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SHORT COMMUNICATION

Properties of nano-Fe₃O₄ incorporated epoxy nanocomposites and nanocomposite coatings from *Cure Index* perspective

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Abstract

The mission of an advanced epoxy-based nanocomposite coating is to help protect a given substrate against an unwelcome guest; e.g. corrosive molecule/media, environmental stress, flame, thermal degradation or microorganisms. In such systems, the degree to which superior properties can be guaranteed depends on the state of network formation in the epoxy in the presence of nanoparticles. For low-filled epoxy nanocomposite coatings, barrierity was taken as the main mechanism controlling over the efficiency of corrosion inhibition in the coating against oxygen or other corrosive moieties, whilst in highly-loaded nanocomposites one should take a closer look at both physical and chemical interaction between the resin and nanoparticles. In this sense, epoxy/ Fe_3O_4 systems were studied here as model nanocomposite coatings and their anti-corrosion and flame retardancy potentials were patterned in terms of qualitative cure analysis made in terms of '*Cure Index*'. Anti-corrosion and flame retardancy properties of the aforementioned nanocomposite coatings were mechanistically described at either low or high loading levels in view of *Cure Index* for postulates of structure-properties association in advanced nano- Fe_3O_4 incorporated epoxy nanocomposite coatings. We hope that speculations about such a relationship are the subject of open discussions between experts working in the field for the sake of generalization of idea to complex systems containing different types of nanoparticles whatever surface functionality.

Keywords: Epoxy nanocomposite coating; *Cure Index*; Corrosion; Flame retardancy; Fe_3O_4

The importance of survey

The state of cure of thermoset nanocomposites depends on the nature [1], size [2, 3], shape [4], surface functionality [5-7], and the concentration [8, 9] of particles of nanoscale dimension. Researchers relish the challenge of property control in thermoset resins, where anticorrosion properties, thermal stability, mechanical properties and flame retardancy have to be adjusted individually and/or simultaneously to guarantee a high-performance material [10-12]. Aside from practical implications, armed with the knowledge of concepts, one can study 3D network formation in thermoset nanocomposites that allows for controlling ultimate properties of complex systems [13-15]. The literature in this area is not replete with proposals that embrace tools and mechanisms undertaking curing phenomenon in the nanocomposites. Therefore, understanding the relationship between network formation and properties of such systems has remained undiscovered. The advent and successful implementation of ‘*Cure Index*’, *CI* as a simple yet powerful criterion for analyzing cure state [16, 17] has opened a promising way for taking molecular image from crosslinking in thermoset nanocomposites. The cure state in epoxy nanocomposites containing different sorts of 0D and then 1D nanoparticles was accordingly patterned as *Poor*, *Good*, or *Excellent* Cure. However, the possibility of prediction of ultimate properties by the *CI* remains critical questions to be answered by the investigators. We do know that taking the first steps towards a convincing experimental framework relying on *CI* requires a huge dataset, but attempts are to speed up the interpretation process.

Choosing a case among individuals

Choosing the best case for survey could reflect the concern about dependency of properties of nanocomposite coatings on the *CI*. The experimental data on both curing and properties of nanocomposite coatings in a given report are rare and spread; hence, a global concern about this survey would be the inability of generalization of the outcome of this discussion to an inclusive framework for future research on the *CI* dependence of properties of nanocomposite coatings. Several epoxy nanocomposites and nanocomposite coatings containing pristine and surface-functionalized Fe_3O_4 nanoparticles have been developed so far and their magnetic and dielectric properties [18], wear rate [19], thermal and electromagnetic behavior [20], impedance matching condition [21], thermal conductivity [22], and mechanical properties [23] have been exhaustively examined. In a series of papers, we investigated cure behavior and kinetics of epoxy nanocomposites at low concentration of Fe_3O_4 nanoparticles (0.1 wt.%, well

below aggregation threshold [5]) with different surface functionality resulting from the attachment of β -cyclodextrin [24], hydroxyapatite and chitosan [25], layer-by-layer chemical functionalization with chitosan, imide-phenylalanine precursors [14], and sulfonic acid precursors [15]. However, sometimes higher nanoparticle concentrations are required to guarantee practical worth of the developed nanocomposites. As an upper limit of highly-loaded systems, a nanocomposite based on diglycidyl ether of bisphenol-A (DGEBA) epoxy resin cured with diaminoxanthone (DAX) in the absence and presence of 10 wt.% of amine-functionalized Fe_3O_4 nanoparticles due to Lakouraj et al. was selected [26]. For the sake of brevity, we named the neat and nanocomposite samples studied in the aforementioned work as DGEBA/DAX and DGEBA/DAX/ Fe_3O_4 , respectively. The promising feature of the work was that it contained nonisothermal cure by differential scanning calorimetry (DSC) at different heating rates (β) of 5, 10, 15 and 20 °C/min. Authors also reported on the corrosion behavior, flame retardancy, and thermal stability of nanocomposite coatings using potentiodynamic polarization, limiting oxygen index (LOI) and thermogravimetric analyses, respectively. Moreover, some cases devoted to corrosion or flame retardancy with their own characterization parts were used in the assigned sections, which are dealt with later.

Analysis of crosslinking by *Cure Index*

Qualitative cure analyses on the low- and high-loaded epoxy/ Fe_3O_4 nanocomposites were performed by using the *CI*, as follows [16]:

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

$$\Delta T = T_{Onset} - T_{Endset} \quad (2)$$

$$\Delta T^* = \frac{\Delta T_C}{\Delta T_{Ref}} \quad (3)$$

$$CI = \Delta H^* \times \Delta T^* \quad (4)$$

where ΔH_C and ΔH_{Ref} are the heat of cure calculated by the DSC analyses for epoxy nanocomposites and blank epoxy, respectively. In these equations, T_{Onset} and T_{Endset} stand for the starting and ending temperatures of cure process, respectively; whilst ΔT_C and ΔT_{Ref} are the

temperature interval required for complete cure of the nanocomposite and blank epoxy, respectively.

Low-concentration epoxy/Fe₃O₄ nanocomposites unconditionally revealed one exothermic peak that made possible explicit calculation of the *CI*. Similarly, Lakouraj et al. [26] claimed that nonisothermal DSC thermograms of their highly-loaded nanocomposites cured stoichiometrically revealed only one exothermic peak whatever the heating rate [26]. However, from both the appearance and detailed analysis of DSC thermograms of DGEBA/DAX/Fe₃O₄ systems one can see two distinct exothermic peaks having completely different sizes irrespective of heating rate. This brought about complication to calculation of ΔT , ΔH_{∞} , thereby problem with obtaining the exact value of the *CI*. In our survey, we used the total area below bimodal DSC thermogram as the target for calculation (**Fig. 1**). The amount of ΔT , ΔH_{∞} , ΔT^* , ΔH^* and correspondingly the value of *CI* of DGEBA/DAX and DGEBA/DAX/Fe₃O₄ systems were extracted and calculated, as given in **Table.1**.

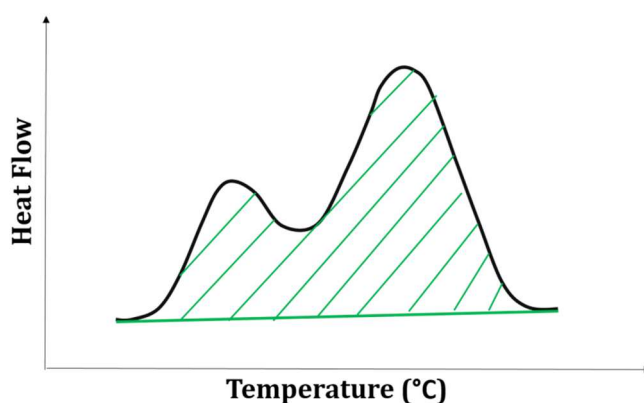


Fig. 1. Total area considered in calculation of ΔH_{∞} under bimodal DSC curves

The presence of two peaks in the DSC curve of DGEBA/DAX/Fe₃O₄ underlines the complexity of curing reaction in epoxy resin in the presence of amine-functionalized Fe₃O₄ due to facilitation of reaction caused by etherification [8]. It is claimed by the authors that the small peak can be ascribed to the cure reaction of DGEBA with amino groups of Fe₃O₄, while the larger peak stands for the reaction of DGEBA with DAX. For calculating the contribution of each reaction, the amount of ΔH of each reaction was determined from the surface of each peak according to **Fig. 2**.

