Influence of carbon nanotube and ionic liquid on properties of natural rubber nanocomposites

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Abstract. Some properties of carbon nanotube (CNT) filled natural rubber (NR) composites were improved by adding an ionic liquid (IL), 1-butyl-3-methyl imidazolium bis (trifluoromethylsulphonyl)imide (BMI). In this work, the CNT and IL (CNT-IL) were mixed with NR by latex mixing method. Cure characteristics, thermo-mechanical properties, Payne effect, electrical conductivity and thermal stability were investigated. It was found that IL (BMI) accelerated vulcanization reactions and reduced scorch time. In addition, Fourier Transform Infrared (FTIR) results confirmed the role of IL in NR composites along with the reaction between CNT and NR molecules. The temperature scanning stress relaxation (TSSR) measurement was used to assess thermo-mechanical properties, and a relaxation peak of IL was found due to interactions of cations and anions in IL (BMI). Furthermore, the Payne effect was used to qualitatively analyze the roles of IL and CNT in three-dimensional CNT networks in the NR matrix. It was found that CNT dispersion was finer in the NR/CNT composites with IL. Furthermore, the NR/CNT-IL composite had higher electrical conductivity and lower percolation threshold concentration than the NR/CNT composite.

Keywords: nanocomposites, natural rubber, carbon nanotubes, Ionic liquid, 1-butyl-3-methyl imidazolium bis(trifluoromethylsulphonyl)imide (BMI)

1. Introduction

Natural rubber (NR) composites with carbon nanotube (CNT) filler have been widely investigated with the main purpose to prepare strong elastic materials with high electrical conductivity. Typically, the addition of CNT could transform NR from electric insulator to conductive material with outstanding flexibility, elasticity and mechanical properties [1–3]. However, the optimum electrical conductivity and other related properties of NR/CNT composites are mainly controlled by localization and three dimensional networks of CNTs in the rubber matrix [4, 5].

That is, the random orientation of CNT can give two-dimensional (2D) and three-dimensional (3D) CNT networks [6]. Normally, three-dimensional CNT networks are formed before reaching the percolation threshold concentration (PTC) of the incorporated filler, creating conductive pathways for electron transfer. Nevertheless, agglomeration of CNT is typical due to interactions of polar functional groups on CNT surfaces via hydrogen bonds and Van-der Waals attraction [7, 8]. This may cause inferior electrical conductivity and mechanical properties of the NR/CNT composites [9, 10].

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To enhance electrical conductivity of the rubber composites, several methodologies have been exploited to improve the CNT dispersion in rubber matrix. One prominent approach is use of CNT mixed with an ionic liquid (IL) [2]. It is noted that IL is typically an organic salt with low melting point (typically $<100^{\circ}\text{C}$), low vapor pressure, and high thermal stability [2]. Typically, the IL molecules consist of a cation and an anion that connect to hydrophobic alkyl groups [11]. In addition, the IL molecules have hydrophilic and hydrophobic parts of the inorganic and organic salts in their molecules. It is noted that the hydrophobic part is capable of interacting with CNT surfaces through cation- π interaction [12]. Also, some ionic liquids contain $-\text{C}=\text{C}-$ in the alkyl chain, and this could interact with diene rubbers via sulfur bridges from sulfur vulcanization [13]. Therefore, IL could bridge CNT surfaces with the rubber matrix [13].

The imidazolium ionic liquid has been widely used in various types of polymer matrix [7, 9, 14–16]. It was found that the imidazolium groups play an important role in improving the ionic conductivity of acrylonitrile butadiene rubber (NBR) [14]. Furthermore, NBR/ SiO_2 in combination with imidazolium ionic liquid gave good elastomeric properties, high tensile strength, and high electrical conductivity [15]. Also, reduced glass transition temperature (T_g) was observed due to the plasticizing effect of IL [15]. In addition, carboxylated nitrile butadiene rubber (XNBR) filled with a layered double hydroxide (MgAl-LDH) in combination with imidazolium ionic liquids improved electrical conductivity and thermal stability [16]. Furthermore, MWCNT has been modified with 1-butyl 3-methyl imidazolium bis(trifluoromethylsulphonyl)imide (BMI) and mixed with styrene butadiene rubber solution (SSBR) [7] and with poly(chloroprene rubber) solution (CR) [17]. The distribution of MWCNT agglomerates and individual tubes was good, with formation of MWCNT conducting networks in SSBR matrix giving electrical conductivity up to 0.01 S/cm. Furthermore, the CR/MWCNT-BMI composites showed improved MWCNT dispersion and related effects [17].

To obtain composites with good CNT distribution and dispersion as well as superior mechanical and electrical properties, preparation technique is practically important. Latex mixing is typically performed by dispersing the MWCNT in water before adding the suspension into natural rubber latex [17]. It was found that a small amount of MWCNT remarkably

improved mechanical, thermal, electrical and barrier properties of NR. Furthermore, segregated CNT networks were found, which gave a low electrical percolation threshold concentration at about 0.043 vol%. A comparison of latex and melt mixing methods was also performed in preparing NR/CNT composites [18]. It was found that the NR composite prepared by latex mixing showed superior tensile properties and electrical conductivity over that prepared by melt mixing. The possible technical potential applications of the investigated material should be an electroactive elastomer (EPA) for strain or pressure sensors, stretchable conductors and actuators together with conductive flexible seals and gaskets.

In the present work, improvement of the CNT dispersion and distribution with high quality CNT networks in NR matrix was pursued. For maximal electrical conductivity an IL was also used, namely 1-butyl 3-methyl imidazolium bis(trifluoromethylsulphonyl)imide (BMI). Therefore, CNT-IL (BMI) was first prepared, and then used to fill NR via latex mixing. In addition, cure characteristics, electrical properties, relaxation behavior and thermal resistance were investigated.

2. Experimental section

2.1. Materials

High ammonia natural rubber latex used as the rubber matrix was manufactured by Von Bundit Co., Ltd (Surat Thani, Thailand). The reinforcing filler used was multi-wall carbon nanotubes (MWCNT), NC7000 with 9.5 nm diameter, 1.5 μm length, and 90% purity, manufactured by Nanocyl S.A. (Sambreville, Belgium). The ionic liquid (IL), 1-butyl-3-methyl imidazolium bis(trifluoromethylsulphonyl)imide (BMI), was manufactured by Ionic Liquids Technologies (Heilbronn, Germany). Other chemicals used in the rubber formulation were zinc oxide (ZnO), stearic acid, 2,2'-dithiobis(benzothiazole) (MBTs) and sulfur, as summarized in Table 1.

2.2. Preparation of CNT, CNT-IL and IL filled-NR composites

NR/CNT, NR/CNT-IL and NR/IL composites were prepared by latex mixing using sodium dodecyl sulphate (SDS) surfactant (0.5 wt%) to stabilize the latex mixture. The CNT or IL or CNT-IL (1:1 by weight) was first mixed in deionized water. The mixture was then conditioned with sonication for about 20 min, and the pH of latex was then adjusted to

Table 1. Chemicals and compounding formulations of CNT and CNT-IL hybrid filled NR compounds.

Chemicals	Suppliers	Contents [phr]
NR latex	Von Bundit Co.,Ltd. (Surat Thani, Thailand)Thani, Thailand	100
Stearic acid	Imperial Chemical Co. Ltd., Pathum Thani, Thailand	1
Zinc oxide (ZnO)	Global Chemical Co. Ltd., Samut Prakarn, Thailand	5
2,2'-Dithiobis-(benzothiazole) (MBTs)	Flexsys Inc., Termoli, Italy	1
Sulfur	Ajax Chemical Co. Ltd., Samut Prakarn, Thailand	2.5
BMI	Ionic Liquids Technologies., Germany	Varied 0–7
CNT	Nanocyl S.A., Belgium	Varied 0–7

about 11 by adding 3 wt% sodium hydroxide solution. Then, the natural rubber latex (10% DRC) was incorporated into the mixture and thoroughly mixed for about 10 min by a mechanical stirrer. The latex mixture was eventually cast on the smooth surface of a glass plate and then dried in a hot air oven at 60 °C for 24 h. The dried film was collected and then compounded with the activator, accelerator and vulcanizing agents in an internal mixer (Brabender® GmbH & Co. KG, Duisburg, Germany), with formulation shown in Table 1. In addition, cure characteristics of the rubber compounds were investigated by a moving die rheometer (MDR 2000) (Alpha Technologies, Ohio, USA) at 160 °C. Vulcanized samples were prepared by compression molding at 160 °C for the respective cure time of each sample.

2.3. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

The ATR-FTIR was used to analyze the chemical interactions of NR, CNT and IL. Thus, the gum NR vulcanizate, together with NR/CNT, NR/IL, NR/CNT-IL composite films without other chemicals (i.e., activator, accelerator and curing agent) were prepared. The FTIR analysis was performed by Thermo Nicolet Avatar 360 FTIR (Thermo Electron Corporation, Thermo Nicolet, Madison, WI, USA) over the wide wavenumber range 4000–500 cm⁻¹ with a resolution of 2 cm⁻¹ and 64 scans for recorded spectrum.

