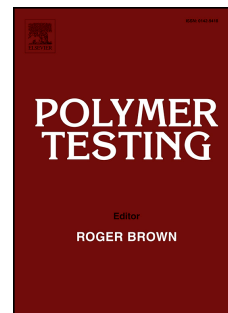


Journal Pre-proof

Highly enhanced electrical and mechanical properties of methyl methacrylate modified natural rubber filled with multiwalled carbon nanotubes

Subhan Salaeh, Anoma Thitithammawong, Arfandee Salae



PII: S0142-9418(19)31637-X

DOI: <https://doi.org/10.1016/j.polymertesting.2020.106417>

Reference: POTE 106417

To appear in: *Polymer Testing*

Received Date: 13 September 2019

Revised Date: 19 January 2020

Accepted Date: 8 February 2020

Please cite this article as: S. Salaeh, A. Thitithammawong, A. Salae, Highly enhanced electrical and mechanical properties of methyl methacrylate modified natural rubber filled with multiwalled carbon nanotubes, *Polymer Testing* (2020), doi: <https://doi.org/10.1016/j.polymertesting.2020.106417>.

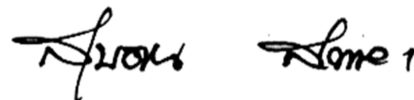
This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier Ltd.

Author Statement

We certify that this manuscript is original and is not under consideration for other publication elsewhere. The figures and tables in the manuscript are the original work of the authors.

Pattani, Thailand (19/01/2020)

A handwritten signature in black ink, appearing to read 'Subhan Salaeh', written in a cursive style.

Dr. Subhan Salaeh

Journal Pre-proof

Highly Enhanced Electrical and Mechanical Properties of Methyl Methacrylate modified Natural Rubber filled with Multiwalled Carbon Nanotubes

Subhan Salaeh^{*}, Anoma Thitithammawong, Arfandee Salae

Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, Pattani 94000, Thailand

^{*}Corresponding author, E-mail: subhan.s@psu.ac.th

Abstract

Developing conductive networks in a polymer matrix with a low percolation threshold and excellent mechanical properties is desired for soft electronics applications. In this work, natural rubber (NR) functionalized with poly(methyl methacrylate) (PMMA) was prepared for strong interfacial interactions with multiwalled carbon nanotubes (MWCNT), resulting in excellent performance of the natural rubber nanocomposites. The MWCNT and methyl methacrylate functional groups gave good filler dispersion, conductivity and tensile properties. The filler network in the matrix was studied with microscopy and from its non-linear viscoelasticity. The Maier-Göritz approach revealed that MWCNT network formation was favored in the NR functionalized with PMMA, with reduced electrical and mechanical percolation thresholds. The obvious improvement in physical performance of MWCNT/methyl methacrylate functionalized natural rubber nanocomposites was caused by interfacial interactions and reduced filler agglomeration in the NR matrix. The modification of NR with poly(methyl methacrylate) and MWCNT filler was demonstrated as an effective pathway to enhance the mechanical and electrical properties of natural rubber nanocomposites.

Keywords; Nano composites; Carbon nanotubes; Mechanical properties; Dynamic mechanical thermal analysis (DMTA); Electrical properties

1. Introduction

Conductive elastomer composites (CECs) have attracted considerable attention for decades now from both academic and industrial communities due to light weight, tunable conductivity, resistance to corrosion, and good processability. They have been exploited in various applications, such as strain sensing materials, electromagnetic interference (EMI) shielding, anti-static shielding, electronic sensors, and stretchable conductors [1-3]. Among the carbon-based fillers, carbon nanotubes (CNTs) are a well-known type of nanofillers with high aspect ratio, high surface area and superior electrical properties. However, obtaining a uniform dispersion of CNT in a rubber matrix is difficult due to their fluffy appearance, strong van der Waals forces, high aspect ratio, and nano-size, which all favor filler aggregation and poor dispersion [4]. Two typical challenges need to be overcome on preparing conductive CNT/elastomer nanocomposites. One is the weak interfacial interactions between CNT and elastomer. The second is the high electrical percolation threshold of rubber/CNT composites. Both these factors degrade mechanical and electrical properties. The physical and chemical interactions between filler and polymer are most important for the performance of CNT/elastomer composites. Therefore, improving the strength of interactions between CNT and polymer is necessary. In this regard, diverse studies have attempted to optimize the dispersion of CNT by improving interfacial interactions in these elastomer nanocomposites, especially assessing the mechanical performance of rubber CNT/composites. Various compatibilization approaches have been reported that fall into two groups: covalent compatibilization and non-covalent compatibilization.

