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Study on curing mechanism of DGEBA/nickel–imidazole system

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Abstract

The role of Im_6NiBr_2 on the polymerization of diglycidyl ether of bisphenol A (DGEBA) was examined. Scanning and isothermal calorimetry experiments were used to investigate the curing behavior over the range of curing catalyst concentration between 0.5 and 42 phr (parts per hundred). Based on the maximum values of reaction enthalpy and glass transition temperature (T_g), the best concentration of the curing catalyst was found to be 15 phr. One exothermic peak was observed at low and at high curing catalyst concentrations, while two exothermic peaks were observed at intermediate concentrations during the scanning calorimetry traces. It is suggested that there are two steps in the polymerization mechanism. The first step is the formation of 1:1 adduct between nickel–imidazole and epoxy oligomers. The second step is a chain growth polymerization reaction. It has been found that at high curing catalyst concentration the epoxy oligomers could react with nickel–imidazole and free imidazole ligand. *In situ* spectroscopy investigations showed that a fraction of nickel–imidazole was dissociated and then regenerated during the curing reaction. The regeneration can be explained by at least two disciplines of *N*-dealkylation and/or Hofmann elimination demonstrating the catalytic nature of the used nickel catalyst at certain conditions.

Keywords: Epoxy; Calorimetry; FT-IR; Nickel–imidazole; Curing mechanism

1. Introduction

Epoxy resins have been commercially servable for about 50 years and are now utilized in many industrial applications where special technical advantages are required. Characteristics like toughness, low shrinkage on curing, high adhesion to many substrates, good mechanical resistance, and versatility in composition make epoxy resins widely used in adhesives, laminates, coatings, and casting applications. Imidazole derivatives are very effective and fast curing catalysts for epoxy resins [1], although compositions of epoxy monomer and imidazoles have the main disadvantage of low storage stability. Efforts have been aimed at further stabilization of imidazoles, developing latent epoxy hardeners [2] by preparing transition-metal imidazole complexes [3–6]. It is known that imidazole derivatives can form complexes with d-block transition metals. These metal–imidazole complexes are able to initiate homopolymerization of epoxide groups via anionic polymerization reaction. Reactions with bifunctional epoxies lead to the formation of polymer network [7]. It was also recognized that the incorporation of metal–imidazole complexes into polymer matrices can improve mechanical, electrical, and thermal properties and chemical resistance [8,9]. Most of the last studies on epoxy/imidazole systems focused on the reaction of phenylglycidylether and imidazole derivatives [10–12]. The mechanism of imidazole cured epoxy resins has been reported in the literature [13,14]. The first step has been postulated to be the attack of the imino nitrogen on the terminal carbon of the epoxy group. This was believed to result in epoxide ring opening with the generation of 1:1 adduct between the imidazole and the resin containing a secondary alcohol group. This initial adduct could then be added to another molecule of epoxide monomer and then the polymerization would be proceeded. Kinetic studies [10,14] exhibited that adduct formation was a fast reaction relative to the polymerization. The proposed

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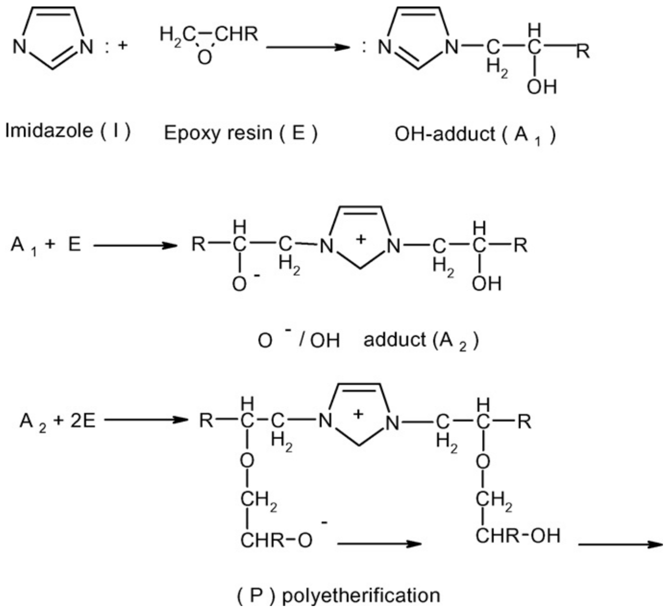

Fig. 1. Proposed mechanism [14] for curing epoxy groups with imidazole.

mechanism [14] for a diepoxide/midazole system consisting of both adducts formation and etherification reaction is shown in Fig. 1.

In the present study we have investigated the polymerization of DGEBA using Im_6NiBr_2 as a curing catalyst. Thermal and spectroscopic analyses were employed to gain insights into the curing mechanism. An extended range of curing catalyst concentrations was employed to clarify the effect of its concentration on the curing mechanism. Knowledge of the mechanism of network formation is of great importance because it can influence the processing conditions and final properties of cured materials. Imidazole–metal complexes could be used to improve the storage stability of epoxide/curing catalyst compositions at room temperatures, promising systems for developing new thermosetting materials.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) with a number average molecular weight of 377 g/mol and epoxy equivalent weight 185 g/eq was purchased from Sigma–Aldrich Canada. Imidazole (Im) and nickel dibromide three hydrates were purchased from Fluka. Acetone was used as a solvent without further purification. The synthesis of hexaquisimidazole–nickel dibromide, Im_6NiBr_2, is described elsewhere [15]. Characterization of the complex with FTIR and TGA produced results in agreement with the literature [15,16]. FTIR bands were observed at 614, 663, 757, 851, 918, 938, 1061, 1091, 1106, 1135, 1160, 1175, 1249, 1257, 1285, 1327, 1415, 1489, 1509, 1536, 1634, 689, 1716, 1792, 1876, 1919, 1942, 2111, 2202, 2268, 2324, 2359, 2574, 2610, 2712, 2862, 2956, and 3059 cm^{-1}. Results from elemental analysis and atomic absorption (ICP-Plasma technique) were in good accord with theoretical values (in parentheses): %C 34.49 (34.6), %H 3.92 (3.9), and % Ni 9.33 (9.4). The curing catalyst was dried under vacuum and then powdered to produce fine particulate. Compositions from 0.5 to 42 phr of the nickel salt were made directly into DGEBA prior to the polymerization experiments by mixing dispersion for a time of 10 min. Fig. 2 shows the structure of the reactants.

