

RESEARCH ARTICLE

Curing kinetics of a novolac resin modified with oxidized multi-walled carbon nanotubes

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Summary

The influence of oxidized multi-walled carbon nanotubes (o-MWCNTs) on the curing kinetics of a novolac resin was studied by means of non-isothermal differential scanning calorimetry. Regarding the kinetics issues, the high concentration of hydroxyl groups on the o-MWCNTs slightly modified the curing reaction of the novolac resin, shifting the differential scanning calorimetry exothermic peak to higher temperatures. The effective activation energy of the curing reaction was calculated by the isoconversional Kissinger-Akahira-Sunose method and increased by the presence of o-MWCNTs with respect to neat novolac. This change was attributed to the increase of the material viscosity. In addition, thermogravimetric analysis revealed that nanocomposites samples containing 0.4 and 1.0 wt% o-MWCNTs presented increased char yield values, indicating an improvement of flame retardancy.

KEYWORDS

differential scanning calorimetry (DSC), isoconversional Kissinger-Akahira-Sunose method, oxidized multi-walled carbon nanotubes (o-MWCNTs), thermogravimetric analysis (TGA)

1 | INTRODUCTION

Phenolic-formaldehyde (PF) resins can be classified as novolac or resole resins, depending on the molar ratio between phenol and formaldehyde and the synthesis conditions.¹ Novolac resins are relatively easy to prepare and thermally stable with a high glass transition temperature. Phenolic-formaldehyde resins can be used in a variety of fields, such as electronic encapsulation, heat insulation foams, fire retardants, or material ablation.^{2,3} Due to their good flame resistance, they are commonly applied in the aerospace industry (spacecraft, rockets, missiles, etc.).⁴ To improve their properties, they have been combined with elastomers,^{5,6} thermoplastic polymers,^{7,8} and nano fillers^{9,10} as well as with different types of fibers.¹¹

The current trend is mainly focused on the study of thermal properties of PF resins. Recently, Park et al¹² have found that the ablation properties and thermal conductivity of PF resins can be improved by the incorporation of carbon nanotubes and carbon fibers. On the other hand, Song et al¹³ have evaluated the presence of multi-walled carbon nanotubes (MWCNTs) and graphene to control the cell morphology of phenolic foams. In addition, Park et al¹⁴ have investigated the kinetics of thermal degradation of resole phenol-formaldehyde/MWCNTs/cellulose nanocomposites through thermogravimetric analysis (TGA). They found that the thermal energies for the decomposition (activation

energy) slightly increased with the amount of MWCNTs while that of the cellulose degradation was independent on the MWCNTs content.

To achieve the desired end-use properties, the curing conditions and the control of the kinetics reaction parameters become critical during the manufacture processing of phenolic-based nanocomposites. Therefore, these parameters have been recently attracted a lot of research interest.^{2-4,14-18}

Several mechanistic or phenomenological models have been used in the literature to analyze the curing kinetics of thermosetting polymers. Mechanistic models are based on the balance of all the species formed or consumed during the curing process; hence, they seem to be more accurate. In the case of PF resins, curing reaction is extremely complicated because it involves the formation of a great number of intermediate compounds such as benzoxazines, benzylamines, amides, imides, and many others.¹⁵ Hence, phenomenological models based on empirical data are found to be more appropriate in this case.^{16,17} Among them, different methodologies can be used for the determination of curing kinetics parameters. Borchardt and Daniels¹⁹ have obtained the kinetic parameters through a single dynamic differential scanning calorimetry (DSC) measurement. In addition, Kissinger²⁰ and Ozawa^{18,21} models use multiple dynamic scans with the same objective. Isoconversional models are another type of kinetic models and provide accurate information as they evaluate the changes in the

activation energy throughout the curing process. These models are especially useful for the study of complex curing process such as those in PF resins. Among isoconversional models, the isoconversional Kissinger-Akahira-Sunose (KAS) model was selected here to analyze the curing kinetics of PF/oxidized MWCNT (o-MWCNT) nanocomposites. The advantage of this model arise from its ability of revealing and handling the complexity of the respective curing kinetics processes. Despite the fact that the activation energies results tend to be effective and tend to vary with the degree of conversion and temperature, they can be used to make reliable kinetic predictions. These predictions are useful to get information about complex mechanisms, and finally, to obtain intrinsic kinetic parameters.²²

To the authors' knowledge at the time of writing, this work presents for the first time the application of the KAS isoconversional model to analyze the curing kinetics of PF/o-MWCNT nanocomposites.

