# Anticorrosion Properties of Epoxy/Nanocellulose Nanocomposite Coating

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Nanocellulose (NC) is an attractive reinforcement agent that can be incorporated into protective coatings because it is a renewable, biodegradable, and biocompatible polymer resource. In this study, a series of epoxy resin-based nanocomposites were prepared in the form of coatings with various amounts of NC loadings, and the coatings were applied onto mild steel at room temperature. The characterizations of the NC and nanocomposites were performed via X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), and Fourier transform infrared spectroscopy (FTIR). The thermophysical properties of the nanocomposites were evaluated using differential scanning calorimetry (DSC) and thermogravimetry (TGA) analyses. The transparency of the nanocomposite specimens was examined by ultraviolet visible (UV-Vis) spectroscopy in the range of 300 to 800 nm. The corrosion protection properties of the coated mild steel substrates immersed in a 3.5% NaCl solution were studied comparatively by electrochemical impedance spectroscopy (EIS). The results showed that all of the nanocomposite coatings with NC noticeably influenced the epoxy-diamine liquid pre-polymer, both physically and chemically. Furthermore, the 1 wt.% NC nanocomposite coating system was found to have the most pronounced anti-corrosion properties, as confirmed by a 30-day EIS study.

*Keywords: Nanocellulose; Nanocomposite; Corrosion; Coating; Electrochemical impedance spectroscopy (EIS)* 

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## INTRODUCTION

The suitability of using biopolymer materials, such as polysaccharides, proteins, and lipids, in film production has been intensively studied recently for the production of biodegradable packaging materials. The development of biomaterials holds great promise to alleviate many sustainability problems and offers the potential of renewability, biodegradability, and a path away from harmful additives. Compared with other materials, cellulose is the most abundant natural carbohydrate biopolymer on earth that is renewable, biodegradable, and non-toxic. It is a hydrophilic polymer composed of repeating  $\beta$ -1,4-linked-D-glucopyranose units and consists of three hydroxyl groups per anhydroglucose unit (AGU), which allows the cellulose molecule to establish strong hydrogen bonds (Zugenmaier 2008).

Knowledge of the molecular structure of cellulose is crucial, as it explains the characteristic properties of cellulose, such as hydrophilicity, chirality, biodegradability, and high functionality. The morphology and the properties of the cellulose nanocrystals

are influenced by its preparation and the dissolution methods used (El-Wakil and Hassan 2008; Chang *et al.* 2010, Chang and Zhang 2011). As a renewable material, cellulose and its derivatives have been comprehensively studied, with a focus on their biological, chemical, and mechanical properties. Nanocellulose (NC) has been generated from microcrystalline cellulose (MCC) *via* acid hydrolysis to improve the physical, mechanical, and gas barrier properties of biopolymer films because of its attractive features, such as high aspect ratio and light weight (Peng *et al.* 2011). These physicochemical properties and wide application prospects have attracted significant interest from both researchers and industrialists.

Along with the development of organic coatings, cellulose nanocrystals are believed to intensify the performance of protective coatings. Thus, the preparation of NC from MCC is important and needs to be considered. Poaty *et al.* (2014) implemented the modification of cellulose nanocrystals with various acryloyl chlorides as reinforcement derivatives for wood coatings, which resulted in an enhanced abrasion resistance of the coatings. Satyamurthy and Vigneshwaran (2013) studied the novel process of preparing spherical NC using anaerobic microbial hydrolysis with MCC and found that the bimodal particle formed by NC has potential in commercial applications. Shankar and Rhim (2016) prepared NC from MCC using an alkaline dissolution method, followed by the regeneration of cellulose, neutralization, and ultrasonication, which decreased the material to the nano-size level as a result.

With the various processes for generating NC, it is possible that it can enhance epoxy elastomer and act as a good reinforcement for transparent composite coatings (Shimazaki *et al.* 2007). The inclusion of NC in epoxy remarkably improves the thermal and mechanical behavior of the composite films, as well as its transparency (Steele *et al.* 2012; Cross *et al.* 2013). Because of the hydrophilic surface of NC, conversion of the congeniality and curtailing the hygroscopicity must be performed. As a result of the reactive surface of the OH side groups, grafting of chemical species can be done to functionalize the NC surface. Herein, NC was obtained from MCC *via* the acid hydrolysis method using sulfuric acid. Generally, the nanocellulose particles resulting from sulfuric acid treatment are easily dispersible in water due to the presence of negatively charged sulfate half-ester groups that result from a reaction of sulfuric acid with the –OH groups on the cellulose surfaces (Wang *et al.* 2007).

