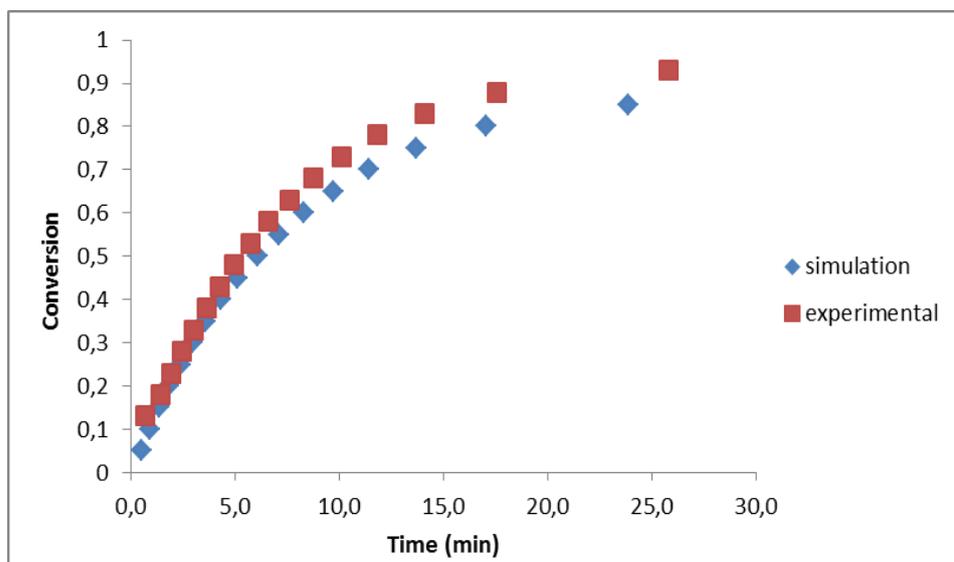


Figure 37. Simulation and experimental conversion-time curves of 15:70:15 GLICMA-HEMA-HDDA at 130°C

It is decided adding a reaction stabilizer to the formulation to see how affects in the reaction. It is tested with two reaction stabilizers: it is added 0,1 phr of Jeffamine (N) or 1 phr of 3-mercaptopropionate (S).

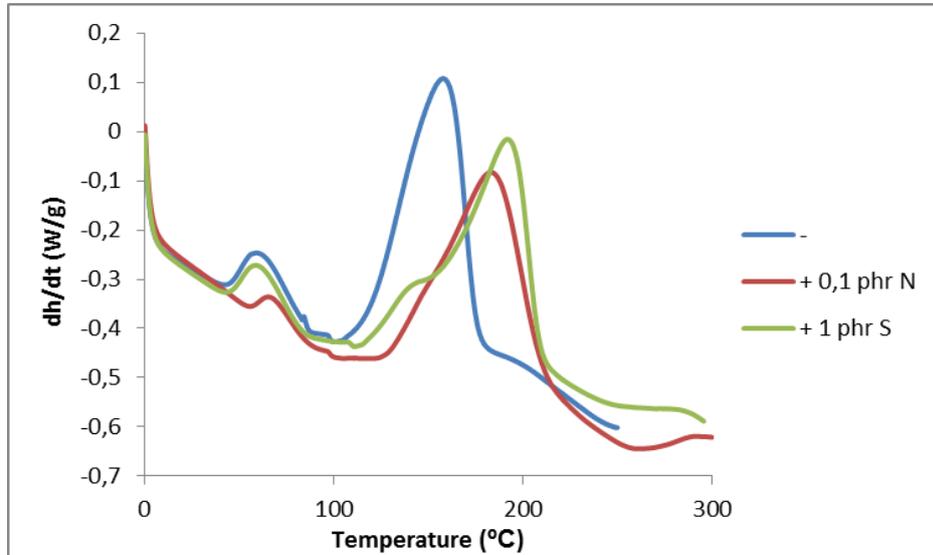


Figure 38. Curves corresponding to the thermal curing of formulation 20:80 GLICMA-HEMA with and without reaction stabilizers

The process to obtain dynamic and conversion-time curves is the same but temperature range is from 0 to 300°C because it is expected that reaction takes place in higher temperature. In Figure 38 it seems that N is better but it is not truly known which one is the best. For that reason, a kinetics analysis is performed. Effect between formulation with and without reaction stabilizer is tested and results are as follows:

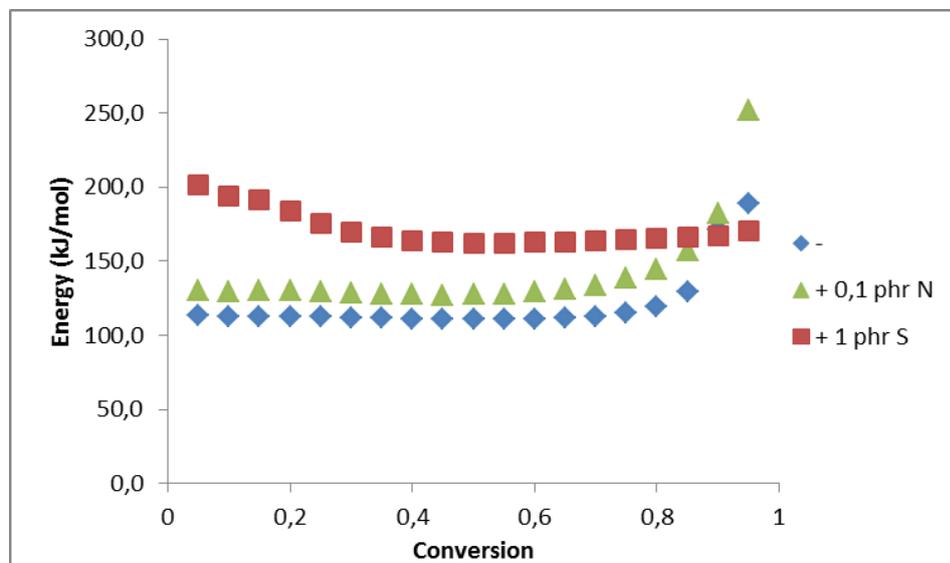


Figure 39. Activation energy of formulation 20:80 GLICMA-HEMA with and without reaction stabilizers

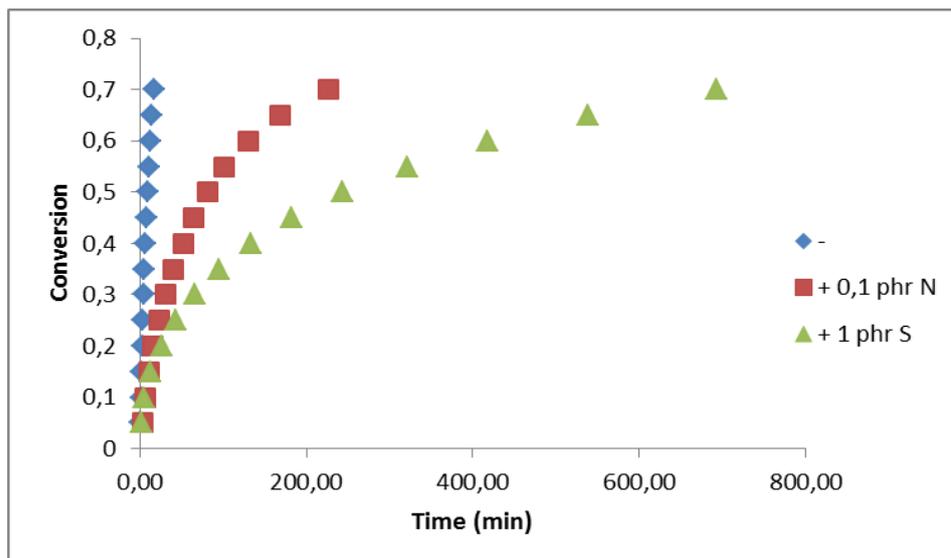


Figure 40. Isothermal curves at 130 °C of formulation 20:80 GLICMA-HEMA with and without reaction stabilizers

As it is expected, reaction stabilizers make reaction slowly and it is needed more time and higher temperature. Considering that values at the beginning and the end of reaction can be inexact, activation energy also increases when a reaction stabilizer is added. The effect of adding a stabilizer with nitrogen is small, in terms of activation energy, but the addition of the stabilizer with sulfur increases significantly the value throughout the process. The simulation of the curing curves at 130 °C reflects the decrease in reactivity associated with the presence of the stabilizer, indicating that longer curing times are required, especially with sulfur, or else higher curing temperatures.

Kinetic curves are also simulated at 43°C to know formulation stability and data are extrapolated to know if formulations are stable at room temperature or not. It is difficult to extrapolate data to lower temperature because real reaction takes place at higher temperature. Values of kinetic curves are shown in the following table:

Table 11. Thermal stability of 20:80 GLICMA-HEMA with and without reaction stabilizers

x	Time (days)		
	-	+ 0,1 phr N	+ 1 phr S
0,05	6	98	~16000
0,1	9	188	~29000
0,15	14	323	~59000

It is appreciated at temperature of 43°C that to achieve 15% as conversion, formulation without reaction stabilizer takes 14 days. Formulation with 0,1 phr N takes 323 days and formulation with 1 phr S takes around 59000 days. As it is predicted, adding reaction stabilizers causes larger thermal stability in intermediate stage. However, true long-term stability has to be tested because of the uncertainty in the extrapolation of data coming from accelerated experiments at high temperature to low temperatures outside the experimental range, and other processes might be taking place slowly that may not be relevant during the relatively short dynamic experiment in the DSC.

7.4. Properties study

In this section, it is studied difference in polymers properties according to its resin composition. Glass transition temperature with DSC and DMA, deformation modulus and decomposition temperature are measured as properties.

7.4.1. DSC analysis

Obtained results are extracted with DSC. These are compared with results obtained with DMA below. Thus, in first instance, it can be known if a material is very crosslinked or not if it is possible to visualize glass temperature with this technique.

First, the results corresponding to the calorimetric analysis of the samples after the photocuring stage are shown. The nominal values of the glass transition temperature were also shown in Table 5.

It is studied in a temperature range from -50 to 150°C to samples without thermal initiator and from 0 to 250°C with thermal initiator, with a heating rate of $\beta=10^{\circ}\text{C}/\text{min}$.

As nomenclature, *UV* means only photocured and *UV+Thermal* means dual-cured. Also, *1p* means first scanning and *2p* means second scanning.

