Epoxidized natural rubber/silane modified silica nanocomposites prepared in latex stage

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Abstract

   Epoxidized natural rubber (ENR) was synthesized from natural rubber (NR) latex via *in situ* epoxidation using HCOOH and H_2O_2. The prepared ENR with 22 mol% epoxidation (ENR-22) was reinforced with silane modified silica (SMS) nanoparticles with different SMS loading in latex stage. The tensile properties, thermal stability, oil resistance and morphology of the ENR-22/SMS nanocomposites were investigated. The tensile strength was improved significantly and gained the maximum point at 7.5 phr SMS content. The thermogravimetric analysis showed an increased initial degradation temperature with the addition of SMS, suggesting higher thermal stability of the nanocomposites. The oil resistance of ENR-22/SMS nanocomposites in IRM 901 oil and IRM 903 oil were increased with the increasing amount of SMS content, indicating having improved oil resistance. The morphology revealed that the dispersions of SMS have been significantly improved since most of the spherical clusters of nanoparticles were individually scattered among the ENR matrix.

1. Introduction

   Natural rubber (NR) exhibits excellent properties such as high mechanical strength, excellent resilience and elasticity, high abrasion resistance, and low heat build-up, which is suitable for various products, e.g., tires, gloves, condoms, balloons, etc [1-2]. However, the use of NR products is limited due to its low stability to oxygen, sunlight, etc. It is also sensitive to most hydrocarbon/hydrophobic solvents including oils mainly due to its unsaturated hydrocarbon chain structure and its non-polar character. These cause limitations in a variety of NR applications. In addition, it is difficult to naturally degrade because of having high molecular weight [3].

   Epoxidation is one of simple and effective methods to increase the polarity of NR. The NR can be chemically modified from *cis*-1,4-polyisoprene rubber into epoxidized natural rubber (ENR), whereby some of the C=C bonds in NR are randomly converted into epoxide groups along the molecular chains [4-9]. As the level of epoxidation in ENR is increased, the NR chain polarity and glass-transition temperature (T_g) is increased [10]. The epoxidation process reduces gas permeability [11]. It also improves the oil and solvent resistance of NR [4-5]. Besides, the weak properties of ENR have been improved by blending with biopolymer such as cellulose [12,13], chitosan [9,14], etc. or reinforcing with inorganic materials such as silica [15-17].

   Incorporation of suitable reinforcing fillers could enhance the phase compatibility of polar/non-polar materials resulting in better properties of the composites. Silica commonly shows hydrophilic property. As in our previous work [18], the polarity of silica nanoparticles was reduced by the introduction of 3-methacryloxypropyltrimethoxy silane onto the silica surface to obtain the fillers having both polar and non polar properties which is similar to that of ENR. Therefore, the present work aims to prepare ENR/silane-modified silica (SMS) nanocomposites by firstly modifying the NR to ENR via epoxidation, then incorporating the SMS into the ENR latex. The chemical structure of ENR was revealed by Fourier transform infrared (FT-IR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. The in-house prepared ENR was reinforced with various amounts of the SMS nanoparticles in latex stage. The effect of SMS content was investigated in this work. The mechanical strength, thermal stability, oil resistance and morphology of the ENR/SMS nanocomposites were investigated.

2. Experimental

2.1 Materials

   High ammonia concentrated NR with 60% dry rubber content (DRC), sulfur (S), zinc oxide (ZnO), zinc diethyldithiocarbamate (ZDEC), zinc 2-mercaptobenzothiazole (ZMBT), Wingstay-L, titanium dioxide (TiO_2), potassium hydroxide (KOH), Terric 16A-16 were supplied by the Rubber Authority of Thailand. Formic acid (HCOOH), hydrogen peroxide (H_2O_2) and Terric 320 were purchased from Sigma-Aldrich Co., Ltd (Thailand). IRM 901 oil and IRM 903 oil were purchased from Chemical Innovation Co., Ltd (Thailand).

