Curing of Phenolic Resins Modified with Chestnut Tannin Extract

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ABSTRACT: Phenolic novolac resins have been modified with chestnut tannin for reduction of phenol content in resins. In this work, rheological and kinetic analysis of curing reactions of these resins with hexamethylenetetramine (hexamine) has been performed. Chemical structure of obtained materials has been analyzed and compared with that of nonmodified resins. Results reveal that cure reactions of resin modified with chestnut tannin are different when compared with nonmodified novolacs not only in the cure kinetics values but also in final chemical structure. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2034–2039, 2006

Key words: novolacs; tannins; cure kinetics; hexamine

INTRODUCTION

Phenol–formaldehyde resins are one of the oldest synthetic polymers, being the first to be synthesized.[1] They were commercialized in 1909 by Baekeland and have been used in numerous applications including refractories, composite materials, adhesives, thermal insulation, and electrical industries.[1] Phenolic resins are the condensation products of phenol and aldehydes, specifically formaldehyde, which are converted into high molecular mass polymer in curing reactions. Two classes of phenol–formaldehyde resins are obtained from the reaction of phenol and formaldehyde usually under either acidic or alkaline conditions, producing novolac or resole resins, respectively.

Phenol and formaldehyde toxicity, combined with the new requirements for increased recycling and reuse of wastes have prompted the use of renewable resources such as wood derivatives[2] as an alternative resource to these materials. Among the possible alternatives, tannin is an excellent renewable resource, which could be used for replacing petroleum-derived phenolic compounds.[3–5] Sekaran et al.[6] have reported the preparation of novolac phenol–formaldehyde–tannin resins with the addition of less than 1% w/w (versus phenol) of tannin powder, recovered from waste water, showing potential applications in the paint industry as a good anticorrosive paint, because of its resistance to strong acids, alkalis, and organic solvents.

Novolac resins are mixtures of linear branched oligomer chains with a relatively low molecular weight. These thermoplastic resins are soluble in several organic solvents. In the curing reaction with hexamethylenetetramine (hexamine), the oligomers become linked into a three-dimensional highly crosslinked network.[1]

Several authors have studied the mechanism of hexamine curing of novolacs, but the numerous possible intermediates complicate the analysis. Hatfield and Maciel[7] have identified 15 possible intermediates in hexamine-cured novolac. Dargaville et al.,[8] de Bruyn et al.,[9] and Zang et al.[10–12] employed monomers and dimers to analyze their curing reactions with hexamine. The proposed mechanism occurs in two stages: formation of initial intermediates such as benzoxazines and benzyl amines and the decomposition, oxidation, and/or further reactions of these initial intermediates into methylene bridges with residual traces of amines, imides, imines, methyl phenol, and others.

In a previous work, the synthesis and the characterization of phenol–formaldehyde–chestnut tannin resin (PFCT) and phenol–formaldehyde–mimosa tannin resin have been presented.[13] In this work, the kinetic analysis of curing reaction of materials obtained from PFCT cured with hexamine has been carried out by rheological and thermal analysis. Fourier transform infrared spectroscopy (FTIR) has also been employed for the determination of the chemical structure of polymeric materials.

MATERIALS AND METHODS

Materials

Commercial powder of chestnut (Castanea sativa) wood extracts was used without purification.

Phenol (P) (99%), formaldehyde (F) 50% w/w, oxalic acid (99%), and fine hexamine (without stabilization) were gently provided by Bakelite Ibérica (Spain).

Synthesis of the resins

The novolac resins (PF) were prepared by polycondensation of P with F in P/F molar ratio of 1 : 0.65 under catalysis by oxalic acid. P and oxalic acid were heated to 100°C and then a 37% w/w solution of F was added dropwise with stirring. The reaction mixture was stirred and refluxed for 60 min. Water and P were stripped off by distillation under vacuum until the level of free P was below 0.2% w/w.

