Abstract: There was a question on “how lanthanides doping in iron oxide affects cure kinetics of epoxy-based nanocomposites?” To answer, we synthesized samarium (Sm)-doped Fe₃O₄ nanoparticles via electrochemical method and characterized it using FTIR, XRD, FE-SEM, EDX, TEM, and XPS analyses. The magnetic particles were uniformly dispersed in epoxy resin to increase the curability of the epoxy/amine system. The effect of the lanthanide dopant on the curing reaction of epoxy with amine was explored by modeling DSC experimental data based on model-free methodology. It was found that Sm³⁺ in the structure of Fe₃O₄ crystal participates in cross-linking of epoxy by catalyzing the reaction between epoxide rings and amine groups of curing agents. In addition, the etherification reaction of active OH groups on the surface of nanoparticles reacts with epoxy rings which prolongs the reaction time at the late stage of reaction where diffusion is the dominant mechanism.

Keywords: Lanthanide; Samarium (Sm)-doped Fe₃O₄ nanoparticles; Epoxy coating; Anticorrosion; Curing reaction.
eye on possibly altering the structure and properties of the parent nanoparticles and creating multifunctional materials, doping of magnetite nanoparticles with other metal ions has been explored.

Lanthanide ions (Ln) are an interesting class of dopants with unique optical and magnetic properties associated with their f-electronic configurations [3]. In addition, the doped particles so prepared have been found to possess physical and chemical characteristics not significantly different from the parent, undoped magnetite nanoparticles. The doping of other metals/metal ions, such as zinc, manganese, copper, nickel, and cobalt, into the Fe₃O₄ enhances the availability of its surface sites [4-6].

In the present study, samarium (Sm)-doped Fe₃O₄ nanoparticles were fabricated via an electrochemical method. The synthesized samples were well characterized by FTIR, XRD, FE-SEM, EDX, TEM, and XPS. Then, the epoxy-based film was reinforced with Ce-doped Fe₃O₄ nanoparticles to obtain an excellent corrosion protection coating. The cure potential of the epoxy-containing Sm-doped Fe₃O₄ nanoparticles was evaluated with dynamic differential calorimetry (DSC) at different heating rates of 2.5, 5, 7.5, and 10 °C/min.

2. Materials and Methods

Iron (II) chloride (FeCl₂·4H₂O), iron(III) nitrate nonahydrate 99.9% (Fe(NO₃)₃·9H₂O), and Samarium(III) nitrate (Sm(NO₃)₃·(H₂O)₂) were supplied by Sigma-Aldrich. Araldite LY 5052 epoxy resin and HY 5052 curing agent were purchased from MIS Hindustan Ciba-Geigy.

2.2. Synthesis of Sm-doped Fe₃O₄ nanoparticles

Sm³⁺-doped Fe₃O₄ nanoparticles were prepared through the cathodic electrodeposition (CED) procedure using a stainless steel cathode (316L, 5 cm × 5 cm × 0.5 mm) inside two graphite anodes. The electrolyte 0.005 molar solution of Iron(III) nitrate nonahydrate (2 g), Iron (II) Chloride (1 g) and Samarium(III) nitrate (0.6 g) was prepared in water. Then, deposition was occurred using Potentiostat/Galvanostat, Model: NCF-PGS 2012, Iran at 25 °C and current density of 10 mA cm⁻² for 30 min followed by rinsing with deionized water several times. Eventually, the dispersed Sm-Fe₃O₄ deposit in deionized water centrifuged at 6000 rpm for 20 min, separated and dried at 70 °C for 1 h.

2.3. Preparation of epoxy/Sm-doped Fe₃O₄ nanocomposite

Epoxy nanocomposites was obtained by mixing 0.1 wt.% of Sm-doped Fe₃O₄ using a mechanical mixer at 2500 rpm for 15 min. Then, Sm-doped Fe₃O₄ in epoxy further mixed by sonication for 5 min. Finally, the curing agent was added to EP/Sm-Fe₃O₄ nanocomposite in the stoichiometric ratio of 38/100 (curing agent/epoxy).

