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Article publicat / *Published paper:*

Jouyandeh, M., et al. (2019) Curing epoxy with ethylenediaminetetraacetic acid (EDTA) surface-functionalized $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ magnetic nanoparticles. *Progress in Organic Coating*, vol. 136, 105248. Doi: 10.1016/j.porgcoat.2019.105248

Curing epoxy with ethylenediaminetetraacetic acid (EDTA) surface-functionalized $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ magnetic nanoparticles

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Abstract

In this work, the bulk and surface composition of Fe₃O₄ supermagnetic nanoparticles were modified for efficient epoxy curing. The bare, ethylenediaminetetraacetic acid (EDTA) capped, and cobalt (Co)-doped EDTA capped Fe₃O₄ nanoparticles were synthesized electrochemically. The crystalline nature and phase information of the nanoparticles, surface capping, morphology and magnetization of nanoparticles were studied by X-Ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM) and vibrating sample magnetometer (VSM), respectively. A low amount of the prepared nanoparticle (0.1 wt.%) was used in preparation of epoxy nanocomposites. Nonisothermal differential scanning calorimetry (DSC) under different heating rates was performed to study the potential of nanoparticles in curing epoxy resin with an aliphatic amine. The heat release data on nanocomposites suggest that EDTA capped Co-doped Fe₃O₄ considerably improved the curing reaction between epoxy resin and the curing agent. Calculations based on *Cure Index* approved qualitatively a shift from *Poor* to *Good* cure by concurrent bulk and surface modifications of magnetic nanoparticles. The approach used in this work can pave the way to enhance curability of epoxy nanocomposites by the combined modification of bulk and surface of nanoparticles.

Keyword: *Cure Index*; Epoxy; Fe₃O₄ Nanoparticle; EDTA; Cobalt Doping

1. Introduction

It was found that addition of fillers and surface functionalization of them has been practiced over the past three decades in order to enhance the ultimate properties of organic coatings [1-5]. and surface functionalization of them has been practiced over the past three decades in order to enhance the ultimate properties of organic coatings Nevertheless, the degree of improvement in properties of coatings containing functionalized nanoparticles was not addressed precisely from a molecular view by monitoring the curability of the surface functionalized nanoparticle to epoxy curing reaction. The other difficulty was that no molecular-level gauge was available for quantifying the status quo of cross-link density of thermoset nanocomposite once nanoparticle was functionalized with reactive groups or molecules [6-8].

The effect of surface modification of a wide variety of nanoparticles with low- and high- molecular weight molecules of amine, carboxylic and hydroxyl on the curability of epoxy resin was addressed in previous works of this group, which are including carbon nanotubes (CNTs) [9- 11], graphene oxide (GO) nanoflakes [12-14], halloysite nanotubes (HNTs) [15-17], silica

nanoparticles with high-molecular weight ethylenediaminetetraacetic acid (EDTA) can affect ultimate properties of cross-linkable polymer nanocomposites. Syuhada et al. showed that EDTA surface functionalized GO dispersed well in chitosan matrix due to interaction of EDTA functional groups with chitosan [21]. Well-dispersed GO-EDTA in chitosan matrix leads to better distribution of stress transfer and resulted in 71% improvement in tensile strength nanoparticles [18, 19] and zinc oxide (ZnO) nanoparticles [20]. Surface functionalization of compared to neat chitosan film.

Fe₃O₄ magnetic nanoparticles were found to be efficiently useful to improve corrosion inhibition and fire retardant properties of epoxy nanocomposites [22]. Improved curability of epoxy/Fe₃O₄

nanocomposites under the influence of nanoparticle surface modification with acid [23], hydroxyl [24, 25], and imide [26] was discussed in previous works of this group. It was also revealed that using *Cure Index* [27, 28], *CI* criterion to study curability of epoxy nanocomposites under nonisothermal differential scanning calorimetry (DSC) could be taken into account as a simple yet reliable procedure to uncover the goodness of cure in terms of *Poor*, *Good*, and *Excellent* cure cases [15, 19]. Nevertheless, effect of bulk composition manipulation of Fe₃O₄, alone or in combination with surface functionalization of Fe₃O₄ was not the subject of investigations.

In this work, the bulk and surface composition of Fe₃O₄ iron oxide nanoparticles (IONs) were respectively modified with cobalt (Co) and ethylenediaminetetraacetic acid (EDTA). The bare IONs, EDTA capped IONs (EDTA-IONs), and Co-doped EDTA-IONs were synthesized based on electrodeposition. The crystalline and phase structure of IONs and their surface characteristics were detected by X-Ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) analyses, respectively. The morphology and magnetization of nanoparticles were also studied by field emission scanning electron microscopy (FE-SEM) and vibrating sample magnetometer (VSM), respectively. Low filled epoxy nanocomposites containing 0.1 wt.% of three aforementioned types of IONs were prepared by mechanical and ultrasound-assisted mixing. Nonisothermal differential scanning calorimetry (DSC) measurements were performed to study the potential of nanoparticles in curing epoxy resin with an aliphatic amine. The heat release data collected varying heating rate in DSC analyses suggested that Co-doped EDTA-IONs assisted in epoxy ring epoxy in a complex manner, while qualitative analyses based on *Cure Index* approved a shift from *Poor* to *Good* cure upon modification of both bulk and surface of IONs. The

outcome of this study unraveled superiority of bulk modification of IONs with Co^{2+} cations almost independent of heating rate applied in DSC, when compared with EDTA-IONs.

2. Experimental

2.1. Materials

Iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), and ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA- Na_2 , 99.9%) were purchased from Sigma-Aldrich. The graphite plates and stainless steel sheets (316L) were provided from local companies. The epoxy resin (Epon-828) and triethylenetetramine (TETA) as curing agent were provided by Hexion Co.

