ISSN 2320-2602

International Journal of Advances in Computer Science and Technology (IJACST), Vol.2 , No.11, Pages : 25 - 28
Special Issue of ICCEeT 2013 - Held during 04-05 November, 2013 Dubai

Effect of ZnO Nano Powder on Mechanical Properties of Epoxy/Polyaminoamide Adduct Coatings

Rawaiz Khan[1,2], Ubair Abdus Samad[1], Mohammad Asif Alam[2], M. Boumaza[1], Saeed M. Al-Zahrani [2, 3]
[1]Department of Chemical Engineering, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia, rawaiz_khan86@yahoo.com
[2]Center of Excellence for Research in Engineering Materials (CEREM), Advanced Manufacturing Institute, King Saud University, P. O. Box 800, Al-Riyadh 11421, Saudi Arabia,
[3]SABIC Polymer Research Center (SPRC) and Department of Chemical Engineering, College of Engineering, King Saud University, P.O. Box 800, Al-Riyadh 11421, Saudi Arabia

Abstract*:* This work reports the effect of Zinc Oxide Nano powder on mechanical properties of Epoxy coating. Bisphenol A diglycidyl ether epoxy resin (DGEBA) formulated with an optimized stoichiometric value of polyaminoamine adduct (ARADUR-PA450) as a curing agent at ambient temperature, is filled with different loadings of ZnO Nano powder (0, 1, 1.5, 2%). Steel and glass substrates were used as coating samples. A thin layer coating was applied by using bird applicator with wet film thickness (WFT) about 60-90 µm. The samples were kept for five days in a dust proof environment for complete curing at ambient temperature. The coated glass samples were used for pendulum hardness measurements while coated steel samples were used for scratch test, mandrel bend and cross hatch test. The dispersion of nano powder and morphology in the epoxy matrix were analyzed by using scanning electronic microscopy (SEM). Nano indentation was used to observe the young's modulus and hardness of the coating at nanometer level.

Key words: Epoxy coating, Morphology, Nano indentation, Polyaminoamine adducts

INTRODUCTION

The polymeric Nano composites possess excellent properties including flame retardancy, elastic stiffness, barrier and scratch resistance, electrical properties and optical characteristics. Recently these Nano composites have attracted researchers' attention due to the properties associated with these composites [1]. Normally polymeric Nano composite comprises two phases including inorganic reinforcement material and polymer matrix. The former consists of nanometer scale particles ranging from 1-100 nm which are dispersed in the later, polymeric matrix [2]. Since particles are of Nano size, they have large surface area per unit volume leading to better phase interactions between nanoparticles and polymeric matrix thus exhibiting remarkable properties [2], [3].

One of the main problems of using nanoparticles is their high tendency to create agglomeration in the polymer matrix due to their high specific surface area, which negatively affects the performance of the nanoparticles as filler [4], [5]. In general, three methods are existed for suitable dispersion of nanoparticles and stopping agglomeration. These three methods comprise: direct mixing of polymer and nanoparticles, in situ polymerization in existence of nanoparticles, and immediate in situ polymerization and nanoparticles formation [6].

Many researchers have worked on the mechanical and morphological properties of epoxy composite. Tang et al. [7] studied the mechanical properties of treated halloysite reinforced epoxy Nano composites. It was described that the fracture toughness of epoxy considerably improved by 78.3% due to the existence of 10 wt. % of added halloysite nanotubes (HNTs). Some of the researchers did surface modification of Nano particles by treating it with amino propyl trimethoxy silane (APS) coupling agents before addition to the epoxy matrix [4], [8]. It has been revealed that ZnO nanoparticles are non-toxic particles which can be used to create ecologically friendly coatings. Excellent optical, chemical, mechanical [9] and biological properties are obtained with nanoparticles. Resistance against photo-degradation is also improved by using ZnO Nano particles [10]-[12].

In this work ZnO nanoparticles were directly incorporated in diluted low viscosity epoxy matrix by using acetone solvent. An optimized quantity of polyaminoamide adducts ARADUR-PA450, which is used as a curing agent. The observed coating samples were characterized for mechanical properties as well morphological properties. The characterization was carried out by using Nano-indentation technique, Konig pendulum Hardness test, SEM, Automatic Scratch resistance, mandrel bend test and impact test.

