

# Influence of an Hyperbranched Aliphatic Polyester on the Cure Kinetic of a Trifunctional Epoxy Resin

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**ABSTRACT:** The influence of an OH-terminated hyperbranched aliphatic polyester on the reaction kinetics and rheology of a trifunctional triglycidyl-*p*-aminophenol (TGAP) epoxy resin cured with an aromatic amine, i.e., diamino-diethyltoluene (DETDA), was investigated. The hyperbranched polymer was expected to enhance the reactivity of the trifunctional epoxy resin; a limited modification in the rheology of the trifunctional epoxy resin with the addition of the hyperbranched polymer, however, was not excluded. The reaction mechanism between DETDA amine and TGAP resin is very complex; therefore, a phenomenological kinetic model was employed. The autocatalytic model chosen was able to fit the experimental calorimetric data for the trifunctional epoxy resin as well as for its mixtures with the hyperbranched polymer. The effect of the OH-terminated hyperbranched aliphatic polyester (H 30) on the reactivity of the

trifunctional epoxy resin was marked, with a decrease of the temperatures at which the crosslinking reactions begin, even though a reduced rate of the curing reactions was observed. However, the completion of the reactions occurred faster and at lower temperatures. The cure mechanism, moreover, remained broadly autocatalytic in nature, regardless of H 30 concentration. Finally, the addition of hyperbranched polymer H 30, even at low percentages, led to a noticeable increase in the viscosity of the resin. This last aspect is believed to restrict to some extent the range of application of such epoxy systems containing the hyperbranched polymer in the traditional processing techniques. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1744–1758, 2008

**Key words:** hyperbranched polymers; curing of thermosets; kinetics of crosslinking; kinetic model

## INTRODUCTION

Thermosetting resins are extensively employed to manufacture composite materials for a variety of structural and electronics applications. High-performance composites based on a thermosetting matrix are produced using different industrial processes. The mechanical properties and the quality of the final product obtained through each process mainly depend on the correct proceeding of the polymerization reactions (“cure process”) of the matrix resin and on an adequate impregnation of the fibers that in turn is influenced by the rheological changes occurring during the crosslinking reactions. Moreover, the cure process is also coupled with a marked heat generation as a result of the exothermic nature of the crosslinking reactions. Uncontrolled polymerization may cause undesired and excessive thermal and rheological variations that could induce microscopic and macroscopic defects in the composite part. Therefore, the processing of polymeric composites based on thermosetting matrices requires the

optimization of the cure cycle parameters as well as an adequate formulation of the reacting system.

Among the others, the resin transfer molding (RTM) technology has been identified as the most indicated process to produce composite components with a complex geometry. However, some basic requirements are demanded to a resin to be suitable for RTM process, i.e.: (i) a low viscosity (not exceeding 0.5 Pa·s) to allow flow through the mold and complete impregnation of the fiber preform; (ii) a sufficient pot life where the viscosity is low enough to allow the complete injection at reasonable pressures; (iii) a low volatile content to minimize the occurrence of voids and porosity; and (iv) a reasonable curing cycle (in terms of curing time and temperature) to produce a fully cured part.<sup>1–3</sup> Low viscosity-elevated pot life thermosetting resins, on the other hand, often present scarce impact resistance and could be, therefore, unsuitable to realize structural components.

Cured thermosetting resins are intrinsically brittle as consequence of their high crosslinking density. For this reason, they are traditionally toughened by dissolving a small proportion (10–20%) of a liquid rubber containing reactive end groups in the liquid epoxy system and inducing the precipitation of crosslinked rubbery particles during curing.<sup>4</sup> The resulting toughened systems possess an increased

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viscosity and require elevated values of temperature and pressure to be injected. While this procedure is still suitable to toughen thermosetting matrices addressed to realize prepregs, it could be inappropriate for those employed, for instance, in RTM process.<sup>3,5</sup>

Several attempts have been recently made to find alternative modifiers for the toughening of thermosetting resins and their composites. To overcome the increase in viscosity due to the addition of a toughening agent, the latter has been added as powder or film directly in the preform of mold. Such solutions, on the other hand, are difficult to realize and do not guarantee an adequate level of toughening. The toughening procedure that employs binders instead of ductile thermoplastics, moreover, permits to substitute only a small percentage of the thermoplastic phase in the matrix resin; the resin, therefore, maintains inadequate levels of viscosity and low pot-life.<sup>6,7</sup>

Among thermosetting resins used as matrices for high-performance composites, multifunctional epoxy resins have been increasingly used in aerospace and load bearing applications, when dimensional stability and good mechanical properties at high temperatures are required. The strong reason for the popularity of these resins lies in their high processability, good dimensional stability, and specific strength; while drawbacks of these systems are their poor fracture toughness and low shelf life. Because of its increased usage, modification of such type of resins by improving toughness and shelf life has been successfully carried out worldwide.<sup>8-11</sup>

Most of the research on toughening of epoxy resins has concentrated on bifunctional and tetrafunctional epoxy systems.<sup>12-16</sup> However, a certain number of advanced composite prepregs contains a significant proportion of the trifunctional epoxy material known as triglycidyl-*p*-aminophenol (TGAP) in combination with tetrafunctional tetraglycidyl diaminodiphenylmethane (TGDDM).<sup>17</sup> The substitution of part of tetrafunctional epoxies with a trifunctional one is potentially desirable, since the resulting lower crosslink density and modulus may be offset by increased toughness when compared to TGDDM-based systems.<sup>18</sup> In addition, the lower viscosity of trifunctional epoxy resins with respect to tetrafunctional ones represents a further attractive advantage for processes with strictly viscosity requirements, such as in RTM technique.

Different studies performed on trifunctional resin systems have demonstrated that only moderate improvement in toughness can be achieved by the addition of a thermoplastic phase.<sup>19-22</sup> In a thermoplastic modified epoxy/amine system, the different components present in the system are initially miscible. As the molecular weight of the epoxy resin

increases as a consequence of the crosslinking reactions, a point is reached where the thermoplastic polymer is no longer miscible in the epoxy/amine mixture. At this point, phase separation occurs giving rise to different morphologies which, in turn, generate different levels of toughness improvement. These different morphologies mainly depend on the chemical affinity existing between the thermoplastic phase and the epoxy resin, on the concentration of the thermoplastic polymer and on the process temperature. Therefore, an incomplete understanding of the effect that the structure and the reactivity of the thermoplastic phase have on both the cure and phase separation processes can limit the possible enhancement in the fracture toughness of the epoxy resin.

The main objective of the present work was to explore the possibility to incorporate novel polymeric molecules in a trifunctional epoxy resin, verifying the modifications in cure kinetics and in processability of the resin brought about by the addition of this polymer. Enhancements in the final toughness of the cured resin due to the addition of the novel polymer are expected and will be the subject of future investigations.

Hyperbranched polymers, belonging to novel dendritic molecules, have recently gained great attention due to their peculiar structure and unique properties. They are characterized by highly branched backbone with a large number of reactive groups, which provide them with excellent flow and processing properties.<sup>23,24</sup>

The term dendritic polymer not only means highly branched tree-like structures and covers both dendrimers as well as hyperbranched polymers, but also other highly branched or fractal molecules. Dendrimers are perfectly branched molecules prepared in a step-wise manner with the potential to come close to structural and molar mass uniformity. On the other hand, hyperbranched polymers are prepared in a random one-pot synthesis from monomers having branching potential but with low control over structure and molar mass.<sup>25</sup> The final properties of hyperbranched polymers are determined by the structure of the repeating unit as well as by the nature of their end groups, by the degree of branching, and by the molar mass and the molar mass distribution. Hyperbranched polymers are usually fully amorphous. When they are blended or used as additives in linear polymers, there is no possibility to exactly predict their effect on the melt viscosity of the polymer. It has been found, in fact, an increase and a decrease of the matrix viscosity, depending not only on the functionality of the hyperbranched molecules but also on its molar mass and molar mass distribution, on the used amount and on the mixing temperature and procedure.<sup>25</sup>

Aliphatic hyperbranched polyesters are mainly based on bis(2-hydroxyethyl) propionic acid or dimethylol propionic acid (DMPA). Their low solution and melt viscosity, low volatility, high molar mass and high variable functionality render these molecules especially suited for those applications in which excellent flow and processing properties are required. Hyperbranched polyesters with different terminations have been successfully employed as multifunctional crosslinkers in coatings and in thermosets, with thermal and UV curing methods. Their addition to resin formulation has been explored to improve the thermal properties and modulus, to change the rheology and to improve the flow and the surface properties, even in sensorics and nanofoam preparation. The OH-terminated hyperbranched polyesters, in particular, show a glass transition temperature ranging from 20 to 40°C, a high solubility in several thermosetting polymers and a high functionality; moreover, their very high branching density leads to a very compact macromolecular structure.<sup>26</sup> They are often regarded as very efficient transfer reagents, being able to speed up the curing reactions of the thermosetting resins to which they are added. A higher final gel content is attained with the full covalent incorporation of the hyperbranched components, providing an enhanced toughness to the resulting coatings and adhesives.<sup>26,27</sup>