Firstly, samples in first stage are compared, in other words, without thermal initiator:

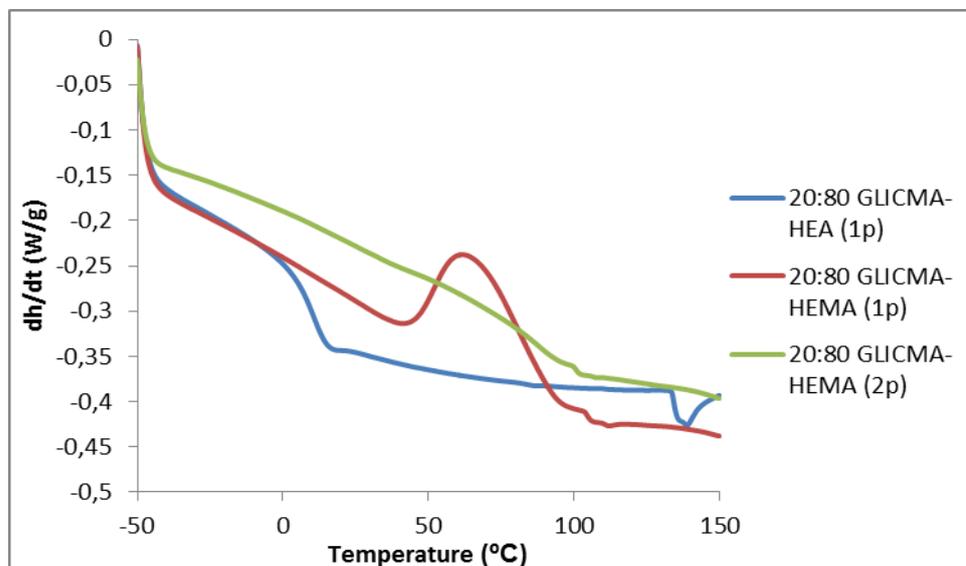


Figure 41 Heat-temperature curves to determinate glass transition temperature of formulations 20:80 after photocuring.

As it is seen before, composition 20:80 GLICMA-HEMA has residual photocuring heat, because its glass temperature is higher than room temperature. For this reason, it is necessary to make a second scan to observe glass transition temperature and not for 20:80 GLICMA-HEA.

Only difference between both compounds are HEA and HEMA resins, in other words, difference between them it is that one has an acrylate group and the other has a methacrylate group. Because of its structure, compounds with methacrylate in comparison with HEA compounds, have glass transition temperature higher. Although not shown above, BMA glass transition temperature also is higher than BA temperature.

Secondly, results with thermal initiators are observed. A comparison between formulation 20:80 GLICMA-HEA with and without CXC is made, in other words, before and after thermal curing:

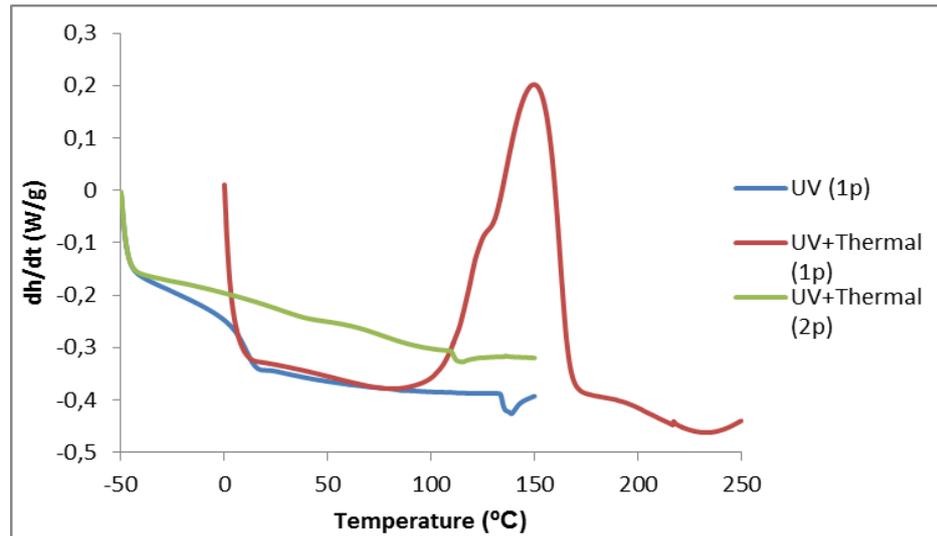


Figure 42. Heat-temperature curves of formulation 20:80 GLICMA-HEA to determinate glass transition temperature.

Glass transition temperature is increased due to thermal curing. With second scan, it is not possible to know T_g clearly because of its crosslinking. For that reason, the thermal-mechanical properties are also analyzed with DMA as it is a more sensitive technique.

In the case of formulation 20:80 GLICMA-HEMA, it cannot be seen glass transition temperature because its higher than room temperature and it has the hypothesis that thermal curing makes go from thermoplastic polymer to a thermoset polymer but formulation structure in first stage is not analyzed.. Structure is crosslinked and molecules are immobile so visualization of glass transition temperature with DSC is difficult.

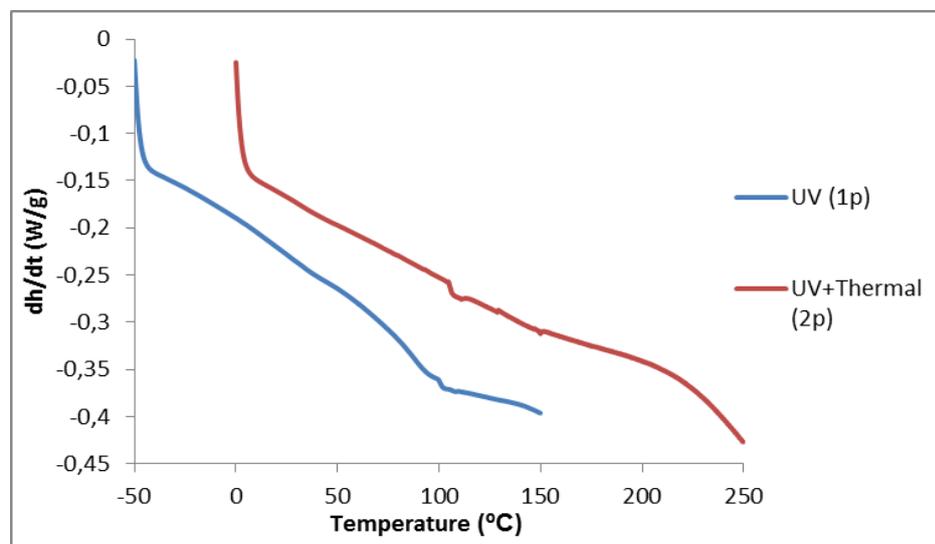


Figure 43. Heat-temperature curves of formulation 20:80 GLICMA-HEMA to determinate glass transition temperature.

Finally, it is studied HDDA effect. Adding HDDA makes samples be crosslinked in first stage. That is the reason why T_g of HDDA is difficult to determinate in preliminary study. It is necessary calculate glass transition temperature through Fox equation.

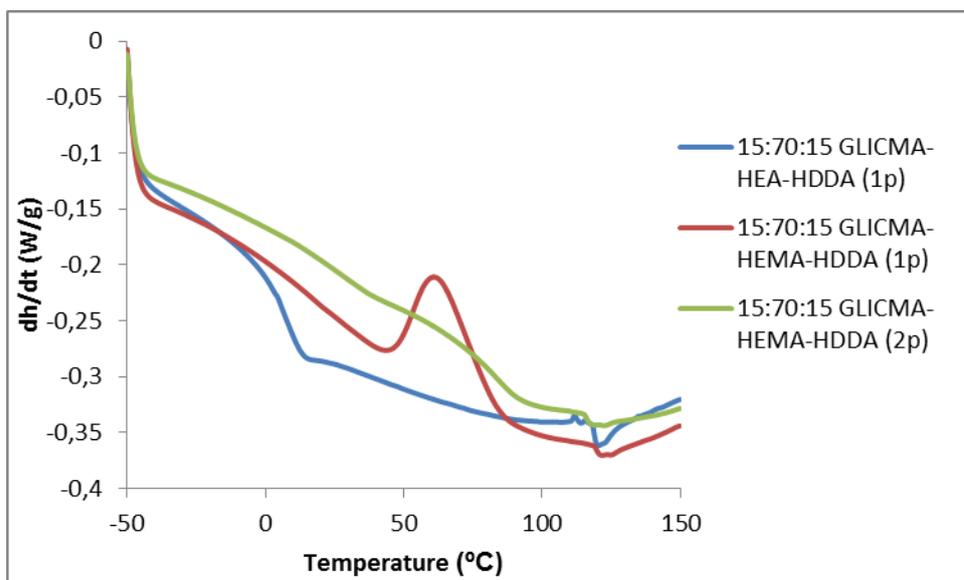


Figure 44. Heat-temperature curves of formulations with HDDA to determinate glass temperature after photocuring.

In this graphic, it is seen glass transition temperature of formulation 15:70:15 GLICMA-HEA-HDDA clearly in comparison with formulation 15:70:15 GLICMA-HEMA-HDDA. As it mentioned before, having a low or similar temperature than room temperature, material is not in vitreous state and can flow so glass transition temperature is easily detectable with DSC. Formulation 15:70:15 GLICMA-HEMA-HDDA has glass transition temperature higher than room temperature as it can be seen in Table 5, so there is post-cured heat because molecule movement is difficult, and glass transition temperature, even it can be detectable, is more complicated to measure than formulation 15:70:15 GLICMA-HEA-HDDA.

7.4.2. Dynamomechanical analysis

Glass transition temperature and deformation modulus are studied in this section. Specifically, only samples with T_g above room temperature were studied. In addition, measurement of dynamomechanical properties is not reliable with extremely soft samples due to instrumental and experimental limitations. For reasons above, formulation 20:80 GLICMA-HEA without thermal initiator, in other words, without thermal curing, cannot be analyzed, but with formulation 20:80 GLICMA-HEMA without thermal initiator is possible, because it is not as flexible as with HEA.

Data which are analyzed are only storage modulus and $\tan \delta$, because loss modulus can be deduced with these two parameters.

Samples in first stage are studied with a heat program from 30 to 160°C and samples with thermal curing are studied from 30 to 220°C, except formulations with HEA, because with DSC, glass transition temperature obtained is low and with final temperature as 105-110°C is enough. All the samples are heated with a heating rate $\beta=3^\circ\text{C}/\text{min}$.

