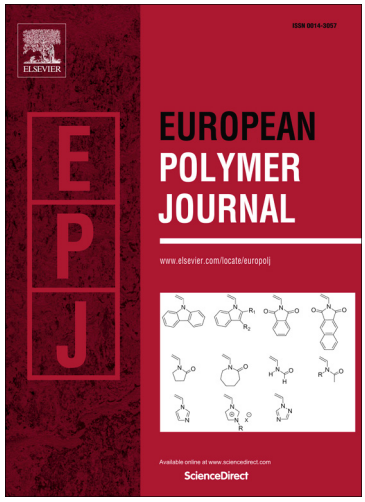

Sequential curing of amine-acrylate-methacrylate mixtures based on selective aza-Michael addition followed by radical photopolymerization

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Sequential curing of amine-acrylate-methacrylate mixtures based on selective aza-Michael addition followed by radical photopolymerization

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ABSTRACT

Dual curing systems find various uses in industry with the process flexibility they provide which allows tailoring properties at different curing stages in accordance with application requirements. A safe and efficient dual curing scheme is proposed here for a set of mixtures containing different proportions of acrylates and methacrylates. The first curing stage is a stoichiometric aza-Michael addition between acrylates and an amine, followed by photo-initiated radical homopolymerization of methacrylates and remaining acrylates. An analysis of aza-Michael reaction kinetics confirmed that amines react selectively with acrylates, leaving methacrylates unreacted after the first curing stage. It was found that acrylate-rich mixtures achieve complete global conversion at the end of the scheme. However, the highest crosslinking density and thermal resistance was observed in a methacrylate-rich formulation. The resulting materials show a wide range of viscoelastic properties at both curing stages that can be tailored to a variety of industrial application needs.

Keywords: acrylate; methacrylate; aza-Michael; dual curing; click reaction; photopolymerization

1 Introduction

Dual curing systems are used in many applications since they provide great flexibility in product design. Taking advantage of the sequentiality of the two reaction steps, one can tailor product properties at both the intermediate and the final curing stages [1]. The first stage of curing in many dual curing schemes is a self-limiting click reaction. These reactions provide high yields with high selectivity, thus making them suitable for a dual curing scheme [2]. A widely used click reaction is the Michael addition as it can be carried out in near-ambient conditions with favorable reaction kinetics and high yields [3–6]. It is essentially a base catalyzed addition of a nucleophile to an activated electrophile. Nucleophiles are referred as Michael donors, whereas electrophiles are called Michael acceptors. Typical Michael donors are amines, thiols, and phosphines. The group of Michael acceptors is more numerous and includes acrylate esters, acrylonitrile, acrylamides, maleimides, alkyl methacrylates, cyanoacrylates and vinyl sulfones [3].

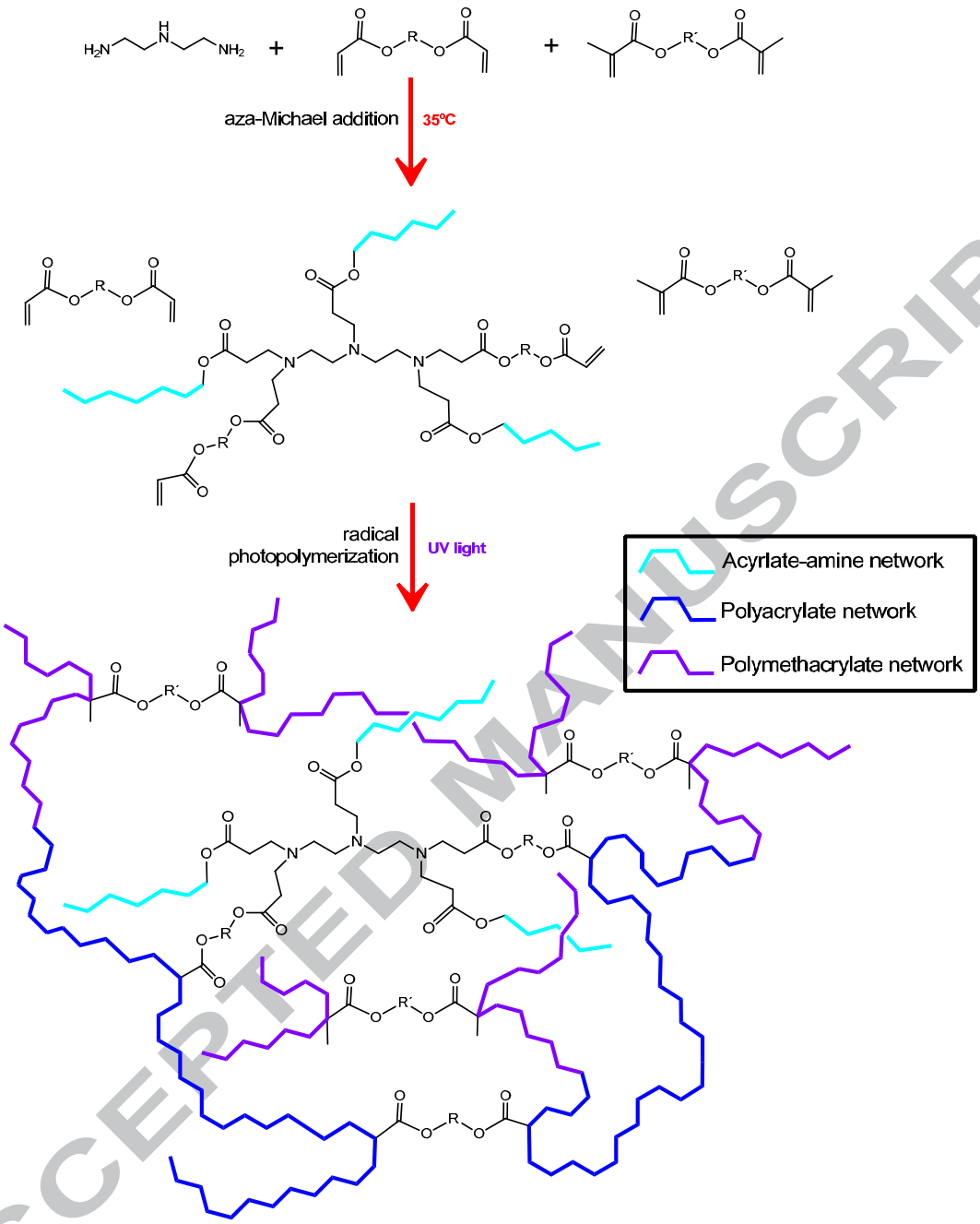
Recently, many researchers have employed a dynamically controlled polymerization designed via Michael addition as a first step and photopolymerization a second step in a dual curing scheme. Nair et al. [1] employed a two-stage curing process consisting of thiol-acrylate Michael addition followed by photopolymerization of excess acrylates to synthesize an array of polymers with a wide range of viscoelastic properties that can be tailored at both curing stages. Peng et al. [7] used base catalyzed thio-Michael addition followed by thiol-ene radical photopolymerization to prepare polymers that can record holographic data. González et al. [5] presented a dual curing process consisting of acrylate-amine Michael addition, followed by photo-initiated radical polymerization to synthesize a wide range of thermosets applicable to various industries. Retailleau et al. [8] used a synthetic strategy based on aza-Michael addition and radical photopolymerization to generate a polymeric network via three time-controlled steps. Their choice of acrylate and amine allows for two consecutive aza-Michael reactions taking place.