2.4. Characterization

The FTIR spectrum of Sm-doped Fe₃O₄ nanoparticles was obtained by Bruker Vector spectrometer, Coventry, UK, between 4000–400 cm⁻¹ wavelength. X-ray diffraction (XRD) of nanoparticles was performed by PW-1800 apparatus (Amsterdam, Netherlands) with Co Kα radiation. The micro- and nano-images of Sm-Fe₃O₄ nanoparticles were obtained by FESEM and EDX-Mapping (Mira 3-XMU) at the voltage of 100 kV and TEM (Zeiss-EM10C-80 kV, Germany). XPS elemental analysis of Sm-Fe₃O₄ nanoparticles was analyzed by a Thermo Fisher Scientific instrument.

The cure reaction of neat epoxy and EP/Sm-Fe₃O₄ nanocomposite investigated by DSC (Perkin Elmer, DSC 4000, Waltham, MA, USA) at four different heating rates (2.5, 5, 7.5 and 10 °C/min).

3. Results and discussion
3.1. Characterization of Sm–Fe$_3$O$_4$ nanoparticles

The FTIR spectrum of the prepared Sm–Fe$_3$O$_4$ nanoparticle is shown in Fig. 1(a). Two sharp bands can be observed at 562 cm$^{-1}$ and 628 cm$^{-1}$ which is ascribed to the splitting of the v1 band of the Fe–O. A wide peak in the range of 415–443 cm$^{-1}$ is because of v2 band of the Fe–O and Sm–O [7]. Appearance of bands at 1648 and 3325 cm$^{-1}$ are attributed to the stretching and deformation vibrations of O–H groups on the surface of Sm–Fe$_3$O$_4$ nanoparticle.

Figure 1(b) shows the XRD pattern of Sm-Fe$_3$O$_4$ nanoparticles, which the cubic spinel structure of Magnetite Fe$_3$O$_4$ [Joint Committee on Powder Diffraction Standards (JCPDS) 76-1849 and Inorganic Crystal Structural Database (ICSD) 28664]. A significant change was not observed in the XRD patterns of doped nanoparticles. The XRD pattern shows that doping Sm does not change the crystal structure of Fe$_3$O$_4$ nanoparticles.

The oxygen atoms in magnetite (Fe$_3$O$_4$) form a close-packed face-centered cubic sublattice with Fe(II) located in octahedral sites and with Fe(III) equally distributed in octahedral and tetrahedral sites (inverse Spinel structure) [8]. The cubic unit cell contains eight formula units and can be denoted as (Fe$^{3+}$)$_8$[Fe$^{3+}$Fe$^{2+}$]$_8$O$_{32}$. Along the (111) axis, the oxygen layers are cubic close-packed. Transition metals can occupy either one of these sites [9]. On the other hand, lanthanide(III) ions exhibit distorted six coordination sites or face-capped octahedral seven coordination sites in the Ln$_2$O$_3$ crystal structure [10]. Therefore, in the present case, lanthanide(III) ions may occupy some of the octahedral sites in the Fe$_3$O$_4$ inverse Spinel structure.

![Fig. 1. (a) FTIR spectra of Ce-doped Fe$_3$O$_4$ and (b) XRD pattern of Sm-doped Fe$_3$O$_4$](image)

Figure 2 shows the FESEM, EDS, mapping, and TEM images of Sm-Fe$_3$O$_4$ nanoparticles. The average particle size is about 20 nm. EDX experiments were performed to confirm the presence of both Fe and Sm in the nanoparticles, as shown in Figure 2 (b). The presence of Sm and Fe is obvious in addition to the peaks corresponding to O and Au. Au stems from the TEM grids used for the analysis and the surfactant molecules.
XPS analysis confirms the presence of Fe and Sm, O, and C in the Sm-Fe$_3$O$_4$ nanoparticles (Figure 3(a)). The Fe2p peaks in the XPS spectrum of Sm-Fe$_3$O$_4$ nanoparticles (Figure 3(b)) show the Fe2p$_{1/2}$ and Fe2p$_{3/2}$ peaks at around 710 and 720 eV, respectively, which confirm the presence of Fe(III) [11]. The Fe2p$_{1/2}$ peak with a shoulder at 708 eV and Fe2p$_{3/2}$ peak with a shoulder at 721 eV indicates the presence of Fe(II) in Fe$_3$O$_4$ [12].