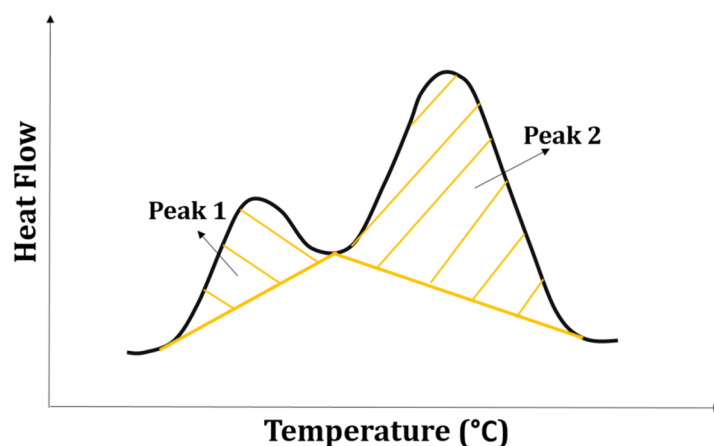


Fig. 2. Total area considered in calculation of ΔH under bimodal DSC curves

We agree with the authors that amine groups grafted to the surface of Fe_3O_4 assist in epoxy ring opening reaction together with the amine groups of DAX curing agent. It is also possible that Fe_3O_4 nanoparticles can react with epoxide rings of resin at lower temperature [26]. Nevertheless, we can hardly accept that cure reaction of epoxy with functional groups in the amine-functionalized Fe_3O_4 is the reason for formation of small peak, Peak 1 in **Fig. 2**, at low temperatures. By contrast, we agree with the authors that reaction of epoxy with DAX takes place at higher temperatures. The contribution of each reaction determined based on **Fig. 2** is statistically given in **Table 1**. As can be observed, due to higher kinetic energy upon increase of heating rate the contribution of amine-functionalized Fe_3O_4 to curing reaction of epoxy would be of higher probability. We provided the statistics, but remain the discussion on this phenomenon to the meticulous readers, those who expect evidence for rationalization of additional exothermic peak, which is appeared in the thermograms.

Table 1. Cure characteristics for neat epoxy and DGEBA/DAX/Fe₃O₄ nanocomposite

Designation	$\beta(^{\circ}\text{C}/\text{min})$	$\Delta T(^{\circ}\text{C})$	$\Delta H_{\infty}(\text{J/g})$	ΔT^*	ΔH^*	CI
DGEBA/DAX	5	204.91	373.12	1.00	1.00	1.00
	10	262.83	374.16	1.00	1.00	1.00
	15	149.75	132.95	1.00	1.00	1.00
	20	275.70	442.13	1.00	1.00	1.00
DGEBA/DAX/Fe₃O₄	5	297.32	767.04	1.45	2.05	2.97
	10	268.23	475.94	1.02	1.27	1.30
	15	290.44	801.99	1.93	6.03	11.64
	20	275.35	865.16	1.01	1.95	1.97
	$\beta(^{\circ}\text{C}/\text{min})$	$\Delta T(^{\circ}\text{C})$	$\Delta H_{\infty}(\text{J/g})$	Contribution to ΔH_{∞} value (%)		
Peak 1	5	81.43	36.84	12.02		
	10	103.41	39.06	19.64		
	15	117.63	60.61	17.82		
	20	130.99	117.65	26.78		
Peak 2	5	215.89	269.61	87.98		
	10	164.82	159.80	80.36		
	15	172.81	279.39	82.17		
	20	145.36	321.59	73.22		

The recently defined *CI* criterion has a very unique ability to track the state of network formation in thermoset nanocomposites. In our first work on the *CI*, we defined schematically duration intervals for the *CI* to in a very simple way give the reader the sense of a measure, where we applied methodology on a series of reliable data collected in our previous works on systems containing 0D nanoparticles with different types and surface functionalities [16]. Then, we assessed the predictability of the *CI* by the implementation of the methodology in a very complex system in which 1D nanoparticles were used as-received, and 1D nanoparticles decorated with 0D nanoparticles followed by functionalization of 1D/0D core/shell particle with hyperbranched macromolecules [17]. We used bar charts as a better way to illustrative the concept and the powerfulness of the *CI* in visualizing how network formation looks like in thermoset nanocomposites. What was surprising was the ability of the *CI* to uncover the positive effect of surface functionalization of nanoparticles on crosslinking, where the *CI* was *Excellent* for all surface-functionalized nanoparticles whatever nanoparticle shape and the amount. Here, we use the third illustrative for the *CI*, which we considered as the best representation explaining network formation in terms of plot of ΔH^* vs. ΔT^* . For making comparison easier, all three representations used for *CI* at low and high loading of Fe₃O₄ are shown in **Fig.3** (ruler format), **Fig.4** (bar charts) and **Fig. 5** (zone diagram).

