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Epoxy/starch-modified nano-zinc oxide transparent nanocomposite coatings: A showcase of superior curing behavior

Morteza Ganjaee Sari^a, Mohammad Reza Saeb^{b,*}, Meisam Shabanian^c, Mahroo Khaleghi^c, Henri Vahabi^d, Christelle Vagner^e, Payam Zarrintaj^f, Reza Khalili^f, Seyed Mohammad Reza Paran^g, Bahram Ramezanzadeh^h, Masoud Mozafariⁱ

^a Department of Nanomaterials and Nanocoatings, Institute for Color Science and Technology, P.O. Box 16765-654, Tehran, Iran

^b Department of Resin and Additives, Institute for Color Science and Technology, P.O. Box 16765-654, Tehran, Iran

^c Faculty of Chemistry and Petrochemical Engineering, Standard Research Institute (SRI), P.O. Box 31745-139, Karaj, Iran

^d Université de Lorraine, Laboratoire MOPS E.A. 4423, Metz F-57070, France

^e Aix Marseille Univ, CNRS, MADIREL UMR 7246, F-13397 Marseille, France

^f School of Chemical Engineering, College of Engineering, University of Tehran, P.O. Box: 11155-4563, Tehran, Iran

⁸ Department of Polymer Processing, Iran Polymer and Petrochemical Institute, P.O. Box: 14965-115, Tehran, Iran

h Department of Surface Coatings and Corrosion, Institute for Color Science and Technology, P.O. Box 16765-654, Tehran, Iran

¹ Department of Nanotechnology and Advanced Materials, Materials and Energy Research Center (MERC), P.O. Box 31787-316, Tehran, Iran

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ABSTRACT

A new class of transparent epoxy-based nanocomposite coatings containing starch-modified nano-zinc oxide (ZnO-St) is presented. ZnO nanoparticles physically decorated with starch carbohydrate polymer increased compatibility with epoxy chains and sterically prevented flocculation of ZnO nanoparticles. Surface characteristics of pristine ZnO and ZnO-St are studied by FTIR spectroscopy corroborating self-assembled starch molecules on ZnO surface until reaching a complete coverage. Curing behaviors of epoxy and transparent nanocomposites containing ZnO and ZnO-St are studied by the aid of nonisothermal calorimetric analyses at four heating rates to compare the curing enthalpies, onset temperatures, peak temperatures, and curing intervals of transparent coatings. The ZnO-St, particularly at low heating rate of 5 °C/min, prolonged curing (corresponding to ΔT increase of ca. 166 for epoxy to 200 °C for Zn-St/epoxy), and increased the amount of heat release (in the same order from 328 to 380 J/g) due to epoxide ring opening by starch hydroxyl groups. Such novel class of epoxy/ZnO-St nanocomposite coatings can be applied as top-coats because of their transparency. Additionally, from an environmental/biological standpoint, one should consider that starch is a carbohydrate polymer and ZnO is antibacterial, which may put more stress on the use of transparent nanocomposite coatings developed in this work.

1. Introduction

The use of advanced epoxy-based materials with superior properties has undergone serious developments in recent years and it is estimated to take a particular place in between versatile thermosetting systems such as nanocomposite coatings [1–3]. Having applied as coating, such nanocomposites show significantly different physical, mechanical and thermal properties compared to their conventional counterparts [4,5]. Nano-zinc oxide (ZnO), as one of the multifunctional inorganic nanoparticles, has drawn a great deal of attention due to its prominent physical and chemical properties, such as chemical stability, low dielectric constant, high luminous transmittance, high catalysis activity, effective antibacterial and bactericide, large band gap, very high excitation binding energy, intensive photo-catalytic effect (ultraviolet and infrared absorption), semiconducting characteristics [6–8].

Epoxy-based coatings comprising nano ZnO have been widely used in the quest for protection of metal substrates against environmental corrosions [9,10]. The nanocomposites based on epoxy resins are usually characterized by the ease of curing and/or processing, excellent resistance against moisture, solvent and chemicals as well as outstanding adhesion strength [11–14]. ZnO nanoparticles can also be used as reinforcing phase to improve wear resistant and anti-sliding properties of composites arising from high elastic modulus and strength [15,16]. It is also of vital importance to know that ZnO nanoparticles

* Corresponding author. E-mail addresses: saeb-mra@icrc.ac.ir, mrsaeb2008@gmail.com (M.R. Saeb).