   SMS nanoparticles were prepared from silica nanoparticles and Silane A174 (Sigma-Aldrich Co., Ltd.) and characterized as reported
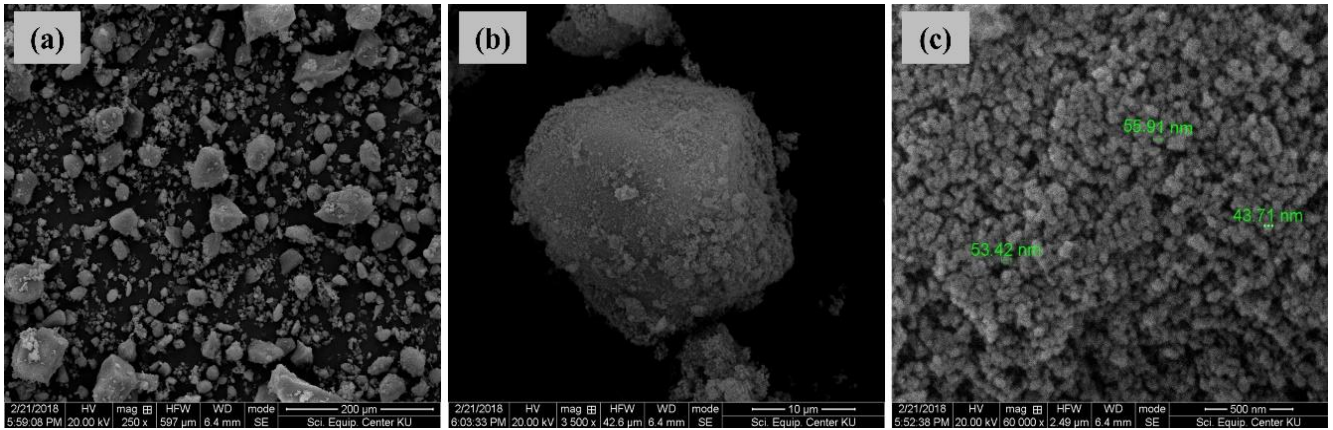
Figure 1. SEM photographs of SMS nanoparticle cluster with magnification of (a) 250x (b) 3,500x, and (c) 60,000x.

in our previous work [18]. The scanning electron micrographs of SMS nanoparticle cluster are depicted in Figure 1. The cluster size is various as shown in Figure 1(a). With the magnification of 3,500 in SEM photograph shown in Figure 1(b), it reveals the size of a 30-μm cluster. Each cluster contains numerous SMS nanoparticles with the size around 50 nm as shown in Figure 1(c).

2.2 Methods

2.2.1 Preparation of ENR

ENR was prepared from NR latex via *in situ* epoxidation using HCOOH and H_2O_2. The NR latex (60% DRC) was first diluted with distilled water to obtain 20% DRC latex. It was stabilized with 15% Terric 320 at 5 wt% of dry rubber content under stirring for 30 min at room temperature to eliminate ammonia. The mixture was heated to 50°C. The assigned amounts of HCOOH and H_2O_2 were added into the stabilized NR latex according to the formulation in Table 1. The 90% w/w HCOOH was first gently dropped into the latex for 60 min,

and then 30% w/w H_2O_2 was then added drop by drop for another 60 min. The reaction was allowed to stir at 50°C for 4 h. To characterize the prepared ENR, the obtained ENR latex was coagulated in 95% v/v methanol, washed with distilled water and soaked in 5% w/v sodium carbonate solution for 18 h to get rid of the remaining acid. It was then washed again until neutral, pressed into thin sheet and dried at 60°C for 48 h.

2.2.2 Preparation of ENR/SMS nanocomposites

ENR/SMS nanocomposites were compounded in latex stage using a mechanical stirrer with various chemicals, according to the amount shown in Table 2. Each ingredient was added one by one followed by stirring for 1.50 min in each addition. Once the SMS was added, the mixture was stirred for 30 min to obtain the homogenization and incubated at room temperature for 72 h. The mixtures were made into sheets by plate-casting. The rubber sheets were allowed to dry for a day and oven-baked at 100°C for 20 min to obtain dried composite sheets.

Table 1. Chemical composition in mole ratio used for the preparation of ENR.

