

# PHYSICAL PROPERTIES AND OIL RESISTANCE OF EPOXIDIZED NATURAL RUBBER/CARBON NANOTUBE NANOCOMPOSITES PREPARED VIA IN SITU EPOXIDATION

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**Abstract-** In this study, epoxidized natural rubber (ENR) was prepared via in situ epoxidation of NR in the latex state using different molar ratios of hydrogen peroxide ( $H_2O_2$ ):formic acid to isoprene unit at 50°C for 4, 6 and 8 h to gain different epoxide levels. ENR with 30 mole% epoxidation referred to as ENR30 was obtained using a molar ratio of  $H_2O_2$ :formic acid of 0.75:0.75 at 50°C for 4 h. Consequently, ENR30/carbon nanotube (CNT) nanocomposites were also prepared using a latex-based process by incorporating five loadings of CNTs (0.5, 1, 1.5, 2 and 2.5 phr) in NR latex and was then followed by in situ epoxidation of NR. The cure time ( $t_{90}$ ), tensile properties (tensile strength, elongation at break and modulus at 300% strain (M300)), glass transition temperature ( $T_g$ ), thermal stability and oil resistance of the nanocomposites were investigated and compared with NR and ENR30. The results showed that the  $t_{90}$  of ENR30/CNT nanocomposites was the longest followed by NR and ENR30. The incorporation of CNTs could increase the tensile strength, M300,  $T_g$ , thermal stability and oil resistance but decrease the elongation at break of the nanocomposites. Among them, the nanocomposite containing 2 phr CNTs exhibited the highest tensile strength, M300,  $T_g$ , thermal stability and oil resistance compared to the NR and ENR30. However, the elongation at break of ENR30 (673.8%) and the ENR30/CNT nanocomposites (591.2–695.3%) was still rather high when compared to that of NR (726.6%). Thus, the CNTs reinforced ENR30 vulcanizates were soft nanocomposites.

**Keywords-** Epoxidized Natural Rubber, Carbon Nanotubes, In situ Epoxidation, Oil Resistance, Nanocomposites.

## I. INTRODUCTION

Natural rubber (NR), a renewable polymeric material, possesses many interesting properties including low cost, low heat build-up, high elasticity and resilience, good formability and high mechanical properties [1–3]. It is well established that NR has high tensile and tear strength owing to its capability to undergo strain crystallization [2]. However, NR has poor oil, ozone and chemical resistance according to its unsaturation hydrocarbon structure and non-polar nature, which limit its applications [1,4]. The introduction of polar group such as epoxide group onto NR backbone is one of the approaches to overcome these drawbacks [4–6]. The epoxidation of NR is a popular chemical modification that can be performed in latex state via in situ epoxidation to gain different epoxide levels, depending on the peracid type and content, reaction time and temperature. Thus, a specific level of epoxidation can be obtained under controlled conditions by converting the double bond (C=C) of NR into epoxide groups to form an epoxidized natural rubber (ENR) [7,8]. Owing to its polarity, ENR exhibited higher oil resistance, gas impermeability, adhesiveness, glass transition temperature ( $T_g$ ) and solubility parameter as the degree of epoxidation is increased when compared to those of the NR [9,10]. Recently, two grades of ENR are commercially available, which have a 25 and 50 mole% epoxidation (ENR25 and ENR50, respectively). Generally, ENR with < 50 mole% epoxide is an elastomer, while those with > 50 mole% epoxidation are harder with a lower resilience and elasticity [11]. Moreover, ENR can be vulcanized in a usual manner as NR using sulfur in

the presence of an accelerator and activator [2,10]. However, the rubbers generally require particular fillers to gain the desired properties as well as to make more suitable rubber compounds of specific use for a variety of applications. Since ENR has a high potential to be used as a matrix for various types of fillers, and so both ENR conventional composites and nanocomposites have been explored [12–14]. This work focused on the use of carbon nanotubes (CNTs) as a nano-filler for the ENR due to their superior properties, such as a very high aspect ratio (up to  $10^4$ ) (Fig. 1), specific surface area, modulus (~103 GPa) and tensile strength (~50 GPa) with a low density (~1.3 g/cm<sup>3</sup>) [15]. In this study, ENR30/CNT nanocomposites were prepared by dispersing various loadings of CNTs (0.5–2.5 parts per hundred parts of rubber, phr) in NR followed by in situ performic acid epoxidation of NR. Their mechanical, thermal and dynamic mechanical properties, as well as their oil resistance, were investigated and compared.