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Fig. 1. Illustrative description of Modification of nano ZnO by starch.





Fig. 2. Schematic demonstration of the chemical structure of the starch-modified nano ZnO.

are nontoxic materials utilized to produce environmentally friendly coatings. Furthermore, it has been found that anticorrosion resistance of the coatings containing this nanoparticle can be superiorly improved [17–19].

However, one must bear in mind that all the above-mentioned advantages will come to reality if only a completed state of dispersion is obtained. It means that ZnO primary particles must be homogeneously distributed and stabilized inside the epoxy matrix. The latter is rare for untreated hydrophilic ZnO particles inside a hydrophobic continuous phase like as epoxy polymers. Surface functionalization of nanoparticles was exploited as the easiest route to conquer such efficacies through modifying the surface physical chemistry properties of filler to increase miscibility between the phases [20,21]. In addition, one can find the best solvent to maintain the dispersing phase inside the matrix to enhance the stability of the dispersion and to prevent the particles to flocculate [22]. By tailoring the functionalities it is possible to simultaneously reach the goals both [23,24].

Starch is a biocompatible macromolecular carbohydrate consisted of large number of glucose units binding together through glycosidic bonds. The structure of this polymer can be divided into two sections of







2000

1500

1000

500

120

60

40

20

4000

3500

3000

Transmittance (%)



Fig. 4. The FTIR spectra of the starch, ZnO, and ZnO-St.







(c)

Fig. 3. The appearance of neat epoxy (a); epoxy/ZnO (b) and epoxy/ZnO-St (c) films for the sake of transparency comparison.

linear helical amylose and the branched amylopectin [25]. The glucose units provide plenty of hydroxyl functional groups that can be used for being covalently grafted on the nano particles such as ZnO. Furthermore, the voluminous construction of starch provides the particles with steric hindrance and prevents them to flocculate, as observed for dendrimer-modified GO in epoxy system [26]. Therefore, it seems that starch can be considered as a potential candidate for surface

functionalization of various nano particles notwithstanding to the best of the authors' knowledge very few studies have been conducted on starch as a natural surface modifier for nanoparticles in the epoxy coating industries.

There is no need to emphasize that almost all properties of the epoxy-based composite coatings are invariably conditional on the curing reactions and the progression in 3D network formed in the course of curing [27,28]. Investigating the cure characteristics of nanocomposite coatings in the absence and in the presence of nanoparticles offers worthwhile evidences about the chemical reactions taking place during the cure process, and consequently deeper understanding of structure-related properties of such coatings. In a previous study [29], the role of the length of the aliphatic amine arm attached to the surface of graphene oxide (GO) nanoplatelets on the curing behavior, cure kinetics and fracture behavior of an epoxy coating was discussed. It was observed that modification of GO causes the crosslinking density to increase through association of excess amine functional groups attached to the modified GO platelets to the epoxy ring opening reactions. The longer the amine chains on the surface of GO the easier the crosslinking of epoxy with amine hardener. Such a preference for curing would be of vital importance at the later stages of reaction, where diffusion predominantly keeps the crosslinking under control.

Karasinski et al. [30] have studied the nonisothermal cure kinetics of nanocomposites based on a solid epoxy matrix filled with ZnO nanoparticles and found that the ZnO particles cause the curing activation energy to reduce. Such phenomenon allows the reaction to continue during a longer period of time and hence enhances crosslinking density in the network. In a previous work, we observed that epoxy coatings containing layered double hydroxides (LDH) based on zinc show no hindered curing due to the catalytic effect of zinc [31]. In the present study, starch carbohydrate polymer is self-assembled on ZnO nanoparticles to gain efficiently crosslinked novel transparent nanocomposite coatings. The surface coverage by starch molecules is characterized by Fourier-transform infrared (FTIR) spectroscopy. Two kinds of transparent nanocomposite coatings containing pristine and surface modified ZnO are prepared and their nonisothermal curing behavior is studied by calorimetric study varying the rate of heating. The potential of coatings to crosslinking is uncovered by measuring curing characteristics as well as comparison between time-dependent conversions of nanocomposites at different heating rates. Cure characteristics of transparent coatings were featured by measuring the enthalpy of cure, onset temperature of cure, and maximum cure temperature to assess the role of ZnO and starch-modified ZnO (ZnO-St) in curing behavior. Surface functionalization and crosslinking behavior of the prepared transparent nanocomposite coatings are mechanistically discussed as well.