2.2. Fabrication of IONs samples

All the electrodeposition experiments were designed based on the cathodic electrodeposition via base generation strategy, previously reported in Refs. [29-33]. The synthesis of bare IONs and EDTA coated IONs were repeated using the same procedure reported in Refs. [32, 33]. The electrochemical cell was a stainless steel sheet centered between two graphite anodes, which all electrodes were immersed into the electrolyte and connected to the external DC power supply by Cu wires. The applied experimental conditions were $i=10 \text{ mA cm}^{-2}$, $t= 25\text{min}$ and $\text{pH}=6.5$. In the deposition of bare IONs, the electrolyte was 2g iron(iii) nitrate + 1g iron(ii) chloride dissolved in one liter distilled H_2O . For deposition of EDTA coated IONs, only 1g/L EDTA polymer as capping agent was added into above mentioned electrolyte. In the synthesis process of EDTA/Co-IONs, a simple aqueous electrolyte containing 1g iron(II) chloride, 0.3 cobalt

chloride, 2g iron(III) nitrate and 1g EDTA was used. After synthesis, the cathode electrodes were removed from the bath solutions i.e. electrolytes, and the deposited black films were separated from the electrode surfaces. Then these powders were washed several times with ethanol and heated at 70 °C for 2h in vacuum oven. The final powders were used in the analyses tests. The schematic illustration of EDTA coated IONs is shown in **Fig. 1**.

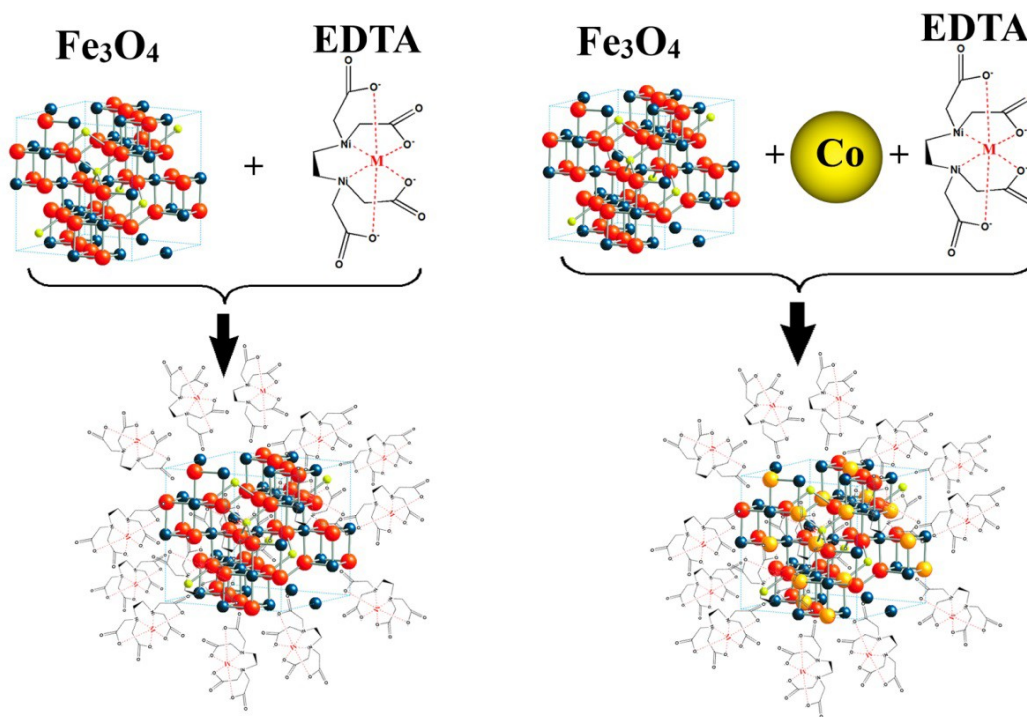


Fig.1. EDTA coating of Fe_3O_4 and Co-doped Fe_3O_4

2.3 Epoxy nanocomposites preparation

Four samples were prepared for further cure analysis: neat epoxy (EP), epoxy nanocomposite containing 0.1 wt.% bare IONs (EP/IONs), EDTA-IONs (EP/EDTA-IONs) and co-doped EDTA-IONs (EP/ Co-doped EDTA-IONs). By adding 0.1 wt.% of nanoparticles into epoxy resin and Sonicated with 50% duty cycle for 5 minutes, the epoxy nanocomposites will be prepared. After that, for getting well dispersal the nanocomposite blended with a mechanical mixer at 2500 rpm for 20 minutes. So as to study cure procedure of epoxy stoichiometric volume of TETA (100:13) was adjoined to epoxy system and combined completely.

2.4. Characterization

The crystalline nature and phase information of the prepared IONs powders were obtained by X-ray diffraction (XRD), using a Phillips PW-1800 diffractometer. The patterns were provided by using Co-K α radiation ($\lambda=1.56\text{\AA}$) in the zone of $10^\circ < 2\theta < 80^\circ$ with steps of 0.015 and acquisition time of 2s/step. The surface capping was confirmed by a Bruker Vector 22 Fourier transform infrared (FT-IR) spectroscope. The IR spectra of sample were collected in the frequency range of $4000\text{--}400\text{cm}^{-1}$ with resolution of 1.5cm^{-1} . The surface morphology observations of the samples were carried out by field-emission scanning electron microscopy (FE-SEM, Mira 3-XMU with accelerating voltage of 100 kV). The magnetization data were collected on Vibrating Sample Magnetometers (VSM, model Lakeshore 7410) at RT in the range of -20000 to 20000 Oe.