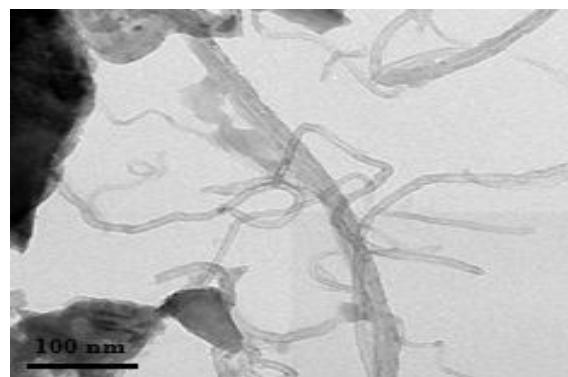


Fig.1. Representative TEM Image of CNTs.

## II. DETAILS EXPERIMENTAL

### 2.1. Materials and Procedures

Concentrated NR latex with a 60% dry rubber content (DRC), polyalcohol ethyleneoxide condensate (Terric 16A- 16), zinc oxide (ZnO), stearic acid, sulfur, n-cyclohexyl-2-benzothiazyl sulphenamide (CBS), voltamol and bentonite were obtained from the Rubber Research Institute of Thailand. Formic acid (98%) and H<sub>2</sub>O<sub>2</sub> (30%) were purchased from Asian Scientific Co. CNTs were supplied by EM-Power Co. Sodium carbonate was from Merck Thailand Co., methanol from RCI Lab Scan Co. and ASTM oil No.1 was from Chemical Innovation Co. All materials were used as supplied without further purification.

### 2.2. Preparation and Characterization of ENR

The ENRs were prepared via in situ epoxidation of NR in the latex state by performic acid generated from the reaction between formic acid and H<sub>2</sub>O<sub>2</sub>. Before epoxidation, NR latex was diluted with distilled water to reduce the dry rubber content from 60% to 20 % DRC and then stabilized with the non-ionic surfactant Terric 16A-16 (3 phr) at room temperature under stirring for 1 h. The assigned amounts of formic acid (0.5, 0.75 and 1 M of isoprene unit) and H<sub>2</sub>O<sub>2</sub> (0.5, 0.75 and 1 M of isoprene unit) were then added to the stabilized NR latex. Formic acid was fed drop by drop into the NR latex within 10–15 min at 40°C, followed by raising the temperature to 50°C within 15 min prior to adding the H<sub>2</sub>O<sub>2</sub> over 5–10 min with continuous stirring. The reaction was allowed to proceed at 50°C for 4, 6 and 8 h. The obtained product was coagulated in the excess 95% (v/v) methanol, filtered, washed well with distilled water, soaked in 5% (w/v) sodium carbonate solution for 5–10 min, washed again until neutral, and pressed into a thin sheet (1.5–2 mm) and dried at 60°C for 48 h until at a constant weight. The prepared ENR was characterized for the mole% epoxidation using Fourier transform infrared spectroscopy (FT-IR) on a Nicolet 6700-FT-IR spectrometer over a frequency range of 400–4000 cm<sup>-1</sup> and by proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR) using a Bruker spectrometer (Advanced 300). The mole% epoxidation was calculated from Eq. (1) using data obtained from the characteristic FT-IR peaks at 870 and 835 cm<sup>-1</sup> as reported [13];

$$\text{Mole\% epoxidation} = [A_{870}/(A_{870} + A_{835})] \times 100, \quad (1)$$

where A<sub>870</sub> and A<sub>835</sub> are the absorbance at wavenumber 870 and 835 cm<sup>-1</sup>, respectively.

To determine the mole% epoxidation from the <sup>1</sup>H-NMR analyses, two characteristic peaks were considered in relation with Eq. (2) [13,15].

$$\text{Mole\% epoxidation} = [A_{2.7}/(A_{2.7} + A_{5.14})] \times 100, \quad (2)$$

where A<sub>2.7</sub> and A<sub>5.14</sub> are the integrated area under the <sup>1</sup>H-NMR peak at ~2.7 ppm (methine proton of the epoxide group) and ~5.14 ppm (olefinic proton of unreacted NR), respectively.