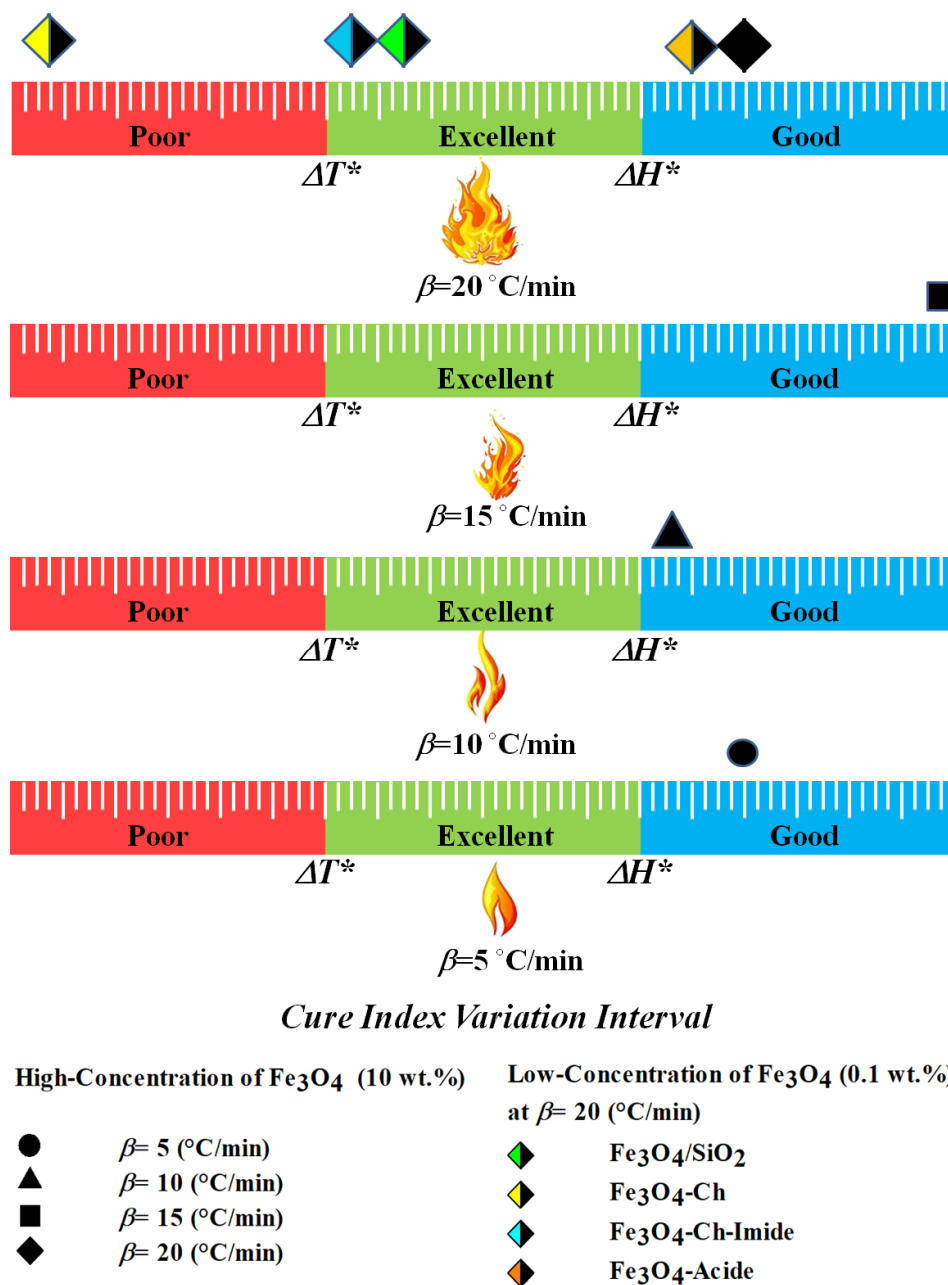


Fig. 3. Ruler representation of *Cure Index* at low-concentration (0.1 wt.%) epoxy nanocomposites with Fe₃O₄/Nanosilica core/shell (Fe₃O₄/SiO₂), Chitosan-modified Fe₃O₄/SiO₂ (Fe₃O₄-Ch), Imide/phenylalanine-modified Fe₃O₄-Ch (Fe₃O₄-Ch-Imide) [14] and 2-acrylamido-2-methylpropanesulfonic acid-modified Fe₃O₄/SiO₂ (Fe₃O₄-Acide) [15]; besides high-concentration (10 wt.%) DGEBA/DAX/Fe₃O₄ systems cured at heating rate of 5, 10, 15 and 20 °C/min [26]. To give the sense of concentration to the reader we used semi-filled and filled symbols for low- and high-concentration systems, respectively.

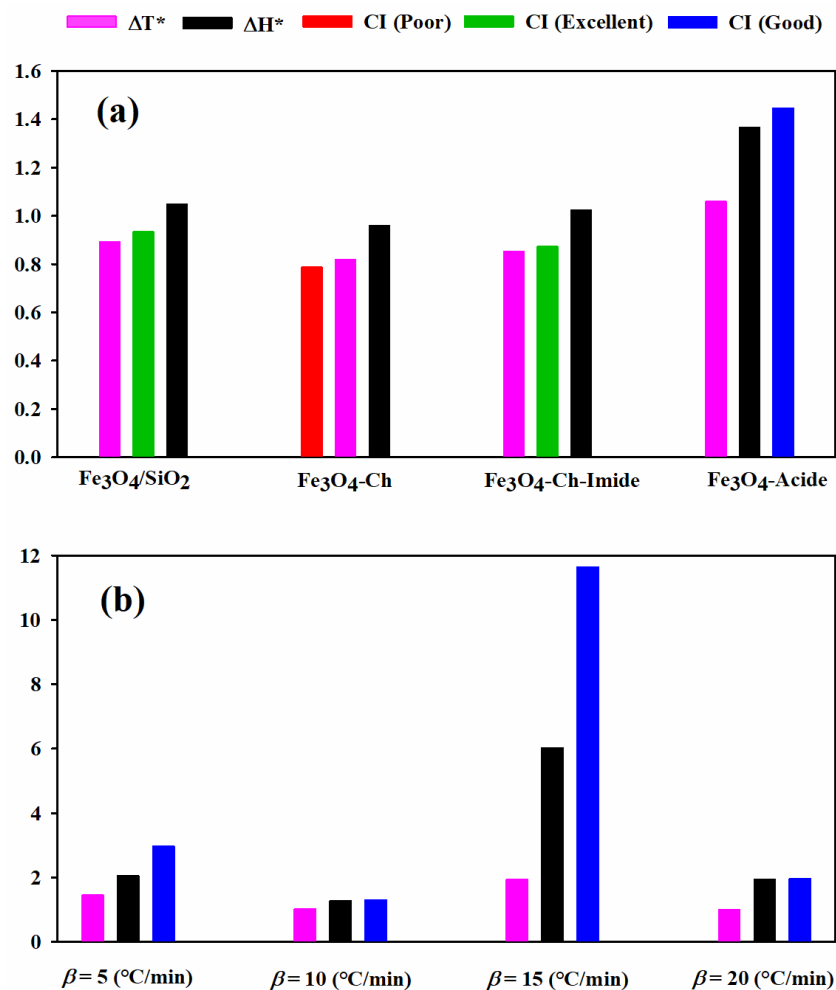


Fig. 4. Bar chart representation of *Cure Index* for (a) low-concentration (0.1 wt.%) epoxy nanocomposites with Fe_3O_4 /Nanosilica core/shell ($\text{Fe}_3\text{O}_4/\text{SiO}_2$), Chitosan-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ($\text{Fe}_3\text{O}_4\text{-Ch}$), Imide/phenylalanine-modified $\text{Fe}_3\text{O}_4\text{-Ch}$ ($\text{Fe}_3\text{O}_4\text{-Ch-Imide}$) [14] and 2-acrylamido-2-methylpropanesulfonic acid-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ($\text{Fe}_3\text{O}_4\text{-Acid}$) [15] and (b) high-concentration (10 wt.%) DGEBA/DAX/ Fe_3O_4 systems cured at heating rate of 5, 10, 15 and 20 °C/min [26]