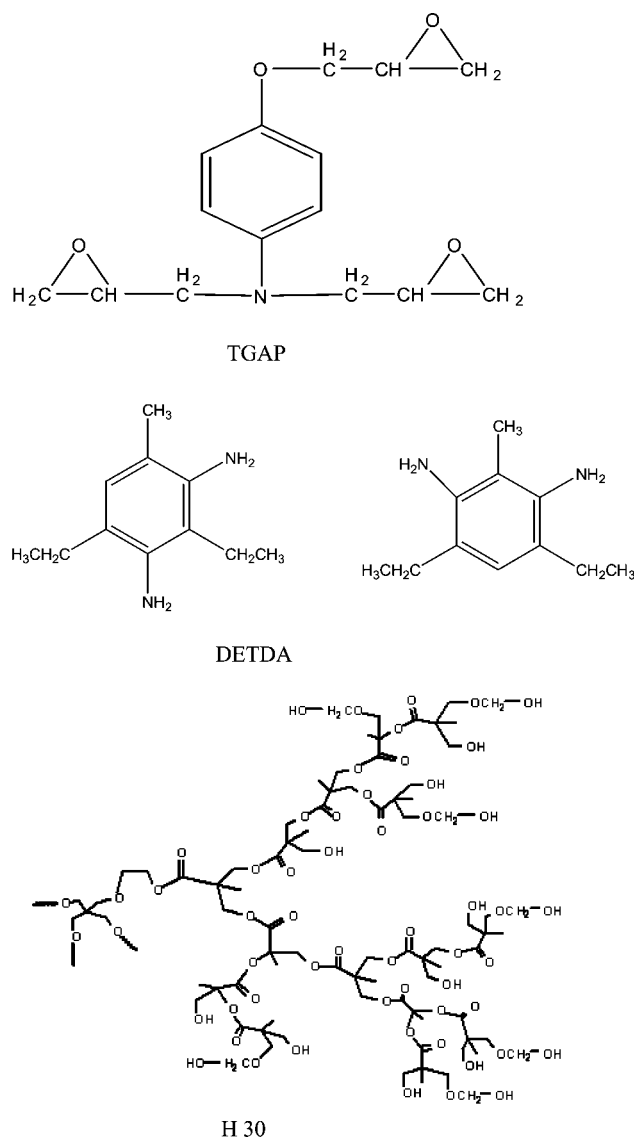
The addition of an OH-terminated hyperbranched aliphatic polyester in a low viscosity TGAP epoxy resin was explored. The influence of the presence of the hyperbranched polymer on the reaction kinetics of the trifunctional epoxy resin was investigated. Only few studies on the kinetics of cure of TGAP resins employing thermal analysis have appeared in literature.<sup>28–30</sup> The rheological characteristics of the modified uncured resin were also examined, to verify that the processability of the resin was not impaired by the addition of the hyperbranched polymer.

## EXPERIMENTAL

### Materials

A trifunctional epoxy resin, i.e., TGAP, whose structure is shown in Scheme 1, produced by Ciba-Geigy with the trademark Araldite MY 0510, was chosen in this study. The molecular weight of MY 0510 is about 300 g/mol. The EEW of the resin is about 101 g/equiv, as reported on data sheet. The trifunctional epoxy resin possesses a low viscosity (i.e., 0.55–0.85 Pa·s at 25°C) and it is particularly suitable for industrial processes implying viscosity requirements.

A low viscosity aromatic amine was selected as curing agent, i.e., diamino-diethyltoluene (DETDA),



**Scheme 1** Chemical structure of: triglycidyl-*p*-aminophenol (TGAP), MY0510, trifunctional epoxy resin; diamino-diethyltoluene, DETDA, hardener; and OH-terminated hyperbranched aliphatic polyester, H 30.

supplied by Aldrich chemicals. It is able to cure epoxy resins at relatively high temperatures and to achieve elevated  $T_g$  values and mechanical properties. The molecular weight of DETDA is 178.28 g/mol and its AEW is 44.57 g/equiv. The chemical structure of the hardener DETDA is also reported in Scheme 1.

A stoichiometric amount of hardener was added to the trifunctional resin, i.e., that corresponding to the molar ratio epoxy/amine = 1 : 1. The corresponding weight ratio was: MY 0510/DETDA 69.38/30.62 wt %. The resin mixture was prepared by adding DETDA to the MY 0510 epoxy at 80°C and mixing until the solution became clear (around 30 min). The hardener was added to the resin before all the calorimetric tests were performed; on the other hand, the

**TABLE I**  
**Details of Composition (wt % by Total Weight of the Mixture and Molar Ratio Between Epoxy, Amine, and Hydroxyl groups) of the Formulations Realized**

Material	0 H30		5 H30		10 H30		15 H30		20 H30	
	wt %	Epoxy, amine, and hydroxyl groups molar ratio	wt %	Epoxy, amine, and hydroxyl groups molar ratio	wt %	Epoxy, amine, and hydroxyl groups molar ratio	wt %	Epoxy, amine, and hydroxyl groups molar ratio	wt %	Epoxy, amine, and hydroxyl groups molar ratio
MY 0510	69.38	1	65.91	1	62.44	1	58.98	1	55.51	1
DETDA	30.62	1	29.09	1	27.56	1	26.02	1	24.49	1
H30	0	–	5	0.068	10	0.144	15	0.228	20	0.324

rheological tests, where the processing properties of the unreacted systems were analyzed, were performed on samples not containing the curing agent.

An OH-terminated hyperbranched aliphatic polyester was evaluated. It is produced by Perstop with the trademark Boltorn H 30. Its chemical structure is again shown in Scheme 1. The molecular weight of H 30, as reported on data sheet, is about 3600 g/mol, the theoretical number of OH groups is 32 and its viscosity, measured at 110°C with a value of shear rate of 30 s<sup>-1</sup>, is 40 Pa·s. Finally, its  $T_g$ , measured through DMA analysis from the Tan  $\delta$  peak, is 35°C, as reported by the suppliers.

Different amounts of H 30, regarded as a filler, were added to the mixture of epoxy/hardener, i.e.: 5, 10, 15, and 20 wt % of H 30 by total weight mixture. The procedure used is the following: the hyperbranched polymer H 30 was first grounded, then dissolved in acetone and added to MY 0510 resin, stirring the mixture for 30 min. The solvent was removed at 50°C using a rotavapor. The hardener DETDA was finally added at room temperature, again stirring the mixture for 30 min. In Table I, the compositions of each formulation realized in terms of weight ratio (in percentage) and of molar ratio between epoxy, amine and hydroxyl groups, are listed.

### Thermal characterization

A complete differential scanning calorimetry (DSC) characterization was undertaken to develop the kinetic models for the crosslinking reactions of MY 0510 and MY 0510/H 30 systems and to calculate their parameters. To this aim, a DSC 822 Mettler Toledo was employed. Each experiment was repeated at least on three samples and the results averaged.

In a first dynamic scan, performed by heating the sample at 5, 10 and 15°C/min in nitrogen atmosphere from 25 to 300°C, the exothermic peak of reaction of any system was analyzed, determining the peak temperature and the heat of the crosslinking reactions. A second scan was always performed at 10°C/min on each sample previously analyzed, to calculate the glass transition temperature ( $T_g$ ) of the system cured in the first scan.

Isothermal tests were performed on some of the formulations realized with MY 0510 resin, i.e., on 0 H 30 and 5 H 30 mixtures, at several temperatures, i.e., 110, 125, 135, and 140°C. After each isothermal test, a second dynamic scan was always performed on the same sample from 25 to 300°C at 10°C/min, to calculate the  $T_g$  of the system and the enthalpy and the peak temperature of the peak of residual crosslinking reactions, if present.

### Dynamic-mechanical analysis

Dynamic-mechanical tests in torsion mode were performed on cured systems 0 H 30, 10 H 30, and 20 H 30, using the Torsional DMA accessory for Rheometric ARES rheometer. The cure process was carried out on samples for 3 h at 135°C, followed by a post cure step, performed for 1 h at 180°C. The dimensions of the specimens were 20.0 × 10.0 × 9 mm. A temperature ramp of 5°C/min from 50 and 250°C, a frequency of 1 Hz, and a strain of 0.5% were used for the dynamic-mechanical analysis. The  $T_g$  of each cured system was determined from the peak temperature of the loss modulus curve ( $G''$ ).

### Rheological characterization

Being the viscosity of H 30 appreciably higher than that of the epoxy resin, even at high temperatures, its inclusion was expected to adversely affect the processability of MY 0510 resin. The influence of the presence of the hyperbranched polymer on the processing characteristics of the epoxy resin was, therefore, investigated by means of rheological tests performed on the control resin, MY 0510, and on mixtures of the resin with different amounts of H 30, i.e., 5 and 20 wt % of H 30 by total weight mixture, i.e., the percentages corresponding to the systems containing also DETDA hardener. The tests were carried out in a strain controlled rheometer Rheometric ARES, with parallel plate flow geometry (radius of the plate = 12.5 mm, gap = 0.6 mm) in steady state mode. Each sample was tested at 25°C, repeating twice the test on the same sample to assess the reproducibility of the results.