Fig. 5. DSC thermographs of prepared samples at four different heating rates of (a) 5; (b) 10; (c) 15; and (d) 20 °C min⁻¹

 Table 1

 Curing parameters of the prepared samples obtained from DSC thermographs recorded at different heating rates.

Designation	Heating Rate (°C/min)	T _{ONSET} (°C)	T _p (°C)	T _{ENDSET} (°C)	ΔT(°C)	$\Delta H_{\infty}(J/g)$
Ероху	5	23.79	84.58	189.98	166.19	328.13
	10	16.60	97.87	230.18	213.58	307.62
	15	23.19	105.33	225.73	202.54	307.96
	20	27.00	110.66	242.65	215.65	294.98
Epoxy/ZnO	5	9.59	85.45	191.46	181.87	354.21
	10	17.46	98.29	216.19	198.73	317.04
	15	15.14	105.43	234.51	219.37	351.90
	20	25.33	111.19	261.62	236.29	331.34
Epoxy/ZnO-St	5	9.31	86.27	209.21	199.9	380.09
	10	16.01	98.16	232.22	216.21	369.22
	15	20.07	105.68	252.58	232.51	356.70
	20	25.89	111.56	267.69	241.80	356.77

2. Experimental

2.1. Materials

Amylum or potato starch $(C_6H_{10}O_5)_n$ was purchased from Merck Chemical Co. and used without further purification. This material is a white fine powder with a bulk density of 3 g/cm³, pH of 6.0–7.5 and water solubility of 50 g/l. Bisphenol A diglycidylether based epoxy resin was purchased from Sigma-Aldrich Co. (USA). This resin is a transparent viscous liquid with an apparent viscosity of 4000–6000 cps at 25 °C. The molecular weight is 340.41 g/mol and an EEW of around 190 g/eq. Cycloaliphatic polyamine curing agent with a viscosity of 55,000 mPa.s (Epikure F205) was provided by Hexion Chemical Co. (USA) and used as the amino curing agent hardener. The active hydrogen equivalent weight (AHEW) of the curing agent is about 105 g/ eq. The curing agent was mixed with the epoxy resin at weight ratio of 21–38 to obtain a stoichiometric network formation. Potato starch (Merck Chemical Co.) was used without further purification. ZnO nanoparticle powder with average particle size of 25–30 nm, 99.983% purity and density 5.6 g/mL was purchased from Tecnan-nanomat Co.

2.2. Surface modification of ZnO by starch

ZnO-St was prepared from ZnO nanoparticles and starch in water



Fig. 6. Schematic of catalytic effect of ZnO particles on the enhancement of the epoxide ring opening.



Fig. 7. Schematic of catalytic effect of ZnO particles along with autocatalytic effect of hydroxyl end-groups of starch on enhancement of the curing reactions.

medium. The procedure began by dispersion of 1 g ZnO powder inside 20 mL of water followed by a sonication process for 20 min. Then, 1.5 g of starch was dissolved in 10 mL water and the solution was gradually added to the ZnO dispersion and was vigorously agitated for 24 h followed by sonication process for 30 min. Having finished the mixing process, the particulate phase was separated by suction filtration and washed with 100 mL of water. The process was repeated three times to ensure the removal of excess unreacted starch. The final product obtained by filtration and dried in a vacuum oven at 60° C for 24 h [32]. Fig. 1 gives an overall view of the modification process.

Fig. 2 schematically demonstrates chemical structure of the ZnO-St nanoparticles used for the preparation of transparent epoxy nano-composite films.

2.3. Preparation of transparent epoxy-based nanocomposite coatings

In order to prepare epoxy-based transparent nanocomposite coatings, 0.1 g of pristine or starch-modified nano ZnO was added to 142.8 g of thinned epoxy (S.C. = 70 wt.%) to ensure a 0.1 wt.% concentration is obtained. The addition process was performed under high shear mechanical agitation and manually controlled to reduce powder waste by the mixer blades and the container walls. The mechanical mixing continued for 20 min after which the dispersion underwent a complimentary ultrasonic process to accomplish the dispersion process