The second stage of many dual curing schemes is a radical polymerization reaction that provides the final product with a high crosslink density and desirable viscoelastic properties [1,5,6]. Xi et al. [7] achieved a temporal control of the two stage thiol-Michael addition and photopolymerization using a mixture of thiol, acrylates and methacrylates. Thiol-methacrylate addition has a significantly lower reaction rate than

thiol-acrylate addition, barely reacting with thiols in the first stage. González et al. [5] demonstrated the same behavior in the preparation of thermosets via two-stage sequential aza-Michael addition and free-radical polymerization of amine-acrylate/methacrylate mixtures.

Taking into consideration these antecedents, in the present work, we utilize acrylate-amine Michael addition (i.e. aza-Michael addition) followed by photo-initiated radical polymerization of methacrylates. Due to the steric hindrance caused by their pendant methyl groups and to the inductive effect, methacrylates are poor Michael acceptors. As a result, they do not partake in the aza-Michael addition, and thus can be used selectively in a dual curing system [5,6]. They can undergo photopolymerization at a subsequent stage of curing via a fast photo-initiated radical curing mechanism to provide the final product with a heterogeneous network structure which would have high crosslink density and desirable mechanical properties [5,9,10].

In the present work, we prepared different mixtures of acrylates, methacrylates and an amine to synthesize thermosets using a solvent-free dual curing scheme carried out at near-ambient conditions. As the first curing step, acrylates are selectively reacted with a stoichiometric amount of an amine through aza-Michael addition. Since an amine performs both as a base and a nucleophile, no additional base catalyst is needed in this reaction [3,5]. After this first curing step, the methacrylates in our mixtures are homopolymerized by a photo-induced free-radical polymerization mechanism. The employed dual curing methodology is schematized in Scheme 1.



Scheme 1. Dual curing methodology and the resulting polymer structure.

We focused on the effect of formulation (i.e. relative acrylate and methacrylate content) on reaction kinetics, the resulting network structure and viscoelastic properties of materials both at the intermediate (i.e. after aza-Michael addition) and final stage (i.e. after photopolymerization). To monitor acrylate and methacrylate conversion, we used Fourier transform infrared spectroscopy (FTIR). To measure viscoelastic properties at

both curing stages, we used dynamic scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). To determine gel time during aza-Michael addition, thermomechanical analysis (TMA) was used. We also used thermogravimetric analysis (TGA) to determine the thermal degradation profiles of our final materials. We performed soluble fraction analyses on intermediate and final materials to shed further light on crosslink density and the extent of conversion. We also carried out a statistical analysis of aza-Michael network build-up in order to support our experimental findings about network structure. In order to check the degree of cure achieved, the final materials were thermally postcured.

2 Experimental

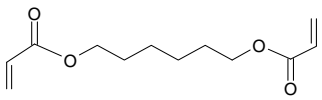
2.1 Materials

We prepared a base acrylate mixture using 75% by weight of hexanediol diacrylate (HDDA, 226.27 $g.mol^{-1}$) and 25% by weight of bisphenol-A glycerolate diacrylate (BisGDA, 484.54 $g.mol^{-1}$). We also prepared a base methacrylate mixture using 12.5% by weight of triethylene glycol dimethacrylate (TEGDMA, 286.3 $g.mol^{-1}$), 37.5% by weight of Bisphenol-A glycerolate dimethacrylate (BGDMA, 512.6 $g.mol^{-1}$) and 50% by weight of hydroxyethyl methacrylate (HEMA, 130.14 $g.mol^{-1}$). HEMA works as a reactive diluent to facilitate higher conversions in methacrylate photopolymerization. As nucleophile for the aza-Michael addition, we used diethylene triamine (DETA, 103.2 $g.mol^{-1}$) in stoichiometric ratio with the acrylate groups present in each formulation. The molecular structure of the chemicals that we used are given in Scheme 2. The choice of the acrylate mixture was based on the research on aza-Michael addition by Gonzáles et al. [5] and the choice of the methacrylate mixture was based on preliminary experimental work (not shown in this paper). Formulations containing *x%* by weight of methacrylate mixture (MA) and *y%* by weight of acrylate-amine mixture (Ac) were prepared and coded as *xMA_yAc*. 2,2-dimethoxy-2-phenylacetophenone (DMAP) was used as radical photoinitiator and added in a proportion of 0.5 phr with respect to the total mixture. The samples were prepared by first mixing the acrylate and methacrylate components and the photoinitiator, and finally addition of the required

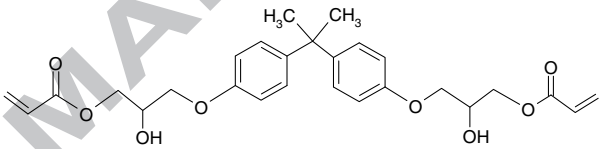
amount of DETA followed by quick stirring and immediate analysis or sample preparation.

Fully cured samples were prepared using a mold with dimensions ca. 1x12x20 mm^3 covered with two glass on both sides to allow UV irradiation. The glass covers were coated with a fine layer of silicone paste to avoid adhesion of the sample. The liquid formulations were poured into the mold and kept in an oven at a controlled temperature of 35 ºC for a number of hours to carry out the aza-Michael reaction. The samples were subsequently irradiated at room temperature in a Vilber Lourmat UV oven equipped with 6 lamps emitting UV light at a wavelength 365 nm and 4 mW/cm^2 total light intensity. The samples were irradiated on both sides, and received a total dose of 3.5 J/cm^2. Thermal postcuring was carried out for 2 hours at 100ºC.

