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Research Article

Effect of an Anhydride Excess on the Curing Kinetics and Dynamic Mechanical Properties of Synthetic and Biogenic Epoxy Resins

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This work analyzes the effect of the anhydride excess on the nonisothermal curing kinetics and on the final properties of synthetic and biobased epoxy resins. Diglycidyl ether of bisphenol A (DGEBA) and epoxidized soybean oil (ESO) were crosslinked using methyltetrahydrophthalic anhydride (MTHPA) as a curing agent and 1-methylimidazole (1MI) as an initiator. It was shown that the ESO/MTHPA/1MI system reacts slower than the DGEBA/MTHPA/1MI system, giving place to a more significant evaporation of the curing agent during the reaction. As a result, an excess of anhydride improves the final thermal properties of the ESO/MTHPA/1MI network, contrary to the behavior observed for DGEBA/MTHPA/1MI. The knowledge of the kinetics of the curing process and the optimal amount of the curing agent for each system is of critical importance for a more efficient processing of these materials.

1. Introduction

The production of polymeric materials has evidenced a very fast and continuous growth since the mid-20th century aimed at satisfying an increasing demand [1, 2]. This trend is still going on in the present day and does not seem that it will be disrupted in the near future. Over the last two decades, however, the environmental problems posed by polymer production were brought into light and were approached by both academic and nongovernmental associations as well as by industrial and commercial partners, with the purpose of finding proper solutions [2]. One of the most important issues currently under discussion is the depletion of oil resources that constitute the main feedstock for the plastic industry. A feasible alternative to replace the petroleum-based chemicals in the polymer manufacture is the use of raw materials derived from the biomass that promise a reduction in the CO_2 fingerprint and an alleviation of the dependence on fossil resources [3–5].

Vegetable oils, which are produced worldwide in large amounts, constitute an economic and readily available material that can be converted into more useful chemical reagents through chemical modification. There are many available modifications for vegetable oils that have been studied and developed so far, including epoxidation, hydroxylation, acrylation, and maleinization among others [6]. These modified oils can be used to obtain different kinds of polymeric materials like epoxy thermosets, [7, 8] polyurethanes [9–11], or polyacrylates, [12] as well as other products such as adhesives and lubricant greases [13, 14]. Epoxidation of fatty acids and vegetable oils can be performed through reaction with a peroxyacid [15] or following a more sustainable