of the nanoparticles and enhance the stability of the epoxy mixture. Nevertheless, the agitation process caused formation of some small bubbles. To erase and remove the bubbles, the resulting mixtures were placed inside a vacuum oven for 2 h. Consequently, to cure the epoxy mixtures, the polyamine hardener was added to the resulting mixtures at room temperature at appropriate ratios. To calculate the right Epoxy to Hardener ratio it must be presumed that epoxy equivalent weight (EEW) of the epoxy resin is around 170.2 g/eq and the average active hydrogen equivalent weight (AHEW) of the amine curing agent is about 105 g/eq. To acquire a stoichiometric curing reaction, 170.2 g of pure epoxy was mixed by 105 g of the curing agent. It should be taken into consideration that there exists a limited time known as pot life for such mixture prior to gel point that is around 30 min and the mixture will be useless after passing this time. After having prepared the inferred samples, they were applied on glass substrates using a film applicator at 120 µm thickness. A flash time of ca. 3 h for the applied films was sufficient before placing samples inside an oven adjusted at 70 °C for 2 h. In the end, the oven was unplugged and the samples left inside for 72 h to make sure that the reactions are perfectly done and the films are fully cured. Free-stand films were also prepared by detaching off the cured films applied on the glass substrates. Fig. 3 demonstartes a clear view of the transparent films of the prepared nanocompsoite coatings containing ZnO nanoparticles modified with starch molecules.

2.4. Measurements and characterizations

Fourier transform infrared (FTIR) spectroscopy was carried out by a Perkin Elmer Spectrum device across the wavenumber range of $4000-400 \text{ cm}^{-1}$ with a resolution of 2 cm⁻¹ to assess and confirm the surface modification of ZnO surface with starch. Differential scanning calorimetry (DSC) was conducted by a Q2000 DSC (TA Instruments USA) to study the curing behavior of the neat and ZnO-filled epoxy resin over the temperature range of 0–300 °C. Inspired by previous studies, 5–10 mg of the prepared nanocomposites were placed into aluminum pans and heated nonisothermally at different heating rates of 5, 10, 15, and 20 °C/min.

3. Results and discussion

3.1. FTIR analysis of the starch grafted ZnO

The FTIR spectra of ZnO, starch and ZnO-St are presented in Fig. 4. The FTIR spectrum of ZnO showed absorption bands at 3440 cm^{-1} , 1630 cm^{-1} and 547 cm^{-1} which are corresponded to O–H stretching, O–H bending and ZnO, respectively [1]. On the other hand, the FTIR spectrum of starch showed characteristic absorption bands at 3410 cm^{-1} related to O–H stretching vibration, at 2933 cm^{-1} corresponded to the aliphatic C–H and a broad band at 1010 cm^{-1} attributed to the C–O stretching of starch. While FTIR spectrum of ZnO-St simultaneously showed the characteristic absorption bands of ZnO structure along with the absorption bands of the starch. As it is clear in the figure, this spectrum showed an absorption band at 3300 cm^{-1} that confirms the presence of the O–H starching vibration of both ZnO and starch. The peak at 2930 cm^{-1} is also attributed to the aliphatic C–H stretching vibration of both ZnO and starch. The peak at 2930 cm^{-1} is also attributed to the aliphatic C–H stretching vibration of the starch part and the band at 1020 cm^{-1} is correlated to the C–O stretching of starch.

3.2. Curing behavior assessment

As it was explained in previous section, the curing behavior of the prepared nanocomposite coatings was investigated by DSC technique. Fig. 5 shows the DSC thermograms of the neat epoxy and its nanocomposites at four different heating rates. The shift of the peaks towards higher temperatures upon increasing the heating rate from 5 to 20 °C/min was to a large extent predictable because of expecting a higher kinetic energy being provided for the system at elevated heating



Fig. 8. Fractional extent of conversion as a function of time for epoxy, epoxy/ZnO and epoxy/ZnO-St at four different heating rates of 5 (a); 10 (b); 15 (c); and 20 (d) °C min⁻¹.

rates. Moreover, unimodal peaks formed in the DSC thermograms confirm the assumption that a single-step kinetic reaction takes place.

In order to study the effect of ZnO and ZnO-St on the curing reaction, curing behavior of the prepared samples was assessed. It is a common practice to assume that increase in the degree of conversion by advancing the curing reaction can be simply termed as:

$$\alpha = \frac{\Delta H_T}{\Delta H_{\infty}} \tag{1}$$

In where ΔH_T and ΔH_{∞} are representing the heat of reaction released at a certain temperature, *T*, and the total heat release during the whole reaction, respectively.