2.2. Instruments

Differential scanning calorimetry (DSC) studies were carried out with TA DSC Q 100 calorimeter under nitrogen atmosphere (50 cm^3/min). Exact weights of samples around 3 mg were run in sealed aluminum pans and an empty aluminum pan was used as reference. Dynamic DSC experiments at heating rate of 20 °C/min were performed from −30 °C to 330 °C with different epoxy/curing catalyst compositions. The glass transition temperature (T_g) was measured during the second scan using the midpoint method available at TA instrument software. Simultaneous thermal gravimetric analysis (TGA) and

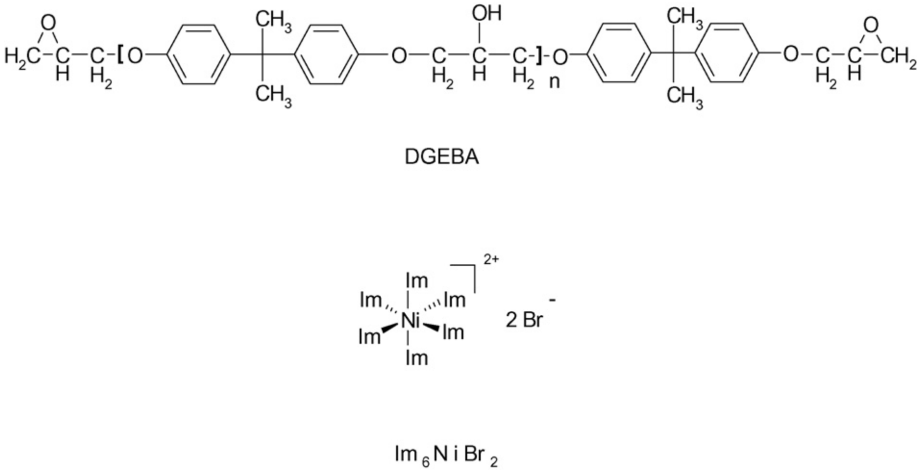

Fig. 2. Structure of the reactants.

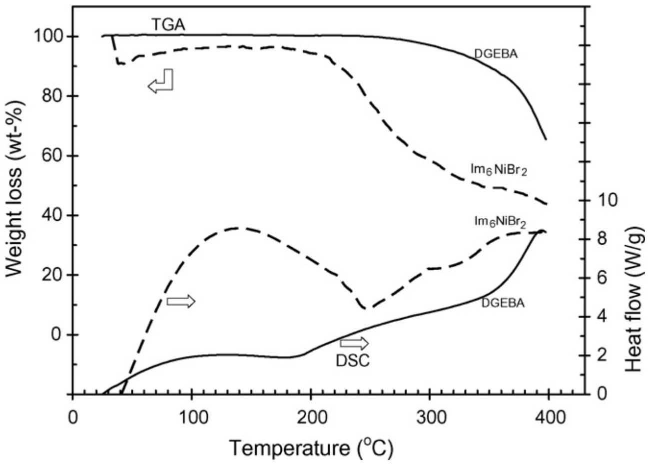

Fig. 3. Simultaneous TGA-DSC thermograms of DGEBA and Im_6NiBr_2 at 20 °C/min.

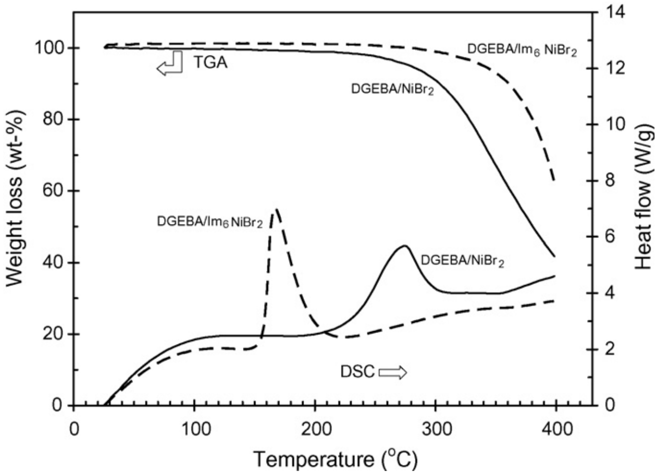

Fig. 4. Simultaneous TGA-DSC thermograms of $DGEBA/NiBr_2$ (15 phr) and $DGEBA/Im_6NiBr_2$ (15 phr) at 20 °C/min.

DSC experiments were made at 20 °C/min under high purity argon (40 cm^3/min) using a NETZSCH STA 409 PC thermal analyzer. *In situ* isothermal curing was carried out between KBr discs placed in a heatable stage inside the Bruker Tensor 27 Fourier transform-infrared (FTIR) spectrometer. Spectra were recorded using OPUS software at different time intervals over a period of up to 150 min. Each spectrum was scanned 32 times at a resolution of 4 cm^{-1}, from 400 to 4000 cm^{-1} wavenumber. The thickness of the film was controlled to provide suitable absorbance readings. Elemental analyses (C and H) were obtained with LECO CHN apparatus. The amount of nickel in the complex was measured by ICP-plasma atomic absorption technique using a Jobin Yvon JY 138 Ultrace instrument.

3. Results and discussion

3.1. Calorimetry of Im_6NiBr_2 and $DGEBA/Im_6NiBr_2$

According to the literature, there are three steps during the thermal decomposition of the Im_6NiBr_2 [16]. The dissociation of imidazole ligands should occur at temperatures below 200 °C. Fig. 3 displays curves of Im_6NiBr_2 and DGEBA recorded in a simultaneous TGA/DSC experiment showing that for the temperature range of interest for curing (<200 °C) there was no decomposition of either curing catalyst or epoxy resin. The thermal decomposition of DGEBA and Im_6NiBr_2 started approximately at 280 °C and 200 °C, respectively. At temperature below 200 °C the process of dissociation of Im_6NiBr_2 may produce free imidazole ligands in equilibrium with $NiBr_2$. It is worthy to note that the deviation observed in the baseline of Fig. 3 (TG curve) is due to instrument limitations (more time was needed to arrive at the equilibration in the first measurement).