2.4. Cure characteristics

Cure characteristics of the gum NR vulcanizate together with the CNT, IL and CNT-IL filled NR compounds were determined by using a moving die rheometer (MDR 2000) (Alpha Technologies, Ohio, USA). The measurements were performed at 160 °C with the fixed oscillation frequency of 1.66 Hz and 1° arc amplitude.

2.5. Vulcanization kinetics

The activation energy of vulcanization for the gum NR as well as CNT, IL and CNT-IL filled NR compounds was investigated by differential scanning calorimetry (DSC) (Mettler-Toledo Ltd., Gießen, Germany). The analysis was performed over the temperature range 10–300 °C with four heating rates: 2, 10, 20 and 30 °C/min.

2.6. Payne effect

The Payne effect was determined by measuring the storage modulus with various strain amplitudes for the rubber composites, by using a rubber process analyzer (RPA) (Alpha Technologies, Ohio, USA). The storage shear moduli (G_0) of cured filled NR compounds at different shear strain rates were determined with strain sweep tests for strains spanning 0.56–100% at the fixed 1 Hz oscillation frequency and 100 °C.

2.7. Temperature scanning stress relaxation (TSSR)

Stress relaxation of the gum NR vulcanizate together with CNT, IL and CNT-IL filled NR composites was investigated by temperature scanning stress relaxation (TSSR) meter (Brabender, Duisburg, Germany). The dumbbell-shaped specimens were first prepared according to ISO 527, type 5A. The samples were first annealed at 100 °C for 30 min, and then cooled down to room temperature for 30 min before testing, in order to avoid the storage hardening phenomenon of NR [19]. The test was then started by extending the sample to 50% strain held at 23 °C for 2 h. Then, the non-isothermal test was performed by raising the temperature from 23 to 220 °C with the constant 2 °C/min heating rate.

2.8. Thermal analysis

Thermal stability of NR vulcanizates together with CNT, IL and CNT-IL filled NR composites was

investigated by thermogravimetric analysis using TGA-SDTA 851 (Mettler Toledo, Zurich, Switzerland). The measurement was performed under nitrogen atmosphere in the temperature range 30–600 °C before switching to oxygen atmosphere and continuously heating to 900 °C at the same 10 °C/min heating rate. Dynamic mechanical thermal analysis (DMTA) was also carried out by using Dynamic Mechanical Thermal Analyzer (DMTA-V, Rheometric Scientific, New Jersey, USA) in tension mode. The samples were scanned over the temperature range from –100 to 25 °C with a heating rate of 3 °C/min, at the fixed mechanical frequency of 10 Hz.

2.9. Electrical properties

Electrical properties in terms of electrical conductivity (σ) of the gum NR vulcanizate as well as CNT, IL and CNT-IL filled NR composites were measured at room temperature by an LCR meter (Hioki IM 3533, Hioki E.E., Corporation, Nagano, Japan). The meter was connected to plate electrodes of a dielectric test fixture (16451B dielectric test fixture, Test Equipment Solutions Ltd., Berkshire, UK) with 5 mm electrode diameter. An approximately 2 mm thick sample was first placed between the plates and then the test was performed over the frequency range 1–10⁵ Hz. The electrical conductivity (σ) was then calculated as Equation (1) [20, 21]:

$$\sigma = \frac{1}{\rho} = \frac{d}{R_p \cdot A} \quad (1)$$

where d and A refer to sample thickness and area of an electrode, respectively. The factor ρ is the volume resistivity, which is the reciprocal of conductivity.

2.10. Morphological properties

Morphological properties of NR composites were investigated by scanning electron microscopy (SEM), FEI-Quanta 400, FEI, (Brno, Czech Republic). Each specimen was first cryogenically fractured in liquid nitrogen to create a freshly fractured cross-sectional surface. Then, the samples were sputter-coated with a thin layer of gold under vacuum before characterizing by SEM.

2.11. Mechanical properties

Mechanical properties of the NR vulcanizates together with CNT, IL and CNT-IL filled NR composites were investigated using a universal tensile testing machine (Tinius Olsen, Co., Ltd., Honey Crock Lane, UK). The tests were carried out with 500 mm/min⁻¹ cross-head speed at room temperature, according to ISO 37.

3. Results and discussion

3.1. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

Figure 1 shows FTIR spectra of the gum NR vulcanizate, together with NR/CNT, NR/IL and NR/CNT-IL composites. Also, the potential FTIR peak assignments are listed in Table 2. It is seen that the

Figure 1. FTIR spectra of the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites (a), and the magnified FTIR spectra of NR/CNT and NR/CNT/IL composites in the wavenumber range from 900 to 1500 cm⁻¹ (b).

Table 2. Peak assignments in FTIR spectra for the gum NR, CNT, IL and CNT-IL filled NR vulcanizates.

Wave number [cm ⁻¹]	Assignment
1643	C=C stretching vibration
1573	C–N stretching vibration
1455	C–H scissoring vibration
1397	–CH ₃ bending vibration
1349	C–N stretching vibration
1221	C–O stretching vibration
1183	C–N stretching vibration
1134	SO ₂ symmetric stretching
1081	C–O stretching vibration
1054	S–N–S stretching vibration
1018	C–O stretching vibration
997	C–H out-of-plane bend
834	=C–H out of plane bending
789	C–C vibrations
740	CF ₃ symmetric bending
720	(CH ₂) rocking
662	C–S stretching vibration
634	C–H bending vibration
615	C–H bending vibration

absorption peak at wavenumber 1643 cm⁻¹, which is assigned to C=C stretching vibrations of NR molecules, was observed [22]. In addition, the absorption peak at 834 cm⁻¹, which indicates =C–H out-of-plane bending, was also observed. Furthermore, absorption peaks at wavenumbers 1455 and 1397 cm⁻¹ were seen, which indicate C–H scissoring and –CH₃ bending vibrations in NR, respectively. In Figure 1, it is clear that addition of CNT in NR gave new FTIR peaks at wavenumbers 1221, 1081 and 1018 cm⁻¹, which are assigned to C–O stretching vibrations [23]. Moreover, the peaks of C=C stretching vibrations in NR at wavenumber 1643 cm⁻¹ completely disappeared upon adding CNT. This might be due to the chemical interactions of CNT and NR, with a proposed reaction shown in Figure 2 (Reaction A). That is, on mixing NR latex and CNT dispersion, CNT was transformed to [CNT⁻]Na⁺ after addition of NaOH solution for adjusting the pH to about 11 [24]. Also, some NR molecular chains might be degraded by thermo-oxidation during drying, which generated ketone groups at NR chain ends [25, 26]. Therefore, the [CNT⁻]Na⁺ can possibly react with NR at the ketone groups to form NR-CNT linkages. Furthermore, high thermal conductivity and thermal diffusion of CNT in the NR matrix might activate the degradation of NR molecules. This might reduce

absorption by C=C at 1643 cm⁻¹ in the NR/CNT composite, relative to the gum NR vulcanizate. In Figure 1, it is also seen that the FTIR spectrum of NR/IL showed an absorption peak at wavenumber 1573 cm⁻¹, which is assigned to C–N stretching vibrations in imidazolium rings [2]. In addition, SO₂ symmetric stretching and CF₃ symmetric bending vibrations in BMI were also observed in the infrared spectrum of NR/IL vulcanizate, at wavenumbers 1134 and 740 cm⁻¹, respectively [2, 27]. Furthermore, S–N–S stretching and C–S stretching vibrations were also observed at 1054 and 662 cm⁻¹, respectively [28]. These peaks indicate various infrared active groups in BMI or the anions of BMI. In addition, the absorption peaks at 789 and 615 cm⁻¹ represent the C–C and C–H in alkyl chain and in imidazolium ring, respectively. In Figure 1, it is also seen that the FTIR spectrum of NR/CNT-IL composite shows the same peak locations as seen in the infrared spectrum of NR/IL vulcanizate. This might be due to the fact that the CNT did not have strong chemical interactions with IL. However, weak physical interactions of dipole-dipole and π - π types might occur between CNT and BMI [2], as proposed in Figure 2 (Reaction B). It is clear that the sp² carbon in CNT might react with the alkoxide ions and cation in imidazodiuim rings of BMI. This is confirmed by the infrared spectra in Figure 1b showing shifted absorption peaks at wavenumbers 1221, 1081 and 1018 cm⁻¹ in NR/CNT to 1183 and 1054 cm⁻¹ in NR/CNT-IL composite [2, 29], respectively. Thus, it can be anticipated that CNT might bridge NR and BMI by π - π interactions of CNT and BMI in the NR/CNT-IL composites (Figure 2, Reaction B).