It can qualitatively be recognized from Fig. 5 that the total enthalpy of the curing reaction of the neat epoxy nanocomposite is less than that of those coatings containing ZnO and ZnO-St nanoparticles. In the same manner, the onset temperatures and the rate of heat buildup within the bulk of nanocomposites are dissimilar to neat epoxy. To quantitatively compare the nonisothermal curing behavior of the transparent coatings, the cure parameter containing the amount of heat released in the course of crosslinking or the enthalpy of curing (ΔH_{∞}) , the onset temperature (T_{onset}) , maximum curing or peak temperature (T_p) , the endset temperature (T_{endset}) and the temperature interval within which curing has been completed (ΔT) have been extracted from the DSC thermographs (Table 1). It is obvious from the table that T_{onset} and T_{endset} , and ΔH_{∞} are being affected by the introduction of ZnO and ZnO-St into the epoxy formulation. On the other hand, the T_p shows almost no obvious change upon addition of nanofillers. Perusing the table, it is also obvious that ΔT is becoming much wider as the ZnO is added to the epoxy, and even becomes enlarged upon addition of ZnO-St. It means that by adding ZnO particles the reactions continue for longer time. In another word, the reactions are being facilitated in the presence of ZnO. On the other side, ΔT is becoming even wider as ZnO-St was used as filler. It declares that the facilitation of the curing reaction is even stronger for ZnO-St. This behavior is observed for nanocomposite coatings independent from the heating rate. Expectedly, the very same trend is seen for ΔH ; so that by adding the nano ZnO particles the enthalpy of curing reaction increased thanks to the facilitation effect of the ZnO. Likewise, the amount of heat released is even more in the case of ZnO-St.

To interpret the curing behavior of the epoxy in the presence of ZnO particles, one must consider that Zn^{2+} as a Lewis acid has the catalytic effect on the curing reaction and eases the epoxide ring opening. This is schematically shown in Fig. 6.

This ring opening facilitation allows for enhancement of the rate of the reaction; thus ΔH increases as well. However, in the case ZnO-St, alongside with the catalytic effect, there exists another phenomenon known as autocatalytic effect of the hydroxyl groups that can contribute to ring opening of epoxide. The starch molecules provide the reactions with multitude of OH end-group. This positively influences the curing reactions that resulted in much faster curing rates and greater amount of heat release. This is also schematically shown in Fig. 7.

The basics of cure kinetics of the existing epoxy-amine system is that the epoxide and amine groups are gradually consumed and converted to C–N bonding due to their mutual chemical tendency. Therefore, the first step in cure kinetics evaluation would be calculation of the extent of the conversion or the magnitude of the curing. It can be equated by the heat generated during the reaction as follows:

$$\frac{d\alpha}{dt} = \frac{1}{H_0} \frac{dH}{dt} \tag{1}$$

In which H_0 is the total heat release during complete curing process and H is the heat release by the curing reactions up to time t.

On the other hand, for nonisothermal curing, presuming the direct relationship between the enthalpy and the curing reaction, fractional extent of conversion, α in curing reaction of the epoxy resin can be phrased using total heat release of the reaction as described in Eq. (1).

$$\alpha = \frac{\Delta H_T}{\Delta H_\infty}$$

To assess if the nanofillers affect the network formation parameters, i.e. conversion, the evolution or the fractional extent of the conversions are captured as a function of reaction time for the epoxy and its nanocomposites at four heating rates, as presented in Fig. 8.

As depicted in Fig. 8, the conversion evolution as a function of time signifies a sigmoidal shape indicating the domination of autocatalytic mechanism. At first look, it seems that α changes insignificantly for the samples at different heating rates. However, a similar pattern can be detected in all plots and that is the higher conversion rate for epoxy/ZnO compared to the other two samples. Epoxy/ZnO-St shows lower conversion rate compared to the epoxy/ZnO, but a higher rate in comparison with the blank epoxy.

It was previously discussed in Fig. 7 that ZnO has the ability to catalyze the curing reaction, but ZnO-St possesses additionally the autocatalytic effect on epoxy ring opening caused by the starch hydroxyl end-groups. Therefore, it is expected that the conversion rate of epoxy/ ZnO-St must be greater than that of the other two. Nevertheless, it should be noted that ZnO particle becomes much bigger after being modified with bulky starch molecules. This, in turn, can prevent the reactants, epoxide rings and amine groups, to collide and react with each other, which may unavoidably retard the curing reactions. Therefore, it can be speculated that modification process has a bilateral effect on the curing reaction. Certainly, what is much more important for curing is the effect of the nanofiller on final conversion and crosslinking density of the network, which is the subject of further investigations. All in all, the transparent epoxy/ZnO-St nanocomposite is a strong candidate for coating applications in view of its enhanced crosslinked network.