For novolac modified with chestnut tannin (PFCT) synthesis, aqueous chestnut tannin extract solution (40% w/w) was added when F addition was finished. Then, residual water and P were removed by distillation as in previous case. Four resins with 4, 14, 21, and 40% w/w chestnut tannin referred to P weight were synthesized (PFCT4, PFCT14, PFCT21, and PFCT40, respectively). Before any analysis, they were stored in a dessicator under vacuum.

Analysis of resins

Rheology

Rheological measurements were performed in a Metravib viscoanalyzer using annular pumping geometry and a probe with a diameter of 6 mm. Scans at 130°C with a frequency of 10 Hz were performed.

Fourier transformed infrared spectroscopy

The FTIR spectra of the resins were obtained with a Nicolet spectrometer. The acquisition conditions were $400–4000$ cm^{-1} spectral range, 10 scans, and a resolution of 4 cm^{-1}. The resin samples were analyzed on KBr pellets.

Thermal analysis

Thermal analysis was carried out with a Mettler DSC20 differential scanning calorimeter (DSC) linked to a TC 15 TA Processor. A 2–6 mg sample was sealed in a medium pressure pan, which could withstand up to 20 bars. A scanning temperature range from 25 to 280°C was employed for thermal characterization. On the basis of the relation of Kissinger, the activation energies were calculated using DSC scans at various
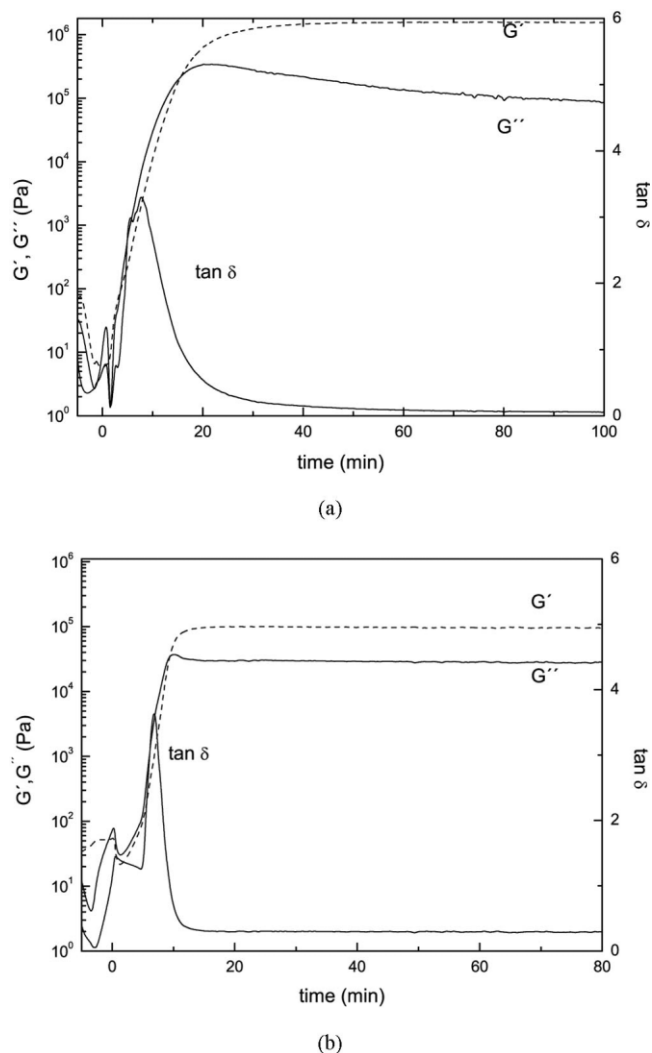

Figure 1 Storage modulus (G'), loss dynamic modulus (G''), and tan δ for the reaction mixture of resin with HMTA (10% w/w) at 130°C. (a) PF resin and (b) PFCT14.

heating rates (1, 5, 10, and 20°C/min) from the maximum temperature of each exothermic peak (T_m).