1.1 | Theory of free kinetic models

The mathematical approach that describes the curing kinetics of thermosets is based on the fundamental rate equation that relates the time dependent progression of conversion at a constant temperature T , $\alpha(t)$, with the concentration of reactants, $f(\alpha)$.^{4,14,15}

Assuming that the curing process is a thermal event, the heat flow measured in a DSC test is directly proportional to the conversion of the curing reaction. Under this hypothesis, the degree of conversion can be defined as

$$\alpha = \frac{\Delta H_{\alpha}}{\Delta H_0}, \quad (1)$$

where ΔH_{α} is the heat released at a given conversion value and ΔH_0 is the total heat released after full conversion.

Most of the phenomenological kinetic models are derived from the following equation, which relates the reaction rate (da/dt) with a conversion function $f(\alpha)$ and a temperature-dependent reaction constant:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = Ae \left(-\frac{E}{RT} \right) f(\alpha), \quad (2)$$

where A is the pre-exponential factor or Arrhenius frequency factor (s^{-1}), E is the effective activation energy (kJ/mol^{-1}), R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), and T is the sample absolute temperature (K).

For isoconversional conditions, the temperature rises at a constant heating rate (β) and the integral form of the single-step kinetic equation can be expressed as

$$g(\alpha) = \int_0^{\alpha} \frac{1}{f(\alpha)} d\alpha = \frac{A}{\beta} \int_{T_0}^T \exp \left[\frac{E}{RT} \right] dT, \quad (3)$$

where $g(\alpha) = \int_0^{\alpha} \frac{1}{f(\alpha)} d\alpha$ is the integral form of the reaction model, and T is the temperature corresponding to a specific degree of conversion.

The use of different approximations to solve the temperature integral leads to the Ozawa and Kissinger solutions,²³ where the effective activation energy is related to the heating rate and the average peak temperature of the exothermic curve (T_p) in a DSC test.

$$\text{Ozawa solution } -\ln \beta = 1.0516 \left(\frac{E}{RT_p} \right) - A' \quad (4)$$

$$\text{Kissinger solution } -\ln \left(\frac{\beta}{T_p^2} \right) = \frac{E}{RT_p} - \ln \left(\frac{A'R}{E} \right) \quad (5)$$

In the present work, the KAS model was used for the determination of kinetic parameters of novolac-based nanocomposites curing over the whole conversion range. The KAS method uses isoconversional integration, in which the temperature integral of T_0 is equal to 0. The resolution of the temperature integral is the crucial step within the integral methods. The temperature integral approximation equation used in the KAS method developed by Coats and Redfern²⁴ is

$$\ln \left(\frac{\beta}{T^2} \right) = A' - \frac{E}{RT}, \quad (6)$$

with $A' = \ln \left(\frac{AR}{E} \right) - \ln g(\alpha)$.

This method does not require the knowledge of the conversion-dependent function, $g(\alpha)$, and only assumes that the process follows the same mechanism of reaction for a given conversion degree, regardless of the crystallization temperature. The linear plot of $\ln(\beta/T^2)$ vs T^{-1} provides the values of the effective activation energy (E) and the Arrhenius frequency factor (A').

2 | EXPERIMENTAL

2.1 | Materials and characterization

Novolac resin (RN 1399) and bisphenol F were provided by Atanor (Buenos Aires, Argentina). The neat novolac resin was prepared by mixing phenol (in excess) and formaldehyde under acidic conditions. Hexamethylenetetramine was used as a curing agent in a proportion of 7 wt%. Different contents (0.1, 0.4, and 1.0 wt%) of MWCNTs (NC7000 from Nanocyl, Belgium), previously oxidized according to the methodology described in a previous work,²⁵ were dispersed in the neat novolac resin through sonication and mechanical mixing. Oxidized MWCNTs will be referred to as o-MWCNTs in the following text.

