Effect of Hydroxypropyl Cellulose in Epoxy Network Formation

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ABSTRACT: Studies on the curing reactions of epoxy systems were carried out in the presence of a cellulose derivative, hydroxypropyl cellulose (HPC). The technique of differential scanning calorimetry (DSC) was applied to characterize the curing reactions/thermal properties. Classical nonisothermal kinetic methods, such as the Kissinger and the Osawa methods (multiple scan) and the Barrett method (single scan) as well as the recently one proposed by Samios et al., were applied to study the reaction kinetics of the epoxy system of diglycidyl ether of bisphenol A (DGEBA) and 4,4′-diaminodiphenylmethane (DDM) with HPC. The Barrett method gives additional information about the process of initiation, gelation, and vitrification. At the beginning of the epoxy curing reaction, HPC acts as a catalyst so that the energy of activation diminishes and the reaction occurs at lower temperatures. Above the minimum temperature T_{min}, it was concluded that HPC behaves as an inhibitor of the reaction (T_{min} is the temperature which corresponds to the minimum point showed by the exotermic peaks during the curing reaction of an epoxy resin measured by DSC). By analyzing the behavior of the kinetic parameters, Ea, k, and $\ln A$, the molecular interactions were shown to be related to the catalyst–inhibitor characteristics of HPC. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 676–683, 2003

Key words: thermosets; liquid-crystalline polymers (LCP); curing of polymers; activation energy; differential scanning calorimetry (DSC)

INTRODUCTION

In the 1990s, a significant number of studies of the curing reactions of epoxy systems, considering the thermal, kinetic, and rheological aspects, were published[1–13] as well as studies of the thermoset properties.[14–19] The research work published by Wisanrakkit and Gillham in the beginning of that decade showed a new development and understanding of the importance of the relationship between the cure reaction and the cured properties; for instance, the glass transition temperature T_g can be related to the extent of a reaction.[11] Besides, light-scattering techniques have improved the research in gelation–vitrification processes.[17,20] Differential scanning calorimetry (DSC), both in isothermal and nonisothermal modes, has been the most widely used technique to characterize the curing reactions/thermal properties and to correlate them. The use of nonisothermal kinetic methods is valid, as, some years ago, it was demonstrated that the isothermal kinetic equations can be extended to nonisothermal reactions.[21] In spite of the differences of the various systems, the analysis techniques, experimental conditions, and mathematical treatments used afforded advanced and consistent results for the understanding of the curing reactions and their products.

The aim of this work was twofold: First, to examine the effect of HPC concentration on the crosslinking kinetics of diglycidyl ether of bisphenol A (DGEBA) with 4,4′-diaminodiphenylmethane (DDM), bearing in mind that epoxy systems are influenced by reactive groups, such as hydroxyl groups present in HPC, during the curing reaction. In addition, HPC shows a liquid crystalline character, which, in turn, may influence the curing kinetics of this epoxy system. Studies on the curing reactions of this epoxy system have been already carried out in the presence of inorganic fillers,[22] but such studies have not been done yet in the presence of organic compounds like cellulose derivatives. Second, to evaluate the application of the Samios method (formerly called half-width method)[22,23] to study the crosslinking kinetics of DGEBA and DDM in the presence of a cellulose derivative (HPC). Classical nonisothermal kinetic methods (multiple scan) such as those of Kissinger[24] and of Osawa[25] as well as the Barrett[26] method (single scan) were also applied.

EXPERIMENTAL

DGEBA (CY-205, Ciba-Geigy, P.A., Brazil) was cured with a stoichiometric amount of a tetrafunctional aro-
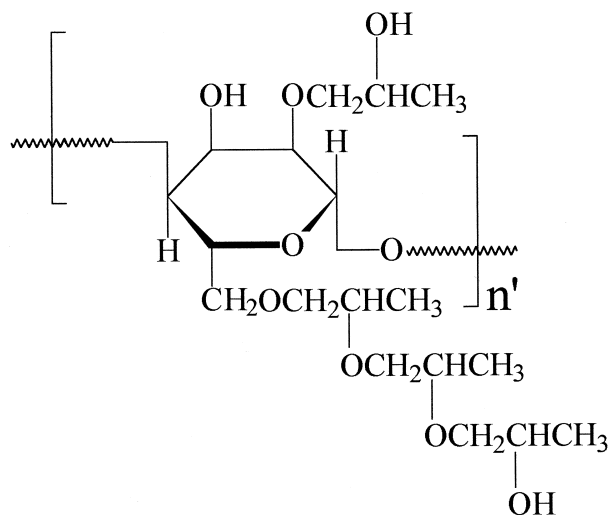
Figure 1 Idealized molecular structure of HPC.

