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Effects of Colloidal Nanosilica on Epoxy-based Nanocomposite Coatings

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ABSTRACT

Epoxy-based nanocomposites were fabricated with different content of colloidal silica nanoparticles such as 10.0, 20.0 and 30.0 wt %, through solution casting. The covalent bonding interfaces, resulting from a ring-opening reaction between silica nanoparticles and epoxy matrix were confirmed by the Fourier transform (FT-IR) infrared spectroscopy. These nanocomposites were characterized for thermal stability, glass transition temperature and adhesive properties using thermogravimetric analyzer (TGA), differential scanning calorimeter (DSC) and cross-cut tape test. In addition, chemical resistance was assessed by immersing the films in different chemical solution (acid, alkali and salt solution) for 21 days. It was found that the properties of the nanocomposites were increased proportionally to the content of silica nanoparticles up to a certain amount of loading. After that the properties were decreased. The surface morphology of the nanocomposites was observed by scanning electron microscopy (SEM), which showed that the silica nanoparticles distributed uniformly. In addition, the nanocomposites were studied on UV radiation absorption by UV-Vis spectrophotometer. Excellent UV radiation was noticed by the nanocomposite films. The oxygen transmission rate (OTR) and water contact angle (WCA) testing of the nanocomposite films was also impressive. Prog. Color Colorants Coat. 12 (2019), 71-82© Institute for Color Science and Technology.

1. Introduction

Epoxy resin was discovered in 1909. It has been widely used as a coating material to protect a substrate from corrosion because of its good adhesive, strong bond strength, durability, toughness, formulation latitude and chemical resistance properties [1]. However, it shows poor coating properties on high-performance application due to some limitations, such as poor adhesive properties and chemical resistance properties [2]. Research has been carried out to prepare epoxy composite by introducing traditional inorganic fillers in epoxy. It shows slight improvement in properties, but it cannot be applied in coating formulation due to phase separation problem which is the biggest disadvantage [2]. In recent years, nanotechnology has become popular in different numbers of application for extraordinary benefits. This technology has also been applied coating to improve the properties [3, 4]. This

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technology has greatly reformed traditional composite material to solve the separation problem between inorganic and organic materials [2]. It also increases the contact area between the organic and inorganic materials [2]. Therefore, it provides an opportunity to develop new classes of advanced materials to apply on the high-tech application [5].

A number of nanoparticles have been used in coating materials as a fillers [6, 7]. Silica nanoparticles are well-known as a filler which has been widely used in engineering composites. They have been used frequently as nanofillers to improve the adhesive and chemical resistance properties of a coating. As a filler, the silica nanoparticles improve the adhesive properties of a coating. They act as an effective physical barrier that protects the substrate against chemicals and corrosion. The interaction and interfacial force between silica nanoparticles and polymer depend on Van der Waals forces and hydrogen bonds. Poor adhesion may also reveal a poor coating application process [8]. Ji et al. indicated that the silica nanoparticles improve the adhesive property of coating. They observed that epoxy with silica nanoparticles showed better corrosion protection due to adhesive between coating and substrate [9]. Caselis et al. studied adhesive properties on epoxy-silica hybrid coating with rhodamine 6G as a dye. They found that the epoxy-silica hybrid coating improves adhesive strength on the substrate than epoxy [10]. Heo et al. investigated research on silica nanoparticles in epoxy with different diameters of particles. From the observation on shear strength, they found the smaller diameter of silica nanoparticles which is 108 nm showed better adhesive properties than the bigger diameter and neat epoxy [11].

The silica nanoparticles are capable of resisting the chemical attack. Epoxy-silica coating has excellent resistance to alkaline, acidic and salt solution [12]. Qian et al. performed chemical impedance test on epoxy with silica nanoparticles in 0.5 M of HCl, 1M of NaOH and 3wt% of NaCl solution. They observed that silica nanoparticles coating was performed better than the epoxy coating. On the other hand, double layer coated showed unaffected even after 49, 42 and 35 days of immersion in salt, acid and alkali solution [13]. Gupta et al. investigated research by modifying epoxy with silicone on chemical resistance test. They observed that it showed good resistance properties against acid solution (1.0 N aqueous solution of H_2SO_4). It improves the resistance properties in a 1.0 N aqueous solution of NaOH with increase content of silicone [12]. Some other researchers performed an analysis on thermal stability. Allahverdi et al. observed that thermal degradation and maximum decomposition temperatures of coating increase with increase content of silica nanoparticles. It also showed higher residual char due to the presence of nanosilica particles [14]. It shows that silica nanoparticles improve the thermal stability of the coating. In the previous study, silica nanoparticles have been used with micro-sized ZnO particles for a better UV-resistivity [15]. In a different study, a hybrid and multi-filler- based epoxy coating has been formulated using silica nanoparticles for heat-resistant coating [16].