Simultaneous TGA/DSC analyses were used to study thermal decomposition of $DGEBA/Im_6NiBr_2$ and $DGEBA/NiBr_2$ systems. In Fig. 4, at intermediary concentration of 15 phr of Im_6NiBr_2 the epoxy system showed a clear exothermic curing peak (DSC) at 170 °C while significant decomposition (TGA) was observed only above 300 °C. To check if $NiBr_2$ could have any effect on the decomposition or curing of DGEBA, the reaction of $DGEBA/NiBr_2$ (15 phr) was also studied (see Fig. 4). In this last case a single exothermic peak was observed with onset at approximately 210 °C. Although the onset of this peak was very similar to the onset of thermal degradation observed on those thermograms in Fig. 3, its intensity was much stronger

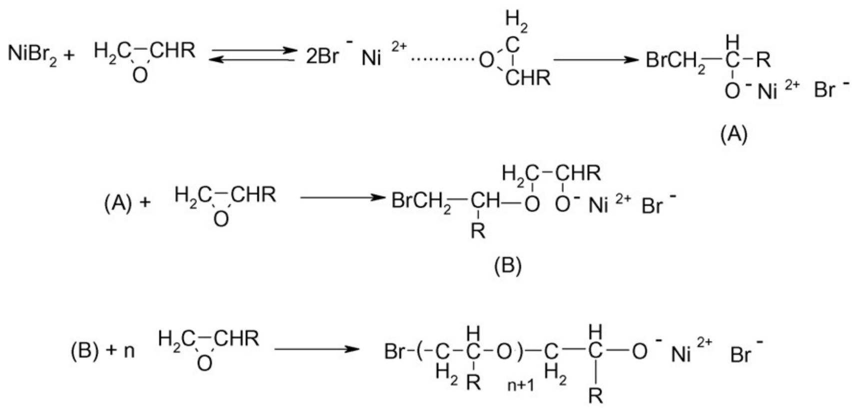

Fig. 5. Possible mechanism of interaction between DGEBA and $NiBr_2$.

and certainly most of the exothermic peak area is at a temperature range where thermal degradation is very slow. The second exothermic peak at intermediate Im_6NiBr_2 concentration (15 phr) with onset temperature of 230 °C is therefore attributed to interactions between DGEBA and $NiBr_2$. A probable mechanism for interaction between epoxy oligomers and $NiBr_2$ is presented in Fig. 5. Although the concentration of epoxy would be very low, this mechanism could be active at temperatures around 250 °C, still below the thermal degradation of DGEBA.

3.2. Scanning calorimetry of DGEBA/Im_6NiBr_2 system

Polymerization of DGEBA with Im_6NiBr_2 at several levels of loading was studied. The epoxy/curing catalyst ratio had a significant effect on the curing mechanism and the final properties of the cured samples. Fig. 6 addresses DSC curves of DGEBA cured with different amounts of 0.5, 1, 2.5, 5, 7.5, 10, 15, 20, and 30 phr Im_6NiBr_2. For this range of concentrations, the enthalpy of reaction increased when the concentration of curing catalyst was increased. From low curing catalyst concentrations (0.5–10 phr) a small exothermic peak was observed at temperatures above 220 °C.

At low concentrations most of the imidazole was consumed at temperatures below 200 °C. After consuming most of the imidazoles, the remaining epoxy groups were available for further reaction. From the simultaneous DSC/TGA curves shown in Fig. 4, it was clear that between temperature of 200 and 300 °C both curing and thermal degradation were present. Therefore, at low curing catalyst concentrations there was a limited curing below 200 °C followed by simultaneous thermal degradation and curing above 200 °C as well. At 15 phr and above loading only one exothermic peak was observed in Fig. 6 indicating that efficient curing took place. However, a clear indication of the influence of curing catalyst concentration on the kinetics of polymerization was found by observing shift in the temperature of the exothermic peak to low temperatures when its concentration was increased. The kinetic interpretation of these results is discussed in a separate paper.

Considering a compromise between the maximum enthalpy of reaction and minimum concentration of curing catalyst the best value of epoxy/Im_6NiBr_2 ratio is recognized to be 15 phr. When a different criterion was used to determine the optimum value of epoxy/Im_6NiBr_2 ratio, i.e. the compromise between the maximum T_g and minimum loading of nickel salt, the value of 15 phr was also evident (Fig. 7). Both the onset temperature and the peak temperature of the exothermic curve obtained during dynamic thermal scans decreased with increased curing catalyst concentration (see Table 1).

One interpretation that might be presented regarding the number of exothermic peaks in Fig. 6 is that at low curing catalyst concentrations (0.5, 1, and 2.5 phr) the network formation was not fully achieved during the first exotherm since the level of incorporated nickel salt was not enough to consume all epoxy groups. Thereby with the increasing temperature, the contribution of thermal degradation becomes more significant and hinders observing a second curing peak.

On the other hand, at the high curing catalyst concentrations typically 20 and 30 phr, the complete cure was obtained during the first exothermic peak. These observations were also verified by the inspection of reaction enthalpy and T_g values in Table 1. This means that most of epoxy groups were polymerized

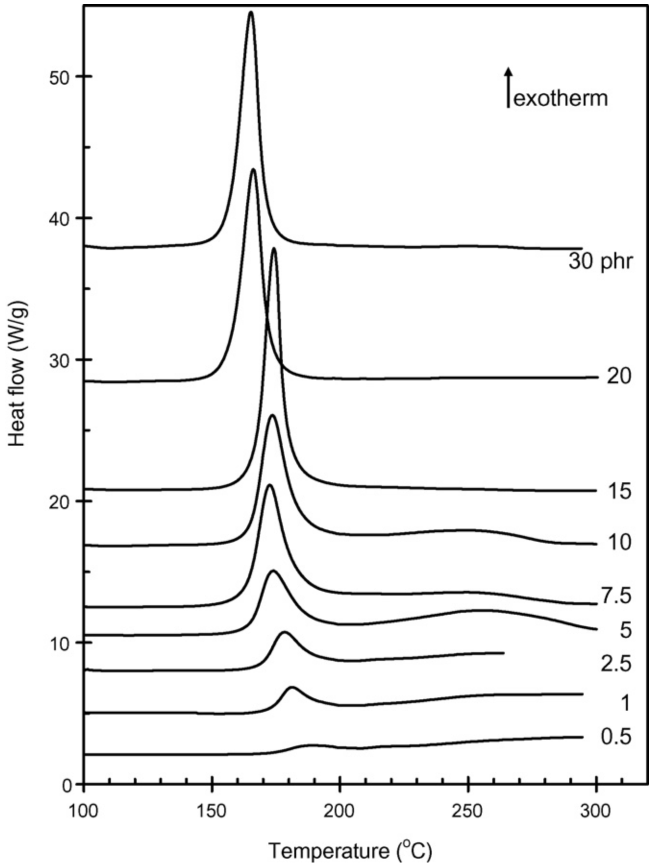

Fig. 6. DSC thermograms of DGEBA/Im_6NiBr_2 system at different concentrations (phr) obtained at scanning rate of 20 °C/min (curves have been stacked horizontally for clarity).