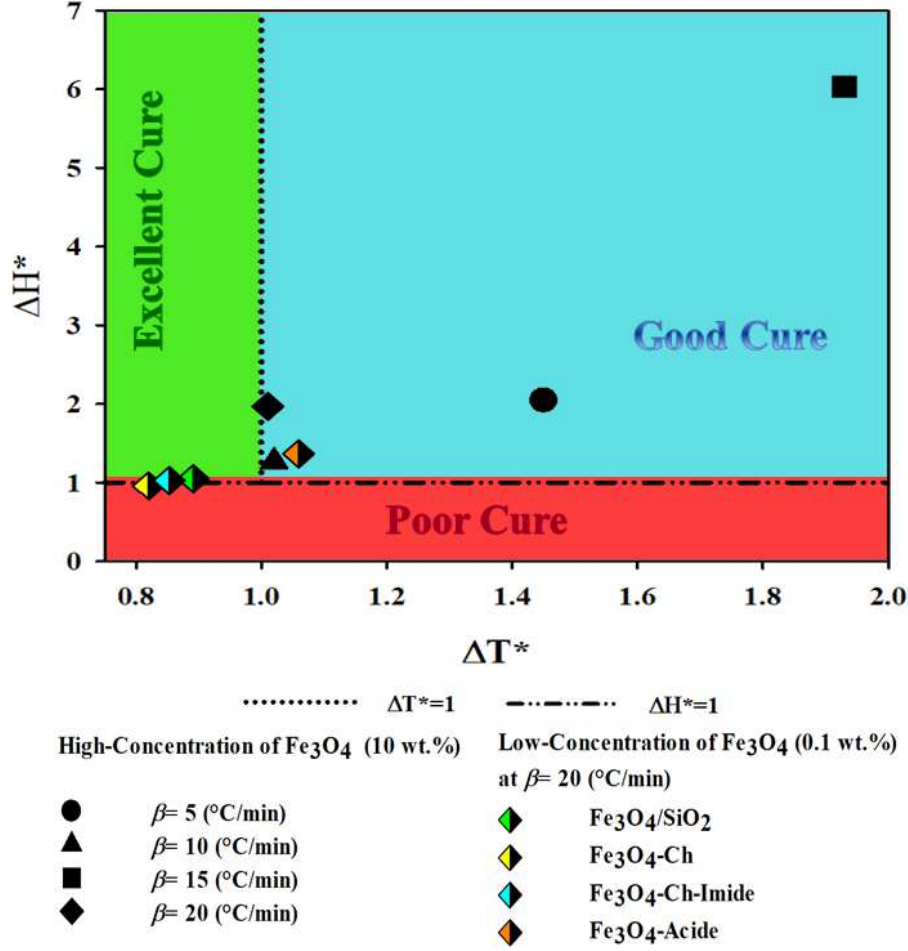


Fig. 5. Zone diagram representation of *Cure Index* for low-concentration (0.1 wt.%) epoxy nanocomposites with Fe_3O_4 /Nanosilica core/shell ($\text{Fe}_3\text{O}_4/\text{SiO}_2$), Chitosan-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ($\text{Fe}_3\text{O}_4\text{-Ch}$), Imide/phenylalanine-modified $\text{Fe}_3\text{O}_4\text{-Ch}$ ($\text{Fe}_3\text{O}_4\text{-Ch-Imide}$) [14] and 2-acrylamido-2-methylpropanesulfonic acid-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ($\text{Fe}_3\text{O}_4\text{-Acide}$) [15]; besides high-concentration (10 wt.%) DGEBA/DAX/ Fe_3O_4 systems cured at heating rate of 5, 10, 15 and 20 $^\circ\text{C}/\text{min}$ [26].

In the zone diagram representation in **Fig. 5**, the green landscape illustrates *Excellent Cure* case ($\Delta T^* < CI < \Delta H^*$), the blue landscape is representative of *Good Cure* ($CI > \Delta H^*$), and the red landscape defines *Poor Cure* ($CI < \Delta T^*$), which are together qualitative representations of crosslinking affected by nano- Fe_3O_4 incorporation into the epoxy. According to statistics given in **Table 1** and **Fig. 3 to 5**, for low-concentration epoxy/ Fe_3O_4 systems, all three types of cure can be reached depending on surface functionality of nanoparticles. We comprehensively discussed about the situation that we face in such systems in a previous work [16]. For highly-loaded system, amine-functionalized Fe_3O_4 nanoparticles keep cure of

DGEBA/DAX systems in a *Good* state irrespective of heating rate, which give sense of proper participation of reactive Fe_3O_4 in cure reaction. It means that amine groups present on the surface of Fe_3O_4 attack to the epoxy groups of resin, and assist in epoxy ring opening reaction leading to a denser crosslinked epoxy network, as indicated by higher ΔH_∞ values compared to the neat epoxy resin.

The effects of low and high concentration of pristine and surface-functionalized Fe_3O_4 nanoparticles on curing reaction of epoxy resin are schematically explained in **Fig. 6**. At low loading of nano- Fe_3O_4 , the probability of nanoparticles aggregation is closely zero, which affects curing potential of epoxy thanks to the large surface to volume ratio of nanoparticles (**Fig.6 (b)**). Moreover, surface modification of Fe_3O_4 nanoparticles has substantial effect on curing reaction of epoxy at low concentration due to effective participation of reactive groups anchored to the surface of Fe_3O_4 nanoparticles in crosslinking reactions (**Fig.6 (c)**). The effective presence of nanoparticles in epoxy matrix leads to a denser crosslinked network. At high concentration of Fe_3O_4 nanoparticles, the success in achieving a well-cured network is dependent on the state of dispersion of nanoparticles throughout the epoxy resin. By choosing suitable mixing method, well-dispersion can be achieved even at high loadings for pristine nanoparticles (**Fig.6 (d and e)**). However, the possibility of nanoparticles' agglomeration at high loading of nanoparticles is usually higher-what ineffectively hinders crosslinking reactions (**Fig.6 (f and g)**).

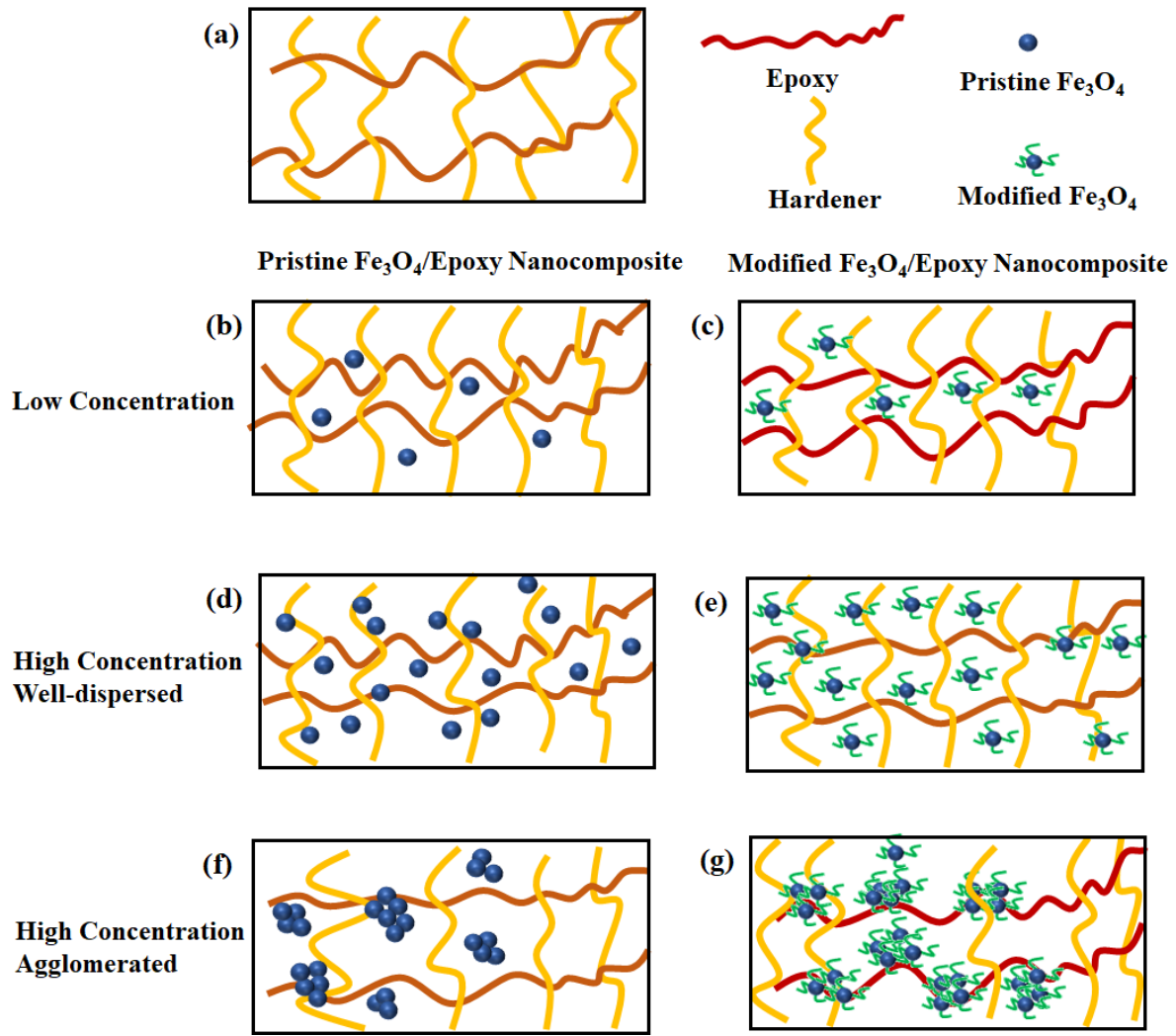


Fig. 6. Schematic illustration of the effect of loading and functionalization of Fe_3O_4 nanoparticles on curing reaction of epoxy resin; (Source: authors)

Desirable dispersion of nanoparticles in the base resin can lead to increase in the crosslinking density of cured system, particularly in the case of surface-functionalized nanoparticles. From application standpoint, an epoxy network with higher crosslinking density due to nanoparticle incorporation in the absence of voids would be on-demand for applications like anticorrosion coating. Well-cured epoxy/ Fe_3O_4 nanocomposites enhance corrosion inhibition through the prevention of diffusion of moisture, oxygen, and other corrosive materials inside the epoxy coatings. However, high amount of nanoparticles may be required for applications like flame retardant coatings. Still achieving complete cure in the presence of nanoparticles is essential. Partially cured systems at high loading of nanoparticles are of higher likelihood of formation and quite often cause undesirable properties [10].