**TABLE II**  
**Results from Dynamic Calorimetric Analysis Performed on MY 0510 and Its Mixtures with the Hyperbranched Polymer H30**

System	Heating rate (°C/min)	$\Delta H$ (J/g)	$\Delta H_{\text{MY 0510}}$ (J/g)	$T_p$ (°C)
0 H30	5	665.5 ± 15.1	959.2	186.6 ± 0.5
	10	658.5 ± 18.5	949.1	206.7 ± 1.3
	15	650.0 ± 2.2	936.9	218.8 ± 1.2
5 H30	5	682.9 ± 13.7	1036.1	174.8 ± 1.8
	10	622.2 ± 22.6	944.0	194.8 ± 1.6
	15	613.8 ± 20.7	931.3	207.8 ± 2.1
10 H30	5	642.8 ± 23.5	1029.5	168.5 ± 1.2
	10	587.4 ± 19.9	940.7	188.6 ± 0.3
	15	548.8 ± 10.1	878.9	200.0 ± 1.4
15 H30	5	597.0 ± 8.0	1012.2	170.3 ± 6.5
	10	579.7 ± 23.2	982.9	188.2 ± 2.7
	15	590.7 ± 21.0	1001.5	200.5 ± 4.1
20 H30	5	501.9 ± 3.2	904.2	163.2 ± 3.2
	10	470.8 ± 22.5	848.1	178.7 ± 1.1
	15	508.1 ± 18.7	915.3	191.1 ± 2.0

Heating rate = rate of the calorimetric scan;  $\Delta H$  = total heat developed during cross-linking reactions;  $\Delta H_{\text{MY 0510}}$  = heat developed during cross-linking reactions normalized to the MY 0510 resin content;  $T_p$  = peak temperature of cross-linking reactions.

To verify if the processability of the 5 wt % of H 30 mixture at temperatures higher than the ambient, a rheological test was performed at 110°C, employing the same instruments and conditions used in the previous experiments (steady state mode, parallel plate, radius of 12.5 mm, gap by about 0.6 mm). The testing temperature was chosen as the typical injection temperature employed for industrial processes, as in the case of RTM process.<sup>31</sup>

## RESULTS AND DISCUSSION

### Thermal analysis—Dynamic tests

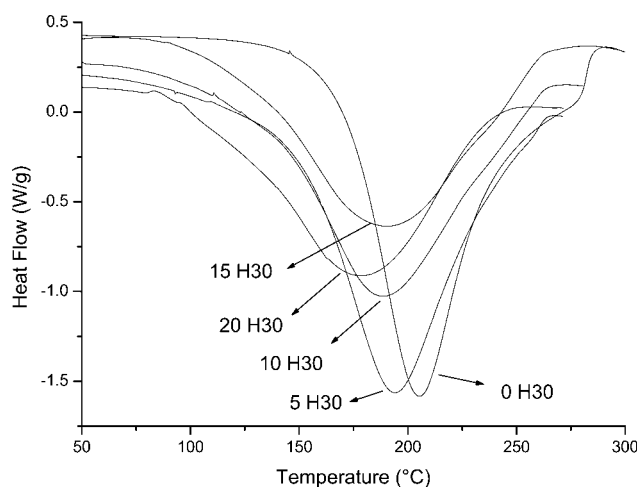
In Table II, the averaged results of the DSC experiments performed at different heating rates on MY 0510/DETDA system and on its mixtures with the hyperbranched polymer H 30, are reported. The total heat of crosslinking reactions and the peak temperature are reported for each formulation. In the same table, the heat developed during crosslinking reactions normalized to the resin/hardener content, is reported, to analyze better the effect of the OH-terminated hyperbranched aliphatic polyester on the reactivity of the trifunctional epoxy resin. The heat of reaction measured for the control system MY 0510/DETDA lies between 650 and 666 J/g, close to the average value (684 J/g) found for the same resin cured with a different aromatic amine, i.e., a diamino-diphenyl sulfone (DDS).<sup>28</sup>

Figure 1 shows the comparison of the first dynamic scan performed at 10°C/min on MY 0150

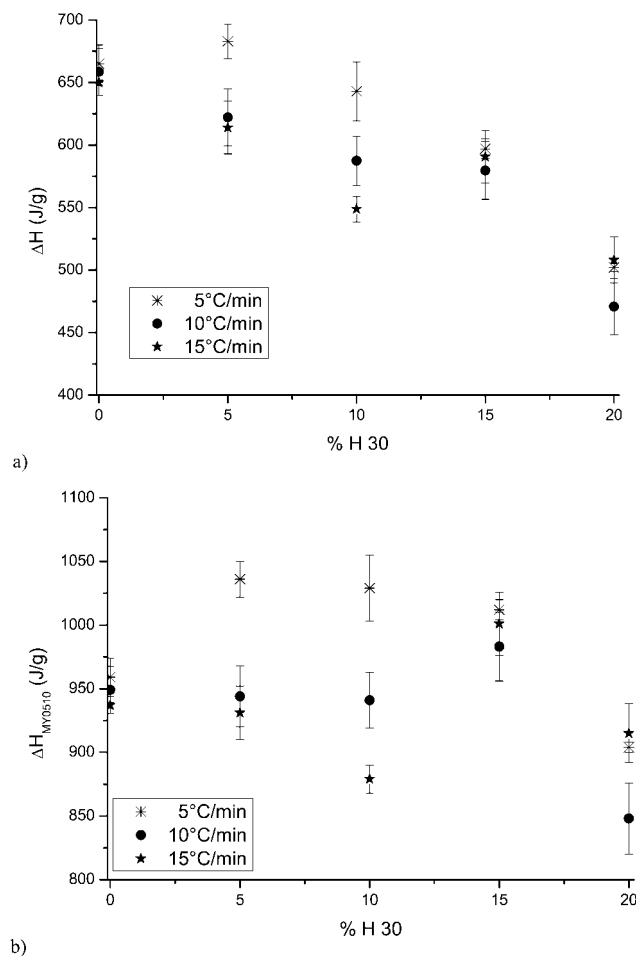
and on its mixtures with different amounts of H 30 polymer. In particular, a “shoulder” can be observed in the last part of the dynamic exothermic peak found for MY 0510/DETDA system. In the case of TGAP based systems, the shoulder was already observed by other researchers and attributed to an increase of the reaction rate occurring at very high temperatures, due to etherification and intramolecular reactions that are favored at higher curing temperatures.<sup>29</sup> In this condition, in fact, the motion of unreacted epoxide units within the matrix is inhibited due to the high degree of conversion achieved.

Referring to the influence of the hyperbranched polymer on the crosslinking reactions of MY 0510 resin, the observation of Figure 1 and the analysis of the data reported in Table II suggest that, by increasing the amount of H 30, both the shape and the range of temperatures of the exothermic peak relative to the crosslinking reactions change, irrespective to the heating rate employed. The range of temperatures at which the curing reactions take place is shifted to lower values by increasing the content of H 30. The peak temperature, in fact, decreases by about 25°C by increasing the percentage of H 30 from 0 to 20 wt %. This occurrence confirms the attitude of H 30 polymer to act as transfer reagent, allowing an early curing reaction of the MY 0510 resin.

On the other hand, the shape of the peak relative to the crosslinking reactions becomes wider by increasing the amount of H 30 polymer. Moreover, the shoulder placed in the last part of the dynamic exothermic peak in the case of the MY 0510 resin and, even if less evident, of its mixtures possessing lower amounts of H 30, i.e., 5–15 wt %, completely disappears when 20% of the hyperbranched polymer is added. Both observations suggest that the mechanism of crosslinking reactions is influenced by the



**Figure 1** Comparison of DSC thermograms relative to the calorimetric scans performed at 10°C/min on MY 0150 and on its mixtures with different amounts of H 30 polymer.



**Figure 2** Comparison of: (a) the total heat developed during crosslinking reactions in DSC dynamic tests relative to MY 0150 resin and its mixtures with different amounts of H 30 polymer; (b) the heat, normalized the effective resin content, developed during crosslinking reactions relative to MY 0150 resin and its mixtures with different amounts of H 30 polymer.

content of H 30. This latter aspect, however, will be discussed in detail in the "cure kinetics" paragraph.

The effect of the hyperbranched polymer on the heat of reaction is unclear. In Figure 2(a) the comparison of the heat developed during crosslinking reactions of MY 0150 resin and of its mixtures with different amounts of H 30 polymer, is reported. The presence of the hyperbranched polymer leads to a reduction of the area of the exothermic peak. When the heat of reaction is normalized to the effective resin content, on the other hand, the area of the exothermic peak remains more or less unaffected, at least up to a 15% content of H 30, as shown in Figure 2(b). This observation suggests that H 30 polymer, possessing OH terminations, could take directly part to the crosslinking reactions of the trifunctional epoxy resin as an additional hardener. The possible reactions taking place between OH terminations of

H 30 polymer and epoxide rings of TGAP resin is depicted in Scheme 2.

After the first calorimetric scan, a second experiment was performed at 10°C/min in DSC module on the same sample, to calculate the  $T_g$  of the system. However, it was possible to measure the  $T_g$  only from few of the calorimetric curves relative to each test performed, with no possibility to calculate the standard deviation. These results, therefore, are not presented. Qualitatively, the addition of hyperbranched polymer H 30 determined a general decrease in the  $T_g$ , down to 40°C when the highest amount of H 30 is added, i.e., 20 wt %. This difficulty in the measurement of the glass transition temperature was attributed to a very dense crosslinked structure that is formed in the case of a trifunctional epoxy resin if compared with the traditional bifunctional DGEBA systems, i.e., the discontinuity in the DSC thermogram is not clearly displayed due to the technical restrains of the instrument.