RESULTS AND DISCUSSION

The formation of the polymer network structure of the PF novolac resins cured with hexamine can be evaluated from dynamic rheological parameters: storage modulus (G'), loss modulus (G''), and loss factor (tan δ). Figure 1 shows the plots obtained for (a) PF and (b) PFCT14 resins with 10% w/w hexamine. A cure temperature of 130°C was chosen because the obtained gelation times are suitable to compare the analyzed systems. G' and G'' initially decrease because of softening of resins, but afterward they increase as a result of network formation. G' increases until a maximum value by entering a plateau and G'' passes through a maximum and again decreases. The loss factor shows
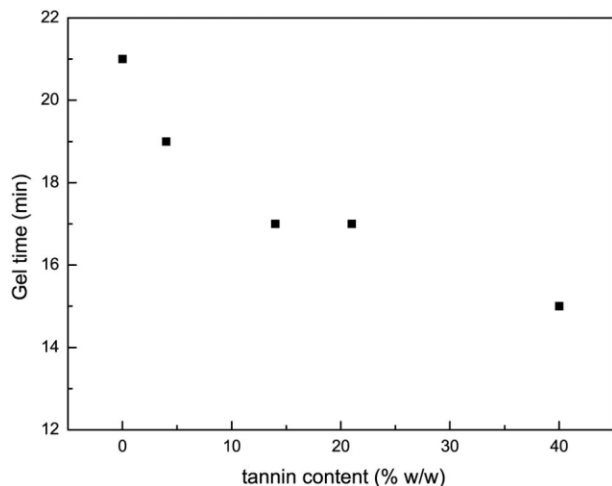
Figure 2 Gelation time evolution with the tannin content extract in resins obtained from the crossover of G'-t and G''-t curves of rheological measurements.

Figure 3 FTIR spectra of PF and PFCT resins containing 14 and 40% w/w chestnut tannin extract cured with 10% w/w HMTA. t_0 and t_f are times for resins with HMTA after and before cure reaction, respectively.

two maxima during heating; the first is due to softening of the resin and the second is linked to network formation. The time when G' reached a minimum was taken as initial time for the beginning of the curing reaction. The gelation time of thermosetting polymers can be determined according to different criteria.[15] These are the peak maximum in loss factor, the crossover of G'-t and G''-t curves, and the intersection point tangent on curve G' (100 kPa) and base line ($G'' = 0$) on the curve G' versus time.[15] The crossover of G'-t and G''-t curves has been chosen in this work as apparent gelation time. In Figure 2, the gelation times are presented as function of tannin contents. As can be seen, the increase in tannin content results in a reduction of gelation times of resins. In a previous work,[13] results of gelation times and flow distance values also indicated that resins modified with chestnut tannin react with hexamine more easily than conventional PF novolacs. Indeed, rheological measurements demonstrate a good agreement with the experimental gelation times obtained in previous works.[13,15,16] It is possible to conclude that PFCT resins react with hexamine more easily than PF novolac resins.