This study was aimed at investigating the effect of NC on the corrosion resistance of mild steel surfaces. Also, the capability of using NC as a reinforcement agent in epoxy (EP) coatings was evaluated, where isophorone diamine (IPDA) was used as the curing agent. The strong hydrogen bonding in the NC is proposed to be an important reason behind the difficulties in obtaining a well-dispersed blend matrix, as well as an underlying cause of agglomeration in the epoxy/NC (ENC) nanocomposite coatings. Herein, the NC loadings into the nanocomposite coatings were only up to 2 wt.% to control the occurrence of high agglomeration in the epoxy resin (EP). Furthermore, the corrosion protection properties of all of the developed coating systems were examined utilizing electrochemical impedance spectroscopy (EIS) with up to 30 days of immersion time and 3.5% NaCl solution as the electrolyte.

## EXPERIMENTAL

### Materials

The medium-viscosity liquid EP was produced from bisphenol A and epichlorohydrin with an unsaturation concentration of approximately 5260 to 5420 mmol/kg and a molar mass of 184 to 190 weight per equivalent. The medium-viscosity liquid EP was supplied by ASAChemicals (Selangor, Malaysia) and used as received without any further modification. ASAChemicals also supplied the isophorone diamine (IPDA) curing agent, which was 3-aminomethyl-3,5,5-trimethylcyclohexylamine, 99.7 wt.% solute content in water solution with a molar mass of 170.30 g/mol and a pH value of 11.6. The raw microcrystalline cellulose (MCC) extracted from softwood pulp was purchased from R&M Chemicals (Essex, U.K.) with 50  $\mu$ m of particle size. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (98 wt.%) and absolute ethanol (EtOH) (99.6%) were purchased from Fisher Scientific (Selangor, Malaysia). Sodium hydroxide (NaOH) (0.5 w/v) was purchased from Bendosen Laboratory Chemicals (Selangor, Malaysia). Ultra-pure water (18 M $\Omega$ ·cm, 25 °C) was provided by INFRA Analytical Laboratory (Kuala Lumpur, Malaysia).

## Preparation of cellulose nanoparticles

First, the MCC was dried in a vacuum at 70 °C for 24 h. Nanocellulose crystals (NCC) were prepared according to a modified method of N. Johar *et al.* (2012) and Shankar and Rhim (2016). For this, three grams of the MCC was then added to a 40 wt.% H<sub>2</sub>SO<sub>4</sub> solution, and the solution was vigorously stirred at 60 °C for 1 h. Then, the suspension was quenched with type-1 ultra-pure water, which was removed by successive centrifugation at 6000 rpm for 10 min. The treated MCC was collected and washed 4 to 6 times with 50 wv.% NaOH and EtOH, followed by centrifugation to remove any remnants of NaOH. After washing, the treated MCC was suspended with EtOH until the suspension reached a pH value of 8 to 10. The suspension was stirred at 400 rpm for 30 min and sonicated for 2 min using a 2-mm probe at 60% amplitude. The dispersed NC was dried overnight and desiccated until further use.

#### Preparation of epoxy/cellulose (ENCs) nanocomposite coatings

The epoxy paint was formulated by directly adding various amounts of dried NC powder (1.0 wt.%, 1.5 wt.%, and 2.0 wt.%) to the EP solution. The mixture was stirred mechanically with a glass rod for 2 min and then sonicated for 30 s at 60% amplitude for dispersion. The blended solution was not held in the sonication probe longer than 30 s to prevent overheating; thus, stirring and sonicating were alternately repeated 3 to 4 times. The diamine curing agent was then added to the mixture with an epoxy/hardener ratio of 4:1 at close to vacuum. The mixture was then coated onto mild steel via brushing. The steel panels were abraded with a sand blaster, followed by acetone degreasing. They were kept in a desiccator until use. Furthermore, the free films of the coating were cast on a Teflon® Petri dish for analytical measurements, and the coated mild steel samples were then dried and cured for seven days at room temperature, which led to the formation of a uniform protection coating for the anticorrosion test. The control samples were labeled ENCO, and the samples labeled ENC1.0, ENC1.5, and ENC2.0 corresponded to the particular amount of nanofiller. Moreover, the thickness of the film was measured by using coating thickness gauge (elcometer® 456, Manchester, England), with a target average thickness of  $60 \pm 5 \,\mu m$  for further characterization measurement.