matic diamine, DDM (HT-972, Ciba-Geigy, P.A., Brazil). The epoxy monomer was a viscous resin with an epoxide equivalent weight (EEW) of 182–196 g/equiv and $n' = 0.14$ (data furnished by the manufacturer), where n' represents the degree of polymerization. The amine curing agent was a crystalline solid (melting point of 90°C) with an amine equivalent weight of 99 g/equiv. The diamine (DDM) was added to the liquid epoxy (DGEBA, preheated at 90°C) in a molar ratio of 2:1 (DGEBA:DDM). HPC was manufactured by Aldrich (Milwaukee, WI) with a nominal molecular weight of 100,000 g mol^{-1} and a polydispersity, as determined by GPC, of 3.5. This cellulose derivative presents a thermotropic liquid crystal behavior whose endothermic transition can be detected by DSC at a temperature range of 165–210°C.[27,28] The idealized molecular structure of HPC is shown in Figure 1. By ^{1}H-NMR,[29] the molar substitution (MS) value was found to be 4.5 {MS represents the average number of hydroxypropyl groups [$CH_2CH(CH_3)O$] per anhydroglucose unit}. HPC was oven-dried for 1 h at 110°C prior to the mixing procedure.

The samples were prepared by adding HPC to the epoxy system at different concentrations (5, 10, 20, and 30 wt %). The resulting viscous mixture of DGEBA/DDM/HPC was carried out under constant stirring and at room temperature. An accurately weighed amount of the reactive mixture (approximately 30–35 mg) was transferred into a DSC pan, which was subsequently sealed and submitted to a DSC temperature scan from −40 to 250°C at temperature scanning rates (ϕ) of 5, 10, 20, and 30°C/min under a dry N_2 flux. The minimum temperature (T_{min})—T_{min} is the temperature which corresponds to the minimum point shown by the exothermic peaks during the curing reaction of an epoxy resin, and at this inflection point, the rate of the curing reaction goes to a maximum—the initial formulation glass transition temperature ($T_{g_{epoxy}}$ or T_{g_0}) of the unreacted epoxy resin, and the total enthalpy ($\Delta H_{epoxy\ sys.}$) evolved were determined using a differential scanning calorimeter, Perkin–Elmer DSC-4.

RESULTS AND DISCUSSION

In our recent articles,[22,23,30] the experimental parameters (T_{min}, $t_{1/2}$, dH/dt, H, H_T, and ϕ) obtained by DSC measurements were related to the equations collected here in Table I with the aim of calculating the energy of activation (Ea), the rate constant (k), and the frequency factor (A). In the present work, the same procedure was applied: The activation energy of the crosslinking reactions of the epoxy resin DGEBA/DDM in the presence of HPC was determined by applying the single-scanning rate method of Barrett[26] as well as the multiple-scanning rate methods of Kissinger,[24] Osawa,[25] and Samios.[22,23]

Evolution of thermal parameters

The curing of epoxy resins is known to be strongly exothermic. Figure 2 shows a typical DSC thermogram for the system under study where the exothermic peaks are characterized by a minimum temperature T_{min}, and at lower temperatures, the initial formulation glass transition temperature (T_{g_0}) can be extracted from the heating ramp. The behavior of these thermal parameters (T_{min} and T_{g_0}) was observed at different concentrations of HPC (0, 5, 10, 20, and 30 wt %) using different temperature scanning rates (5, 10, 20, and 30°C min^{-1}).

TABLE I
Differential Methods Used in Nonisothermal Kinetic Analysis
(Linear Plots: $y = mx + c$)