Differential scanning calorimetry experiments were performed in a DSC-60 Shimadzu. The instrument sensitivity and temperature were previously calibrated with a set of Hg, In, Sb, Bi, and Zn standards. A series of non-isothermal scans was conducted from room temperature to 250°C with different heating rates β : 5°C/min, 10°C/min, 15°C/min, and 20°C/min. All DSC measurements were performed under the gas flow of high-purity N_2 . Average and deviation values were obtained from the results of three DSC experiments.

Thermogravimetric analysis was performed for different samples in a TGA-50 Shimadzu analyzer. About 5.5 ± 0.3 mg of samples of neat novolac and novolac/o-MWCNTs nanocomposites were submitted to a heating process from room temperature to 800°C at 10°C/min under dynamic nitrogen flow (30 mL/min).

3 | RESULTS AND DISCUSSION

Figure 1 shows non-isothermal thermograms of heat flow as a function of temperature for the neat novolac resin at different heating rates β . As expected, the DSC exothermic peak shifted to higher temperatures with increasing heating rate as a result of the increase of crosslinking reactions.^{4,15,26} All curves exhibited the exothermic peak within the temperature range of 140°C to 180°C highlighting the optimum processing window to assure the highest cure temperature for performance of the end product. In addition, the full width at half maximum became wider with increasing β value, indicating that the number of crosslinking reactions occurred at higher temperatures within shorter times.²⁶

Figure 2 presents degree of conversion vs temperature plots at different heating rates for neat novolac. These plots displayed a typical sigmoidal profile characterized by a slow increase of α value at the beginning and at the end of the reaction and a high increase of α at the intermediate stage. The progress of the curing reaction can be divided into 3 stages.^{4,26} During the initial stage, although the curing

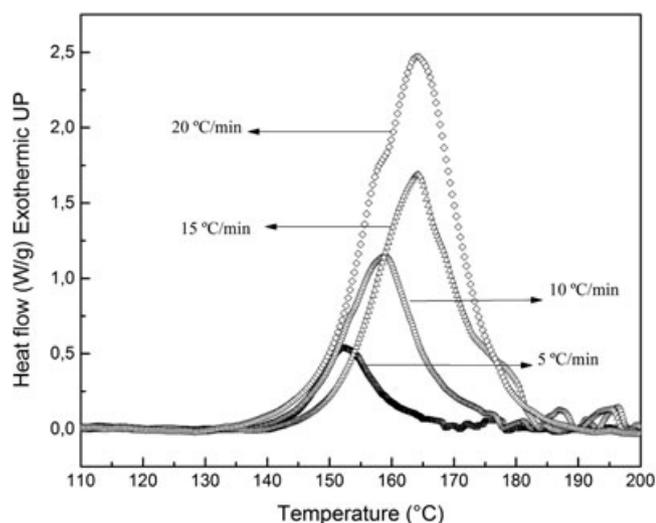


FIGURE 1 Heat flow as a function of temperature for the novolac resin with 7 wt% HMTA catalyst at different heating rates β

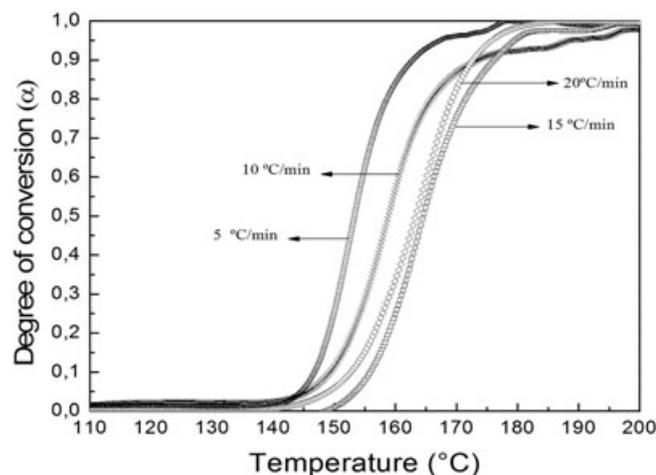


FIGURE 2 Degree of conversion as a function of the reaction temperature at different heating rates for neat novolac

rate is slow, there is a short time before the resin reaches the gel point. Along with the transformation into the gel state, the reaction rate increases rapidly, the maximum velocity corresponds to the peak heat flux. During intermediate time points, crosslinking degree of the network structure advances, and the resin transforms gradually into the glassy state. With the increased crosslinking degree, the curing rate decreases. In the last stage, when the curing degree reaches its maximum value, the curing rate decreases because of high viscosity.²⁷