First comparison is made with formulation 20:80 GLICMA-HEMA with and without thermal initiator, and also formulation 20:80 GLICMA-HEA with thermal curing:

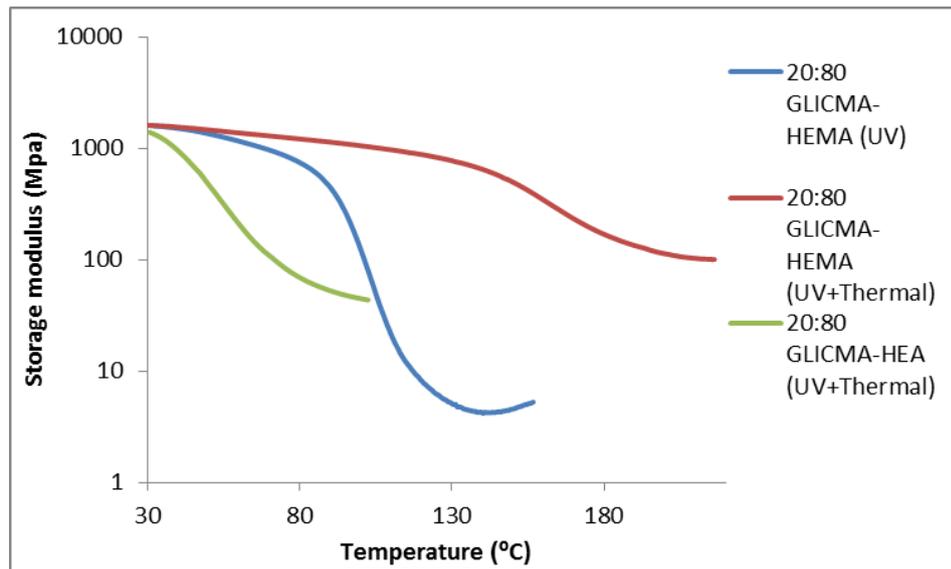


Figure 45. Storage modulus-temperature curves of HEA-HEMA system.

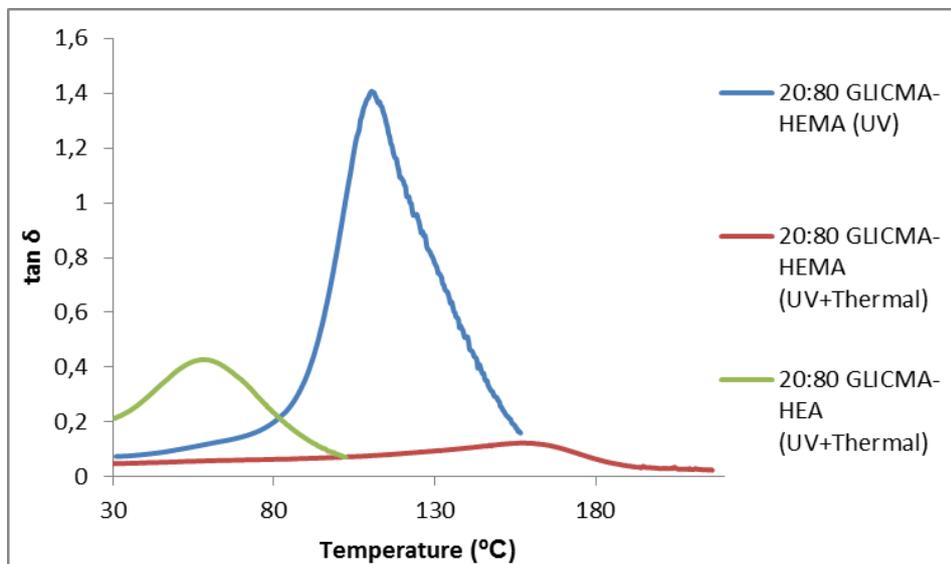


Figure 46. $\tan \delta$ -temperature curves of HEA-HEMA system.

$Tan \delta$ allows identifying mechanics relaxations of materials as maxim in viscous dissipation, in other words, it is related with glass transition of material. For this reason, where there is an important fall of storage modulus, also there is a maxim peak in representation $\tan \delta$ respect temperature. In formulations after photocuring, peak is more expanded because material softens during relaxation and dynamomechanical properties are less accurate.

With $\tan \delta$, it can be observed material rigidity: formulation 20:80 GLICMA-HEMA with thermal curing is more rigid than the others, because it doesn't have a pronounced change in its peak. Firstly, it is seen thermal curing causes samples with more rigidity. Secondly, in comparison between formulations with thermal curing, it is reasonable that storage modulus of compound with HEA is lower than compound with HEMA, because it is not completely in vitreous state for its glass transition temperature.

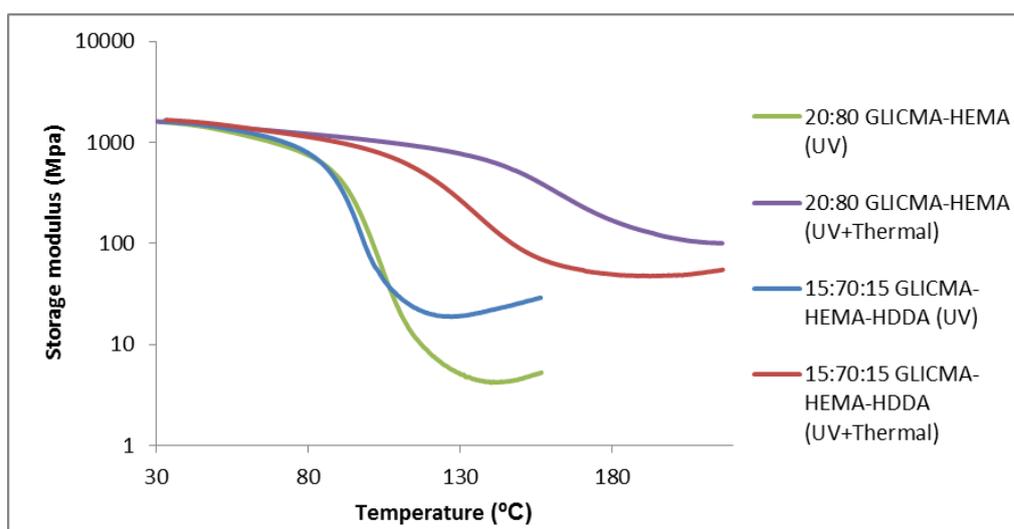


Figure 47. Storage modulus-temperature curves. Comparison of formulation with and without HDDA.

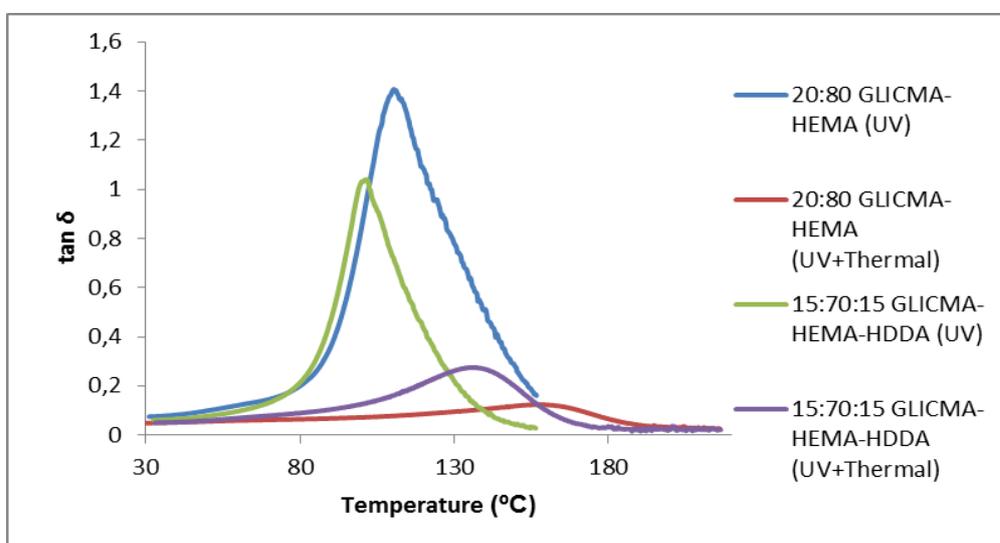


Figure 48. $\tan \delta$ -temperature curves. Comparison of formulation with and without HDDA.

With HDDA, all formulations are thermosets in first stage, so it's logical that rigidity increases because of molecule immobility and its structure. But glass transition temperature of HDDA is lower than HEMA, so in first stage, molecules of formulation with HDDA have more mobility. For this reason, a variation can be seen in formulations in second stage: both are thermosets and they have low $\tan \delta$ intensity respect temperature, but compound with HDDA have more chain mobility giving a more pronounced pick. Regarding formulations in first stage, it is compared a thermoplastic and a thermoset giving a more pronounced curve to thermoplastic, but thermoset curved with HDDA is far more intense than other thermosets. As conclusion, HDDA gives an elasticity effect and it can clearly be seen in following comparison:

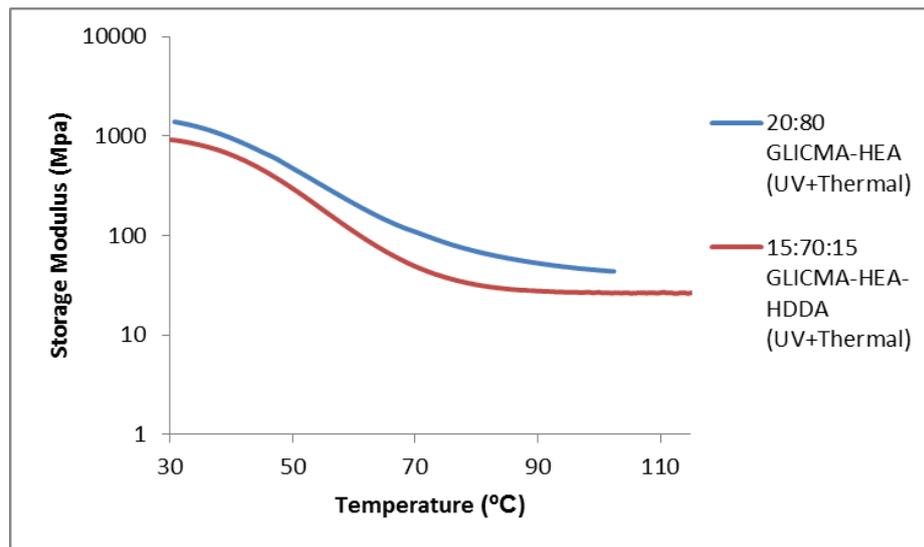


Figure 49. Storage modulus-temperature curves. Comparison of HEA formulation with and without HDDA.