Covalent compatibilization is adding or grafting desired functional groups onto CNT particles using covalent surface chemistry [5, 6]. This technique would damage the sp^2 -hybridized network, which is required for electron transport and conductivity, degrading the mechanical and electrical properties of the CNTs themselves. Non-covalent compatibilization means coating or wrapping the CNT surfaces with a surfactant, ionic liquid or polymer without covalent bonds between CNT and the modifying substance [5]. This technique does not change the structure and properties of CNT. For example, Becker et al. [7] also studied the dispersion of MWCNT in two different polyamides (PAs). They found that mixing MWCNT into aromatic PA provide better dispersion and filler distribution due to the π - π interactions between the aromatic hexagons and the carbon nanotubes. Moreover, several studies have dealt with cation- π and π - π interactions between compatibilizer and CNT [4, 8]. Subramaniam et al. [4] modified CNT with ionic liquid in chloroprene rubber (CR) and they found uniform dispersion in the modified CNT/CR composites. However, the surfactants that can be used for non-covalent compatibilization are very limited, and some cannot be used to modify CNTs with different functionalities. Therefore, novel effective and convenient approaches for compatibilization in CNT nanocomposites are highly desirable.

Herein, we developed an effective non-covalent compatibilization between MWCNT and NR using chemical functionalization of NR molecules with poly(methyl methacrylate) (PMMA). This functionalization technique is easy and scalable for compatibilizing CNT in polymer composites. The functionalization of NR with PMMA was done to prevent CNT aggregation and improve its dispersion in the NR matrix. This work aims to clarify structure-property relationships of NR and acrylic modified NR nanocomposites. High conductivity and reduction of percolation threshold, while keeping excellent mechanical properties, were also expected. Our results show beneficial effects of grafting the copolymer when incorporating CNT as filler in NR. The functionalization of NR with PMMA and the

fabrication of electrically conductive elastomer nanocomposites are schematically illustrated in Fig. 1.

2. Experimental

Materials. High ammonia (HA) concentrated latex containing 61% dry rubber was manufactured by Yala Latex Co., Ltd. (Thailand). Methyl methacrylate (MMA) monomer was purchased from Sigma-Aldrich (USA). The MMA was purified by a standard procedure before synthesis. Cumene hydroperoxide (CHP) and tetraethylene pentaamine (TEPA) were purchased from Fluka (Buchs, Switzerland). Phenolic resin (HRJ-10518) was manufactured by Schenectady International Inc., New Port, USA. *N*-(1,3-Dimethylbutyl)-*N'*-phenyl-p-phenylenediamine (6PPD) was manufactured by Eliokem Inc., OH, USA. Multiwall carbon nanotubes (MWCNT) with trade name NC7000TM were purchased from Nanocyl S.A., Belgium. These MWCNT have an average diameter of 9.5 nm, average length of 1.5 μm , aspect ratio >150 and specific surface area of 250-300 m^2/g .

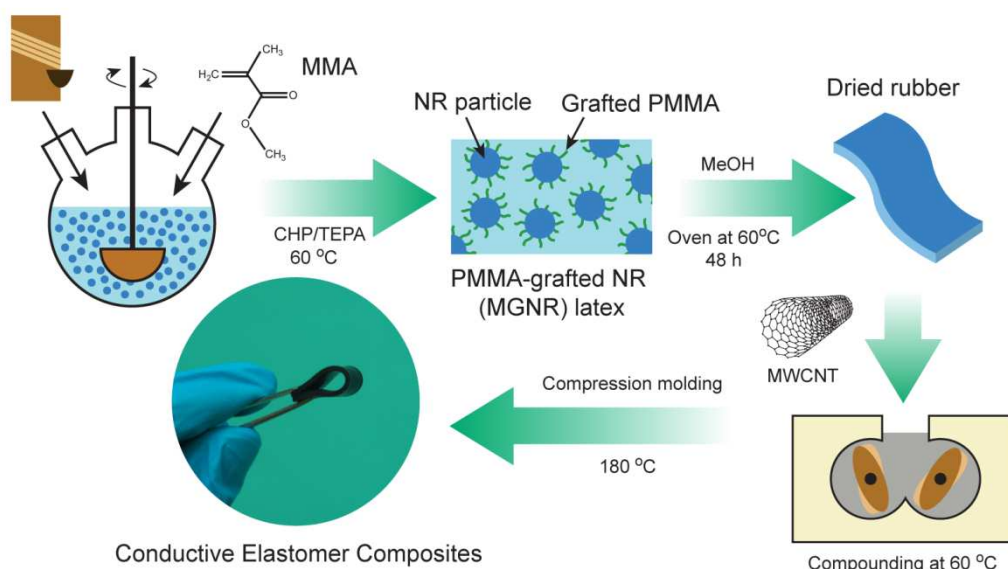


Fig. 1. Schematic diagram for the preparation of conductive elastomer composites from methacrylate modified natural rubber by filling with multiwalled carbon nanotubes.