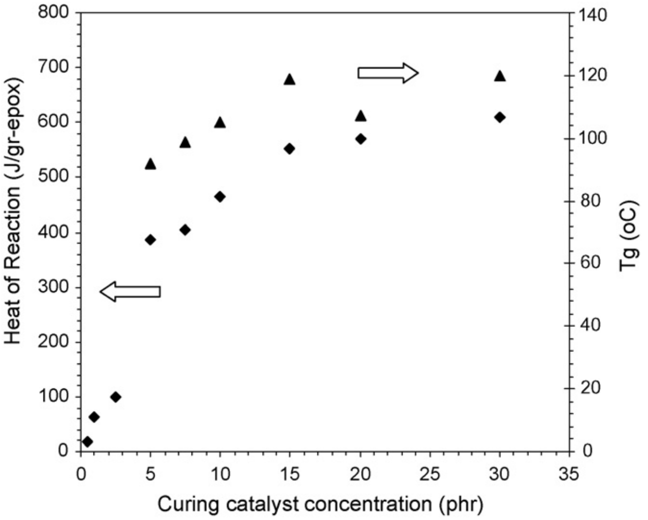

Fig. 7. Effect of curing catalyst concentration on enthalpy of reaction and glass transition temperature of the cured samples.

Table 1
DSC thermograms data of DGEBA/Im_6NiBr_2 cure obtained at 20 °C/min

Im_6NiBr_2 (phr)	$T_{1,\text{onset}}$ (°C)	$T_{1,\max}$ (°C)	ΔH^* (J/g-epoxy)	$T_{2,\text{onset}}$ (°C)	$T_{2,\max}$ (°C)	T_g (°C)
0.5	165	187	19	–	–	–
1	159	181	64	–	–	–
2.5	153	178	99	–	–	–
5	150	174	387	207	258	92
7.5	145	173	406	224	253	99
10	143	174	466	217	253	105
15	139	174	553	–	–	119
20	134	166	572	–	–	107
30	134	165	610	–	–	120

T_1 and T_2 are corresponding to the first and the second exothermic peaks, respectively.

[*] ΔH shows the total reaction heat in terms of Joule per gram epoxy resin.

and there were minimal free epoxy groups for further reaction responsible for the appearance a second exotherm. However, the first exothermic peak finished at 206 and 189 °C for 20 and 30 phr, respectively. At these relatively low temperatures the contribution of thermal degradation on the curing reaction is expected to be negligible.

To clarify the contribution of thermal degradation on the dynamically cured samples, we have examined simultaneous DSC/TGA thermograms of the epoxy involving the lowest and the highest amount of the nickel salt, see Fig. 8. Thermal degradation for the lowest concentration was reasonable at temperatures above 230 °C. Also, there was no thermal degradation for the epoxy loaded with 30 phr nickel salt in the temperature range of the first exothermic peak.

At intermediate concentrations of 5, 7.5, and 10 phr a second distinct exotherm was clearly observed. This showed that at the end of the first exothermic peak there were still free epoxy groups capable of additional reactions. This also means that the network obtained with these intermediate concentrations were more stable towards thermal degradation and consequently a second exothermic peak is seen as well.

Two important results are derived from the dynamic DSC measurements. First, the heat of reaction for the first exothermic peak was proportional to initial concentration of the curing catalyst. Second, at the end of the first exothermic peak there might be species in the reaction environment which were able to react with the remained epoxy groups leading to the second exotherm, most likely with some contribution from free $NiBr_2$.

3.3. Isothermal calorimetry of DGEBA/Im_6NiBr_2 system

It was shown in the literature [14,18] that curing of epoxy resin with 1-unsubstituted imidazoles exhibited different exothermic peaks. It should be noted that interactions between DGEBA and Im_6NiBr_2 could be feasible at temperatures lower than the Im_6NiBr_2 dissociation temperature. A qualitative test was carried out to verify the cure of DGEBA with Im_6NiBr_2 at low temperatures. The time necessary to achieve apparently fully cured materials was measured. As it is shown in Fig. 9, increasing the temperature from 60 to 70 °C decreased the time to complete curing. This effect was more noticeable at low concentrations. From results in Fig. 9, one can only conclude that curing of DGEBA with Im_6NiBr_2 was active at temperatures well below those of exothermic peaks observed in Fig. 6.

Isothermal DSC experiments were conducted with different epoxy/curing catalyst compositions to obtain further insights into the curing mechanism and structural properties. In Fig. 10,

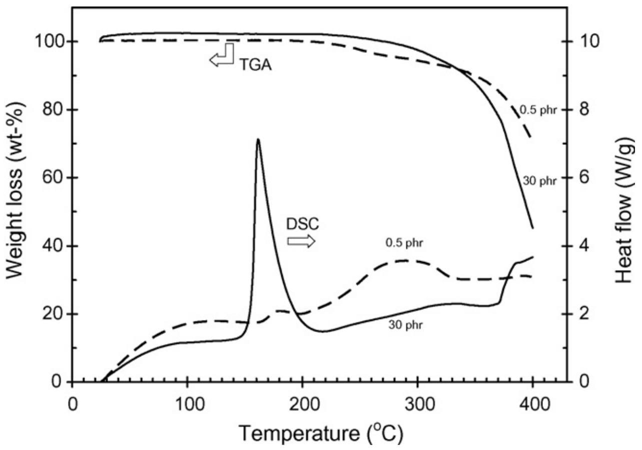

Fig. 8. Simultaneous DSC-TGA curves of the DGEBA cured with 0.5 phr (- -) and 30 phr (–) of Im_6NiBr_2 obtained with scanning rate of 20 °C/min.