Sm-3d$_{5/2}$ regions of Sm-Fe$_3$O$_4$ nanoparticles are shown in Figure 3(c). By evaluating the binding energy values (3d$_{5/2}$) of Sm(III) (1079 and 1107 eV) present in the nanoparticles with their standards [Sm$_2$O$_3$ (1082 and 1108 eV) [13], it can be concluded that this lanthanide is present in its +3 oxidation states in the nanoparticles. Subtle changes observed may be due to the different coordination environments occupied in the crystal structure as observed by others in other europium-oxo compounds.
3.2. Curing analysis

Figure 4 displays nonisothermal DSC thermographs of neat epoxy and EP/Sm-Fe$_3$O$_4$ cured with a stoichiometric amount of amine curing agent at heating rates of 2.5, 5, 7.5, and 10 °C/min. One exothermic peak can be observed for both samples at different heating rates, which revealed that the presence of Sm-Fe$_3$O$_4$ nanoparticles in the epoxy matrix does not change the domination of the chemically controlled reaction mechanism [14,15].

The Cure characteristics of EP and EP/Sm-Fe$_3$O$_4$ nanocomposite include $T_{\text{Onset}}$, $T_{\text{Endset}}$, $T_p$, $\Delta T$, and $\Delta H_{\infty}$, which are the onset, endset, the exothermal peak temperature, temperature interval, and the enthalpy of complete cure, respectively, are reported in Table 1. $T_{\text{Onset}}$, $T_{\text{Endset}}$, and $T_p$ shifted towards elevated temperatures by increasing heating rates from 2.5 to 10 °C/min to compensate for reducing curing time [16,17].

The addition of Sm-Fe$_3$O$_4$ nanoparticles decreased $T_{\text{Onset}}$ and $T_p$ of epoxy/amine reaction, indicating that Sm doped magnetic nanoparticles accelerate cross-linking reaction. The surface activity of Sm-Fe$_3$O$_4$ nanoparticles can ascribe this increment in the system’s reactivity due to the presence of Sm$^{3+}$ in the crystal structure of nanoparticles.
that catalyze the reaction between epoxy and amine curing agents [4,18]. However, \( T_{\text{Endset}} \), \( \Delta T \) increased for EP/Sm-Fe\(_3\)O\(_4\) nanocomposite compared to neat epoxy, which means that at the late stage of cure reaction, the OH groups on the surface of nanoparticles participate in etherification reaction and prolong the cross-linking of epoxy reaction.

The effect of etherification reaction of OH groups on the surface of Sm-Fe\(_3\)O\(_4\) nanoparticles besides the catalyzing effect of Sm\(^{3+}\), which acts as Lewis acid increase total heat of cure (\( \Delta H^\infty \)) of EP/Sm-Fe\(_3\)O\(_4\) nanocomposite in comparison to neat epoxy [19].

### Table 1. Cure characteristics of EP and EP/Sm-Fe\(_3\)O\(_4\) nanocomposite as a function of heating rate.

| Sample     | Heating rate (°C/min) | \( T_{\text{Onset}} \) (°C) | \( T\_P \) (°C) | \( T_{\text{Endset}} \) (°C) | \( \Delta T \) (°C) | \( \Delta H - (J/g) \) | \( \Delta T^* \) | \( \Delta H^* \) | CI       |
|------------|-----------------------|-----------------------------|-----------------|-----------------------------|-----------------|------------------|--------------|--------------|---------|
| EP         | 2.5                   | 25.71                       | 90.367          | 159.93                      | 134.22          | 329.62           | N.a.        | N.a.        | N.a.   |
|            | 5.0                   | 37.37                       | 101.69          | 171.72                      | 134.35          | 336.21           | N.a.        | N.a.        | N.a.   |
|            | 7.5                   | 40.65                       | 110.28          | 180.68                      | 140.03          | 344.05           | N.a.        | N.a.        | N.a.   |
|            | 10                    | 41.43                       | 119.15          | 225.3                       | 183.87          | 404.33           | N.a.        | N.a.        | N.a.   |
| EP/Sm-Fe\(_3\)O\(_4\) | 2.5                   | 30.8                        | 89.407          | 170.6                       | 139.8           | 385.77           | 1.04        | 1.17        | 1.22    |
|            | 5.0                   | 35.69                       | 101.5           | 175.2                       | 139.51          | 363.72           | 1.04        | 1.08        | 1.12    |
|            | 7.5                   | 39.13                       | 107.66          | 207.02                      | 167.89          | 296.34           | 1.2         | 0.86        | 1.03    |
|            | 10                    | 40.1                        | 115.14          | 225.97                      | 185.87          | 403.44           | 1.01        | 1.01        | 1.02    |