## Methods

### Morphology and characterization

The surface morphologies of the raw MCC, NC, neat epoxy, and ENC nanocomposite sample pieces were examined by field-emission scanning electron microscopy (FESEM) (Quanta FEG 450, EDX-OXFORD, Eindhoven, Netherland) after being coated with gold by using gold sputter coater (Bio-Rad, Watford, England).

Fourier transform infrared spectroscopy (FTIR) was performed using an FTIR spectrometer (FTIR-Spectrum 400, Perkin Elmer, Wokingham, UK) at a resolution of 4 cm<sup>-1</sup> and in the range of 400 to 4000 cm<sup>-1</sup>.

The crystalline nature of the MCC and NC, and the crystalline phases present in the ENC nanocomposite samples, were determined by X-ray diffraction (XRD) (EMPYREAN, PANalytical, EA Almelo, Netherland) at room temperature. The spectra were recorded using Cu K $\alpha$  radiation at 40 kV and 30 mA with scanning at a 2 $\theta$  of 10° to 50°. The crystallinity index (CI) of the MCC and NC was calculated using the Segal method, given by Eq. 1,

$$CI(\%) = (I_{200} - I_{am}) / I_{200} * 100$$
<sup>(1)</sup>

where  $I_{200}$  is the intensity of the (2 0 0) peak and  $I_{am}$  is the intensity of the amorphous minimum region between the (2 0 0) and (1 0 1) peaks. The crystallite size (CS) was calculated using Scherrer's equation, given by Eq. 2,

$$CS = K\lambda / \beta_{1/2} \cos\theta \tag{2}$$

where *K* is the Scherrer constant (0.94),  $\lambda$  is the X-ray wavelength (0.154060),  $\beta_{1/2}$  is the full width at half maximum (FWHM) of the deflection peak, and  $\theta$  is the Bragg's angle (°).

Thermal properties and ultraviolet visible (UV-Vis) analyses of ENC nanocomposite films

The thermal stability of the nanocomposite samples was analyzed by thermosgravimetric analysis (TGA). The TGA tests were conducted using a Mettler Toledo TGA Q500 (Columbus, USA). The samples were heated from room temperature to 800 °C at a rate of heating of 50 °C/min under nitrogen gas with a flow rate of 60 mL/min.

Differential scanning calorimetry (DSC) analysis was performed to investigate the influence of the NC reinforcement filler on the thermal properties of the coating systems. The DSC tests were performed using a TA Instruments Q200 DSC (New Castle, USA) under nitrogen flow. Each sample was heated from -30 to 300 °C at a heating rate of 10 °C/min.

Ultraviolet visible (UV-Vis) analysis of the nanocomposite films was performed using a UV-3101PC (Shimadzu, Kyoto, Japan) UV-Vis spectrometer in transmission mode and a wavelength range of 400 to 800 nm.

## *Electrochemical impedance spectroscopy (EIS)*

The electrochemical response, barrier performance, and corrosion protection of all of the prepared coating systems with up to 30 days of immersion in 3.5% NaCl solution were investigated using EIS. To accomplish this, a classical three-electrode cell with an exposed area of 3 cm<sup>2</sup> as the working electrode, a saturated calomel electrode SCE as the reference electrode, and a platinum electrode as the counter electrode were utilized to

perform the EIS tests after placement in a Faraday cage to reduce the noise during measurement.

A Gamry PC14G300 potentiostat (Warminster, PA, USA) with a frequency range of 300 kHz to 10 MHz and an amplitude of sinusoidal voltage at 10 mV was utilized for data measurement. All of the EIS data were analyzed by the software Gamry Echem Analyst, Version 6.03 (Warminster, PA, USA).

# **RESULTS AND DISCUSSION**

# Morphologies of Nanocellulose (NC) and Epoxy/Nanocellulose (ENC) Nanocomposite Coatings

Cellulose nanoparticles were prepared from raw MCC by an acid hydrolysis treatment with sulfuric acid solution. The morphology of the raw MCC and the prepared NC was observed by FESEM, as shown in Fig. 1. Substantial agglomerations of raw MCC granules that varied in length were observed (Fig. 1a), and they were seemingly in fiber form. This indicated the strong composition of the hydrogen bonding within the cellulose microfibrils (Kumar *et al.* 2014). However, after the acid hydrolysis treatment, the size decreased and NC was produced (Fig. 1b) with an average length and width of 80 to 500 nm and 10 to 70 nm, respectively. The NC had a rod-like shape due to losing of amorphous region on the microfibrils of MCC. The results indicated a favorable reaction due to the acidic treatment.