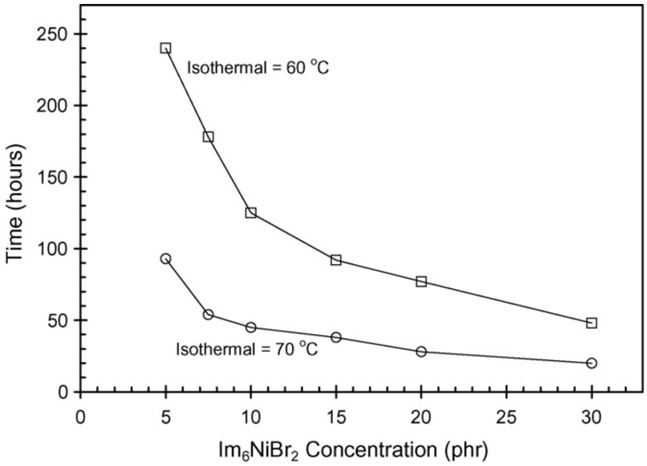

Fig. 9. Times necessary to achieve complete cure for DGEBA/Im_6NiBr_2 polymerization at isothermal conditions.

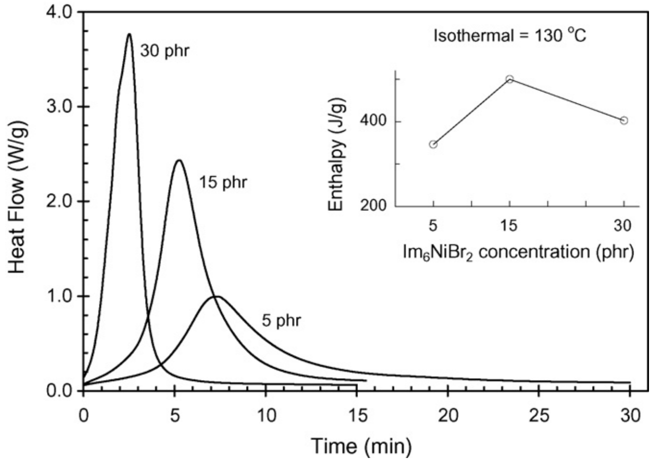

Fig. 10. DSC thermograms for DGEBA/Im_6NiBr_2 polymerization obtained isothermally at 130 °C from concentrations of 5, 15, and 30 phr.

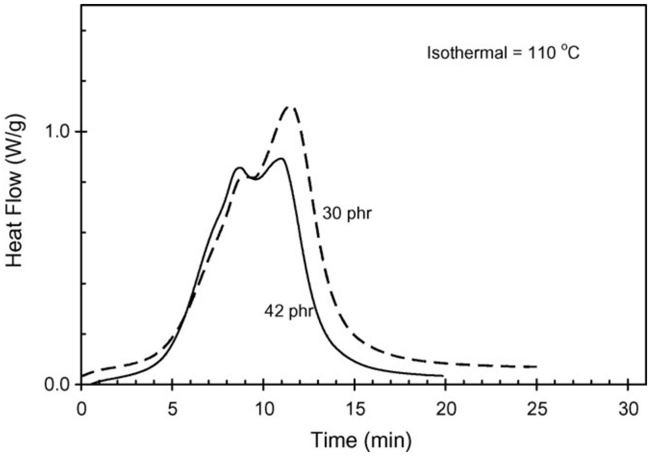

Fig. 11. DSC thermograms for DGEBA/Im_6NiBr_2 polymerization obtained isothermally at 110 °C from concentrations of 30 and 42 phr.

one exothermic peak was observed for the samples cured isothermally at 130 °C for the curing catalyst concentrations of 5, 15, and 30 phr. As expected, for curing at same isothermal temperature it was observed that increasing Im_6NiBr_2 concentration has decreased the time needed to complete curing. A shoulder prior to the maximum of the DSC curve was observed for the system loaded with 30 phr nickel salt.

For samples cured isothermally at 130 °C, the reaction enthalpy showed a maximum at the intermediate concentration 15 phr (see Fig. 10). Most likely at high curing catalyst concentration (30 phr) fast reaction in the beginning of curing reaction decreased mobility of epoxy groups and consequently affected the capacity to achieve maximum conversions. This observation is in agreement with the literature [14]. It was decided then to extend this investigation by running high curing catalyst concentrations at a smaller isothermal temperature in an attempt to obtain further information about the curing mechanism. As it was displayed in Fig. 11, for curing catalyst concentration of 30 phr two exothermic peaks were recognized at isothermal curing at 110 °C. Increasing the curing catalyst concentration even further to 42 phr which could be a very high level of loading in terms of practical applications also showed two peaks. The reaction enthalpy was 477 and 450 J/g-epoxy for 30 and 42 phr, respectively. Again, increasing the concentration of Im_6NiBr_2 has decreased the total reaction enthalpy. Since the selected isothermal temperature (110 °C) was lower than the T_g (about 120 °C in Table 1), system will first vitrify and then if give enough time undergo gelation. In many systems the mobility in the vitrified state is too low to guarantee additional reaction. However, it seems that there is a restriction to reach full curing at high concentrations of curing catalyst under isothermal conditions.

According to the above observations, a model having two steps in polymerization mechanism is proposed for the studied curing reaction and illustrated in Fig. 12. Similar mechanism has been used to describe the use of 1-substituted imidazoles

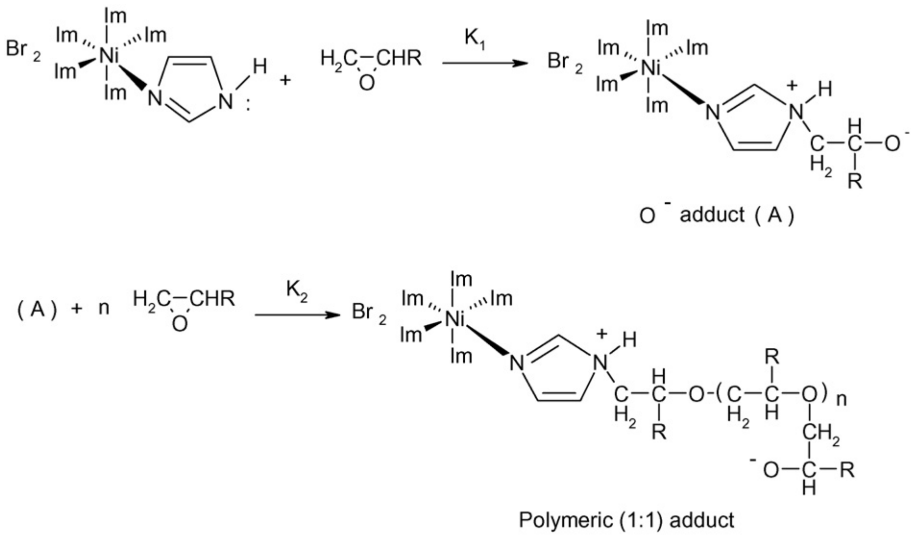

Fig. 12. Proposed model for a two-step mechanism in the DGEBA/Im_6NiBr_2 polymerization.