Anti-corrosion mechanism

Evolution in 3D network formation in thermoset resins during the cure process involves densification of system followed by decline in volume. In the case of epoxy resin, this decrement fluctuates between 0.5 and 10% leading to a considerable volumetric shrinkage. Additionally, the curing process in a constrained mold increases the possibility of having higher tensile stress. These phenomena together assist in formation of voids [27], the main cause of corrosion in most engineering contexts. To tackle this problem, as a very basic corrosion protection method, the use of nanoparticles makes possible to hinder diffusion of corrosive moieties into the resin [28].

Fig. 7 demonstrates anti-corrosion barrier mechanism of neat epoxy and its nanocomposite with the bare and functionalized Fe_3O_4 nanoparticles dispersed poorly or well in the resin. It can be seen that moisture, oxygen, and other corrosive materials can easily reach the metal substrate in the absence of nanoparticles through the pathways void provide with the resin (Top scheme in **Fig. 7**). By the immersion time, the interface between the polymer and metal substrate undergoes cathodic delamination [29]. On the other hand, based on an experimental study done by Zhang et al. [30], it was demonstrated that even at low concentration of Fe_3O_4 nanoparticles (1 wt.%) uniformly dispersed in the epoxy matrix an improved corrosion inhibition could be expected with respect to the blank epoxy coating (**Fig. 7a**). It was reported that SiO_2 -coated (surface-modified) Fe_3O_4 had a relatively good dispersion ability in the epoxy due to chemical stability brought about by the silica layer, as schematically shown in **Fig. 7b**. There was evidence that SiO_2 -coated Fe_3O_4 nanoparticles were able to provide the epoxy coating with acceptable anti-corrosion properties with respect to the bare- Fe_3O_4 /epoxy nanocomposite and similarly than that of the neat epoxy matrix [30]. Elsewhere, Fe_3O_4 nanoparticles treated with indole-3 butyric acid (IBA) appeared as a corrosion inhibitor when incorporated by 3 wt.% in an epoxy-polyamide coating [31]. It was indicated that the coating acted as an efficient corrosion inhibitive layer in the presence of IBA- Fe_3O_4 nanoparticles, like what we visualized in **Fig. 7b**. Overall, the impedance results revealed that incorporation of bare and surface-coated Fe_3O_4 nanoparticles into the epoxy matrix kept anti-corrosion properties at a satisfactory level in the face with sodium chloride electrolyte. Furthermore, it was understood from the bending test results that the interaction between metal surface and the coating has been improved by surface modification of nanoparticles.

It is generally accepted that at high loading levels the bare Fe_3O_4 nanoparticles are prone to poor dispersion in the epoxy system (**Fig. 7c**). Lakouraj et al. [26] showed that addition of 10 wt.% of amine-functionalized Fe_3O_4 nanoparticles to epoxy leads to an R_p value of ca. $2.6 \text{ M}\Omega\cdot\text{cm}^2$ for the resulting nanocomposite coatings, which was about 1.6 times higher than the value of R_p obtained for the neat epoxy coating. As disclosed by the *CI*, the curing process of highly-loaded DGEBA/DAX/modified- Fe_3O_4 gives the cure sense of *Good* (**Fig. 3-5**). This was featured by a rise in the total heat release upon addition of amine-modified Fe_3O_4 . The functional groups of well-dispersed amine-modified Fe_3O_4 contributed to crosslinking reactions with epoxy leading to a denser 3D network with fewer voids with respect to the neat epoxy coating, hence allowed for barrier property promotion (**Fig. 7d**). It should be noted that there might be a critical concentration at which agglomerates are formed significantly or partially depending on surface functionality of nanoparticles (see **Fig. 7b** and **7c**). In such a situation, enlargement of void size would take place that deteriorates corrosion resistance of the coating. Above the aforementioned critical concentration, addition of nanoparticles might be destructive due to the van der Waals attractive forces being boosted between the Fe_3O_4 nanoparticles and also magnetic attraction acting on them that intensifies agglomeration and hence deteriorates barrier property. Fe_3O_4 surface modification can be employed in order to tackle the attractive forces caused by stearic repulsions [32]. It is well-accepted that proper dispersion of nanoparticles in a polymeric media can improve the corrosion resistance of coating by lowering the number of open voids. However, improper surface modifications of Fe_3O_4 may increase the risk of agglomeration.

According to the aforementioned context, the cure situation of epoxy thermoset systems in the presence of nanoparticles has an important role on their final properties. Well-dispersed nanoparticles with reactive chemical groups anchored to surface can effectively participate in curing reaction of epoxy leading to *Excellent* or *Good* cure based on the *CI* criterion. In these situations, the final network is denser with fewer voids that prevents moisture and corrosion materials' diffusion through the epoxy matrix that leads to a coating with higher corrosion inhabitation property with respect to blank coating.

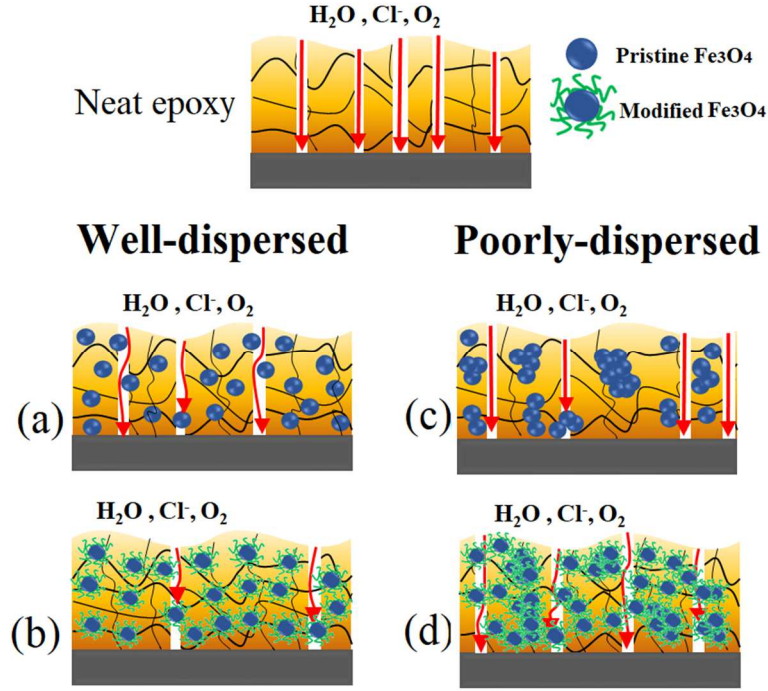


Fig. 7. Possible barrier and corrosion protection mechanisms of the neat epoxy (Top scheme) and Fe_3O_4 /epoxy nanocomposite coatings: (a) Well-dispersed bare- Fe_3O_4 /epoxy nanocomposite; (b) Well-dispersed Modified- Fe_3O_4 /epoxy nanocomposite; (c) Poorly-dispersed bare- Fe_3O_4 /epoxy nanocomposite; and (d) Well-dispersed modified- Fe_3O_4 /epoxy nanocomposite; (Source: authors)