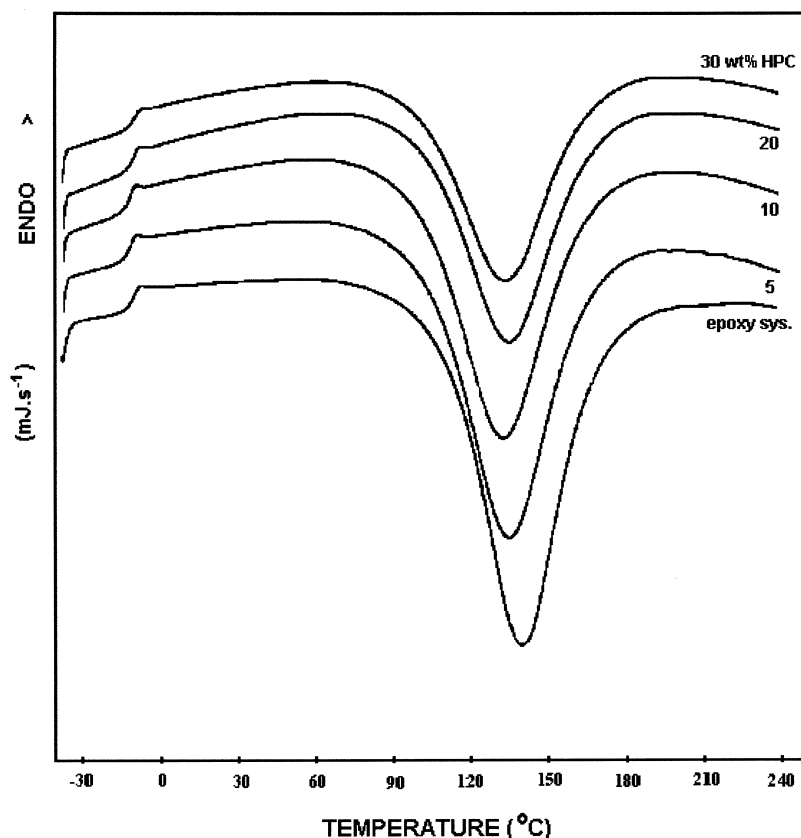| Method	y	x	Slope (m)	Reference
Kissinger	$\ln[\phi/(T_{min})^2]$	$1/T_{min}$	$-Ea/R$	24
Osawa	$\ln \phi$	$1/T_{min}$	$-Ea/R$	25
Samios	$\ln t_{1/2}$	$1/T_{min}$	Ea/R	22, 23
Barrett	$\ln k^a$	$1/T$	$-Ea/R$	26

^{a} $k = (dH/dt)/(H_T - H)$.

Figure 2 DSC typical thermograms obtained during the curing process for the epoxy system (DGEBA/DDM/HPC) with different HPC concentrations (0, 5, 10, 20, and 30 wt %) measured at 5°C min^{-1}.

It was observed that the T_{min} and T_{g_0} values remain practically constant with increase of the HPC concentration. However, when the scanning rate is increased, these parameters increased for all systems under investigation. The average values of T_{min} ($\langle T_{min} \rangle$) and T_{g_0} ($\langle T_{g_0} \rangle$) in each temperature scanning rate can be seen in Table II. The average values of T_{min} and T_{g_0} show an increase of 141 to 197°C and -13.4 to -7.4, respectively. In absolute values, the increase of T_{min} is larger than that of T_{g_0}. This indicates that T_{min} is more sensitive to the increase of the temperature scanning rate in this epoxy system. It was observed that T_{min} values increase with the scanning rate for all systems under investigation. Similar behavior was previously reported for other epoxy systems.[23]

TABLE II
Average values of T_{min} ($\langle T_{min} \rangle$) and $T_{g_0}(\langle T_{g_0} \rangle$) at Different Temperature Scanning Rates During the Cure Reaction of Epoxy System (DGEBA/DDM) in the Presence of HPC

ϕ (°C min^{-1})	$\langle T_{min} \rangle$ (°C)	$\langle T_{g_0} \rangle$ (°C)
5	141 ± 4	−13.4 ± 0.6
10	159 ± 5	−11.8 ± 0.5
20	182 ± 3	−9.6 ± 0.6
30	197 ± 3	−7.4 ± 0.6

Applying the Barrett method

The Barrett method has been used as a very efficient tool in the investigation of the different stages of the crosslinking reaction process and in the calculation of kinetic parameters. Besides these investigations, already accomplished in past works,[19,26,23] the effect of the variation of the temperature scanning rate (5, 10, 20, and 30°C min^{-1}) for different concentrations of HPC (0, 5, 10, 20, and 30 wt %) was also studied. Figures 3 and 4 show the behavior of the crosslinking reaction for different temperature scanning rates (namely, 5, 10, 20, and 30°C min^{-1}) with respect to the rate constant and the extent of reaction (α), respectively.