Acrylates

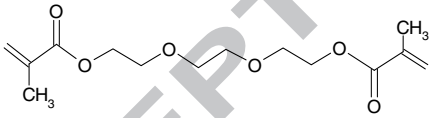


HDDA

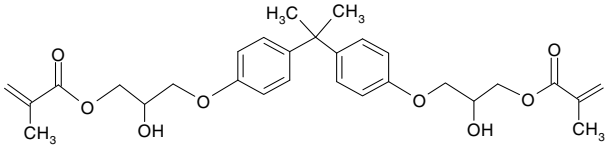


BisGDA

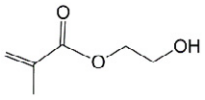
Methacrylates



TEGDMA

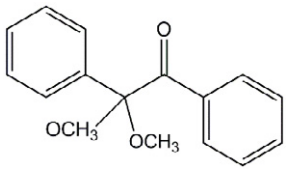


BGDMA

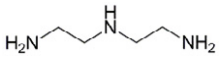


HEMA

Photoinitiator **Amine**



DMPA



DETA

Scheme 2. Molecular structures of the chemicals used

Table 1: Composition of the formulations used in this work

Formulation	Acrylate-amine			Methacrylate		
	Wt.% HDDA	Wt.% bisGDA	Wt.% DETA	Wt.% TEGDMA	Wt.% bisGMA	Wt.% HEMA
0MA_100Ac	64.8	21.7	13.6	0	0	0
25MA_75Ac	48.6	16.2	10.2	3.1	9.4	12.5
50MA_50Ac	32.4	10.8	6.8	6.3	18.8	25.0
75MA_25Ac	16.2	5.4	3.4	9.4	28.1	37.5
90MA_10Ac	6.5	2.2	1.4	11.3	33.8	45.0
100MA_0Ac	0	0	0	12.5	37.5	50.0

2.2 Fourier-transform infrared spectroscopy (FTIR)

We used a Brucker Vertex 70 FTIR spectrometer equipped with an attenuated total reflection (ATR) accessory (GoldenGate^{TM}, Specac Ltd.) which is temperature controlled in order to monitor the aza-Michael reaction and to verify the degree of cure of the samples after the aza-Michael reaction, photocuring and thermal postcuring. Spectra were collected in absorbance mode with a resolution of 4 cm^{-1} in the wavelength range from 4000 to 600 cm^{-1} averaging 20 scans for each spectrum. Scans were carried out every 15 minutes for a duration of time sufficient to observe the highest achievable conversion in aza-Michael reaction. Additional scans were performed on photocured and postcured samples as well. The conversion of functional groups is denoted as α and it is defined by Equation 1.

$$\propto = 1 - \frac{A'}{A_0'} \qquad (1)$$

where A' is taken either as the absorbance of the acrylate groups (area under the absorbance peak at 1407 cm^{-1}) or as the absorbance of the total of acrylate and methacrylate groups (area under the absorbance peaks at 1620 cm^{-1} and 1636 cm^{-1}),

both normalized with that of the ester group of the acrylate mixtures (1720 cm^{-1}) and A_0' is the value of this absorbance at time 0. The former absorbance gives acrylate conversion, whereas the latter gives global (total of acrylate and methacrylate) conversion.

2.3 Differential Scanning Calorimetry (DSC)

To determine thermal glass transition temperatures (T_g) and conversions, calorimetric scans of materials at intermediate and final stages, after postcure, and also filtrates of the soluble fraction analyses were carried out on a Mettler DSC822e thermal analyzer. The DSC822e analyzer was calibrated using an indium standard (heat flow calibration). Samples of approximately 5 mg were placed in aluminum pans with pierced lids and analyzed by choosing a temperature ramp of 10°C/min from -100°C to 250°C.

2.4 Dynamic mechanical analysis (DMA)

Fully cured materials were analyzed using a TA Instruments DMA Q800 device. Prismatic rectangular samples (ca. 1x12x20 mm^3) were analyzed by DMA using a single cantilever clamp at a frequency of 1 Hz and 0.05% strain at 3ºC min^{-1} from -50ºC up to a temperature high enough for complete network relaxation. The peak temperatures of tan δ curves were taken as α-relaxation temperatures.

2.5 Thermomechanical analysis (TMA)

A Mettler thermo-mechanical analyzer SDTA840 was used to determine the gel point during aza-Michael addition. A silanized glass fiber disc about 5mm in diameter was impregnated with the liquid (uncured) formulation and sandwiched between two aluminum discs. The sample was placed in 35ºC for 3h and subjected to an oscillatory force from 0.005 to 0.1N with an oscillation frequency of 0.083 Hz. The gel time was taken as the onset in the decrease of the oscillation amplitude measured by the probe. The conversion at gel point was determined as the conversion reached in FTIR at the gel time.

2.6 Soluble fraction analysis

After each curing step, each material was weighed and placed in a 250ml three-necked flask. To extract the soluble fraction, chloroform was added in the flask in an amount sufficiently high to ensure solubility of all soluble material. The mixture was boiled at 60ºC under atmospheric conditions and was kept under constant reflux using a water cooled condenser for 24 hours. The flask content was then filtered to separate the soluble and gel fractions. Each filtrate was dried at 80ºC in an electric oven. Weight measurements were performed between drying cycles and drying was continued until no further weight change was measured. For each formulation, the dried filtrate weight was taken as the gel fraction; the difference between the initial weight and gel fraction was taken as the soluble fraction. Solutes and filtrates were analyzed in FTIR. Filtrates were further analyzed in DSC.

2.7 Network build-up analysis

In spite of the complexity of the reaction mechanism, the aza-Michael addition to acrylates is a step-wise reaction from the network build-up point of view and can be modeled using well-established methods [11]. Two straightforward and useful relationships that can be used to analyze the network build-up process are the conversion at gelation x_{gel} and the critical stoichiometric ratio r_c, assuming ideal random step-wise reaction:

$$x_{gel} = \sqrt{\frac{r}{(f-1)\cdot(g-1)}} \tag{2}$$

$$r_c = \frac{1}{(f-1)\cdot(g-1)} \tag{3}$$

where f and g are the functionalities of the amine crosslinker and acrylate monomer respectively, x refers to the acrylate conversion and r is the amine:acrylate equivalent ratio.

Other relevant network build-up parameters such as the gel fraction w_{gel} can also be calculated. A statistical method based on the random combination of structural fragments [11] has been used to simulate the evolution of network formation and to

calculate the gel point conversion and gel fraction after aza-Michael addition. Details on the procedures and the expressions used for their calculation are found in the appendix.

3 Results and discussion

3.1 Reaction kinetics of the aza-Michael addition

The aza-Michael reaction has been monitored with FTIR at 35 ºC. Figure 1 shows the spectra collected during reaction of formulation *50MA_50Ac*.