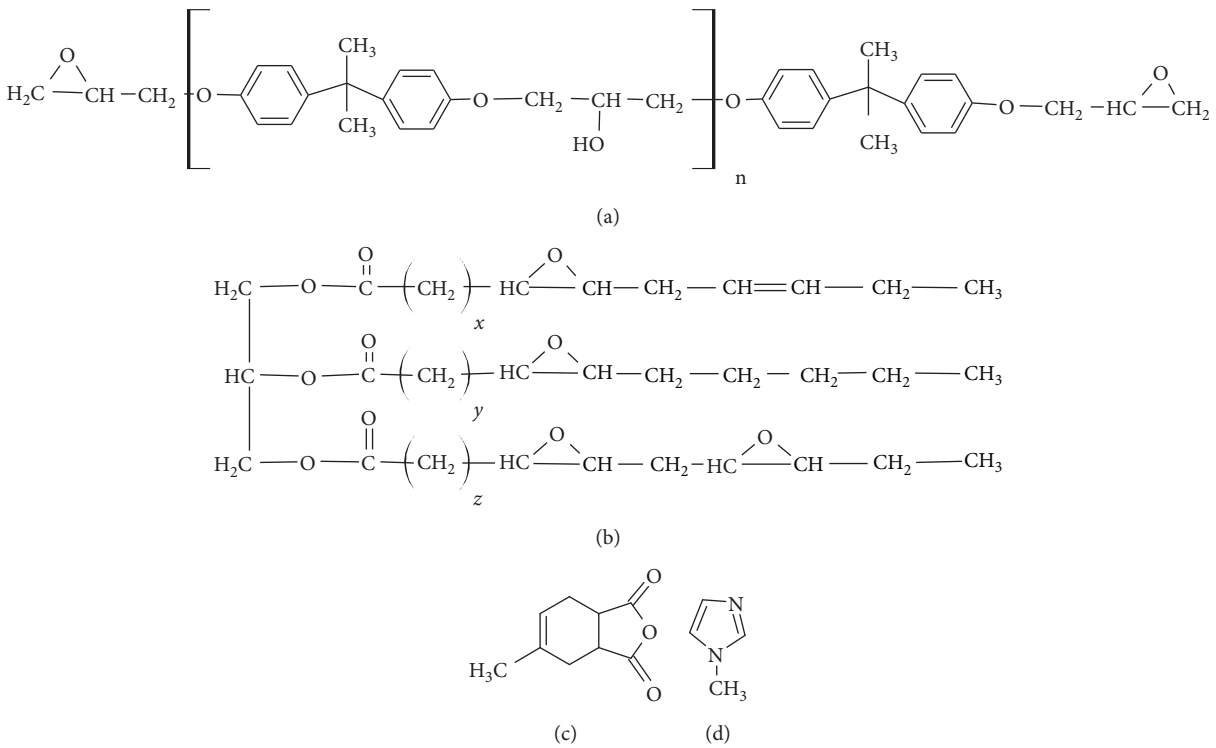

Figure 1: Representative chemical structures of (a) DGEBA ($n = 0.109$) and (b) ESO and chemical structures of (c) MTHPA and (d) 1MI.

route like enzymatic epoxidation [16, 17]. Epoxidized vegetable oils (EVOs) are nowadays produced at an industrial scale and used mainly as a plasticizer for polyvinyl chloride (PVC) [16]. Presently, there are numerous research groups devoted to the development of thermosetting epoxy polymers using EVOs as a green alternative to—or at least as a partial replacement or a modifier for—synthetic epoxy resins, which is generating a growing body of literature describing the curing kinetics [18–20] and the properties of such materials [7, 8, 21, 22].

We already studied the curing process of stoichiometric DGEBA/MTHPA/1MI and ESO/MTHPA/1MI systems [7] and performed a thorough characterization of the resulting networks [7, 23]. The nonisothermal curing kinetics of the stoichiometric systems was also studied, and a phenomenological model was used to fit the experimental results and to explain the behavior of DGEBA-ESO mixtures during curing [18].

Nevertheless, the effect of an excess of anhydride on both the curing kinetics and the final properties has been somewhat overlooked in spite of their importance when the end-use of the material is considered. It is known that anhydride evaporation can take place during the polymerization reaction, leading to an undesired change in the stoichiometric relation and yielding a final material with a lower curing agent/epoxy resin ratio. This change in the proportion of the curing agent with respect to the epoxy precursor must be accounted in order to properly explain the material behavior. Moreover, a prediction of the evaporation amount, when possible, can be proved useful to improve the performance of the material and lead to important savings in energy and raw materials [24]. Indeed, it is a common practice in the industry to use an excess of anhydride in order to compensate the evaporation [25].

In the present manuscript, we study the effect of different amounts of anhydride excess on the properties of thermosetting polymers obtained using synthetic and bio-based epoxy precursors (diglycidyl ether of bisphenol A and epoxidized soybean oil, respectively). We discuss how the different reaction kinetics lead to different anhydride evaporation rates and ultimately affect the network stoichiometry and performance.

2. Experimental

2.1. Materials. The diglycidyl ether of a bisphenol A-based epoxy prepolymer (DGEBA; Araldite GY250; epoxide equivalent weight (EEW) = 185 g/eq) and the hardener methyltetrahydrophthalic anhydride (MTHPA; >99%; anhydride equivalent weight (AEW) = 166 g/eq) were obtained from Distraltec (Buenos Aires, Argentina). Epoxidized soybean oil (ESO; iodine value = 2.4; EEW = 242 g/eq; average molar mass = 929 g/mol; and average functionality = 3.8) was kindly provided by Unipox S.A. (Buenos Aires, Argentina). Both chemicals, DGEBA and ESO, were vacuum dried overnight before use. 1-Methylimidazole (1MI; >99%; molar mass = 82.1 g/mol) was purchased from Huntsman (Buenos Aires, Argentina) and was used as received. The chemical structures of DGEBA, ESO, MTHPA, and 1MI are shown in Figure 1.