Since various corrosion test methods are available, we may need an auxiliary function simplifying the comparison of coating corrosion resistance performances. In this sense, '*Anti-corrosion Performance Enhancement*' was simply defined based on available experimental data by normalizing the difference in the corrosion resistances of the neat and the nanoparticle-containing matrix to the one of the blank epoxy, as follows:

Anti-corrosion Performance Enhancement in percent based on Electrochemical Impedance Spectroscopy (EIS) was defined as:

$$\left| \frac{\log Z(\text{Nanoparticle-containing}) - \log Z(\text{Neat epoxy})}{\log Z(\text{Neat epoxy})} \right| \times 100 \quad (5)$$

$$\left| \frac{Rt(Nanoparticle - containing) - Rt(Neatepoxy)}{Rt(Neatepoxy)} \right| \times 100 \quad (6)$$

Anti-corrosion Performance Enhancement based on salt spray test was also defined as:

$$\left| \frac{Rustcreepage(Nanoparticle - containing) - Rustcreepage(Neatepoxy)}{Rustcreepage(Neatepoxy)} \right| \times 100 \quad (7)$$

Anti-corrosion Performance Enhancement based on potentiodynamic polarization:

$$\left| \frac{Icorr(Nanoparticle - containing) - Icorr(Neatepoxy)}{Icorr(Neatepoxy)} \right| \times 100 \quad (8)$$

The results of calculations by the use of related data in the literature are given in **Table 2**.

Table 2. Summary of available experimental data on corrosion inhibition of epoxy coatings caused by Fe_3O_4 based on *EIS, **Salt spray data, and ***Potentiodynamic polarization data

Media	Nanoparticle type	Nanoparticle concentration (wt.%)	Anti-corrosion Performance Enhancement (%)	Reference
*Epoxy	Fe_3O_4 / ^a TEA	1	11.88	[33]
	^b APTMS- Fe_3O_4	1	1.81	
	APTMS- Fe_3O_4 /TEA	1	37	
*Epoxy	Fe_3O_4	1	41.44	[30]
	$\text{Fe}_3\text{O}_4/\text{SiO}_2$	1	135.98	
**Epoxy-polyamide	Fe_3O_4	3	37.79	[31]
	^c IBA- Fe_3O_4	3	49.6	
***Epoxy	Fe_3O_4	10	83.00	[26]

^a TEA is triethanolamine

^b APTMS is 3-aminopropyltrimethoxysilane

^c IBA is indole-3 butyric acid

Fig. 8 gives a brief view of variation interval of corrosion inhibition of epoxy-based nanocomposite coatings based on data provided in **Table 2**. While sufficient data points are not available, it can be roughly interpreted that a higher concentration of the nanoparticles cannot necessarily increase the corrosion inhibition of the coating. Additionally, nanoparticle surface modification generally alters the corrosion inhibition depending on the nanoparticle and surface modification types. It is worth noting that even at very low level of Fe_3O_4 - SiO_2 loading (1 wt.%) about 136 % improvement in corrosion inhibition was gained, while using more quantities of surface-modified nanoparticles could not significantly enhance corrosion inhibition.

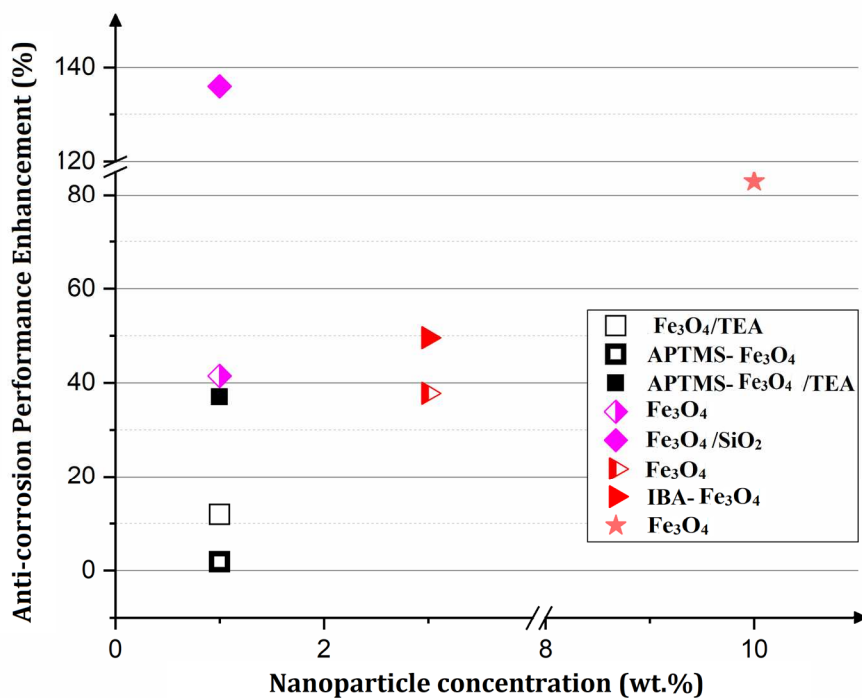


Fig. 8. Anti-corrosion Performance Enhancement (%) of epoxy-based coatings in the presence of bare and modified Fe_3O_4 nanoparticle as a function of weight percent

Flame retardancy mechanism

The formation of residue/char during combustion is a signature of flame retardancy action of polymers. It is obvious that the transformation of a part of polymer into residue/char during combustion decreases fuels evolved from the combustion [33]. Furthermore, the presence of residue/char on the surface of polymer may insulate and protect the underlying polymer from the flame. It can slow down the transfer of gases from the pyrolysis zone to the flame, and act as a barrier for oxygen penetration from the surface into condense phase during the combustion [34]. The efficiency of a residue/char as a barrier during the combustion depends on both its chemical and physical properties.

As described earlier, network formation in thermoset epoxy resins during cure process leads to volumetric shrinkage that is responsible for void formation. Therefore, these voids facilitate oxygen diffusion through the epoxy resin coating. Typically, pyrolysis can lead to formation of the char layer on the surface of polymers. The neat epoxy sample generates a very thin brittle char microlayer whilst it burns [35]. The existence of cracks and voids in the char layer leads

to low barrier efficiency, thereby facilitates diffusion of oxygen inside the epoxy matrix followed by facile transfer of evolved products of combustion of matrix to gaseous phase (**Fig. 9 (a)**).

Addition of nanoparticles to the epoxy matrix can improve flame retardancy and thermal stability of base epoxy, depending on the type and concentration of nanoparticles. Likewise, flame retardancy action of epoxy nanocomposites depends on the type of nanoparticles at low or high loading levels, which itself determines partial or complete curing of epoxy. In some previous works, we underlined the effects of halloysite nanotube as low-cost mineral and expandable graphite as superior flame retardants [36] at low and high loading levels (3 and 9 wt.%, respectively) as well as dependency of cure state of epoxy (denoted as partial and complete cures) [10] on flame retardancy of epoxy coatings were thoroughly discussed. In case of magnetic nanoparticles, investigations are indeed limited. At low loading levels, the effects of iron oxide green ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and iron oxide brown ($\text{Fe}_2\text{O}_3 + \text{FeO} \cdot n\text{H}_2\text{O}$) nanoparticles on smoke-suppression properties and flame retardancy behavior of epoxy were reported in almost twin papers by a Chinese group [37, 38]. They added very low amounts of the aforementioned nanoparticles (0.5-3 wt.%) to an epoxy highly loaded (ca. 60 wt.%) with ammonium polyphosphate (APP) and pentaerythritol (PER) intumescent flame retardant additives. They declared that synergistic effects between iron oxide and APP/PER was responsible for significant smoke suppression they observed, while cone calorimetry curves were almost similar for samples having different amount of iron oxide. Since no jump was seen in cone calorimetry curves of epoxy-based composites caused by addition of iron oxide nanoparticles, very high contents of APP and PER in the system were responsible for intumescent character of epoxy. Elsewhere, Fe_3O_4 -doped sepiolite was added at 2 and 4 wt.% to epoxy and its flame retardancy performance was compared correspondingly with sepiolite [39]. Although *Flame Retardancy Index*, in brief *FRI*, is defined for thermoplastic composites, we believe in its worth for evaluating the effect of doping Fe_3O_4 in sepiolite based on cone calorimetry data provided by the authors on thermoset epoxy nanocomposites [40]. Calculations unraveled that *FRI* values were 0.98 and 1.26 for epoxy systems containing 2 and 4 wt.% neat sepiolite additives, respectively. This shows that at higher content addition of this filler changed performance of system from *Poor* to *Good*, but still very limitedly. The *FRI* values of 0.93 and 1.15 were also calculated for the corresponding epoxy systems filled with the same amounts of Fe_3O_4 -doped sepiolite, signifying even worsening of sepiolite performance by structural changes made by

magnetic nanoparticles. Overall, estimations suggest that at low concentration Fe_3O_4 has no serious effect on the flame retardancy of epoxy.

