

Cure Kinetic of Polyurethane/Fluorinated POSS Hybrid

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ABSTRACT

One of the decisive factors in obtaining the desired properties in coatings is their complete curing, which necessitates the study of kinetics of curing. In recent years, many studies have been conducted on the use of polyhedral oligomeric silsesquioxane (POSS) in coatings. Creating functional groups on POSS and using it in formulation can create new or improve the properties of coatings. In this study, the cure kinetics between hydroxyl functional acrylic resin, aliphatic polyisocyanate and fluorinated POSS with terminal hydroxyl group (F-POSS-OH) was studied using both the Malek and model-free isoconversional method (Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose) by DSC. The parameters of the cure kinetic equation for both systems were calculated and the effect of F-POSS-OH on the activation energy of polyurethane systems is investigated by free models. The results are shown that the m parameter in the cure kinetic equation for the coatings containing the F-POSS-OH increased, which indicates an increase in the autocatalytic effect of the curing system. Also, in the free model, the F-POSS-OH was reduced the activation energy of reaction. Prog. Color Colorants Coat. 13 (2020), 63-73 © Institute for Color Science and Technology.

1. Introduction

Recently, the use of hybrid compounds has increased because they exhibit advantageous properties of organic compounds, such as flexibility, as well as those of inorganic compounds, such as thermal stability and high hardness [1]. One of the newly used hybrid compounds in polymers is polyhedral oligomeric silsesquioxane (POSS). Due to the cage structure, and 1-3 nm particle size range, POSS improves some properties of polymers such as physical and chemical properties, dielectric properties, thermal stability, etc [2].

The POSS compounds can appear as three forms in the matrix of polymers. In the first case, the POSS

compounds are dispersed as filler and a neutral composition in the polymer matrix. In second case, the POSS compounds with an active agent group on their structure are appeared at the end of the chains or on the chains [3-6]. The third case, the POSS compounds with more than two active groups, can participate in chemical reactions and react chemically with polymer chains and be placed in the polymer structure to formed hybrid material [7-10]. If the POSS compounds have more than two functional groups and are involved in the reaction between the resin and the hardener, they can affect the kinetics of curing. The influences of functional nano particles and POSS have been investigated in various studies. In some studies, the

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improvement of some polyurethane properties such as thermal stability with using of POSS compounds has been reported. In some cases, the nonfunctional POSS has been added as nano filler to the polyurethane system; in some cases, the POSS compounds with active hydroxyl groups are used as the polyol in polyurethane system; and in other cases, the compound of the POSS with NCO active groups as the curing agent is used in the polyurethane system [11-16].

In this study, the effect of functional POSS with hydroxyl groups and fluorine groups on the curing kinetics of a polyurethane coating composed of acrylic polyol and aliphatic polyisocyanate has been investigated. The curing behaviors of both neat polyurethane system and F-POSS-OH/PU system were investigated by the curing kinetics using DSC. And, the curing temperature and the curing degree parameters obtained from DSC measurement at various heating rates showed the curing reactivity of both systems. And, activation energy and reaction order of both systems could be obtained to explain their curing behaviors. The curing kinetics was simulated by Málek method.

2. Experimental

2.1. Materials

Fluorinated polyhedral oligomeric silsesquioxane with hydroxyl group (F-POSS-OH) prepared from Institute for

Color Science and Technology (Iran), Hydroxyl-functional acrylic resin (60 % solution in 1:1 xylene/methoxy propyl acetate mixture) as polyol from Taak Resin Co. (Iran) and aliphatic polyisocyanate (75 % solution in 1:1 xylene/MPA mixture) as hardener from Bayer Co. (Germany). The schematic preparation and structure of F-POSS-OH presented in Figure 1.

2.2. Sample preparation and DSC measurement

The samples were prepared via gentle mixing of the hydroxyl-functional acrylic resin, aliphatic polyisocyanate as a curing agent and F-POSS-OH at the ambient temperature, while the ingredients were previously dried at 90 °C for 4 h in a vacuum oven under 10 mbar vacuums. The sample compositions and codes are tabulated in Table 1.

