CYCLOPENTYL TRISILANOL SILSESQUIOXANES – MODIFIED NATURAL RUBBER ($CpSSQ(OH)_3$ – ENR-50) NANOCOMPOSITE IN THE PRESENCE OF TIN (II) CHLORIDE DIHYDRATE

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ABSTRACT

A nanocomposite comprising cyclopentyl trisilanol silsesquioxanes ($CpSSQ(OH)_3$) and 50% epoxidized natural rubber (ENR-50) was prepared at reflux temperature with Tin (II) chloride dihydrate ($SnCl_2.2H_2O$) as catalyst. $SnCl_2.2H_2O$ was found to be an affective catalyst to promote ring opening in ENR-50 and tailored it to $CpSSQ(OH)_3$ via chemical reaction. The generation of carbonyl functional groups arising from epoxide ring opening can be clearly seen in FTIR spectra. ^1H and ^{29}Si NMR analyses further proved that the incorporation of $CpSSQ(OH)_3$ in ENR-50 occured. TGA studies showed a degradation temperature with 10% weight decreased and DSC thermogram indicates a single T_g. Single peak in XRD diffractogram at 2-Theta angle further confirmed the surface modification.

Keywords: *silsesquioxanes, ENR-50, oxirane ring opening, hybrid*

INTRODUCTION

Silsesquioxanes are compounds of general formula $(RSiO_{1.5})_n$, where R is an organic group or hydrogen [1-3]. Silsesquioxane is subclassed into the polymer species and the monomer species [4]. Polymer species of silsesquioxane, also known as polysilsesquioxane [5, 6], comprised of discrete structures constituted by the same or different monomer units. Monomer species of silsesquioxane or oligosilsesquioxane is represented by assembly of Si-O-Si structural components via a particular degree of condensation. Thus these oligosilsesquioxanes can be either the fully condensed or the incompletely condensed [7-10]. Fully condensed oligosilsesquioxane is known as the polyhedral oligomeric silsesquioxane (POSS). Generally either type of the above oligosilsesquioxane with reactive functionalities are suitable for polymerization, grafting [11] or surface bonding [12]. Thus they offer potential functionalization with a wide variety of polymer matrices for the preparation of polymer nanocomposites and hybrids. The properties of these materials are intermediate between those of organic polymer and ceramics. Hybrid polymeric materials that contain segments of oligosilsesquioxanes may exhibit a number of potential useful properties and may combine the advantages of the polymer matrix and nanosize oligosilsesquioxane filler used.

Cyclopentyl trisilanol silsesquioxane $[(C_5H_9)_7Si_7O_9(OH)_3]$ [in this work abbreviated as $(CpSSQ(OH)_3)$] is an example of the incompletely condensed oligosilsesquioxane with three active silanol groups. $CpSSQ(OH)_3$ has almost similar property to the respective fully condensed oligosilsesquioxane, cyclopentyl-POSS. $CpSSQ(OH)_3$ has low solubility in a variety of common organic solvents [7], nonetheless, the incorporation of $CpSSQ(OH)_3$ into polymers can lead to the composite material property improvement, such as temperature and resistant to oxidation, surface hardening and reduced flammability. ENR-50 is a natural rubber with 50 percent epoxidation of 1,4-polyisoprene [13-15]. ENR-50 exhibits excellent properties such as oil resistance [16], gas permeability, good wet rip and high damping characteristics. Thus it is a potential substitute to many synthetic elastomers [17]. The oxirane ring in the ENR-50 offers synthetic manipulability through its reactivity. The oxiranes are found to be effective in causing specific interactions in ENR blends [18] and contribute to crosslink between ENR chains. The oxirane in ENR is sensitive to acid (i.e. low pH) and it has been found that oxirane ring opening is achievable through the acid catalysis [16, 19]. Tin (II) chloride dihydrate ($SnCl_2.2H_2O$) is one of the promising acidic catalyst [20] with the ability of promoting oxirane ring opening in the ENR-50 and subsequent tailoring towards the silanol groups of the $CpSSQ(OH)_3$. In this study, we investigated the silanoxy (Si-O-C) bonds formation in the $CpSSQ(OH)_3$-ENR-50 composite catalyzed by tin (II) chloride dihydrate.