### 2.3. Preparation and Characterization of ENR/CNT Nanocomposites

The CNTs were first prepared in an aqueous dispersion at 2 wt% using Voltamol (2 wt%) and bentonite (1 wt%) as dispersant in distilled water by ball milling at 200 rpm for 72 h. The ENR/CNT nanocomposites were prepared by incorporating various loadings of CNTs (0.5, 1, 1.5, 2 and 2.5 phr) into NR latex and was then followed by in situ performic epoxidation of NR. The mole% epoxidation of ENR in the ENR/CNT nanocomposites were also characterized using FT-IR analysis. The obtained nanolatex was coagulated as described above.

### 2.4. Compounding, Cure Characterization and Vulcanization

The dry rubber was compounded with ZnO (5 phr), stearic acid (2 phr), CBS (1 phr) and sulfur (2 phr) in an internal mixer (MX500-D75L90) at 70°C for 9 min, and then sheeted on an open two-roll mill at room temperature for 3 min. The cure behaviors in terms of the scorch time (t<sub>s2</sub>) and cure time (t<sub>90</sub>) were determined using a moving die rheometer (MDR, A0225-rheo Tech MD) according to ASTM D2084. The cure rate index (CRI), which is a measure of the rate of the cure reaction, was then calculated from Eq. (3) [14],

$$\text{CRI} = 100/(t_{90} - t_{s2}) \quad (3)$$

The rubber compound was compressed and cured in a compression molding machine (LP-S-20, LabTech Engineering) at 130°C according to the t<sub>90</sub> obtained from the MDR.

### 2.5. Tensile Properties

The tensile test of the sample was measured according to ASTM D 412 using a universal testing machine (Techpro T-TS01) with a 1 kN load cell and at a cross-head speed of 500 mm/min on the dumbbell-shape sample. At least five specimens were tested for the tensile strength, modulus at 300% strain and elongation at break and the average values were reported.

### 2.6. Dynamic Mechanical Analysis

The dynamic mechanical analysis (DMA) of the sample was performed on a Mettler Toledo DMA/SDTA 861<sup>e</sup> instrument under a shear mode at a constant frequency of 1 Hz and a heating rate of 3°C/min over a temperature range of -60 to 80°C and under a nitrogen atmosphere.

### 2.7. Oil Resistance

The oil resistance was determined by measurement the percentage volume change of the sample after a 72 h immersion period in ASTM Oil No.1 at 100°C. Before immersion, the test specimen was weighed in both air and in distilled water at room temperature. After immersion, the test specimen was removed from the oil, cooled to room temperature by

transferring to a cool and clean test oil for about 30 min, and then dipped quickly in acetone at room temperature and wiped lightly with filter paper to remove the excess oil from the surface before weighing again in both air and distilled water. The percent change in volume was then calculated using Eq. (4) according to ASTM D471-79;

$\% \Delta V = [(M_3 - M_4) - (M_1 - M_2)] / (M_1 - M_2) \times 100$  (4)

where  $M_1$  and  $M_2$  are the initial mass (g) of the specimen in air and distilled water, respectively, and  $M_3$  and  $M_4$  are the mass (g) of the specimen in air and distilled water after immersion, respectively.

### III. RESULTS AND DISCUSSION

#### 3.1. FT-IR and $^1\text{H-NMR}$ Analysis of Epoxide Content

Representative FT-IR spectra of NR, ENR and ENR/CNT nanocomposites are shown in Fig. 2. The absorption bands of NR at 2860, 1650, 1450, 1375 and 835  $\text{cm}^{-1}$  in Fig. 2(a) are assigned to the C-H stretching, C=C stretching, -CH<sub>2</sub>- deformation, C-H deformation and =C-H deformation, respectively [9,13]. New absorption bands at 870 and 1240  $\text{cm}^{-1}$  in Fig. 2(b) are assigned to the asymmetric and symmetric stretching of the epoxide ring, respectively [13]. This confirmed the formation of oxirane ring (epoxide) from the reaction of performic acid (generated in situ by the reaction of formic acid and  $\text{H}_2\text{O}_2$ ) with the C=C bond on the NR molecules. By varying the  $\text{H}_2\text{O}_2$ :formic acid ratio and reaction time, the prepared ENRs possessed different epoxide contents as shown in Table 1. As can be seen, the level of epoxidation increased with increasing either formic acid or  $\text{H}_2\text{O}_2$  contents, as a consequence of the increasing performic acid content, and was in the range of 27.5–60.4 mole %. Moreover, the prolonged reaction time increased the reaction chance between performic acid and the C=C bond in the NR molecule to yield more epoxide groups. According to the mole% epoxidation, the ENR with medium epoxide content (~30 mole% epoxidation, ENR30) was then selected for preparing the ENR30/CNT nanocomposites to obtain the products with comparable resilience and elasticity to NR but a higher oil resistance. Therefore, the conditions for preparing the ENR30 (molar ratio of  $\text{H}_2\text{O}_2$ :formic acid to isoprene unit of 0.75: 0.75 at 50°C for 4 h) were also used to prepare the ENR30/CNT nanocomposites.