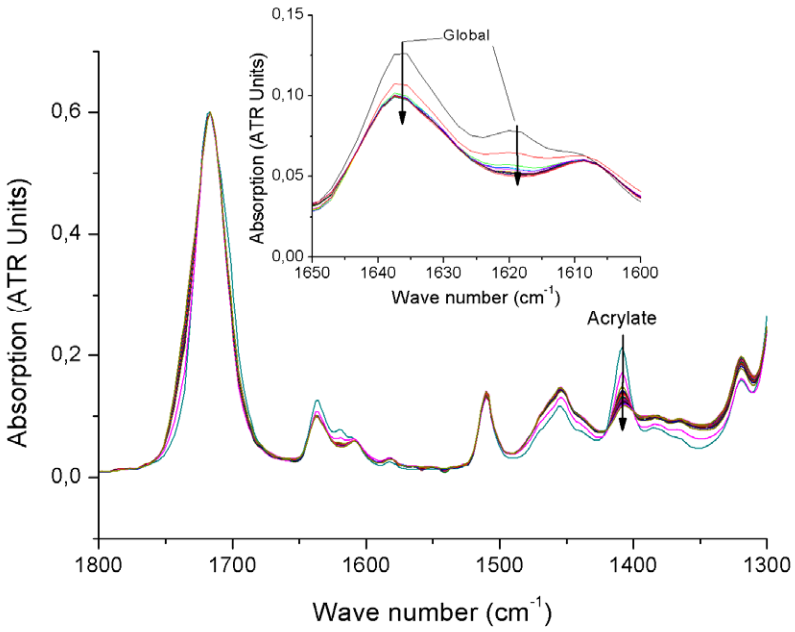


Fig 1. Evolution of FTIR spectra for *50MA_50Ac* monitored during aza-Michael reaction for 4 hours. Spectra were taken every 15 minutes. Curves are normalized using the carbonyl ester band at 1720 cm^{-1}

A reduction of intensities can be observed in the relevant peaks. To investigate the extent of the selectivity of the aza-Michael reaction towards acrylates, for each formulation, the acrylate conversion determined from the 1407 cm^{-1} band was multiplied by the acrylate mole fraction in that formulation. The result was checked against the global conversion directly determined from the peaks at 1620 cm^{-1} and 1636 cm^{-1}. In all cases, the two conversions were found to be virtually equal, thus proving selectivity. For space considerations, we present the results of *50MA_50Ac* only. The

acrylate mole fraction in this formulation is 0.516. Therefore the global conversion is calculated by equation 4.

$$x_{global\ (1407\ cm^{-1})} = 0.516 * x_{acrylate\ (1407\ cm^{-1})} \quad (4)$$

Figure 2 shows that, taking into account the experimental error and that of the mathematical deconvolution of the FTIR bands needed for the analysis, the total number of reacted acrylate and methacrylate groups is practically equal to the number of reacted acrylate groups. This confirms that the aza-Michael reaction is selective towards acrylates, and that methacrylates are poor Michael acceptors [3].

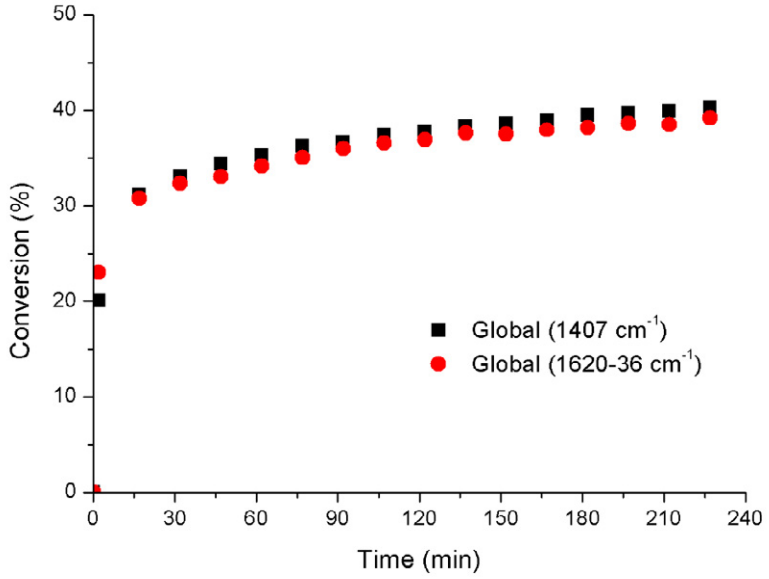


Fig 2. Global conversion of *50MA_50Ac* determined from two different absorption regions.

In Figure 3, acrylate conversion profiles obtained from FTIR data in the aza-Michael addition of different formulations are given.

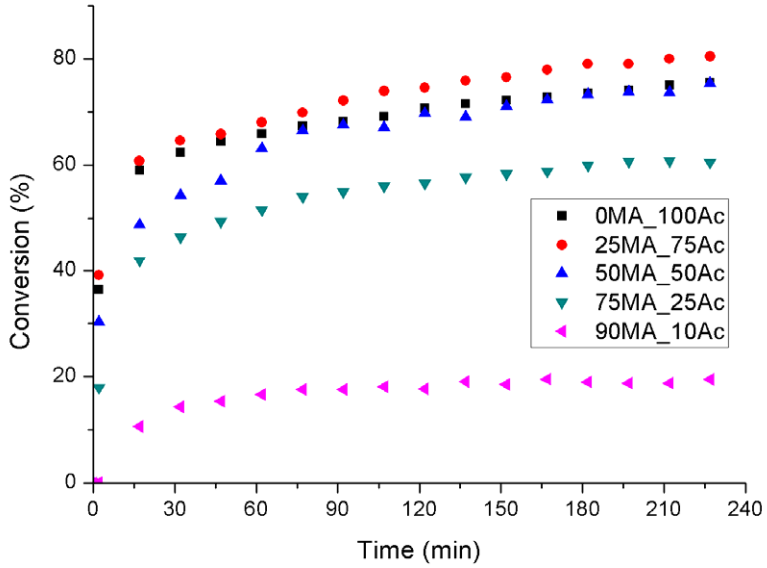


Fig 3. FTIR acrylate conversion of formulations with different compositions.

As can be seen, when the weight percentage of acrylate groups in the formulation is below 50, aza-Michael reaction rate and final acrylate conversion decrease significantly. In the first 4 hours, the acrylate conversion of *25MA_75Ac* was observed to be the highest among all formulations. However, the final conversion of *100Ac* was observed to be the highest when aza-Michael reaction is continued for longer times, as will be shown in following subsections. Since the methacrylate groups do not take part in aza-Michael addition, they dilute the reactant concentration and therefore slow down the reaction. This retardance is more significant in formulations that have a methacrylate weight percentage higher than 50.