3.2. Curing characteristics

Figure 3 shows the curing curves of gum NR compound together with CNT, IL and CNT-IL filled NR compounds. Also, Table 3 shows scorch time (t_{s2}), cure time (t_{c90}), minimum torque (M_L), maximum torque (M_H) and torque difference ($M_H - M_L$) for various types of NR compounds. Reversion with decreasing torque after the optimum cure level was found in all compounds studied. Furthermore, the reversion phenomenon was more pronounced after the addition of CNT, IL and CNT/IL. This might be due to more breakdown of sulfidic linkages in the presence of CNT, IL and CNT-IL, and also the breakdown of chemical interactions of rubber with the polar functional groups on filler surfaces. Moreover,

Figure 2. Proposed reaction mechanisms of NR and CNT (Reaction A) as well as NR, CNT and IL (BMI) (Reaction B).

Figure 3. Cure curves of gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

the CNT might activate thermal oxidation and/or degradation of NR and the sulfur linkages because CNT has high thermal conductivity [30]. In Table 3, it is also seen that the scorch time (t_{s2}) of gum NR compound was shortened by addition of CNT due to its high thermal conduction and diffusion in the NR

Table 3. Cure properties of the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

Sample	M_L [dNm]	M_H [dNm]	$M_H - M_L$ [dNm]	t_{s2} [min]	t_{c90} [min]
Gum NR	1.18	5.99	4.81	1.33	3.32
NR/CNT 5 phr	1.83	7.90	6.07	0.71	2.79
NR/IL 5 phr	1.34	4.01	2.67	1.77	2.56
NR/CNT-IL 5 phr	2.45	6.35	3.90	1.05	2.63

Figure 4. A proposed reaction mechanism between MBTS and 1-butyl-3-methyl imidazolium bis (trifluoromethylsulfonyl) imide (BMI) during vulcanization.

matrix, which increased the rate of sulfur vulcanization. On the other hand, addition of IL (BMI) and CNT/IL prolonged t_{s2} from that of the NR/CNT compound. This might be because BMI retarded vulcanization reactions by reacting with 2,2'-Dithiobis(benzothiazole) (MBTs) accelerator, as described in Figure 4. It is seen that the accelerator (MBT) can react with BMI via π - π interactions between mercaptobenzthiazole and imidazolium rings. This would lower the reactivity of MBT in vulcanization of NR and delay scorch, as compared to the gum NR and NR/CNT compounds. However, in the NR/CNT-IL compound, the t_{s2} and t_{90} were significantly decreased from those of the gum NR compound due to the formation of CNT-IL (BMI) bridges that activated the vulcanization of the compound. Moreover, decreased t_{s2} and t_{90} might be due to reactions of CNT-IL bridges with NR that consumed C=C double bonds in NR by the reaction mechanism shown in Figure 2. Thus, active C=C bonds in NR decreased and vulcanization of NR compounds had faster curing. This matches the disappearance of the IR absorption peak at 1643 cm^{-1} , which is assigned to stretching vibrations of $\text{C}=\text{C}$ (Figure 1), upon addition of CNT, IL and CNT-IL. In Table 3, it is also seen that the torque difference or delta torque increased with addition of CNT but decreased with addition of IL (BMI). This might be due to CNT network formation in the NR matrix, which increased crosslink density and reinforced the rubber vulcanizates. However, incorporation of imidazolium salt reduced torque by plasticizing and lubricating the rubber compound [31]. In addition, the IL (BMI) also acts as a retarder

that delays vulcanization reactions of NR. Hence delta torque and crosslink densities of both NR/IL and NR/CNT-IL were below those of the gum NR and NR/CNT vulcanizates, because vulcanization was retarded by IL (BMI).

Kinetics of vulcanization was investigated by DSC performed at different heating rates (q). The main aim was to analyze the exothermic temperature (T_p) for each heating rate. Then, the relationship between $\log q$ and $1/T_p$ (temperature) was plotted in accordance with the Ozawa equation (Equation (2)). The slope in $\log q$ versus $1/T_p$ plot was evaluated to estimate the activation energy (E_a) of vulcanization for each rubber sample, as follows [32]:

$$E_a = -2.3R \frac{d \log q}{d\left(\frac{1}{T_p}\right)} \quad (2)$$

where R is the gas constant ($8.31\text{ J/(K}\cdot\text{mol)}$), T_p is the temperature at the exothermic peak and q is the heating rate.

Figure 5 shows the relationships of $\log q$ and $1/T_p$ with E_a indicated for each curve. Also, the insert in Figure 5 shows the DSC thermogram of each rubber sample. Furthermore, Table 4 summarizes the activation energy and conversion for the gum NR vulcanizate and the NR filled with CNT, IL and CNT-IL, at each heating rate. It can be seen that the activation energies (E_a) of gum NR, CNT, IL and CNT-IL filled NR vulcanizates are 87.17, 124.36, 100.07 and 113.13 kJ/mol, respectively (Table 4). A higher E_a means the compound needs more energy to start vulcanization. It is seen in Figure 5 and Table that the gum NR had the lowest activation energy, while

Figure 5. Relationship between $\log q$ and $1/T_p$ for the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

incorporation of CNT, IL and CNT-IL increased the activation energy of vulcanization. This might be due to CNT hindering reactions of active sulfur atoms and C=C double bonds, by adsorbing polymer chains on the CNT surfaces (i.e., rubber-filler interactions) and by CNT and IL interfering with the accelerator molecules [33]. In NR/IL compound, a higher activation energy was observed because the IL (BMI) interact with MBT accelerator. Also, the alkyl chains in BMI could interact with NR via Van-der Waals forces [34]. This could hinder the vulcanization in NR/IL compound requiring more energy to start vulcanization than in the gum NR compound. It is also seen in

Table 4 that the NR/CNT-IL compound showed activation energy between NR/CNT and NR/IL compounds. This may relate to the absorption of rubber on CNT surfaces increasing activation energy. In addition, lower E_a was found for the NR/CNT-IL compound than for the NR/CNT compound. This might be attributed to finer dispersion for CNT in the rubber matrix in the NR/CNT-IL compound. This is because the IL (BMI) acted as a plasticizer or dispersing agent for CNT in NR matrix, improving the dispersion of CNT. This might reduce the activation energy of vulcanization reactions.

Degree of conversion by vulcanization can be estimated from the exothermic peaks in DSC thermograms according to Equations (3) and (4) [35]:

$$\alpha(T) = \frac{\Delta H_{\text{part}}}{\Delta H_{\text{tot}}} \cdot 100 \quad (3)$$

$$= \frac{\int_{T_0}^T \Phi(T) dT}{\int_{T_0}^{T_1} \Phi(T) dT} \quad (4)$$

where ΔH_{part} is the partial area of the DSC peak below the actual temperature, and ΔH_{tot} is the total area of the peak. T_0 and T_1 are the initial and end temperatures of reaction, respectively.

Figure 6 shows the degree of conversion of gum NR, together with CNT, IL and CNT-IL filled NR

Table 4. Activation energy and conversion of the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

Sample	Heating rate [°C/min]	T_p [°C]	E_a [kJ/mol]	T_0 [°C]	T_1 [°C]	Conversion [%]
Gum NR	2	150.52	87.17	126	209	50
	10	179.37		152	223	
	20	196.32		158	234	
	30	200.51		166	236	
NR/IL 5 phr	2	162.06	100.07	125	176	51
	10	193.75		146	230	
	20	199.06		156	237	
	30	209.49		160	246	
NR/CNT 5 phr	2	162.16	124.30	108	209	82
	10	183.02		124	237	
	20	193.31		134	256	
	30	199.42		158	240	
NR/CNT-IL 5 phr	2	166.05	113.13	126	209	65
	10	178.39		152	223	
	20	197.74		158	234	
	30	204.62		166	236

Figure 6. Conversion of the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

compounds. Also, Table 4 shows the conversion degrees of the various compounds estimated from Figure 6 and Equations (3) and (4). It can be seen that the gum NR together with NR/CNT, NR/IL and NR/CNT/IL compounds had degrees of conversion of 50, 82, 51 and 65%, respectively. Therefore, it is clear that the NR/IL (BMI) compound showed similar degree of conversion by vulcanization as the gum NR compound. On the other hand, the CNT effectively increased the degree of conversion (i.e., 82%) probably by good thermal conduction and diffusion in the NR matrix [36], so that at the regular vulcanization temperature a higher degree of conversion was found than for the gum NR compound. Furthermore, the NR/CNT-IL compound showed less conversion than the NR/CNT compound, because IL (BMI) may cover CNT surfaces effectively preventing thermal diffusion along CNT, and may deactivate MBT by reactions with the IL (BMI). In summary, CNT in the NR matrix increases the energy required to vulcanize the rubber (higher E_a), from that of the gum NR compound. However, shorter t_{s1} and t_{90} were found owing to the high thermal conductivity of CNT that increased the degree of conversion. These properties

were significantly altered after CNT-IL was incorporated into the NR compound. That is, the vulcanization started later than for the NR/CNT compound (i.e., higher t_{s2}). This might be due to reactions of imidazolium rings with accelerator retarding vulcanization, as shown in Figure 4. This reduces E_a and the conversion by vulcanization, as seen in Figures 5 and 6, and Tables 3 and 4.