2.2. Sample Preparation. DGEBA/MTHPA and ESO/MTHPA reactive systems were prepared with different stoichiometric ratios (R = anhydride equivalents/epoxy equivalents) of 1.0, 1.2, and 1.4. For every system, 0.06 mol of 1MI per epoxy equivalent was added, and the mechanical mixing was performed by hand.

2.3. Characterization

2.3.1. Differential Scanning Calorimetry (DSC). The curing kinetics was evaluated from data obtained by differential scanning calorimetry (DSC). Tests were carried out on a DSC Shimadzu 50 in dynamic mode at different heating rates (q = 2, 5, 10, and 20°C/min) under a nitrogen atmosphere (20 ml/min). From these tests, the heat of reaction (ΔH_r, expressed in kJ per epoxy equivalent) and the temperature for the maximum value of the reaction exothermic peaks (T_p) were measured.

2.3.2. Conversion and Reaction Rate Measurement. Conversion values (α) and reaction rate ($d\alpha/dt$) were obtained from DSC tests according to the procedure previously reported [18]. Briefly, by considering that at any given moment the partial heat released is proportional to the conversion (α), the following equation can be written:

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_T}, \tag{1}$$

where $\Delta H(t)$ is the partial heat released until the time t and ΔH_T is the total heat of reaction, calculated by integrating $\Delta H(t)$ for the whole curing reaction.

Analogously, the reaction rate $d\alpha/dt$ can be calculated from DSC data as

$$\frac{d\alpha(t)}{dt} = \frac{1}{\Delta H_T} \cdot \frac{dH(t)}{dt}, \tag{2}$$

where $dH(t)/dt$ is the instantaneous heat released, directly measured by the DSC.

2.3.3. Reaction Kinetics Fitting. The reaction kinetics was adjusted to the autocatalytic model proposed by Kamal and Sourour [26].

$$\frac{d\alpha(t)}{dt} = (k_1 + k_2.\alpha^n)(1-\alpha)^m, \tag{3}$$

with the rate constants k_1 and k_2 displaying Arrhenius-type dependence with temperature:

$$k_i = A_i.\exp\left(-\frac{Ea_i}{R.T}\right), \tag{4}$$

where Ea_i are the activation energies and A_i are the preexponential factors.

Though this phenomenological model does not provide information about the reaction mechanism, it can be very useful to predict the conversion profile of the reactive systems under different conditions when the temperature-time relation is known or when it is coupled with the heat balance equation, especially when a number of species involved in the reaction make difficult to use a mechanistic model.

In a previous work [18], it was found that the exponents n and m are close to 1 for stoichiometric systems (R = 1); hence, this value was used for all the formulations. Activation energies Ea_1 and Ea_2 are assumed to be independent of R for each system, since the reactions involved the same species regardless of the stoichiometric ratio, and therefore, the values obtained previously were used.

The values for the activation energy for the DGEBA/MTHPA/1MI systems are Ea_1 = 65.1 kJ/mol and Ea_2 = 69.6 kJ/mol, and those for ESO/MTHPA/1MI systems are Ea_1 = 65.7 kJ/mol and Ea_2 = 86.9 kJ/mol.

A multiparametric fitting was used to obtain the preexponential factors (A_i) by minimizing the difference between the calculated conversions and the experimental measurements [27]. The evaporation of the curing agent during the polymerization reaction was neglected in the first approach to obtain the kinetic parameters. As it will be discussed later, this hypothesis was not correct for all the formulations analyzed, though the changes introduced in the reaction kinetics can be regarded as nonsignificant.