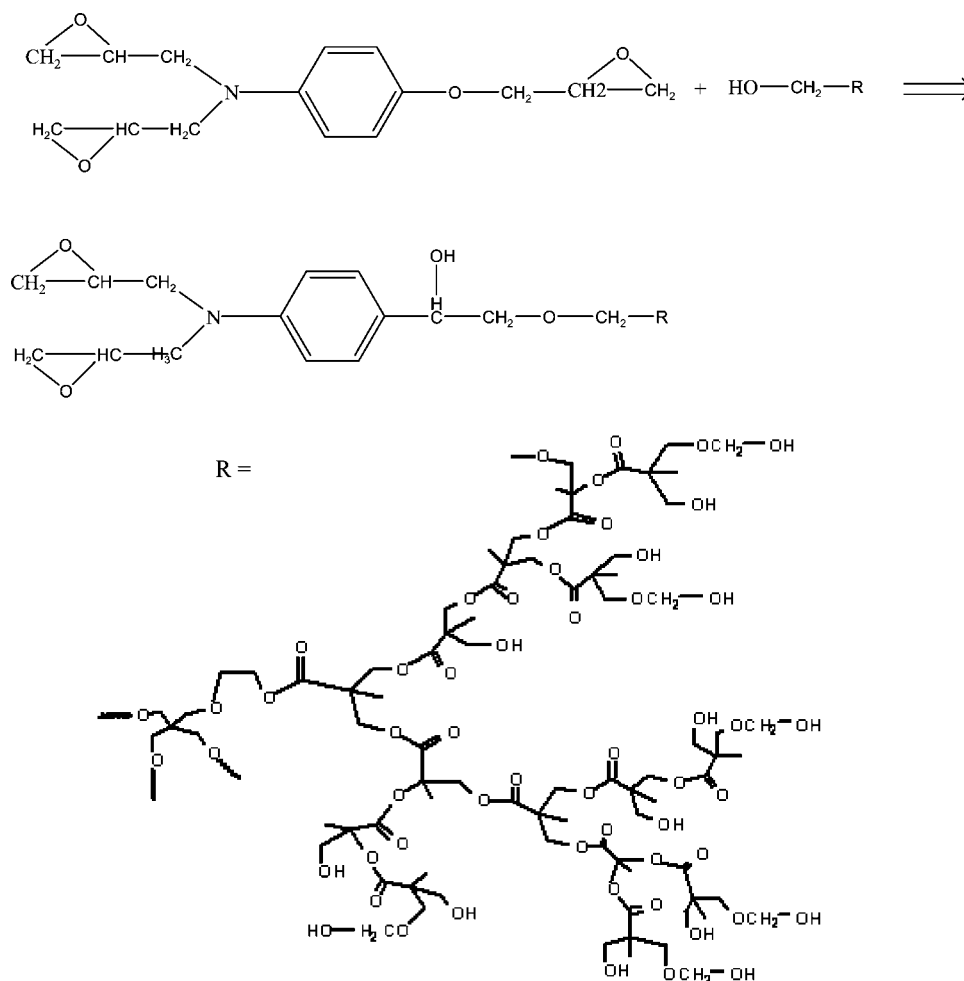
#### Thermal analysis—Isothermal tests

In Table III, the averaged results of the isothermal tests performed on MY 0510 resin and on its 5 wt % mixture with the hyperbranched polymer H 30, are reported. In Figure 3(a), a typical isothermal DSC curve, i.e., that relative to the test performed at 110°C on TGAP plus 5 wt % of H 30, is shown.

From the comparison of the results reported in Table III, the total heat of reaction measured on both systems increases by increasing the isothermal test temperature, as expected.

Referring to the effect of H 30 on the heat of reaction, in Figure 4(a), the crosslinking enthalpy, normalized to the effective MY 0510 resin content, as function of the isothermal test temperature, is reported for both the pure resin and its 5 wt % mixture with H 30. The increase in  $\Delta H$  with the temperature test is continuous, even though not perfectly linear, for the TGAP resin; on the other hand, for the 5 wt % mixture the expected increase in crosslinking enthalpy with the isothermal test temperature is only rough. Certain uncertainty, however, does exist in the calculation of the heat of reaction from all the isothermal tests, since, especially for the highest isothermal temperatures, the reaction would begin before the instrument begins the acquisition of the data. For this reason, the comparison of the heats of reaction measured at different isothermal test temperatures between the pure resin and its 5 wt % mixture must be considered only indicative.

In Figure 4(b), the maximum degree of reaction,  $\alpha_m$ , measured in each isothermal test performed on the pure TGAP resin, is reported as a function of the test temperature. The temperature dependence of  $\alpha_m$  seems to follow the Dibenedetto equation<sup>32,33</sup>:



**Scheme 2** Chemical reactions taking place between an epoxide ring of TGAP resin and the OH terminations of the hyperbranched polymer, H 30.

$$\alpha_m = \frac{T_C - T_{g0}}{T_C(1 - C_2) - T_{g0}(1 - C_1)} \quad (1)$$

where  $T_C$  is the curing temperature,  $T_{g0}$  is the  $T_g$  of the uncured resin, and  $C_1$  and  $C_2$  are the model parameters. On the other hand, a consistent calculation of  $\alpha_m$  was not possible for the 5 wt % mixture with H 30.

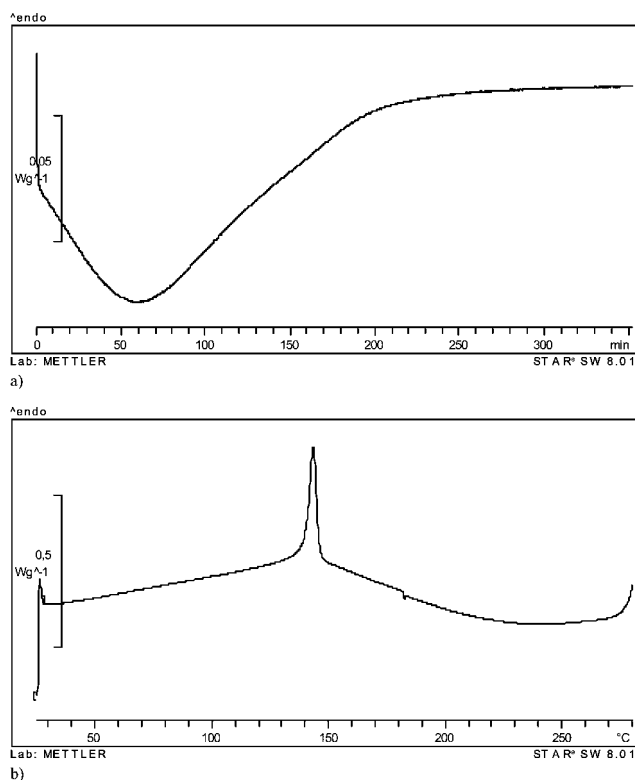
**TABLE III**  
Results from Isothermal Calorimetric Analysis Performed on MY 0510 and on Its 5% Mixtures with the Hyperbranched Polymer H 30

System	$\Delta H$ (J/g)			
	$T_{iso} = 110^\circ\text{C}$	$T_{iso} = 125^\circ\text{C}$	$T_{iso} = 135^\circ\text{C}$	$T_{iso} = 145^\circ\text{C}$
0 H30	474.8	563.3	606.7	612.1
5 H30	391.5	551.4		491.6

$T_{iso}$  = isothermal testing temperature;  $\Delta H$  = total heat developed during cross-linking reactions measured during the isothermal test.

A more accurate calculation of the heat of reaction developed by both the systems analyzed at each isothermal temperature as the difference between the total heat of reaction, calculated through dynamic scans, and the residual heat of reaction, calculated from the dynamic scan performed on the same samples after each isothermal experiment, was again not feasible. Difficulties in the calculation of the residual heat of crosslinking reactions, in fact, were always found. In Figure 3(b), for instance, the dynamic scan performed at  $10^\circ\text{C}/\text{min}$  on MY 0510 plus 5 wt % of H 30 after the isothermal experiment at  $110^\circ\text{C}$ , is reported: it is clear that the residual heat of reaction is not calculable. A similar behavior for dynamic scans performed after an isothermal test on MY 0510 resin cured with DDS amine hardener is reported also by other authors.<sup>28</sup>

The uncertainty of the results obtained by isothermal DSC experiments suggested to use the data from dynamic tests to develop suitable kinetic models for the pure TGAP resin and for its mixtures with H 30.



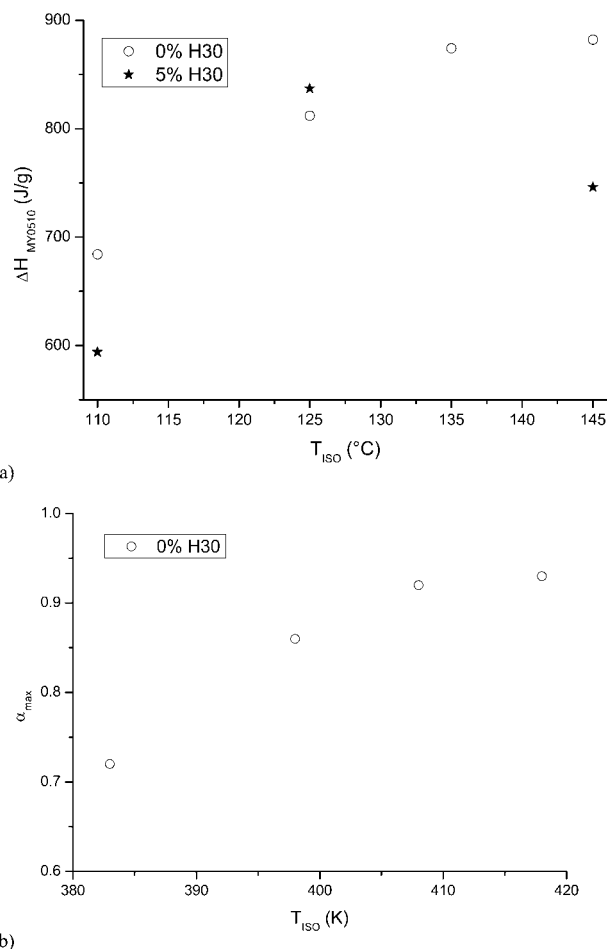
**Figure 3** DSC curves relative: (a) to the isothermal test performed at 110°C on MY 0510 plus 5 wt % H 30; (b) to the second calorimetric scan performed at 10°C/min on the same system.