In this paper, surface modification of nanosilica toward the preparation of nanocomposite by colloidal silica with easily homogenous dispersion and tailorable surface property. The scope of the present study to analyze and characterize epoxy coatings with different content of colloidal silica nanoparticles. This work examines the effect of silica nanoparticles on the curing process, adhesive, chemical resistance, thermal stability, morphological and UV absorption properties. In addition, oxygen gas transfer rate analysis performance was performed to qualify the protection ability to the substrate.

2. Experimental

2.1. Materials

A liquid diglycidyl ether of bisphenol A (DGEBA) as epoxy resin of number average molecular weight of ≤ 700) was purchased from Momentive Specialty Chemicals, Singapore. Fatty acid amido amine as curing agent was purchased from Hexion Specialty Chemicals, Nederlands. Silica nanoparticles with density of 1.22 g/mL at 25 ^{o}C and surface area of 320 - 400 m^2/g was purchased from Sigma-Aldrich. Hydrochloric acid (37 wt% in water) was purchased from Sigma-Aldrich. Sodium Hydroxide (NaOH) with (99.0 wt%) was purchased from Systerm. Sodium chloride was purchased from Merck. Acetone was purchased from Bendosen with min 99.9% of purity.

2.2. Preparation of the Epoxy/ SiO_2 coating

The epoxy coatings were prepared with different percentage of silica nanoparticles. Firstly, silica nanoparticles (10, 20, and 30 wt %) were added in 30g of DGEBA. The solutions were stirred by mechanical stirrer in 100 mL of beaker for 2 hours at 120 °C. After that, the temperature of the solution was reduced to room temperature, and 1.5 mL of acetone was added into the composite solution and stirred for 1 hour. For curing process, 6.5 g of hardener was added into the epoxy solution and stirred for 10 minutes. Finally, the coating was applied on an aluminum substrate for further characterization. The formulation of different samples is presented in Table 1.

2.3. Characterization

The curing time of the nanocoatings was measured by observing and recording time of coating till completely cure at room temperature to study the effect of silica nanoparticles on the curing process. The coating was checked by observing one-finger touch on coating which is coated on an aluminum substrate. The time was recorded once no fingerprint present on the coating.

The adhesive test was carried out by cross-cut tape test which measured by following ASTM D3359-09E2. This analysis was done after coating cured on substrate by cut dry film with space cuts 2 mm apart and make six cuts (vertically and horizontal) by a sharp razor blade. Scotch tape (pressure-sensitive tape) were used to analysis adhesive of coating on the substrate by removing tape which placed on the grid of coating.

The chemical resistance was carried out on coating by soaking the substrate which coated by composite coating in three different types of chemical which are acid, base and salt solution. Firstly, 5M of hydrochloric acid (HCl) was prepared by diluting 20.5ml of HCL (37% w/w) in 29.5 mL of H_2O. Then, 13.2 mL of NaOH (50 % w/w) were diluted in 36.8 mL of H_2O to prepare 5 M of NaOH for a base solution. Finally, 5 M of NaCl was prepared by diluting 14.61g of NaCl in 35.39 mL of H_2O. Each of composite coating was immersed in three different types of solution which are 5M of HCl, 5M of NaOH and 5M of NaCl. The coatings were observed and weight loss was measured after 21 days (3 weeks).

Fourier transform infrared (FT-IR) spectroscopy (Thermo Scientific, USA) was employed to determine the functional groups of the nanocoatings. The spectra were recorded in the transmission mode at a resolution of 4 cm^{-1} in the range of 400-4000 cm^{-1}. The UV radiation absorption by the coating was analyzed by Ultraviolet-Visible Spectrophotometer (Perkin-Elmer UV/Vis Spectrophotometer Lambda EZ210). The samples were placed in glass cuvette and the absorbance was scanned in the range of 190 – 900 nm. Acetone was used for cleaning purpose to clean glass cuvette. The thermal stability of nanocomposite coatings was analyzed by Thermogravimetric analysis (TGA) using Mettler Toledo dynamically from 30°C to 700°C at a heating rate of 20°C/min under nitrogen gas with a flow rate of 60 mL/min. Differential scanning calorimetry (DSC) analyses were performed using a Mettler Toledo TGA/DSC instrument under nitrogen flow. Each sample heated as a temperature range from 30 °C to 700 °C at a heating rate of 20 °C/min. Scanning electron microscopy (SEM) (Phenom ProX, Netherlands) was carried out to analyze surface morphology of the nanocoatings. The samples were dried and fixed to a metal-based specimen holder with double-sided sticky carbon tape. The oxygen transmission rate was measured by MOCON Oxygen Transmission Rate tester (OX-TRAN) with a test gas containing 100% oxygen, nitrogen (containing 2 vol % hydrogen) as a carrier gas. The thickness of the films was fixed to 0.2 mm, area of 20 cm^2.

Table 1: Quantity of used materials in different coatings.