Chemicals	Formula								
	1	2	3	4	5	6	7	8	9
NR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
HCOOH	0.25	0.25	0.25	0.50	0.50	0.50	0.75	0.75	0.75
H_2O_2	0.25	0.50	0.75	0.25	0.50	0.75	0.25	0.50	0.75

Table 2. Formulation of the rubber compound and composite.

Ingredients	Amount (phr)
20% ENR latex	100.0
10% KOH	0.6
10% Teric 16A-16	0.1
50% Sulfur	2.4
50% ZDEC	1.2
50% ZMBT	1.2
50% Wingstay L	3.0
50% TiO_2	3.0
50% ZnO	3.0
10% SMS	0, 1.0, 2.5, 5.0, 7.5, 10.0

2.3 Characterization and testing

2.3.1 Fourier transform infrared spectroscopy (FT-IR)

The prepared ENRs were characterized for their mol% epoxidation using Fourier transform infrared spectroscopy (FT-IR) over a frequency range of 650 cm^{-1} to 4,000 cm^{-1} (Perkin Elmer: spectrum 100, Waltham, USA). The mol% epoxidation was calculated from Equation (1) in according to Davey and Loadman where A_{870} and A_{835} are areas under the characteristic FT-IR peaks at 870 and 835 cm^{-1}, respectively [19].

$$Mol\% \; epoxidation = \frac{A_{870}}{A_{870}+A_{835}} \times 100 \qquad (1)$$

2.3.2 Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy

The obtained ENRs were also confirmed their structures using proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy (Bruker DPX-400, USA). Deuterated chloroform was used as NMR solvent.

2.3.3 Mechanical properties determination

The tensile test was performed on ten pieces of dumbbell specimens according to ASTM D412 using a universal testing machine (Instron, USA). The properties such as tensile strength, modulus at 100% strain and elongation at break were analyzed.

2.3.4 Thermogravimetric analysis (TGA)

The thermal stability was determined by thermogravimetric analysis (TGA) using a Mettler Toledo TGA/SDTA 851e analyzer. The analysis was performed under a nitrogen atmosphere over a temperature range of 30°C to 800°C at a heating rate of 20°C·min^{-1}.

2.3.5 Oil resistance

The oil resistance was determined by the measurement of volume change. The samples were immersed into ASTM oil No. 1 (IRM 901 oil) and ASTM oil No. 3 (IRM 903 oil) at 100°C for 70 h according to ASTM D471. The volume change was calculated from Equation (2) where m_1 and m_2 are the initial mass (g) of the sample in air and distilled water, respectively. The m_3 and m_4 are the mass (g) of sample in air and distilled water after immersion, respectively.

$$Volume\ change = \frac{(m_3 - m_4) - (m_1 - m_2)}{(m_1 - m_2)} \quad (2)$$

2.3.6 Morphology

The morphology of the tensile fractured surface of the sample was observed by scanning electron microscopy (ThermoFisher Scientific: Model Quanta 450, FEI, USA) with a magnification of 20,000. The samples were sputtered with gold prior examination to improve the surface conductivity.

3. Results and discussion

3.1 FT-IR analysis of ENR

The FT-IR spectra of NR and ENR with different mol% epoxidation are shown in Figure 2. The characteristic peaks of NR as shown in Figure 2(a) appeared at 2960, 2925, 2860, 1660, 1450, 1375 and 835 cm^{-1} are assigned to the –CH$_3$ stretching, -CH$_2$- asymmetric stretching, -CH$_2$- symmetric stretching, C=C stretching, -CH$_2$- deformation, C-H deformation and C=C bending, respectively. As the epoxidation took place, the double bonds in NR molecules were randomly converted into epoxide groups, resulting in the decrease in the peaks at 1660 cm^{-1} and 835 cm^{-1}. New characteristic peaks at 1240 cm^{-1} and 870 cm^{-1} increased correspondingly as the mol% epoxidation increased, attributed to the symmetric stretching and asymmetric stretching of epoxide (C-O-C) ring, respectively [20] as appeared on the spectra of ENR

shown in Figure 2(b-d). This confirmed the formation of epoxide rings generated *in situ* from the reaction of HCOOH and H$_2$O$_2$ with the C=C bonds on the NR backbones.