Functionalization of NR with PMMA. The graft copolymer of natural rubber with methyl methacrylate (NR-*g*-PMMA) was synthesized at fixed NR/MMA monomer ratio of 80/20, as previously described elsewhere [9]. In brief, potassium laurate as stabilizer and tetraethylene pentaamine (TEPA) as redox initiator were added into high ammonia NR latex, which was the main reactant. The mixture was diluted to 50% total solids content (TSC) with distilled water and then it was stirred for at least 30 min at 60°C with N₂ purging. In the feed tank, the MMA was mixed with CHP and was thereafter dropped into the main reactor. The emulsion polymerization was carried out at 60°C for 3 h with constant stirring. The PMMA grafted natural rubber latex was coagulated using methanol, washed with distilled water, and then dried in an oven at 50 °C until constant weight. For convenience, the poly(methyl methacrylate)-grafted natural rubber prepared in this work is here labeled MGNR.

Preparation of rubber/MWCNT nanocomposites. The compounds of NR or MGNR with MWCNT as filler were prepared by shear mixing in a 50 ml Bradender Plasticorder. The amounts of additives are reported as parts per hundred of rubber by weight, or in “phr” units. The compounding and curing formulations had 1 phr 6PPD, 7 phr HRJ-10518 and 0-20 phr MWCNT. The shear mixing was performed at 60°C and 60 rpm mixing speed for a total mixing time of 10 minutes. Then 2 mm thin rubber films were prepared using a hydraulic press at 180°C for the appropriate cure times derived from curing curves.

Characterization. IR spectra of purified NR and MGNR samples were recorded using an attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrophotometer (Tensor 27, Bruker Optics, Ettlingen, Germany), equipped with a germanium ATR crystal probe, at 4 cm⁻¹ resolution with 32 scans per sample over the wavenumber range 4000–400 cm⁻¹. Raman spectra were recorded using a Raman spectrometer (RAMA Nforce, Nanophoton, Osaka, Japan) with a laser of 785 nm wavelength

to excite the samples at 1 mW. Mechanical tests of the composites were performed according to ASTM D412 using a universal tensile testing machine (Hounsfield Tensometer, model H 10KS, Hounsfield Test Equipment Co., Surrey, UK) at crosshead speed of 500 mm/min. The alternating current (ac) conductivity of a nanocomposite was determined at room temperature over the frequency range 10^2 - 10^6 Hz using a Precision Impedance Analyzer (Agilent 4294A, Keysight Technologies, Santa Rosa, CA, USA) with dielectric test fixture 16451B. Thin samples of 10 mm diameter and thickness of about 1.5 mm were used in the measurements. A dynamic mechanical analyzer (DMA 8000, Perkin-Elmer, Inc., Waltham, MA, USA) was used to test the storage modulus and $\tan \delta$, sweeping the temperature from -80 to 100°C at a rate of 3°C/min. Rectangular samples were tested in tension mode at the fixed 10 Hz frequency. The dynamic rheological measurements of the crosslinked composites were recorded with a Rubber Process Analyzer (RPA 2000, Alpha Technologies, Akron, OH, USA) at 60°C. In these determinations the strain amplitude was increased in logarithmic steps from 0.3 to 100% at a frequency of 1 Hz. The MWCNT dispersion in the rubber matrix was investigated by imaging with field emission scanning electron microscope (FESEM, Apreo, FEI Ltd., Hillsboro, OR, USA) and transmission electron microscope (TEM, JEM-2010, JEOL Ltd., Tokyo, Japan), which were operated at 5 kV and 200 kV, respectively. For SEM observation, the samples were cryogenically fractured in a liquid nitrogen bath. The dried fracture surfaces were then sputter coated with a thin layer of gold prior to imaging. For TEM imaging, ultrathin films were prepared by using a microtome (Boeckler Instruments, Inc., Arizona, USA) at -100°C.

3. Results and discussion

3.1 Structural characterization

The functionalization of NR with PMMA was initially verified from FTIR spectra, shown in the Supporting information, Fig. S1. NR and MGNR show similar absorption bands

as *cis* 1,4-polyisoprene: 749 (CH₂ rocking), 839 cm⁻¹ (=C-H out of plane bending vibration), 1309 cm⁻¹ (CH₂ wagging), 1373 cm⁻¹ (CH₃, asymmetrical stretching), 1450 cm⁻¹ (CH₂ symmetrical stretching and CH₃, asymmetrical deformation), 1660 cm⁻¹ (C=C stretching), 2725 cm⁻¹ (overtone of CH₃ asymmetrical deformation), 2852 cm⁻¹ (-CH₂- and -CH₃, symmetrical stretch), 2924 (-CH₂- asymmetrical stretching), 2965 (-CH₃ asymmetrical stretching), and 3039 cm⁻¹ (=CH stretching) [10, 11]. In contrast, the FTIR spectrum of MGNR has new evident bands of acrylic group of PMMA: 988 cm⁻¹ (C-O-CH₃ rocking), 1148 and 1192 cm⁻¹ (C-O stretching vibration), and 1730 cm⁻¹ (C=O stretching) [12-14]. This confirms the successful grafting of PMMA onto NR backbones. Fig. S2 shows ¹H-NMR spectra of NR and MGNR. The success in graft copolymerization was confirmed by appearance of the peak at 3.61 ppm in the ¹H-NMR spectra, which corresponds to methoxy proton of the acrylic group in the grafted PMMA, as shown in Fig. S2b [15]. The mole percentage of grafted PMMA was calculated from integrated peak areas at 5.13 ppm and 3.61 ppm, as previously described elsewhere [15]. In this work, it was found that the MGNR had 15 mol% of grafted PMMA.