3.3. Payne effect

Figure 7 shows the storage modulus as a function of strain amplitude for the gum NR, together with CNT, IL and CNT/IL filled NR compounds. It can be seen that incorporation of IL lowers the storage moduli from that of the gum NR compound due to the plasticizing effect of IL [31]. However, the addition of CNT in NR showed the reverse effect by abrupt increase of the storage modulus for the NR/CNT composite. Moreover, the NR/CNT-IL composite showed a surprising synergy with the highest storage modulus. This might be due to the fine dispersion of CNT in the NR matrix. The dipole-dipole and π - π interactions between CNT and BMI decreased re-agglomeration of CNT bundles [7]. It is noted that the Payne

Figure 7. Storage modulus as a function of strain amplitude for the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

effect of filled rubber compounds can be assessed from the dynamic storage modulus (G') at various strain amplitudes. It indicates the filler-filler and filler-rubber interactions in a rubber composite. Furthermore, the Payne effect in CNT-filled NR compounds could inform about CNT network formation [13]. The G' modulus tends to decrease with strain as the extension breaks filler networks [13], and a decreasing trend of G' at high applied strains is observed in Figure 7 also for the gum NR vulcanizate without any filler. This might be caused by the breakdown of NR crosslinks and entanglements [14]. It is noted that the Payne effect is typically estimated from moduli at very low and at very high strains ($G'_0 \rightarrow G'_\infty$) [37] as Equations (5) and (6):

$$\Delta G' = G'_0 - G'_\infty \quad (5)$$

$$\% \Delta G' = \frac{G'_0 - G'_\infty}{G'_\infty} \cdot 100 \quad (6)$$

where G'_0 and G'_∞ are the maximum and minimum moduli.

Table 5 shows the $\Delta G'$ (Eq. (5)) and $\% \Delta G'$ (Eq. (6)) of gum NR together with CNT, IL and CNT-IL filled

NR compounds as the Payne values for the filled NR compounds. It is noted that, to observe the Payne effect for the filled NR composites, the effects of NR matrix alone are canceled, so that the Payne effect [%] of NR/CNT composite = $\% \Delta G'_{\text{NR/CNT}} - \% \Delta G'_{\text{Gum NR}}$ and the Payne effect [%] of NR/CNT-IL composite = $\% \Delta G'_{\text{NR/CNT-IL}} - \% \Delta G'_{\text{NR/IL}}$, giving 68 and 88%, respectively. It is noted that a larger Payne effect indicates more filler-filler interactions. Furthermore, it has been claimed that a finer dispersion of CNT also increases the Payne effect in rubber/CNT/ionic liquid hybrid composites [28]. Therefore the combination of CNT and IL that improved the CNT dispersion and gave larger Payne effect, as in the model of Figure 8. It can be seen that chain entanglement of NR molecules occurs due to the high molecular weight and coil-like conformations, as shown in Figure 8a. This is reflected by the about 44% $\% \Delta G'$ of the gum NR compound (Table 5). However, addition of IL in the NR matrix reduced $\% \Delta G'$ by about 23% (Table 5). This might be due to plasticizing effect of the IL (BMI) that reduced physical interactions (friction) of NR molecules and allowed slippage and disentanglement, as described in Figure 8b. Furthermore, the addition of CNT in NR increased $\% \Delta G'$ by increasing filler-filler interactions of CNT bundles, as described in Figure 8c. Moreover, the largest Payne effect was observed for the NR/CNT-IL composite. This might be attributed to the π - π interactions of alkyl chains in BMI and CNT that broke down CNT bundles. This means that the CNT particles could interact with each other, producing a strong Payne effect, as shown in Figure 8d. Likewise, the imidazolium rings in BMI interacted with the CNT particles via π - π interactions, as described in Reaction B (Figure 2). Therefore, the alkyl chains in IL (BMI) might expand CNT bundles by diffusing into them. However, the IL (BMI) might reduce filler-filler interactions of CNT but still strongly affect the CNT network formation in NR/CNT-IL composites. This gave the strongest Payne effect for the NR/CNT-IL composites.

Table 5. Payne effect (calculated from Equations (6) and (7)) for the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

Sample	G'_0 [MPa]	G'_∞ [MPa]	$\Delta G'$ [MPa]	$\Delta G'$ [%]	Payne effect of filled NR [%]
Gum NR	0.1236	0.08570	0.0379	44	–
NR/IL 5 phr	0.0997	0.08140	0.0183	23	–
NR/CNT 5 phr	0.1905	0.08970	0.1008	112	68
NR/CNT-IL 5 phr	0.2138	0.10124	0.1126	111	88

Payne effect was calculated based on Equations (6) and (7).

Figure 8. A proposed model for chain entanglement of natural rubber molecules (a), and NR filled with IL (b), CNT (c) and CNT-IL (d).

3.4. Temperature scanning stress relaxation (TSSR)

Relaxation behavior under thermal treatment of the gum NR compound together with IL, CNT and CNT-IL filled NR compounds was characterized by the novel TSSR technique. The TSSR curves, or the relations of stress relaxation to temperature, are shown in Figure 9. Also, Table 6 summarizes the TSSR results in terms of initial stress (σ_0) and relaxation temperature (T_x). It is noted that the T_x stands for the temperature at which the force has decreased by $x\%$ from its initial value (F_0) [38]. Thus, T_{10} , T_{50} and T_{90} indicate the temperatures at which the stresses have decreased by 10, 50 and 90% from the initial stress. In Figure 9, it can be seen that addition of IL increased the stress in NR/IL compound from that of the gum NR compound. In contrast, the plasticizing effect of IL (BMI) should give a lower stress. However, the IL (BMI) can act differently in un-vulcanized and vulcanized NR/IL compounds. That is, the IL (BMI) decreased the torque difference (Figure 3 and Table 3) and storage modulus (Figure 7 and Table 5) in un-vulcanized natural rubber compounds, but gave higher stiffness in the NR/IL vulcanizate. This might be due to the random localization of BMI

Figure 9. Stress relaxation of the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

Table 6. TSSR results in terms of σ_0 and T_x for the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

Sample	σ_0 [MPa]	T_{10} [°C]	T_{50} [°C]	T_{90} [°C]
Gum NR	0.32	132.0	158.6	202.1
NR/IL 5 phr	0.42	128.8	163.2	220.0
NR/CNT 5 phr	0.59	84.2	141.3	181.0
NR/CNT-IL 5 phr	0.87	89.1	148.1	199.3

Figure 10. A proposed model for the localization of IL in un-vulcanized (a), and in vulcanized NR samples (b).

molecules that can link to NR molecules via sulfur linkages, as described in Figure 10. That is, the IL in the NR matrix could freely move and lubricate the NR molecular chains during shear deformation of the un-vulcanized NR sample. On the other hand, after vulcanization of NR, the IL (BMI) formed small domains dispersed in the NR matrix. Hence, the restriction of molecular movement was due to the sulfur crosslinks [39], as seen in Figure 10b.

It is also seen in Figure 9 that the stress-temperature curve of NR/CNT is above that of the gum NR vulcanizate, particularly at temperatures below 150 °C. This indicates the reinforcement effect of CNT in the NR matrix. Moreover, the combination of CNT and IL in NR vulcanizate (i.e., NR/CNT-IL) showed the highest stress-temperature curve. This might be due to the IL (BMI) effectively improving the dispersion of CNT so that stronger three-dimensional networks of CNT were produced. In Figure 9, it is also seen that the initial gradient of the stress-temperature curve slightly increased, due to the entropy effect of NR similar to other crosslinked networks or gels [19]. Therefore, it is clear that incorporation of CNT and CNT-IL increased the entropic effect from that in the gum NR vulcanizate. This might be attributed to more physical interactions of NR that was adsorbed on the CNT surfaces [5]. It is clear in Figure 9 that a plateau stress-temperature relation was observed in the temperature range from 50 to 120 °C for the gum NR and NR/IL vulcanizates. On the other hand, the NR/CNT and NR/CNT-IL composites showed a slightly decreasing stress with temperature in this range. This

Figure 11. A proposed model of adsorbed rubber layer and its breakdown in NR/CNT-IL composite.

might be due to the breakdown of some physically adsorbed rubber layers on CNT surfaces [8], as depicted in Figure 11. It can be seen that the rubber chains reacted with CNT particles and NR was deposited on CNT surfaces. Also, the IL (BMI) could interact with CNT via dipole-dipole interactions. However, the weak interactions of NR with CNT or CNT-IL might be degraded at elevated temperatures from 50 to 120 °C.