Differential scanning calorimeter (DSC) is used to study thermal analysis kinetics. According to the DSC curves, the curing degree of resins and the relationships among reaction rate, time and temperature can be measured, and therefore the kinetic equations can be determined. The rate of reaction $d\alpha/dt$ as a function of time was obtained from the rate of heat flow measured in DSC experiments (Eq. 1) [17].

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_T} = \frac{d(H_t/\Delta H_T)}{dt} \quad (1)$$

Table 1. The samples compositions.

Sample code	OH-functional acrylic resin (%)	aliphatic polyisocyanate (%)	F-POSS-OH (%)
A	73	27	0
B	69.35	25.65	5

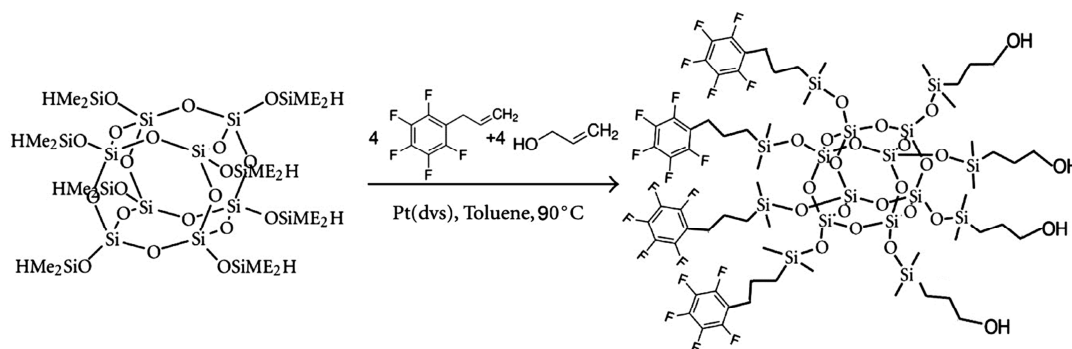


Figure 1: The schema preparation and structure of F-POSS-OH.

where H_t is the reaction heat released up to a time t , ΔH is the total reaction heat. So the degree of conversion at different times can be obtained by integrating the curve. By substituting them into the kinetic equation, kinetic parameters can be determined. Therefore, the basic equation describing curing process is obtained.

The non-isothermal reactions were investigated by using differential scanning calorimeter (DSC) Maia 200 F3, Netzsch (Germany). For this purpose, about 10 mg fresh mixtures were accurately measured, enclosed in an aluminum DSC crucible, and scanned from 298 to 573 K with an identical empty crucible as the reference. Dry nitrogen was used as protective gas, and the heating rates were controlled at 5, 10 and 15 K/min. Also, reaction characterization was done by Fourier transform infrared spectroscopy (Perkin Elmer FT-IR spectrophotometer) in the range of 4000–400 cm^{-1} .

3. Results and Discussion

3.1. FT-IR spectroscopy results

Fourier transformed infrared spectra of blank polyurethane and F-POSS-OH polyurethane before and after curing are shown in Figure 2. FT-IR spectrum of both systems before curing (Figure 2, a and b) showed very strong absorption peak at 2249 cm^{-1} attributed to the isocyanate ($-\text{N}=\text{C}=\text{O}$) group whereas after curing in both systems (Figure 2, c and d) the disappearance of the NCO peak at 2249 cm^{-1} are showed. These results confirm the complete cure process of materials.

3.2. Cure kinetics

3.2.1. Non-isothermal curing reaction kinetics

DSC thermograms for samples A and B at three different heating rates are shown in Figure 3. The initial reaction temperature (T_i), peak reaction temperature (T_p), and final reaction temperature (T_f) can be obtained from Figure 3, which are listed in Table 2.