Samples	DGEBA (g)	30% colloidal silica (g)	Acetone (mL)	Hardener (g)
EPOXY	30	-	1.5	6.5
ES 10%	30	3 g	1.5	6.5
ES 20%	30	6 g	1.5	6.5
ES 30%	30	9 g	1.5	6.5

3. Results and Discussions

3.1. Physical properties

3.1.1. Physico-chemical Properties

The density of the samples is presented in Table 2. The density of the neat epoxy, ES10, ES20, and ES30 was 0.7438, 0.8787, 1.0510 and 1.0852 g/mL, respectively. The nanocoatings showed higher density than neat epoxy samples due to increase of surface area contributed by silica nanoparticles [17]. On the other hand, it was observed that higher content of silica nanoparticles presence in epoxy showed an increased density of sample due to increases of surface area of sample [17].

The curing time of the nanocoatings was determined. The results are listed in Table 2. It was observed that curing time of epoxy coating was 450 min which was decrease to 430, 420 and 435 min for ES10, ES20, and ES30, respectively. Its showed that higher concentration of silica nanoparticles presence, improved the curing process of coating due to higher specific surface area actively participated in the curing process [17], but when silica nanoparticles content increase more than 20 wt %, curing reaction of coating become weaker by showing longer time taken to cure than other composite coatings.

3.1.2. Adhesive properties

The adhesive property of the nanocoatings on aluminum substrates was evaluated using the cross-cut tape test method. This test was analyzed by measuring the percentage area where flacking or detached (coating removal) occur due to the removal of an adhesive tape. Results are classified as follows: 0 (>65% coating detached); 1 (35-65%); 2 (15-35%); 3 (5-15%); 4 (<5%); 5 (0% or none). The results are presented in Figure 1. The results are summarized in Table 2. It was found that the silica nanoparticles improved the adhesion properties of the coating [9]. The neat epoxy coating showed poor adhesive properties and classified as 3. On the other hand, increased concentration of silica nanoparticles (30 wt %) showed weaker adhesive strength with less than 5% of the area were flaked on coating. This is because of poor dispersion into the epoxy system. The ES20 showed a little flake on coating than ES30 and classified as 4 which less than 5% of area were flaked observed as seen from Figure 1. This result indicates that the silica nanoparticles improved adhesive properties even at high concentration of SiO_2. These results also help to explain the reason why silica nanoparticles coatings showed better chemical resistance, as mentioned earlier in chemical immersion tests.

3.1.3. Chemical Resistance

The chemical resistivity of the coatings was observed by immersing the samples in different solution which was acid (5M HCl), 5M of NaCl and alkali (5M NaOH) for 21 days. The weight loss was also measured after the testing. The results are presented in Table 2. It was found that neat epoxy coating showed poor chemical resistance in acid, salt and alkali solution. From observation, the color of epoxy coating was changed to dark yellow and it showed weight loss after the immersion period in acid and alkali solution. On the other hand, epoxy with silica nanoparticles coatings showed improved chemical resistance properties against acid, alkali and salt solution than neat epoxy coating [13].

Table 2: Physical properties of different coatings.

Samples	Density (g/mL)	OTR (cc m^{-2} day^{-1})	Curing time (min)	Adhesive test	Chemical resistance		
					HCl	NaCl	NaOH
EPOXY	0.7438	2.1×10^6	450	3 (5 – 15%)	Bad	Bad	Bad
ES10%	0.8787	1.9×10^6	430	5 (0%)	Good	Best	Best
ES20%	1.0510	1.5×10^6	420	4 (< 5%)	Good	Best	Good
ES30%	1.0852	1.5×10^6	435	4 (< 5%)	Good	Good	Good

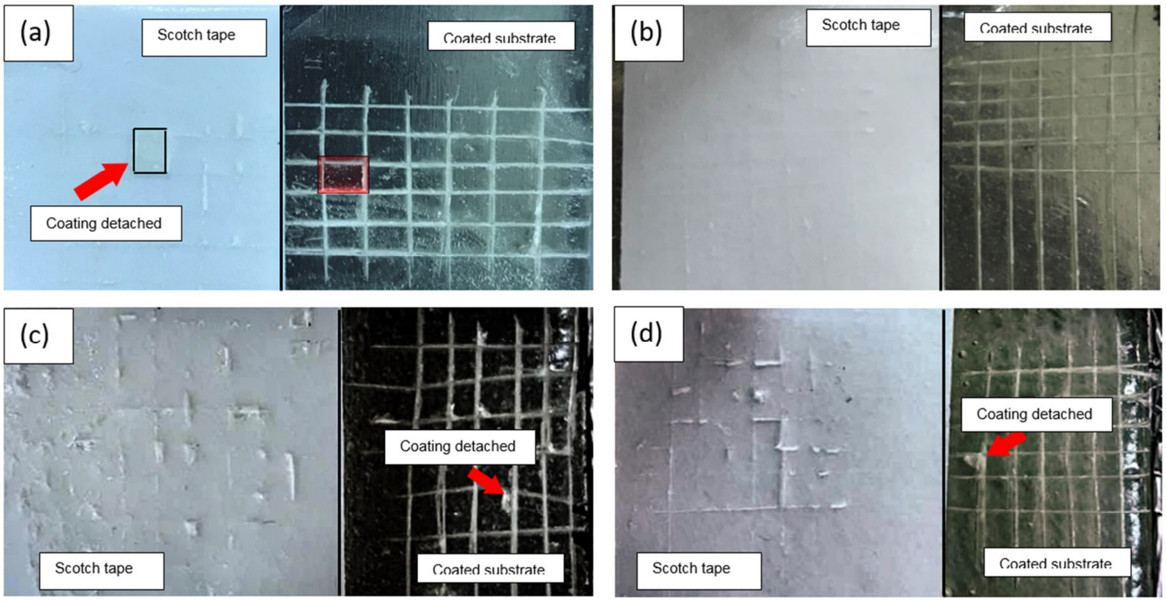


Figure 1: Adhesive properties of coating by Cross-Cut Tape Test: (a) Epoxy, (b) ES10, (c) ES20 and (d) ES30.