To analyze the chemical structures, resins were cured with hexamine at 165°C during 150 min and their structures compared by FTIR analysis. In Figure 3, PF and PFCT resins with several chestnut tannin contents are shown before and after cure with hexamine (t_0 and t_f, respectively). A decrease of peak intensities at 810, 1007, 1240, 1375, and 1460 cm^{-1} due to hexamine disappearance is observed in all spectra. The intensity of bands at 1770 and 1690 cm^{-1} of modified resins also decreases. These bands have been attributed in a previous work[13] to the carbonyl stretching vibration of ester groups linked to aromatic ring units and to the carbonyl in-plane stretching vibration, respectively.
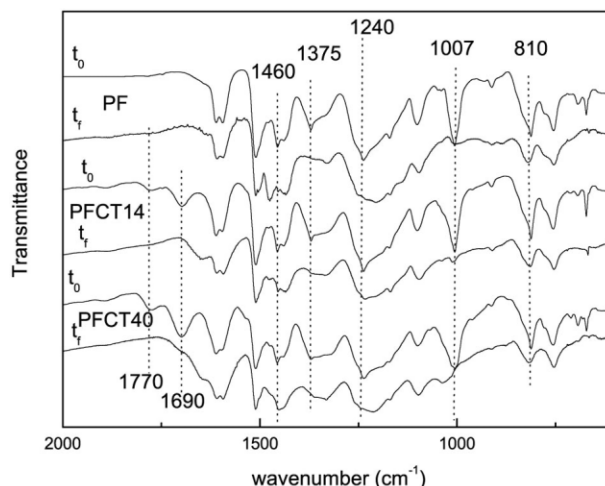
Differences between PF and PFCT final cured resins are shown in Figure 4. Reduced intensity of the band at 1475 cm^{-1} in modified resins is observed. Modified resins show a band at 1454 cm^{-1}, which correspond to the same wavenumber of that methylene groups of hexamine. Then, this fact could indicate that the presence in final cured resins of amine groups near to the methylene bridges. These groups could be a result of the reactions between PFCT resins and PFCT intermediates of the decomposition of hexamine. The amine group presence could also be proved by the presence of a band at 1033 cm^{-1}.

The presence of a new band around 1645 cm^{-1} could be due to the formation of amide groups (band of amide I) or to the formation of azomethine groups
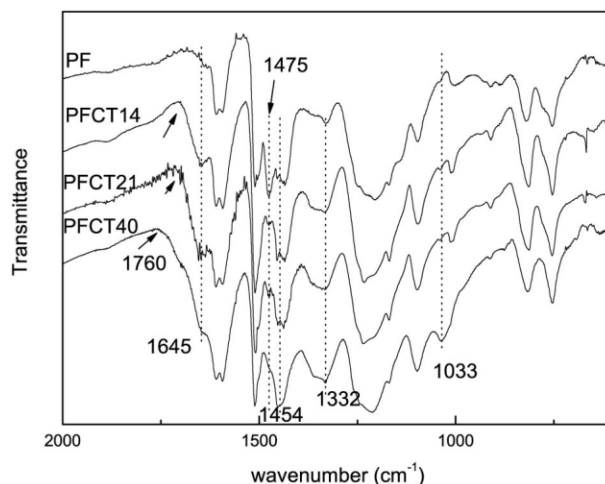

Figure 4 FTIR spectra of cured PF and PFCT resins containing 14, 21, and 40% w/w of chestnut tannin and cured with 10% w/w hexamine.
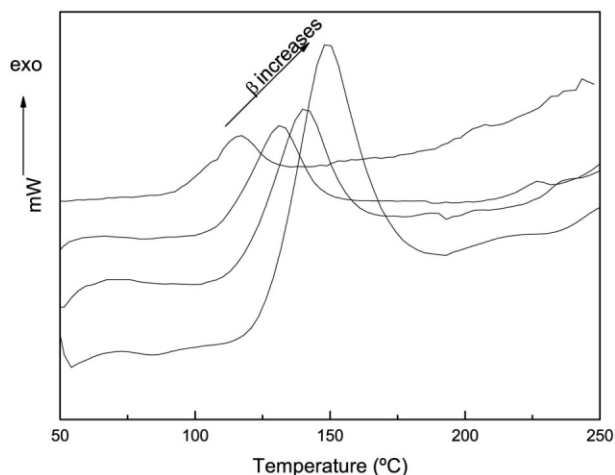
Figure 5 DSC thermograms of PFCT resin containing 14% w/w chestnut tannin extract at several heating rates (1, 5, 10, and 20°C/min).

Figure 6 Plot of $-\ln(\beta\,T_m^{\,2})$ versus $T_m^{\,-1}$ for the modified and nonmodified resins.