Furthermore, stress relaxation was clearly observed for temperatures of 120–220 °C in all samples studied. This might be due to the thermo-oxidative degradation of rubber [40]. In Table 6, it is also seen that the lowest T_{10} (i.e., the temperature at which the force has decreased by 10% from the initial force) was observed for the NR/CNT composite, while the highest

was for the gum NR and NR/IL vulcanizates. This might be related to the higher thermal conductivity of NR/CNT compound that favored thermal stress relaxation. Also, the physical desorption of rubber adsorbed on CNT might also play an important role. In addition, the NR/IL composite exhibited the highest T_{50} and T_{90} , which indicate better thermal resistance of the NR. This might be attributed to the high thermal stability of IL (BMI) [7] that improved thermo-oxidative resistance of the rubber composite. In contrast, the NR/CNT composites exhibited the lowest T_{50} and T_{90} due to high thermal conductivity and thermal diffusion in CNT, which facilitated thermo-oxidative degradation of NR [23, 30]. However, the combination of CNT-IL improved thermal stability due to the proper combination of high thermal stability of IL (BMI) and high thermal conductivity of CNT, as described in Figure 11. It is seen that the phonon charges had freedom of movement along the NR matrix through the CNT network in the NR/CNT composite. This induced faster thermo-oxidative degradation at T_{50} and T_{90} in the NR/CNT than in the NR/CNT-IL composite [30]. As expected, the CNT surfaces might be covered by high thermal stability IL (BMI), which caused scattering of phonon ions in the CNT-IL pathway, as shown in Figure 11. Thus, thermal diffusion was limited and therefore the T_{50} and T_{90} of NR/CNT-IL composites were higher than for the NR/CNT composite.

The relaxation spectrum ($H(T)$) was obtained by differentiating the non-isothermal relaxation modulus ($E(T)$), it is per definition calculated from the stress ' σ ' by division of the applied constant strain ' ϵ ' (in this case $\epsilon = 0.5$ (50%)) for a constant heating rate ($v = 2^\circ\text{C}/\text{min}$), as Equations (7) and (8) [41, 42]:

$$E = \frac{\sigma}{\epsilon_0} \quad (7)$$

$$H(T) = -T \left[\frac{dE(T)}{dT} \right]_{v=\text{const}} \quad (8)$$

where σ is the stress at a given time (t) or temperature (T) and ϵ_0 is the applied strain, which is kept constant.

Figure 12 shows the relaxation spectra of gum NR compound, together with CNT, IL and CNT-IL filled NR compounds, with a magnification of the spectra for the temperature range 23–220 °C. It can be seen that the NR/CNT composites showed the higher relaxation peaks than the gum NR compound. This

Figure 12. Relaxation spectrum of the gum NR vulcanizate together with NR/CNT, NR/IL and NR/CNT-IL composites, with magnified temperature range 23–100 °C in the in the left corner.

might be attributed to more rubber-filler and filler-filler interactions in the CNT filled NR compound. Furthermore, two relaxation peaks were observed in NR/IL and NR/CNT-IL composites in the temperature range 23–100 °C. That is, *peak I* is in the temperature range 35–60 °C, while *peak II* is in the temperature range 70–100 °C. It is noted that *peak I* might be attributed to the desorption of physically bound rubber, while *peak II* might be assigned to the degradation of IL (BMI) molecules. In addition, each compound showed a relaxation peak in the temperature range 100–200 °C, which indicates relaxation of NR. It is clear that the addition of filler increased relaxation peak intensity, with a synergistic effect in the NR/CNT-IL composite. This might be due to stronger interactions or bonds between NR and CNT. Furthermore, the IL by improving the dispersion of CNT may have enabled stronger three-dimensional CNT networks, which increased the relaxation energy, as described in Figure 8d.

3.5. Electrical properties

Figure 13 shows electrical conductivity of IL, CNT and CNT-IL filled NR vulcanizates with various filler loadings. Normally, the electrical conductivity of a composite with conductive filler has a percolation threshold concentration (f_c), which is the critical filler concentration that suffices for conductive pathways through the insulating matrix [43]. The percolation threshold concentration (f_c) can be estimated using percolation theory Equations (9) and (10) [44]:

$$\sigma_{DC} = k(f - f_c)^t, f > f_c \quad (9)$$

$$\log \sigma_{DC} = \log k + t \cdot \log(f - f_c) \quad (10)$$

where σ_{DC} is the *DC* conductivity of the composite, the parameters f and f_c are the volume fraction of filler and the volume fraction at percolation threshold, respectively, k is a constant and parameter t is related to the type of network formed by the filler in the matrix.

In Figure 13, it is clearly seen that adding IL in NR slightly increased electrical conductivity, but the loading level of IL (BMI) had no significant effect the conductivity of an NR vulcanizate. This might be because the IL (BMI) was encapsulated by the insulating NR as the imidazolium IL could be more compatible with the hydrophobic rubber matrix [7]. This leads to the poor electrical conductivity of the NR/IL vulcanizate, with no detectable percolation threshold. On the other hand, the NR/CNT and NR/CNT-IL composites showed percolation threshold concentrations (based on Equations (9) and (10)) at 3.64 and 2.92 phr, respectively. Therefore, the NR/CNT-IL composite exhibited comparatively high electrical conductivity with lower percolation threshold than in the NR/CNT composites. This might be due to the synergy of plasticizing by IL (BMI) that contributed to good dispersion of CNT, which then could form three-dimensional networks in the NR matrix, assisted by the physical interactions of CNT particles, as described in Figure 2 (Reaction B). Therefore, the plasticizing effect and physical interactions facilitated CNT network formation and reduced CNT

agglomeration, as shown in Figure 8d. This matches the Payne effect (Figure 7) and the initial stress relaxation (Figure 9) of the various NR vulcanizates.

3.6. Thermal degradation

Figures 14 and 15 show TGA and DTG thermograms of gum NR vulcanizate together with IL, CNT and CNT-IL filled NR vulcanizates. It is noted that TGA was performed under nitrogen atmosphere in the temperature range from 23 to 600 °C, with switching to oxygen atmosphere for the temperature range from 600 to 900 °C. It can be seen in Figure 14 that the NR/CNT and NR/CNT-IL composites show immediate weight losses at the initial temperature (a). This might be due to the thermal degradation of hydroxyl groups on the CNT surfaces in temperature range 100–200 °C [45]. On the other hand, the NR/IL and gum NR vulcanizates showed no significant difference in the initial TGA thermograms. In addition, the NR/CNT and NR/CNT-IL composites still exhibited faster decomposition at the higher temperatures in region (b), which matches the DTG thermogram peaks (i) in Figure 15. This might be due to the high thermal conductivity of CNT which enabled thermal diffusion in the composites and hence caused a faster thermo-oxidative degradation. Furthermore, the NR/IL composite showed slightly decreasing trend of weight in this region. This might be due to the thermal decomposition of short alkyl chains in the imidazolium molecules. Nevertheless, in the temperature region (c), the last region under the nitrogen atmosphere (Figure 14), it can be seen that the NR/CNT-IL composite exhibited the most residue, on comparing to

Figure 13. Electrical conductivity of NR/CNT, NR/IL and NR/CNT-IL vulcanizates with various filler loadings.

Figure 14. TGA thermograms of gum NR vulcanizate together with NR/CNT, NR/IL and NR/CNT-IL composites.

the NR/CNT and NR/IL composites. On the other hand, the gum NR vulcanizate exhibited the least residue. Therefore, the IL (BMI) improved CNT dispersion and three-dimensional networks in the NR matrix with more rubber-filler interactions in the NR/CNT-IL composite. This gave the highest residue amount after heating under nitrogen atmosphere until 600 °C. It is also seen in Figure 14 and Table 7

Figure 15. DTG thermograms of gum NR vulcanizate together with NR/CNT, NR/IL and NR/CNT-IL composites.

that the decomposition temperature (T_d) of gum NR and NR composites are clearly established in the temperature range 385–390 °C, which is confirmed by the DTG thermograms, *peak (ii)*. That is, the T_d s of gum NR vulcanizate, and NR/IL, NR/CNT and NR/CNT-IL composites are 390.66, 388.82, 390.11 and 385.33 °C, respectively.

In Table 7, it is also seen that weight losses of gum NR vulcanizate, as well as NR/CNT, NR/IL and NR/CNT-IL composites under nitrogen atmosphere at the end of step I are 94.10, 90.57, 93.21 and 88.10%, respectively. It is noted that the weight loss arises from the decomposition of moisture and organic

Table 7. Weight loss and degradation temperature (T_d) for the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

Step	Weight loss [%]			
	Gum NR	NR/CNT	NR/IL	NR/CNT-IL
Step 1 (under N ₂ atmosphere)	94.10	90.57	93.21	88.10
Step 2 (under O ₂ atmosphere)	0.83	4.35	0.91	5.26
	Degradation temperature (T_d)			
	390.66	390.11	388.82	385.33

components in the composites, in particular the NR molecules. It is clear that the gum NR vulcanizate showed the most weight loss (94.10%) while the NR/IL vulcanizate had 93.21%. The gum NR vulcanizate had the most easily degraded NR while some of the NR was replaced by IL(BMI) in the NR/IL vulcanizate. The NR/CNT and NR/CNT-IL composites exhibited less weight loss at 90.57 and 88.10%, respectively. This might be due to the high thermal conductivity of CNT promoting degradation in the NR/CNT composite while the NR/CNT-IL composite benefited from the low MW component IL (BMI). In Table 7, it is also seen that the decomposition under oxygen atmosphere could be correlated to the small but sharp DTG thermogram *peaks (iii)* in Figure 15. That is, the weight losses of gum NR, NR/IL, NR/CNT and NR/CNT-IL composites are 0.83, 0.91, 4.35 and 5.26%, respectively. The remaining char residues from gum NR vulcanizate (i.e., 0.83%) might represent various inorganic minor components. In addition, the large weight losses of NR/CNT and NR/CNT-IL could be from degradation of CNT and/or IL together with other components under the oxygen atmosphere.