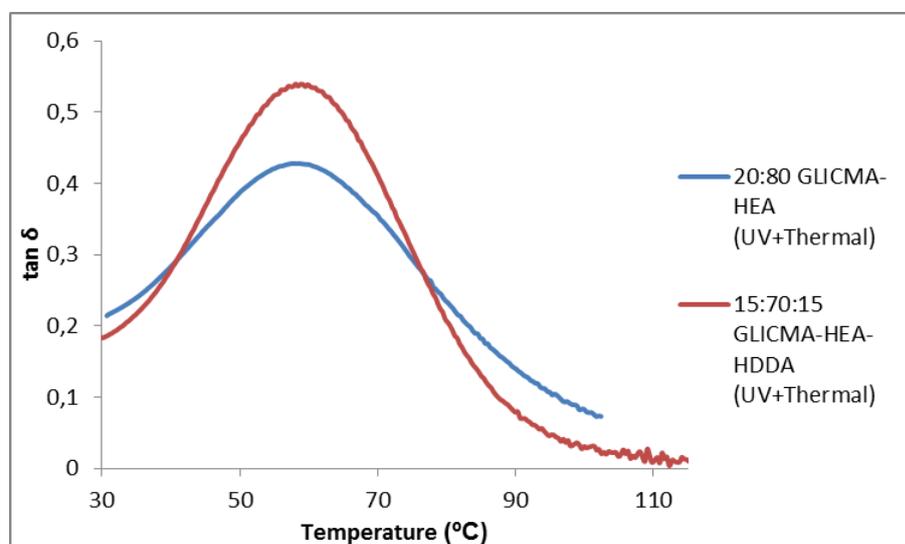


Figure 50. $\tan \delta$ -temperature curves. Comparison of HEA formulation with and without HDDA.

Moreover, to verify what GLICMA effect in formulations is, it is prepared a new sample with 40% of GLICMA and 60% of HEMA as proportions. Only it is possible to analyze the dual-cured sample.

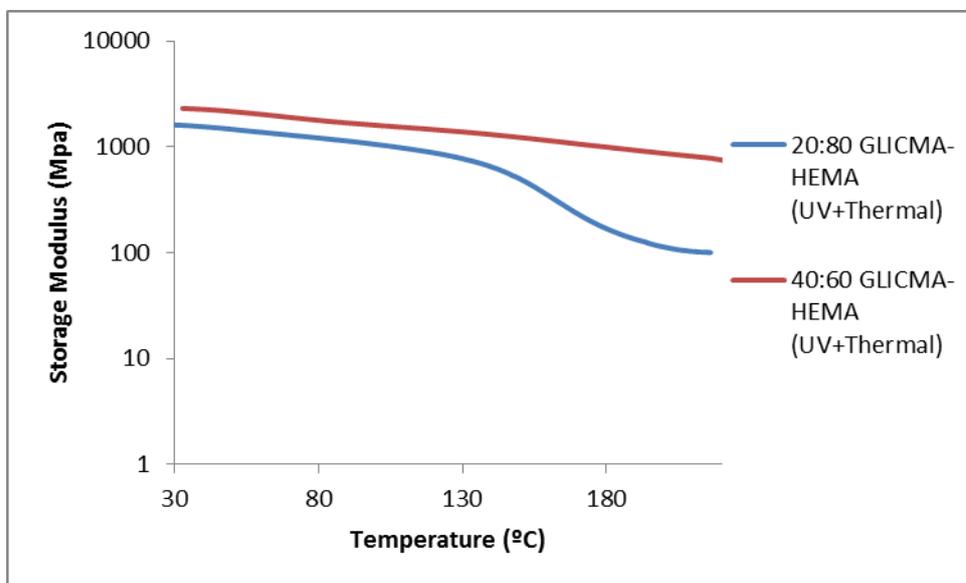


Figure 51. Storage modulus-temperature curves. Effect of GLICMA resin.

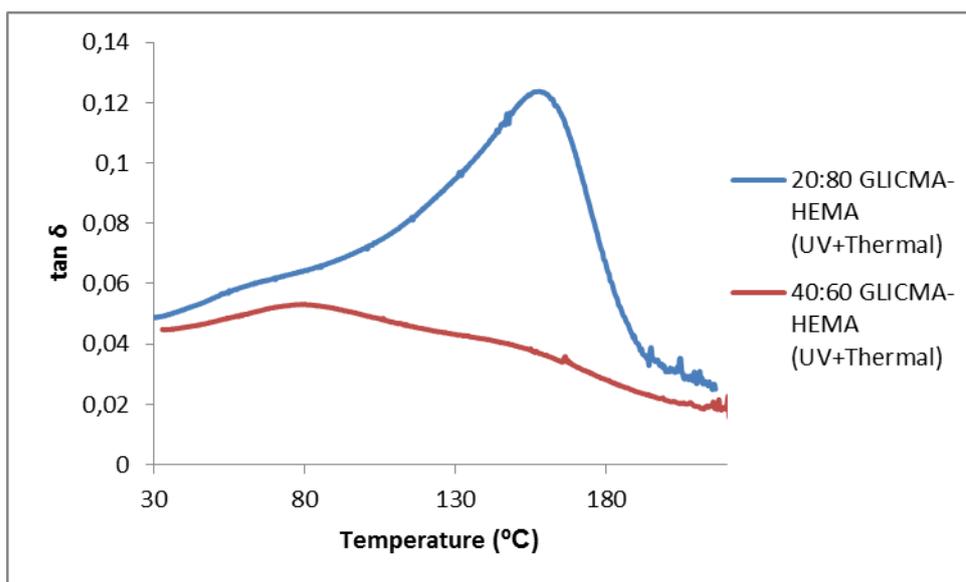


Figure 52. tan δ-temperature curves. Effect of GLICMA resin.

Adding more GLICMA in formulation should produce materials with a lower intermediate T_g , after photocuring, because of the lower T_g of GLICMA in comparison with HEMA. After thermal curing, sample becomes much more rigid because having more GLICMA also causes more epoxy links, in other words, final structure is much more crosslinked and molecules are more fixed with each other. In this case, it is not possible to see relaxation clearly; storage modulus fallen and $\tan \delta$ results are very low due to its crosslinked that provokes low mobility.

With this last example, it is clearly seen the wide variation of properties that can be obtained with dual curing.

Finally, glass transition temperatures obtained with DSC and DMA are compared to verify results:

Table 12. Comparison of glass transition temperatures with DSC and DMA

Composition	UV curing		UV and thermal curing
	T_{gDSC} (°C)	T_{gDMA} (°C)	T_{gDMA} (°C)
20:80 GLICMA-HEA	-3	-	58
20:80 GLICMA-HEMA	86	110	158
15:70:15 GLICMA-HEA-HDDA	8	-	58
15:70:15 GLICMA-HEMA-HDDA	85	100	136

Results obtained with DMA are different of DSC results because they calculate properties in different ways, but it can be seen that glass transition temperature of samples with thermal initiator is increased after thermal curing.

7.4.3. Thermogravimetry Analysis:

Thermobalance is used to determinate decompose temperature of each polymer made. It is studied stability with respect to temperature with sample pieces cured previously. All the samples are subjected to a thermal program from 30 to 800°C with a heating rate $\beta=10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. It can be seen difference between samples and the effect of having a certain composition.

In the first place, it is studied polymers with only photocuring. It is analyzed difference between thermoplastics prepared, in other words, formulations 20:80 GLICMA-HEA and 20:80 GLICMA-HEMA. Weight is represented as a percentage:

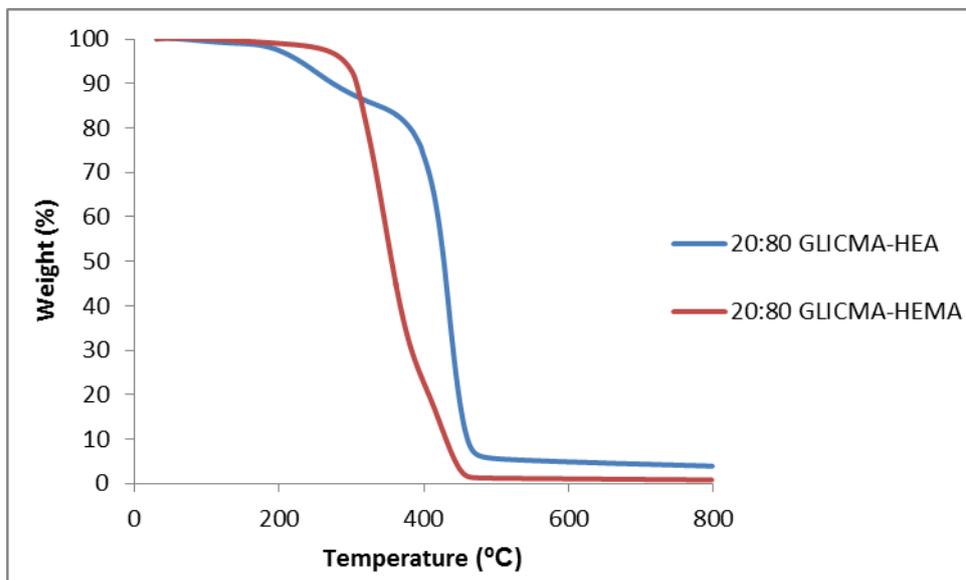


Figure 53. Mass loss with respect to temperature of 20:80 formulations after photocuring.