—CH=N— in agreement with the results reported by Aranguren et al.[17] for the analysis of the reaction of novolacs with hexamine in closed mold. In spectra of the nonmodified novolac resin, the presence of a small band at 1645 cm^{-1} is also clear. The same band is present in the PFCT spectra, but with a broader width from 1760 until around 1645 cm^{-1}, which increases with tannin extract content. This can be explained by the presence of several groups: ester (1750–1740 cm^{-1}), aldehydes (1740–1720 cm^{-1}), carboxilic acid (1710–1690 cm^{-1}), and imines (1690–1640 cm^{-1}). The presence of these bands indicates that many chemical groups are obtained as a result of curing reactions.

Kinetic analysis of cure reactions between resins and hexamine was performed by DSC using Kissinger model.[18] According to this method, the activation energy is obtained from the variation of maximum reaction rate upon inverse temperature. Figure 5 shows the thermograms obtained for PFCT14 at 1, 5, 10, and 20°C/min. The Kissinger method assumes that the peak represents a point of constant conversion for each heating rate. The resulting relation can be expressed as:

$$-\ln\left(\frac{\beta}{T_m^{\,2}}\right) = \frac{E}{RT_m} - \ln\left(\frac{ZR}{E}\right) \qquad (1)$$

where β is a constant heating rate, E the activation energy, Z the collision frequency or Arrhenius frequency factor, and R the universal gas constant. Therefore, a plot of $\ln(\beta\,T_m^{\,-2})$ versus $T_m^{\,-1}$ gives the apparent activation energy and Z without a specific assumption on the conversion dependent function. Figure 6 shows the linear relationships obtained for analyzed resins with 10% w/w hexamine. A good fitting with
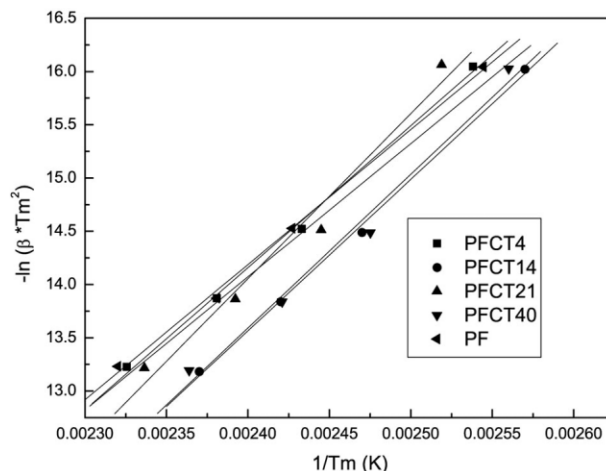
regression coefficients higher than 0.99 was obtained for all systems.

From activation energy and frequency factor, apparent rate constant (k) dependence with tannin extract content in resins can be obtained (Fig. 7). From curves, it can be deduced that k increases when tannin extract content increases. This result is in good agreement with gelation times obtained by rheological technique. In both cases, PFCT resins react with hexamine more easily than PF resin.

From results obtained by Kissinger, relatively few information can be obtained because the kinetic parameters are calculated for a degree of conversion, which correspond to the maximum of exothermic peak. Li and Järvelä[19] and Vyazovkin and Sbirrazzuoli[20] have employed a model-free isoconversional method to analyze the cure of phenolic resins and epoxy-amine systems, respectively. The isoconversional methods of kinetic analysis allow one to reveal a dependence of the activation energy on the extent of
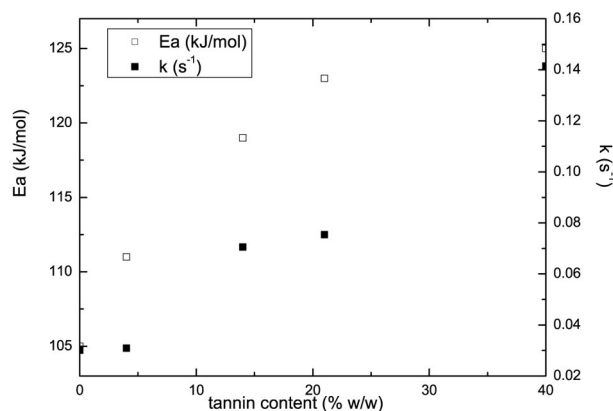