Further experimental work was carried out in order to optimize the duration of the aza-Michael reaction, using the *50MA-50Ac* formulation. The formulation was kept at 35 ºC for 4, 24 and 48 hours and subsequently analyzed by FTIR. As seen in Figure 4, the aza-Michael reaction apparently stagnated after 24 hours as no further decrease was observed in neither the acrylate peak at 1407 cm^{-1}, nor the peaks at 1620 and 1636 cm^{-1}.

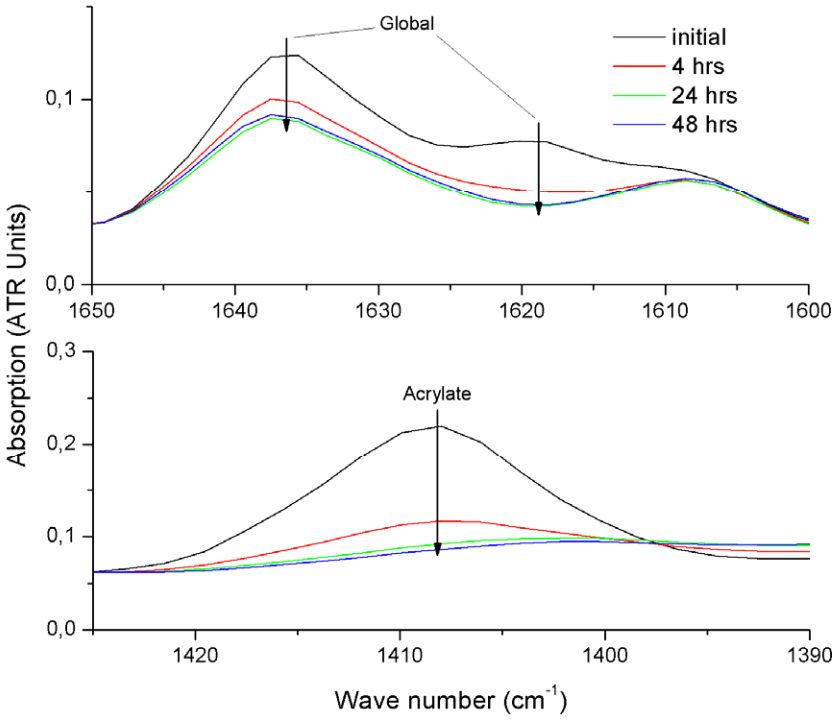


Fig 4. FTIR spectra of *50MA_50Ac* sample showing conversion of reactive groups during aza-Michael addition. Top: Reduction of acrylate + methacrylate absorption. Bottom: Reduction of acrylate absorption. Curves are normalized using the carbonyl ester band at 1720 cm^{-1}

In Figure 5, one can see the conversions obtained by analyzing FTIR data taken during aza-Michael reaction. The slight divergence between acrylate conversion and global conversion after the fourth hour indicates conversion of methacrylates as well. However, it was confirmed by DSC that in comparison to the change in T_g when the samples are photocured, this small methacrylate conversion has no practical significance. These results show that the intermediate materials have storage stability.

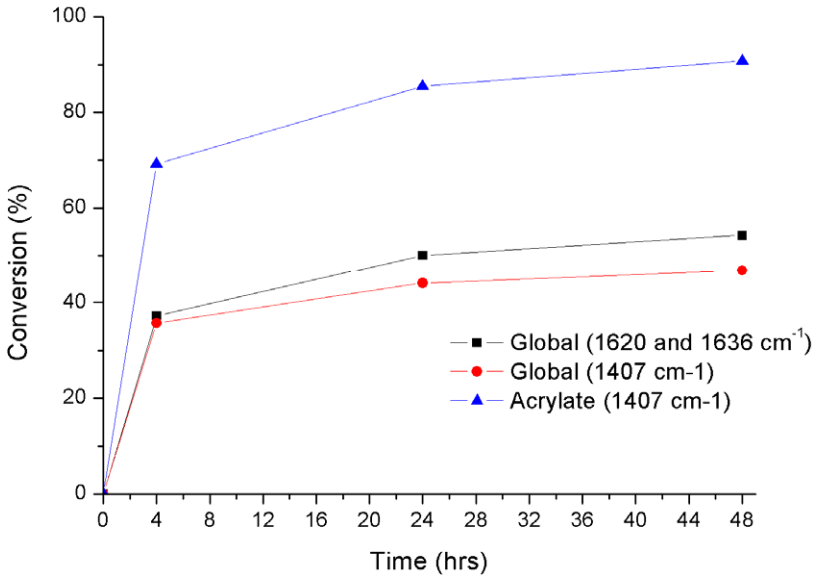


Fig 5. Evolution of acrylate and global conversion of *50MA_50Ac* during 48 hours of aza-Michael addition

Comparable relaxation ranges were observed in the two samples obtained after aza-Michael reaction was carried out for 24 and 48 hours. This indicates that the network structure of these materials are similar. Taking into account these preliminary findings on aza-Michael reaction kinetics and product properties, in the further characterization of our materials, 24 hours of aza-Michael reaction was established as a standard procedure for material preparation.

3.2 Network build-up analysis

Aza-Michael addition follows a step-wise polymerization process that can be analyzed using well-established statistical methods [11]. It is known that the reactivity of the formed secondary amines during aza-Michael addition is lower than that of primary amines and original secondary amines in the amine crosslinker due to strong steric hindrance [4,5]. However, from a practical point of view, the effect of negative substitution effects on the gel point conversion is not very significant [11], and the same is expected for other network build-up parameters. Two relevant parameters have been

determined experimentally, the acrylate conversion at the gel point and the gel fraction, and compared with the predictions made assuming ideal step-wise polycondensation (see Appendix).

The gel time was determined by TMA under isothermal conditions following a similar procedure as the one described in the literature [12] and the conversion was determined by comparing it with FTIR measurements. In Table 1, the gel times determined by TMA are given, together with the corresponding conversions from FTIR measurements, and also the Tg of filtrates obtained after fully solubilizing the intermediate materials. It can be observed that gel time increases significantly on increasing the methacrylate content, due to the decrease in the reaction rate caused by the lower concentration of amine and acrylate groups that participate in the aza-Michael addition.

Table 1: Intermediate material properties at gel point. T_g are obtained by DSC.