The higher concentration of silica nanoparticles in epoxy which is ES30 showed poor chemical resistivity properties. It showed lighter color change than ES10 and ES20 after immersed in HCl ES10 and ES20 showed comparatively best resistivity to the alkali and salt solution [12]. From overall observation, epoxy with higher concentration of silica nanoparticles showed poor chemical resistivity than lower content of nanosilica particles due to uneven dispersion in epoxy as confirmed by the SEM observation. Moreover, presence of silica nanoparticles did not show weight loss in the coating. Silica nanoparticles improved chemical resistance properties may be due to the presence of a stable aromatic ring in the poly alkyl chains by modified with nanoparticles [18].

3.2. UV absorption

The epoxy coating containing various amount of silica nanoparticles were compared with neat epoxy by UV-Visible spectrophotometer. Figure 2 shows light absorbance of neat epoxy and nanocomposite coating were studied on UV, Vis and NIR absorbance properties. Typically, the UV region is considered to extend from 190 to 350 nm, the Vis from 350 to 800 nm and the NIR from 800 to 1000 nm. From observation, silica nanoparticles coating shows higher absorbance in UV, Vis and NIR range, while in composite coatings this value increase by increasing the content of nanosilica particles except on Vis at a range of 350-500 nm [14]. The epoxy with different concentration of nanosilica particles showed very similar absorbance, but some difference can still be detected. ES30 showed maximum absorption on the near-infrared range than other composite coatings. It can be said that the effect of silica nanoparticles in NIR absorbance properties by absorption is directly proportional to silica nanoparticles concentration in the coating. From overall observation, epoxy with silica nanoparticles showed better absorbance properties with increasing the concentration of filler than neat epoxy [14].

3.3. Oxygen transmission rate analysis

The high barrier property towards oxygen permeation is the most important characteristics of coating [19]. A diffusion of oxygen through an organic coating is considered one of the major causes of corrosion on a substrate [20]. The oxygen permeability of the nanocomposite coatings with an average thickness of 0.20 mm was characterized for the oxygen transmission rate (OTR) analysis and are reported in Table 2. The modified nanosilica particles in epoxy matrix (ES20) showed an improved barrier property, showing lower oxygen transmission rate than epoxy coating. It shows that the interaction of crosslinking density between nanoparticles and polymer matrix was stronger with reduced pinholes on coating. The higher loading of 20 or 30 wt % of silica nanoparticles in the epoxy resin showed increased barrier properties of coating.