3.7. Dynamic mechanical analysis (DMA)

Figure 16 shows the storage modulus (G') and the loss tangent ($\tan \delta$) as functions of temperature for the gum NR vulcanizate together with NR/CNT, NR/IL and NR/CNT-IL composites. Also, Table 8 shows glass transition temperature (T_g) and $\tan \delta_{\max}$ for the same cases. Higher storage moduli were seen in the glassy regions of NR/CNT, NR/IL and NR/CNT-IL composites than for the gum NR vulcanizate. This might be due to the reinforcement of NR

Figure 16. Storage modulus and $\tan \delta$ as functions of temperature for the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

Table 8. Glass transition temperature (T_g) and $\tan \delta_{\max}$ for the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

Sample	T_{g1} [°C]	T_{g2} [°C]	$\tan \delta_{\max}$
Gum NR	-52.7	—	1.38
NR/IL 5 phr	-55.3	-32.2	0.93
NR/CNT 5 phr	-55.8	—	1.09
NR/CNT-IL 5 phr	-51.4	-36.5	1.18

matrix by CNT and the mixture of CNT and IL. Likewise, the plasticizing effect of IL favored orientation of rubber molecules and the formation of three-dimensional CNT networks in the NR matrix.

In the glass transition state, the moduli of all samples abruptly decreased with temperature. It is clear that the composites with IL showed two decreasing stages while the ones without IL exhibited only a single stage of decreasing storage modulus. This correlates to the double $\tan \delta$ peaks of the composites with IL, but a single $\tan \delta$ peak for the composites without IL. This reflects the glass transitions of NR and BMI at different temperatures. Therefore, the gum NR compound and NR/CNT composite showed a single glass transition temperature (T_g) at -52.7 and -55.8 °C, respectively. On the other hand, the NR/IL composite showed double T_g s at -55.3 and -32.2 °C, which reflect the T_g s of NR and IL (BMI) phases, respectively. Hybridization in the CNT-IL filled NR matrix shifted the T_g of NR phase to a higher temperature (i.e., -51.4 °C) that was lower than the T_g of IL (BMI) at -36.5 °C. It is noted that shift of T_g might be due to the amorphous structure of rubber chains [46]. In Table 8, it can be seen that addition of CNT or IL decreased T_g of the NR phase. This is due to the increased free volume in the NR matrix, from CNT agglomeration which left NR molecular chains to move freely [34]. Moreover, the plasticizing effect of IL (BMI) favors molecular mobility [34], which reduced the level of entanglements of NR molecules. However, the NR/CNT-IL composite showed higher T_g of NR phase but lower T_g of IL (BMI) phase. This might be due to the good filler-rubber interactions favoring formation of CNT networks. Thus, the NR molecular mobility or flexibility was restricted by the formed CNT networks. Moreover, the addition of CNT-IL shifted T_g s of NR and IL (BMI) phases toward each other (i.e., the NR phase shifted to higher temperature while the IL (BMI) shifted to lower temperature). This suggests partial miscibility of the blend components [47]. In Table 8, it can be seen

that the incorporation of CNT, IL, and especially CNT-IL hybrid filler in the NR matrix reduced $\tan \delta$ max or the energy loss, meaning worsened damping properties.

3.8. Morphological properties

Figure 17 shows SEM micrographs of NR/IL (BMI), NR/CNT and NR/CNT-IL composites. White spots (Figure 17a) and large cavities (Figure 17b) were dispersed in the NR matrix of the NR/IL vulcanizate. The white spots might be accumulated BMI (crystalline salt) and/or ZnO particles dispersed in the NR matrix. Also, pores or voids could be the result of incompatibility between NR and BMI. In addition, the sample preparation for SEM inspection by cryogenic fracturing in liquid nitrogen could cause cracks or fractures on sample surfaces. In Figure 17c, both CNT particles and agglomerates are clearly seen in

the NR/CNT composite. However, a finer dispersion of CNT with smaller aggregates is also seen in the NR/CNT-IL composite (Figure 17d). Therefore, the plasticizing effect of IL effectively reduced CNT agglomeration and supported stronger three-dimensional network formation of CNT bundles. This might be attributed to the IL (BMI) reducing the Van der Waals forces between CNT bundles. The CNT particles were eventually covered by the IL molecules (as seen in Figure 11) that hindered the Van der Waals forces. Therefore, it is concluded that the morphological properties corroborate improved dispersion of CNT and formation of three-dimensional CNT networks in NR matrix by hybrid CNT-IL filler, which matches also other observations, of torque difference (Figure 3), storage modulus (Figure 7) and electrical properties (Figure 13).

Figure 17. SEM micrographs of NR/IL (focused on the white spots) (a), and NR/IL (focused on the cavitations) (b), NR/CNT (c) and NR/CNT-IL (d) composites.

3.9. Mechanical properties

Figure 18 shows stress-strain curves of gum NR vulcanizate together with NR/CNT, NR/IL and NR/CNT-IL composites. Also, tensile properties in terms of 100 and 300% moduli, tensile strength, and elongation at break are summarized in Table 9. It is seen that the addition of CNT, IL and CNT-IL affected the stress-strain behavior of NR vulcanizates. Furthermore, addition of IL (BMI) significantly increased the modulus of NR composite from that of the gum NR vulcanizate, which matches well the initial relaxation moduli (Figure 9 and Table 6). Also, this result agrees with the addition of IL (5 phr) in the ENR matrix increasing the Young's modulus [48]. This might be due to the physical interactions by π bonds of NR molecules and imidazolium rings [48]. In addition, lower 100% but higher 300% moduli were observed for the NR/IL than for the NR/CNT composite. This means that the NR/IL composites gained rigidity from added IL (BMI) via the physical interactions of NR and IL, as well as from the crystalline IL(BMI) phase in the matrix [48]. However, the hybrid CNT-IL filler gave the highest moduli with synergy of CNT and IL (BMI), along with the interactions among IL, CNT and NR described in Figure 2 (Reaction B).

Figure 18. Stress-strain curve of the gum NR vulcanizate together with NR/CNT, NR/IL and NR/CNT-IL composites.

Table 9. Mechanical properties in terms of tensile strength, elongation at break, and 100 and 300% moduli for the gum NR compound together with NR/CNT, NR/IL and NR/CNT-IL composites.

Sample	100% modulus [MPa]	300% modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]
Gum NR	0.73±0.20	1.63±1.85	15.59±2.78	709.30±10.57
NR/IL 5 phr	1.35±0.45	5.47±1.82	14.89±1.92	514.64±52.28
NR/CNT 5 phr	1.67±0.06	4.47±0.15	16.50±0.36	606.93±29.31
NR/CNT-IL 5 phr	2.36±0.69	7.73±1.88	15.13±2.31	418.02±53.87

This result matches well the initial moduli from the TSSR measurements (Figure 9) and the storage moduli from DMA measurements (Figure 16). In Table 9, lower tensile strength and elongation at break were seen with the addition of IL (BMI) than for the gum NR vulcanizate. Furthermore, higher tensile strength was observed for the NR/CNT composites for the gum NR and NR-IL vulcanizates. Moreover, slightly lower tensile strength and elongation at break were observed for the NR/CNT-IL than for the NR/CNT composites. This might be because the small IL molecules freely dispersed in the NR matrix and acted as defects that initiate failure, similar to that in the ENR/IL composite [48].

Effects of CNT, IL and CNT-IL on strain-induced crystallization of NR composites can be assessed from plots of reduced stress as functions of extension, according to the Mooney–Rivlin Equation (11) [49]:

$$\sigma^* = \frac{\sigma}{\lambda - \frac{1}{\lambda^2}} \quad (11)$$

where σ and λ are the stress and the extension ratio, respectively.