For the novolac resin investigated, 2 different behaviors were observed. At low heating rates (5°C/min and 10°C/min), more time was available for the network to develop; hence, the peak temperature for the reaction conversion was the lowest. For high heating rates (15°C/min and 20°C/min), on the other hand, the curves presented practically the same reaction rate. As the higher heating rate did not allow enough time for the reactive groups to react, then, the reaction conversion shifted to a higher peak temperature.^{4,15,27}

Figure 3 shows the exothermic peak for neat novolac and the different novolac/o-MWCNTs nanocomposites studied at $\beta = 10^\circ\text{C}/\text{min}$ as an example. In addition, Table 1 shows the curing onset temperature (T_o), peak temperature (T_p), endset temperature (T_e), and enthalpy (ΔH) for neat novolac and the different nanocomposites investigated. For heating rates higher than 10°C/min, an increase of T_o and T_p values was found. Furthermore, with the increase of the amount of o-MWCNTs, the peak temperature increased. This means that the addition of o-MWCNTs retarded the initiation of the curing reaction and this effect became more significant for the composite with 1.0 wt% o-MWCNTs. Moreover, at the heating rate of 5°C/min, no significant changes of T_o and T_p with the addition of o-MWCNTs were observed. On the other hand, enthalpy energy increased with the incorporation of o-MWCNTs for all heating rates, indicating that the curing parameters (ΔH , T_o , and T_p) changed with respect to neat novolac. Choi et al²⁷ have already reported similar results. They found that the incorporation of pure and functionalized carbon nanotubes (azomethine ylide groups) into an epoxy matrix led to a shift of the peak temperature to higher values. In addition, an increase of enthalpy and activation energy values was observed, reflecting its influence on the curing reactions.

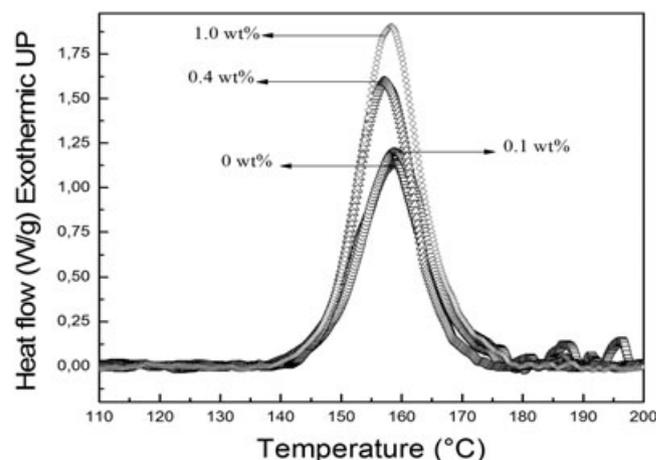


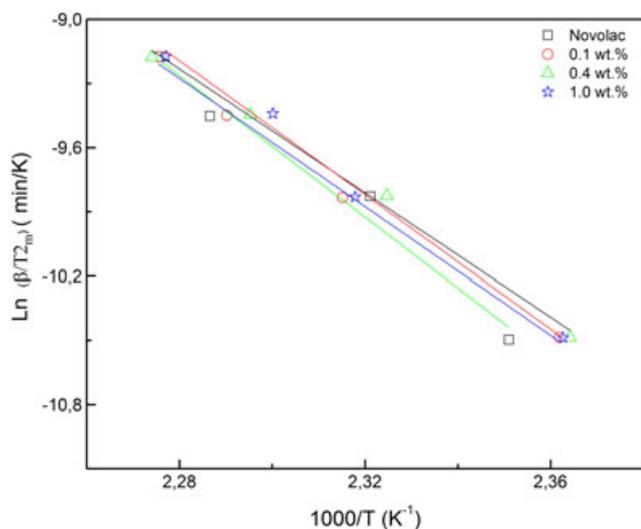
FIGURE 3 Heat flow as a function of temperature for neat novolac and novolac/o-MWCNTs nanocomposites at a heating rate of $\beta = 10^\circ\text{C}/\text{min}$