The mol% epoxidation of the prepared ENRs was calculated using Equation (1) and listed in Table 3. It was in the range of 6 mol% to 45 mol%. The results showed that the mol% epoxidation increased with either HCOOH or H$_2$O$_2$ content. It is known that ENR with lower mol% epoxidation provides lower oil resistance, but higher resilience and elasticity than the one with higher mol% epoxidation [4,5,21]. The ENR with medium mol% epoxidation, prepared from 1.00 mol NR, 0.50 mol HCOOH and 0.75 mol H$_2$O$_2$ (Formula 6), was chosen to prepared ENR/SMS nanocomposites with different SMS loading. Consequently, this ENR with mol% epoxidation of 22% was denoted as ENR-22.

3.2 ^{1}H-NMR spectroscopy of ENR

The structural study of NR and ENR was also carried out using ^{1}H-NMR spectroscopy technique (Figure 3). In the ^{1}H-NMR spectrum, the peaks at δ 1.70 (-CH$_3$; *a*), 2.08 (-CH$_2$; *b*) and 5.15 (=CH-; *c*) were the characteristic peaks of NR. The successful epoxidation was confirmed as seen from new peaks at δ 1.28 (-CH$_3$; *d*), 1.57 and 2.18 (-CH$_2$-; *e*) and 2.70 ppm (-CH-; *f*) shown in Figure 3(b).
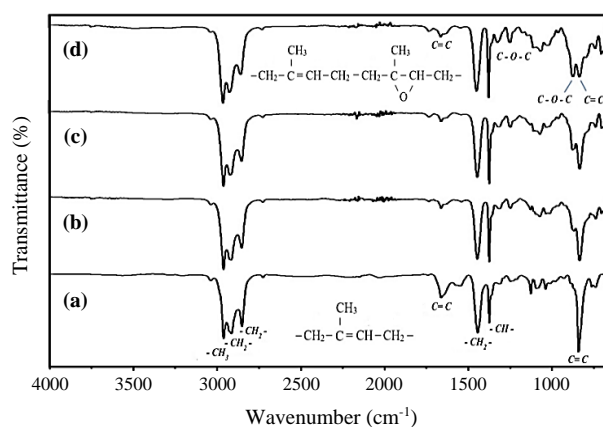
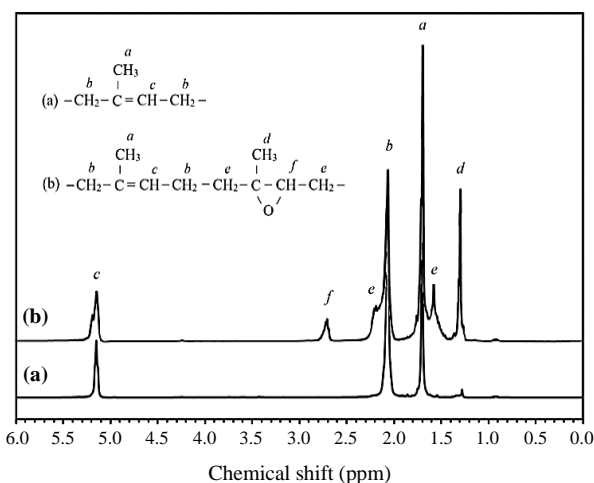**Figure 2**. FT-IR spectra of the (a) NR, (b) ENR-15, (c) ENR-22, and (d) ENR-45.

Figure 3. ^{1}H-NMR spectra of the (a) NR and (b) ENR-22.

Table 3. Mol% epoxidation of the prepared ENR.

Character	Formula								
	1	2	3	4	5	6	7	8	9
Mol% Epoxidation	6	10	15	8	18	22	15	36	45

3.3 Mechanical properties of ENR/SMS nanocomposites

The mechanical properties in terms of tensile strength, elongation at break and modulus at 100% strain of ENR-22 and its composites are illustrated in Figure 4. In Figure 4(a), the tensile strength of SMS-filled ENR-22 was improved significantly and gradually increased with increasing filler loading. It reached the maximum point when SMS was added at 7.5 phr. The better reinforcement efficiency may be attributed to intermolecular attraction between ENR-22 and SMS particles. The smaller nanoparticle size of SMS provides a larger surface area for the interaction between the rubber matrix and its reinforcing filler. Figure 4(b) shows that the elongation at break was lower than that of the neat ENR-22 and decreased with increasing SMS content. The modulus at 100% elongation increases with increasing SMS loading. These may be attributed to the higher crosslink density and good distribution of SMS in ENR matrices.