2.5. Dynamic DSC measurement

The curing state of epoxy resin and its nanocomposites consist of 0.1 wt% EDTA-IONs and Co-doped EDTA-IONs was examined nano-isothermally on Perkin Elmer DSC 4000. Dynamic DSC was worked at heating degree (β) of 5, 10, 15, and 20 °C min⁻¹ in temperature range of 15–250 °C under nitrogen with the current speed of 20 mL min⁻¹.

3. Results and discussion

3.1. Structure and morphology

The powder X-ray diffraction (i.e. XRD) patterns of the electro-deposited IONs powders are provided in **Fig. 2**. For all sample, well-defined diffractions of (111), (220), (311), (400), (422), (511), (440), (620) and (533) are present in **Fig. 2**. These planes are well-fitted with those mentioned for Fe₃O₄ crystal phase of iron oxide (JCPDS No.85-1436) [29-32, 34]. The average crystallite sizes of bare IONs, ESTA/IONs and EDTA/Co-IONs samples were assessed through Debye Scherrer relation, i.e. $D = k\lambda/\beta\cos\theta$, where β is the full width of (311) plane at its half maximum (FWHM), λ is the X-ray beam wavelength ($\lambda_{Co}=1.56\text{\AA}$), θ is the Bragg angle for the actual peak and k is a shape function, where k=0.9 was applied. It was found that the average crystalline size were 9.1nm, 8.2nm and 13.9nm for bare IONs, EDTA/IONs and EDTA/Co- doped IONs, respectively.

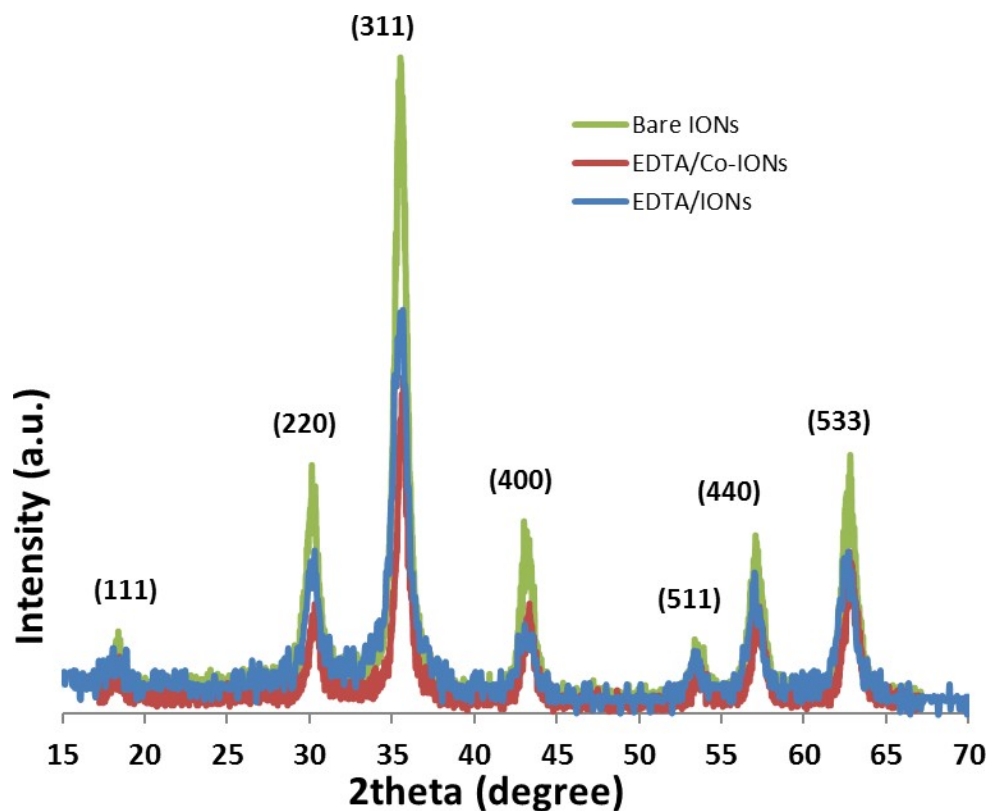


Fig. 2. XRD patterns of the synthesized bare IONs [32], EDTA/ IONs [33] and EDTA/Co-doped IONs.

FT-IR spectra of the fabricated Bare IONs, EDTA/IONs and EDTA/Co-doped IONs are presented in Fig. 3. In all spectrum, the IR bands located at $\nu \leq 700 \text{ cm}^{-1}$ and 661 cm^{-1} are related to ν_1 and ν_2 vibration modes of the $\text{Fe}^{2+}\text{---O}^{2-}/\text{Co}^{2+}\text{---O}^{2-}$ and $\text{Fe}^{3+}\text{---O}^{2-}$ chemical bonds [29-32]. For EDTA capped IONs, in the wavenumbers of $700\text{-}1700 \text{ cm}^{-1}$, various IR bands are observed; e.g. $\nu_{\text{stretching}}=3280\text{-}3285 \text{ cm}^{-1}$ for N-H bonds, $\nu_{\text{stretching}}=2875\text{-}2880 \text{ cm}^{-1}$ for N-C-H bonds, $\nu_{\text{stretching}}=1625\text{-}1630 \text{ cm}^{-1}$ for C=O groups, $\nu_{\text{stretching}}=1475\text{-}1480 \text{ cm}^{-1}$ for C-O bonds, $\nu_{\text{wagging}}=1380\text{-}1385 \text{ cm}^{-1}$ for CH_3 groups, $\nu_{\text{stretching}}=1135\text{-}1140 \text{ cm}^{-1}$ for C-N bonds and $\nu_{\text{stretching}}=1025\text{-}1030 \text{ cm}^{-1}$ for C-O-C bonds [29-33], where these IR bands confirmed the EDTA layer onto the surface of the electrodeposited IONs particles.