TABLE 1 Onset temperature T_o , peak temperature T_p , endset temperature T_e , and enthalpy ΔH at different heating rates (β)

Sample	Heat Rates (β)	Onset (T_o), °C	Peak (T_p), °C	Endset (T_e), °C	ΔH (J/g)
Novolac	5°C/min	143.9 ± 0.3	152.2 ± 0.3	159.4 ± 0.3	24.4 ± 0.1
0.1 wt% MWCNTs		143.0 ± 0.4	150.2 ± 0.4	159.1 ± 0.4	28.8 ± 0.2
0.4 wt% MWCNTs		143.3 ± 0.3	149.8 ± 0.3	157.0 ± 0.2	30.3 ± 0.3
1.0 wt% MWCNTs		143.9 ± 0.2	150.1 ± 0.4	156.9 ± 0.3	32.6 ± 0.3
Novolac	10°C/min	146.8 ± 0.4	157.6 ± 0.4	164.9 ± 0.4	29.0 ± 0.1
0.1 wt% MWCNTs		148.3 ± 0.5	158.7 ± 0.3	166.6 ± 0.3	29.8 ± 0.2
0.4 wt% MWCNTs		148.0 ± 0.3	157.0 ± 0.2	165.2 ± 0.3	29.7 ± 0.2
1.0 wt% MWCNTs		149.4 ± 0.2	158.2 ± 0.3	167.0 ± 0.6	41.9 ± 0.3
Novolac	15°C/min	147.7 ± 0.5	160.6 ± 0.3	175.5 ± 0.4	29.7 ± 0.1
0.1 wt% MWCNTs		150.0 ± 0.4	163.4 ± 0.2	170.8 ± 0.5	34.1 ± 0.3
0.4 wt% MWCNTs		151.4 ± 0.4	161.5 ± 0.2	172.4 ± 0.3	31.5 ± 0.4
1.0 wt% MWCNTs		155.2 ± 0.2	166.0 ± 0.3	176.3 ± 0.2	33.2 ± 0.2
Novolac	20°C/min	148.9 ± 0.3	164.2 ± 0.2	176.1 ± 0.5	30.2 ± 0.2
0.1 wt% MWCNTs		153.1 ± 0.4	166.3 ± 0.4	176.7 ± 0.5	30.7 ± 0.4
0.4 wt% MWCNTs		154.6 ± 0.5	166.5 ± 0.3	177.3 ± 0.3	34.4 ± 0.5
1.0 wt% MWCNTs		155.2 ± 0.2	166.0 ± 0.3	176.3 ± 0.2	33.2 ± 0.2

Abbreviation: MWCNTs, multi-walled carbon nanotubes.

In this work, the effective activation energy of the curing reaction was determined by means of the KAS method taking into account the slope of the linear plots of $\ln(\beta/T_m^2)$ vs $(1000/T)$ at different heating rates (Figure 4). Table 2 shows the effective activation energy values for neat novolac and the different nanocomposites investigated. The effective activation energy value for neat novolac was lower than that for the novolac/o-MWCNTs nanocomposites during the crosslinking reaction. The formation of bridges was easier in neat novolac, leading to a lesser crosslinked network.²⁵ In addition, samples containing 0.1 and 0.4 wt% o-MWCNTs presented the highest values of the effective activation energy. The presence of high concentration of OH groups from the modified nanotubes surface in the sample containing 0.1 and 0.4 wt% o-MWCNTs, increased the crosslinking effective