3.4 Thermal stability

TGA was used to evaluate the thermal stability of ENR-22 and its composites. The degradation behaviors of SMS, ENR-22 and ENR-22 reinforced with SMS (7.5 phr) nanocomposite are shown in Figure 5, while the values of T_{onset}, $T_{end\,set}$ and T_{max} are summarized in Table 4. The TGA curves of ENR-22 and ENR-22/SMS (7.5) nanocomposite showed a similar degradation characteristic. This indicated that the addition of SMS did not change the degradation mechanism of the ENR-22, whereas the degradation temperatures were affected. As it can be observed from Table 4, all the nanocomposites exhibited the increases in T_{onset}, $T_{end\,set}$ and T_{max} with increasing SMS content compared to that of the neat ENR-22. This indicated from the increasing of T_{onset} that SMS could delay the initial degradation of ENR-22. $T_{end\,set}$ and T_{max} were all shifted to the higher temperatures with the addition of SMS, suggesting the higher interaction between the ENR-22 and SMS at higher temperature and so increased the thermal stability of the nanocomposites.

3.5 Oil resistance

Figure 6 shows the change in volume of ENR-22 and ENR-22/SMS nanocomposites after being immersed in IRM 901 oil and IRM 903 oil at 100°C for 70 h. As the IRM 901 oil is lower polar hydrocarbon oil, the IRM 903 oil is a higher polar one. Percentage volume change in IRM 901 oil of all samples was lower than that in IRM 903 oil, indicating that ENR-22 exhibited a polar character. Swelling of ENRs in oils was substantially less than that of NR since epoxidation has brought about substantial improvement in oil resistance. The swelling levels of ENR-22/SMS nanocomposites in both types of oil were decreased when the amount of SMS content was increased, indicating superior oil resistance. This might be because ENR and SMS contain both polar and non-polar parts in the molecules, resulting in better molecular interaction between the two. On the other hand, the interaction between ENR and SMS chains promotes the formation of rubber-filler network, which can help the distribution of SMS and resist the swelling of rubber in oil. Therefore, the addition of SMS into ENR-22 not only improved the mechanical properties of the composites but also enhanced the oil resistance of these nanocomposites.
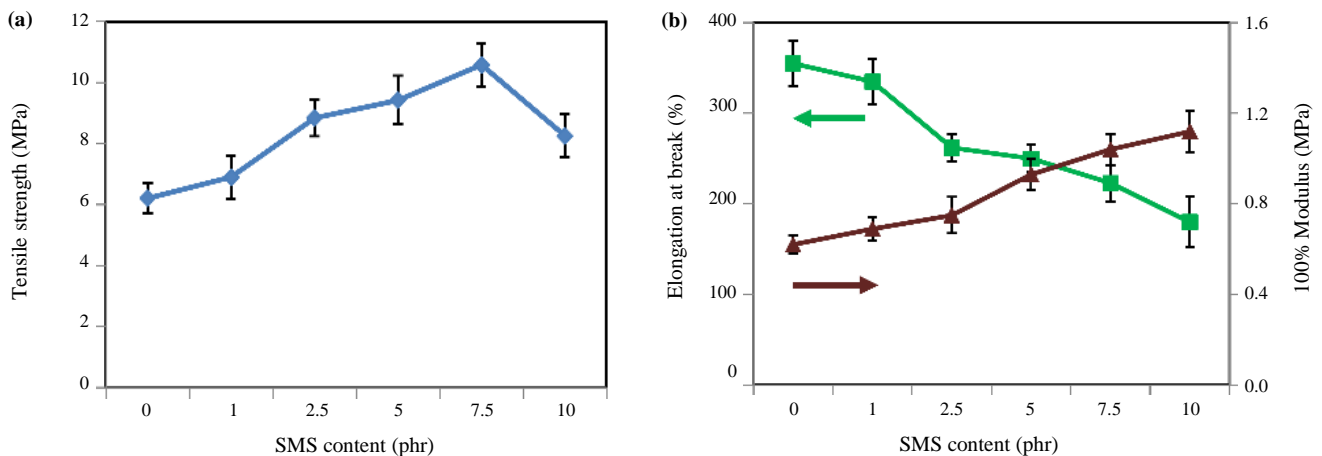

Figure 4. The (a) tensile strength and (b) elongation at break and modulus at 100% strain of the ENR-22 and ENR-22/SMS nanocomposites.