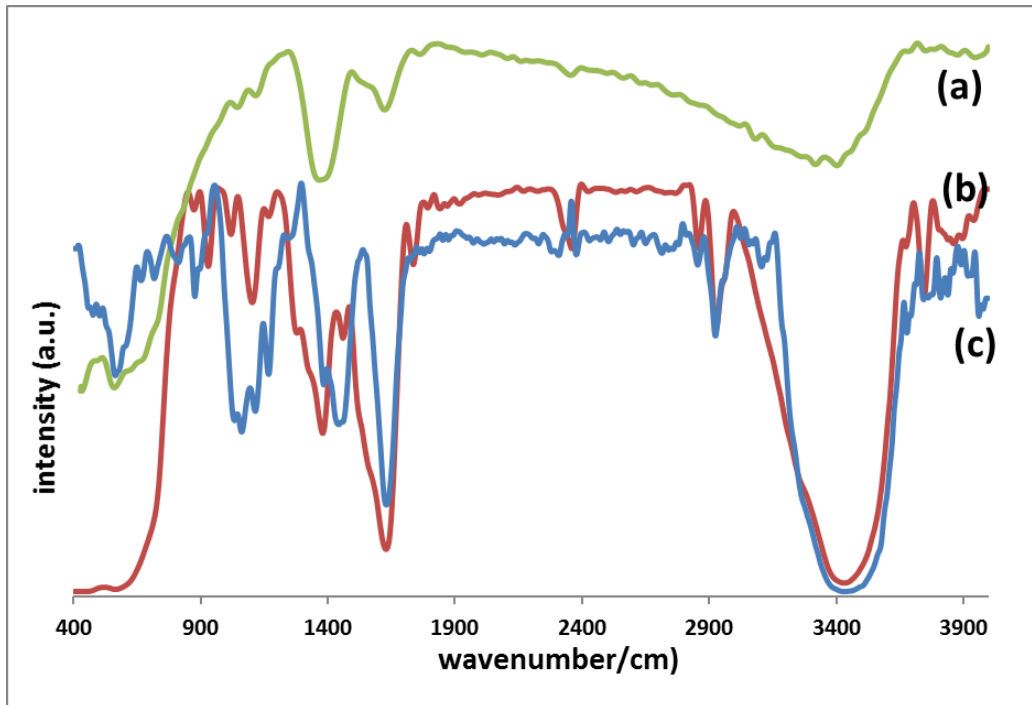


Fig. 3. FT-IR spectra of the fabricated (a) bare IONs [32], (b) EDTA/IONs [33] and (c) EDTA/Co-doped IONs.

Surface morphology texture of the prepared IONs was characterized through FE-SEM technique and their FE-SEM images are given in **Fig. 4**. It is clearly seen that all deposited IONs samples have spherical particles. The average diameters of 20nm, 40nm and 35nm were measured for bare IONs, EDTA/IONs and EDTA/Co-doped IONs, respectively (**Fig. 4**).