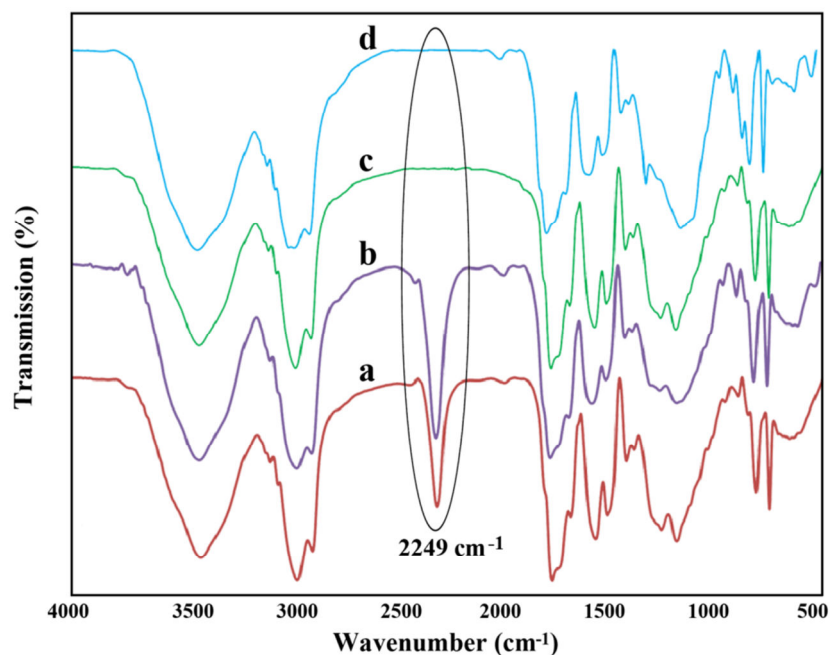
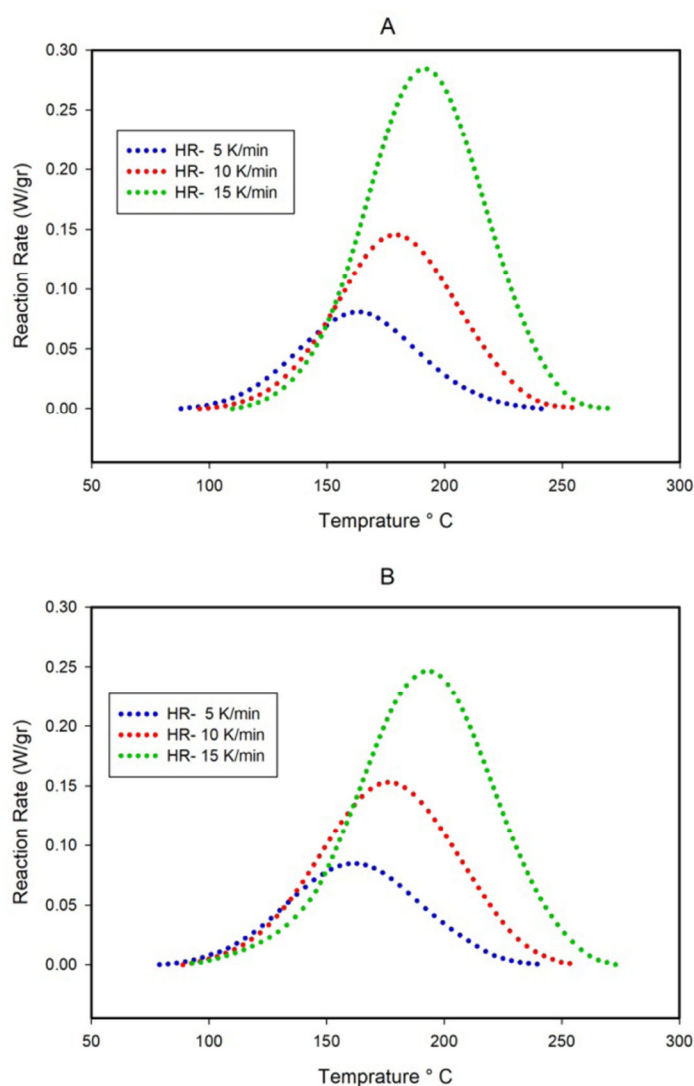


Figure 2: FT-IR spectra, a) blank PU before curing, b) F-POSS-OH/PU before curing, c) blank PU after curing, d) F-POSS-OH/PU after curing.