Intermediate Material	Gel time (min)	FTIR conversion	T_g of the filtrate (ºC)
0MA_100Ac	25.9	0.61	-5.4
25MA_75Ac	27.1	0.63	-12.3
50MA_50Ac	34.7	0.55	-8.0
75MA_25Ac	83.1	0.54	-7.4

Taking into account that all formulations have a stoichiometric amine-acrylate ratio, the theoretical conversion at the gel point assuming ideal step-wise behaviour should be 0.5. The FTIR conversions at gel point are in relatively good agreement with this theoretical value. Furthermore, the gel point determined for *100Ac* is in agreement with the paper by González et al. [5] in which the researchers use TMA to determine gel time of the same formulation. However, the experimental values are slightly higher than theoretical ones, probably due to the lower reactivity of formed secondary amine groups. In addition, one also has to take into account the experimental differences due to the pairing of data from two different sources: TMA and FTIR.

Table 1 also shows that the T_g's of filtrates are similar in all formulations. All filtrates are composed of a fully crosslinked acrylate-amine network. This is confirmed both by the similarity of T_g values of all filtrates to that of the fully cured *0MA_100Ac* material (see Table 3), and also by the similarity of their FTIR spectra shown in the

bottom part of Figure 6. Also in this figure, one can see that the soluble fractions consist mainly of unreacted acrylate or methacrylate mixtures depending on the formulation content. The selectivity of the aza-Michael reaction can be confirmed given that soluble fractions of all methacrylate containing formulations and the neat methacrylate mixture produce absorption peaks with comparable intensities.

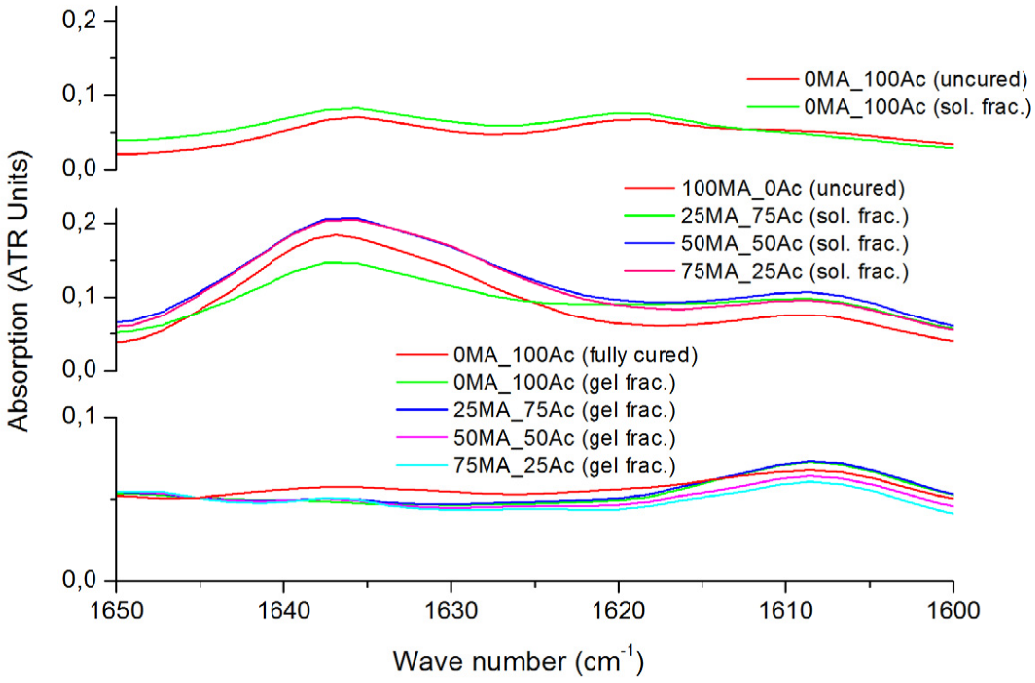


Fig. 6. FTIR absorption peaks at 1620 and 1636 cm^{-1} (corresponding to the total of acrylate and methacrylate groups) of gel and soluble fractions of all intermediate materials. Curves are normalized using the carbonyl ester band at 1720 cm^{-1}

Table 2 gives the results of gel fraction analysis for all intermediate materials after 4 hours of aza-Michael addition, in comparison with the theoretical gel fractions calculated by the statistical method [11], assuming that methacrylates do not react during the aza-Michael stage. Reasonable agreement is observed in all cases, which also confirms the hypothesis of the non-reactivity of methacrylates.

Table 2: Experimental and theoretical soluble fraction analysis for intermediate materials after 4 hours of aza-Michael addition.

Intermediate material	Exp. gel fraction (%)	Theo. gel fraction (%)
0MA_100Ac	86	95
25MA_75Ac	72	72
50MA_50Ac	46	48
75MA_25Ac	22	24

3.3 Characterization of the materials

Table 3 summarizes important parameters regarding the curing of our dual curing formulations. For all formulations, the final T_g are significantly higher than the intermediate T_g owing to the photo-polymerization of unreacted acrylate and methacrylate groups remaining at the intermediate stage, leading to more densely crosslinked networks. Formulations with higher methacrylate content achieved lower acrylate conversions at the intermediate stage due to their lower aza-Michael reaction rates (i.e. due to the dilution effect of methacrylates). Furthermore, a high methacrylate content results in a tighter poly(methacrylate) network which introduces mobility restrictions for further polymerization, imposing yet another barrier to higher conversions at the final stage. However, it can be noticed that the higher the methacrylate content, the higher is the final T_g, regardless of the intermediate acrylate conversion and intermediate T_g, indicating the dominant contribution of the poly(methacrylate) network in the viscoelastic properties of the materials.

Table 3: Conversion of acrylate and methacrylate groups, T_g, gel fractions, and thermal degradation characteristics of the materials. T_g are obtained by DSC.

	Intermediate stage		Final stage					
Material	Acrylate conv. (%)	T_g (ºC)	Acrylate conv. (%)	Global conv. (%)	T_g (ºC)	Gel frac. (%)	Temp. at 2% wt. loss (ºC)	Temp. at 5% wt. loss (ºC)
0MA_100Ac	86	-22.3	94	92	-9.2	97.4	204	222
25MA_75Ac	83	-37.5	97	95	8.8	97.6	209	227
50MA_50Ac	80	-46.4	99	89	26.3	100	206	228
75MA_25Ac	66	-67.4	89	84	52.0	100	221	250

Soluble fraction analyses were also carried out on final materials in order to verify completeness of cure. As can be seen in Table 3, gel fractions of materials with methacrylate weight percent greater than or equal to 50 are unity. This indicates that, even though complete conversion is not achieved due to mobility and topological restrictions towards the end of the polymerization process, monomers are effectively incorporated into the network structure.