Finally, from the second dynamic scan, the calculation of the  $T_g$  of the system, previously cured in the first isothermal experiment, was again possible only for few of the samples analyzed and are not reported. The  $T_g$  values increase by increasing the isothermal temperature, as expected, being always considerably higher than the isothermal temperature, of about 35–45°C. This last aspect will be discussed in the next paragraph. Moreover, no relevant differences in the  $T_g$  values were observed by comparing the two compositions analyzed, i.e., the addition of a small amount of H 30 seems to leave almost unaffected the  $T_g$  of the cured MY 0510 system.

The mentioned uncertainty in the calculation of  $T_g$  by DSC analysis suggested to perform a dynamic-mechanical analysis on TGAP based cured systems to measure more accurately the variation in the glass transition temperature due to the inclusion of the hyperbranched polymer.

#### Dynamic-mechanical analysis

DMA tests were employed to evaluate the glass transition temperature of systems based on MY 0510 resin previously cured. The glass transition temperatures of each sample analyzed, calculated from the peak of  $G''$  curve, are listed in Table IV. A single  $T_g$  was observed for all the systems analyzed.



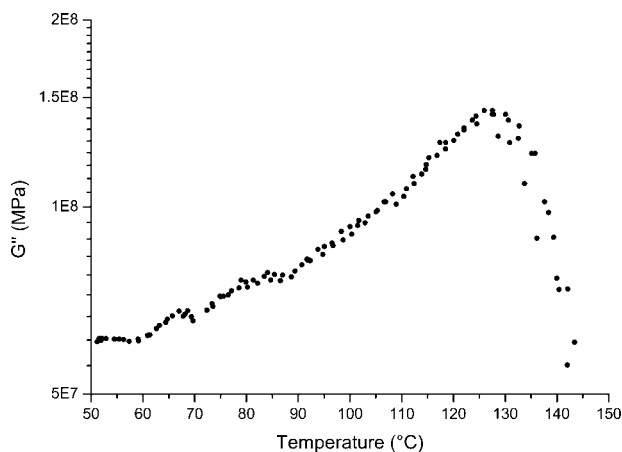
**Figure 4** (a) Comparison of the heat, normalized the effective resin content, developed during crosslinking reactions in DSC isothermal tests relative to MY 0510 resin and its mixture with 5 wt % of H 30 polymer, as a function of test temperature; (b) degree of reaction developed by MY 0510 resin during isothermal tests, as a function of test temperature.

The glass transition temperature for the cured neat resin MY 0510 was found to be about 245°C, i.e., well above both the curing and postcuring temperatures, i.e., 135 and 180°C, respectively. This feature, observed also by other authors, was explained with the high functionality of TGAP resin, having very reactive sites in close proximity. When the  $T_g$

**TABLE IV**  
Glass Transition Temperatures ( $T_g$ ) Calculated from Dynamic-Mechanical Analysis (Torsion Mode) Performed on MY 0510 Based Mixtures, Previously Cured for 3 h at 135°C, Plus a Post-Cure Step Performed for 1 h at 180°C

System	$T_g$ (°C)
0 H30	245.4
10 H30	215.5
20 H30	127.6





**Figure 5** Loss modulus ( $G''$ ) curve from DMTA experiment relative to the system MY 0150 plus 20 wt % of H 30 polymer.

approaches the curing temperature causing the reduction in chain mobility and, in turn, in rate of reaction, the system vitrifies; at this point, reactive sites are still available even when they are locked into the network and interchain reactions or etherification can continue at a reasonable rate, as already pointed out.<sup>28,29</sup> The highest  $T_g$  that was achieved for TGAP/DDS system after repeated curing cycles, for instance, was  $\sim 264^\circ\text{C}$ , confirming the highly crosslinked structure of the TGAP network.<sup>28</sup>

A dramatic decrease in  $T_g$  values was registered by increasing the H 30 content added to the TGAP resin. In particular, the addition of 20 wt % of H 30 by total weight mixture leads to a halving in  $T_g$ . In Figure 5, the DMTA spectra of this system, is reported. The decrease in  $T_g$  can be restrained to  $30^\circ\text{C}$  by limiting the content of H 30 to 10%. A possible explanation of the decrease in  $T_g$  is that H 30 acts as an additional hardener for the epoxy resin, as already hypothesized. This leads to an excess of amine hardener DETDA in the epoxy rich phase. Moreover, H 30 itself can plasticize the cured system, possessing a flexible structure with a high mobility. Both phenomena would concur to produce a structure with a lower crosslink density and, hence, a looser and more mobile network.

### Cure kinetics from thermal analysis

The processing of polymeric composites, based on thermosetting matrices, requires the optimization of the curing parameters, especially when the composites are employed in structural applications where specific properties of the components are required. Curing is coupled with heat generation as a result of exothermic thermosetting reactions. The relative rates of heat generation and transfer, thus, determine the values of the composite temperature, and, hence,

of the progress of the reaction and the viscosity through the thickness of the laminate. Therefore, uncontrolled polymerization may cause undesired and excessive thermal and rheological variations inducing microscopic and macroscopic defects in the composite part. Moreover, the increase in viscosity taking place in the resin in the first stage of curing can be responsible of an excessive time to fill the mold and it can even avoid the complete filling.

Kinetic and rheological models correlating the thermal and the chemo-rheological behavior of different matrices to the molecular and chemical characteristics of the reactive systems must be integrated into a heat transfer model, to produce a general model for the description of the thermochemo-rheological behavior of thermosetting matrices during the processing of thermoset-based composites. The obtained master model is able to describe the behavior of the main variables (temperature, degree of reaction, viscosity) during the processing of the composite, and it represents an invaluable means for simulation, control, and optimization of the process parameters under different conditions.

The study of cure kinetics of thermosetting resins can be approached using mechanistic or phenomenological models. When a mechanistic kinetic model instead than an empirical one, generally expressed as a simple rate equation, is employed several advantages can be obtained. However, even though a mechanistic model is able to provide more information and more accurate prediction on the reaction rate, conversion degree and the consumption of individual reacting species, it requires a detailed characterization of the resin and a very complicated parameter estimation. Therefore, simple phenomenological models are often preferred in practical studies of the cure processes of commercial resins. As an example, kinetics of TGAP based systems are reported to be more complex than other DGA derived epoxies, such as the largely employed tetrafunctional DGEBA systems. Therefore, a phenomenological approach is generally preferred.<sup>29</sup>

To the best of our knowledge, only few studies on the kinetics of cure of TGAP resins based on thermal analysis have appeared in literature.

In particular, for a TGAP/DDS system the average activation energy was determined by employing the Kissinger equation and the results from different dynamic scans by Varley et al.<sup>28</sup> It was found to be  $50.9\text{ kJ/mol}$  and it compared well to the value of  $55.4\text{ kJ/mol}$  reported by other authors for the same resin/hardener system.<sup>34</sup> However, the use of a kinetic model such as the Kissinger equation makes a large number of theoretical assumptions. The main is that the reaction mechanism consists of one predominant reaction step (i.e., hypothesizing a first order reaction), in this case epoxy/amine addition,

ignoring other possibilities, such as polyetherification which can occur under specific conditions.<sup>28</sup>

The same authors used other kinetic models by processing the results from DSC isothermal experiments:  $n$ th order, autocatalytic, diffusion controlled mechanism.<sup>28</sup> However, they applied the mentioned models to the data from any single experiment, obtaining for each conversion degree, corresponding to a specific isothermal temperature, the activation energy for that degree of reaction. This method, even if useful for general purposes, cannot be effective in estimating the progress of crosslinking reactions in any potential curing condition.

In the present study, an autocatalytic mechanism is proposed for the polymerization reaction of the TGAP epoxy resin with DETDA curing agent. This reaction mechanism consists in a cationic polyaddition reaction catalyzed first by hydroxyl groups initially present in the system and then by hydroxyl groups produced during the primary amine/epoxide reaction.<sup>30</sup> It was previously verified for TGAP resin hardened by DDS amine, proving to be effective in particular in the early stages of cure; however, the diffusional processes, occurring at higher conversions, were not well reproduced by the same model.<sup>28</sup>

An autocatalytic kinetic model, as first proposed by Smith<sup>35</sup> and subsequently modified by Ryan and Dutta for epoxy systems,<sup>36</sup> is expressed by the following equation:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (2)$$

where  $\alpha$  represents the actual degree of reaction,  $m$  and  $n$  represent the reaction orders, not depending on temperature.  $k_1$  and  $k_2$  represent the temperature-dependent rate coefficients for the reaction catalyzed by proton donors initially present in the system and proton donors that are produced during cure, respectively. Each of them is given by an Arrhenius type equation:

$$k_1 = k_{01}e^{(-E_1/RT)} \quad (3)$$

$$k_2 = k_{02}e^{(-E_2/RT)} \quad (4)$$

where  $k_{01}$  and  $k_{02}$  are the rate constants and  $E_1$  and  $E_2$  represent the activation energies for  $k_1$  and  $k_2$ , respectively.