EXPERIMENTAL SECTION

Materials

All the chemicals were obtained commercially and used without further purification unless otherwise stated. 1,3,5,7,9,11,14-heptacyclopentyltricyclo [7.3.3.1] heptasiloxane-*endo*-3,7,14-triol, [$CpSSQ(OH)_3$] 95% was purchased from Aldrich, USA. Deuterated chloroform, $CDCl_3$ is from Fluka Chemicals,

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Switzerland. n-Hexane from Merck, Germany. Toluene is from Systerm, Malaysia. Tetrahydrofuran is from J.T. Baker, New Jersey. Tin (II) chloride dihydrate, 97% is from Acros Organic, USA. Epoxidized natural rubber with 50% epoxidation (ENR-50) was supplied by Guthrie Polymer Sdn Bhd, Malaysia and purified according to literature [18].

Nanocomposite preparation

Mol ratio between $CpSSQ(OH)_3$ and ENR-50 was fixed 1:1 in this experiment. The molecular weight of ENR-50 is 152.33 g mol^{-1} based on its mass repeating units. 10% (w/w) of $SnCl_2.2H_2O$ was used as catalyst based on the total mass of $CpSSQ(OH)_3$ and ENR-50. In a typical preparation, 40 mg (4.57×10^{-5} mol) of $CpSSQ(OH)_3$ and 4.70 mg (2.08×10^{-5} mol) of $SnCl_2.2H_2O$ were added to 5.46 mL (4.57×10^{-5} mol) of ENR-50 (1.28 mg mL^{-1}) stock in toluene. Toluene was then added to the mixture until the final volume was 20 mL. Then, 5 mL of THF was added in the mixture, stirred until homogenous and refluxed for three hours. The solvent was then removed using rotary evaporator and the nanocomposite obtained was dried in vacuum oven at 50 °C for 24 hours.

Measurements and characterization techniques

The FTIR spectra were obtained on a Perkin-Elmer 2000 at room temperature (25 °C). A thin layer of ENR-50 solution was drop cast as a thin film onto a ZnSe window. For $CpSSQ(OH)_3$ and the prepared nanocomposite were ground and the powder was mixed with KBr and pressed into thin pellets. In all cases 64 scans at 2 cm^{-1} resolution were used to record the spectra in the range of 600 to 4000 cm^{-1}. The ^1H NMR measurements were carried out on an Advanced Bruker 400 MHz. The samples were dissolved with deuterated chloroform. The ^{29}Si NMR spectra were obtained using an Advanced Bruker 97.5 MHz. The range of chemical shift recorded was 100 – 400 ppm with spectral width of 600 ppm and the number of scan is 2000. The set number of points and set size for processing in dimension were 64000. The inversed probe was used to minimize nuclear overhauser effect (NOE). The calorimetric measurements were carried out using a Perkin Elmer Pyris-6 (Shelton CT). The samples (about 10 mg) were sealed in aluminium pan and thermograms were recorded at a heating rate of 20 °C min^{-1} over a range of -50 to 200 °C. A Perkin Elmer TGA-7 thermal gravimetric analyzer was used to investigate the thermal stability of the samples. The samples (about 10 mg) were heated under nitrogen atmosphere from 30 °C until 900 °C at the heating rate of 20 °C min^{-1} in all cases. X-ray diffractogram (XRD) of the powdered samples were collected on a SIEMENS D5000 X-ray diffractometer with monochromatic Cu-Kα radiation filter in the 2-Theta range from 0 – 100°.