Subsequently, the NC in powder form was reinforced into the EP polymer, and the morphologies of the ENC nanocomposite films were further characterized by FESEM, as shown in Fig. 2. The figure shows a featureless surface of the neat EP, and also reveals a rough surface characteristic of the film in which the NC particles were embedded in the epoxy matrix (Shi *et al.* 2009). The surface of the ENC nanocomposites was observed to be relatively rough and eventful compared to the neat resin. The reason may have been that the NC embedded in the resin caused a cross-linking reaction, which resulted in the matrix surface to become more abrasive during dispersion. Because of this change in abrasiveness, the NC may have limited the smoothness of the surface of the nanocomposite films.

The surface roughness indicated the occurrence of deformation when nanoparticles were added with some forces applied during the dispersion through sonication. As shown in Fig. 2b, the surface roughness was homogeneous and less aggregated, which meant that the dispersion of 1 wt. % of NCs were good enough for the NC to be embedded within the EP matrix. That, in turn, could be considered as a clear evidence of the competence of the sonication process in developing an acceptable level of nanoparticles dispersion within the utilized polymeric matrix.

The agglomeration of nanoparticles was due to the heterogeneous reaction between the NC and epoxy matrices when more NC is added. This was because the resin had enough force to strengthen the bonding in the NC, which caused difficulty with dispersion in the epoxy surface. Moreover, as the loading ratio of NC nanoparticles exceeds 1 wt. % up to 1.5wt. % and 2 wt. %, the number of the nanoparticles in unit area increased; therefore, the tendency of the utilized nanoparticles to be attracted to each other increased.

It is worth mentioning that a good dispersion of nanoparticles in the epoxy matrix led to having a stabilized cross-linking network (Kadhim *et al.* 2013) when more

nanoparticles were added. However, this explanation does not fully clarify the nanocellulose systems seen in Fig. 2b. The surface morphology of the 2.0 wt.% NC nanocomposite (ENC2.0) was found to be relatively smooth and rough in the same vicinity. This observation indicated that the stiffness of the surface, which led to the adhesion behavior of the films, was increased due to the strong intermolecular bonding within the cross-linking networks (Preghenella *et al.* 2005; Lu and Hsieh 2010). However, agglomeration still remained within the matrix, even though both the mechanical mixing and ultrasonication were performed in this work. Sufficient energy force to disperse the particles could not be exerted. The ultrasonic mixing technique could have reduced the size of the particles and dispersed them homogeneously if the compatibility between the NC surfaces and matrix was adequate. Thus, only ENC1.0 showed good dispersion in epoxy/diamine pre-polymer.



Fig. 1. FESEM images of (a) raw MCC and (b) NC



**Fig. 2.** FESEM images of (a) neat epoxy (ENC0), and (b) 1.0 wt.% (ENC1.0), (c) 1.5 wt.% (ENC1.5), and (d) 2.0 wt.% (ENC2.0) NC nanocomposite films

# X-Ray Diffraction Spectra of Nanocellulose (NC) and Epoxy/Nanocellulose (ENC) Nanocomposite Coatings

The crystalline nature and size of the NC produced from the MCC was determined by XRD, and the materials further characterized with ENC nanocomposite coatings, as shown in Fig. 3. The MCC and NC exhibited characteristic crystalline peaks around a  $2\theta$  of 14.6°, 16.5°, 20.0°, 22.6°, and 34.6°, which are considered to be characteristic peaks of typical cellulose structures that correspond to (-110), (110), (102), (200), and (004) on the lattice plane, respectively (Ciolacu *et al.* 2011; Johar *et al.* 2012; Sheltami *et al.* 2012). The crystallite sizes of the MCC and NC, calculated using Eq. 2, were 18.39 and 11.03 nm, respectively. This indicated that the crystallite size of the MCC decreased after treatment with acid hydrolysis using sulfuric acid dissolution. The CIs of the MCC and NC were 88% and 79%, respectively, which showed that the NC possessed a greater CI because of the isolation from water dispersion during acid hydrolysis and alkaline neutralization (Nam *et al.* 2016; Shankar and Rhim 2016).