Equation (2) was properly modified for TGAP/DDS systems to take into account for the diffusion control phenomena occurring at the later stages of the polymerization reactions.<sup>28</sup>

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(\alpha_m - \alpha)^n \quad (5)$$

The parameters of eq. (5) are typically obtained by processing calorimetric data belonging from isothermal experiments. Equation (5), in fact, predicts that the rate of reaction during an isothermal polymerization approaches 0 when  $\alpha = \alpha_m$ . This condition represents the effect on the kinetic behavior of a dramatic decrease of the molecular mobility due to the transition to a glassy state. The effect of vitrification on the reaction kinetics, associated with evolution of the glass transition temperature as a function of the degree of polymerization and crosslinking, is considered by replacing 1 by  $\alpha_m$  in eq. (2).

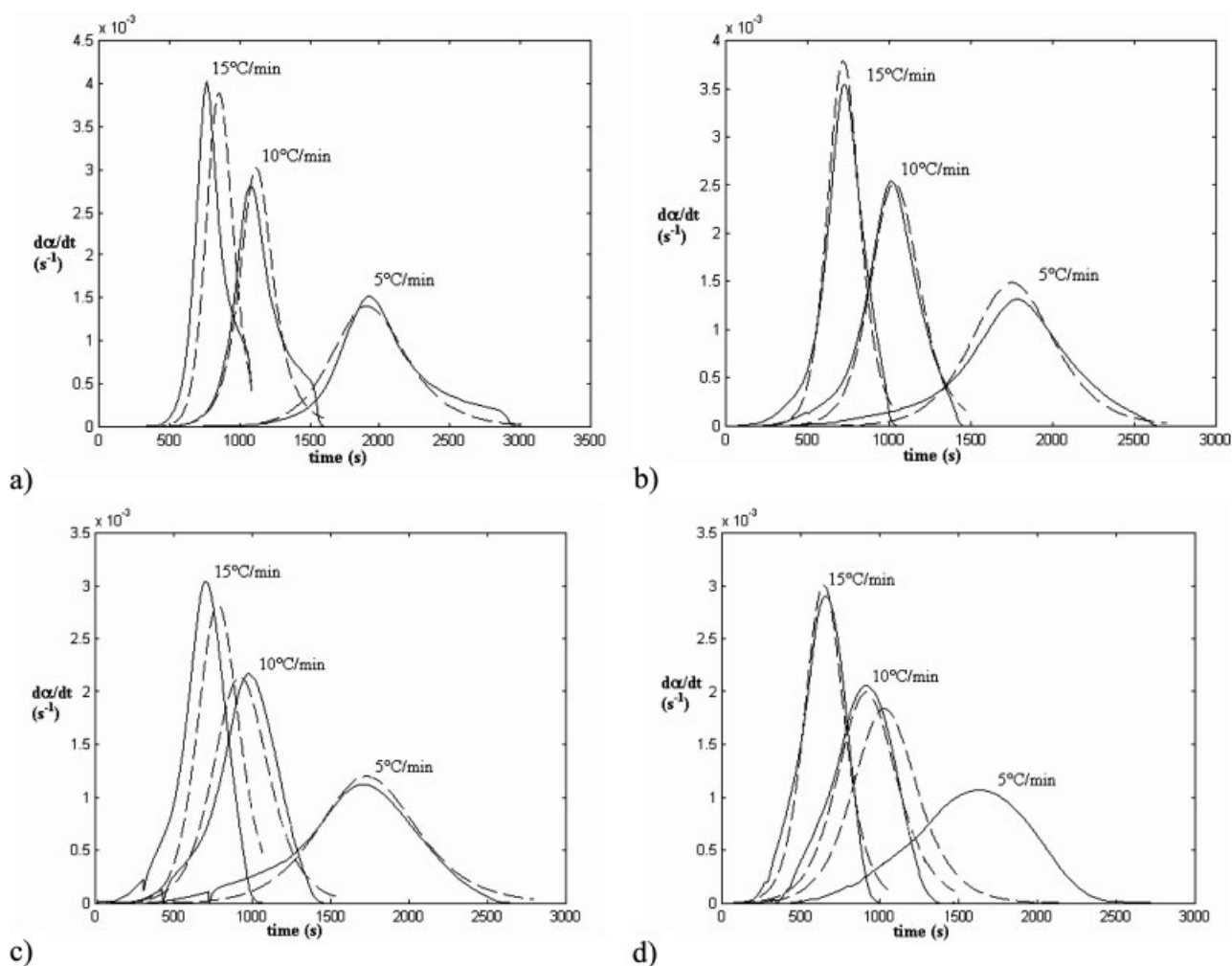
The values of the kinetic parameters of all the reported models can be determined by regression of DSC dynamic and isothermal experiments, assuming that the heat evolved during the polymerization reaction is proportional to the extent of crosslinking reactions.

In our case, due to the mentioned difficulties in calculating precise crosslinking enthalpies from isothermal experiments, only the data from dynamic calorimetric tests were used to develop kinetic models for TGAP resin and its mixture with H 30 polymer. The complete kinetic model represented by eq. (2) was employed, since from the observation of isothermal calorimetric curves found for pure TGAP resin and for its mixtures with H 30 [see Fig. 3(a)], the initial reaction rate has a finite value (therefore  $k_1$  cannot equal to 0) and the behavior is autocatalytic (therefore  $k_2$  cannot equal to 0).

The kinetic parameters of eqs. (2)–(4) calculated for neat resin MY 0510 and for its mixtures containing different amounts of H 30, are reported in Table V. The comparison of the model predictions with the experimental DSC data is presented in Figures 6 and 7. Referring to the graphs of the rate of conversion versus time for each system analyzed [Fig. 6(a,d)], a good matching between theoretical and experimental curves is generally obtained, indicating the validity of the kinetic model adopted. It is confirmed that the model is not able to fit the shoulder placed in the last part of the dynamic exothermic peak, i.e., to simulate the diffusional processes taking place at higher conversions. The only exception is given by the mixture containing the highest amount of H 30 polymer, i.e., 20 wt %. As can be seen from the

**TABLE V**  
Kinetic Parameters of eqs. (2)–(4) Calculated for MY 0510 Resin and for Its Mixtures with the Hyperbranched Polymer H 30

System	$K_{01}$ (s <sup>-1</sup> )	$E_1$ (kJ/mol)	$k_{02}$ (s <sup>-1</sup> )	$E_2$ (kJ/mol)	$m$	$n$
0 H30	$1.33 \times 10^7$	88.09	$5.45 \times 10^4$	94.76	1	2
5 H30	$1.83 \times 10^{-8}$	13.71	$1.67 \times 10^7$	62.32	0.96	1.04
10 H30	$0.8 \times 10^{-6}$	18.12	$1.61 \times 10^7$	64.06	0.96	1.04
20 H30	$1.83 \times 10^{-6}$	14.54	$1.83 \times 10^7$	63.99	0.96	1.04



**Figure 6** Comparison of the model predictions (discontinuous lines) with the experimental DSC data (continuous lines) in terms of rate of conversion versus time for the systems: (a) MY 0150 resin; (b) MY 0150 plus 5 wt % of H 30 polymer; (c) MY 0150 plus 10 wt % of H 30 polymer; and (d) MY 0150 plus 20 wt % of H 30 polymer.

observation of Figure 6(d), the model predictions are quite far from the experimental data but only for the lowest heating rate value, i.e., 5°C/min. To the same conclusions conducts the observation of the graphs of the degree of conversion versus time [Fig. 7(a,d)]: the agreement between theoretical and experimental curves is good for the system not containing H 30 and for the mixture containing 5 and 10 wt % of H30. The comparison is again lacking for the mixture containing 20 wt % of the hyperbranched polymer analyzed at the lowest heating rate, i.e., 5°C/min.