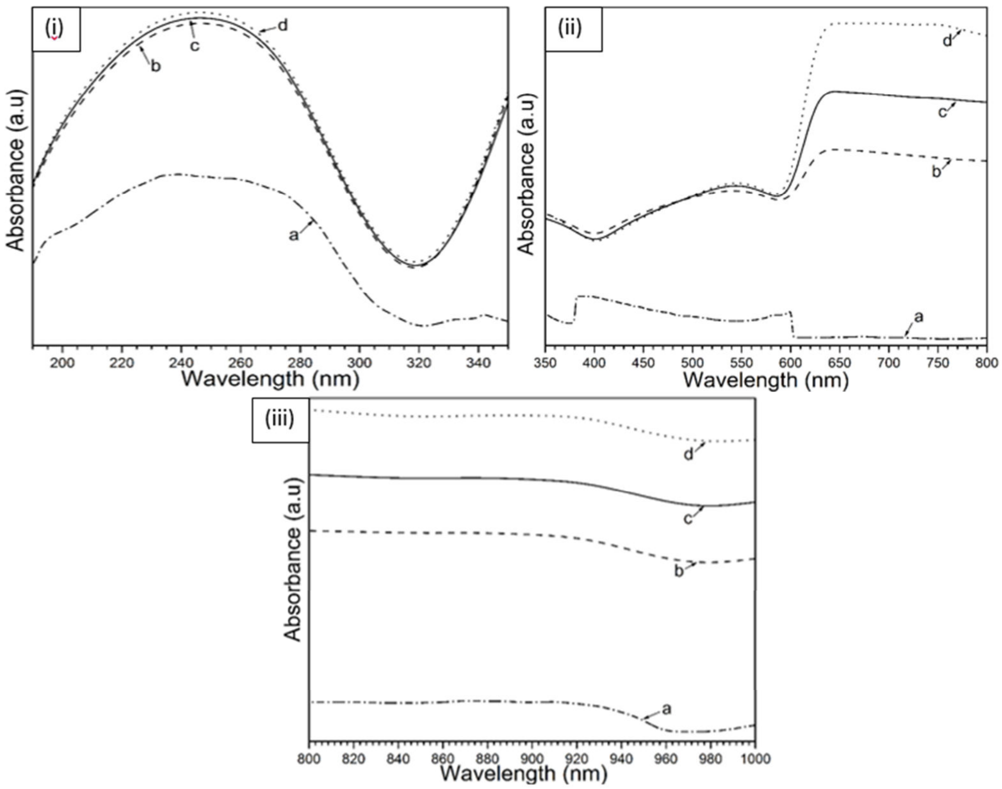


Figure 2: UV-Vis Spectrophotometer analysis: (i) UV, (ii) Vis and (iii) NIR; (a) epoxy, (b) ES10, (c) ES20 and (d) ES30.

Although, the epoxy coating showed smooth surface as seen from the SEM observation, the OTR was higher than composite coating might be due to the presence of pinhole defects in the coating, small spikes or pits on the coating surface cause pinhole defects in the barrier film [21, 22].

3.4. Thermal properties analysis

The effect of silica nanoparticles on thermal stability was investigated by TGA. Figure 3 shows the thermograms of epoxy nanocoatings filled with different concentration of silica nanoparticles. The results for initial decomposition temperature (T_{onset}), temperature at 50% weight loss (T_{50}), and the amount of char residual at 600 ^{o}C are presented in Table 3. The analysis showed major weight losses in the range of 300-500 ^{o}C. As the initial decomposition temperature (T_{onset}) at 5% of weight loss are listed in Table 3, ES20 showed higher temperature range than other composite coatings. Primary degradation appears caused by the decomposition of functional groups on the skeleton [23]. The ES20 also showed better thermal stability on temperature degradation at weight loss of 50%. Nearly 50% of weight loss was occurred at 412^{o}C for ES20 which is higher than ES10 (389 ^{o}C), ES30 (406 ^{o}C) and epoxy (407 ^{o}C), respectively. An increase of T_{50} was generally considered as an indication of enhancement on thermal stability [23]. It can be said that nanoparticles improved thermal stability of the coatings due to the formation of strong polymeric-inorganic char [24]. The increase in thermal stability due to nanofillers inhibit on molecular mobility of polymer chains which are Si-O bond [25]. From overall observation, ES20 showed better thermal stability which shown good interaction between the organic matrix and inorganic particles [23]. Moreover, presence of silica nanoparticles showed higher residual char than epoxy. In Figure 4, epoxy with silica nanoparticles coatings showed peak at higher temperature than epoxy in DTG analysis. It clearly evident that presence of silica nanoparticles improved the thermal stability in coating. The ES20 showed better properties even ES30. This is may be due to unstable nanosilica cross-linking with epoxy and elimination of water from the Si-OOH group to form in SiO_2 [26].

Table 3: FT-IR peaks corresponding to functional groups in different coatings.

Wavenumber (cm^{-1})	Functional group
799 – 825	C-O-C stretching of oxirane group
1023 – 1035	C-O-C of ethers
1459	C=C of aromatic group
3300	OH groups
2922 – 2925	symmetrical C-H stretch of CH_2 group
1248 – 1251	C-O stretch of aromatic ring
2843	C-H stretching
1177 – 1182	Si-O-Si of silica groups
1100 – 1105	Si-O-C groups
3100	Si-OH groups

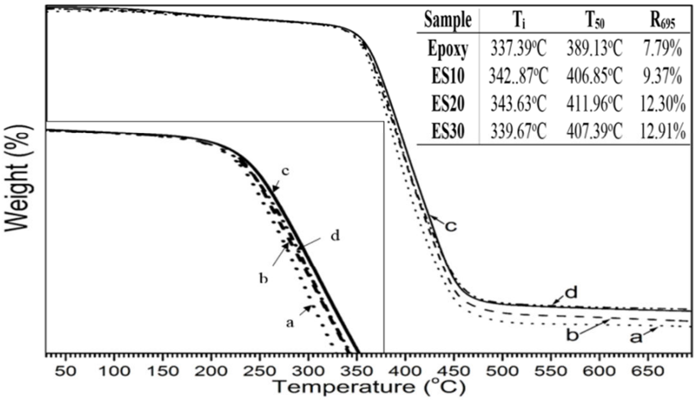


Figure 3: Thermal analysis of coatings: (a) Epoxy, (b) ES10, (c) ES20 and (d) ES30.