The materials were thermally postcured at 100ºC for 2 hours in order to achieve complete conversion of all functionalities, after which their FTIR spectra and thermomechanical properties were measured. As a result, slight improvements in T_g were observed especially in *50MA_50Ac* and *75MA_25Ac* formulations, since these two formulations had achieved relatively lower global conversions at the end of our curing scheme. However, these improvements were deemed practically insignificant, considering that the increases in T_g were lower than 5ºC in both materials, and that they consist of highly heterogeneous polymer networks and thus exhibit broad network relaxation behavior (See Figures 8 and 9). As a result, we may argue that our dual curing process is highly efficient from a kinetic point of view.

In Figures 7 and 8 we present the storage moduli and tan δcurves obtained by DMA measurements on final materials prepared from the different formulations detailed in Table 1. For comparison purposes, we present our results together with that of the neat poly(methacrylate) mixture which is named as *100MA_0Ac*. The mixture *100MA_0Ac* was cured using the same UV curing scheme, but was postcured thermally at 100ºC for 2 hours to ensure complete conversion. As can be seen in both figures, a wide range of glass transition properties can be imparted to the final materials by changing the formulation. The α-relaxations vary between 10 and 150ºC, corresponding to both neat acrylate, *0MA_100Ac*, and to neat methacrylate thermosets, *100MA_0Ac*, respectively. With their different contents of poly(amino-ester), poly(acrylate) and poly(methacrylate) networks, the α-relaxations of all the other materials span this range. The broader relaxation ranges of methacrylate-rich formulations imply that the poly(methacrylate) part of the network has a bigger contribution to network heterogeneity in comparison to the poly(amino-ester) and poly(acrylate) parts. Each material has a storage modulus in the unrelaxed state between 2 and 3 GPa. The moduli after relaxation was in the range of 10-15 MPa, the differences were deemed insignificant due to low stiffness of the materials after relaxation of the network

structure. Due to its HEMA content, the neat poly(methacrylate) material has a low α-relaxation comparable to the other formulations. Overall, the wide range of relaxation behaviors achieved by adjusting the contribution of aza-Michael addition and radical double bond homopolymerization suggest that the dual curing scheme proposed in this research can be suitable for a wide range of industrial applications. Only in the case of more densely crosslinked materials, a thermal postcuring at a moderate temperature might be necessary to ensure complete reaction of all the double bonds and achieve optimal properties.

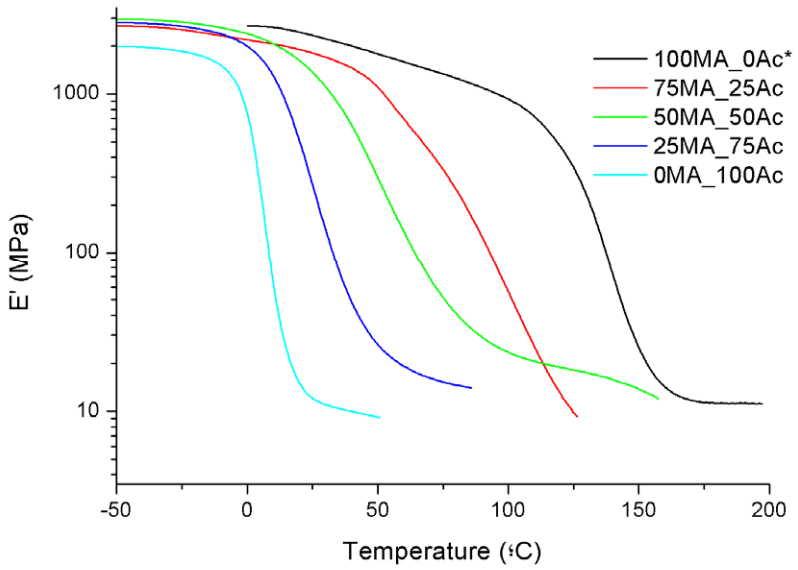


Fig 7. Evolution of storage moduli of different formulations processed via 24h of aza-Michael reaction and subsequent photocuring. The asterisk sign (*) indicates this sample was postcured at 100 ºC for 2 hours. DMA run was discontinued for *75MA_25Ac* above 127ºC as the stiffness of the sample fell below the minimum sensitivity of the equipment.

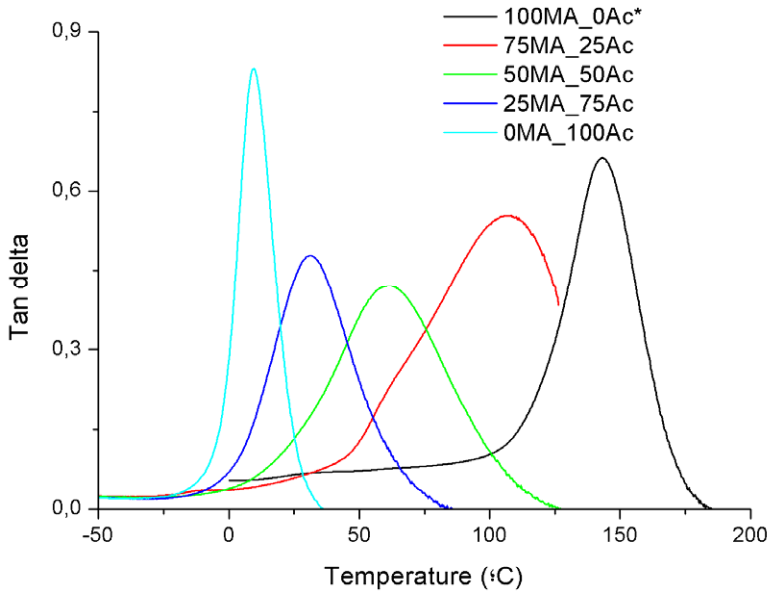


Fig 8. Evolution of tan δ of different formulations processed via 24h of aza-Michael reaction and subsequent photocuring. The asterisk sign (*) indicates this sample was postcured at 100 ºC for 2 hours. DMA run was discontinued for *75MA_25Ac* above 127ºC as the stiffness of the sample fell below the minimum sensitivity of the equipment.

The thermal stability of the thermosets was studied by thermogravimetric analysis. As can be seen in Figure 9, all formulations with methacrylate content (i.e. *75MA_25Ac*, *50MA_50Ac*, and *25MA_75Ac)* exhibit degradation in two stages. The acrylate-rich materials degrade much faster than others due to their dominating poly(aminoester) structure which contains relatively weaker C-N bonds. On the other hand, methacrylate-rich materials, with their stronger C-C bonds of the poly(methacrylate) network, show a slower initial degradation between 200ºC and 300ºC. In all cases the degradation of the poly(acrylate) or poly(methacrylate) network occurs at temperatures higher than 350ºC. The two right-most columns of Table 3 show the temperatures at 2% and 5% weight loss. The materials with lower methacrylate content show similar thermal degradation behavior; temperatures that result in 2% and 5% weight loss are comparable in these materials. However, the material *75MA_25Ac* has outstanding thermal resistance as can be seen especially from its temperature of 5% weight loss which is 22ºC higher than the second best performing material. This suggests that the high crosslinking density of *75MA_25Ac* makes up for its relatively

lower final acrylate conversion (see Table 3). Given the relatively low decomposition temperatures, in comparison to neat poly(acrylates) and poly(methacrylates), these materials might be more suitable for applications in which thermal reworkability is necessary for the recovery of valuable substrates at the end of the service life of components [13].