**FIGURE 4** Isoconversional plot for neat novolac resin and their nanocomposites [Colour figure can be viewed at wileyonlinelibrary.com]**TABLE 2** Values of the effective activation energy E , A' , and R^2 for neat novolac resin and their nanocomposites obtained from dynamic differential scanning calorimetry tests at different heating rates

o-MWCNT content	E , kJ/mol	A'	R^2
0	198 ± 1	23.8 ± 0.3	0.99
0.1 wt%	220 ± 2	26.5 ± 0.4	0.98
0.4 wt%	236 ± 2	28.4 ± 0.4	0.96
1.0 wt%	207 ± 3	24.9 ± 0.5	0.99

Abbreviation: o-MWCNT, oxidized multi-walled carbon nanotube.

activation energy of the crosslinking reaction. These OH functional groups reacted with methylene groups of the novolac resin, leading to the attachment of phenolic molecules to the o-MWCNTs and delaying the curing onset temperature. In a previous work, it was shown that in epoxy and epoxy-phenolic resins beyond 0.4 wt%, the o-MWCNTs strongly tend to agglomerate.²⁵ In the case of the sample containing 1.0 wt% o-MWCNTs, agglomeration is expected to be higher, and hence, the amount of OH groups available to react with the resin are expected to significantly decrease. This dispersion effect can be related to the decrease of the effective activation energy observed for sample containing 1.0 wt% o-MWCNTs.

The thermal decomposition process of the nanocomposites was studied by TGA. Figure 5 shows the different stages observed within this process in dotted lines. Below 120°C, a slight weight loss (about 3%) associated to the removal of the absorbed moisture was observed. Between 120°C and 390°C, a weight loss of about 9% to 11%, which can be attributed to structural changes in the novolac resin, was found. After 400°C, the rate of degradation of the samples rapidly increased. The remaining weights at 800°C were 49% and 52% for sample neat novolac and the containing 1.0 wt% o-MWCNTs, respectively. In this stage, samples presented similar decomposition behavior, characterized by the thermal dissociation of the relatively weak bonds with the release of gaseous phenol, methyl derivatives and other

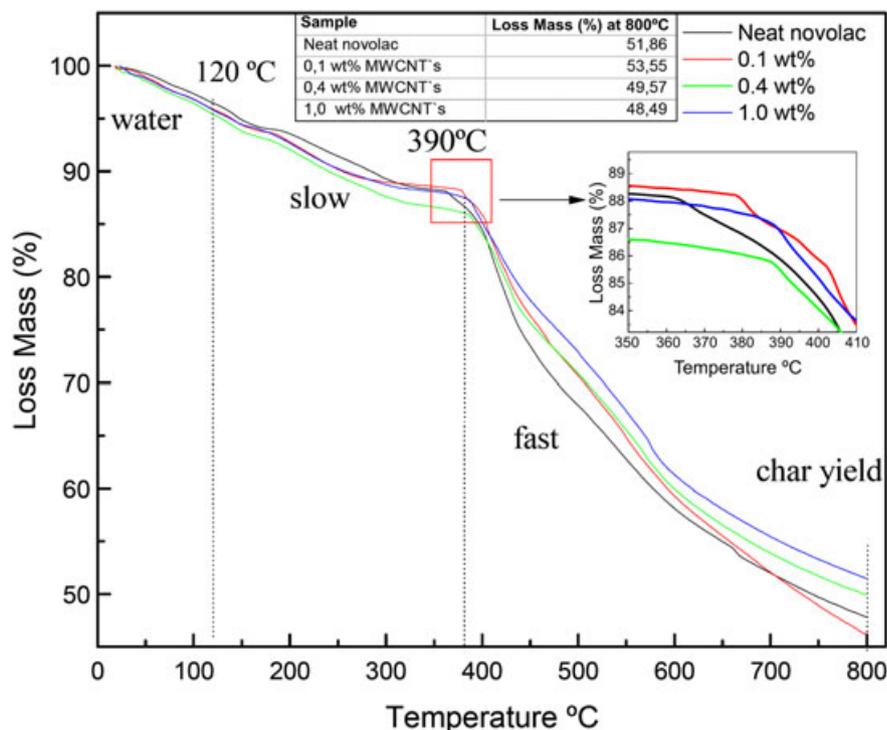


FIGURE 5 Thermogravimetric analysis curves for neat novolac resin and the nanocomposites at $\beta = 10^\circ\text{C}/\text{min}$ in N_2 [Colour figure can be viewed at wileyonlinelibrary.com]

products.²⁸ In addition, an increasing trend of char yield values in samples containing 0.4 and 1.0 wt% o-MWCNTs was observed indicating the better flame retardant properties induced by the presence of the o-MWCNTs.