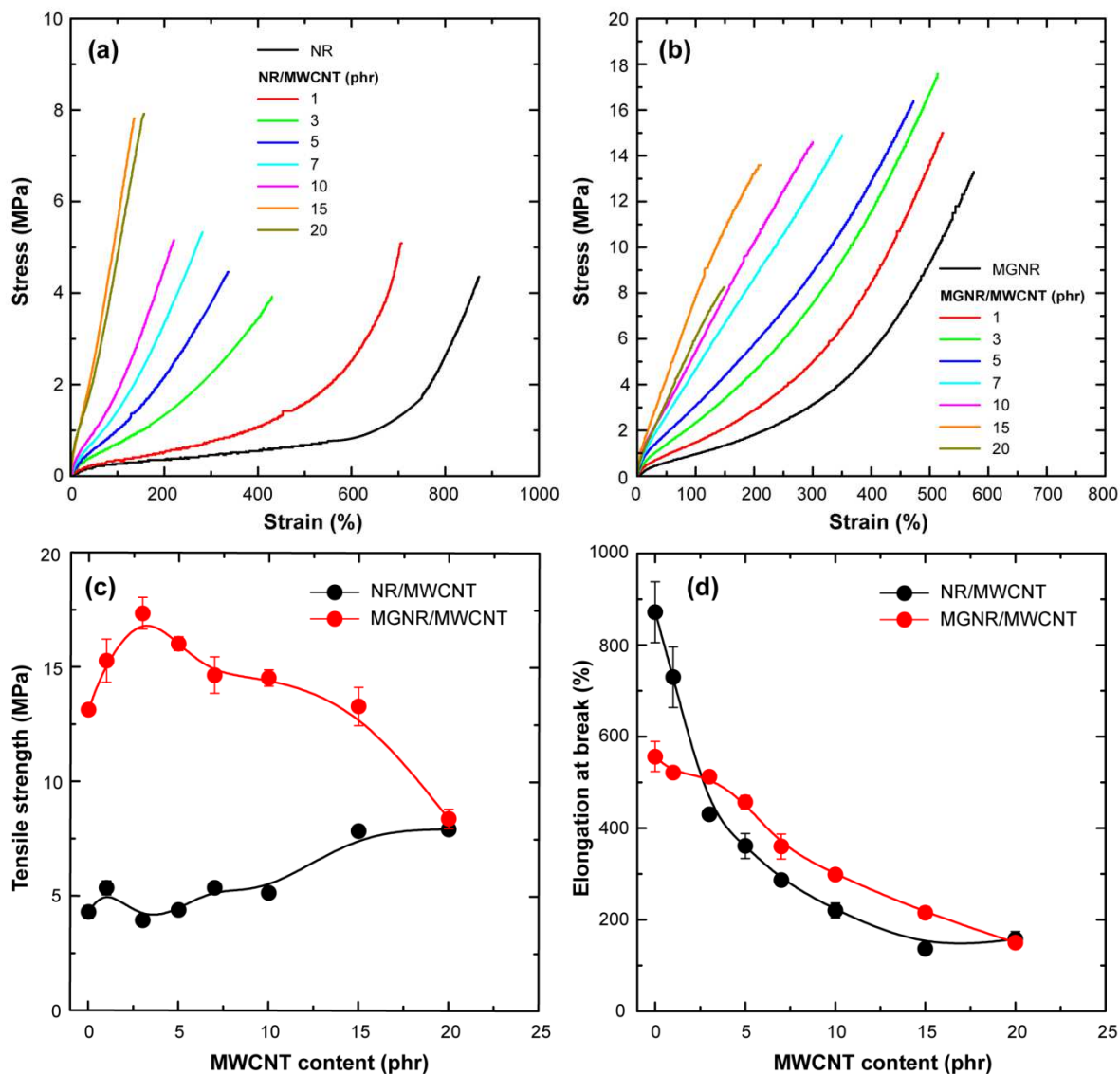


Fig. 2. The tensile stress versus strain curves of (a) NR/MWCNT, and (b) MGNR/MWCNT. (c) Tensile strength, and (d) elongation at break as functions of MWCNT loading.