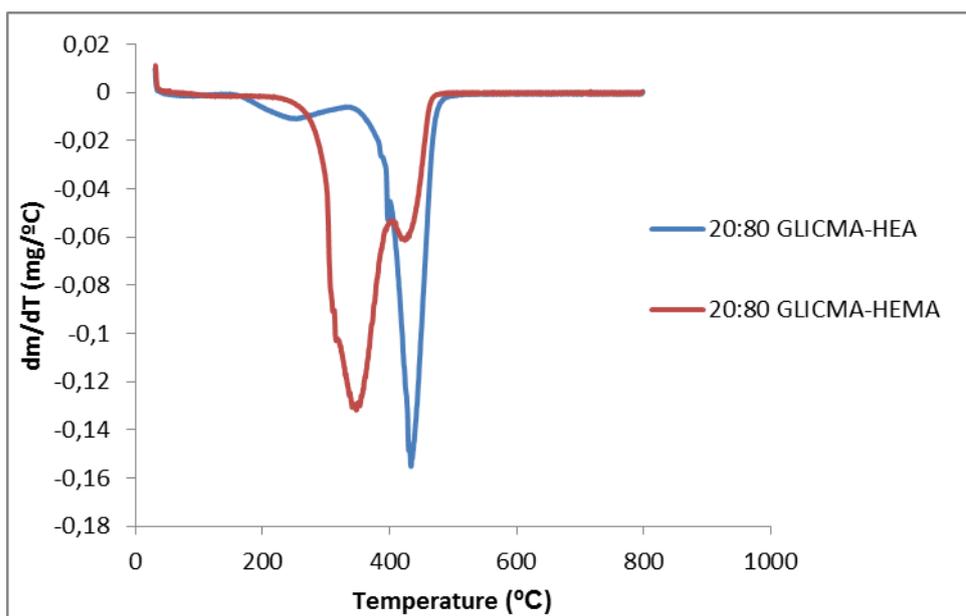


Figure 54. Degradation rate with respect to temperature of 20:80 formulation after photocuring.

These two formulations are similar, difference between them is methyl group existence or not. It can be seen that methacrylate group has decompose temperature lower than acrylate group, but it is more stable.

Then, it is compared previous samples with samples of the second stage to see thermal initiator effect in thermal stability.

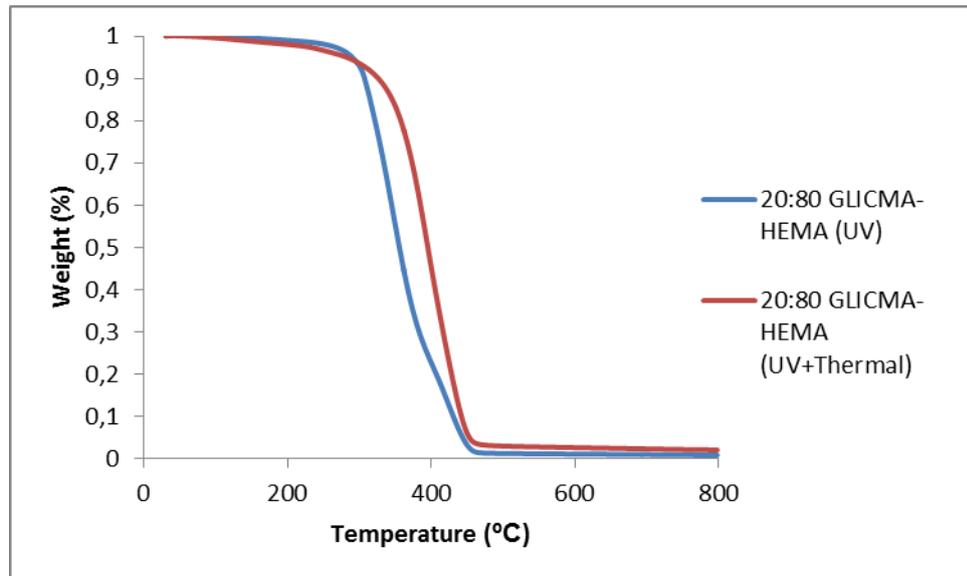


Figure 55. Mass loss with respect to temperature. Effect of thermal initiator in formulation 20:80 GLICMA-HEMA.

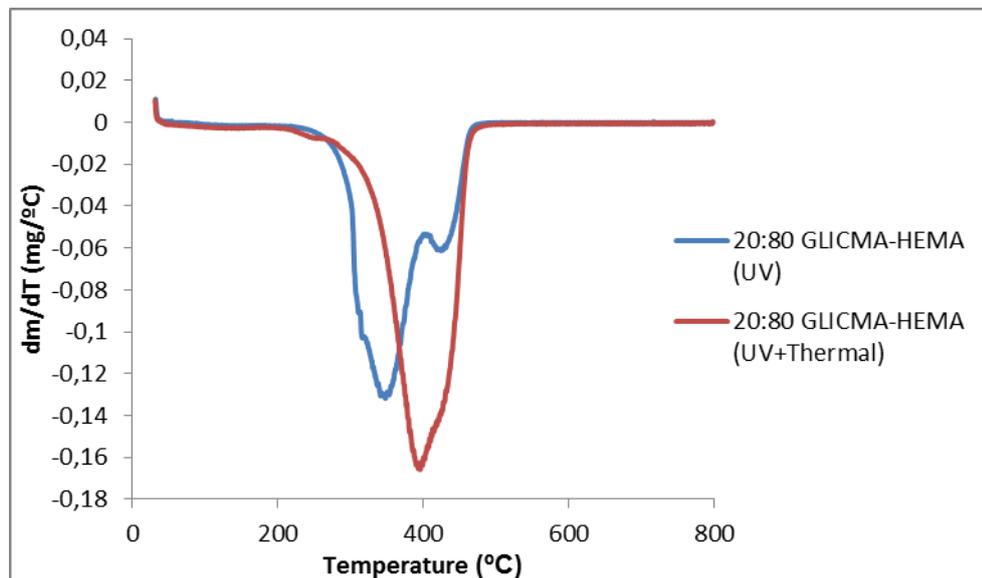


Figure 56. Degradation rate with respect to temperature. Effect of thermal initiator in formulation 20:80 GLICMA-HEMA.

Formulation changes its linear structure to a crosslinked structure, in other words, from thermoplastic to thermoset. Decompose temperature is higher and also its thermal stability, because it can be seen its decompose rate more abruptly and decomposes all quickly, as not thermoplastic.

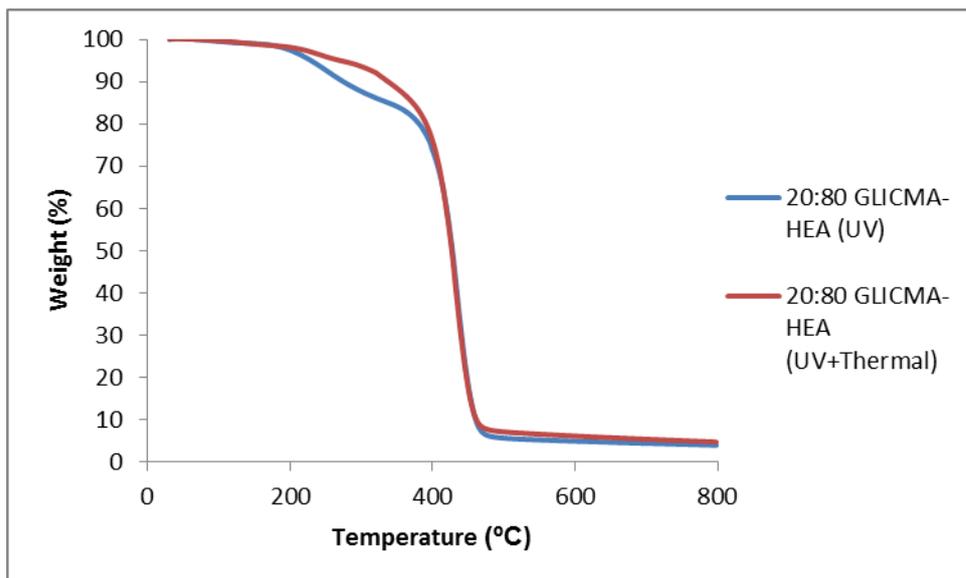


Figure 57. Mass loss with respect to temperature. Effect of thermal initiator in formulation 20:80 GLICMA-HEA.

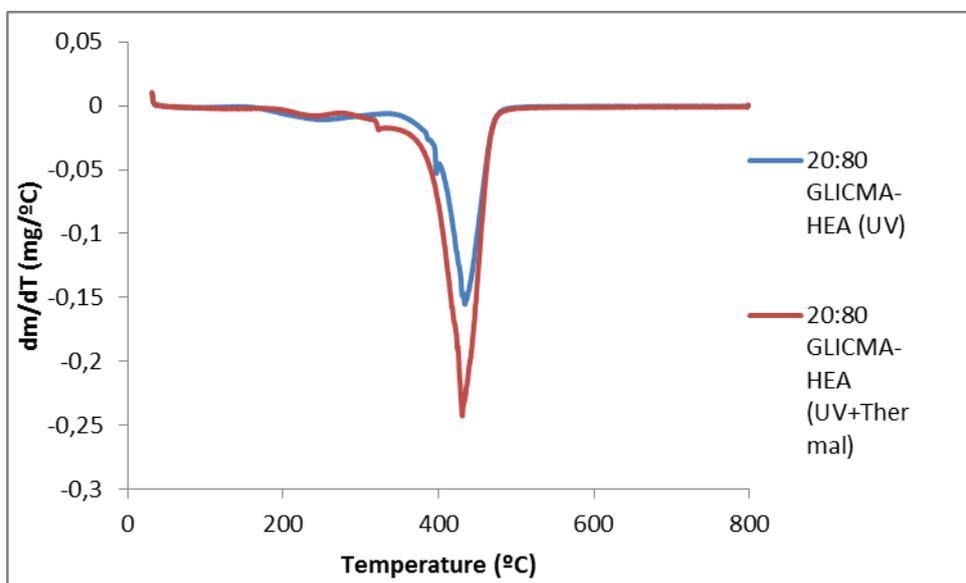


Figure 58. Degradation rate with respect to temperature. Effect of thermal initiator in formulation 20:80 GLICMA-HEA.

In 20:80 GLICMA-HEA cases, it can be observed how decomposition temperature does not change too much and it can be supposed that it is the same, but thermal stability is higher as 20:80 GLICMA-HEMA cases.

Adding a thermal initiator and being thermal cured, makes formulation be thermosets and its thermal stability is higher due to epoxy cationic polymerization. Decomposition temperature increases in 20:80 GLICMA-HEMA system but it doesn't in 20:80 GLICMA-HEMA system, because it has high enough its decomposition temperature.

Finally, it is compared HDDA effect with compounds without HDDA, and also it is compared formulations with HDDA in first and second stage.