XRD micrographs also were obtained for epoxy/nanocellulose nanocomposites with variation in nanocellulose content, as shown in Fig. 3. The control film of the neat epoxy showed a broad amorphous peak from  $12.2^{\circ}$  to  $28.5^{\circ}$ , thus exhibiting the amorphous nature of epoxy. However, no change in the peak position of the neat epoxy was observed with the presence of nanocellulose in the nanocomposite systems, which might have been because of the smaller concentration of NC in the epoxy matrix. Pan *et al.* (2012) reported that no obvious peak was seen in the 2 wt.% ENC nanocomposite spectrum because of the low content of nanofiller, and visible peaks were observed in the nanocomposites that were 4 wt.% to 8 wt.% of loaded nanofiller. The disappearance of all of the maxima ( $2\theta = 14.6^{\circ}$ ,  $16.5^{\circ}$ ,  $20.0^{\circ}$ ,  $22.6^{\circ}$ , and  $34.6^{\circ}$ ) from the layered structure of the NC indicated the intercalation or exfoliation of the nanofiller to form the nanocomposite with the EP matrix.



Fig. 3. XRD patterns of the raw MCC, NC, and ENC nanocomposite coatings

# Fourier Transform Infrared Spectroscopy of Nanocellulose (NC) and Epoxy/Nanocellulose (ENC) Nanocomposite Coatings

FTIR was performed to understand the change in the chemical structures of the NC, EP, IPDA, and ENC nanocomposite samples, as shown in Fig. 4. In general, the

change in the crystalline structure of the cellulose led to the disappearance or reduction in intensity of certain FTIR peaks of the crystalline domains of the cellulose. In the functional region of the FTIR, the broad band located in the ranges of 3000 to 3500 cm<sup>-1</sup> and 2790 to 2982 cm<sup>-1</sup> corresponded to the hydroxyl (O-H) and aliphatic alkyl (C-H) stretching vibrations, respectively (Lani *et al.* 2014).

In contrast, the amorphous band was assigned to the peak at 895 cm<sup>-1</sup>, which was attributed to the C-O-C stretching vibration at the  $\beta$ -(1,4)-glycosidic linkages of cellulose (Ciolacu *et al.* 2011; Xu *et al.* 2013), and the disappearance of the band at 1062 cm<sup>-1</sup> was attributed to the symmetrical C-O-S vibration resulting from the presence of H<sub>2</sub>SO<sub>4</sub> in the acid hydrolysis treatment.

All of the infrared-active modes, such as deformation, twisting, and wagging of the anhydroglucopyranose unit, were observed in the 1800 to 700 cm<sup>-1</sup> regions. The absorption peaks at 1315, 1160, 1108, and 1054 cm<sup>-1</sup> were due to H-C-H wagging, the C-C ring stretching band, the C-O-C glycosidic ether band, and the C-O-C pyranose ring stretching, respectively (Lu and Hsieh 2010; Sheltami *et al.* 2012; Voronova *et al.* 2012; Kumar *et al.* 2014). The peak at 1642 cm<sup>-1</sup> was attributed to the OH bending of the absorbed water, due to the strong water-interaction in the cellulose (Morán *et al.* 2008; Neto *et al.* 2013). No difference was found in the spectrum of the NC compared with that of the MCC, which suggested that in the case of acid hydrolysis, the molecular structure of the cellulose did not undergo any vital changes. However, a slight reduction in the absorption number indicated that the change in the size of the NC was accompanied by a decreased degree of crystallinity, as shown by the XRD and FESEM.

In the fingerprint region, the crystallinity band at 1428 cm<sup>-1</sup> was attributed to the CH<sub>2</sub>- bending vibration, which indicated the reduction in the degree of crystallinity of the cellulose due to the decrease in the absorption. Figure 4 depicts the FTIR spectra obtained from the unreacted epoxy, IPDA, and neat cured EP. The absorption peaks at 915 and 3100 cm<sup>-1</sup> were attributed to the presence of the C-O deformation and the C-H stretching of the oxirane group in the epoxy matrix, respectively. The bands located at 1032 cm<sup>-1</sup> corresponded to a C-O-C linkage because of the unreacted epoxide group. Fraga *et al.* (2008) reported that the bands at 1507 and 820 cm<sup>-1</sup> could be assigned to the p-phenylene groups in the unreacted epoxide group. The disappearance of bands, as observed in the neat epoxy (ENCO), indicated that all of the epoxide groups reacted during curing and were well blended with the isophorone diamine curing agent (Nunez *et al.* 1995; Fraga *et al.* 2008).