The absorption bands at 1240 and 870  $\text{cm}^{-1}$  of the ENR30/CNT nanocomposites (Fig. 2(c)) also confirmed the formation of epoxide rings via the in situ epoxidation in the presence of CNTs in NR latex. It was found that the mole % epoxidation of ENR in the nanocomposites was slightly higher than that in the neat ENR30 and was in the range of 33.6–34.2%. This may be due to the acidity of CNTs, since commercial CNTs usually possess carboxylic acid groups on their surfaces [16]. Moreover, FT-IR spectra of ENR30 and ENR30/CNT nanocomposites (Figs.

2(b) and 2(c)) did not exhibit carbonyl peak at 1716  $\text{cm}^{-1}$  and hydroxyl peak at 3430  $\text{cm}^{-1}$ , suggesting that there was no side reaction from ring-opening reaction of epoxide groups [13].

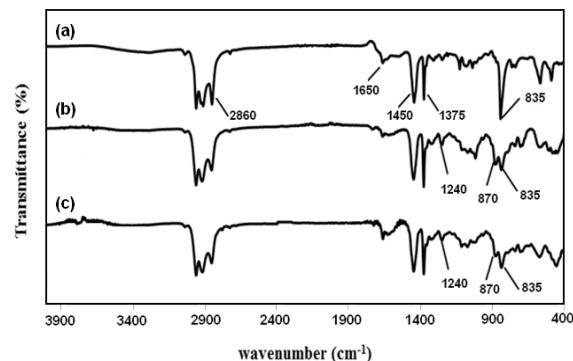


Fig.2. Representative FT-IR Spectra of (a) NR, (b) ENR and (c) ENR/CNT Nanocomposite.

Time (h)	Mole% epoxidation				
	$\text{H}_2\text{O}_2$ :formic acid				
	0.5:0.75	0.75:0.75	1:0.75	0.75:0.5	0.75:1
4	27.5	30.3	41.9	32.3	45.8
6	32.0	37.1	47.8	36.2	51.0
8	36.5	43.3	53.2	42.2	60.4

Table 1: Mole % Epoxidation of the Prepared ENR

The  $^1\text{H-NMR}$  spectrum of the prepared ENR sample shown in Fig. 3 revealed two peaks at about 2.7 ppm and 1.3 ppm, which represent the proton attached to the epoxide ring and the proton from a methyl group attached to epoxide ring, respectively, while the peak at about 5.14 ppm represented olefinic proton of unreacted NR [6,15]. The calculated mole% epoxidation of the prepared ENR (using Eq. (2) and the  $^1\text{H-NMR}$  data) was about 27.4%, and so are in accord with the successful preparation of ENR30.

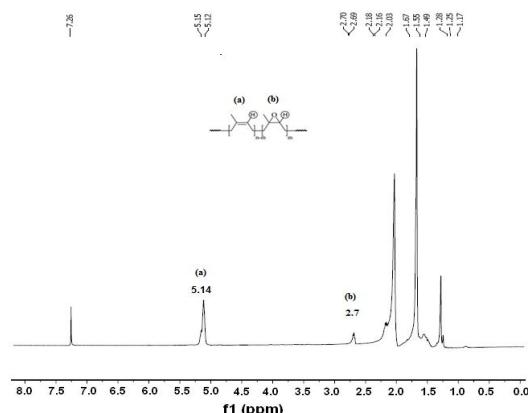


Fig.3. Representative  $^1\text{H-NMR}$  Spectrum of the ENR30 Sample.