2.3.4. Dynamic Mechanical Analysis (DMA). Dynamic mechanical analysis (DMA) was carried out on samples cured following a nonisothermal program in a convection oven. The program consisted in heating from 25°C to 240°C, at a heating rate of 2°C/min. Cured samples were cut to suitable dimensions ($1 \times 4 \times 25\ mm^3$) and tested on an AntonPaar Physica MCR 301 rheometer in a torsion mode, with a span of 15 mm. DMA tests were carried out at a heating rate of 2°C/min, from 0°C to 180°C for ESO/MTHPA/1MI and from 0°C to 200°C for DGEBA/MTHPA/1MI.

3. Results and Discussion

Figure 2 shows the DSC thermograms for DGEBA/MTHPA/1MI and ESO/MTHPA/1MI systems with different R values and q = 10°C/min. Thermograms for the rest of the q values are shown in the Supplementary Information File (available here) and show essentially the same shape as those shown here. Each curve displayed a clear and single exothermic peak, owed to the copolymerization reaction, as the only event in the examined temperature range. Qualitatively, it is possible to observe in the thermograms that the reaction peak (and its area) become lower with the increase in the stoichiometric ratio R. This was expected since, as it will be discussed later, the additional anhydride (20 or 40% over the stoichiometric amount) was prevented to react due to the consumption of the epoxy groups, thus lowering the total heat of reaction on the basis of the sample weight.

The temperatures of the exothermic reaction peak (T_p) for the different heating rates are summarized in Table 1. For the same q and R values, the ESO/MTHPA/1MI systems exhibit higher T_p values than the DGEBA/MTHPA/1MI

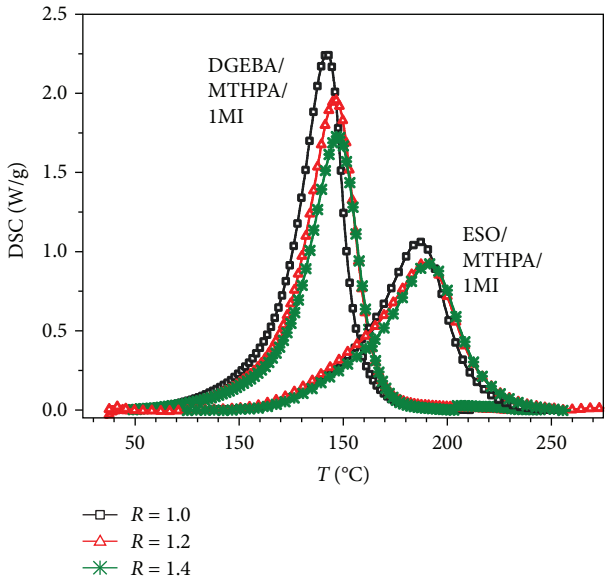

Figure 2: DSC thermograms for the curing of DGEBA and ESO with MTHPA and 1MI with different stoichiometric ratios R, at a heating rate $q = 10$°C/min.

Table 1: Peak reaction temperatures (T_p), measured in °C, for DGEBA/MTHPA/1MI and ESO/MTHPA/1MI with different stoichiometric ratios R.

q (°C/min)	DGEBA/MTHPA/1MI			ESO/MTHPA/1MI		
	$R = 1$	$R = 1.2$	$R = 1.4$	$R = 1$	$R = 1.2$	$R = 1.4$
2	113	116	117	153	158	158
5	129	133	134	173	177	176
10	142	146	147	187	190	190
20	157	162	163	203	207	208

mixtures, due to its lower reactivity, attributed to the increased steric hindrance and electronic effects of the internal oxiranes of ESO [7, 29]. For any given q, T_p values increase with R for both systems, probably due to a dilution effect of the initiator (1MI) and epoxy groups, as a consequence of the higher concentration of MTHPA. The reaction mechanism [24, 30–33] is shown in Figure 3 for terminal epoxides (though it also applies for internal ones) and involves an initiation step whose kinetics strongly depends on the concentration of the initiator and epoxy groups. Hence, the higher T_p values can be associated to the lower concentrations of both 1MI and DGEBA.