At higher loadings, hybridization of nano- Fe_3O_4 with MgAl layered double hydroxide (LDH) nanoparticles amalgamated with phytic acid and hydroxypropyl-sulfobutyl- β -cyclodextrin sodium (CDBS) flame retardant additives loaded at 8 wt.% in epoxy resulted in 55 % decline in the peak of heat release rate (pHRR) and 34% in total smoke production (TSP) [41]. Though decline in pHRR is itself a signature of flame retardancy behavior of system, calculation of *FRI* of 2.29 after 600 s exposure to flame in cone calorimetry measurements suggests that still the amount of additive should be higher for performance enhancement. Analyses on micro-calorimetry of combustion was also served to study high-contraction epoxy/ Fe_3O_4 nanocomposites. A report on surface functionalization of Fe_3O_4 nanoparticles with conductive polypyrrole polymer and its incorporation into epoxy at 30 wt.% was indicative of 50% fall in the total heat release (THR) of epoxy [42]. Nevertheless, no information on cure state of the aforementioned systems was given by the authors. Lakouraj et al. [26] showed that amine-functionalized Fe_3O_4 nanoparticles enhanced char formation and improved the thermal stability of epoxy coatings through the LOI and TGA analysis. As discussed in cure section, from *CI* standpoint the cure state of epoxy system becomes *Good* in the presence of amine-functionalized Fe_3O_4 nanoparticles. *Good* cure represents a network with higher crosslink density which can provide a reasonable justification for increasing thermal stability and flame retardancy of their epoxy nanocomposite coating.

Overall, a mechanism together with possible reasons are presented here for flame retardancy of epoxy system containing Fe_3O_4 nanoparticles. The results of Lakouraj et al. are considered as a particular case. In the presence of Fe_3O_4 nanoparticles, a more compact network can be formed. Metal nanoparticles are usually used to improve the thermal stability of char layer [41]. Ions in intermediate metals accelerate the formation of char layer and increase the flame retardant efficiency. Intermediate metals act as a catalyst for crosslinkable macromolecules that increase char formation [41]. However, forasmuch as the interaction of Fe_3O_4 nanoparticles with epoxy resin is physical, the movement of polymer chains in the vicinity of nanoparticles takes place easily under heat, which leads to induction of free volume in the system, while oxygen still can diffuse into the bulk material. However, the transfer paths of oxygen into the material and pyrolysis products into the flame area are to some degree more difficult than the neat epoxy resin because of existence of fewer holes in nanocomposite system. High thermal conductivity of these nanoparticles allows evacuation of heat at the surface of sample and

delays thermal decomposition [43]. As a result, the presence of nanoparticles leads to less polymer degradation and higher residue formation with higher thermal stability because of formation of denser crosslinked network during cure process (**Fig. 6 (b)**). By the way, char contains cavities and cracks, which cause mass and heat, transfer in system (**Fig. 9 (b)**).

Increasing the concentration of nanoparticles leads to a denser network with fewer cavities, which improves the barrier effect of the char layer (**Fig. 9 (C)**) pertinent to fine dispersion of nanoparticles for well-cured network formation shown in **Fig. 6 (c)**. However, by passing a critical concentration, nanoparticles tend to interact with themselves rather than interacting with polymer matrix chains because of Van der Waals forces, which hinder curing reaction of epoxy system (**Fig. 6 (f)**). Consequently, they form agglomerates, which leads to more pathways for oxygen diffusion associated with degradation of polymer chains. The resulting degradation products can easily transfer through the gaseous phase, which cause flammability resistance becoming worse than the neat sample. The char also contains large cracks that do not show any barrier effect (**Fig. 9 (d)**).

Functionalization of Fe_3O_4 nanoparticles leads to strong interactions between the particles and the epoxy matrix with benefits to formation of 3D network with higher crosslink densities (**Fig. 6 (c)**). This denser network makes diffusion of oxygen into the material harder resulting in less degradation of sample and less flammable products. The combustion products are also trapped inside the crosslinked network to reduce refueling the flame (**Fig. 9 (e)**). Increasing the concentration of these nanoparticles will also result in a more compact 3D network with very small amount of molecular diffusion that enhances flame retardancy performance of nanocomposite. Increasing the amount of char residue in this sample as well as its higher thermal stability leads to a further reduction in the total amount of released volatiles and heat transfer (**Fig. 9 (f)**). The nanocomposite that was prepared by Lakouraj et al. [26] can be placed in this class, as confirmed by *Cure Index*, where 10 wt.% of amine-modified Fe_3O_4 is well dispersed in epoxy matrix to improve crosslink density through decrease of oxygen and combustion products pathways (**Fig. 9 (f)**). However, by passing the critical concentration of these nanoparticles due to their high surface area, they tend to hug each other and forms agglomerate. This aggregation decreases crosslink density featured by *Poor* cure case based on the *CI* (**Fig. 6 (g)**). As a result, the diffusion pathways increase and the flammability of this sample decreases (**Fig. 9 (g)**). Overall, from all the aforementioned scenarios it is obvious that characteristics of the formed residue/char such as porosity, cohesion, thermal stability, thermal

conductivity, hardness, and thickness are directly affected by the curing state of resin as well as the state of interaction of nanoparticles with matrix during curing process.