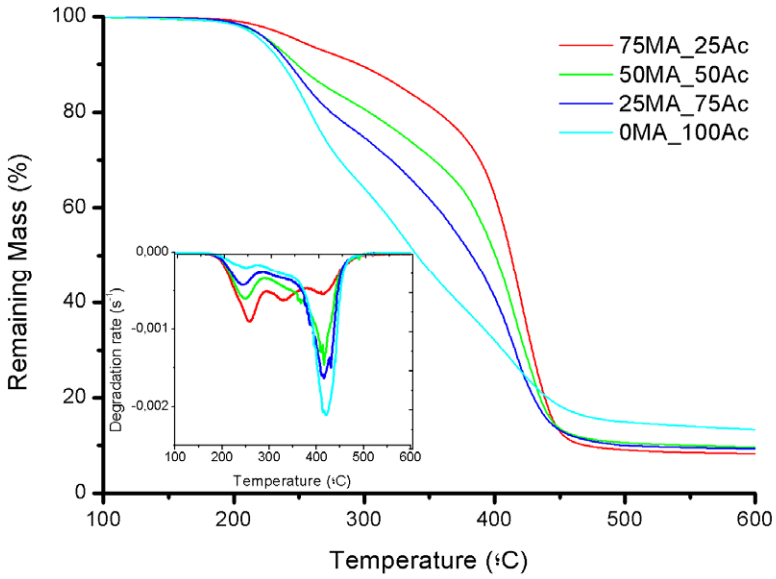


Fig 9. TGA curves of the different formulations in N_2 atmosphere.

4 Conclusions

We have demonstrated a novel approach to design thermosets based on poly(aminoester) and poly(methacrylate) chemistry using an efficient two-stage process which can be carried out in near-ambient temperature conditions. By conducting kinetic experiments and carrying out detailed analyses on network structure, we have shown selectivity of the aza-Michael addition towards acrylates. This selectivity allows tailoring intermediate material properties to meet requirements posed by various industrial applications. The final material properties are attained after a photo-initiated radical polymerization mechanism which is quick and effective. We have shown that practically complete conversions of all reactive species can be achieved at the end of the process.

The resulting materials exhibit a wide array of glass transition temperatures depending on the relative contribution of the aza-Michael and radical double bond homopolymerization reactions, making these systems easily custom-tailorable and adaptable to different application demands. Utilizing this room-temperature environmentally friendly dual-curing processing scheme, further tailoring could be achieved by choosing acrylates and methacrylates with different functionalities and structures. Finally, owing to their facile thermal degradability, these materials might be better candidates than neat poly(acrylates) and poly(methacrylates) for applications requiring thermal reworkability where recovery of valuable substrates is necessary after the end of service life of components [13].

5 Acknowledgments

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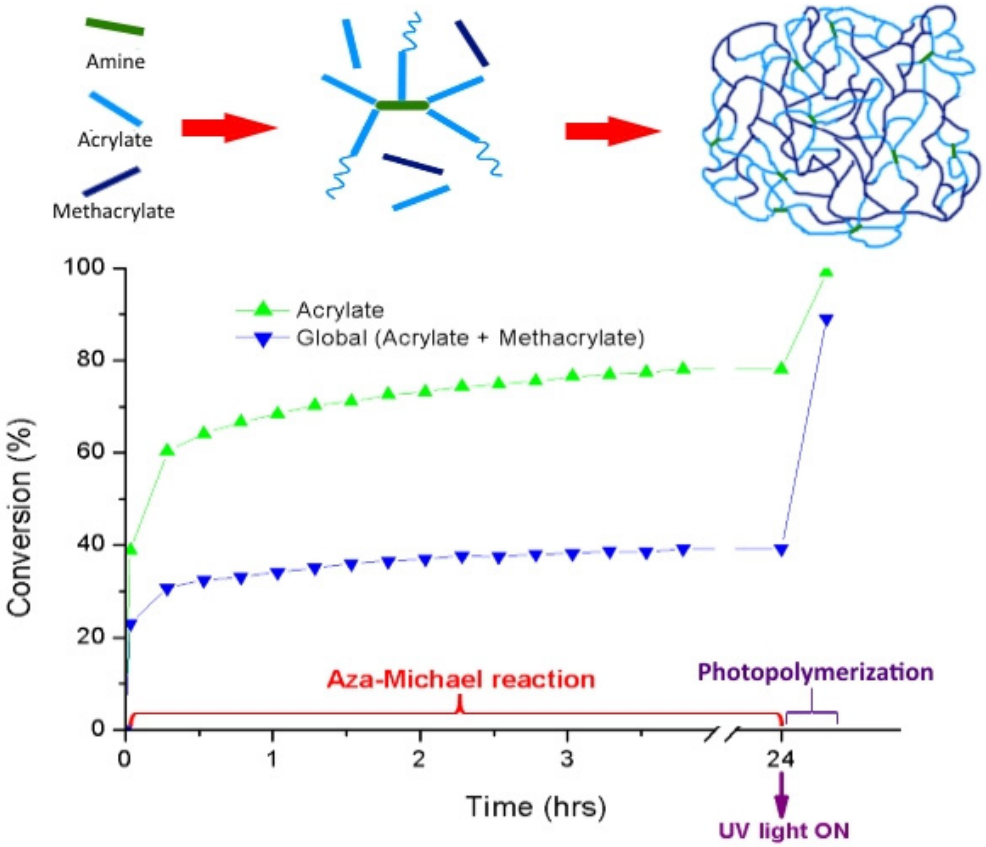
Graphical abstract



Sequential curing of amine-acrylate-methacrylate mixtures based on selective aza-Michael addition followed by radical photopolymerization

Highlights

- Dual curing process is carried out under ambient conditions and is solvent-free
- Acrylate-rich mixtures achieve remarkably high conversions at the end of the scheme
- Highest Tg and thermal resistance was observed in a methacrylate-rich formulation
- Final materials are versatile with alpha-relaxation temperatures ranging from -9 to 52ºC.