RESULT AND DISCUSSION

Spectroscopic Evidence of Si-O-C Bond Formation

FTIR analysis was conducted on each of the starting material and the resultant nanocomposite. From Fig 1, the characteristic peaks of the C=C at 3034, 837 cm^{-1} and the epoxide ring at 876 cm^{-1} [21] of the ENR-50 are clearly seen. The presence of $CpSSQ(OH)_3$ is indicated by the silanol group absorption peaks at 3189 and 877 cm^{-1} [22]. The existence of silsesquioxane skeleton, Si-O-Si is indicated by the broad but sharp absorption peak at 1102 cm^{-1} [23]. The peaks at 1246 cm^{-1} is due to the Si-C arising from the cyclopentyl group attach to the silsesquioxane skeleton [23].

The FTIR spectrum of resultant nanocomposite showed peak appearing at 1713 cm^{-1} attributed to the C=O group that arise from the secondary ring opening of isolated epoxide ring [13, 14, 24, 25]. The epoxide ring opening causes the carbonyl formation and the subsequent interaction via hydrogen bonding between –OH of the trisilanol and the carbonyl of the ring opened of ENR. Hence, the observed silanol group peak shifted from 3189 cm^{-1} to 3197 cm^{-1} [22]. FTIR technique is insufficient to determine the formation of Si-O-C bond resulting from the interaction between the silanol group, Si-OH of $CpSSQ(OH)_3$ and the oxirane of ENR-50. This is because the expected peak for Si-O-C was masked by strong and sharp absorption band of Si-O-Si [22].

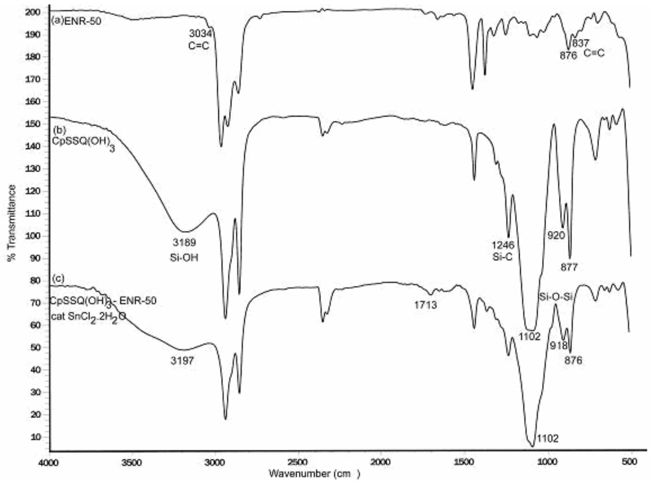


Fig 1. FTIR spectra of (a) ENR-50, (b) $CpSSQ(OH)_3$ and (c) nanocomposite $CpSSQ(OH)_3$ – ENR-50 with catalyst $SnCl_2.2H_2O$.

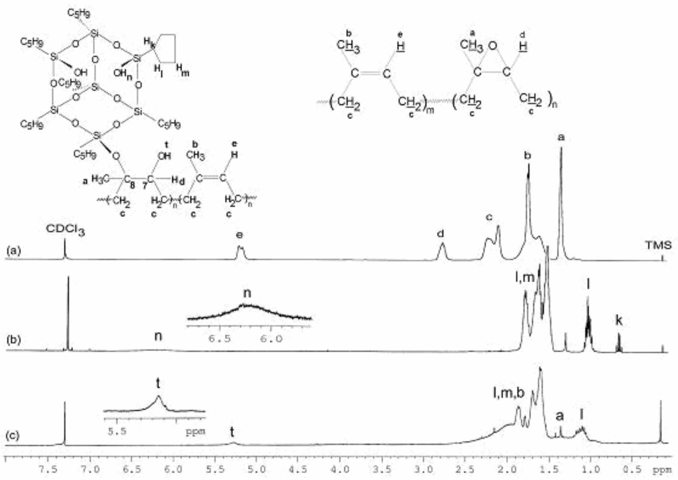


Fig 2. ^{1}H NMR spectra of (a) ENR-50, (b) CpSSQ$(OH)_3$ and (c) nanocomposite CpSSQ$(OH)_3$ – ENR-50 with catalyst $SnCl_2.2H_2O$.