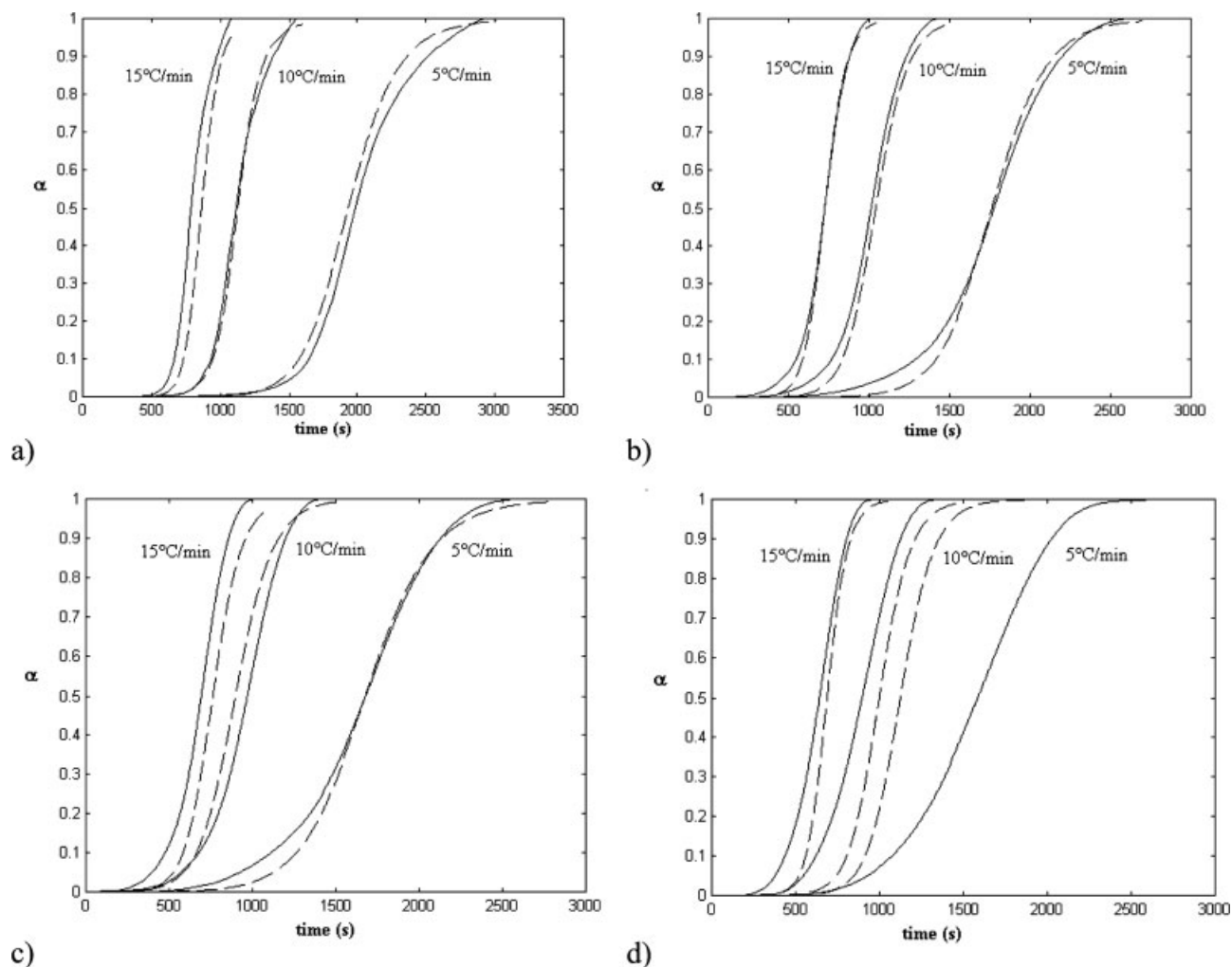
The analysis of the kinetic parameters calculated for MY 0510 and for its mixtures with H 30 polymer, reported in Table V, can reveal interesting features.

The reaction orders, i.e.,  $m$  and  $n$ , are often imposed integer, as  $m = n = 1$ ,  $m = 1$  and  $n = 2$ , or  $m + n = 2$ .<sup>37-39</sup> In accordance with other authors, for the control system MY 0510 a second order reaction was set in our study, i.e., the value of  $n$  was

assigned to 2, while  $m$  was assumed to be 1.<sup>28-30</sup> On the other hand, for the modified systems, we found a better fitting of the experimental data by using  $m + n = 2$ .

When  $m = n = 1$  in Eq. (2), the step determining the reaction rate is a bimolecular interaction between an hydroxyl group and either an amine group or an amine-epoxide species. If  $m = 1$  and  $n = 2$ , it is suggested that the rate-determining step is a termolecular reaction among hydroxyl, amine, and epoxide groups. On the other hand, some researchers choose to fix  $m + n = 2$ , since they approximately found that both  $m$  and  $n$  are close to 1.<sup>28</sup>

As reported in Table V, by choosing the reaction orders as  $m = 1$  and  $n = 2$ , the values obtained for the activation energies of the MY 0510 neat resin were about 88 kJ/mol for  $E_1$  and 95 kJ/mol for  $E_2$ . These values are relatively close to those calculated using the model represented by Eq. (2) for TGAP resin cured with different aromatic amines (DDS



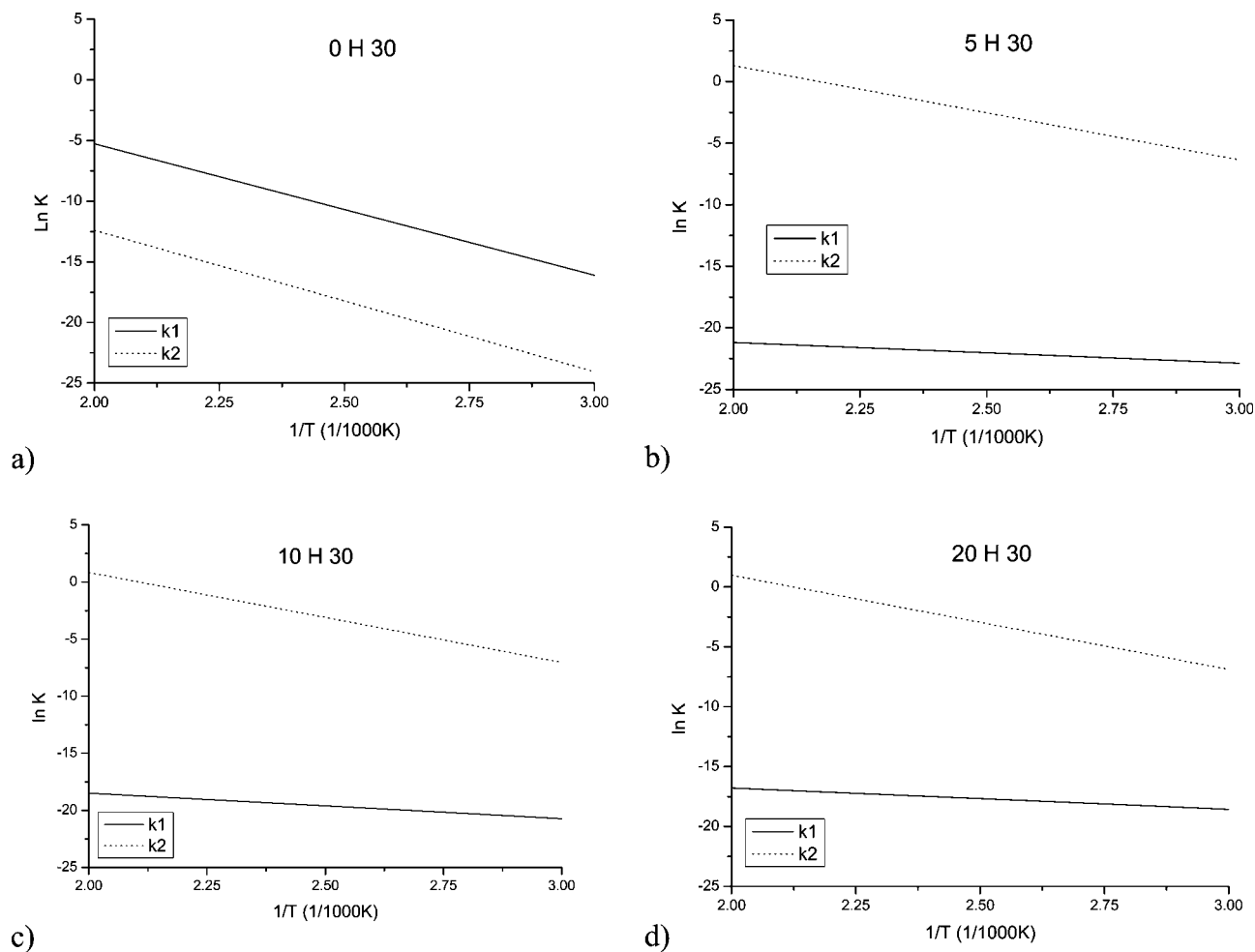
**Figure 7** Comparison of the model predictions (discontinuous lines) with the experimental DSC data (continuous lines) in terms of degree of conversion versus time for the systems: (a) MY 0150 resin; (b) MY 0150 plus 5 wt % of H 30 polymer; (c) MY 0150 plus 10 wt % of H 30 polymer; and (d) MY 0150 plus 20 wt % of H 30 polymer.

and MCDEA, i.e., 4,4' methylene bis [3-chloro 2,6-diethylaniline]), i.e., 80 or 104 kJ/mol for  $E_1$  and 60, 62, or 72 kJ/mol for  $E_2$ .<sup>28,29</sup> Referring to the rate coefficients, i.e.,  $k_{01}$  and  $k_{02}$ , a consistent comparison with the corresponding values reported in the same studies cannot be made, due to the substantial differences in experimental DSC data used to calculate them (single isothermal tests or a single dynamic scan performed at 10°C/min).

The use of alcohols to modify the curing process of epoxy systems is reported by several researches.<sup>40-42</sup> It is thought that the occurrence of a chain transfer reaction involving the OH groups causes the change of kinetics of the process and, in turn, of the properties of the cured network. The comparison of the kinetic data reported in Table V for MY 0510 resin and for its mixtures with H 30 polymer confirms that the addition of the hyperbranched polymer modifies the reaction mechanism of the TGAP resin, since almost all the kinetic pa-

rameters are substantially influenced by the addition of the hyperbranched polymer. The effect of the content of H 30 polymer on all the parameters, on the other hand, is almost insignificant.