MATERIALS AND METHODS

Materials

In this study Bisphenol A diglycidyl ether epoxy resin (DGEBA, Hexion Chemicals), is used which is a low viscosity transparent material is made of Bisphenol A and epichlorohydrin. polyaminoamine adducts ARADUR 450 (PA450, Huntsman Advanced Materials), is used as a curing agent at ambient temperature and acetone (Merck, 99%), is used as a solvent to have ease of dispersion and to avoid agglomeration. ZnO Nano powder (Sigma Aldrich, <50nm, >97%) was used as filler, to improve the mechanical properties of the coating. Glass substrates were coated to perform pendulum hardness test while steel substrates were used to perform Dry film thickness (DFT) measurement, scratch resistance, impact resistance, mandrel bend and Nano indentation tests.

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Preparation of Epoxy Nano-composite Coating

Epoxy resin was diluted by adding Acetone and stirred at about 500 RPM for 5 minutes. ZnO Nano powder was directly added to the resin acetone solution and stirred at a speed of 2500 rpm for at least 1 hr, using mechanical stirring (DisperMaster S_2, Sheen Instruments. Ltd, UK). To avoid overheating a cooling bath has been used. After mechanical stirring the solution was sonicated for 90 minutes at 50 ºC. Acetone was used as a solvent because the study of Fourier transform infrared spectroscopy (FTIR) and FT-Raman [13] revealed that mixing and sonication in acetone did not induce any chemical change in epoxy network. The hardener ARADUR 450 was also diluted with acetone before addition to the solution with 1:1 weight ratio, followed by mechanical stirring at a speed of 600 rpm for few minutes. The solution was kept for 10 minutes for stabilization. The chemical composition for different coating samples are given in Table 1.

Table 1 Chemical Composition of Coating Samples

Sample code	Epoxy Resin	PA-450	Acetone	ZnO	Air Release
EPZ-1	100	10	40	0	0.2
EPZ-2	100	10	40	1	0.2
EPZ-3	100	10	40	1.5	0.2
EPZ-4	100	10	40	2	0.2

Preparation of Coating Samples

The coatings substrates were degreased and thoroughly cleaned by using acetone. Four sided applicator (80mm width, Gap sizes 30/60/90/120µm, Sheen Instruments. Ltd, UK) was used with 60 Gap size to coat both glass and steel substrates. The coated samples should have a uniform WFT, and should be kept on a smooth surface in a dust free environment. The curing and cross linking process of the wet film will take at least 5 days to complete at ambient temperature and 5 to 8 hours in oven at 80-90 ºC.

Morphology and Dispersion Analysis

The dispersion of Nano powder and morphological studies was carried out by using Scanning electron Microscopy (JEOL JSM7600F). The sticky carbon tape is used to mount the cured film sample on aluminum stubs. A thin layer of gold was coated on the sample in order to avoid charging before the observation by SEM.

Mechanical Properties

Automatic scratch tester (REF705, Sheen Instruments Ltd, UK) is used to check the scratch resistance of coating samples by applying scratch probe with different applied loadings. The sample is placed in the sample holder and by turning on the machine the probe automatically travels along the sample surface and applies the scratch load. The probe is mounted with different weights. The load is increase until the probe damage the coating surface.

Impact strength is measured by dropping a standard weight distance apart, so as to strike an indenter that damages the coating and the substrate. The damage can either be an intrusion or an extrusion. The dropping weight distance is gradually increased to determine the failure point. The failure occurs in films is mostly cracking, which can be more visible by using magnifier. The height at which the film cracks is noted as the failure point as Force-inch-pound (f-in-lb). The apparatus used is impact tester (Ref BG5546, Sheen Instruments. Ltd, UK).

Mandrel bend test was performed to determine the flexibility, elongation and resistance to cracking of the coated film on steel substrate. The conical mandrel tester is a metal cone with rotating panel-bending arm, and panel clamps. The length of the cone is 200 mm with diameter of 3mm at one end and 38mm at the other end. The lever is moved through about 180º at uniform velocity to bend the specimen approximately 135º. The purpose of the test is to check if there any crack after bending the specimen. The bending time is about 1 second. The surface of the specimen is examined for cracking immediately after bending with unaided eye.

Pendulum hardness tester (BYK-Gardner, Germany) is used to determine Konig hardness while Nano indenter (Micromaterials.Co.Uk) is used to determine Nano hardness and elastic modulus of the coating film. The indentation was carried out at 250 mN maximum load using Berkovich type indenter, 25 indents for each sample in different locations. Table 2 shows the specifications for konig pendulum.