3.2 Mechanical properties and morphology of nanocomposites

Typical stress-strain curves of NR/MWCNT and MGNR/MWCNT composites with various MWCNT contents are shown in Figs. 2a and 2b, respectively. The unfilled MGNR showed higher tensile strength but lesser extensibility than unfilled NR. This is because grafting PMMA onto NR increased the stiffness of rubber and decreased chain mobility. Incorporation of MWCNT in NR and MGNR increased stiffness whereas flexibility was reduced by restricted chain mobility. The effects of MWCNT content on the tensile strength

and elongation at break in NR and MGNR nanocomposites are shown in Figs. 2c and d. The NR/MWCNT nanocomposites showed no significant increase in tensile strength. In contrast, the tensile strength of MGNR/MWCNT nanocomposites initially increased and reached the maximum value of 17.4 MPa when only 3 phr of MWCNT was added, indicating that a small loading of MWCNT considerably improved the mechanical properties of MGNR. The increase in tensile strength at low loading levels of a nanofiller is mainly attributed to the strong interfacial interactions between the nanofiller and the polymer matrix, inducing good dispersion of the nanofiller in the matrix [16-18]. Beyond 3 phr, the tensile strength of MGNR/MWCNT nanocomposite gradually decreased but remained still higher than that of the NR/MWCNT nanocomposite. The decrease in tensile strength at high loading levels might be due to MWCNT filler agglomeration [19]. Regarding the elongation at break, it tended to decrease with MWCNT content for both types of matrices. Meanwhile, the elongation at break of MGNR/MWCNT nanocomposites was slightly higher than that of NR/MWCNT nanocomposites with MWCNT in the range of 5 – 15 phr. The decreasing trend of elongation at break with MWCNT loading is typical in polymer nanocomposites because MWCNT has high specific surface area, stiffness, and aspect ratio, contributing to stiffness and restricting the movements of polymer chains [8, 20]. In addition, the dominance of filler-filler interaction over polymer-filler interactions at high filler loadings decreased elongation at break and caused loss of flexibility [21]. Such deterioration of extensibility was clearly observed for both types of nanocomposites, as shown in Fig. 2d.