At high-temperature scanning rates, the behavior of the epoxy matrix does not show differences in the presence of several concentrations of HPC. This can be verified by the tendency of the curves to superimpose for the temperature scanning rates of 20°C min^{-1} and, more significantly, for 30°C min^{-1}. The curves in Figure 3 present two slopes, indicating that the reaction already presents two stages: initiation (5 to approximately 45% of the extent of the reaction) and gelation–vitrification (from 45 to about 95%), which includes the theoretical gel point. Taking into account the Flory
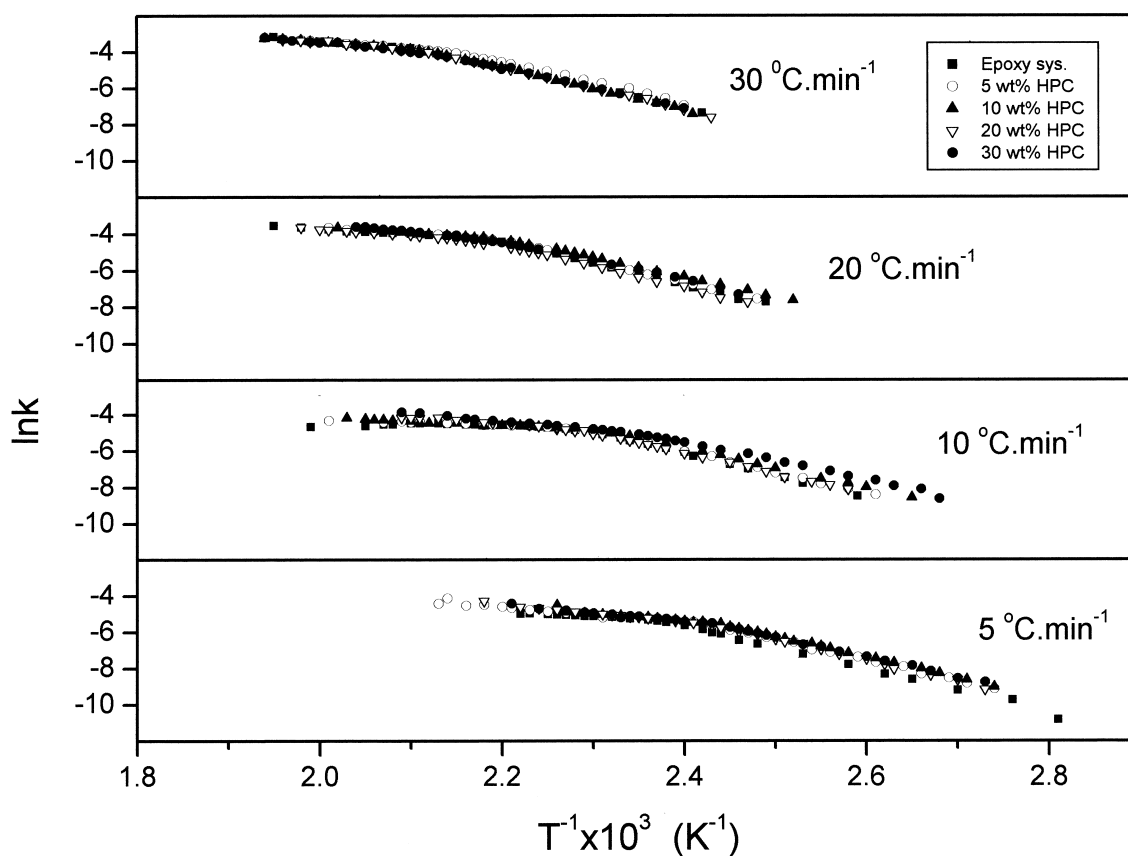
Figure 3 Behavior of ln k versus T^{-1} at different temperature scanning rates and HPC concentrations.

theory of gelation,[31] the theoretical extent of the reaction of this epoxy system[1] is 0.58. It is known that the gel point corresponds to the point where a transformation of a viscous liquid to an elastic gel takes place. The gelation process is dependent on the stoichiometry, functionality, and reactivity of the reagents. Thus, with increase of the temperature scanning rate, independent of the concentration of HPC, the theoretical gel point also shifts to higher temperatures. These points are marked in Figure 4. For the temperature scanning rate of 5°C min^{-1} at different concentrations of HPC, the curves are located in the temperature range from 115 to 177°C. For the epoxy system without and with HPC, in the first stages (initiation), the temperature limits are, respectively, (105–138°C) and (115–145°C). At the first stages, a superposition of the curves with HPC occurs, and for the concentrations above 5 wt % HPC, there is no distinction among them.

For the rate of 5°C min^{-1}, one can also notice that the addition of HPC to the epoxy system increases the rate constant values, suggesting a slight accelerating effect of HPC in the curing reaction of the epoxy system. In the second stage, this effect is also detectable for all curves with HPC. Besides, the theoretical gel point also decreases, in temperature aspects, from

150°C (0 wt % of HPC) to a value around 143°C (for the other curves).