Table 4. TGA data of the ENR-22 and ENR-22/SMS nanocomposites.

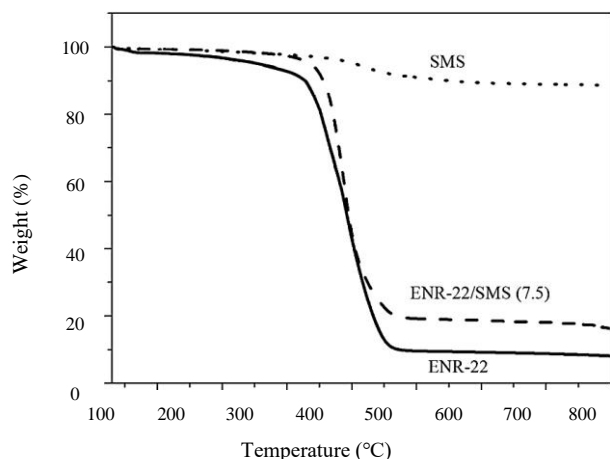| SMS contents (phr)	T_{onset} (°C)	$T_{end\,set}$ (°C)	T_{max} (°C)
0.0	360	416	386
1.0	362	425	388
2.5	366	431	390
5.0	368	434	394
7.5	370	439	397
10.0	371	440	400

Figure 5. TGA thermograms of SMS, ENR-22 and ENR-22 reinforced with SMS (7.5 phr) nanocomposite.

3.6 Morphology

To investigate the morphology of the nanocomposites, SEM was employed to view the tensile fractured surface of the samples. The SEM images of the composites reinforced with nanosilica are shown in Figure 7. Compared with the SEM image of NR/unmodified silica nanocomposite shown in Figure 7(a), the SMS nanoparticles were scattered uniformly throughout the composites as shown in Figure 7(b) and (c). The dispersions of SMS have been significantly improved since most of the spherical clusters of nanoparticles were individually scattered among the ENR matrix. This is in agreement with the results of tensile strength and 100% modulus. It may be due to the good interfacial bonding between ENR-22 and SMS as aforementioned.
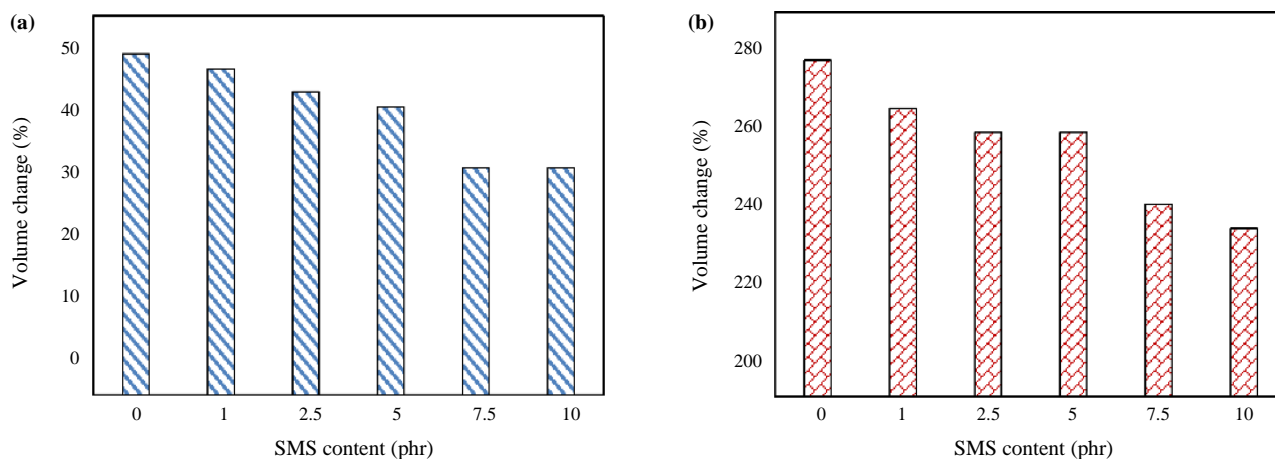