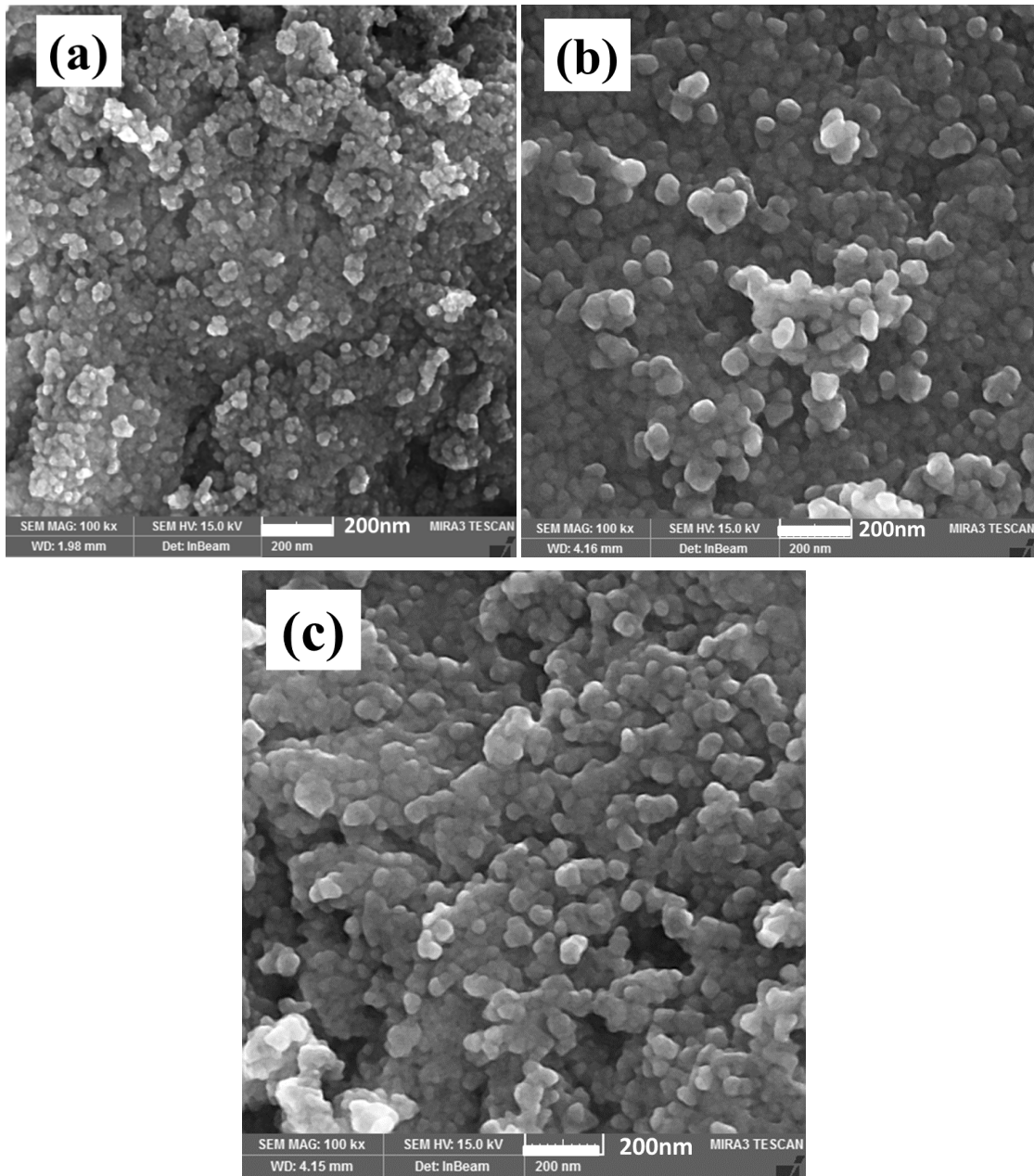


Fig. 4. FE-SEM images of bare IONs [32], (b) EDTA/ IONs and (c) EDTA/Co-doped IONs.

Fig. 5 shows the VSM curves for the prepared IONPs particles. The VSM profiles of all three IONs exhibited a complete S shape and hence their superparamagnetic behaviors. From **Fig. 5**, the saturation magnetization (M_s), remanence (M_r) and coercivity (H_{ci}) values were measured to be $M_s=72.96$ emu/g, $M_r=0.82$ emu/g and $H_{ci}=2.9$ Oe (for bare IONs as reported in Ref. [32]), $M_s=51.89$ emu/g, $M_r=0.59$ emu/g and $H_{ci}=0.85$ Oe (for EDTA-IONs as reported in Ref. [33])

and $M_s=33.68$ emu/g, $M_r=0.72$ emu/g and $H_{ci}=1.04$ Oe (for EDTA/Co-IONs). The low H_{ci} and negligible M_r for all three fabricated IONs proved their superparamagnetic properties. These data indicated that the magnetization of IONs is reduced as a result of surface coating with EDTA, and Co^{2+} -doping into their crystal structures, which is due to the reduction of magnetite fraction of the samples. The measured low values for the H_{ci} and M_r quantities indicated an improvement in the superparamagnetic performances of both EDTA-coated IONs and Co-doped EDTA-IONs sample as compared with bare IONs.

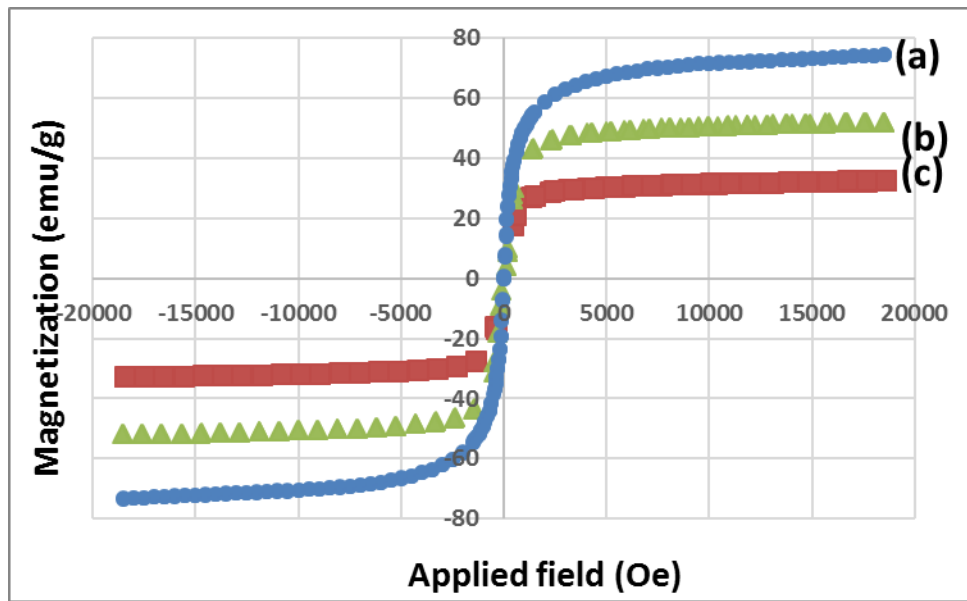


Fig. 5. VSM curves of the fabricated (a) bare IONs, (b) EDTA/ IONs and (c) EDTA/Co-doped IONs.

3.2. Cure analysis

The cure curves that achieved based on nonisothermal DSC at β of 5, 10, 15 and 20 °C/min are indicated in Fig. 6. It is just an exothermic peak in all the samples at four heating rates which

means other side reactions are subordinate by epoxy ring opening and amine groups of curing agent [35].