Figures 3 and 4 show also the behavior of the epoxy matrix for the temperature scanning rate of 10°C min^{-1} in regard to the different concentrations of HPC. The curves are located in the temperature range of 130–204°C. In analyzing this temperature scanning rate, the rate constant values increase with the concentration of HPC and an accelerating effect of HPC is again verified in the curing reaction of the epoxy system. In the second stages, this effect is also detectable for the curves of concentrations of 10 and 30 wt % of HPC. The theoretical gel point also decreases, in temperature terms, from 166°C (0, 5, and 20 wt % of HPC) to a value around 160°C (only for the other curves with 10 and 30 wt % of HPC).

By analyzing the curves at the temperature scanning rate of 20°C min^{-1}, a different behavior from the other rates was verified, suggesting a limiting condition: Starting from this temperature scanning rate, the method loses sensitivity in the evaluation of the effect of the presence of HPC in the epoxy matrix. Finally, in observing the behavior of the epoxy matrix for the temperature scanning rate of 30°C min^{-1} in relationship to the different concentrations of HPC, their
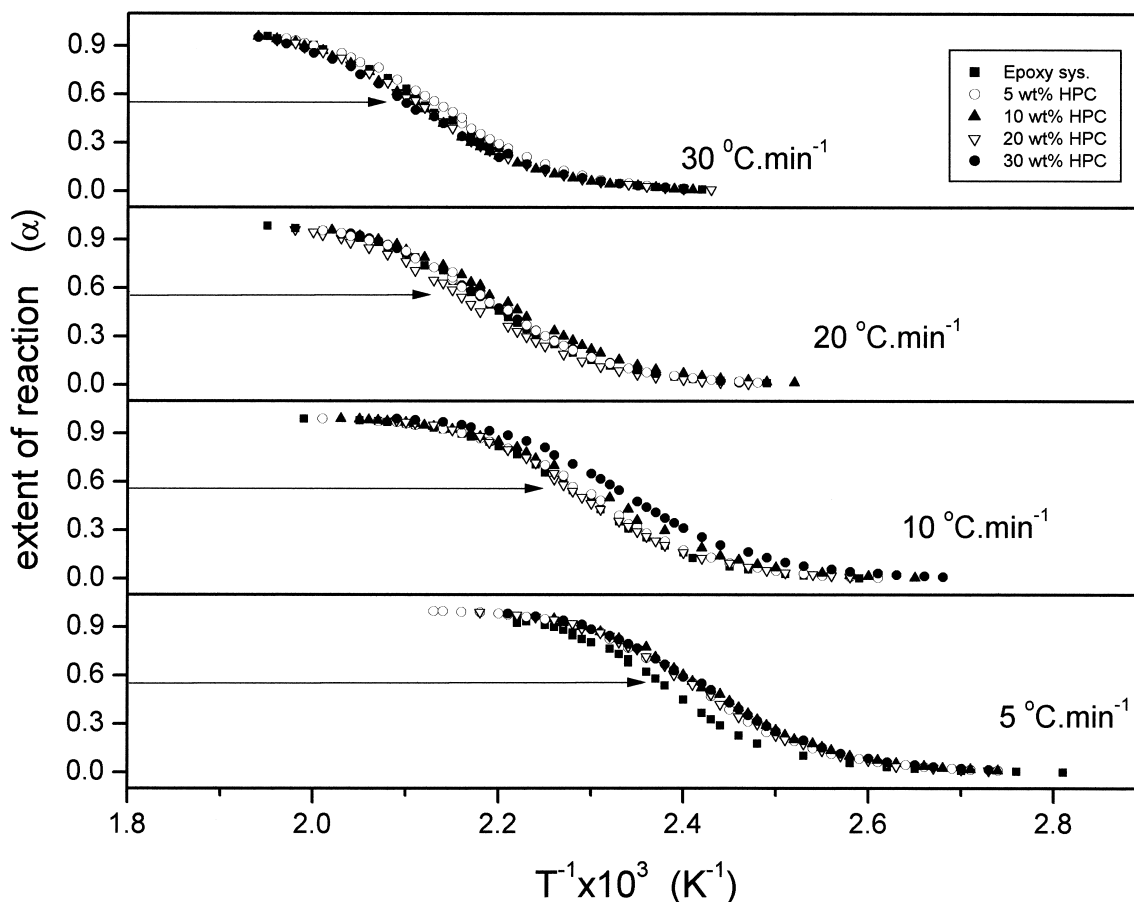
Figure 4 Behavior of the extent of reaction (α) versus T^{-1} at different temperature scanning rates and HPC concentrations. The arrows indicate the theoretical gel point.

curves are located in the temperature range from 155 to 234°C.