N.a.: Not applicable

The effect of curability of Sm-Fe\(_3\)O\(_4\) nanoparticles in epoxy/amine system are specified by Cure Index:

\[
CI = \Delta T^* \times \Delta H^*, \quad \Delta T^* = \frac{\Delta T_{\text{nanocomposite}}}{\Delta T_{\text{Reference}}} \quad \text{and} \quad \Delta H^* = \frac{\Delta H_{\text{nanocomposite}}}{\Delta H_{\text{Reference}}},
\]

\( \Delta T \) is temperature window within which curing occurs, with subscripts of “nanocomposite” and “Reference” for nanocomposite and blank epoxy systems, respectively. Similarly, \( \Delta H^\infty \) of such systems are defined. The asterisk terms in each case are dimensionless. Good, Poor, and Excellent curing reaction of nanocomposites occurs at CI>\( \Delta H^\infty \), CI < \( \Delta T^* \), and \( \Delta T^* < CI < \Delta H^\infty \), respectively. The addition of Sm-Fe\(_3\)O\(_4\) nanoparticles in the epoxy matrix resulted in a Good cure reaction, which means that Sm\(^{3+}\) participates in cross-linking of epoxy by catalyzing the reaction between epoxide rings and amine groups of curing agents. In addition, the active OH groups on the surface of nanoparticles react with epoxy polar groups that increase both \( \Delta T \) and \( \Delta H \) and result in Good CI.

Figure 5 shows the conversion (\( \alpha \)) of curing reaction as a function of temperature which obtained from Eq. 2:

\[
\alpha = \frac{\Delta H_T}{\Delta H_\infty},
\]

where \( \Delta H_T \) is the enthalpy of reaction at a specific temperature.

In the initial stage of the curing reaction, cross-linking occurs rapidly until reaching gel point under the control of chemical reaction between the epoxy ring and amine groups of curing agent. By contrast, at the late stage of cure, where diffusion is dominant, the cross-linking occurs slowly. Also, Sm-Fe\(_3\)O\(_4\) nanoparticles accelerate cross-linking of epoxy after vitrification which indicated an acceleration of diffusion mechanisms due to the presence of OH groups on the surface of nanoparticles [20].
Fig. 5. The fractional extent of conversion as a function of reaction time for EP and EP/Sm-Fe$_3$O$_4$ nanocomposite at heating rates of 2.5, 5, 7.5, and 10 °C/min.

Isoconversional model-free Friedman and Kissinger-Akahira-Sunose (KAS) were employed to obtain the apparent activation energy ($E_\alpha$) of curing reaction (Supporting Information, Eqs. S1 and S2, Figures S1 and S2) [21,22]. The apparent activation energy of neat epoxy and EP/Sm-Fe$_3$O$_4$ nanocomposite as a function of $\alpha$ based on both Friedman and KAS are shown in Figure 6. $E_\alpha$ reduced for neat epoxy and its nanocomposite in $\alpha$ higher than 0.5 due to the participation of OH groups in epoxide ring-opening at a later stage of curing reaction revealing the autocatalytic mechanism of epoxy cure reaction [23,24]. The higher $E_\alpha$ values for EP/Sm-Fe$_3$O$_4$ nanocomposite compared to neat epoxy can be attributed to the higher viscosity of the epoxy system in the presence of Sm-Fe$_3$O$_4$ nanoparticles [25].

Fig. 6. Evolution of activation energy for EP and EP/Sm-Fe$_3$O$_4$ nanocomposite estimated by (a) differential Friedman model and (b) integral KAS model.