In the ^{1}H NMR, Fig 2; the doublet at δ 5.2 ppm indicated the **e** proton attached to the isoprene carbon. While singlet peak at δ 2.7 ppm indicated that the **d** proton is attached to oxirane carbon. The aliphatic protons ($-CH_2-$), **c** are represented by two doublet peaks at δ 2.2 of isoprene and 2.1 ppm of oxirane structure respectively. The methyl protons, **b** and **a** are at δ 1.7 ppm and 1.3 ppm respectively [13, 26, 27]. The chemical shift of isoprene proton is at a higher magnetic field as compared to oxirane proton as shown in Fig 2(a).

From Fig 2(b), the chemical shift at δ 0.5 ppm indicated the **k** proton which is directly attached to silicon atom of silsesquioxane framework. The multiplet at δ 0.9 ppm represented the **l** proton. Also the multiplet peak at δ 1.3 – 1.8 ppm represented the **m** proton and partial of the **l** proton which was not shown at δ 0.9 ppm [7]. A single broad peak at δ 6.0 ppm is due to the silanol group of CpSSQ$(OH)_3$ [4].

The ^{1}H NMR analysis of the resultant nanocomposite in Fig 2(c), showed the peak of silanol group, **n** disappeared. The proton was replaced by the **t** proton belonged to new hydroxyl group due to ring opening reaction of ENR-50 of **C7**. Proton **a** and **b** of ENR-50 respectively was shown at δ 1.3 – 1.4 ppm and δ 1.5 – 1.9 ppm. It were appeared as broadening of spectrum baseline and addition of proton integration compare to same peak region of CpSSQ$(OH)_3$. The c proton is shifted to the new region of δ 2.1 – 2.3 ppm proving that there was a tether formed between ENR-50 and CpSSQ$(OH)_3$ via Si-O-C bonding. Thus the results of ^{1}H NMR also suggest Si-O-C bond formation similar to the finding of FTIR analysis as described above.

CpSSQ$(OH)_3$ is an organosilicon compound with C_{3v} symmetry. Generally there are three environment for silicon available and these correspond to silicon atom at the centre of symmetry (Si_a), silanol silicon (Si_b) and silicon positioned at the closed vertex position (Si_c) [28], Fig 3. These three different environments for silicon have been observed via ^{29}Si NMR if CpSSQ$(OH)_3$ compound is analyzed in (v/v) 75% $CDCl_3$ and 25% pyridine solvent mixture [7]. However the product composite involves ENR-50 as the polymer matrix which is highly sensitive to strong electrophilic solvent such as pyridine [29]. Thus using pyridine in the solvent mixture may cause degradation of the composite obtained. To overcome this CpSSQ$(OH)_3$ was analyzed in 100% $CDCl_3$. The spectrum of the composite in 100% $CDCl_3$ only displayed two overlapping peaks at δ -99 ppm and at δ -106 ppm corresponding to Si_c and Si_b silicon respectively, Fig 4a. Both peaks (δ -99 ppm, δ -106 ppm) were individually tested with variable temperature experiments using same sample to prove that these two peaks were obtained from CpSSQ$(OH)_3$ compound [30,31]. After the conformation of the sample peaks, the same sample solution then was added with a drop of D_2O in order to differentiate between Si_b and Si_c silicon [29].