Figure 4 shows experimental conversion-temperature curves for DGEBA/MTHPA/1MI and ESO/MTHPA/1MI systems with $R = 1$ and $R = 1.4$, at a heating rate of $q = 10$°C/min (calculated with equation (1)) and the fitting to the proposed model (equations (3) and (4)). Curves corresponding to systems with $R = 1.2$ are placed between those for $R = 1$ and $R = 1.4$ and are not shown here for the sake of clarity. The fitting shows an excellent agreement between the experimental data and the Kamal model. Unsurprisingly, the general trends mentioned for DSC thermograms are repeated here: a decrease in reactivity (curves shifting to higher temperatures) with the increase of R due to a dilution effect and a higher reaction rate for DGEBA/MTHPA systems compared with that ESO/MTHPA, owed to the different reactivity of the epoxide groups.

The obtained values for preexponential factors A_1 and A_2 for both systems, used to fit the experimental data in Figure 4, are listed in Table 2. For both the DGEBA/MTHPA/1MI and ESO/MTHPA/1MI systems, the decrease in the reactivity with increasing R values is reflected in a decrease in A_1 and A_2, being the decrease more prominent when R is raised from 1 to 1.2. The general reduction in the preexponential factors is the result of a lower reaction rate for both the initiation and the propagation steps, which involves two alternating reactions (see Figure 3): an epoxy-carboxylate reaction is followed by an anhydride-alkoxide reaction, which produces a new carboxylate that starts the cycle again by reacting with another epoxy group. As the carboxylate is more stable than the alkoxide, the carboxylate-epoxy reaction is the slower one, and thus, it determines the overall reaction rate [28]. Considering this reaction mechanism, the lower concentration of epoxy rings as R is increased accounts for the decrease of the preexponential values. Moreover, it can be noted that a similar decrease in both A_1 (20% decrease for $R = 1.2$ with respect to $R = 1$ and 22% for $R = 1.4$) and A_2 (26% and 33%, respectively) was observed for the DGEBA curing reaction with increasing MTHPA excess. On the other hand, the effect of MTHPA excess for ESO/MTHPA/1MI systems is much more important in A_2 (46% for $R = 1.2$ and 52% for $R = 1.4$) than in A_1 (less than 1% and 4%, respectively). Assuming that the A_2 constant is more related with the propagation step, one could infer that since it involves the attack of a bulky anion to a hindered internal (in the case of ESO) epoxy group, it is more sensitive to the oxirane concentration than A_1, more related with the initiation step.

A remarkable aspect found in the DSC analysis is the increase of the reaction heat with the increase of MTHPA concentration (Table 3). The higher reaction heat per epoxy equivalent indicates a larger amount of reacted epoxy groups as the anhydride concentration increases. This finding reveals that a significant amount of oxirane moieties remained unreacted in stoichiometric mixtures, leading to the formation of pendent chains that contribute in reducing the thermal and mechanical properties of the formed networks. This behavior can be attributed to the anhydride evaporation taking place during the curing cycle, which leads to obtaining a final material with an R value different to that of the initial mixture. To evaluate this fact, the mass loss during dynamic DSC tests was measured, and dynamic mechanical tests were performed on the polymers cured in a convection oven in a nonisothermal mode at 2°C/min.

The average mass loss for each system is shown in Table 4. It can be assumed, due to the low volatility of the DGEBA and ESO and the low concentration of1MI (which is in a high proportion bonded to DGEBA, ESO, or heavier oligomers), that all the mass losses correspond to evaporated