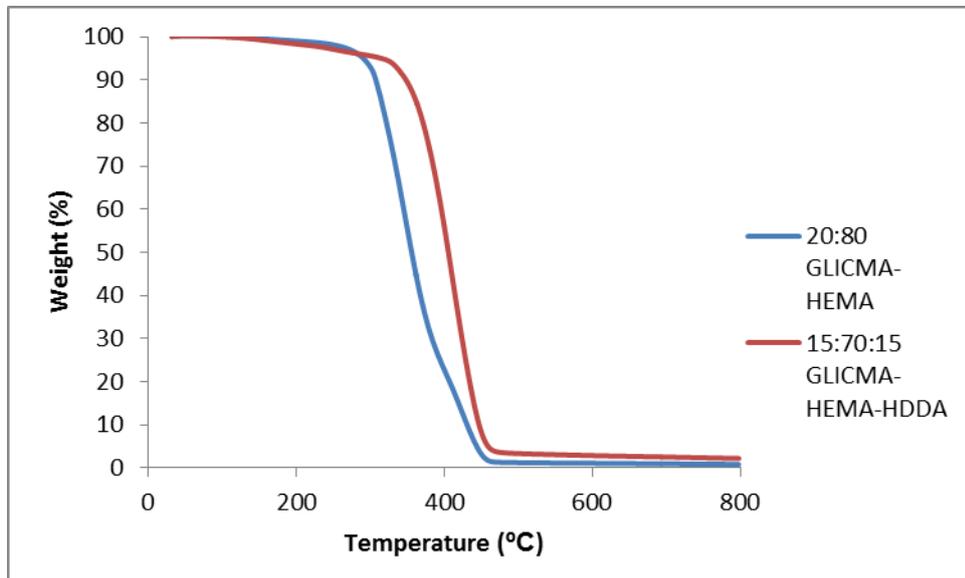


Figure 59. Mass loss with respect to temperature. Effect of HDDA in formulation with HEMA after photocuring

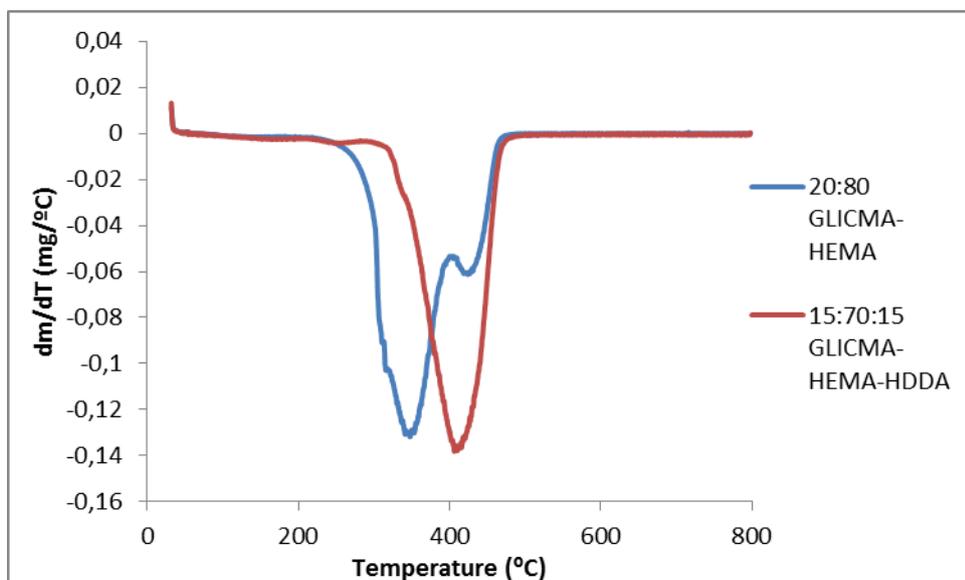


Figure 60. Degradation rate with respect to temperature. Effect of HDDA in formulations with HEMA after photocuring

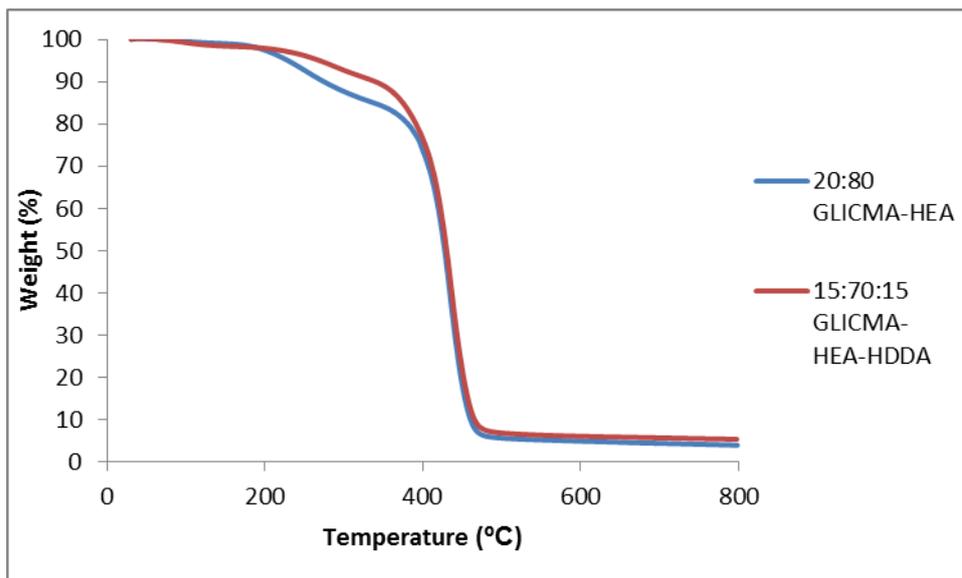


Figure 61. Mass loss with respect to temperature. Effect of HDDA in formulations with HEA after photocuring

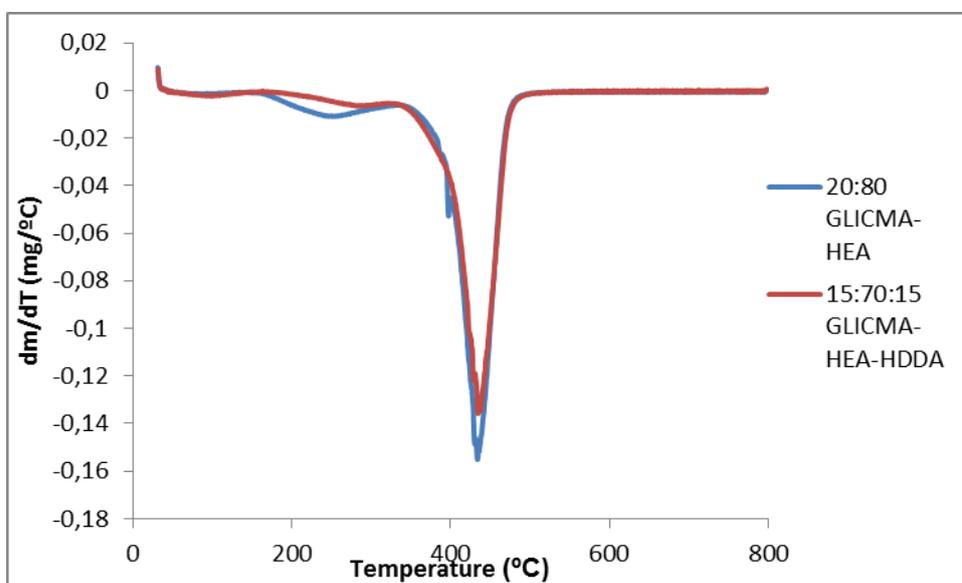


Figure 62. Degradation rate with respect to temperature. Effect of HDDA in formulations with HEA after photocuring

HDDA effect is very similar to adding thermal initiator to second stage of dual-curing: thermal stability is given because adding HDDA makes sample be thermoset. Regarding decomposition temperatures, it is the same as previous cases: in formulations with HEMA, it helps to increase decomposition temperature, but formulations with HEA, decomposition temperature is almost identical.

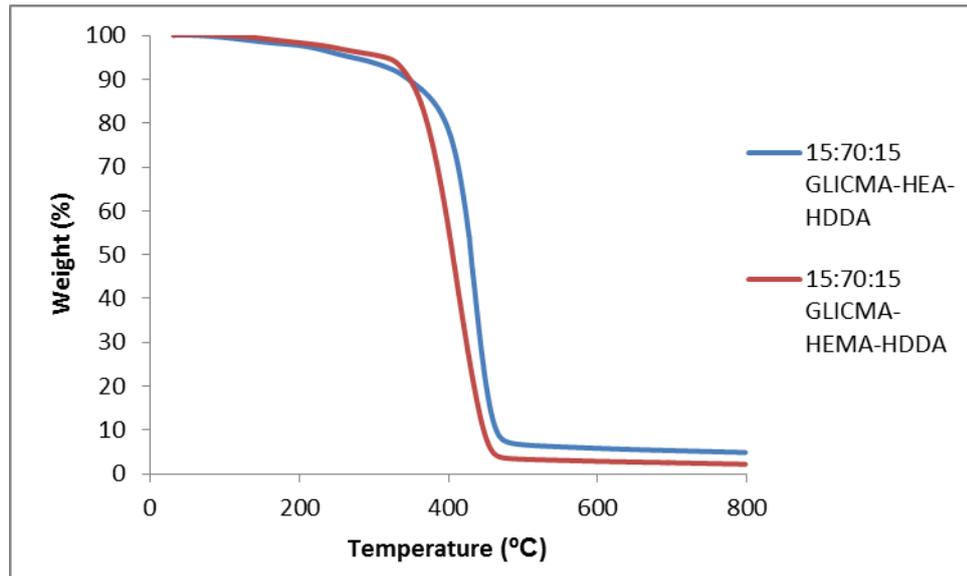


Figure 63. Mass loss with respect to temperature. Comparison of systems with HDDA after dual curing.

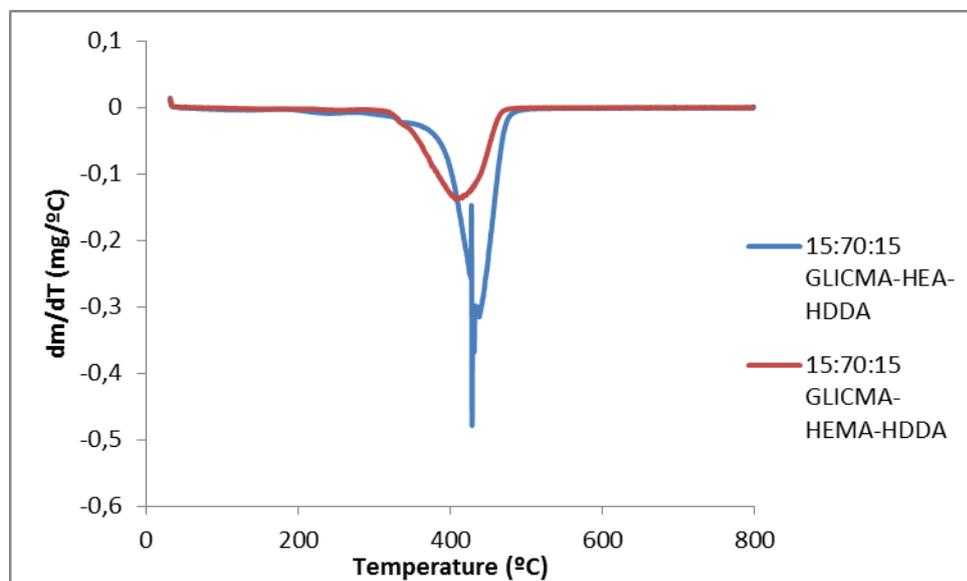


Figure 64. Degradation rate with respect to temperature. Comparison of systems with HDDA after dual curing.