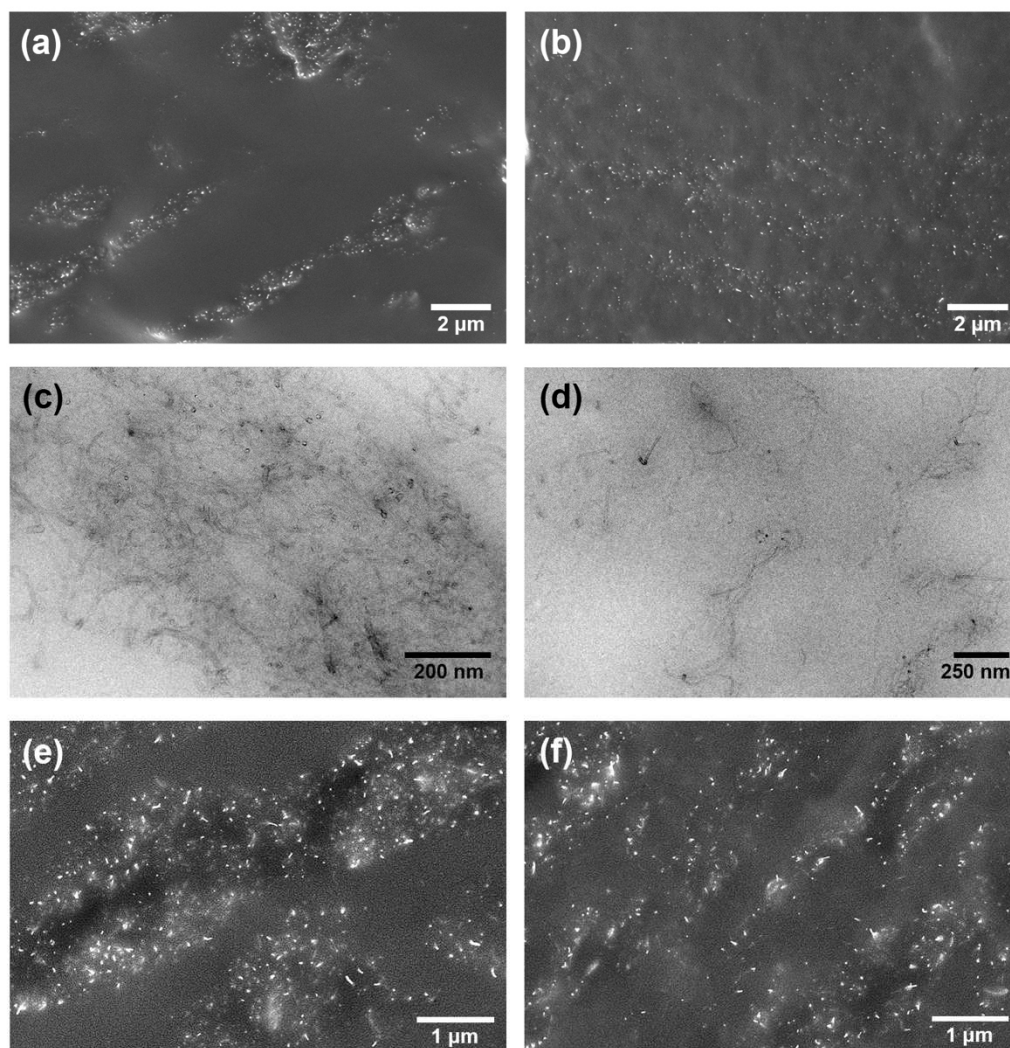


Fig. 3. FESEM and TEM micrographs of rubber nanocomposites with (a-d) 3 phr and (e and f) 5 phr MWCNT loadings; (a, c, and e) NR/MWCNT (b, d and f), MGNR/MWCNT nanocomposites.

The morphology of the composites was studied using SEM and TEM imaging to assess the state of dispersion of MWCNT filler in rubber matrix. The FESEM and TEM micrographs of NR/MWCNT and MGNR/MWCNT, shown in Figs. 3 and S3, demonstrate that the dispersion of MWCNT in MGNR is much better than in NR/MWCNT composites. As the MWCNT content increases to 5 phr (Fig. 3e and f), MGNR nanocomposites still show fairly uniform filler dispersion as compared to NR nanocomposites. The agglomeration of MWCNT observed in unmodified NR matrix is caused by low MWCNT-NR affinity, strong

van der Waals forces between the individual MWCNTs, and high aspect ratio of MWCNT [22].

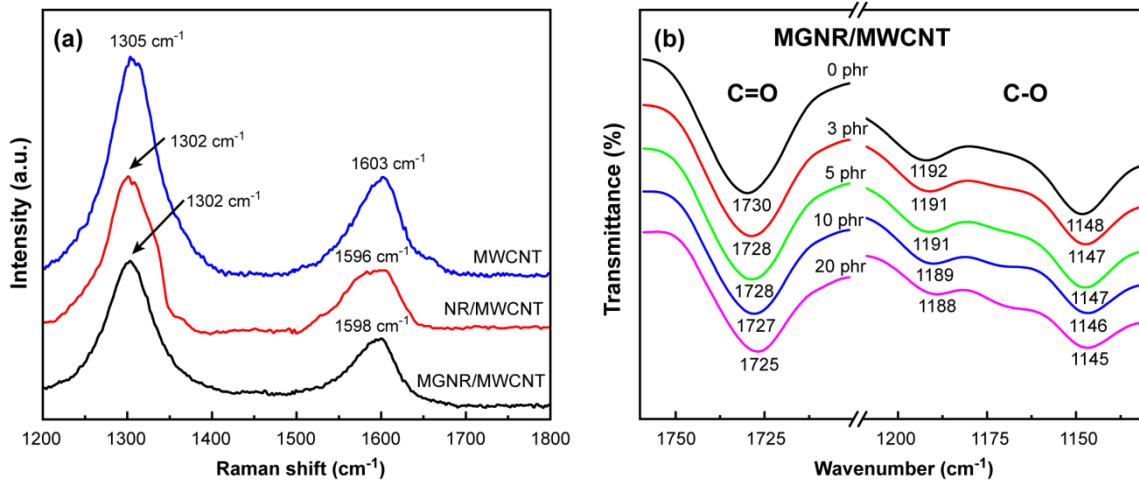


Fig. 4. Raman spectra of pure MWCNT and rubber nanocomposite containing 5 phr MWCNT, and (b) variations of C=O group (~ 1730 cm⁻¹) as well as C-O group (~ 1192 and ~ 1148 cm⁻¹) in FTIR spectra of MGNR/MWCNT nanocomposites with various amounts of MWCNT.

In the reinforced nanocomposites, it is also believed that the enhanced interfacial interactions between nanofiller and polymer matrix play an importance role affecting the mechanical properties and dispersion of nanofillers [8]. Raman spectroscopy is widely used to evaluate the interactions between MWCNT and a polymer matrix [23, 24]. Fig. 4 shows Raman spectra of the MWCNT and the rubber nanocomposite containing MWCNT at 5 phr. The nanotubes show D-band and G-band at 1341 and 1598 cm⁻¹, respectively. The D-band represents defects in the graphitic structure of MWCNT. The G-band represents the C–C vibrations of delocalized π -electrons with sp^2 hybridization [23, 25]. It is noteworthy that an upshift by 5 cm⁻¹ was observed for the G-band of MGNR nanocomposites. Although the upshift of G-band for this composite is lower than that reported in Refs. [23, 26], small upshifts of G-band have also been observed for other CNT-polymer composites [27, 28]. The