4. Conclusion

In the current study, ZnO was physically modified by starch macromolecules to increase the compatibility of such nanofiller with epoxy resin as well as to sterically prevent the particles to flocculate. The surface characteristics of ZnO and starch-modified ZnO (ZnO-St) are studied by FTIR technique. The results confirm that starch molecules have been successfully adsorbed on the surface of ZnO particles; so that they were self-assembled on the surface of nanoparticles thanks to surface concentration gradient. The curing behavior assessment demonstrated that curing mechanism remains almost unaffected by the introduction of ZnO and ZnO-St nanofillers in spite of considerable change observed for total heat release, ΔH , and the temperature change across which reaction continued. It was found that by adding ZnO particles ΔH increases due to catalytic effect of Zn^{2+} acting as a Lewis acid that enhances the ring opening of epoxide groups. The use of ZnO-St even resulted in a greater value of ΔH as an indication of catalytic effect of ZnO, moreover an autocatalytic effect caused by starch hydroxyls that positively drive curing reactions at elevated conversions. Furthermore, investigation on conversion rates demonstrates that although the rates are not significantly affected by the nanofiller addition, ZnO has been more successful to increase the conversion rate compared to ZnO-St, most probably due to the steric hindrance of the bulky starch molecules. The novel epoxy/ZnO-St nanocomposites developed in this work are suitable for developed highly crosslinkable transparent coatings.