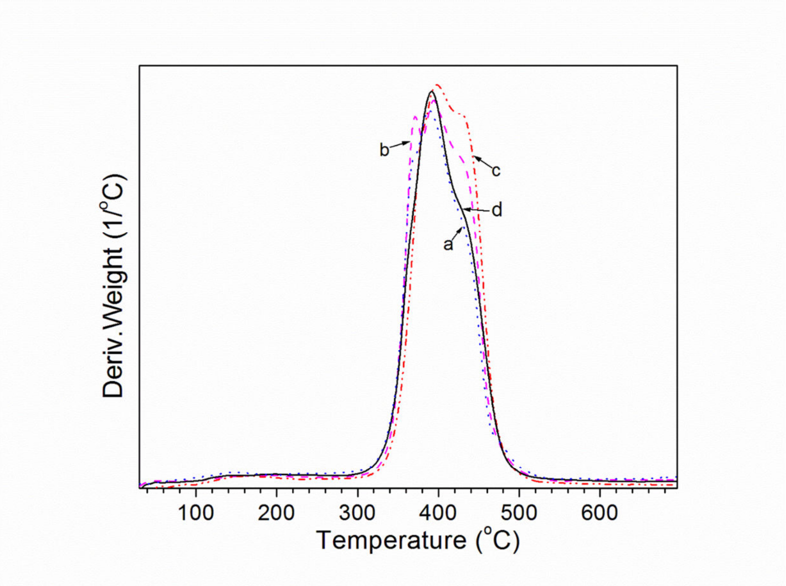


Figure 4: DTG analysis of coatings: (a) Epoxy, (b) ES10, (c) ES20 and (d) ES30.

The glass transition temperature (T_g) and melting temperature (T_m) of epoxy composites with different concentration were observed on DSC thermogram shown in Figure 5. The results are tabulated in Table 3. From observation, epoxy/silica nanoparticles showed higher T_g than neat epoxy coating due to interfacial adhesive between epoxy and silica nanoparticles control the motion of the segmental chains [10]. On the other hand, T_g of ES20 is 76.5 °C, which is higher than ES10 and ES20. It showed that 20 wt % content of silica nanoparticles in epoxy having strong interaction between polymer and nanoparticles [21]. The value of the T_g of ES30 was decrease to 71.7 °C and that of ES10 were showed at 72.6°C which higher than ES30. The significant increase of T_g due to the introduction of the silica nanoparticles which limit the movement of polymer chains in ES10 and ES20 [22]. The melting temperature of ES10 and ES20 was 402 and 404 °C, respectively. The increased melting temperature at higher loading is probably due to the presence of silica nanoparticles in epoxy coatings [23].

3.5. Fourier transform infrared spectroscopy

The FT-IR spectra of different samples are presented in Figure 6. From the figure, the silica nanoparticles were confirmed by the peak at 1177-1182 cm^{-1}, assigned to the stretching vibrations of -Si-O-Si- group [30]. The peaks at around 1100-1105 cm^{-1} were assigned to the stretching vibrations of Si-O-C group [30]. The absorption peak of Si-OH was almost disappeared at 3100 cm^{-1} due to the crosslinking by the colloidal silica during the curing process to form Si-O-Si [31]. For epoxy resin, the characteristic absorption peak of C-O-C was found at 799-825 cm^{-1} due to the stretching of oxirane group [32]. The characteristic peak of C-O-C of ethers was found at 1023-1035 cm^{-1} [32]. The absorption peak at 1459 cm^{-1} in the coatings related to the C=C aromatic group was weakened during the processing [33]. The presence of –OH group was confirmed by the peak at 3300 cm^{-1}, which was classified as weak peak for the evidence of the ring opening reaction of epoxide between DGEBA and acetone [30]. Moreover, the peak showed in range of 2922 – 2925 cm^{-1} was correspond to the symmetrical C-H stretch of the CH_2 group [34]. The peak at 1248 – 1251 cm^{-1} was correspond to the C-O stretching in aromatic ring of epoxy resin [34]. The existence and interaction of epoxy groups with the particles were confirmed by the presence of the characteristic band of C-H stretching at 2843 cm^{-1} [23]. The chemical structure and interaction between the epoxy and the fillers are shown in Scheme 1.