Table 2: Calorimetric data of N75/OH-functional acrylic resin system and N75/OH-functional acrylic/F-POSS-OH system.

Samples	Heating rates $^{\circ}\text{C}/\text{min}^{-1}$	Initial reaction temperature $T_i/^{\circ}\text{C}$	Peak reaction temperature $T_p/^{\circ}\text{C}$	Final reaction temperature $T_f/^{\circ}\text{C}$	Exothermic enthalpy $\Delta H/\text{J g}^{-1}$
N75/OH-functional acrylic resin	5	87.82	163.48	241.12	61.2
	10	95.79	179.4	255.06	57.3
	15	109.72	191.35	270.98	68.1
N75/OH-functional acrylic/F-POSS-OH system	5	78.86	161.4	243.11	71.28
	10	88.8	176.42	254.06	65.88
	15	92.8	193.34	271.98	70.24

**Figure 3:** Reaction rate of A and B for blank PU and 5 % wt F-POSS-OH/PU system as a function of temperature at different heating rates.

It can be found from Table 2 and 3 that the average of exothermic enthalpy of neat polyurethane system is about 7 J/g lower than that of F-POSS-OH polyurethane system. However, the peak reaction temperature and final reaction temperature of both neat polyurethane system and F-POSS-OH polyurethane system are basically the same. OH-functional acrylic resin and F-POSS-OH can both react with polyisocyanate. The schematic reaction is shown in Figure 4. In F-POSS-OH polyurethane system there is more functional group to reaction, therefore that is why the exothermic enthalpy was higher than neat polyurethane system. The reaction between OH-functional acrylic resin and polyisocyanate is the main reaction compared to the reaction between F-POSS-OH and polyisocyanate, which is why the peak reaction temperature and final reaction temperature of neat polyurethane system and F-POSS-OH polyurethane system are similar.

3.2.2. Determination of curing mechanism functions and reaction kinetic parameters

When polyurethane resin is cured at a constant heating rate β , the curing reaction rate can be expressed as a function of conversion and temperature (Equation 2).

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (2)$$

where A is pre-exponential factor and E_a is the

activation energy, $f(\alpha)$ is the reaction model, R is the gas constant, T is the absolute temperature and α is the reaction conversion that can be determined from the DSC runs as a fractional heat release. In this study, Málek method [18, 19] can be applied to determine an appropriate reaction model $f(\alpha)$ as shown in the following steps:

1) Using appropriate methods to obtain activation energy E_a .

2) According to the shapes and characteristic values of two special functions $y(\alpha)$ and $z(\alpha)$ to determine mechanism function $f(\alpha)$. Two special functions $y(\alpha)$ and $z(\alpha)$ are constructed with reaction could be identified by equations 3 and 4.

3) According to the mechanism function $f(\alpha)$, choosing proper methods to calculate kinetic parameters including n, m, and pre-exponential factor A.

$$y(\alpha) = \frac{d\alpha}{dt} \exp(\chi) \quad (3)$$

$$Z(\alpha) = \pi(\chi) \frac{d\alpha}{dt} \exp \times \frac{T}{\beta} \quad (4)$$

where χ is the reduced activation energy E_a/RT , $\pi(\chi)$ represents the integral of temperature. The expression is the approximate temperature integral proposed by Senum and Yang [20] as equations 5.

$$\pi(\chi) = \frac{\chi^3 + 18\chi^2 + 88\chi + 96}{\chi^4 + 20\chi^3 + 120\chi^2 + 240\chi + 120} \quad (5)$$