Figure 6. The change in volume of ENR-22 and ENR-22/SMS nanocomposites in (a) IRM 901 oil and (b) IRM 903 oil.
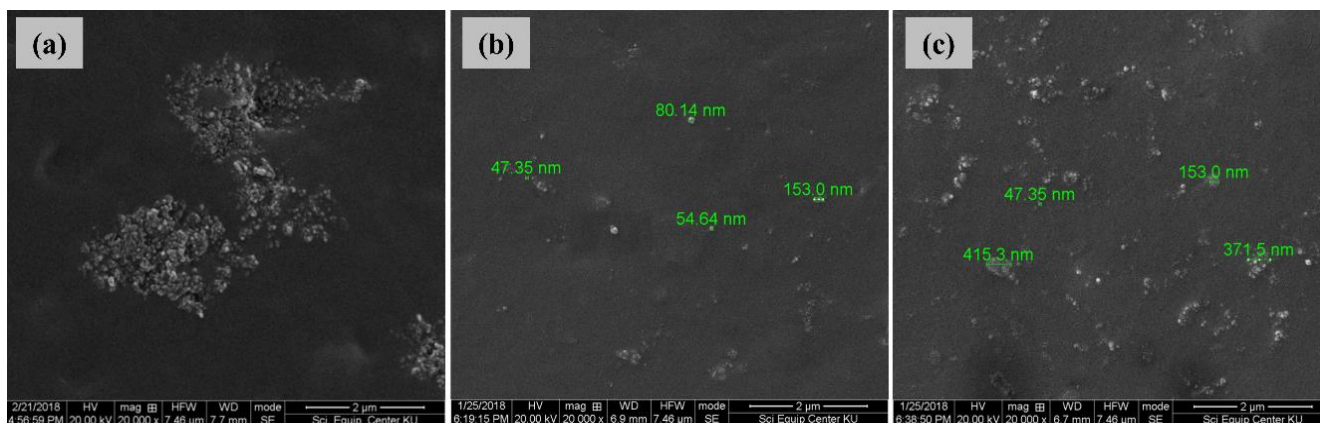

Figure 7. SEM photographs (20,000 × magnification) of the (a) NR reinforced with unmodified silica (7.5 phr), (b) ENR-22 reinforced with SMS (2.5 phr), and (c) ENR-22 reinforced with SMS (7.5 phr).

4. Conclusions

Epoxidized natural rubber with 22 mol% epoxidation (ENR-22) was successfully prepared from 1 mol concentrated natural rubber latex via *in situ* epoxidation using 0.50 mol formic acid and 0.75 mol hydrogen peroxide in the presence of Terric 320 at 50°C for 4 h. The structural study of ENR was carried out using FTIR and ^{1}H-NMR spectroscopy techniques and the mol% epoxidation was calculated using the data from FT-IR analysis. Silane modified silica (SMS) nanoparticle was used as a reinforcing filler into the prepared ENR-22

at different SMS content (0 phr to 10 phr). The ENR-22/SMS nano-composites were compounded in latex stage and plate-casted into sheets. As the amounts of SMS in the composites increased, tensile strength and modulus at 100% strain were increased, while the elongation at break was decreased. It should be noted that the tensile strength was gained the maximum point at 7.5 phr SMS content. The values of T_{onset}, $T_{end\ set}$ and T_{max} from the thermal analysis of the nanocomposites containing SMS were increased. The dispersions of SMS revealed by SEM technique have been significantly improved since most of the spherical clusters of nanoparticles were individually scattered among the ENR matrix. Furthermore, the oil resistance of ENR-22/SMS nanocomposites in IRM 901 oil and IRM 903 oil were increased with the increasing amount of SMS content, indicating superior oil resistance.

Acknowledgements

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