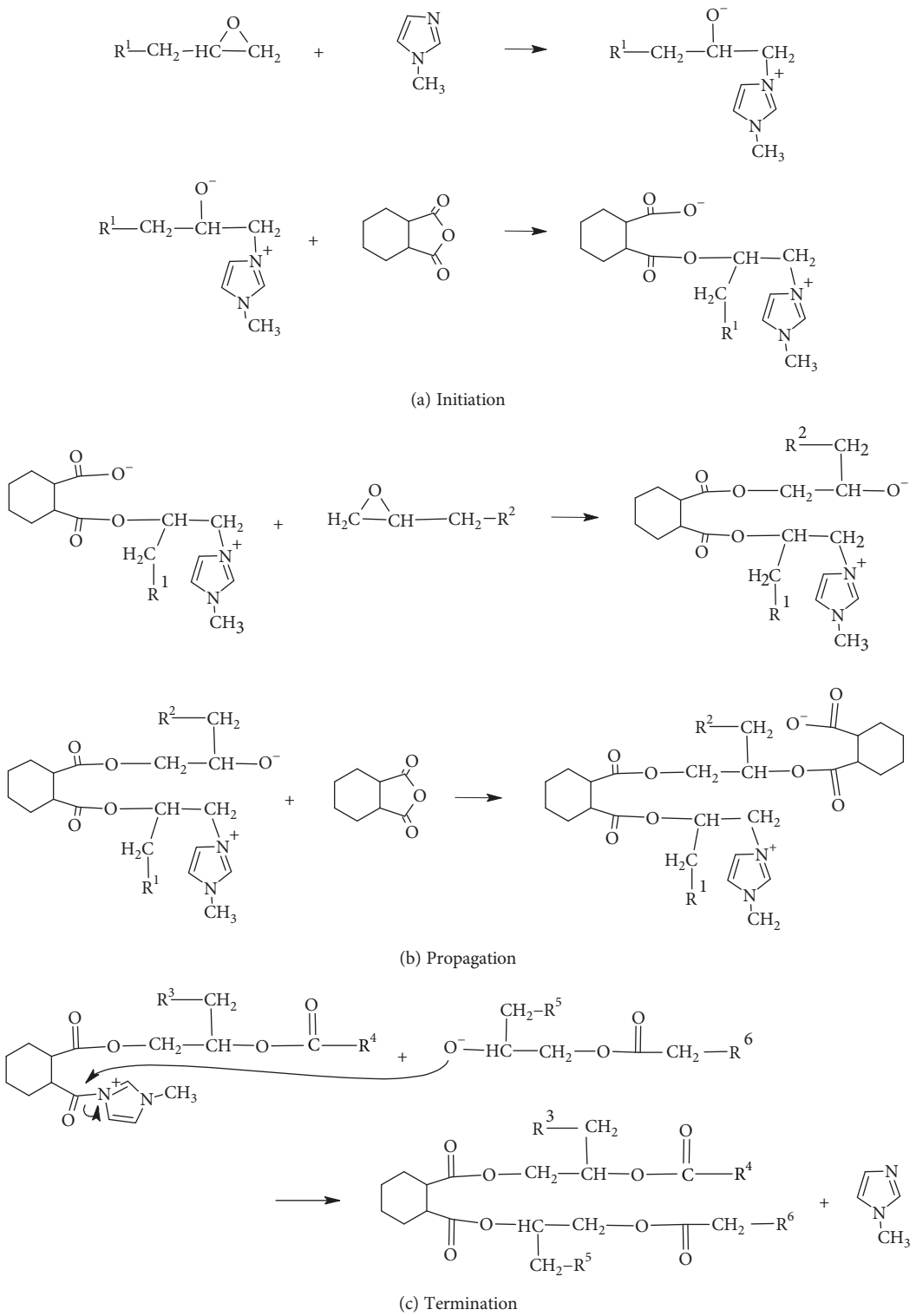

Figure 3: Reaction mechanism for the imidazole initiated epoxy-anhydride copolymerization, including a termination step [28].

MTHPA. The effective anhydride equivalents/epoxy equivalents relation (R_{eff}) was calculated for the cured polymers.

Mass loss, as expected, increases with the initial excess of MTHPA, and for a given R value, it is greater for ESO/MTHPA systems, since DGEBA/MTHPA systems react faster, leaving less time for free MTHPA to be released through evaporation.