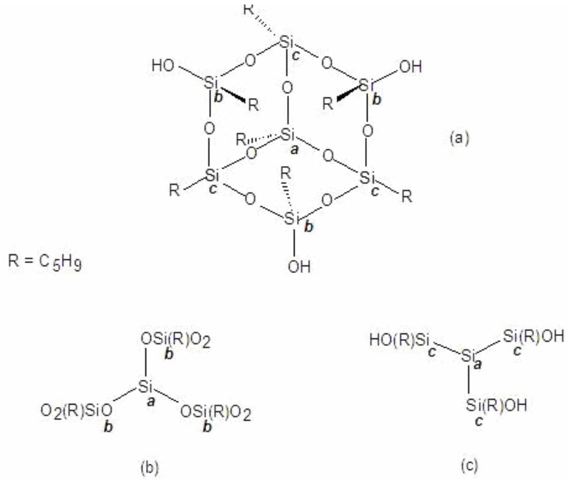


Fig 3. Molecule symmetry of CpSSQ$(OH)_3$ (a) Si_a silicon atom position as symmetry centre to (b) silanol silicon atom, Si_b and (c) silicon atom at closed vertex position, Si_c.

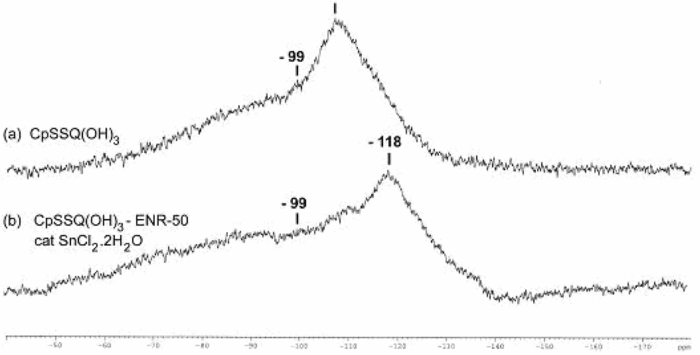


Fig 4. ^{29}Si NMR spectra of (a) CpSSQ$(OH)_3$ and (b) nanocomposite CpSSQ$(OH)_3$ – ENR-50 with catalyst $SnCl_2.2H_2O$.

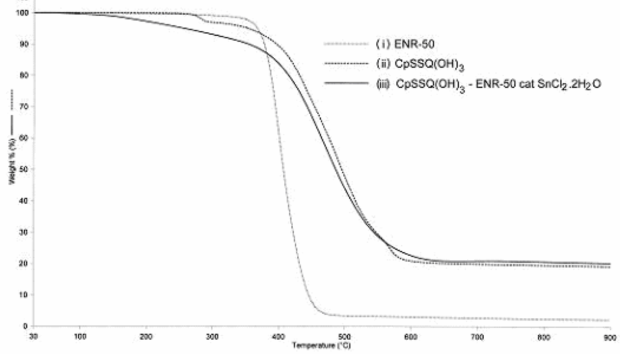
The ^{29}Si NMR spectrum of the resultant nanocomposite recorded a change in silanol Si_b chemical shift to δ -118, Fig 4b. It was due to the formation of a silanoxy Si-O-C bond [32] between the silanol of $CpSSQ(OH)_3$ and the oxirane of ENR-50. A difference in chemical shift in range of 10 to 12 ppm strongly suggest that the environment of Si_b silicon has changed [4]. While the peak of Si_c silicon positioned at δ -99 ppm remained unchanged because of these Si_c silicons are undisturbed and are not reactive toward oxirane ring of ENR-50.