Figure 19 shows Mooney–Rivlin plots for the gum NR vulcanizate together with NR/CNT, NR/IL and NR/CNT-IL composites. According to the James and Guth approach [50], the reduced stress (σ^*) indicates the elastic modulus of composites [48] together with degree of strain-induced crystallization in the rubber vulcanizates, which can be estimated from the initial slope with $(1/\lambda) < 0.01$. It is seen that the gum NR vulcanizate showed the highest slope of 0.08, while the NR composites with IL, CNT and CNT-IL showed lower slopes at 0.02, 0.05 and 0.03, respectively. Therefore, the addition of CNT or CNT-IL affected significantly the crystallization behavior of NR during extension. This might be attributed to the interactions of CNT with NR by physical crosslinks that hindered orientation of the NR [5]. In the NR/IL composite, the crystalline BMI also restricted NR mobility, consequently reducing strain induced crystallization

Figure 19. Mooney–Rivlin plot of gum NR vulcanizate together with NR/CNT, NR/IL and NR/CNT-IL composites.

of the NR. Thus, incorporation of CNT-IL gave a slope (0.03) between those of the NR/CNT (0.05) and the NR/IL (0.02) composites. It is anticipated that some of the BMI reacted with CNT by physical adsorption. This could decrease the amount of crystalline BMI dispersed in the NR matrix. Therefore, adding IL (BMI) in the NR decreased torque difference (Figure 3) and storage moduli (Figure 7), but increased the initial moduli (Figure 9) and 100% moduli (Figure 18). In summary the combination CNT-IL had synergistic effects by enabling the CNT to form an infinite three-dimensional network in the NR matrix. This enhanced the dynamic properties (Figures 7 and 16), mechanical properties (Figures 18 and 19) and electrical properties (Figure 13) of NR composites from those of the gum NR vulcanizate.

4. Conclusions

The NR/CNT, NR/IL and NR/CNT-IL composites were prepared by latex mixing method. ATR-FTIR was then used to confirm the presence of IL and to assess the interactions of IL with CNT and NR. It was found that the C=C bonds in NR decreased and even disappeared after addition of CNT in NR matrix. This might indicate chemical interactions of NR and CNT. Furthermore, the dipole-dipole and π - π interactions of CNT and IL (BMI) were confirmed. It was also found that IL significantly influenced the vulcanization reaction kinetics in NR compounds. That is, the BMI might act as a cure retardant increasing the scorch time to favor safe processing of the NR compound. Also, the plasticizing effect of BMI contributed to

finer CNT dispersion in the NR matrix and three-dimensional filler network formation, and hence reduced the activation energy of vulcanization. However, conversion by vulcanization in the NR/IL compound decreased owing to reactions of imidazolium rings in IL (BMI) and mercaptobenzthiazole rings in MBT. This consumed some accelerator that initiates and propagates the vulcanization. In addition, the highest Payne effect was found in NR/CNT-IL composite, attributed to the three-dimensional CNT network formation in the NR matrix. Also, T_g increased with the addition of CNT-IL indicating mobility restrictions of NR. Furthermore, the NR/CNT-IL composites showed improved storage modulus, initial stress (σ_0), and 100 and 300% moduli of the composites from those of the gum NR vulcanizate. Incorporation of CNT-IL in NR matrix also had a synergistic effect on the electrical conductivity, because both CNT and IL (BMI) support electron transport. This effectively enhanced the electrical conductivity of the NR composites, by formation of three-dimensional CNT networks. Therefore, the NR/CNT-IL showed the best electrical conductivity and the least percolation threshold concentration.

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References

- [1] Tamil Selvan N., Eswaran S. B., Das A., Stöckelhuber K. W., Wießner S., Pötschke P., Nando G. B., Chervanyov A. I., Heinrich G.: Piezoresistive natural rubber-multiwall carbon nanotube nanocomposite for sensor applications. *Sensors and Actuators A*, **239**, 102–113 (2016).
<https://doi.org/10.1016/j.sna.2016.01.004>
- [2] Deng F., Ito M., Noguchi T., Wang L., Ueki H., Niihara K., Kim Y. A., Endo M., Zheng Q.-S.: Elucidation of the reinforcing mechanism in carbon nanotube/ rubber nanocomposites. *ACS nano*, **5**, 3858–3866 (2011).
<https://doi.org/10.1021/nn200201u>

- [3] Jose T., Moni G., Salini S., Raju A. J., George J. J., George S. C.: Multifunctional multi-walled carbon nanotube reinforced natural rubber nanocomposites. *Industrial Crops and Products*, **105**, 63–73 (2017).
<https://doi.org/10.1016/j.indcrop.2017.04.047>
- [4] Jin S., Park Y. J., Min H. S.: A three-dimensional simulation of quantum transport in silicon nanowire transistor in the presence of electron-phonon interactions. *Journal of Applied Physics*, **99**, 123719/1–123719/10 (2006).
<https://doi.org/10.1063/1.2206885>
- [5] Krainoi A., Kummerlöwe C., Nakaramontri Y., Vennemann N., Pichaiyut S., Wisunthorn S., Nakason C.: Influence of critical carbon nanotube loading on mechanical and electrical properties of epoxidized natural rubber nanocomposites. *Polymer Testing*, **66**, 122–136 (2018).
<https://doi.org/10.1016/j.polymertesting.2018.01.003>
- [6] Ma H. M., Gao X.-L.: A three-dimensional Monte Carlo model for electrically conductive polymer matrix composites filled with curved fibers. *Polymer*, **49**, 4230–4238 (2008).
<https://doi.org/10.1016/j.polymer.2008.07.034>
- [7] Subramaniam K., Das A., Simon F., Heinrich G.: Networking of ionic liquid modified CNTs in SSBR. *European Polymer Journal*, **49**, 345–352 (2013).
<https://doi.org/10.1016/j.eurpolymj.2012.10.023>
- [8] Nakaramontri Y., Nakason C., Kummerlöwe C., Vennemann N.: Influence of modified natural rubber on properties of natural rubber–carbon nanotube composites. *Rubber Chemistry and Technology*, **88**, 199–218 (2015).
<https://doi.org/10.5254/rct.14.85949>
- [9] Subramaniam K., Das A., Steinhauser D., Klüppel M., Heinrich G.: Effect of ionic liquid on dielectric, mechanical and dynamic mechanical properties of multi-walled carbon nanotubes/polychloroprene rubber composites. *European Polymer Journal*, **47**, 2234–2243 (2011).
<https://doi.org/10.1016/j.eurpolymj.2011.09.021>
- [10] Ahmadian Hoseini A. H., Arjmand M., Sundararaj U., Trifkovic M.: Significance of interfacial interaction and agglomerates on electrical properties of polymer-carbon nanotube nanocomposites. *Materials and Design*, **125**, 126–134 (2017).
<https://doi.org/10.1016/j.matdes.2017.04.004>
- [11] Umapathi R., Venkatesu P.: Thermo-responsive triblock copolymer phase transition behaviour in imidazolium-based ionic liquids: Role of the effect of alkyl chain length of cations. *Journal of Colloid and Interface Science*, **485**, 183–191 (2017).
<https://doi.org/10.1016/j.jcis.2016.09.034>
- [12] Fukushima T., Kosaka A., Yamamoto Y., Aimiya T., Notazawa S., Takigawa T., Inabe T., Aida T.: Dramatic effect of dispersed carbon nanotubes on the mechanical and electroconductive properties of polymers derived from ionic liquids. *Small*, **2**, 554–600 (2006).
<https://doi.org/10.1002/smll.200500404>
- [13] Das A., Stöckelhuber K. W., Jurk R., Fritzsche J., Klüppel M., Heinrich G.: Coupling activity of ionic liquids between diene elastomers and multi-walled carbon nanotubes. *Carbon*, **47**, 3313–3321 (2009).
<https://doi.org/10.1016/j.carbon.2009.07.052>
- [14] Marwanta E., Mizumo T., Nakamura N., Ohno H.: Improved ionic conductivity of nitrile rubber/ionic liquid composites. *Polymer*, **46**, 3795–3800 (2005).
<https://doi.org/10.1016/j.polymer.2005.02.113>
- [15] Marzec A., Laskowska A., Boiteux G., Zaborski M., Gain O., Serghei A.: The impact of imidazolium ionic liquids on the properties of nitrile rubber composites. *European Polymer Journal*, **53**, 139–146 (2014).
<https://doi.org/10.1016/j.eurpolymj.2014.01.035>
- [16] Laskowska A., Marzec A., Boiteux G., Zaborski M., Gain O., Serghei A., Maniukiewicz W.: Improving the ionic conductivity of carboxylated nitrile rubber/LDH composites by adding imidazolium bis(trifluoromethylsulfonyl)imide ionic liquids. *Macromolecular Symposia*, **342**, 35–45 (2014).
<https://doi.org/10.1002/masy.201300232>
- [17] George N., Bipinbal P. K., Bhadrar B., Mathiazhagan V., Joseph R.: Segregated network formation of multiwalled carbon nanotubes in natural rubber through surfactant assisted latex compounding: A novel technique for multifunctional properties. *Polymer*, **112**, 264–277 (2017).
<https://doi.org/10.1016/j.polymer.2017.01.082>
- [18] Nakaramontri Y., Nakason C., Kummerlöwe C., Vennemann N.: Enhancement of electrical conductivity and filler dispersion of carbon nanotube filled natural rubber composites by latex mixing and in situ silanization. *Rubber Chemistry and Technology*, **89**, 272–291 (2016).
<https://doi.org/10.5254/rct.15.84848>
- [19] Vennemann N., Wu M.: Thermoelastic properties and relaxation behavior of S-SBR/silica vulcanizates. *Rubber World*, **246**, 18–23 (2012)
- [20] Du F., Fischer J., Winey K.: Coagulation method for preparing single-walled carbon nanotube/poly(methyl methacrylate) composites and their modulus, electrical conductivity, and thermal stability. *Journal of Polymer Science Part B*, **41**, 3333–3338 (2003).
<https://doi.org/10.1002/polb.10701>
- [21] Safadi B., Andrews R., Glurke E. A.: Multiwalled carbon nanotube polymer composites: Synthesis and characterization of thin films. *Journal of Applied Polymer Science*, **84**, 2660–2669 (2002).
<https://doi.org/10.1002/app.10436>
- [22] Coates J.: Interpretation of infrared spectra, A practical approach. in ‘Encyclopedia of analytical chemistry’ (eds.: Meyers R. A.) Wiley, New York, 6–15 (2006).
<https://doi.org/10.1002/9780470027318.a5606>
- [23] Laskowska A., Marzec A., Boiteux G., Zaborski M., Gain O., Serghei A.: Investigations of nitrile rubber composites containing imidazolium ionic liquids. *Macromolecular Symposia*, **341**, 18–25 (2014).
<https://doi.org/10.1002/masy.201300150>