#### 3.2. Cure Characteristics

The  $t_{s2}$ ,  $t_{90}$  and CRI of NR, ENR30 and ENR30/CNT nanocomposites are summarized in Table 2. The  $t_{s2}$  is a measure of premature vulcanization while  $t_{90}$  is the

optimum cure time of the vulcanizates. As can be seen, both  $t_{s2}$  and  $t_{90}$  of ENR30 exhibited a similar trend, which were shorter than of NR, according to the fact that the isolated double bonds react more rapidly than the continuous C=C bonds [8,17], and also the epoxide groups in ENR can activate the adjacent C=C bonds that make them more susceptible to vulcanize, and therefore, lower the  $t_{s2}$  and  $t_{90}$  [13,14], and as a consequence, the CRI of ENR30 was higher than that of NR, indicating that ENR30 had higher rate of curing than NR. However, the  $t_{s2}$  and  $t_{90}$  of ENR30/CNT nanocomposites increased with increasing CNTs content up to 2 phr. This is owing to the carboxyl groups on CNT surfaces have absorbed the basic accelerator, and thereby, delay the  $t_{s2}$  and  $t_{90}$  of the nanocomposites [14,17]. Thus, the CRI decreased with the addition of CNTs. When the CNTs were 2.5 phr, the decreased  $t_{s2}$  and  $t_{90}$  and the increased CRI were owing to the agglomeration of CNTs that lower the accelerator absorption.

**Table 2: Cure Characteristics of NR, ENR30 and ENR30/CNT Nanocomposites.**

Sample	$t_{s2}$ (min)	$t_{90}$ (min)	CRI (%·min <sup>-1</sup> )
NR	8.5	17.1	11.6
ENR30	8.1	16.0	12.7
<i>ENR30/CNT</i>			
100/0.5	8.7	17.2	11.8
100/1.0	9.7	18.4	11.5
100/1.5	10.2	19.0	11.4
100/2.0	10.5	19.5	11.1
100/2.5	9.5	17.5	12.5

### 3.3. Mechanical Properties

The tensile properties (tensile strength, elongation at break (EB) and modulus at 300% strain (M300)) of NR, ENR30 and ENR30/CNT nanocomposites are presented in Table 4. As can be seen, the tensile strength of NR was slightly higher than that of ENR30, because NR has higher capability to undergo strain-induced crystallization than ENR30. However, the tensile strength of nanocomposites at 0.5 and 1 phr CNTs was not improved compared to that of NR and ENR30, but rather was lower, which may be due to an insufficient level of CNT dispersion and uniform transmission of stress in the ENR30 matrix. As the CNT loadings were increased to 1.5 and 2 phr, the tensile strength increased up to a maximum value at 2 phr, suggesting a better CNT dispersion in the ENR30 matrix and also a better stress transfer at the interface of CNTs and ENR30, due to the very high specific area and aspect ratio of the CNTs that give rise to a higher interaction between the CNT and ENR30. At the highest CNTs loading of 2.5 phr, a remarkable decrease in the tensile strength was

observed. This may be due to the agglomeration of CNTs that restricted the strain-induced crystallization of ENR30 and allowed less stress transfer across each phase.

The EB value for all the ENR30 and ENR30/CNT nanocomposites was lower than that of NR. This is because of the polar nature of ENR30 that tightly held the ENR molecules and the high stiffness of CNTs that restricted the mobility of rubber chains and also reduced the EB of the vulcanizates. However, the EB of ENR30 (673.8%) and ENR30/CNT nanocomposites (591.2–695.3%) was still rather high when compared to that of NR (726.6%).

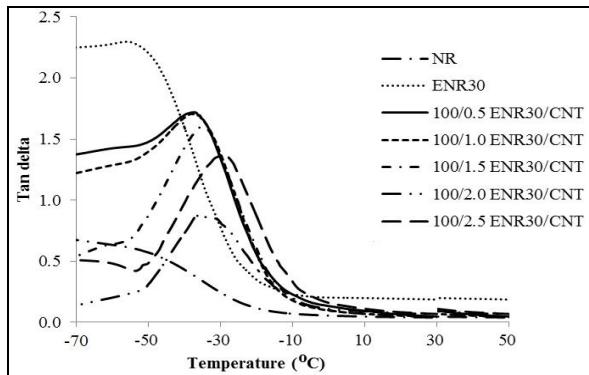
Moreover, the M300 of the ENR30 and ENR30/CNT nanocomposites were all higher than that of NR, which was attributed to the polar epoxide groups that tightly held the ENR30 molecules together, and also the higher stiffness of CNTs would reduce the mobility of the rubber chains and consequently increase the nanocomposite stiffness. However, the M300 of all the samples was rather low and was in the same range (1.8–2.4 MPa). Thus the CNTs reinforced ENR30 vulcanizates were soft nanocomposites.