Fig. 4. FTIR of the NCC and epoxy/NCC nanocomposite coating systems

In the ENC nanocomposites, the epoxide group could react with the hydroxyl groups on the NC surfaces. If an epoxide group reacted with a NC hydroxyl group, the result would be an ether group and a hydroxyl group. The band at 3200 to 3450 cm<sup>-1</sup> of the ENC nanocomposite spectrum confirmed that an interaction occurred within the hydroxyl group and suggested there was an increase in hydrogen bonding between the NC nanofiller and epoxy matrix. The band at 1606 cm<sup>-1</sup> was possibly due to the overlapping of the C=C stretching of the epoxide group and the -NH<sub>2</sub> scissoring of the amine group. It is worth noting that the observed peaks of the N-H stretching (3283 cm<sup>-1</sup>) and the N-H deformation (1602 cm<sup>-1</sup>) of the diamine group quantitatively appeared because of the strong -OH absorption bands and corresponded to the other organic band region. Also, the peak at 1032 cm<sup>-1</sup> clearly showed an increase in the peak intensity that corresponded with the NC loading. This confirmed that a strong interaction occurred between the ether linkage of the epoxy matrix and the glycosidic ether linkages of the NC. Other bands at 895, 1229, 1455, and 1606 cm<sup>-1</sup> increased in intensity after the addition of the NC nanofiller, and these bands were attributed to the C-O-C stretching vibration, H-C-H wagging, CH<sub>2</sub>- bending vibration, and C=C stretching, respectively.

# Optical Transmittance of Epoxy/Nanocellulose (ENC) Nanocomposite Coatings

The UV-Vis transmittance spectra of the EP and NC nanocomposite specimens in the visible wavelength range of 300 to 800 nm at 2.0 nm intervals are shown in Fig. 5. The transmittance of the 2.0 wt.% NC nanocomposite (ENC2.0) was the lowest, with less than 20% light transmittance. Incidentally, the specimen with 1 wt.% NC nanocomposite (ENC1.0) was clearly transparent, with the highest light transmittance of 73% at 400 nm. The transparency of the nanocomposites was dependent upon the amount of the nanofillers. The light transmission rates of the specimens with 1.5 wt.% and 2.0 wt.% NC nanocomposite (ENC1.2 and ENC2.0) were reduced to 43% and 45%, respectively.

Moreover, the drop off of light transmission for all of the samples was observed at approximately 300 to 350 nm, which meant there was high light absorption at this point and that no light reflection occurred in the ultraviolet region (300 to 400 nm). The high transparency of the 1 wt.% NC in the ENC nanocomposite possibly resulted from the difference in the refractive index between the nanofiller and the epoxy matrix, which suppressed light transmission through the epoxy/NC interphase. This indicated that the difference in the refractive index of the filler and matrix also played an important role in controlling the optical transmittance of the composite films.



Fig. 5. UV-Vis spectra for the ENC nanocomposite specimens

# **Thermal Analysis of Epoxy/Nanocellulose (ENC) Nanocomposite Coatings** *Thermogravimetric analysis (TGA)*

The TGA results of the neat epoxy and ENC nanocomposite coating samples are given in Fig. 6, which includes weight loss *versus* temperature. The initial degradation temperature ( $T_{IDT}$ ), temperature at the maximum weight loss rate ( $T_{max}$ ), and residue at 700 °C are tabulated in Table 1. Herein,  $T_{IDT}$  is used as the thermal stability indicator and defined as the temperature corresponded to the 5 wt.% loss in weight.

Figure 6 shows that there was less than 5% weight loss at approximately 65 to 160 °C, and the water or small molecule loss in this range was considered to be minimal. The NC nanocomposite coating samples exhibited about 5 wt.% weight loss in between approximately 300 and 390 °C, which corresponded to the initial degradation temperature, but the overall thermal stability showed little change due to the NC content. As shown in Fig. 6, the thermal decomposition of the neat EP consisted of one step (Ammar *et al.* 2016c).

Furthermore, from Table 1, the  $T_{IDT}$  for thermal degradation for the ENC nanocomposite coating samples increased from approximately 367 to 384 °C, which was relatively high compared to the neat epoxy coating. The change in the temperature may have been due to dehydration, depolymerization, and decomposition of the glycosyl unit accompanied by char formation. The drastic weight loss that occurred up to 460 °C could be attributed to the breakdown and oxidation of the char residue.

Moreover, as the NC content increased, the temperature at the maximum weight loss rate for the first degradation step decreased, but was still greater than for the neat epoxy coating. The temperature at the maximum weight loss rate for the second degradation step was greater than the temperature of the first degradation for the same NC content.