To enlighten the effect of the inclusion of H 30 on the kinetic of crosslinking reactions of TGAP resin, in Figure 8 the logarithm of the apparent rate coefficients  $k_1$  and  $k_2$  are plotted for each system analyzed against the reciprocal temperature, by substituting in eqs. (3) and (4), respectively, the parameters of Table V.  $k_1$  coefficient significantly decreases in systems containing the hyperbranched polymer (reduced  $k_{01}$  found for all mixtures). Even small amounts of H 30 polymer are able to inhibit the proton donors (hydroxyl groups) initially present in the system and the initial rate of the reactions, as a consequence, is lowered. This can be explained by the "active-surface" of the hyperbranched polymer H 30 which is able to attract and link the reacting molecules in charged to speed up the crosslinking reactions. On



**Figure 8** Plots of the apparent rate coefficients  $k_1$  and  $k_2$  as a function of the reciprocal temperature for systems: (a) MY 0150 resin; (b) MY 0150 plus 5 wt % of H 30 polymer; (c) MY 0150 plus 10 wt % of H 30 polymer; and (d) MY 0150 plus 20 wt % of H 30 polymer.

the other hand, the presence of the hyperbranched polymer leads to reduced values of the activation energy  $E_1$ . This is consistent with the shift to lower temperatures of the beginning of curing reactions by increasing the content of H 30, as observed in dynamic calorimetric experiments, and explained with the attitude of H 30 to act as transfer reagent, allowing an early curing reaction. In conclusion, referring to the first stage of the crosslinking reactions of the trifunctional epoxy resin, the presence of the hyperbranched polymer H 30 would determine the reduction of the starting temperature of the reaction (due to the transfer reagent nature of H 30) along with the slowing down of the reaction (due to the active surface of H 30).

The reduction of  $k_1$  is scarcely affected by the content of H 30 polymer. Moreover, the influence of the temperature on  $k_1$  coefficient calculated for the systems containing H 30 polymer is negligible if compared to the that relative to the MY 0510 resin, even

when low contents of the hyperbranched polymer are employed (reduced  $E_1$ ).

A noticeable increase in  $k_2$  value is observed when the hyperbranched polymer is added to the MY 0510 resin, irrespective to the H 30 content. This indicates that a larger number of proton donors are available to accelerate the last stage of curing when H 30 is present. The activation energy calculated for the mixtures, almost independent from the H 30 content, is lower than that calculated for TGAP resin. In addition, the presence of the hyperbranched polymer significantly increases  $k_{02}$  parameter, indicating a faster completion of crosslinking reactions. This, again, is in agreement with the lower end temperatures of crosslinking exothermic peaks found for the systems containing the H 30 polymer. It can be hypothesized that the presence of a "flexible-transfer reagent," responsible for the reduction in the crosslinking density of the TGAP resin, enhance the mobility of the reactive species, accelerating the comple-

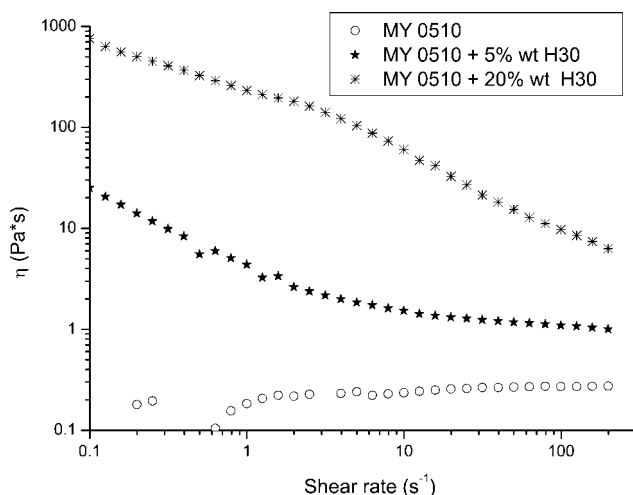
tion of crosslinking reactions at lower temperatures. The disappearance of the shoulder observed for TGAP resin at high temperatures in dynamic DSC thermograms, indicating that the diffusional processes dominate the crosslinking reactions at higher degrees of conversion (corresponding to high temperatures), when high contents of hyperbranched polymer are added can be also explained by the enhanced mobility of the network.

### Rheological analysis

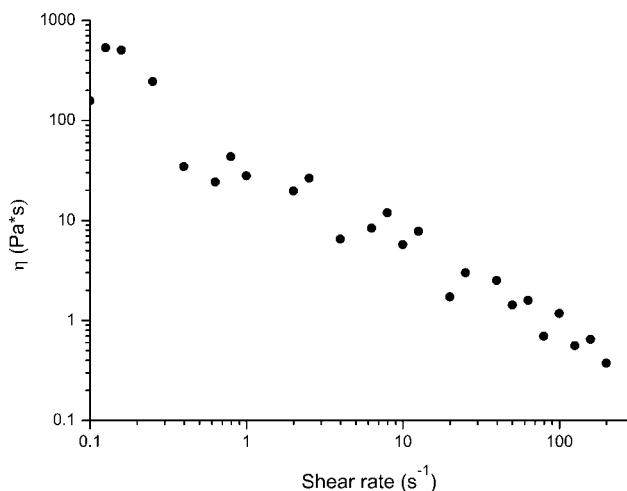
In Figure 9, the rheological behavior in steady state mode of uncured TGAP resin and of its mixtures with H 30 polymer at ambient temperature, is reported.

From the comparison between the first and second runs, performed on the same sample, it was observed that the viscosity measured in the second experiment was slightly lower than that measured in the first run only for the mixture containing the highest amount of H 30, i.e., 20 wt %. A possible small effect of aggregation of the micro particles of the OH-terminated hyperbranched can explain the observed behavior. However, the viscosity of this mixture remains well above that of pure MY 0510 resin, even in the second rheological experiment. In Figure 9, in particular, the rheological curves relative to the second scan are reported for all the systems analyzed.

The TGAP resin shows a low Newtonian viscosity at ambient temperature. On the other hand, when the OH-terminated hyperbranched aliphatic polyester H 30 is added, even in small percentages (i.e., at 5 wt % H 30), the viscosity of the mixture consider-



**Figure 9** Results of rheological tests (second run) performed in steady state mode at 25°C on MY 0510 resin, MY 0510 plus 5 wt % H 30 system, MY 0510 plus 20 wt % H 30 system.



**Figure 10** Results of rheological test performed in steady state mode at 110°C on mixture of MY 0150 with 5 wt % of H 30 polymer.

ably increases. The rheological behavior of both mixtures is not Newtonian, with a pseudoplastic feature.

It is reported that OH-terminated hyperbranched aliphatic polyester H 30 exhibits shear-thinning behavior, both under steady shear and oscillatory shear conditions, due to the interactions between the functional groups on the molecular periphery.<sup>43</sup> Moreover, the shear-thinning dominance has been frequently reported for polymer blends consisting of components with different rheological characteristics, as, for instance, in the case of blends of Thermotropic Liquid Crystalline Polymers (TLCP), showing a strong shear-thinning behavior, and flexible polymers.<sup>44</sup>

The rheological measurement performed at 110°C on the mixture of TGAP resin containing 5 wt % of H 30, reported in Figure 10, indicates that, by increasing the temperature up to a typical injection temperature of industrial processes, the viscosity of the mixture appreciably reduces, even if in correspondence of very high shear rate values.

It can be, finally, concluded that the modification of the TGAP resin through the addition of low percentages (i.e., 5 wt %) of hyperbranched polymer H 30 leads to a noticeable increase in the viscosity of the resin. The resulting system will be, therefore, suitable only in industrial processes for the production of composites that do not require severe restraints on the viscosity of the resin.

### CONCLUSIONS

The modifications in reaction kinetics of a trifunctional epoxy resin (TGAP) when an OH-terminated hyperbranched aliphatic polyester was added to it in percentages ranging from 5 to 20 wt %, were analyzed.

Since several difficulties were found in the calculation of the crosslinking enthalpy through isothermal calorimetric tests, dynamic DSC experiments were employed to develop appropriate kinetic models.

The mechanism of crosslinking reactions of the trifunctional epoxy resin is influenced by the presence of the hyperbranched polymer and this was attributed to chemical interactions occurring between the molecules of hyperbranched and epoxy polymers. However, the cure reactions remained autocatalytic in nature across the range of composition analyzed. The attitude of OH-terminated hyperbranched polymer to act as transfer reagent, allowing an early curing reaction to the TGAP resin, as reported in previous studies, was confirmed also by our results. A noticeable decrease in activation energy was, in fact, measured. However, the initial rate of reaction was found to decrease with the addition of even small amounts of the hyperbranched polymer. The completion of crosslinking reactions, on the other hand, occurs faster and at lower temperatures.

Moreover, the addition of large amounts of the OH-terminated hyperbranched aliphatic polyester leads to an excessive decrease in the final  $T_g$  of the cured systems based on the TGAP resin. The hyperbranched polymer was thought to act as an additional hardener for the epoxy resin, leading to an excess of amine hardener DETDA in the epoxy rich phase. This in turn would produce a network with a lower crosslink density and, hence, a looser and more mobile network with a reduced  $T_g$ .

The modification of the TGAP resin through the addition of low percentages of hyperbranched polymer (i.e., 5 wt %), however, produces a noticeable increase in the viscosity of the resin, even at elevated injection temperatures. However, the pseudoplastic nature of the mixture yields to a continuous reduction in viscosity by increasing the shear rate value.

A complete analysis of the mechanical and toughness properties of the cured resin and of its mixture with the hyperbranched polymer analyzed is recommended. The verification of a noticeable increase in toughness of the cured TGAP resin by adding small amount of the hyperbranched polymer, in fact, could suggest the choice of a suitable technique to process the modified resin.

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