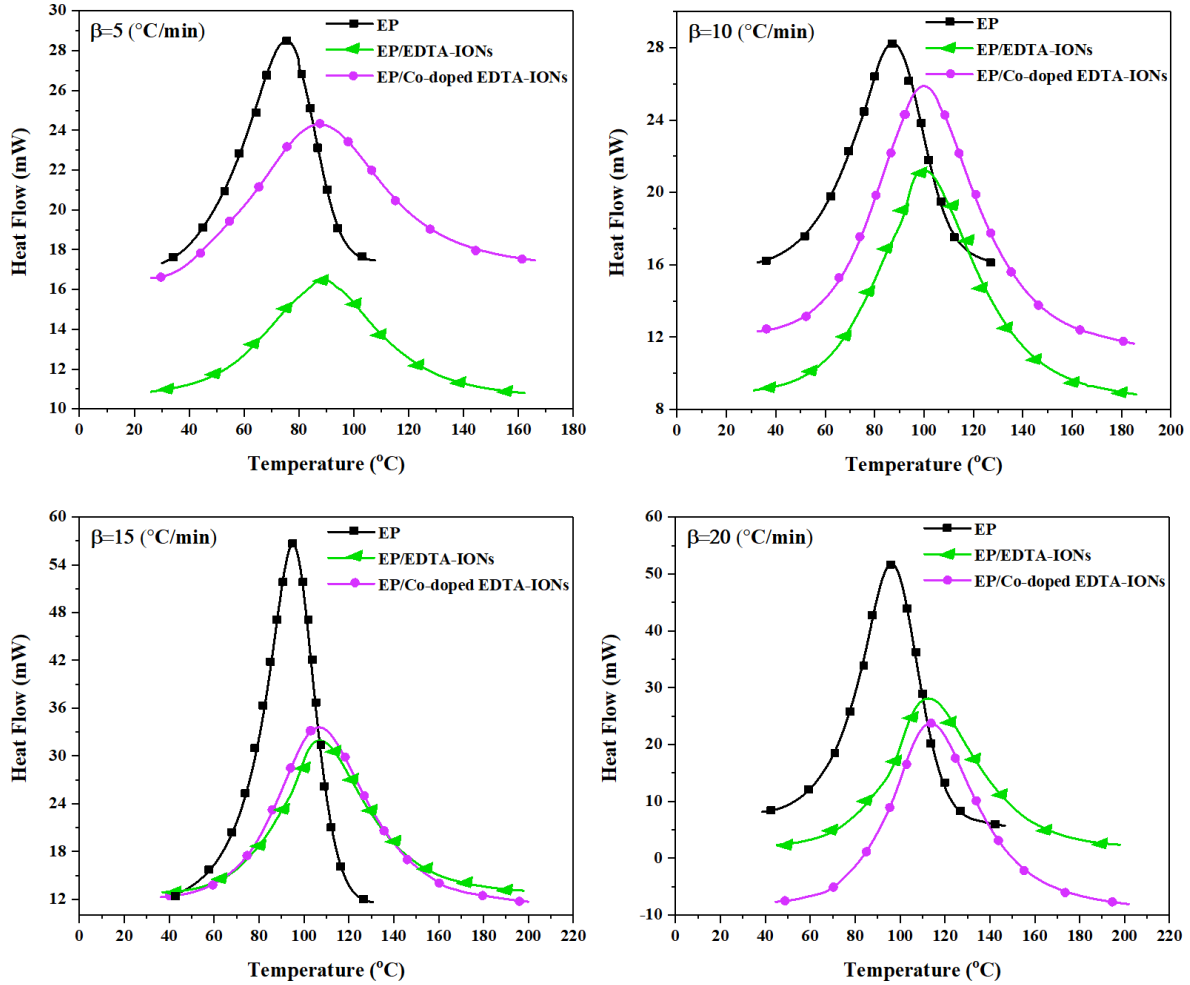


Fig.6. Dynamic DSC thermograms of EP, EP/EDTA-IONs and EP/Co-doped EDTA-IONs at different heating rates.

3.2.1. Qualitative cure analysis (CI)

Cure situation of epoxy containing EDTA coated pristine and Co-doped IONs was studied qualitatively by CI, according to dynamic cure protocol of thermoset system [28]. Cure situation

of epoxy nanocomposites can be evaluated by CI as a dimensionless and simple criterion which can be calculated as follows:

$$\Delta H^* = \frac{\Delta H_C}{\Delta H_{Ref}} \quad (1)$$

$$\Delta T^* = \frac{\Delta T_C}{\Delta T_{Ref}} \quad (2)$$

$$CI = \Delta H^* \times \Delta T^* \quad (3)$$

ΔH_C , ΔT_C and ΔH_{Ref} , ΔT_{Ref} are the heat released during the whole cure process and temperature interval for epoxy nanocomposite and blank epoxy that has mentioned in the above equation.

The values of ΔT^* , ΔH^* and CI for EP/IONs, EP/EDTA-IONs and EP/Co-doped EDTA-IONs nanocomposites at different heating rates of 5, 10, 15 and 20 °C/min are presented in Table 1.

The onset and endset cure temperature (T_{onset} and T_{endset}), total temperature interval (ΔT), the maximum temperature of DSC curve (T_p) and total enthalpy of cure (ΔH) are also listed in Table 1.

According to Table 1, by addition of nanoparticles T_{onset} shifted to higher temperature compared to neat epoxy due to the steric hindrance effect of nanoparticles, which led to the viscosity build up [36]. In the case of EDTA-IONs and Co-doped EDTA-IONs incorporated epoxy system the presence of EDTA with COOH groups significantly increased the total time of cure. Moreover, EDTA on the surface of EDTA-IONs and Co-doped EDTA-IONs also improved ΔH values compared to EP/IONs which indicates formation of denser cross-linked network [37].