In thermal curing of second stage, thermal stability doesn't change significantly in formulations with and without HDDA. So, HDDA effect is similar to adding thermal initiator effect and has thermal curing regarding thermal stability. Difference is that with dual curing it is obtained different properties in first and second stage, and with HDDA, it is obtained thermal stability properties in first stage.

The reason of not exactly results is because device is very sensitive with movements, i.e. receiving a nitrogen flow to prepare an inert atmosphere makes results change. Furthermore, mass derivative with respect to temperature is a numerical derivative, not a polynomial regression with subsequent derivative, with consequences of error involved.

It is seen a clearly comparison between all formulations in the following table:

Table 13. Comparison decomposition temperature and 5% mass loss temperature before and after thermal curing.

Composition	UV curing		UV curing + thermal curing	
	$T_{5\%} (^{\circ}\text{C})$	$T_{max} (^{\circ}\text{C})$	$T_{5\%} (^{\circ}\text{C})$	$T_{max} (^{\circ}\text{C})$
20:80 GLICMA-HEA	230	434	271	430
20:80 GLICMA-HEMA	290	341	283	392
15:70:15 GLICMA-HEA-HDDA	270	435	271	428
15:70:15 GLICMA-HEMA-HDDA	315	406	315	408

7.5. Thermal latency study

In this study, it is analyzed 20:80 GLICMA-HEA and 20:80 GLICMA-HEMA formulations for 1 month to see reaction stabilizers effect and testing if low temperature extrapolations are correct.

Six compounds are prepared in total: of each formulation mentioned before, it is prepared one sample without reaction stabilizers, one with 0,1 phr N and on with 1 phr S. It is prepared 5 capsules of each formulation, so there are 30 capsules in total. All of them are photocured and every week one sample of each formulation is thermal cured, and also it is measured one sample just after having photocuring, to have a sample as reference. Samples are left in a silicone bath at the temperature of 43°C for as long as it is necessary until they have to be measured. They are subjected to a dynamic thermal program with a heating rate $\beta=10^{\circ}\text{C}/\text{min}$ from 0 to 300°C.

Firstly, 20:80 GLICMA-HEA curves are compared:

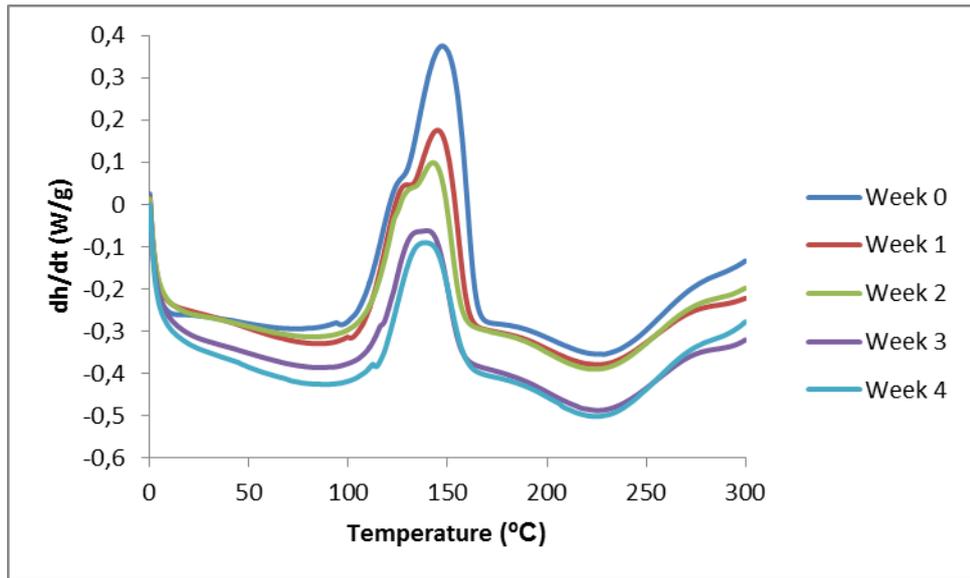


Figure 65. Thermal curing of 20:80 GLICMA-HEA.

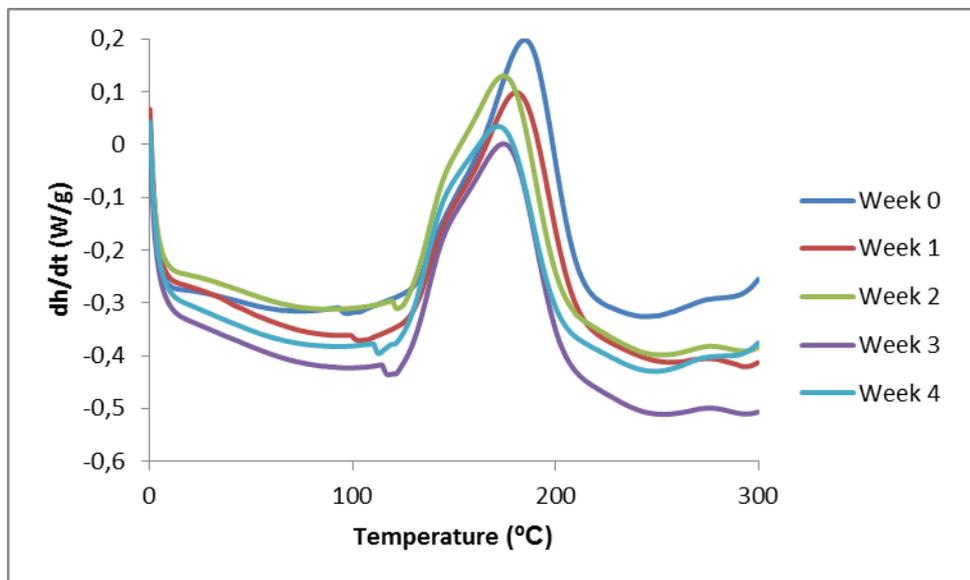


Figure 66. Thermal curing of 20:80 GLICMA-HEA with 0,1 phr N.

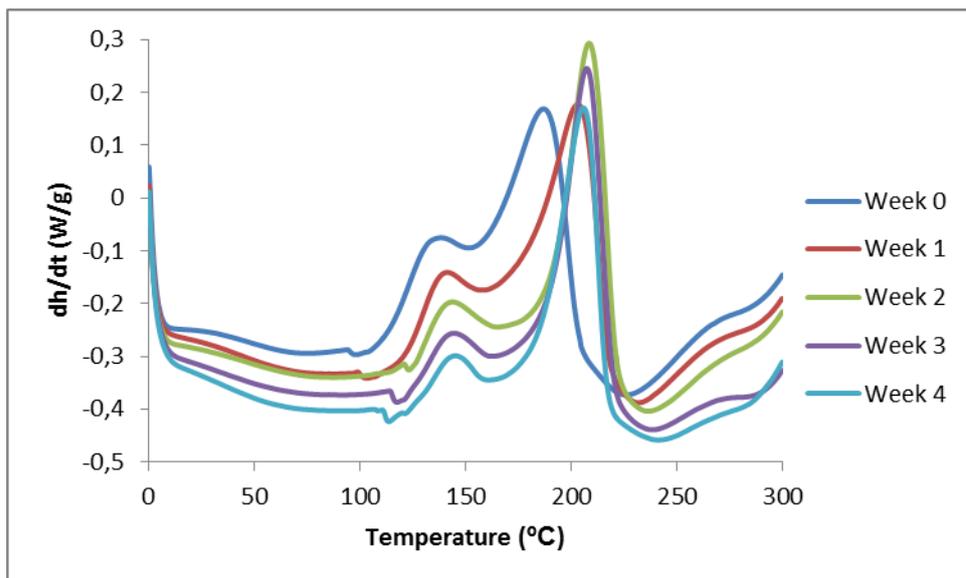


Figure 67. Thermal curing of 20:80 GLICMA-HEA with 1 phr S.

Table 14. Thermal curing heats and conversion of formulations 20:80 GLICMA-HEA.

Week	-		+ 0,1 phr N		+ 1 phr S	
	Δh (J/g)	Conversion (%)	Δh (J/g)	Conversion (%)	Δh (J/g)	Conversion (%)
0	147,23	0	153,76	0	164,75	0
1	112,13	23,8	153,58	0,1	160,62	2,5
2	94,23	36,0	152,43	0,9	144,88	12,0
3	75,03	49,0	147,72	3,9	133,22	19,1
4	74,49	49,4	141,40	8,0	117,98	28,4

Results show how reaction stabilizer which allows a higher thermal latency is N. As expected, formulation without stabilizer still reacting with time. This instability with time is caused by photoinitiator and humidity that provides plasticity and chain movement, so sample has facility to react. Also it is appreciated how stabilizer S moves reaction curves to the right and curves tendency is not the same as the others cases. There is a hypothesis that low temperature processes are activated and it is the reason why curves are so different.