in the curing of epoxy resins [13,17]. The two-step mechanism is particularly important to describe the two peaks observed in isothermal curing with high concentrations of Im_6NiBr_2 (30 and 42 phr). Heise and Martin [18] have also reported two distinct exothermic peaks when 2-ethyl-4-methyl imidazole was used as curing catalyst for epoxy resin at low and at high concentrations. These authors attributed the first and the second exotherms to adduct formation and anionic chain growth polymerization, respectively.

3.4. FTIR spectroscopy of DGEBA/Im_6NiBr_2 polymerization

In order to obtain more details on the curing mechanism of DGEBA/Im_6NiBr_2 system, *in situ* FTIR study was carried out using a series of Im_6NiBr_2 concentrations (5, 7.5, 10, 15, 20, and 30 phr) over the temperature range from 145 to 175 °C. Four isothermal temperatures were selected for each composition. A broad range of curing catalyst concentrations was preferred to help clarifying the contribution of Im_6NiBr_2 in the mechanism. The isothermal temperature of 160 °C was common to the all compositions. Fig. 13 shows an example of FTIR spectra obtained at different times (from 1 to 120 min) for DGEBA cured with 15 phr of Im_6NiBr_2 at 160 °C.

Similar spectra were obtained for all other concentrations and temperatures investigated here. The epoxy group asymmetric stretching can be observed at 760, 914, and 970 cm^{-1}. The curing catalyst Im_6NiBr_2 showed 6 vibration bands in the region of 2700–3200 cm^{-1}. The N–H stretching of the free imidazole ligands should also be present in the same region. The hydroxyl group vibration band can be observed at 3300 cm^{-1}. It should be noted that the quantitative analysis of the N–H and epoxy group vibration (at 914 cm^{-1}) was not possible due to superposition. As it is seen in Fig. 13, the intensity of the band at 970 cm^{-1} decreased over time indicating curing to be complete. Similarly, the intensity of the band at 3300 cm^{-1} (OH group) increased over time. Changes in area of peaks were used to understand the mechanism. The vibrations of carbonyl group and carbon double bond appeared after certain curing times for the most compositions. The curing times necessary for observation of those groups were dependent on temperature and epoxy/curing catalyst ratios. Several authors have already reported the appearance of double bond stretching in the

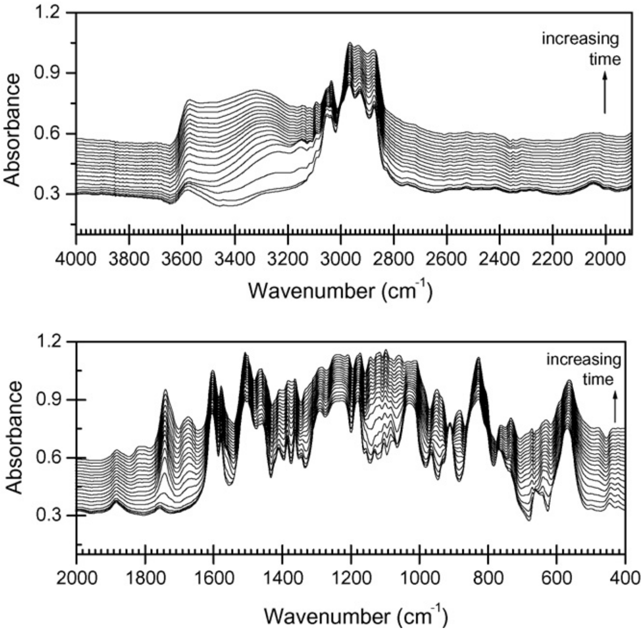

Fig. 13. FTIR spectra obtained at different times (from 1 to 120 min) for DGEBA cured with 15 phr of Im_6NiBr_2 at 160 °C (curves have been stacked for clarity).

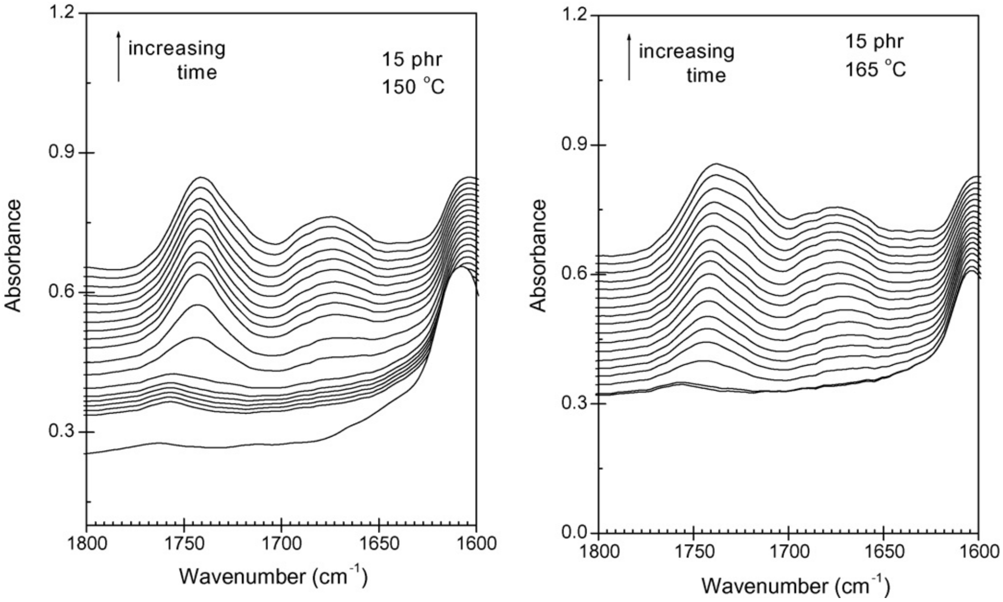

Fig. 14. Evolution of carbon double bond and carbonyl groups with time (from 1 to 120 min) during the cure of DGEBA with 15 phr of Im_6NiBr_2 at 150 and 165 °C (curves have been stacked for clarity).

range from 1650 to 1770 cm^{-1} in epoxy curing with imidazoles [13,19,20]. Fig. 14 shows the evolution of the carbon double bond and carbonyl group vibrations during the curing of epoxy resin with 15 phr of Im_6NiBr_2 at 150 and 165 °C at various curing times.