Figure 5 shows the storage torsion modulus (G'; Figure 5(a)) and the damping factor (tan δ; Figure 5(b)) as a function of temperature for nonisothermally cured

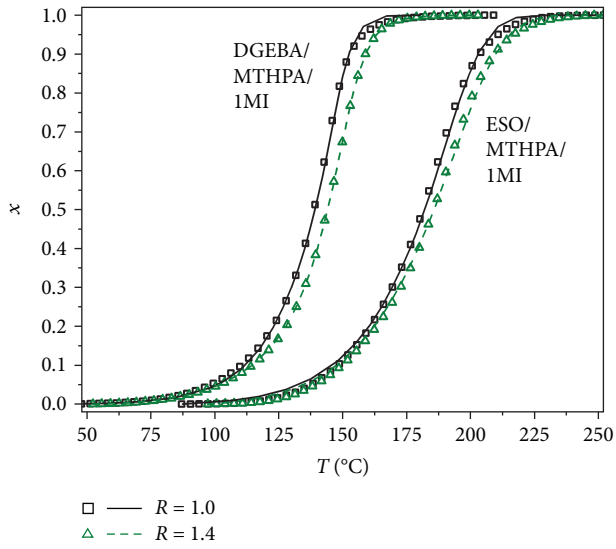

Figure 4: x-T curves for the curing of DGEBA and ESO with MTHPA and 1MI, with stoichiometric ratios $R = 1.0$ and $R = 1.4$, corresponding to $q = 10$°C/min. Solid lines show the obtained fittings to equations (3) and (4).

Table 2: Kinetics parameters of the DGEBA/MTHPA/1MI and ESO/MTHPA/1MI systems with different stoichiometric ratios R.

System	R	$A_1 \cdot 10^{-5}(s^{-1})$	$A_2 \cdot 10^{-6}(s^{-1})$
DGEBA/MTHPA/1MI	1.0	7.11	8.35
	1.2	5.69	6.18
	1.4	5.55	5.63
ESO/MTHPA/1MI	1.0	1.30	51.6
	1.2	1.29	27.8
	1.4	1.25	25.0

Table 3: Total heat of reaction (ΔH_r), measured on the basis of epoxy equivalents for the DGEBA/MTHPA/1MI and ESO/MTHPA/1MI systems with different stoichiometric ratios R.

System	R	ΔH_r (kJ/epoxy eq)	Variation
DGEBA/MTHPA/1MI	1.0	132	
	1.2	140	+6.1%
	1.4	144	+9.1%
ESO/MTHPA/1MI	1.0	108	
	1.2	120	+11.1%
	1.4	130	+20.4%

DGEBA/MTHPA and ESO/MTHPA polymers. For DGEBA/MTHPA systems, increasing R values produce a significant decrease in glass transition temperature (T_g), measured as the maximum of the tan δ curve. In these systems, MTHPA evaporation is not as important as in ESO/MTHPA, and although a higher conversion of epoxy groups is achieved by increasing R, there is a large amount of unreacted or partially reacted MTHPA, exerting a plasticizing effect and forming pendent chains.

Table 4: Mass percentage evaporated during the dynamic curing for the DGEBA/MTHPA/1MI and ESO/MTHPA/1MI systems with different stoichiometric ratios R.

System	R	Δm (%)	R_{eff}
DGEBA/MTHPA/1MI	1.0	1.5	0.97
	1.2	3.5	1.12
	1.4	7.9	1.20
ESO/MTHPA/1MI	1.0	7.6	0.81
	1.2	7.9	0.99
	1.4	11.9	1.06

For ESO/MTHPA, the opposite behavior was found. In these systems, a significant amount of MTHPA evaporates due to a slower polymerization reaction. Hence, a higher final conversion of epoxy groups is obtained with the increase of R, leading to an increase in T_g value. The R_{eff} values show that an excess of MTHPA between 20% and 40% is needed to attain the stoichiometric condition for the cured networks.

It must be also taken into account that for DGEBA/MTHPA systems, an increase in the proportion of MTHPA decreases the concentration of phenyl groups, providing the network with an enhanced mobility at molecular level and decreasing its T_g, [7] which has not occurred with the ESO/MTHPA systems, since no aromatic groups are present in the ESO chemical structure.