The autocatalytic reaction model ($f(\alpha)$, Eq. 3) of neat epoxy and its nanocomposite was obtained by Friedman and Malek model (Supporting Information, Eqs. S2-S5, Figures S3 and S4).

$$f(\alpha) = \alpha^m (1 - \alpha)^n,$$  \hspace{1cm} (3)

The reaction model parameters, including the pre-exponential factor (lnA), non-catalytic (n), and autocatalytic (m) reaction orders, were determined from Eqs. S6 and S7 and Figs. S5 and S6 and reported in Table 2. As can be observed, both n and m increased for EP/Sm-Fe$_3$O$_4$ nanocomposite compared to neat epoxy. Increment of n indicated the catalyzing effect of Sm$^{3+}$ as a Lewis acid in the reaction between the epoxy ring and amine curing agent and enhancement of m is because of reaction of OH groups on the surface of Sm-Fe$_3$O$_4$ nanoparticles with epoxide rings. The retardation effect Sm-Fe$_3$O$_4$ nanoparticles on cure reaction of epoxy is reflected in higher lnA values.
Table 2. The kinetic parameters evaluated for the curing of EP and EP/Sm-Fe\textsubscript{3}O\textsubscript{4} nanocomposite based on Friedman and KAS models at different heating rates.

| Designation     | Heating rate (°C/min) | Friedman | KAS     |
|-----------------|-----------------------|----------|---------|
|                 |                       | $m$      | $n$     | $lnA$ (s$^{-1}$) | $m$      | $n$     | $lnA$ (s$^{-1}$) |
| EP              | 2.5                   | 0.14     | 1.32    | 12.09       | 0.09     | 1.36    | 13.3       |
|                 | 5.0                   | 0.29     | 1.38    | 12.71       | 0.24     | 1.42    | 13.9       |
|                 | 7.5                   | 0.29     | 1.36    | 12.76       | 0.24     | 1.4     | 13.92      |
|                 | 10                    | 0.25     | 1.69    | 12.57       | 0.2      | 1.74    | 13.71      |
| EP/Sm-Fe\textsubscript{3}O\textsubscript{4} | 2.5                   | 0.16     | 1.58    | 14.5        | 0.13     | 1.62    | 15.39      |
|                 | 5.0                   | 0.23     | 1.47    | 14.8        | 0.20     | 1.5     | 15.66      |
|                 | 7.5                   | 0.34     | 1.72    | 15.05       | 0.30     | 1.75    | 15.9       |
|                 | 10                    | 0.31     | 1.85    | 14.9        | 0.28     | 1.89    | 15.73      |

The validation of isoconversional methods (Friedman and KAS) are obtained by comparison with the experimental data and shown in Fig. 7. Clearly, both KAS and Friedman approaches can predict the curing rate of cross-linking reaction for neat epoxy and Sm-Fe\textsubscript{3}O\textsubscript{4} nanoparticles incorporated epoxy system.

5. Conclusions
Sm-doped Fe\textsubscript{3}O\textsubscript{4} nanoparticle was synthesized through electrochemical method to investigate its effect on curability of Epoxy/amine system. XPS results indicated that samarium is present in its +3 oxidation states in the structure of Fe\textsubscript{3}O\textsubscript{4} lattice. The XRD pattern revealed that Sm\textsuperscript{3+} ions occupy the octahedral sites in the Fe\textsubscript{3}O\textsubscript{4} crystal structure. DSC analysis at different heating rate showed that addition of Sm-Fe\textsubscript{3}O\textsubscript{4} nanoparticles accelerate cross-linking reaction due to the catalyzing effect of Sm\textsuperscript{3+} in the crystal structure of Fe\textsubscript{3}O\textsubscript{4} nanoparticles on the reaction between epoxy and amine curing agent which reflected in lower $T_{\text{Onset}}$ and $T_p$. Obtaining Good CI by addition of Sm-Fe\textsubscript{3}O\textsubscript{4} nanoparticles in epoxy matrix showed that Sm\textsuperscript{3+} participate in cross-linking of epoxy by catalyzing the reaction between epoxide rings and amine groups of curing agent and etherification reaction of active OH groups on the surface of nanoparticles reacts with epoxy rings. The apparent activation energy that determined by isoconversional Friedman and KAS methods indicated complex curing reaction of epoxy in the presence of Sm-Fe\textsubscript{3}O\textsubscript{4} nano-
particles which cause increment of average Eα value from 47.3 for neat epoxy to 52.6 kJ/mol. The autocatalytic reaction model was validated by experimental data.

**Supplementary Materials:** The Supplementary Materials are available online at www.mdpi.com.

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