For each composition the time necessary to observe the carbon double bond peak was reduced with increased curing temperature. To set a better comparison, it was assumed that the minimum time necessary to observe the carbon double bond peak was the time when the normalized area under A1/A2 was higher than 0.1. These two peak areas are corresponding to the carbon double bond (A1, about at 1670 cm^{-1}) and the internal standard (A2, 1184 cm^{-1}) peaks. At low curing cat-

Table 2
Times necessary to observe (column 2) and to reach maximum peak area (column 3) of the carbon double bond from the analysis of FT-IR spectra at 160 °C

Im_6NiBr_2 concentration (phr)	Minimum time A1/A2 > 0.1 (min)	Time to reach maximum A1/A2 (min)
5	20	45
7.5	15	35
10	20	45
15	9	45
20	90	120
30	–	–

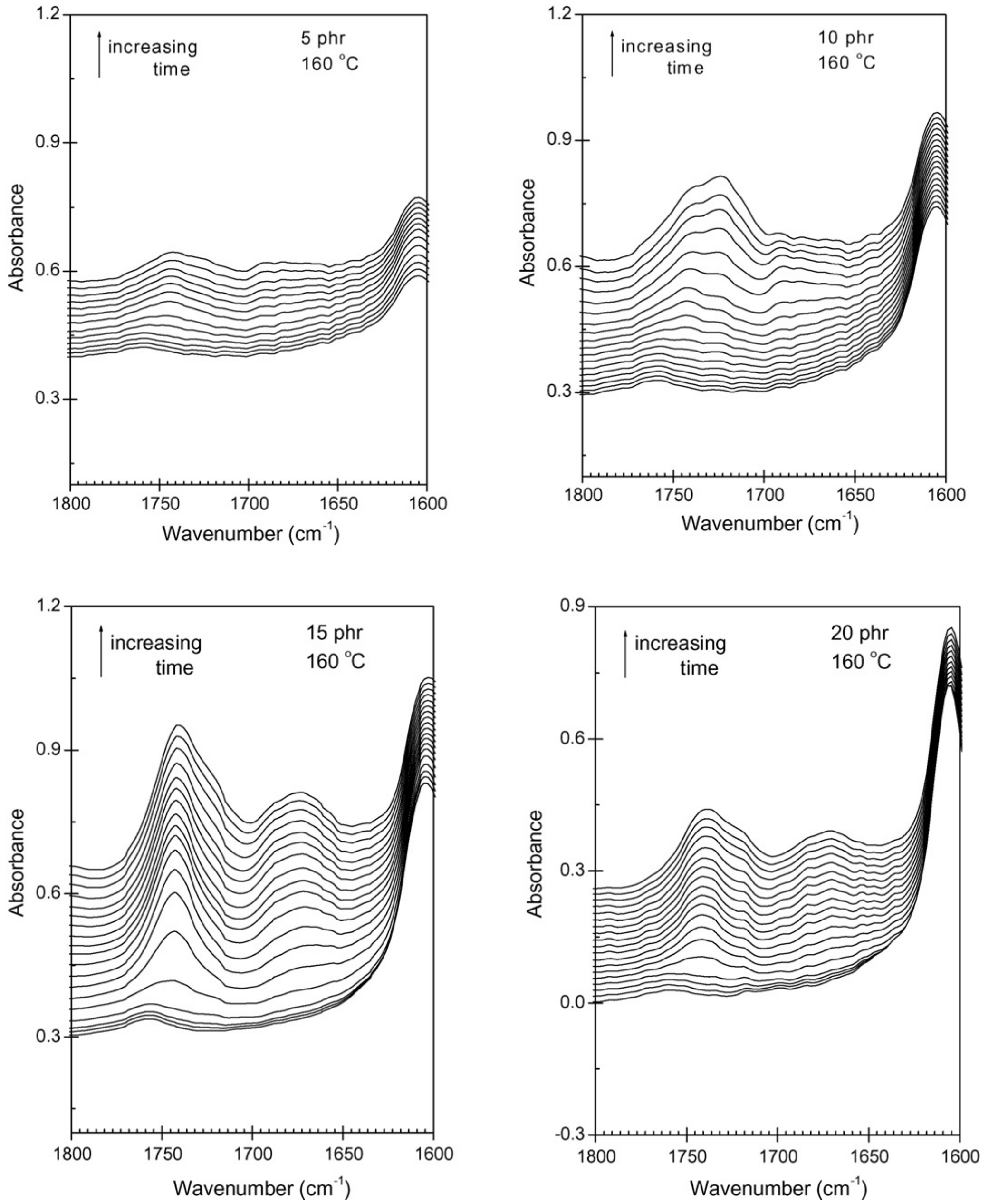

Fig. 15. Evolution of carbon double bond and carbonyl group with time (from 1 to 120 min) during the cure of DGEBA with different concentration of Im_6NiBr_2 at 160 °C (curves have been stacked for clarity).

alyst concentrations of 5, 7.5, and 10 phr the time necessary to observe the carbon double bond formation did not change considerably, see Table 2. The appearance of the carbon double bond was more noticeable in initial steps (9 min) of the curing reaction when it was carried out with concentration 15 phr. Further increase of curing catalyst concentration to 20 phr caused to observe the carbon double bond formation at longer times.

No peak for carbon double bond vibrations was observed when the epoxy cured with 30 phr of Im_6NiBr_2 at 160 °C. At temperatures lower than 160 °C there was evidence of carbon double bond formation at longer times only. This effect was significant at high concentration of Im_6NiBr_2. Also, this means that the contribution of the reaction path leading to carbon double bond formation is decreased at high curing catalyst concentration. There might be a competition between the catalytic polymerization pathway and the free imidazole interaction pathway at high level of nickel salt loading. More evidence supporting this suggestion was given by analysis of the area corresponding to carbon double bond in the FTIR spectra in Fig. 15.