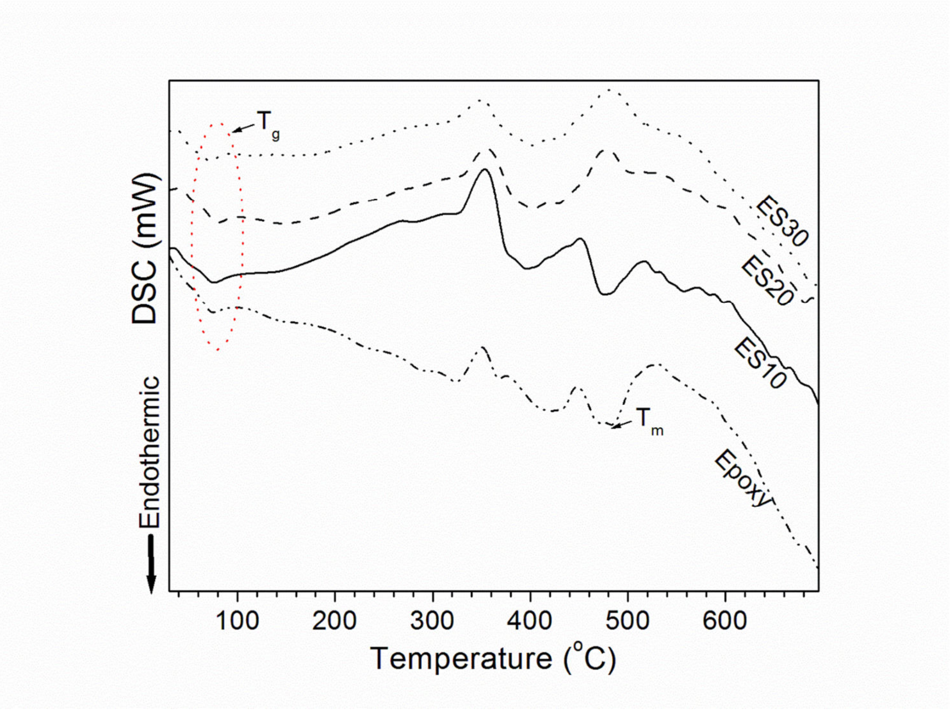


Figure 5: The DSC curves of epoxy with different concentration of silica nanoparticles.

Table 4: Thermal properties of composite coatings.

Samples	T_i (ºC)	T_{50} (ºC)	R_{695} (%)	T_g (ºC)	T_{m1} (ºC)	T_{m2} (ºC)
Epoxy	337.39	389.13	7.79	68.43	419.37	475.75
ES10	342..87	406.85	9.37	72.69	395.45	473.99
ES20	343.63	411.96	12.30	76.53	404.59	-
ES30	339.67	407.39	12.91	71.71	402.30	-

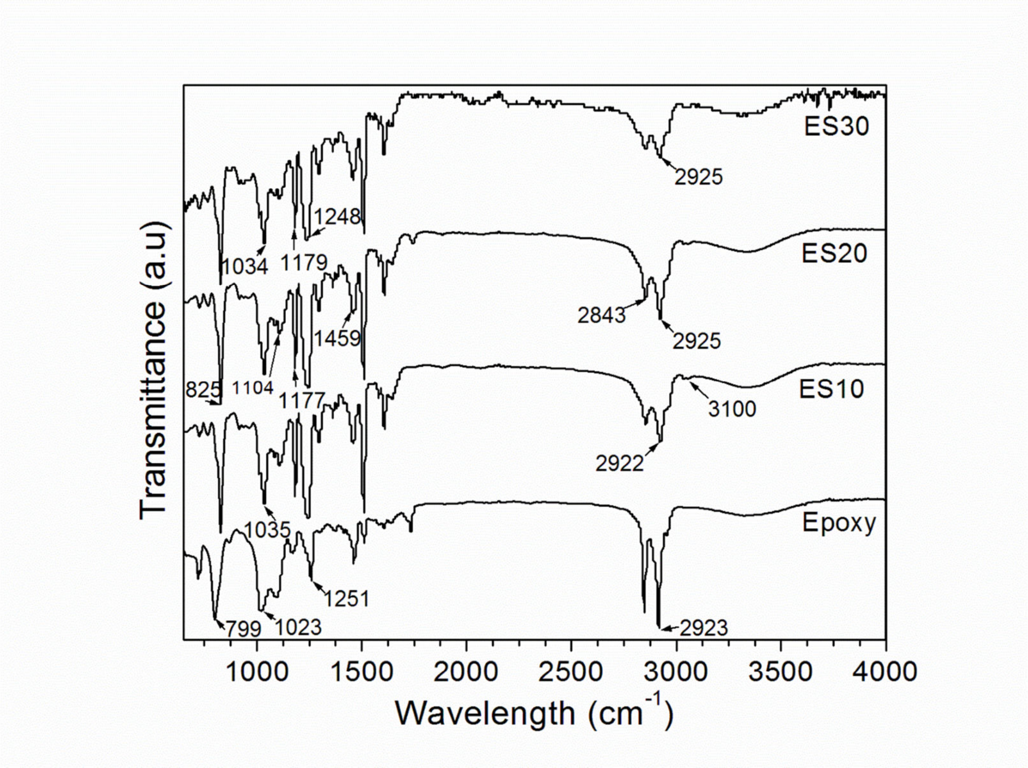
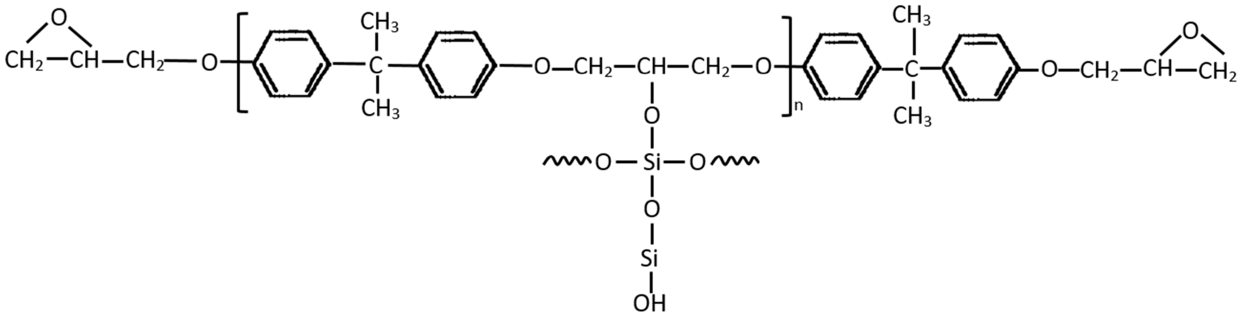


Figure 6: FT-IR spectra of Epoxy, ES10, ES20 and ES30.