**Fig. 6.** TGA thermograms of the neat epoxy (ENC0) and NC nanocomposite coating systems (ENC1.0, ENC1.5, and ENC2.0)

<b>Table 1.</b> Initial Degradation Temperature ( $T_{IDT}$ ), Temperature at Maximum
Weight Loss Rate ( $T_{max}$ ), and Char Residue at 700 °C, Determined from TGA
Data

Sample	ENC0	ENC1.0	ENC1.5	ENC2.0
T <sub>IDT</sub> (°C)	367.25 ± 0.36	384.63 ± 0.23	385.13 ± 0.63	384.16 ± 0.88
T <sub>max</sub> (°C)	365.51 ± 0.24	395.59 ± 0.15	395.30 ± 0.57	393.99 ± 0.44
Char Residue, 700 °C (wt.%)	9.07	7.41	6.43	7.12

#### Differential scanning calorimetric (DSC) analysis

The DSC curves and glass transition temperature  $(T_g)$  values of the neat epoxy and ENC composite samples are shown in Figs. 7 and 8, respectively. Figure 7 shows the DSC thermograms for the second cycle scanning of the endothermic measurement for all of the coating samples. The two-cycle scanning was adopted to eliminate the moisture content of the samples, which might affect the DSC measurements or the thermal degradation. In this study, the  $T_g$  was approximately 135 to 150 °C, although the baseline step was somewhat small. The baseline step may have been small because of the anhydroglucopyranose units in the NC.

A maximum increase of approximately 15 °C of the  $T_g$  was observed at a NC loading of 1.0 wt.% and 1.5 wt.%, and the  $T_g$  slightly decreased for the 2.0 wt.% loading, as shown in Fig. 8. This trend of an increased  $T_g$  corresponded with the good bonding system between the polymer network and reinforced filler. This indicated the good physical or chemical mobility interactions between the epoxy matrix and the inclusion of NC particles.

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**Fig. 7.** DSC thermograms at the second scan of the neat epoxy (ENC0) and NC nanocomposite coatings (ENC1.0, ENC1.5, and ENC2.0)

#### Electrochemical Impedance Spectroscopy (EIS) Measurement

EIS measurements were performed to investigate the effects of the addition of NC on the barrier and corrosion protection properties of the epoxy coating in a 3.5 wt.% solution with different immersion times.



Fig. 8.  $T_g$  of the neat epoxy and NC nanocomposites determined from the DSC data

Figures 9 and 10 present the Bode plots of the epoxy coating and the coatings reinforced with various amounts of NC after 1 day and 30 days of immersion, respectively. To study the influence of NC nanoparticles on the corrosion protection performance of the EP, EIS measurements were conducted periodically after exposing the coated steel panels to the 3.5% NaCl solution. The obtained results were expressed graphically using Bode plots after 1 day and 30 days of immersion, as illustrated in Figs. 9 and 10, respectively. Furthermore, two different models, as shown in Fig. 11, of the equivalent circuit were utilized to achieve the best numerical fitting of the recorded EIS data over the different periods of immersion and the corresponded impedance values for all the resistance components of the utilized equivalent circuit models were tabulated in Table 2.

After 1 day of immersion, as shown in Fig. 9, the electrochemical responses of all of the prepared coating systems, revealed that only the neat epoxy coating system, ENCO, demonstrated a Bode plot with two-time constants. This finding could be considered clear evidence that the film coating of the unmodified polymeric matrix suffered penetration of electrolytes towards the substrate surface with the weakest barrier ability. The electrochemical behavior of the ENCO coating system at this stage of degradation could be perfectly described with model B of the equivalent circuit. In contrast, all of the prepared coating systems reinforced with different loading rates of NC nanoparticles demonstrated better corrosion protection properties after the first day of immersion. The good anticorrosion performance of the NC nanocomposite coatings was confirmed by the Bode plots illustrated in Fig. 9. The impedance plots demonstrated a one-time constant, and the EIS data was fitted with model A of the equivalent circuit (Mostafaei and Nasirpouri 2013; Ammar *et al.* 2016a).

To further investigate the ability of the NC nanoparticles to enhance the corrosion protection performance of the epoxy coating systems, the EIS studies continued to 30 days of immersion, and the Bode plots were recorded and illustrated in Fig. 10. As shown in Fig. 10, the impedance plot of the ENC0 coating system continued to demonstrate two-time constants with the lowest impedance modulus |Z|, which indicated that the unmodified polymeric matrix of the EP did not withstand the exposure to the aggressive corrosive medium. This resulted in the creation of diffusion pathways and the penetration of the corrosive agents towards the substrate surface, and therefore, corrosion occurred.