For the isothermal temperature of 160 °C the normalized peak area of the carbon double bond (A1/A2 in Fig. 16) was reduced at high curing catalyst concentration at the same time. It was also observed that for the same Im_6NiBr_2 concentration, increasing the curing temperature has increased the A1/A2. This behavior was general for the other epoxy/curing catalyst compositions studied here. Evidences provided by literatures suggested that starting imidazole curing catalyst can be regenerated during the curing reaction [21,22]. It has been shown that there are two main pathways namely *N*-dealkylation and Hofmann elimination to regenerate the curing catalyst. The mechanism presented in Fig. 17 is in agreement with those previously proposed in the literature. The final product shown in Fig. 17 may also attribute to the isomerization of epoxy to aldehyde on a heating treatment [23].

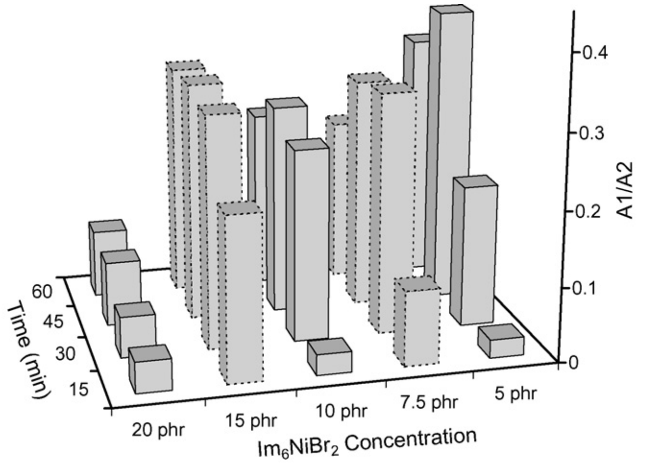

Fig. 16. Normalized area under peak of the carbon double bond for various DGEBA/Im_6NiBr_2 compositions cured at 160 °C.

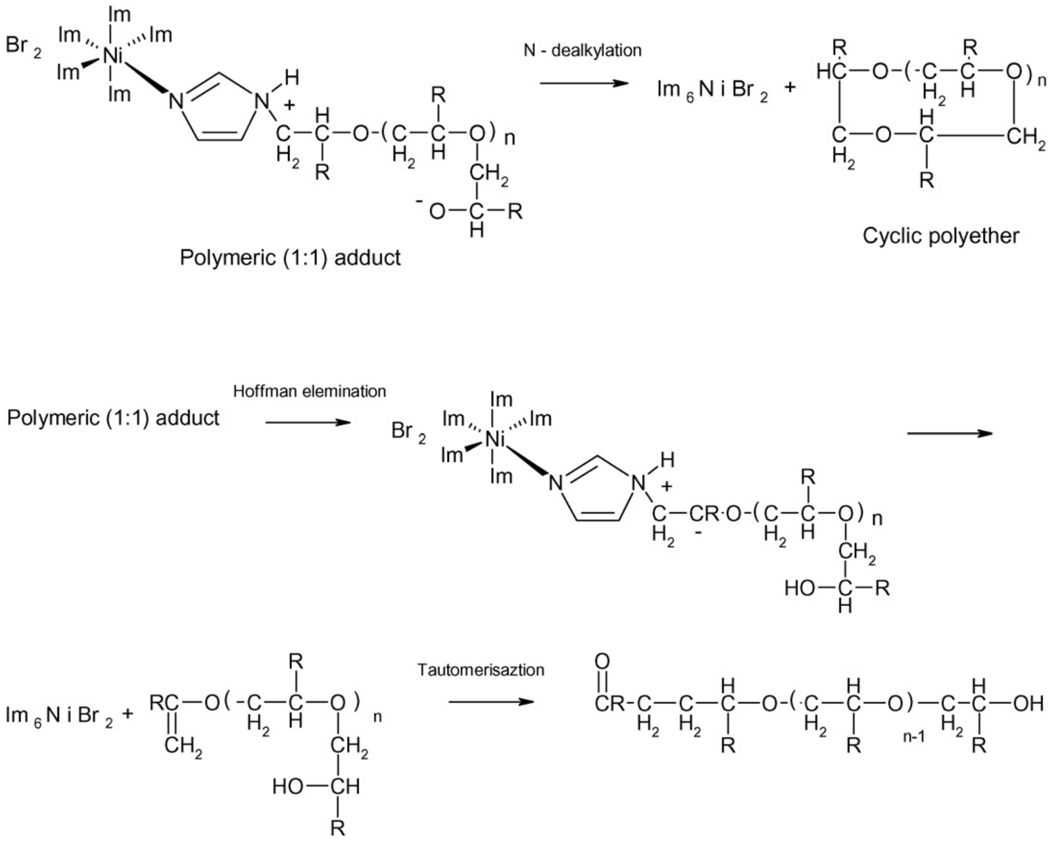

Fig. 17. Proposed mechanism for double bond formation during curing of DGEBA with Im_6NiBr_2.

4. Conclusions

Hexaquisimidazole–nickel dibromide was an effective curing catalyst for epoxy diglycidyl ether of bisphenol A. When the complex was incorporated into epoxy resin at room temperature, very slow reaction took place. Scanning calorimetry studies on samples with different compositions showed that at low curing catalyst concentration two exothermic peaks were observed and at high curing catalyst concentration only one exothermic peak was seen. The second exotherm observed at low Im_6NiBr_2 concentrations (0.5, 1, and 2.5 phr) were attributed simultaneous to curing and thermal degradation reactions. When the concentration of the curing catalyst was increased, the first exotherm became prominent and there was no evidence of the second exotherm at concentrations higher than 15 phr. Isothermal calorimetry traces indicated that there was only one exothermic peak at low concentrations of Im_6NiBr_2. A new shoulder/peak prior to the main exotherm was also observed with increasing nickel salt level of loading. Therefore, at low Im_6NiBr_2 concentrations the curing reaction proceeded through a two-step polymerization mechanism. The formation of 1:1 adduct between the epoxy resin and Im_6NiBr_2 (first step) was followed by chain growth polymerization reaction (second step).

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