Table 1. Cure characteristics of the prepared epoxy nanocomposites as a function of heating rate

Designation	β (°C/min)	T_{onset} (°C)	T_{endset} (°C)	T_p (°C)	ΔT (°C)	ΔH_c (J/g)	ΔT^*	ΔH^*	CI
EP	5	30.04	107.62	75.31	77.58	340.41	n.a.	n.a.	n.a.
	10	29.7	165.3	98.4	135.7	319.4	n.a.	n.a.	n.a.
	15	36.64	191.89	107.89	155.25	377.61	n.a.	n.a.	n.a.
	20	38.62	146.67	96.09	108.05	374.39	n.a.	n.a.	n.a.
EP/IONs	5	40.7	140.4	90.3	99.6	186.6	0.83	0.55	0.45
	10	40.7	166.0	99.1	125.3	310.8	0.92	0.97	0.90
	15	46.1	174.4	113.0	128.3	127.7	0.83	0.34	0.28
	20	46.9	191.5	118.0	144.7	164.3	0.90	0.44	0.40
EP/EDTA-IONs	5	26.05	162.14	88.78	136.09	277.46	1.75	0.81	1.42
	10	31.11	285.95	100.3	154.84	306.07	1.14	0.96	1.09
	15	37.03	197.78	106.90	160.75	310.28	1.03	0.82	0.84
	20	45.20	197.88	112.69	152.68	315.41	1.41	0.84	1.18
EP/Co-doped EDTA-IONs	5	26.12	165.94	87.55	139.82	416.96	1.80	1.22	2.19
	10	32.61	184.96	100.02	152.35	352.29	1.12	1.10	1.24
	15	36.19	199.95	106.76	163.76	375.35	1.05	0.99	1.04
	20	45.54	201.90	114.59	156.35	389.45	1.45	1.04	1.51

n.a. – not applicable (reference measurements)

As can be observed from Table 1, addition of pristine IONs hindered curing reaction of epoxy. While by surface functionalization of IONs nanoparticles by EDTA, T_{onset} and T_{endset} at all the heating rates decreased and increased compared to EP/IONs, respectively. It means that reaction of EDTA on the surface of IONs raise cure temperature interval. At the same time, ΔH increased

due to reaction of carboxyl groups of EDTA with epoxide groups of resin. But still the amount of heat released of cure is lower than neat epoxy. On the other hand, EDTA coated Co-doped IONs nanoparticles are able to increased ΔH of cure compared to neat epoxy and its nanocomposites containing pristine and EDTA functionalized IONs nanoparticles. COOH groups of EDTA on the surface of Co-doped IONs nanoparticles participate in epoxide ring opening and facilitate curing reaction (**Fig. 7**). The main process of the reaction between COOH and epoxy is to yield β -hydroxypropyl ester which may react with a second COOH group at high temperature to yield a diester. This cross-linking reaction can occurs at lower temperatures with the use of tertiary amines as catalyst [38]. Since the COOH groups is in the second priority in comparison with amine groups of curing agent in epoxide ring opening the total temperature of cure increase because their nucleophilicity is much lower than the abovementioned N-containing curing agents [39].

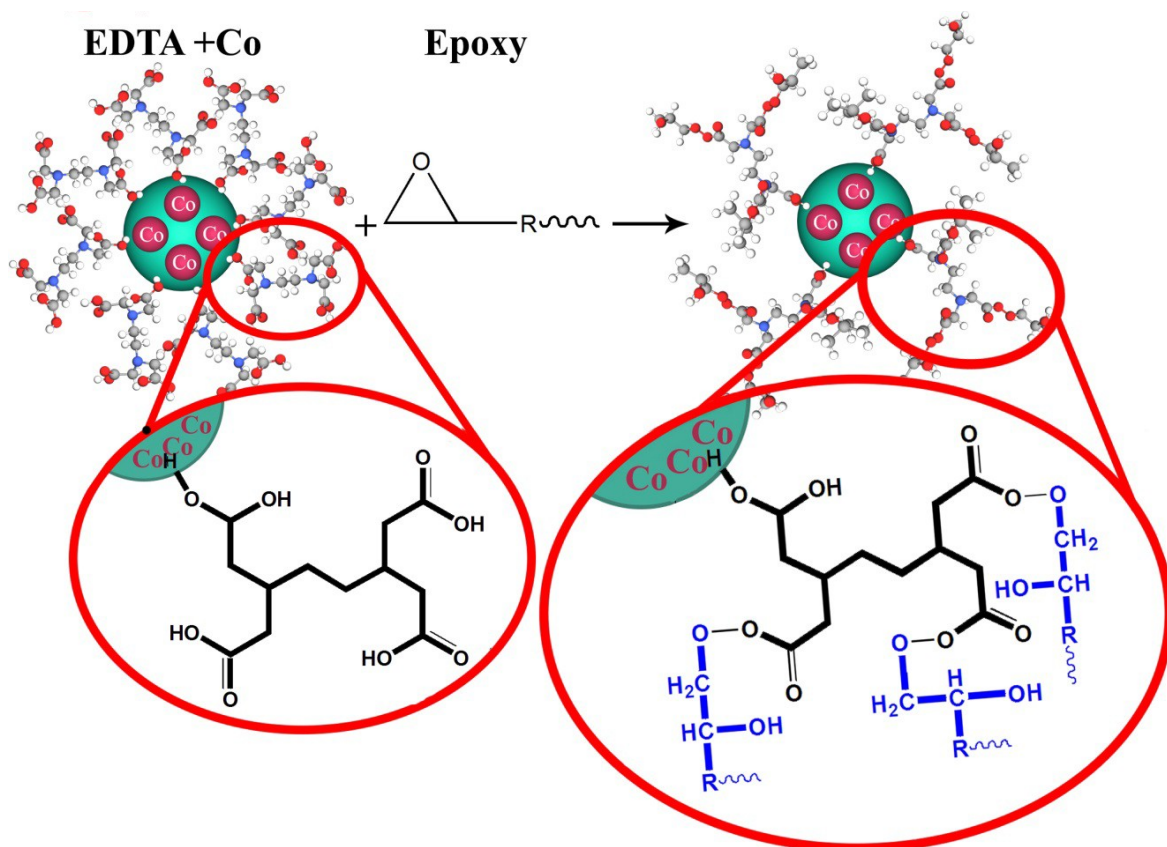


Fig. 7: Reaction between EDTA on the surface of Co-doped IONs and epoxy.