upshift of G-band is associated with physical and chemical interactions between the grafted PMMA chains on MGNR and the MWCNTs [27, 29]. However, the G-bands of NR/MWCNT nanocomposites shifted to lower wave numbers. Thomas et al. [30] also observed the shifting of G-band to lower wave number for the MWCNT composites with high filler loading. FTIR analysis further supports interfacial interactions, by the strong shifts of absorption bands for C=O and C-O groups of PMMA chains, as shown in Fig. 4b. These shifts towards lower wavenumbers of the functional groups in PMMA chains with MWCNT content indicate interfacial interactions between carbonyl groups of the MGNR matrix and MWCNT [27]. In the case of NR/MWCNT, the absorption bands belonging to C=C vibrations did not shift in the IR spectra, as shown in Fig S4. The absence of a shift indicates that the unsaturated bonds (C=C) in unmodified NR did not interact with the nanotubes. However, a clear shift of C=C vibrations in NR was observed only at a high MWCNT loading (20 phr). As shown in Fig. S5, the absorption bands at 3383 and 1741 cm^{-1} of the pristine MWCNTs specimens represent stretching vibrations of hydroxyl groups (-OH) and carbonyl groups (C=O) in the MWCNTs, respectively. Although this MWCNT is not functionalized, the surface of pristine MWCNT generally has oxygen-containing functional groups: epoxy, hydroxyl, carbonyl, and carboxyl groups, induced during production in the purification process [31, 32]. Therefore, the upshift of G-band in Raman spectra and absorption bands of the PMMA groups in FTIR spectra, discussed above, are likely due to dipole-dipole interactions between carbonyl groups in the MGNR and oxygen-containing functional groups in MWCNT filler [24, 33]. Moreover, the upshift of the G-band to higher frequencies can be attributed to interactions of polymer chains with MWCNT aggregates during melt mixing [22, 34]. Therefore, grafted PMMA chains in MGNR may facilitate penetration of MGNR into MWCNT bundles and improve the dispersion of MWCNT in MGNR matrix, as compared with unmodified NR, supported by our morphology assessment.

Uniform dispersion and interfacial interactions affect eventual stress-transfer between MWCNT filler and MGNR matrix, and this can dramatically affect the mechanical properties of the MGNR/MWCNT nanocomposites [17, 18, 35].

3.3 Electrical properties

Fig. 5 displays the frequency dependence of ac conductivity for NR/MWCNT and MGNR/MWCNT nanocomposites with the tested MWCNT contents. The ac conductivity of pure rubber and of the non-conductive composites increased with frequency. The ac conductivity with both types of matrix increased with MWCNT content over the whole frequency range. The nanocomposites with 5 phr MWCNT in NR and with 3 phr in MGNR had a low-frequency plateau, indicating the transition from insulating to conductive, as the MWCNT formed an electrically conductive network in the matrix already at a low concentration.

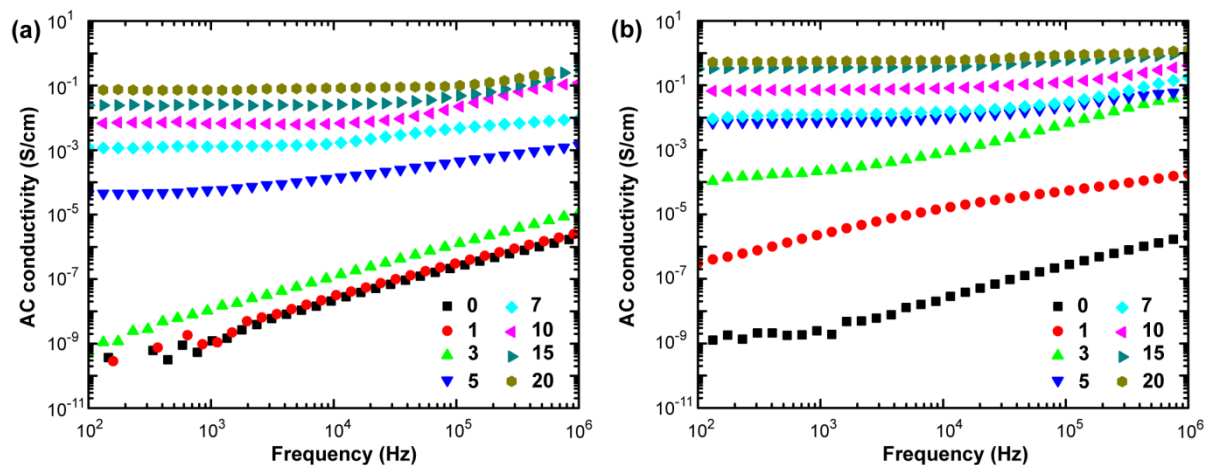


Fig. 5. AC conductivity versus frequency for (a) NR/MWCNT, and (b) MGNR/MWCNT.