Similar behavior in terms of thermal stability in inert atmosphere of polymer/MWCNTs nanocomposites has been previously reported in the literature. Wu et al²⁹ found that for polylactide-based nanocomposites, the presence of carboxylic and purified MWCNTs retards the thermal depolymerization of polylactide. Bikiaris et al³⁰ also observed a significant increase of thermal stability of isotactic polypropylene nanocomposites due to the presence of MWCNTs. This improvement of thermal stability was attributed to superficial modification, barrier effects, and thermal conductive effects of MWCNTs.^{29,30}

4 | CONCLUSIONS

The curing behavior of neat novolac and its nanocomposites with o-MWCNTs was studied by means of dynamic DSC analysis. Comparison of the kinetic parameters indicated that the curing mechanisms of neat novolac and its nanocomposites are similar. The dependence of the activation energy on the curing conversion was determined using the isoconversional KAS method. The results revealed that the effective activation energy (E) of both, neat novolac and its nanocomposites, depends on the curing conversion, suggesting the complexity of the overall reaction kinetics. Moreover, the presence of o-MWCNTs led to an increase of the effective activation energy values respect to that of neat novolac. This change in the effective activation energy was attributed to an increase of viscosity, due to the addition of o-MWCNTs. The results obtained from TGA analysis showed that the thermal decomposition of the novolac system was enhanced by increasing the o-MWCNTs content and for samples containing 0.4 and 1.0 wt% o-MWCNTs presented increased char yield values,

indicating an improvement of flame retardancy. From the above results, it is clear that the presence of carbon nanotubes significantly affects the curing kinetics and the thermal stability of the novolac resin being this effect more important as the filler content increases.

REFERENCES

1. Reghunadhan Nair CP. Advances in addition-cure phenolic resins. *Prog Polym Sci.* 2004;29:401-498.
2. Wu H, Chu P. Degradation kinetics of functionalized novolac resins. *Polym Degrad Stab.* 2010;95:1849-1855.
3. Bu Z, Hu J, Li B. Novel silicon-modified phenolic novolac resins: non-isothermal curing kinetics, and mechanical and thermal properties of their biofiber-reinforced composites. *Thermochimica Acta.* 2014;575:244-253.
4. Zhang C, Binienda W, Zeng L, Ye X, Chen S. Kinetic study of the novolac resin curing process using model fitting and model-free methods. *Thermochimica Acta.* 2011;523:63-69.
5. Zhong Y, Wu W, Wu R, Luo Q, Wang Z. The flame retarding mechanism of the novolac as char agent with the fire retardant containing phosphoro use nitrogen in thermoplastic poly(ether ester) elastomer system. *Polym Degrad Stab.* 2014;105:166-177.
6. Bahramian AR. Pyrolysis and flammability properties of novolac/graphite nanocomposites. *Fire Saf J.* 2013;61:265-273.
7. Jackson DM, Oliveira FB, Derval SR, Christian G, Alain C, Elisabet F. Renewable resources as reinforcement of polymeric matrices: composites based on phenolic thermosets and chemically modified sisal fibers. *Macromol Biosci.* 2007;7:1121-1131.
8. Faulstich P, Elisabete F. Unmodified and modified surface sisal fibers as reinforcement of phenolic and lignophenolic matrices composites: thermal analyses of fibers and composites. *Macromol Mater Eng.* 2006;291:405-417.
9. Natali M, Monti M, Puglia D, Kenny JM, Torre L. Ablative properties of carbon black and MWNT/phenolic composites. *Composites: Part A.* 2012;43:174-182.
10. Zabihi O, Khodabandeh A, Mostafavi SM. Preparation, optimization and thermal characterization of a novel conductive thermoset nanocomposite containing polythiophene nanoparticle using dynamic thermal analysis. *Polym Degrad Stab.* 2012;97:3-13.