The cure situation of epoxy nanocomposites including 0.1 wt.% of EDTA coated pristine and Co-doped IONs nanoparticles are explained based on CI situation in the plot of ΔH^* versus ΔT^* (**Fig. 8**). **Fig.8** shows the green area as an *Excellent* cure situation ($\Delta T^* < CI < \Delta H^*$), the blue area as *Good* curing situation of nanocomposite ($CI > \Delta H^*$) and the red area as *Poor* curing for EDTA coated pristine and Co-doped IONs nanoparticles incorporated epoxy ($CI < \Delta T^*$).

As shown in **Fig.8**, at low heating rates ($\beta = 5$ and 10 °C/min) the reaction is slow and curing moieties specially COOH groups of EDTA on the surface of Co-doped IONs nanoparticles have

enough time to participate in curing reaction of epoxy which led to the situation that CI became higher than ΔH^* which means that *Good* cure situation. On the other hand, high β (20 °C/min) reduce the reaction time but raise the kinetic energy per molecules which increase the curing reaction mobility and improve the curing situation in to *Good* condition.

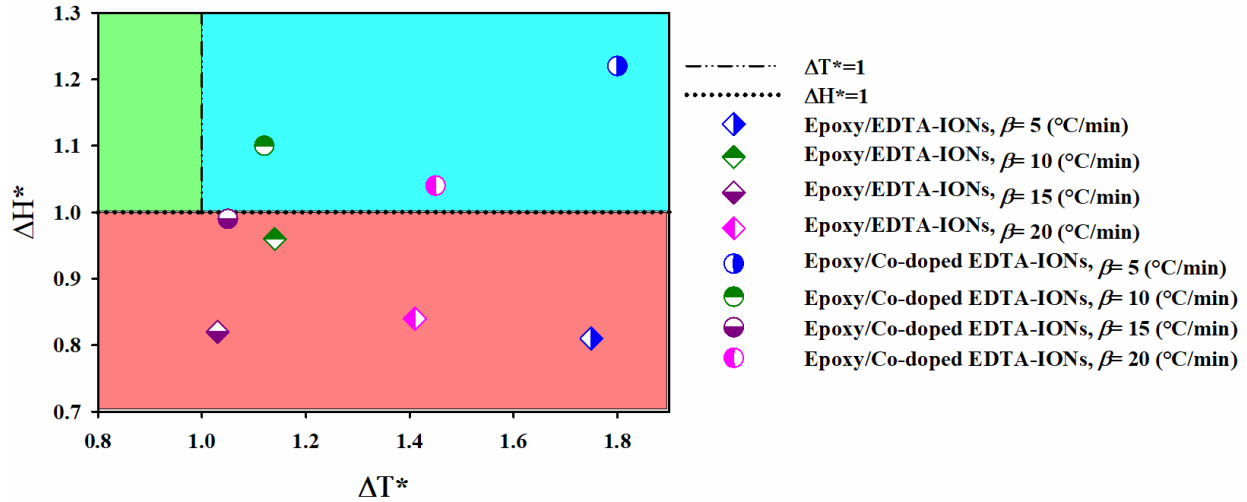


Fig. 8. Cure situation of EP/EDTA-IONs and EP/Co-doped EDTA-IONs nanocomposites at heating rates of 5, 10, 15 and 20 °C/min.

Conclusion

Pristine IONs and EDTA coated IONs and Co^{2+} doped IONs nanoparticles were prepared based on the cathodic electrodeposition via base generation strategy. The crystalline nature and phase information of the Pristine IONs and EDTA coated IONs and Co^{2+} doped IONs powders were studied by XRD. From Debye Scherrer relation using XRD data the average crystalline size of bare IONs, EDTA/IONs and EDTA/Co-doped IONs were calculated 9.1 nm, 8.2 nm and 13.9 nm, respectively. The surface capping was confirmed by FT-IR. FESEM images showed that the average diameters of 20 nm, 40 nm and 35 nm for Pristine IONs and EDTA coated IONs and Co^{2+} doped IONs, respectively. The potential of the prepared nanoparticles on cure reaction of

epoxy resin at low level of particles (0.1 wt.%) was investigated by dynamic DSC at heating rates of 5, 10, 15 and 20 °C/min. DSC results show that pristine IONs hindered epoxy curing reaction with amine hardener as reflected in a significant drop in ΔH values even more than 50%

($\Delta H^*=0.34$ at $\beta=15$ °C/min). While EDTA- IONs increased ΔH_{∞} compared to bare IONs at all heating rates. The value of ΔH increased from 127 J/g for EP/IONs to 310 J/g for EP/EDTA-

IONs. Catalyzing effect of COOH of EDTA on the surface and Co^{2+} in the bulk of IONs led to the shift of cure state of epoxy/amine system from Poor to Good at $\beta = 5, 10$ and 20 °C/min.

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