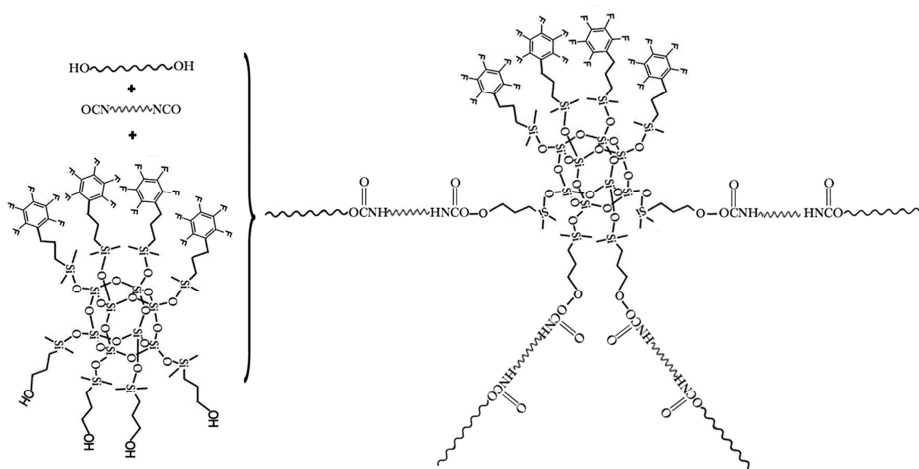


Figure 4: The schematic reaction of OH-functional acrylic resin and F-POSS-OH with polyisocyanate.

In this study to evaluate the apparent activation energy E_α , peak-maximum-evolution Kissinger method is used [21] as equation 6.

$$\ln \left[\frac{\beta/T_p^2}{1/T_p} \right] = -\frac{E_\alpha}{RT} \quad (6)$$

According to this method, E_α is obtained from the maximum reaction rate, where $d(\frac{d\alpha}{dt})/dt$ is zero at a constant heating rate. Therefore E_α is calculated by the fitting straight line of $\ln \left[\frac{\beta/T_p^2}{1/T_p} \right]$ versus $1/T_p$. The E_α for

neat polyurethane system is about 58.09 kJ/mol and for F-POSS-OH polyurethane system is about 50.21 kJ/mol.

The values of α_p , α_M and α_p^∞ can be determined by plotting $d\alpha/dt$ and normalized, $y(\alpha)$ and $z(\alpha)$ versus conversion. α_p was the curing degree corresponding to the maximum of $d\alpha/dt$, α_M was the curing degree corresponding to the maximum of $y(\alpha)$, and α_p^∞ was the curing degree corresponding to the maximum of $z(\alpha)$. The curves $y(\alpha)$ and $z(\alpha)$ are shown in Figure 5 and Table 3 shows the specific data.

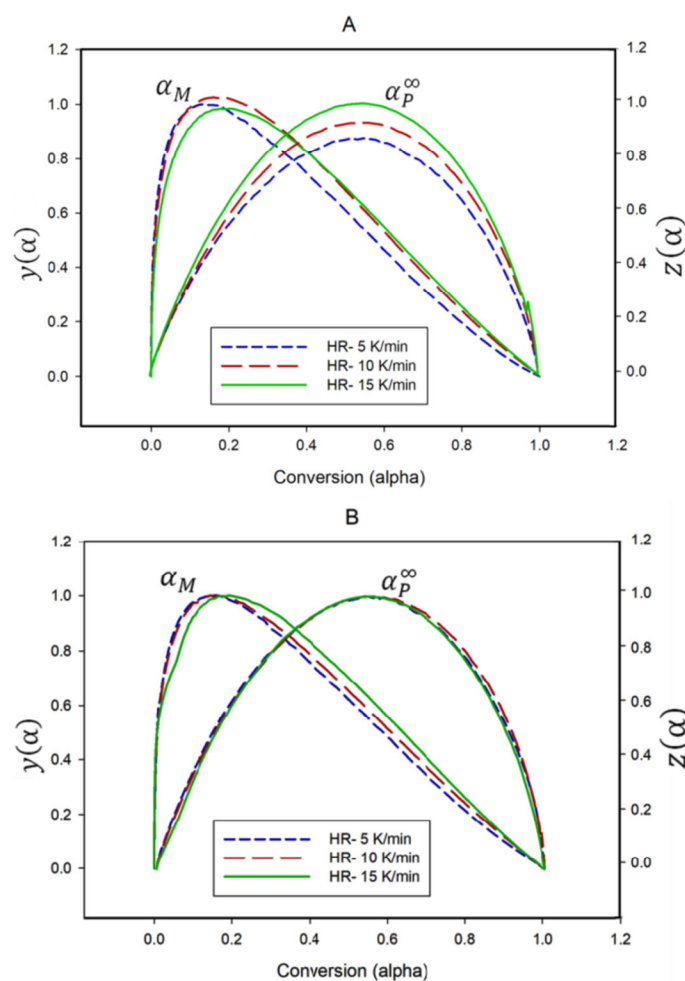


Figure 5: Normalized $y(\alpha)$ and $z(\alpha)$, and the dependence of reaction rate on conversion degree, A and B for blank PU and 5% wt F-POSS-OH /PU system.