Table 2 Specification of Konig Pendulum

Parameter	Specification
Weight	200 g ± 0.2
Diameter	0.2 in (5 mm)
Deflection start	6°
Deflection end	3°
Period of Oscillation	1.4 s
Damping Time on Glass	250 ± 10 s

RESULTS AND DISCUSSIONS

Fig 1 (a-d) shows the top view FESEM low magnification micrographs, while Fig 1 (e-g) shows the cross sectional view FESEM micrographs. The EPZ-1 coating sample micrographs Fig 1 (a,e) has a smooth coating surface and it can be observed that It has a homogeneous morphology. The cross sectional micrograph of EPZ-1 coating sample shows no cracks, which indicates good elasticity and flexibility. EPZ-2 coating micrographs (b,f) have comparatively inhomogeneous surface but dispersion of the nanoparticles is good with no agglomeration. The cross section does not show cracks which are sign for good elastic modulus and flexibility. EPZ-3 samples micrographs (c, g) analysis shows rough surface with some particle agglomerations that found to increase as filler content increased due to the increase in matrix viscosity.. The coating cross sectional indicates some sort of cracking which could be because of the brittleness in the coating film which can also be a reason for the decrease in impact strength of the coating. EPZ-4 FESEM images (d,h) reveal poor dispersion and high degree of agglomeration in the coating film. The micro cracks are prominent in the cross sectional view. The surface is rough and inhomogeneous morphology.

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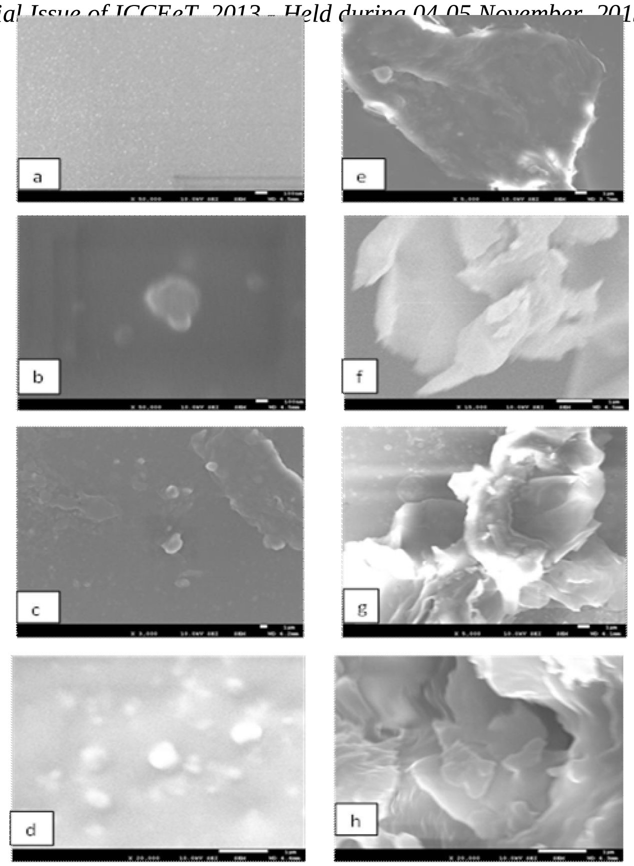

Fig 1 (a),(b),(c) and (d): Surface Images for EPZ- (1,2,3and 4) Respectively , and **Fig 1(e),(f),(g) and (h):** Cross Section SEM Images for EPZ-(1,2,3 and 4) Respectively

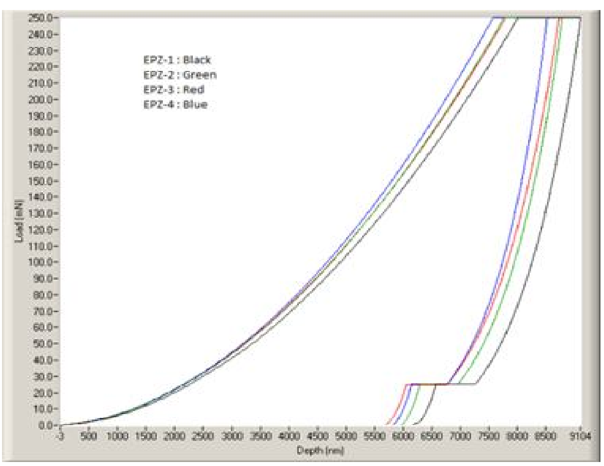

Fig 2a: Nano Indentation Curves

Fig- 2a displays the load-depth curve for epoxy coating samples contain different percentage of Nano particles. It is very clearly seen that at maximum load of 250mN, the maximum indentation depth is decreased with increasing Nano powder loading. Decrease in maximum indentation depth from 9104nm for EPZ-1 to approximately 8000nm for EPZ-4 indicates the improved load-bearing property of the Nano composite coatings [14], [15]. The reduced modulus and Nano hardness of the coating sample is also improved (Fig-2b) with the addition ZnO nano particles. Table 3 shows Nano indentation results for coating samples. The results indicate a significant increase in the reduced modulus and hardness of the plain epoxy coating from 3.5 and 0.15 GPa to 4.95 and 0.18 GPa, respectively.