At the first stages, the curves with HPC do not shift to lower temperatures and it is not possible to detect differences between the curves with HPC and the curve of the pure epoxy system (0 wt % of HPC). In this temperature scanning rate, increase of the rate constant values, with increase of the concentration of HPC, is slightly detectable for the curve of a concentration of 5 wt % of HPC for the extent of reaction values nearby the theoretical gel point. In the second stages, this effect is also detectable at an extent of reaction values close to the theoretical gel point only for the curve of 5 wt % of HPC. The decrease of the

theoretical gel point is not clear. Concerning these kinetic studies at different temperature scanning rates of the cure of this epoxy system in the presence and without HPC, and in applying Barrett method, it can be concluded that the recommended temperature scanning rate should not be higher than 10°C min^{-1} as shown in Figures 3 and 4.

The activation energy (Ea) and frequency factor (A) were evaluated by the Barrett method before the theoretical gel point (Table III) at different concentrations of HPC (0, 5, 10, 20, and 30 wt %). Taking into account that the Ea and ln A evaluated at the same concentration of HPC for different temperature scanning rates (5, 10, 20, and 30°C min^{-1}) showed no significant

TABLE III
Results of Ea and ln A Applying the Barrett Method to the Epoxy System (DGEBA/DDM/HPC) Before the Gel Point

Measurement	Wt % HPC				
	0	5	10	20	30
$\langle Ea \rangle$ (kJ mol^{-1})	100 ± 1	93 ± 1	91 ± 1	93 ± 1	88 ± 1
$\langle \ln A \rangle$	21 ± 0.4	20 ± 0.2	20 ± 0.3	20 ± 0.4	19 ± 0.3

TABLE IV
Results of Ea and ln A Obtained by Multiple-scanning Methods

	Kissinger	Osawa	Samios	
Wt % HPC	Ea (kJ mol^{-1})	Ea (kJ mol^{-1})	Ea (kJ mol^{-1})	ln A
0	51 ± 2	59 ± 2	49 ± 1	8.6 ± 0.3
5	47 ± 2	54 ± 2	44 ± 1	7.6 ± 0.2
10	41 ± 2	49 ± 2	39 ± 2	6.0 ± 0.1
20	42 ± 2	50 ± 2	40 ± 2	6.4 ± 0.7
30	39 ± 4	47 ± 4	38 ± 3	5.7 ± 0.9

changes, the average activation energy $\langle Ea \rangle$ and the average frequency factor $\langle \ln A \rangle$ values were used in Table III. When Ea and ln A values are determined at the same temperature scanning rate, a significant decrease was verified by these values as the concentration of HPC increases. In fact, the average values of Ea decreased from 100 kJ mol^{-1} (0 wt % of HPC) to 88 kJ mol^{-1} (30 wt % of HPC). These values of Ea are comparable to those obtained through the application of the time–temperature superposition method[11] using different techniques such as DSC[1,19] and TBA,[12] where T_g is the basic parameter used for the calculations of Ea. The comparison between the mentioned methods is valid,[1,19] even considering the inherent simplification of the Barrett method—which assumes order of the reaction equal to 1—and knowing that the calculation of Ea is obtained only for the first stages (initiation), where, theoretically, there are neither diffusion effects nor vitrification processes.

Application of Kissinger, Osawa, and Samios methods

In recent works,[22,23] the half-width method as well as Kissinger and Osawa methods were used and compared for the crosslinking reaction of similar epoxy systems. The Samios method consists of plotting the natural logarithm of the half-width time versus the inverse of $T_{\min}$ (Table I). The half-width time is obtained from the DSC thermogram as follows: At the peak temperature $T_{\min}$, one locates the half-height. At the half-height, one measures the half-width in temperature units. By dividing this half-width by the tem-

perature scanning rate, one obtains the half-width in time units, that is, the "half-width time." If the scanning rate is increased, the half-width time becomes shorter. An exponential dependence is observed. Table IV collects the results of the energy of activation (Ea) by the Samios method (38–49 kJ mol^{-1}), which are comparable to those given by the Osawa and Kissinger methods (values between 39 and 59 kJ mol^{-1}). The results of Table IV showed a slight Ea decrease with increase of the HPC concentration. Concerning the results of Figures 3 and 4, it can be concluded that HPC acts as an accelerator in the early stages of the cure reaction. The HPC component acts also as a catalyst, since it lowers the energy of activation correspondent to the first stage of the reaction (Tables III and IV). On the other hand, the Barrett method gives much higher Ea values than those given by the multiple-scanning methods. The Barrett method is able to differentiate kinetics before the gel point while the dynamic methods consider an average value of all the kinetic processes. Only in the case where we have an unique kinetic process would we expect to have the same Ea values of Barrett and the multiple-scan methods of Kissinger, Osawa, and Samios et al.