Figure 7 Evolution of apparent activation energy and rate constant with tannin extract content.
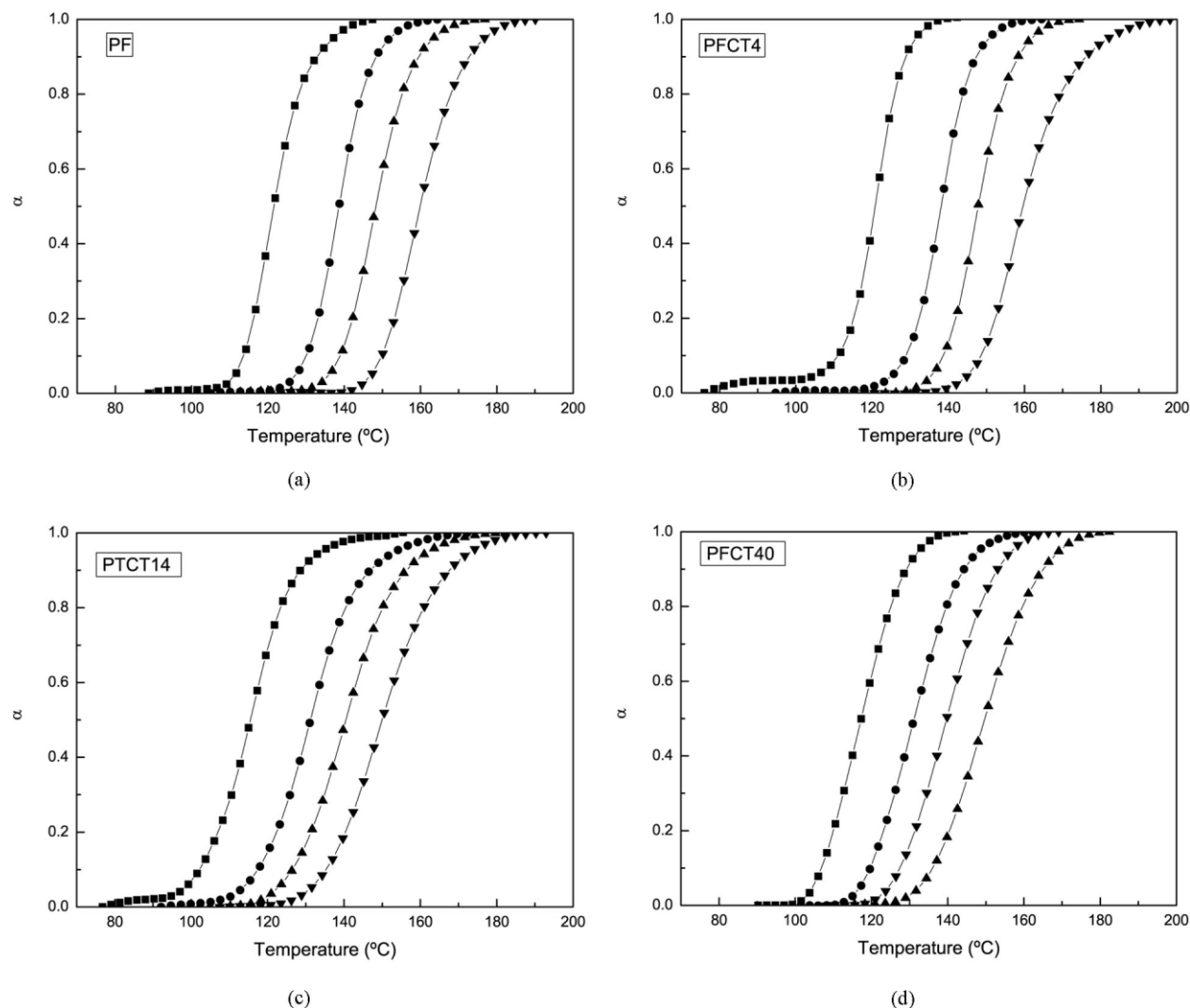
Figure 8 Integral kinetic curves obtained for PF and PFCT resins with hexamine at different heating rates (1, 5, 10, and 20°C/min).