11. da Silva Santos R, de Souza AA, De Paoli M-A, de Souza CML. Cardanol-formaldehyde thermoset composites reinforced with buriti fibers: preparation and characterization. *Composites Part A*. 2010;41:1123-1129.
12. Park JM, Kwon D-J, Wang Z-J, et al. Effects of carbon nanotubes and carbon fiber reinforcements on thermal conductivity and ablation properties of carbon/phenolic composites. *Compos Part B Eng*. 2014;67:22-29.
13. Song SA, Chung YS, Kim SS. The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles. *Composites Science and Technology*. 2014;103:85-93.
14. Park B, Kadla J. Thermal degradation kinetics of resole phenol-formaldehyde resin/multi-walled carbon nanotube/cellulose nanocomposite. *Thermochimica Acta*. 2012;540:107-115.
15. Tejado A, Kortaberria G, Labidia J, Echeverria JM, Mondragon I. Isoconversional kinetic analysis of novolac-type lignophenolic resins cure. *Thermochimica Acta*. 2008;471:80
16. Domínguez JC, Alonso MV, Oliet M, Rojo E, Rodríguez F. Kinetic study of a phenolic-novolac resin curing process by rheological and DSC analysis. *Thermochimica Acta*. 2010;498:39-44.
17. Guo J, Lin K, Xu Z. Curing kinetic analysis of phenolic resin filled with nonmetallic materials reclaimed from waste printed circuit boards. *Thermochimica Acta*. 2013;556:13-17.
18. Ozawa T. Kinetic analysis of derivative curves in thermal analysis. *J Thermal Anal*. 1970;2:301-324.
19. Borchardt HJ, Daniels F. The application of differential thermal analysis to the study of reaction kinetics. *J Am Chem Soc*. 1956;79:41-46.
20. Kissinger HE. Reaction kinetics in differential thermal analysis. *Anal Chem*. 1957;29:1702-1706.
21. Popescu C. Integral method to analyze the kinetics of heterogeneous reactions under non-isothermal conditions: a variant on the Ozawa-Flynn-Wall method. *Thermochimica Acta*. 1996;285:309-323.
22. Vyazovki S, Sbirrazzuoli N. Isoconversional kinetic analysis of thermally stimulated processes in polymers macromol. *Rapid Commun*. 2006;27:1515-1532.
23. Kandelbauer A, Wulleza G, Mahendran A, Taudes I, Widsten P. Model-free kinetic analysis of melamine-formaldehyde resin cure. *Chem Eng J*. 2009;152:556-565.
24. Coats CAW, Redfern JP. Kinetic parameters from thermogravimetric data. *Nature*. 1964;201:68.
25. Morales Arias JP, Escobar MM, Vazquez A. Modeling of dynamic mechanical properties of epoxy and epoxy-phenolic reinforced with multi wall-carbon nanotubes. *Journal of Composite Materials*. 2014;48:2001-2009.
26. Wan J, Wang S, Li C, et al. Effect of molecular weight and molecular weight distribution on cure reaction of novolac with hexamethylenetetramine and properties of related composites. *Thermochimica Acta*. 2012;530:32-41.
27. Choi W, Shanmugaraj A, Ryu S. Study on the effect of phenol anchored multiwall carbon nanotube on the curing kinetics of epoxy/novolac resins. *Thermochimica Acta*. 2010;506:77-81.
28. Wang J, Jiang H, Jiang N. Study on the pyrolysis of phenol-formaldehyde (PF) resin and modified PF resin. *Thermochimica Acta*. 2009;496:136-142.
29. Wu D, Wu L, Zhang M, Zhao Y. Viscoelasticity and thermal stability of polylactide composites with various functionalized carbon nanotubes. *Polym Degrad Stab*. 2008;93:1577-1584.
30. Bikiaris D, Vassiliou A, Chrissafis K, Paraskevopoulos K, Jannakoudakis A, Docoslis A. Effect of acid treated multi-walled carbon nanotubes on the mechanical, permeability, thermal properties and thermo-oxidative stability of isotactic polypropylene. *Polym Degrad Stab*. 2008;93:952-967.

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