However, the 1.0 wt.% NC and 1.5 wt.% NC coating systems demonstrated a remarkable stability against the corrosion initiation for up to 30 days of immersion, as their respective impedance plots continued with the one time constant and remained wellfitted with model A of the equivalent circuit. Ammar et al. (2016b) and other researchers (Zhou et al. 2014; Ramezanzadeh et al. 2016) have attributed the better corrosion protection performance of the nanocomposite coating systems, compared to the unmodified polymeric systems, to the ability of the nanoparticles to fill up the porosity of the polymeric matrices and further enhance the quality of the coating film by promoting the possibility of achieving the optimal defect-free coating film. This forced the corrosive agents to travel longer distances to reach the surface of the substrate. However, it is worth noting that as the loading ratio of the NC nanoparticles increased up to 2 wt.%, the impedance modulus |Z| value decreased, and two-time constants were observed with the impedance plot after 30 days of immersion. This was due to the degradation of the film coating, and was a sign that the corrosion occurred at the coating-substrate interface. The performance of the 2.0 wt.% NC coating system could be attributed to the tendency of nanoparticles to agglomerate at high loading ratios (Ammar et al. 2016c, d).



**Fig. 9.** Representative Bode plots in terms of (a) impedance and (b) phase angle of the neat epoxy (ENC0) and NC nanocomposite coating systems (ENC1.0, ENC1.5, and ENC2.0) after 1 day of immersion



**Fig. 10.** Representative Bode plots in terms of (a) impedance and (b) phase angle of the neat epoxy (ENC0) and NC nanocomposite coating systems (ENC1.0, ENC1.5, and ENC2.0) after 30 days of immersion

System	<i>R</i> <sub>c</sub> (Ω cm²)	R <sub>ct</sub> (Ω cm²)	R <sub>diff</sub> (Ω cm²)	The equivalent circuit model used in fitting EIS data
ENC0	$(4.55 \pm 0.18) \times 10^4$	(8.69 ± 0.23) ×10 <sup>5</sup>	(7.32 ± 0.98) ×10 <sup>5</sup>	В
ENC1.0	$(2.28 \pm 0.27) \times 10^8$	(1.52 ± 0.04) ×10 <sup>9</sup>	-	А
ENC1.5	$(1.33 \pm 0.97) \times 10^7$	$(5.47 \pm 0.34) \times 10^8$	-	A
ENC2.0	$(6.24 \pm 0.95) \times 10^5$	$(3.87 \pm 0.14) \times 10^7$	$(1.96 \pm 0.03) \times 10^8$	В

**Table 2.** Fitted Impedance Values of the Equivalent Circuit Elements Along with the Utilized Model after 30 Days of Immersion



**Fig. 11.** The equivalent circuits used for fitting the impedance plots.  $R_s$  is solution resistance,  $R_c$  is the coating resistance,  $CPE_c$  is the constant phase element of coating capacitance,  $CPE_{dl}$  is the constant phase element of double layer capacitance,  $R_{ct}$  is the charge transfer resistance,  $CPE_{dl}$  is the constant phase element of diffusion capacitance, and  $R_{diff}$  is the diffusion resistance (correlated to the diffusion process used in the presence of corrosion products)

# CONCLUSIONS

- 1. This study reported the preparation of NC from the raw material MCC by acid hydrolysis. The NC was then used as a reinforcement nanofiller in epoxy coating systems. The effect of the NC as reinforcement nanofiller on the corrosion protection properties of the epoxy/diamine coatings was studied.
- 2. The results showed that embedding the NC into the epoxy/diamine pre-polymer enhanced the coating's thermal, physical, and chemical properties. The  $T_g$  increased as the content of NC increased, and the transparency of the film coating decreased with higher NC loadings into the epoxy matrices. This indicated that there was good reinforcement of the epoxy/diamine matrices, and the water content and thermal stability were not degraded with the addition of NC. Some aggregation of NC was seen on the coating surfaces. These results are worthy of further investigation in future studies.
- 3. The EIS studies were performed with immersion in a 3.5% NaCl solution up to 30 days in order to investigate the corrosion protection performance and the barrier properties of all the developed coating systems. The results of EIS studies revealed the ability of NC to alter the corrosion protection performance of the coating film. Higher impedance values were recorded for the coating systems that contain NC even after 30 days of immersion time. The best barrier properties and the most pronounced enhancement over the corrosion protection performance were observed for the 1.0 wt.% NC coating system.
- 4. The NC incorporated into the epoxy matrices helped to improve their properties physically and chemically. In that regard, epoxy/nanocellulose nanocomposite coatings enhanced the barrier properties as anticorrosion protection.
- 5. Overall, these results indicated that the nanocomposite or another type of polymer nanocomposite might support the assertion that such structure-property relationships can be applied in a broad range of applications in the future.

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