conversion. The general approach takes kinetics as phenomenological in nature, which ignores the complexity of cure in kinetic calculations. In this work, the isoconversional principle has been used in the integral method of Kissinger. Figure 8 shows the integral kinetic curves obtained for PF and PFCT resins with hexamine at different heating rates (1, 5, 10, and 20°C/min). The activation energy can be evaluated by the following expression

$$\ln\left(\frac{\beta}{T_i^2}\right) = \frac{-E_\alpha}{RT_i} + \ln\left(\frac{ZR}{E_\alpha}\right) \qquad (2)$$

where T_i is the temperature to reach a given degree of conversion. A plot of $\ln(\beta\,T_i^{-2})$ versus T_i^{-1} is a straight line from which the activation energy at a given conversion can be obtained.

From kinetic values obtained from isoconversional method, apparent rate constant (k) can also be ob-

tained for different conversions (Fig. 9). As can bee seen, for PF resin and PFCT resins with low tannin content (4% w/w), differences in rate constant values between different conversions are small. For example, for PF system, differences between the higher and lower rate constants are 0.1, while 0.4 for PFCT40. Then, it is possible to conclude that in the cure process of PF resins with hexamine, similar reactions are present independently of conversion grade. On the contrary, the cure process of PFCT with hexamine is the result of several complex reactions, which can be slightly different at each conversion. This result could be expected if the chemical structure of PF and PFCT resins described in a previous work[13] is considered. The PF novolac resins' chemical structure can be described as P molecules linked each other with methylene groups. As Lim et al.[21] and others[5–10] have proved by several techniques, PF novolac resins cure reactions with hexamine result in the formation of
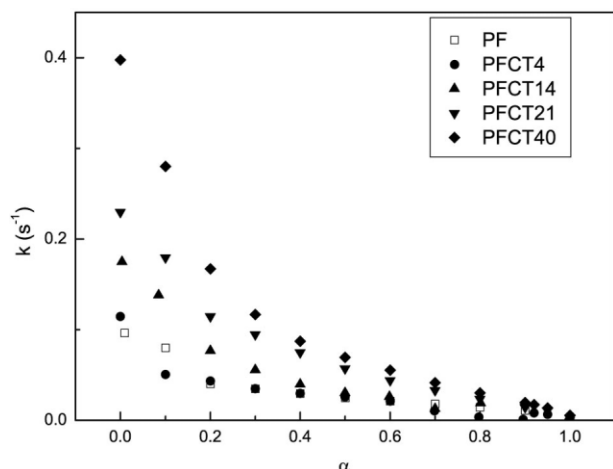
Figure 9 Evolution of apparent rate constant with conversion.

methylene linkages and other minor nitrogen-containing structures as a result of several intermediate molecules as benzylamines and benzoxazines. On the contrary, PFCT resins present not only ring reactive positions, but also others as ester and acid groups.[13] The presence of several reactive sites in resins could result in a complex sum of reactions, which lead to a complex kinetic behavior.

CONCLUSIONS

Phenolic resins modified with commercial chestnut extract tannin have been characterized. From rheological measurements, it has been proved that PFCT resins with hexamine have gelation times shorter than the ones for PF resins, which confirms results obtained by other techniques that have been presented in previous work.[14]

Kinetic parameters obtained from Kissinger equation and chemical structures of cured materials indicate that PF and PFCT resins present different cure reactions. From results obtained by rheological and kinetic analysis, it can be concluded that PFCT resins react with hexamine more easily than PF resins. The presence of new linkages in FTIR spectra after curing and the variations in rate constant prove the complexity of cure reactions.

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