By applying the Barrett method (Table V) or the Samios method (Table VI) at $T_{\min}$, a rate constant analysis was performed. It can be verified that rate constants do not change with increasing of the HPC concentration inside the epoxy matrix. Although HPC seems to have an accelerator–catalyst behavior at temperatures lower than $T_{\min}$, at temperatures higher than $T_{\min}$, its presence probably leads to an inhibiting

TABLE V
Results of k Applying the Barrett Method to the Epoxy System (DGEBA/DDM/HPC) at $T_{\min}$

	Wt % HPC				
	0	5	10	20	30
ϕ (°C min^{-1})			[$k \times 10^3$ (s^{-1})]		
5	3.6	3.9	4.1	3.9	4.0
10	7.4	7.1	6.7	7.7	9.1
20	12.2	12.5	12.4	12.1	11.5
30	18.7	17.1	18.4	18.2	16.4

TABLE VI
Results of k Applying Samios Method to the Epoxy System (DGEBA/DDM/HPC) at $T_{\min}$

	Wt % HPC				
	0	5	10	20	30
ϕ (°C min^{-1})			[$k \times 10^3$ (s^{-1})]		
5	4.0	5.3	4.4	5.1	4.4
10	6.9	9.6	7.4	9.7	6.4
20	12.4	17.2	14.4	17.3	12.6
30	18.9	22.4	19.0	22.0	18.2
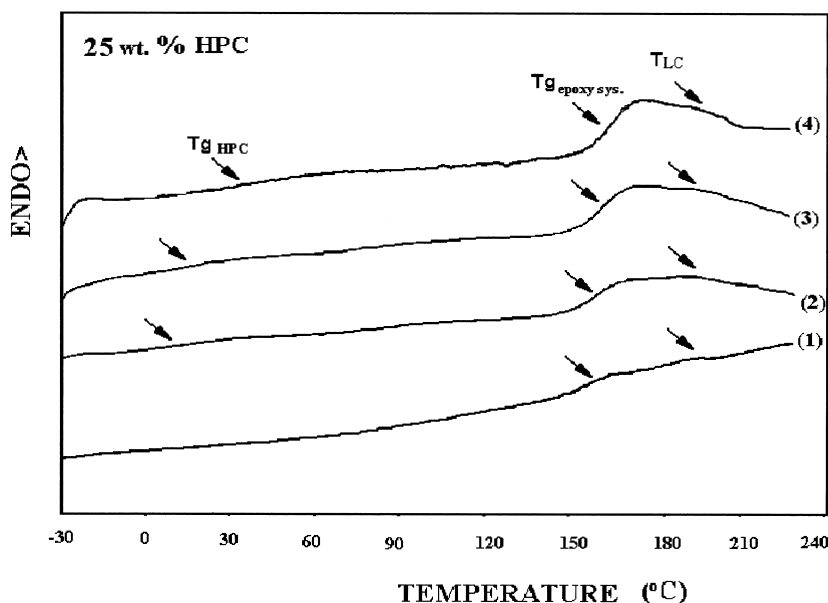
Figure 5 DSC curves of cured epoxy–HPC systems (25 wt % of HPC) measured at (1) 10°C min^{-1}, (2) 20°C min^{-1}, (3) 30°C min^{-1}, and (4) 40°C min^{-1}, indicating the $T_{g_{HPC}}$ (glass temperature of HPC), $T_{g_{epoxy\ sys.}}$ (glass temperature of the epoxy system), and T_{LC} (liquid crystal transition temperature of HPC).

factor. This inhibition effect was inferred, bearing in mind that at the beginning of the reaction the rate constants increase but at T_{min} they become constant (Tables V and VI). The reasons for this inhibiting behavior are not totally clear but can be related to the liquid crystalline transition of HPC that takes place at the temperature range after the theoretical gel point, hindering the remaining reaction to continue. As can be seen in Figure 5, the HPC liquid crystal endothermic transition ($\Delta H = 3.6$ J g^{-1}) takes place at the range of 160–205°C.[30] The peak position of the liquid crystal transition (T_{LC}) of HPC does not suffer any effect, indicating that the liquid crystal behavior was retained during the process formation of the epoxy network. This behavior can be related to the phase separation that takes place at the final stages of the crosslinking process when the HPC content is as high as 25 wt %.