Table 3: Parameters of SB(m, n) and α_p , α_M , and α_p^∞ of samples for different heating rates.

Samples	Heating rates °C/min	α_p	α_M	α_p^∞	n	m	lnA
N75/OH-functional acrylic resin	5	0.5198	0.1293	0.5510	1.29	0.19	10.46
	10	0.5173	0.1556	0.5641	1.15	0.21	10.64
	15	0.5119	0.1773	0.5437	1.31	0.28	10.51
Average	-	-	-	-	1.25	0.22	10.54
N75/OH-functional acrylic/F-POSS-OH system	5	0.5142	0.16	0.5430	1.38	0.26	8.36
	10	0.5206	0.17	0.5349	1.50	0.30	8.86
	15	0.5357	0.19	0.5496	1.14	0.27	8.30
Average	-	-	-	-	1.34	0.28	8.50

According to Málek method [19], when the value of $\alpha_p^\infty \neq 0.632$ and $0 < \alpha_M < 1$, the best description of the non-isothermal reaction rate is given by the empirical SB(m, n) model which is shown as equations 7.

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E\alpha}{RT}\right) \alpha^m (1 - \alpha)^n \quad (7)$$

where m and n are reaction orders. To find values of Málek's parameters for investigated samples which are presented in Table 3, equation 7 can be rewritten in the form is shown as equation 8.

$$\ln\left[\left(\frac{d\alpha}{dt}\right) \pi(\chi)\right] = \ln A + n \ln[\alpha^p (1 - \alpha)] \quad (8)$$

where $p = m/n$ is calculated using $P = \alpha_M / (1 - \alpha_M)$ [22]. By plotting $\ln\left[\left(\frac{d\alpha}{dt}\right) \pi(\chi)\right]$, versus $n \ln[\alpha^p (1 - \alpha)]$ For $0.2 < \alpha < 0.8$, values of Málek's parameters were obtained. N was obtained from the slope, m was calculated according to the values of n and p, and the

value of lnA was obtained from the intercept of fitting straight line. Results are shown in Table 3.

By replacing the values of parameters of SB in equation 7, the curing kinetic fitting equations of neat polyurethane system and F-POSS-OH polyurethane system were achieved, as equations 9 and 10.

$$\frac{d\alpha}{dt} = 37900 \exp\left(\frac{-6987.63}{T}\right) \alpha^{0.22} (1 - \alpha)^{1.25} \quad (9)$$

$$\frac{d\alpha}{dt} = 4920 \exp\left(\frac{-6039.63}{T}\right) \alpha^{0.28} (1 - \alpha)^{1.34} \quad (10)$$

Compared equation 9 with equation 10, was shown that the value of m of neat polyurethane system in equation 9 is less than that of F-POSS-OH polyurethane system in equation 10. That is to say, F-POSS-OH increases the autocatalytic effect in polyurethane curing. Compared the model fitting curves with experimental curves are shown in Figure 6.