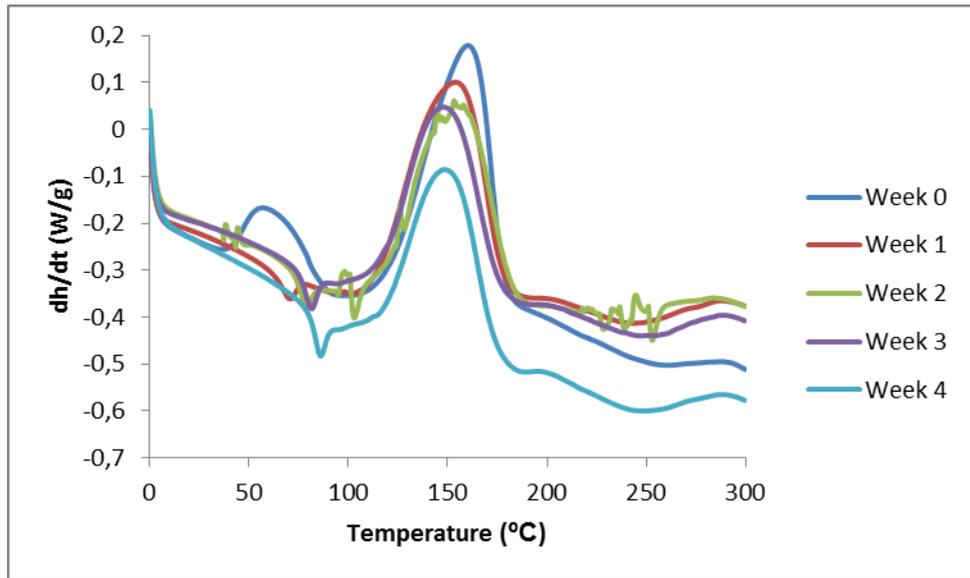


Figure 68. Thermal curing of 20:80 GLICMA-HEMA.

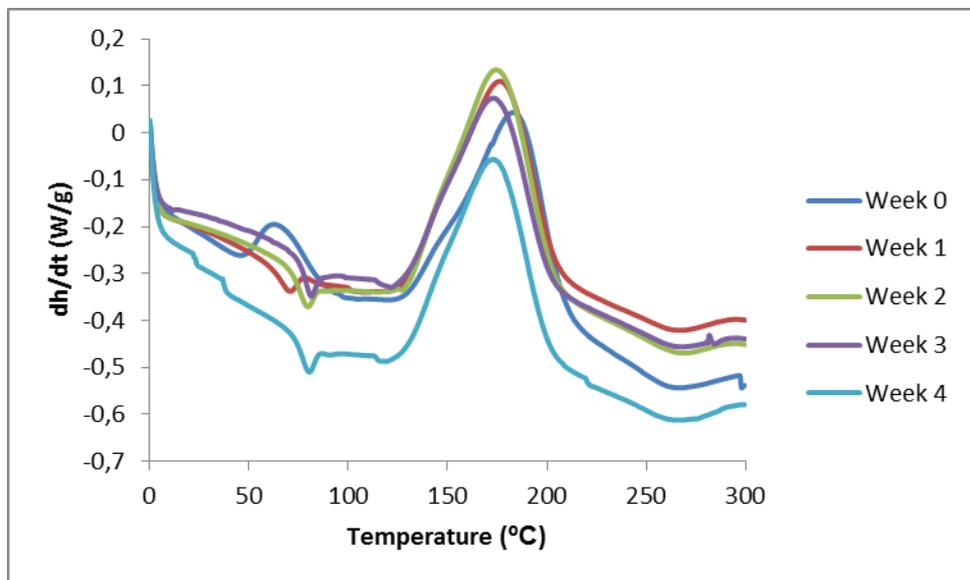


Figure 69. Thermal curing of 20:80 GLICMA-HEMA with 0,1 phr N.

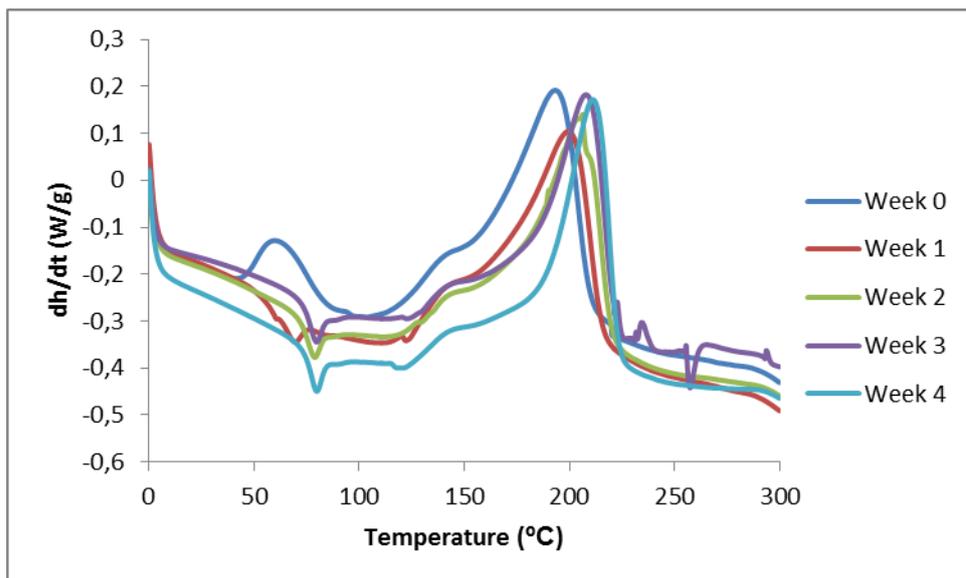


Figure 70. Thermal curing of 20:80 GLICMA-HEMA with 1 phr S.

Table 15. Thermal curing heats and conversion of formulations 20:80 GLICMA-HEMA.

Week	-		+ 0,1 phr N		+ 1 phr S	
	Δh (J/g)	Conversion (%)	Δh (J/g)	Conversion (%)	Δh (J/g)	Conversion (%)
0	148,06	0	150,04	0	152,4	0
1	127,53	13,9	148,37	1,1	143,5	5,8
2	121,91	17,7	147,86	1,5	136,4	10,5
3	99,82	32,6	139,13	7,27	124,9	18,0
4	92,86	37,28	129,39	13,8	124,1	18,6

Results of 20:80 GLICMA-HEMA formulations verify previous results of formulation 20:80 GLICMA-HEA. With data of sample without stabilizer, it is seen how residual heat disappears in one week. This is a sign that sample still reacts with time, and glass transition temperature decrease because of plasticity when sample takes humidity. In a certain point, sample is saturated with water and for this reason glass transition temperature doesn't change in the coming weeks, consuming part of the thermal curing heat.

As compounds with HEA case, it is verified that N is better stabilizer than S because sample reacts lower with time and there is no modified curves effect as curves with S. This fact is unknown and there is the hypothesis of low temperature reaction existence.

If these results are compared with simulated results in Kinetic Analysis Results section, it is seen that it was expected that stabilizer S was better than N but reality shows that simulation is wrong. The reason of this mistake is because it is extrapolating data which have been studied at high temperatures to a low temperature analysis and unknown processes are activated at low temperature.

8. Environment evaluation

Environment aspects are considered in the present project, as set in directives of this School to perform Bachelor's thesis and according to the concept of sustainability that should be regulate at any project.

Principal environment impact difference between dual-curing and B-stage process is the no required use of solvents by systems to be able to react. Also, there should not be volatile or soluble fragments. Regarding obtained materials, as mentioned before, thermosets once cured, it cannot be mold so recycle also is not possible.

Referring to the experimental part of the project, during all the study, it is taken care to depositing waste (remains of material, vials, gloves, etc) in habilitated deposits for this usage. Later, all the waste is sent to required disposal plants to apply ideal treatment under appropriate conditions.

9. Economic evaluation

It is performed an economic evaluation of the total project cost. It is considered all the costs in terms of material expenses, instrumentation costs and time dedicated of human resources.

In material costs, quantity of the product that has been used is considered. It is used 1 g of each resin to preliminary study and it is produced 2 g of each formulation to be able to test and make samples for photocuring and dual-curing. The following table shows quantity, material price and total price of expenditure on material:

Table 16. Materials costs

<i>Product</i>	<i>Quantity (g)</i>	<i>Price per unit (€/g)</i>	<i>Total price (€)</i>
<i>GLICMA</i>	<i>8</i>	<i>0,332</i>	<i>2,66</i>
<i>HEA</i>	<i>10,2</i>	<i>0,191</i>	<i>1,95</i>
<i>HEMA</i>	<i>13</i>	<i>0,420</i>	<i>5,46</i>
<i>HDDA</i>	<i>2,8</i>	<i>0,346</i>	<i>0,97</i>
<i>BA</i>	<i>2,4</i>	<i>0,217</i>	<i>0,52</i>
<i>BMA</i>	<i>2,4</i>	<i>0,173</i>	<i>0,42</i>
<i>DMPA</i>	<i>1,17</i>	<i>1,184</i>	<i>1,39</i>
<i>N</i>	<i>0,012</i>	<i>0,148</i>	<i>0,01</i>
<i>S</i>	<i>0,12</i>	<i>0,231</i>	<i>0,03</i>
Total cost (€)			13,4

Regarding expenses of instrumentation, it is counted for each test the instrumental amortization, the maintenance, required consumed material, power consumption and cryogenics and inert gases service during the tests. Moreover, it is counted 550€ approximately in terms of laboratory equipment such as spatulas, syringes, globes, etc.

Table 17. Instrumentation costs

Tests	Price per test (€/test)	Nº tests	Total price (€)
<i>Photo-DSC</i>	50	48	2.400
<i>DSC</i>	50	48	2.400
<i>DMA</i>	100	7	700
<i>TGA</i>	50	8	400
Total cost (€)			5.900

Finally, it is accounted staff costs. In the present project, it is counted two directors and one technical researcher as research scholar with their dedication time:

Table 18. Human resources costs

Human resources	Price per hour (€/h)	Dedication (h)	Total price (€)
<i>Technical researcher</i>	10	600	6.000
<i>Director 1</i>	25	120	3.000
<i>Director 2</i>	25	120	3.000
Total cost (€)			12.000

Adding all the costs of the above tables and 550 € of laboratory equipment, the total project cost is approximately 18.463€.

10. Conclusions

The most relevant findings are the following:

- It is possible to design materials following a two-stage procedure with controlled reactivity and tailorable intermediate properties.
- Properties in the intermediate stage between photocuring and thermal curing can be controlled essentially by the different rigidity of methacrylate and acrylate polymers and the presence of chemical crosslinking.
- Properties after the thermal curing reflect a significant increase in crosslinking and rigidity of the samples.
- The addition of reaction stabilizers makes it possible to prepare photocured materials and store them safely under controlled conditions before application and final thermal curing.
- The use of highly hydrophilic monomers such as HEA and HEMA, however, can facilitate moisture absorption and therefore affect the long term properties of the photocured and completely cured materials.
- Less hydrophilic monomers with adequate reactivity should be explored to overcome this drawback.
- The copolymer composition, molecular weight and soluble fraction of the polymers in the intermediate stage should be studied in more depth to understand the structure-properties relationships.
- Possible applications such as the easy preparation of components with complex shapes are envisioned.

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