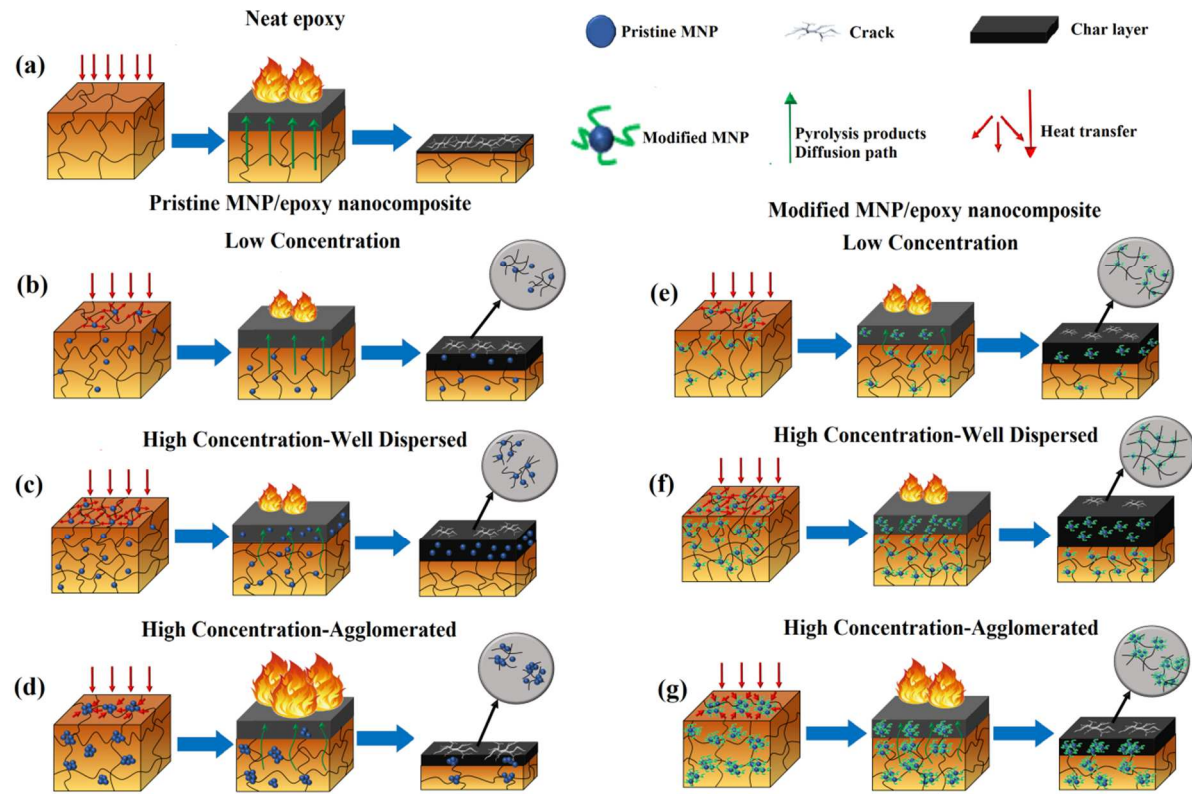


Fig. 9. Schematic diagrams of char formation and flame retardancy mechanism of neat epoxy and its MNPs nanocomposite coatings: (a) neat epoxy, (b) low concentration of pristine Fe_3O_4 , (c) low concentration of modified- Fe_3O_4 , (d) high concentration of well-dispersed pristine Fe_3O_4 , (e) high concentration of agglomerated pristine Fe_3O_4 , (f) high concentration of well-dispersed modified- Fe_3O_4 and (g) high concentration of agglomerated modified- Fe_3O_4 (HC-M-P); (Source: authors)

A close view at anti-corrosion and flame retardancy performance of epoxy coatings containing low and high concentration of pristine and modified Fe_3O_4 must be interpreted on account of *Cure Index*. It helps to deepen understanding of performance of organic composite coatings from a qualitative molecular perspective. Fe_3O_4 nanoparticles, depending on their content and functionality, can affect cure in epoxy, and consequently change anti-corrosion and flame retardancy performances. Network formation in thermoset epoxy resins during cure process leads to volumetric shrinkage, which is responsible for void formation and allows diffusion of oxygen, corrosion and combustion products through the coating, and; therefore, weakens barrier property. However, Fe_3O_4 at sufficient level and with proper functionality can facilitate

dispersion of particles in epoxy matrix, block the diffusion paths and improve barrier property of epoxy coating for anti-corrosion and flame retardancy application. For a comprehensive conclusion, a large pull of data on engineered systems in terms of cure, anti-corrosion, and flame retardancy characteristics are necessary.

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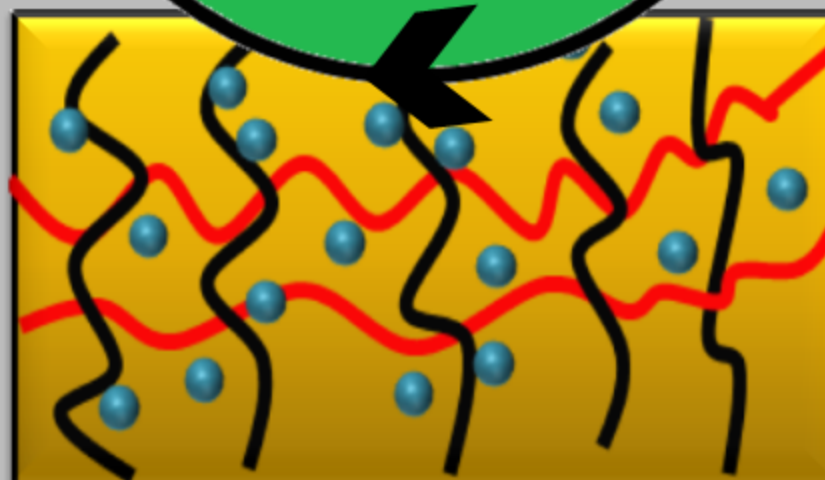
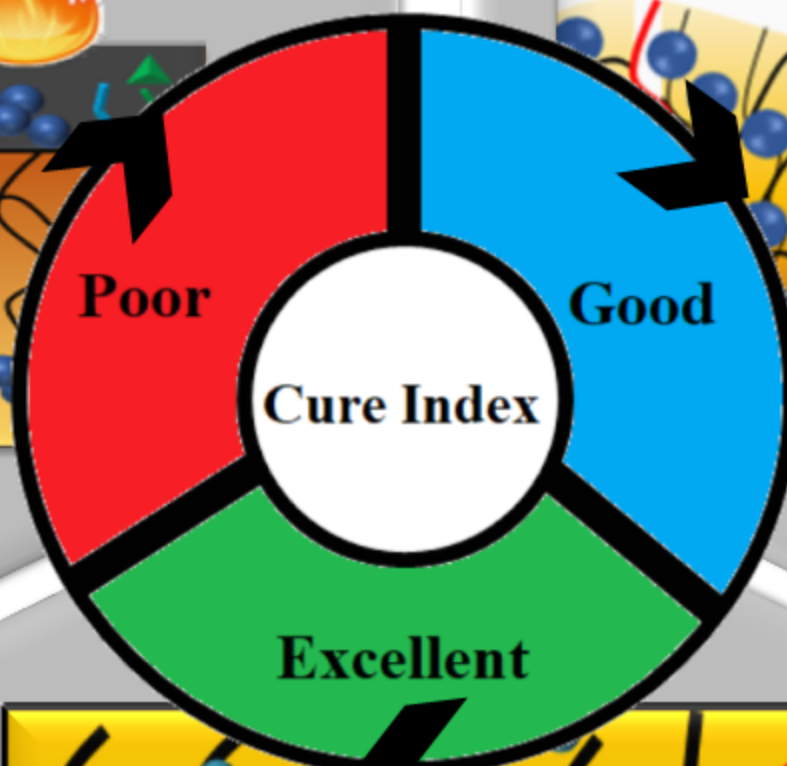
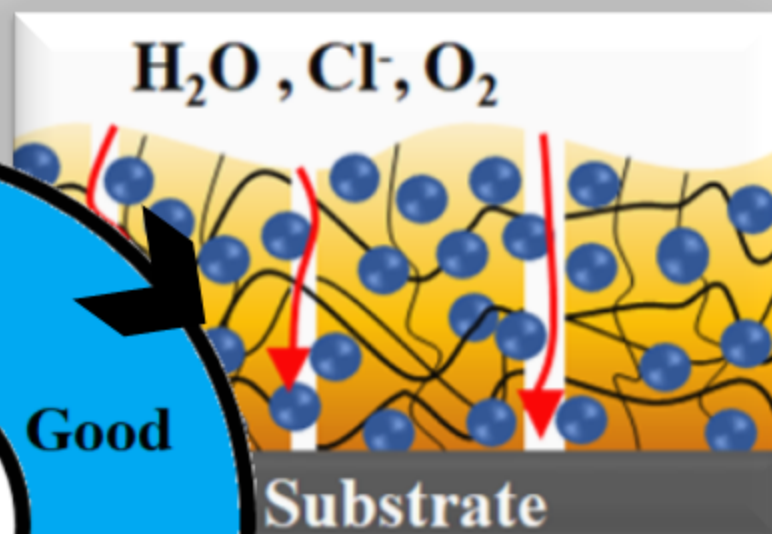
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Flame Retardant Coating



Anti-corrosive Coating



Well-cured Network