Thermal characteristics

Fig 5 showed the respective TGA and DTGA thermograms of ENR-50, $CpSSQ(OH)_3$ and the nanocomposite. Decomposition of ENR-50 occurred in a single step at temperature range of 388 °C to 500 °C, Fig 5a(i). Pyrolysis of ENR-50 involved the breakdown of the main and side chain and also depolymerization [33]. The 10% weight loss of ENR-50 occurred at 393 °C. While the peak of maximum weight loss appeared at 416 °C, Fig 5b(i). The residue left was 2.4%. While $CpSSQ(OH)_3$ displayed multistages decomposition [34] over temperature range of 238 – 600 °C, Figure 5b(ii). The onset temperature occurred at 238 °C and the 10% weight loss take place at the same temperature as ENR-50 i.e. at 393 °C, Fig 5a(ii). The first stage of decomposition involved the evaporation of water as shown by maximum weight loss at 280 °C. While the second stage of decomposition at 441 °C only partial decomposition of cyclopentyl group occur. The remainder of cyclopentyl decomposed simultaneously with Si-O-Si cage rearrangement at 493 °C [34, 35]. The residue left was 19.2%. The thermal decomposition of composite obtained displayed thermal degradation over a range of 180 to 650 °C with 10% weight loss after elimination of trace water occurred at 373 °C, Fig 5a(iii). The residual water was originally from the catalyst used. A decrease in degradation temperature and the 10% weight loss was due to a good mixing of the composite producing a strong interaction between the ENR-50 matrix and the $CpSSQ(OH)_3$. The composite inherits the thermal stability of both the matrix and the filler. A broad degradation curve with maximum peak at 300 - 550 °C was refers to the pyrolysis of ENR-50, cyclopentyl group and tin chloride that occurred in distinguishable stages [36, 37]. This was followed by Si-O-Si cage rearrangement at 473 °C, Fig 5b(iii). The percentage residue increased arising from amount of hydrocarbon from both entities as well as the catalyst used.

The DSC analysis was carried out to study the glass transition temperature (T_g) of the composite obtained and comparison with that of the $CpSSQ(OH)_3$ and ENR-50 was made. From Fig 6(c), the composite displayed a single T_g at 0.4 °C. This value is lower than the T_g of $CpSSQ(OH)_3$ but higher than the T_g of ENR-50. However, the enthalpy value for the composite obtained is 0.07 J g^{-1} °C^{-1} and was almost the same as of $CpSSQ(OH)_3$ but is less when compared to the ENR-50 which is 0.50 J g^{-1} °C^{-1}, Fig 6. Therefore DSC study further established the formation of the silanoxy (Si-O-C) bond. The presence of tin (II) catalyst in the $CpSSQ(OH)_3$-ENR-50 composite has produced a new hybrid material as represented by a new single T_g value [38, 39].

(5a) TGA thermograms



(5b) DTGA thermograms

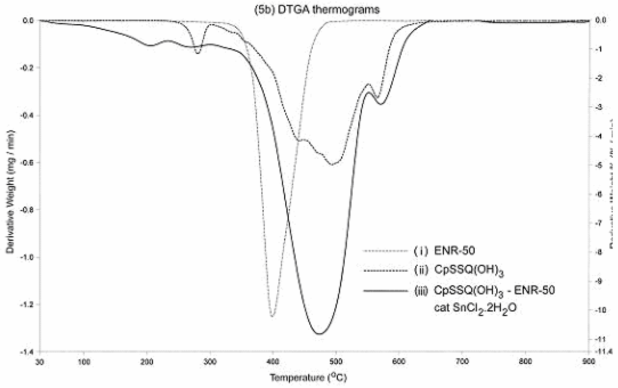


Fig 5. (a) TGA and (b) DTGA thermograms of (i) ENR-50, (ii) $CpSSQ(OH)_3$ and (iii) nanocomposite $CpSSQ(OH)_3$ – ENR-50 with catalyst $SnCl_2.2H_2O$.