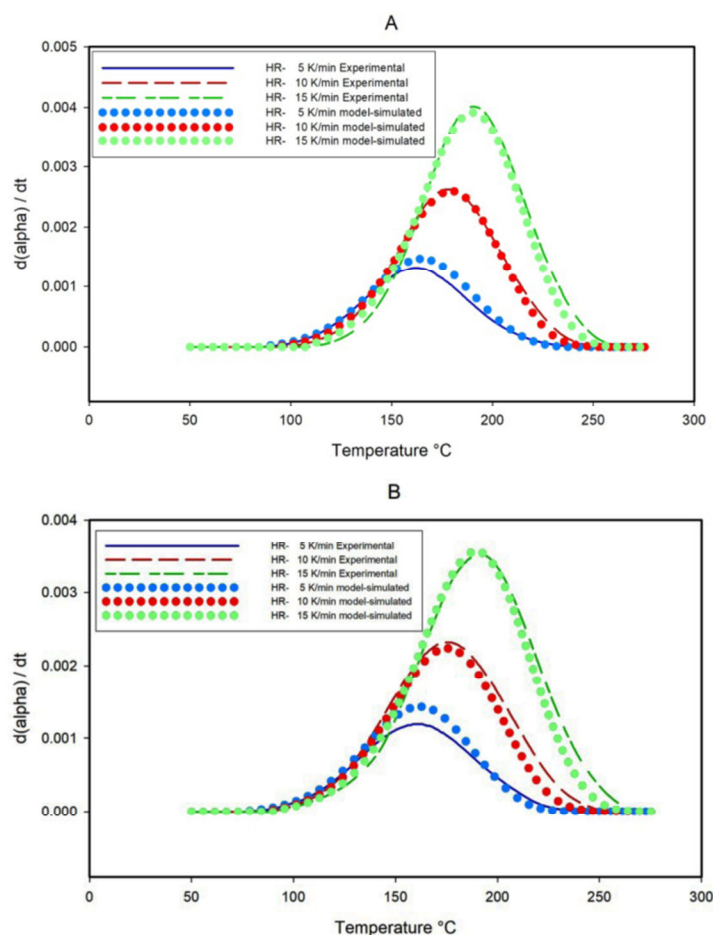


Figure 6: The variations of da/dt for the samples of A and B for blank PU and 5% wt F-POSS-OH/PU system. The experimental data were compared with the model-simulated reaction rate in SB(m, n) model.

3.3. Model-free isoconversional method

3.3.1. Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose analysis

If the activation energy is changing throughout the reaction as a function of the degree of cure, then the model-free isoconversional methods can be used to study kinetic of reaction. Flynn-Wall-Ozawa (FWO) analysis [23] and Kissinger-Akahira-Sunose (KAS) analysis [24] are two types of the model-free isoconversional methods. The value of activation energy is calculated according to equations 11 and 12 for FWO and KAS methods.

$$n\beta_i = \text{constant} - \frac{1.052 E_\alpha}{RT_{\alpha,i}} \quad (11)$$

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{constant} - \frac{E_\alpha}{RT_{\alpha,i}} \quad (12)$$

where the subscript α represents the conversion rate, E_α is the activation energy, $T_{\alpha,i}$ is the temperature at the heating rate β_i and conversion rate α . Under different heating rates, the dependence of non-isothermal curing conversion degree α on the temperature is shown in Figure 7.

The activation energy variations of the samples blank PU system and F-POSS-OH/PU system are shown in Figure 8. In both systems, E_α rises by increasing of reaction conversion. In F-POSS-OH/PU system, E_α rises steadily by increasing of the conversion. Whereas in blank PU system, initially by increasing of conversion, E_α rises steadily and at high conversion by a sharp rise. As known as that m parameter at Málek method stand for the contribution of autocatalytic reactions and this parameter for blank PU system was 0.22 and for F-POSS-PU system was 0.28. This is the reason of different results for activation energy in both systems.