References

- [1] P.P. Vijayan, D. Puglia, H. Rastin, M.R. Saeb, B. Shojaei, K. Formela, Cure kinetics of epoxy/MWCNTs nanocomposites: isothermal calorimetric and rheological analyses, Prog. Org. Coat. 108 (Suppl. C) (2017) 75–83, http://dx.doi.org/10.1016/j. porgcoat.2017.04.005.
- [2] M.R. Saeb, H. Rastin, M. Nonahal, M. Ghaffari, A. Jannesari, K. Formela, Cure kinetics of epoxy/MWCNTs nanocomposites: nonisothermal calorimetric and rheokinetic techniques, J. Appl. Polym. Sci. 134 (35) (2017).
- [3] M.R. Saeb, H. Rastin, M. Nonahal, S.M.R. Paran, H.A. Khonakdar, D. Puglia, Cure kinetics of epoxy/chicken eggshell biowaste composites: isothermal calorimetric and chemorheological analyses, Prog. Org. Coat. 114 (2018) 208–215, http://dx. doi.org/10.1016/j.porgcoat.2017.10.018.
- [4] G. Bahlakeh, B. Ramezanzadeh, M.R. Saeb, H. Terryn, M. Ghaffari, Corrosion protection properties and interfacial adhesion mechanism of an epoxy/polyamide coating applied on the steel surface decorated with cerium oxide nanofilm: complementary experimental, molecular dynamics (MD) and first principle quantum mechanics (QM) simulation methods, Appl. Surf. Sci. 419 (2017) 650–669.
- [5] G. Bahlakeh, M. Ghaffari, M.R. Saeb, B. Ramezanzadeh, F. De Proft, H. Terryn, A close-up of the effect of iron oxide type on the interfacial interaction between epoxy and carbon steel: combined molecular dynamics simulations and quantum mechanics, J. Phys. Chem. C 120 (20) (2016) 11014–11026.
- [6] T.M. Hafshejani, A. Zamanian, J.R. Venugopal, Z. Rezvani, F. Sefat, M.R. Saeb, et al., Antibacterial glass-ionomer cement restorative materials: a critical review on the current status of extended release formulations, J. Controlled Release 262 (2017) 317–328.
- [7] R. Dhahri, M. Hjiri, L. El Mir, H. Alamri, A. Bonavita, D. Iannazzo, et al., CO sensing characteristics of In-doped ZnO semiconductor nanoparticles, J. Sci.: Adv. Mater. Devices 2 (1) (2017) 34–40.
- [8] K.H. Ng, M.R. Khan, Y.H. Ng, S.S. Hossain, C.K. Cheng, Restoration of liquid effluent from oil palm agroindustry in Malaysia using UV/TiO 2 and UV/ZnO photocatalytic systems: a comparative study, J. Environ. Manage. 196 (2017) 674–680.
- [9] E. Bakhshandeh, A. Jannesari, Z. Ranjbar, S. Sobhani, M.R. Saeb, Anti-corrosion hybrid coatings based on epoxy-silica nano-composites: toward relationship between the morphology and EIS data, Prog. Org. Coat. 77 (7) (2014) 1169–1183.
- [10] S. Singha, M.J. Thomas, Influence of filler loading on dielectric properties of epoxy-ZnO nanocomposites, IEEE Trans. Dielectr. Electr. Insul. 16 (2) (2009).
- [11] T. Gao, B. Sang, B. Shao, R. Li, Z. Li, Flame retardancy and mechanical properties of a novel zinc Hydroxystannate/Epoxy resin nanocomposite, J. Nanosci. Nanotechnol. 17 (12) (2017) 8856–8863.
- [12] M. Rostami, S. Rasouli, B. Ramezanzadeh, A. Askari, Electrochemical investigation of the properties of Co doped ZnO nanoparticle as a corrosion inhibitive pigment for modifying corrosion resistance of the epoxy coating, Corros. Sci. 88 (2014) 387–399.
- [13] B. Ramezanzadeh, M. Attar, Cathodic delamination and anticorrosion performance of an epoxy coating containing nano/micro-sized ZnO particles on Cr (III)-Co (II)/Cr (III)-Ni (II) posttreated steel samples, Corrosion 69 (8) (2013) 793–803.
- [14] B. Liu, H.C. Zeng, Hydrothermal synthesis of ZnO nanorods in the diameter regime of 50 nm, J. Am. Chem. Soc. 125 (15) (2003) 4430–4431.
- [15] J.W. Kang, C.H. Lee, H.S. Shin, D.H. Yeo, Jeong D.Y. Resistance, Wear resistance control in ZnO substrates for electrostatic discharge-Safe ceramics through variation of sintering temperature and additives, Nanosci. Nanotechnol. Lett. 9 (1) (2017) 85–88.
- [16] C. Yang, F. Wang, W. Li, J. Ou, C. Li, A. Amirfazli, Anti-icing properties of superhydrophobic ZnO/PDMS composite coating, Appl. Phys. A 122 (1) (2016) 1.
- [17] Z. Mahidashti, T. Shahrabi, B. Ramezanzadeh, The role of post-treatment of an ecofriendly cerium nanostructure Conversion coating by green corrosion inhibitor on the adhesion and corrosion protection properties of the epoxy coating, Prog. Org. Coat. 114 (2018) 19–32.
- [18] B. Ramezanzadeh, M. Rostami, S. Niroumandrad, Enhancement of the physical/ mechanical properties of an epoxy composite by addition of aluminum nanoparticles through modification with cerium oxides and functionalization by SiO2-NH2 thin films, Prog. Org. Coat. 112 (2017) 244–253.
- [19] B. Ramezanzadeh, M. Attar, M. Farzam, Effect of ZnO nanoparticles on the thermal and mechanical properties of epoxy-based nanocomposite, J. Therm. Anal. Calorim. 103 (2) (2010) 731–739.
- [20] M.R. Saeb, E. Bakhshandeh, H.A. Khonakdar, E. Mäder, C. Scheffler, G. Heinrich, Cure kinetics of epoxy nanocomposites affected by MWCNTs functionalization: a review, Sci. World J. 2013 (2013).
- [21] M.R. Saeb, F. Najafi, E. Bakhshandeh, H.A. Khonakdar, M. Mostafaiyan, F. Simon, et al., Highly curable epoxy/MWCNTs nanocomposites: an effective approach to functionalization of carbon nanotubes, Chem. Eng. J. 259 (2015) 117–125.
- [22] E. Bakhshandeh, S. Sobhani, A. Jannesari, A.S. Pakdel, M.G. Sari, M.R. Saeb, Structure-property relationship in epoxy-silica hybrid nanocomposites: the role of organic solvent in achieving silica domains, J. Vinyl Add. Tech. 21 (4) (2015) 305–313.
- [23] M.R. Saeb, H. Rastin, M. Shabanian, M. Ghaffari, G. Bahlakeh, Cure kinetics of epoxy/β-cyclodextrin-functionalized Fe 3 O 4 nanocomposites: experimental analysis, mathematical modeling, and molecular dynamics simulation, Prog. Org. Coat. 110 (2017) 172–181.