CONCLUSIONS

In summary, it was demonstrated that the effect of HPC inside an epoxy matrix can be studied through the kinetic methods applied. The values of Ea obtained by the Samios method agree well with the classical multiple-scanning methods in spite of their differences. In kinetic aspects, in analyzing only Ea values, the role of HPC inside the epoxy matrix can be understood as follows: At the beginning of the reaction, HPC acts as an accelerator–catalyst until T_{min}, and beyond T_{min}, the behavior of the rate constant (k) and frequency factor (A) indicates that the crosslinking process suffers a slowdown where HPC behaves as an inhibitor of this reaction. The molecular interactions between the HPC hydroxyl groups and the epoxy–amine reaction seem to be related to the catalyst–inhibitor characteristics of HPC.

References

1. Miranda, M. I. G. Dissertation, Instituto de Química, UFRGS, Porto Alegre, 1993.
2. Corcuera, M. A.; Mondragon, I.; Riccardi, C. C.; Williams, R. J. J. J Appl Polym Sci 1997, 64, 157.
3. Abuin, S. P. Polym Commun 38, 3117. 1997,
4. Sanz, G.; Garmendia, J.; Andres, M. A.; Mondragon, I. J Appl Polym Sci 1995, 55, 75.
5. Casalini, R.; Corezzi, S.; Livi, A.; Levita, G.; Rolla, P. A. J Appl Polym Sci 1997, 65, 17.
6. Parodi, F.; DeMeuse, M. T.; Gillham, J. K. J Appl Polym Sci 1997, 64, 15.
7. Vallely, A. S.; Gillham, J. K. J Appl Polym Sci 1997, 64, 39.
8. Venditti, R. A.; Gillham, J. K. J Appl Polym Sci 1997, 64, 3.
9. Matsuoka, S.; Hale, A. J Appl Polym Sci 1997, 64, 77.
10. Barral, L.; Cano, J.; Lopez, J.; Nogueira, P.; Abad, M. J.; Ramirez, C. J Therm Anal 1997, 50, 409.
11. Wisanrakkit, G.; Gillham, J. K. J Appl Polym Sci 1990, 41, 2885.
12. Zukas, W. X. J Appl Polym Sci 1994, 53, 429.
13. Núñez, L.; Taboada, J.; Fraga, F.; Núñez , M. R. Z. J Appl Polym Sci 1997, 66, 1377.
14. Tarifa, S.; Bouazizi, A. J Therm Anal 1997, 48, 297.
15. Tsagaropoulos, G.; Eisenberg, A. Macromolecules 1995, 28, 396.
16. Johari, G. P.; Mikolajczak, G.; Cavaille, J. Y. Polymer 1987, 28, 2023.

17. Mangion, M. B. M.; Wang, M.; Johari, G. P. J Appl Polym Sci 1992, 30, 445.
18. Barral, L.; Cano, J.; Lopez, J.; Lopez-Bueno, I.; Nogueira, P.; Abad, M. J.; Ramirez, C. J Therm Anal 1998, 51, 489.
19. Miranda, M. I. G.; Samios, D. Eur Polym J 1997, 33, 325.
20. Samios, D.; Castiglia, S.; da Silveira, N. P.; Stassen, H. K. J Polym Sci Part B Polym Phys 1995, 33, 1857.
21. Sesták, J. J Therm Anal 1979, 16, 503.
22. Miranda, M. I. G.; Bica, C. I. D.; Tomedi, C.; Samios, D. Polymer 1997, 38, 1017.
23. Miranda, M. I. G.; Bica, C. I. D.; Samios, D. Polymer 1997, 38, 4843.
24. Kissinger, H. E. Anal Chem 1957, 1702.
25. Osawa, T. Bull Chem Soc Jpn 1965, 38, 1881; J Therm Anal 1970, 2, 301.
26. Barrett, K. E. J. J Appl Polym Sci 1967, 2, 1617.
27. Rials, T.; Glasser, W. J Appl Polym Sci 1988, 36, 749.
28. Gray, D. G. J Appl Polym Sci Appl Polym Symp 1983, 37, 179.
29. Ho, F. F.-L.; Kohler, R. R.; Ward, G. A. Anal Chem 1972, 44, 178.
30. Miranda, M. I. G. Ph.D. Thesis, Instituto de Química, UFRGS, Porto Alegre,1998.
31. Flory, P. J. Principles of Polymer Chemistry; Cornell University: Ithaca, NY, 1953.