### 3.4. Thermal Behaviors

The loss factor ( $\tan \delta$ ) as a function of temperature (from -60 to 80°C) for NR, ENR30 and ENR30/CNT nanocomposites are shown in Fig. 4. The temperature at the maximum  $\tan \delta$  peak was assigned to the glass transition temperature ( $T_g$ ) of the sample, and the derived  $T_g$  values are listed in Table 4. The  $T_g$  of ENR30 was higher than that of NR, owing to the epoxide groups in ENR30 that provided a stronger intermolecular attraction and so restricted the motion of segment chains. The incorporation of CNTs (0.5–2 phr) also caused a dose-dependent increase in  $T_g$  of these nanocomposites. This is due to the stiffness of CNTs that restricted the movement of rubber chains. However, at higher CNT loading of 2.5 phr the nanocomposites exhibited a slightly lower  $T_g$  than the ENR30/CNT nanocomposite with a 2 phr loading, owing to the agglomeration of CNT particles.

**Table 3: Tensile Properties of NR, ENR30 and ENR30/CNT Nanocomposites.**

Sample	Tensile strength (MPa)	EB (%)	M300 (MPa)
NR	24.0	726.6	1.8
ENR30	23.3	673.8	2.1
<i>ENR30/CNT</i>			
100/0.5	21.2	709.6	2.1
100/1.0	22.9	683.7	2.2
100/1.5	24.1	691.6	2.3
100/2.0	26.5	695.3	2.4
100/2.5	19.2	591.2	2.3



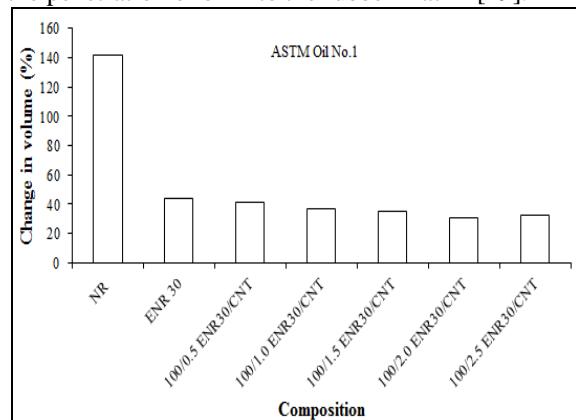
**Fig.4. Loss Tangent ( $\tan \delta$ ) of the NR, ENR30 and ENR30/CNT Nanocomposites.**

**Table 4:  $T_g$  of the NR, ENR30 and ENR30/CNT Nanocomposites.**

Composition	$T_g$ (°C)
NR	-60.0
ENR30	-51.0
<i>ENR30/CNT</i>	
100/0.5	-49.2
100/1.0	-40.0
100/1.5	-39.0
100/2.0	-38.9
100/2.5	-40.5

### 3.5. Oil Resistance

The percentage of volume change of the NR, ENR30 and ENR30/CNT nanocomposites after being immersed in ASTM Oil No.1 at 100°C for 72 h is shown in Fig. 5. The ASTM Oil No. 1 is a low polar hydrocarbon oil having a high aniline point at 123.8°C [18]. As can be seen, the percentage volume change of NR after immersion in oil was much higher than that of ENR30 and ENR30/CNT nanocomposites, indicating that the epoxidation significantly increased their ASTM Oil No. 1 resistance. Moreover the ENR30/CNT nanocomposites exhibited higher oil resistance than the ENR30 because CNTs restricted the penetration of oil into the rubber matrix [19].



**Fig.5. Change in the Volume of the NR, ENR30 and ENR30/CNT Nanocomposites After Immersion in Oil at 100°C for 72 h.**

## CONCLUSIONS

The ENR30/CNT nanocomposites were successfully prepared by adding five different loadings of CNTs (0.5, 1, 1.5, 2 and 2.5 phr) to NR latex prior to in situ epoxidation. The epoxidation was performed using a molar ratio of formic acid:H<sub>2</sub>O<sub>2</sub> to isoprene unit of 0.75:0.75 at 50°C for 4 h. The  $t_{s2}$  and  $t_{90}$  obtained from the MDR showed that the ENR30/CNT nanocomposites exhibited longer  $t_{s2}$  and  $t_{90}$ , presumably due to the absorption of the accelerator by the carboxyl groups on the CNT surface. Among the five ENR30/CNT nanocomposites, one that filled with 2 phr CNTs exhibited the highest tensile strength, EB, M300,  $T_g$  and ASTM Oil No. 1 resistance.

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