Table 3: Nano indentation results

Sample coding	Reduced Modulus (Gpa)	Hardness (Gpa)
EPZ-1	3.5	0.14
EPZ-2	4.28	0.16
EPZ-3	4.87	0.17
EPZ-4	4.95	0.18

The scratch resistance of the coating samples was also determined by using automatic scratch tester (REF705, Sheen Instruments Ltd, UK) with a dry film thickness (DFT) of 70-80 µm. It is clear from the results that the scratch resistance of the coating decreased with increasing percentage of the Nano particles. EPZ-1 has highest scratch resistance while EPZ-4 has lowest scratch resistance value. The higher scratch resistance of the coating film can also be correlated to the polar hydroxyls and oxirane moieties present in the backbone of the polymeric chain of the PA450 epoxy resin [16].

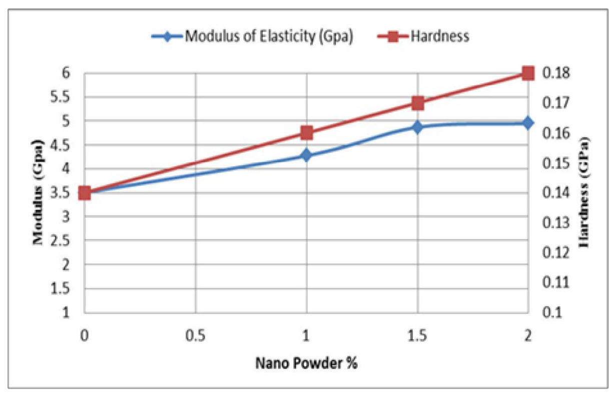

Fig 2b: Effect of Nano Powder on Modulus and Hardness

Konig pendulum hardness is measured on glass panel with film thickness of 70-90 µm by using pendulum tester (BYK-Gardner, Germany). Table 4 shows the results for Konig hardness, scratch resistance, impact resistance and mandrel bend test of different samples. The results show that the Konig hardness is increase with the increase in ZnO Nanoparticles content while scratch resistance and impact resistance has an inverse effect. According to the ASTM standard a minimum DFT of 25 µm is required for Konig Pendulum hardness test to minimize the effect of the substrate [17]. In the literature it is reported [18] that the hardness value is directly related to the proportion of cross-linking between epoxide groups and curing agents. On the basis of which it can be said that the crosslinking between between epoxide groups and the curing agent is highest in EPZ-4. The mandrel bend test is also passed perfectly with no visible cracking. This is useful for bending the steel during manufacturing of different articles.

Table 4: Dry film thickness, Impact resistance, scratch resistance load, Konig hardness and mandrel bend results

Sample Code	DFT(µm)	(f-in-lb) at Impact Failure	Scratch resis. load at failure (Kg)	Konig hardness after 10 days	Mandrel bend test
EPZ-1	(70-90)	280	7.5	75	Pass
EPZ-2	(70-90)	224	6.75	83	Pass
EPZ-3	(70-90)	176	6	91	Pass
EPZ-4	(70-90)	152	4.5	103	Pass

Conclusion

Different percentage of ZnO Nano powder was added to an optimized formulation of Bisphenol A diglycidyl ether epoxy resin (DGEBA) and polyaminoamine adduct (ARADUR-PA450) as a curing agent. Various mechanical properties including reduced modulus, Nano hardness (indentation), scratch resistance, Konig hardness, Impact resistance and mandrel bending have been described. All the four formulations passed mandrel bend test perfectly. The scratch resistance and impact resistance test results reported that as the Nano powder loading increased in the formulation, the resistance to scratch and impact also decreased accordingly. Conversely the modulus of elasticity and Konig hardness increased with increasing ZnO Nano powder loading in the polymeric matrix. It is also reported from the SEM results that the dispersion of the Nano powder in the polymer matrix is a great challenge when going for higher loading. The dispersion of the Nano powder has great effect on the mechanical properties of the coating. It is recommended to have surface modification of Nano powder by using 3-aminopropyl trimethoxysilane (APS) as a coupling agent.

Acknowledgement

Authors wish to express their gratitude to Saudi Arabian oil company (Saudi ARAMCO) and the Center of Excellence for Research in Engineering Materials (CEREM) for the financial support. The authors would also like to express their thanks to Mr. Muhammad Ali and Mr. harry of CEREM Mechanical Lab for their help and support in SEM analysis. The thanks is extended to Mr. Xianming Shi from Montana State University, Bozeman USA for advising and responding via emails.

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