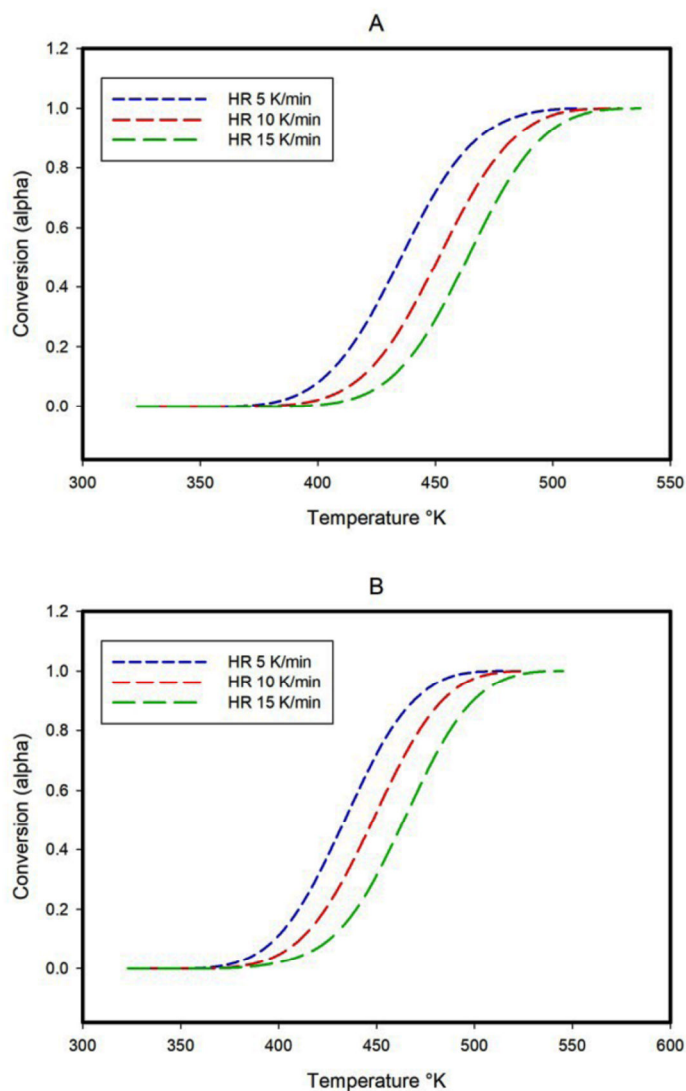


Figure 7: Dependence of non-isothermal curing conversion degree α on the temperature at different heating rates.

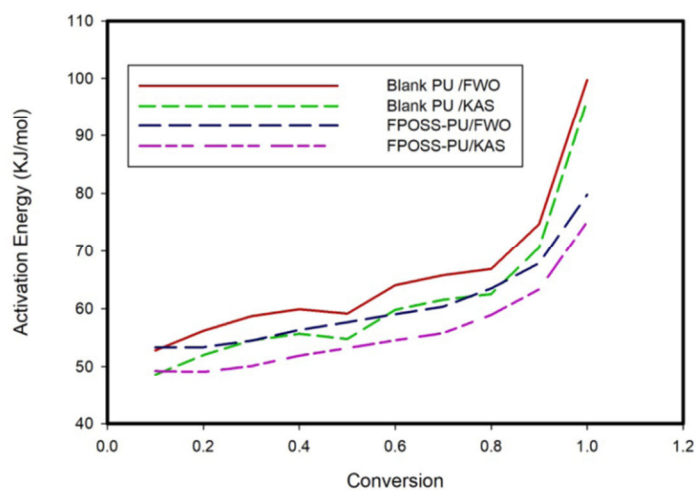


Figure 8: The variations of the activation energy versus conversion calculated by FWO and KAS methods for the samples of blank PU system and F-POSS-OH/PU system.

4. Conclusion

In this research the cure kinetic between hydroxyl functional acrylic resin, aliphatic polyisocyanate and F-POSS-OH to formation polyurethane/F-POSS-OH hybrid was studied. The results of FT-IR test showed that F-POSS-OH/polyurethane hybrid has been successfully to be formed. Then, the cure kinetics was studied by Malek and model-free isoconversional method. In F-POSS-OH/PU system for more functional group to react with polyisocyanate, exothermic enthalpy of neat polyurethane system is about 7 J/g lower than that of F-POSS-OH/PU system. Value of m parameter in Malek kinetic equation for neat

polyurethane system is less than that of F-POSS-OH/PU system that means F-POSS-OH increases the autocatalytic effect in polyurethane curing. In both systems activation energy rises by increasing of reaction conversion. In F-POSS-OH/PU system, activation energy rises steadily by increasing of the conversion. Whereas in blank PU system, initially by increasing of conversion, activation energy rises steadily and at high conversion by a sharp rise. With increase the conversion, the activation energy is increased, which can make it harder the access of active groups in curing process.

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