4. Conclusions

Kinetic parameters, useful to predict conversion values for a given temperature profile, were obtained from the study of the curing kinetics for the DGEBA/MTHPA/1MI and ESO/MTHPA/1MI systems with different anhydride/epoxy equivalent ratios. The obtained kinetic parameters reflect the lower reactivity of the ESO with respect to DGEBA as well as a delay of the reaction as the content of MTHPA is increased, probably due to a dilution effect on both the epoxy groups and the 1MI.

The final properties of the DGEBA/MTHPA networks vary significantly with R, showing a decrease in the T_g value. Instead, a moderate increase of T_g was observed for ESO/MTHPA systems when the MTHPA amount increased. The results showed that in the stoichiometric ESO/MTHPA polymers, a significant fraction of epoxy functionalities remains unreacted. This occurs in part not due to steric hindrance but mainly because of the evaporation of the curing agent that leads to R_{eff} values significantly lower than expected. In this case, when the processing of ESO-based systems is evaluated for different applications, it is desirable to use an anhydride excess in order to obtain a cured material with better mechanical and thermal properties.

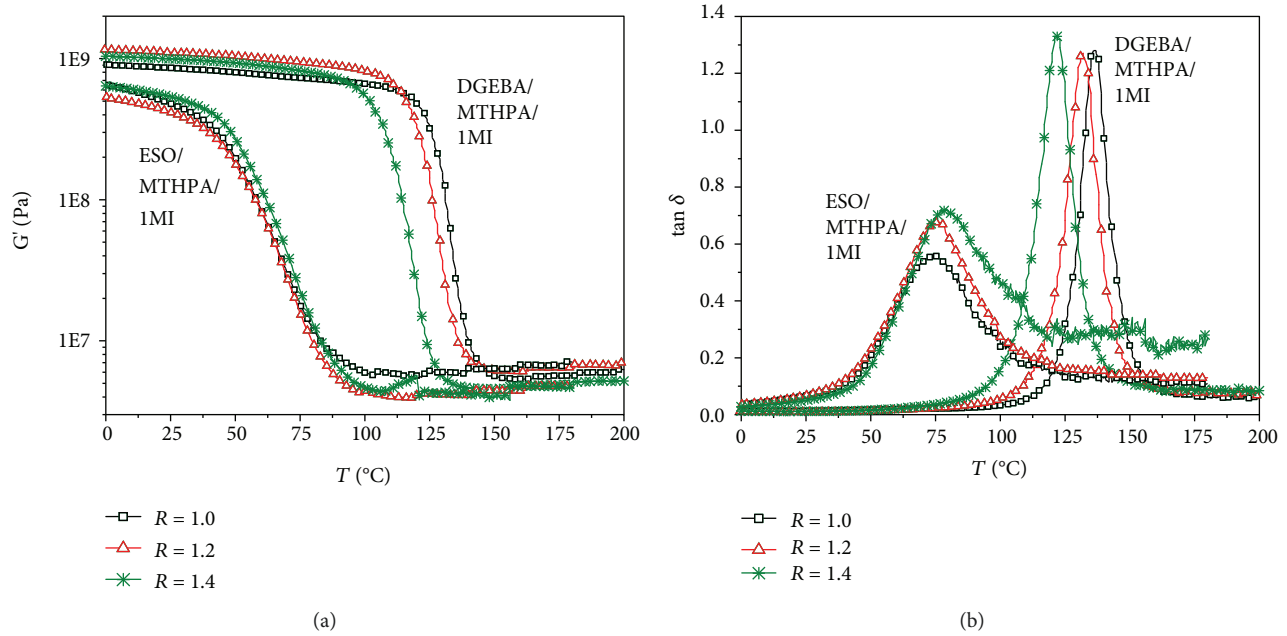

FIGURE 5: (a) G' and (b) tan δ curves for the DGEBA/MTHPA/1MI and ESO/MTHPA/1MI networks with different stoichiometric ratio R values, cured at 2°C/min.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

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Supplementary Materials

Effect of an anhydride excess on the curing kinetics and dynamic-mechanical properties of synthetic and biogenic epoxy resins. *(Supplementary Materials)*

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