- [24] Sun H., Song X., Xu M., Zhang Y., Que W., Yang S.: Functionalization of carbon nanotubes via Birch reduction chemistry for selective loading of CuO nanosheets. *New Journal of Chemistry*, **39**, 4278–4283 (2015).
<https://doi.org/10.1039/C5NJ00283D>
- [25] Bevilacqua E. M., English E. S.: The scission step in hevea oxidation. *Journal of Polymer Science*, **49**, 495–505 (1961).
<https://doi.org/10.1002/pol.1961.1204915229>
- [26] Zheng W., Jia Z., Zhang Z., Yang W., Zhang L., Wu S.: Improvements of lanthanum complex on the thermal-oxidative stability of natural rubber. *Journal of Materials Science*, **51**, 9043–9056 (2016).
<https://doi.org/10.1007/s10853-016-0157-4>
- [27] Kiefer J., Fries J., Leipertz A.: Experimental vibrational study of imidazolium-based ionic liquids: Raman and infrared spectra of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-ethyl-3-methylimidazolium ethylsulfate. *Applied Spectroscopy*, **61**, 1307–1311 (2007).
<https://doi.org/10.1366/000370207783292000>
- [28] Subramaniam K., Das A., Stöckelhuber K. W., Heinrich G.: Elastomer composites based on carbon nanotubes and ionic liquid. *Rubber Chemistry and Technology*, **86**, 367–400 (2013).
<https://doi.org/10.5254/rct.13.86984>
- [29] Wang J., Chu H., Yan Li.: Why single-walled carbon nanotubes can be dispersed in imidazolium-based ionic liquids. *ACS Nano*, **2**, 2540–2546 (2008).
<https://doi.org/10.1021/nn800510g>
- [30] Wang Q.: Atomic transportation via carbon nanotubes. *Nano Letters*, **9**, 245–249 (2009).
<https://doi.org/10.1021/nl802829z>
- [31] Marzec A., Laskowska A., Boiteux G., Zaborski M., Gain O., Serghei A.: Properties of carboxylated nitrile rubber/hydrotalcite composites containing imidazolium ionic liquids. *Macromolecular Symposia*, **341**, 7–17 (2014).
<https://doi.org/10.1002/masy.201300149>
- [32] López-Manchado M. A., Arroyo M., Herrero B., Biagiotti J.: Vulcanization kinetics of natural rubber–organoclay nanocomposites. *Journal of Applied Polymer Science*, **89**, 1–15 (2003).
<https://doi.org/10.1002/app.12082>
- [33] Perez L. D., Zuluaga M. A., Kyu T., Mark J. E., Lopez B. L.: Preparation, characterization, and physical properties of multiwall carbon nanotube/elastomer composites. *Polymer Engineering and Science*, **49**, 866–874 (2009).
<https://doi.org/10.1002/pen.21247>
- [34] Salaeh S., Boiteux G., Cassagnau P., Nakason C.: Flexible 0–3 ceramic-polymer composites of barium titanate and epoxidized natural rubber. *International Journal of Applied Ceramic Technology*, **12**, 106–115 (2015).
<https://doi.org/10.1111/ijac.12129>
- [35] Jürgen E. K.: Collected application thermal analysis. *Schwerzenbach, Switzerland* (2002).
- [36] Wei C., Srivastava C., Cho K.: Thermal expansion and diffusion coefficients of carbon nanotube-polymer composites. *Nano Letters*, **2**, 647–650 (2002).
<https://doi.org/10.1021/nl025554>
- [37] Payne A. R., Whittaker R. E.: Low strain dynamic properties of filled rubber. *Rubber Chemistry and Technology*, **44**, 440–478 (1971).
<https://doi.org/10.5254/1.3547375>
- [38] Pongdong W., Kummerlöwe C., Vennemann N., Thithammawong A., Nakason C.: A comparative investigation of rice husk ash and siliceous earth as reinforcing fillers in dynamically cured blends of epoxidized natural rubber (ENR) and thermoplastic polyurethane (TPU). *Journal of Polymers and the Environment*, **26**, 1145–1159 (2018).
<https://doi.org/10.1007/s10924-017-1022-5>
- [39] Gatos K. G., Sawanis N. S., Apostolov A. A., Thomann R., Karger-Kocsis J.: Nanocomposite formation in hydrogenated nitrile rubber (HNBR)/organo-montmorillonite as a function of the intercalant type. *Macromolecular Materials and Engineering*, **289**, 1079–1086 (2004).
<https://doi.org/10.1002/mame.200400214>
- [40] Le H. H., Ilisch S., Radusch H. J.: Characterization of the effect of the filler dispersion on the stress relaxation behavior of carbon black filled rubber composites. *Polymer*, **50**, 2294–2303 (2009).
<https://doi.org/10.1016/j.polymer.2009.02.051>
- [41] Barbe A., Bökamp K., Kummerlöwe C., Sollmann H., Vennemann N.: Investigation of modified SEBS-based thermoplastic elastomers by temperature scanning stress relaxation measurements. *Polymer Engineering and Science*, **45**, 1498–1507 (2005).
<https://doi.org/10.1002/pen.20427>
- [42] Ferry J. D.: *Viscoelastic properties of polymers*. Wiley, New York (1980).
- [43] Pham G. T.: Characterization and modeling of piezoresistive properties of carbon nanotube-based conductive polymer composites. PhD thesis, Florida State University, Tallahassee (2008).
- [44] Ma P.-C., Siddiqui N. A., Marom G., Kim J.-K.: Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review. *Composites Part A: Applied Science and Manufacturing*, **41**, 1345–1367 (2010).
<https://doi.org/10.1016/j.compositesa.2010.07.003>
- [45] Li L., Yao X., Li H., Liu Z., Ma W., Liang X.: Thermal stability of oxygen-containing functional groups on activated carbon surfaces in a thermal oxidative environment. *Journal of Chemical Engineering of Japan*, **47**, 21–27 (2014).
<https://doi.org/10.1252/jcej.13we193>
- [46] Bai J., Goodridge R. D., Hague R. J. M., Song M., Okamoto M.: Influence of carbon nanotubes on the rheology and dynamic mechanical properties of polyamide-12 for laser sintering. *Polymer Testing*, **36**, 95–100 (2014).
<https://doi.org/10.1016/j.polymertesting.2014.03.012>

- [47] Nakason C., Panklieng Y., Kaesaman A.: Rheological and thermal properties of thermoplastic natural rubbers based on poly(methyl methacrylate)/epoxidized-natural-rubber blends. *Journal of Applied Polymer Science*, **92**, 3561–3572 (2004).
<https://doi.org/10.1002/app.20384>
- [48] Matchawet S., Kaesaman A., Vennemann N., Kumerlöwe C., Nakason C.: Effects of imidazolium ionic liquid on cure characteristics, electrical conductivity and other related properties of epoxidized natural rubber vulcanizates. *European Polymer Journal*, **87**, 344–359 (2017).
<https://doi.org/10.1016/j.eurpolymj.2016.12.037>
- [49] Bhattacharyya S., Sinturel C., Bahloul O., Saboungi M-L., Thomas S., Salvétat J-P.: Improving reinforcement of natural rubber by networking of activated carbon nanotubes. *Carbon*, **46**, 1037–1045 (2008).
<https://doi.org/10.1016/j.carbon.2008.03.011>
- [50] James H. M., Guth E.: Theory of the elastic properties of rubber. *The Journal of Chemical Physics*, **15**, 455–481 (1943).
<https://doi.org/10.1063/1.1723785>