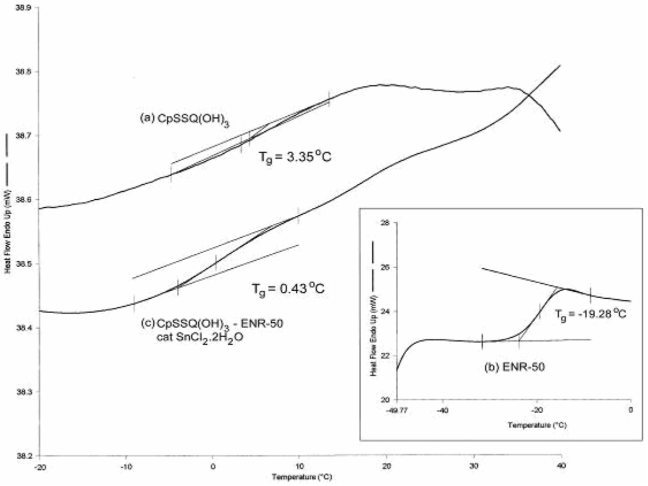


Fig 6. DSC thermograms of (a) $CpSSQ(OH)_3$, (b) ENR-50 and (c) nanocomposite $CpSSQ(OH)_3$ – ENR-50 with catalyst $SnCl_2.2H_2O$.

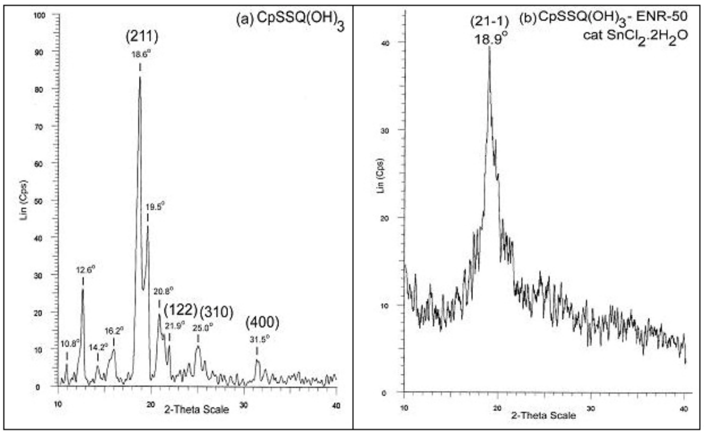


Fig 7. XRD diffractograms of (a) $CpSSQ(OH)_3$ and (b) nanocomposite $CpSSQ(OH)_3$ – ENR-50 with catalyst $SnCl_2.2H_2O$.

X-Ray Diffraction

Fig 7(a) showed powder XRD diffractogram of $CpSSQ(OH)_3$ exhibiting ten peaks at 2θ of 10.8, 12.6, 14.2, 16.2, 18.6, 19.5, 20.8, 21.9, 25.0 and 31.5°. The peaks at 2θ of 18.6°, 21.9°, 25.0° and 31.5° correspond to the Miller indices of (211), (122), (310) and (400) respectively [40]. Most of –$[Si_7O_9]$- cage frameworks with three silanol functionalities exist in the crystal structure of β-crystobalite or β-trydinamite [3]. XRD powder analyses of $CpSSQ(OH)_3$ is more useful to extend data collection of composite than single X-ray. This limitation is due to amorphous characteristic of ENR-50. XRD diffractogram of the composite obtained showed a broad single peak at 2θ of 18.9° and indicate Miller of (21-1), Fig 7(b). The incorporation of ENR-50 as the matrix was shown by the broad peak [41, 42] of the halo-amorphous of ENR-50 at 2θ range of 15 – 22°.

CONCLUSION

In conclusion, preparation of nanocomposite from $CpSSQ(OH)_3$ and ENR-50 was successfully carried out via chemical reaction at reflux temperature with addition of $SnCl_2.2H_2O$ through the reaction between the silanol group of $CpSSQ(OH)_3$ and epoxide ring opening of ENR-50. The approach provides way of functionalizing $CpSSQ(OH)_3$ with convenient one step methodology. The ^{1}H NMR, ^{29}Si NMR. TGA, DSC and XRD analysis of the nanocomposite further confirmed the properties of the interactive blend obtained.

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