Scheme 1: Chemical structure of Epoxy with silica nanoparticles.

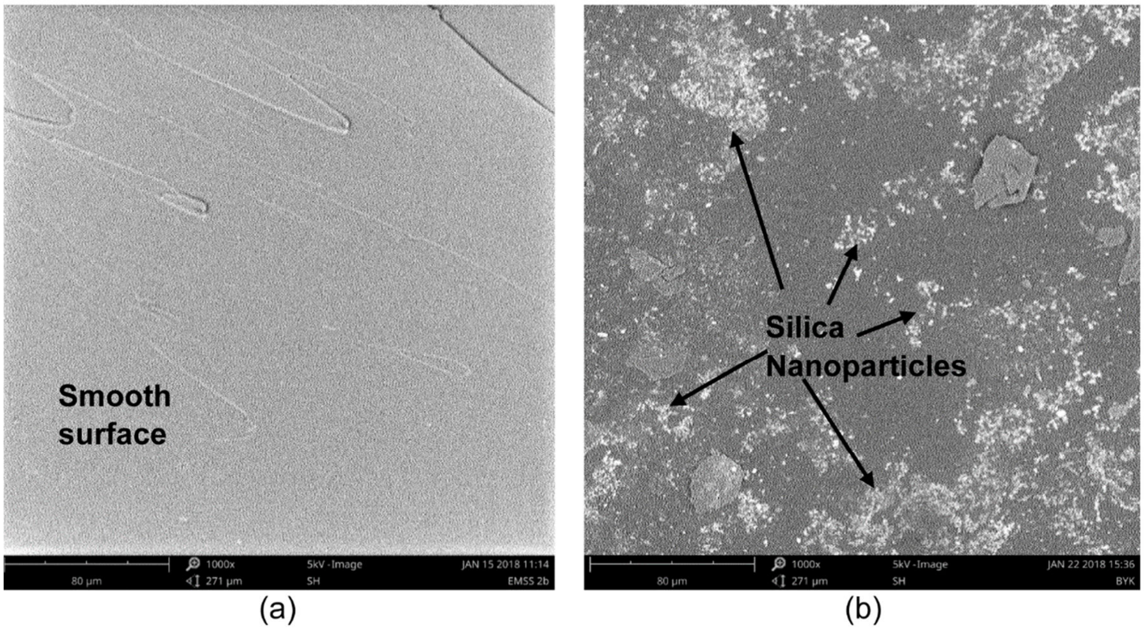


Figure 7: SEM micrographs of different samples.

3.6. Surface morphology

The dispersion of the silica nanoparticles in the epoxy, and the interfacial properties between the epoxy and the nanoparticles were observed by the SEM analysis. The surface micrographs of the nanocoatings are presented in Figure 7. Figure 7a shows the surface of the epoxy coating, whereas Figure 7b shows the surface of the ES20. The surface morphology of the epoxy coating was smooth (Figure 7a). On the other hand, in the morphology of ES20, the silica nanoparticles (20 wt %) were well-dispersed as seen from the uniform and smooth surface of the sample (Figure 7b) [1]. However, no sign of nanoparticles agglomeration was found. This helps to achieve the better adhesive and thermal stability of the coating [35]. The nanoparticles with higher surface area participated actively in the curing process. Therefore, a good dispersion of the nanoparticles and cross-linking with epoxy helped to improve the properties of the coating [1].

4. Conclusions

The epoxy/silica coatings were prepared using different amount (10, 20 and 30 wt %) of colloidal nanosilica particles. The nanocomposite coatings were characterized by various physico-chemical properties such as density, curing time, chemical resistance, UV-absorbance, adhesive strength and oxygen gas transmission rate analysis. In addition, their thermal, structural and morphological properties were also investigated. The properties of the epoxy/silica nanocoating were influenced by the interfacial strength between epoxy and silica nanoparticles. Overall, good adhesive properties with curing time of 420 min to 450 min were observed by the nanocoatings. In addition, the presence of silica nanoparticles in the coatings showed better chemical resistance against acid, alkali and salt solution. Moreover, the nanocoatings showed an excellent UV absorbance than the epoxy. The range of OTR was 1.5×10^6 to 2.1×10^6 cc m^{-2} day^{-1}. Among the composite coating, the ES20 showed the better thermal and chemical resistance than other coatings. The glass transition temperature of the nanocomposites coatings was changed, meaning the toughness and stiffness of the composite coatings were also changed. Overall, the thermal stability of the nanocomposite coating was increased.

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