The ac conductivity was constant over low frequencies, more so as CNT loading increased, corresponding to dc conductivity as characteristic of conductive materials. With increasing CNT content, the plateau region extended to cover the range of frequencies tested. The conductivity of a composite at a low frequency can be estimated from

$$\sigma'(\omega) = \sigma(0) + \sigma_{AC}(\omega) = \sigma_{DC} + A\omega^s \quad (1)$$

where σ_{AC} and σ_{DC} are the ac and dc conductivities, respectively. A is a temperature-dependent constant and s is an exponent dependent on both frequency and temperature. The first term in Eq. 1 is the true dc-conductivity (σ_{DC}) of the material, which is frequency-independent, and is the asymptote of ac conductivity at very low frequencies ($\omega \rightarrow 0$). The frequency-independence of ac conductivity emerges when continuous conductive networks are formed in the polymer matrix. The second term σ_{AC} or $A\omega^s$ is frequency dependent, due to the mechanism of electron transport by hopping over gaps.

The variation of dc conductivity for NR/MWCNT and MGNR/MWCNT composites with CNT loading is shown in Fig. 6. When a small loading of CNT was introduced into the rubber matrix, the conductivity slightly improved despite the insulating rubber matrix. However, at the same 1 phr amount of MWCNT the conductivity of MGNR/MWCNT composite is higher than that of NR/MWCNT composite. A dramatic increase in conductivity was observed with further increase in CNT loading, indicating the formation of conductive networks in NR and MGNR matrices, and this transition takes place at the percolation threshold concentration of the conductive filler. The electrical percolation threshold can be estimated from percolation theory, by the well-known scaling law.

$$\sigma = \sigma_0(p - p_c)^t \quad \text{when } p > p_c \quad (2)$$

In Fig. 6, the best fits to experimental data with Eq. 2 are shown with $p_c = 4.61$ phr for NR/MWCNT and $p_c = 2.25$ phr for MGNR/MWCNT. These values indicate conductive nanotube networks in the rubber matrices. Moreover, it was found that the critical exponent t was about 1.97 for MGNR/MWCNT, which is less than that for NR/MWCNT composites ($t=2.8$). The lower percolation threshold ($p_c = 2.25$) and universal value ($t = 1.97$) of MGNR/MWCNT composites is attributed to better dispersion of MWCNT in the MGNR

matrix and indicates a three-dimensional conductive network [36]. In contrast, the NR/MWCNT composites showed a higher percolation threshold ($p_c = 4.61$) and a larger critical exponent ($t = 2.8$), suggesting larger distances between MWCNT bundles in the NR matrix. Evidently, the low percolation threshold of MGNR/MWCNT nanocomposites suggests excellent dispersion of MWCNT and non-covalent compatibilization between grafted PMMA and MWCNT, as discussed earlier. Moreover, MGNR as the matrix not only reduced the percolation threshold but also improved the conductivity above the percolation threshold, as seen in Fig. 6, indicating that the specific interactions between functionalized PMMA and MWCNT aided in the formation of conductive networks, and improved the electrical properties of these polymer nanocomposites. The low percolation threshold, high flexibility and good mechanical properties of conductive MGNR/MWCNT nanocomposites indicate potential for use as a strain sensor or in smart polymer materials [37, 38].

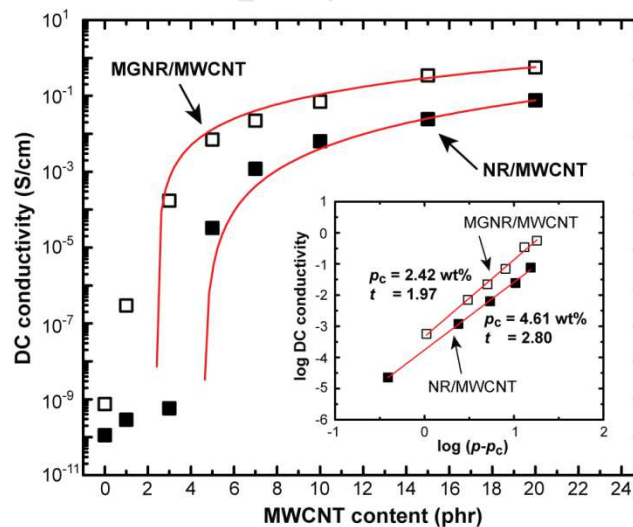


Fig. 6. DC conductivity (σ) as function of MWCNT content in NR and MGNR. The inset shows the log-log plot of σ versus $p - p_c$ with least squares fitted lines and parameter estimates from the fits.

3.4 Non-linear viscoelastic studies

The effects of strain amplitude on shear modulus at various CNT concentrations in the conductive nanocomposites are shown in Fig. 7. Generally, unfilled rubber does not show any dependency of the dynamic modulus on strain while filled rubber composites show strong dependencies. That is, the storage modulus typically decreases with strain amplitude due to the breakdown of filler-filler interactions [4, 39-41]. The difference in shear modulus between low and high strain is known as the Payne effect, and this got significantly stronger with increasing MWCNT loading in both NR/MWCNT and MGNR/MWCNT nanocomposites. As shown in Fig. 7, the G' of MGNR/MWCNT is higher than that of NR/MWCNT as the same filler loading.

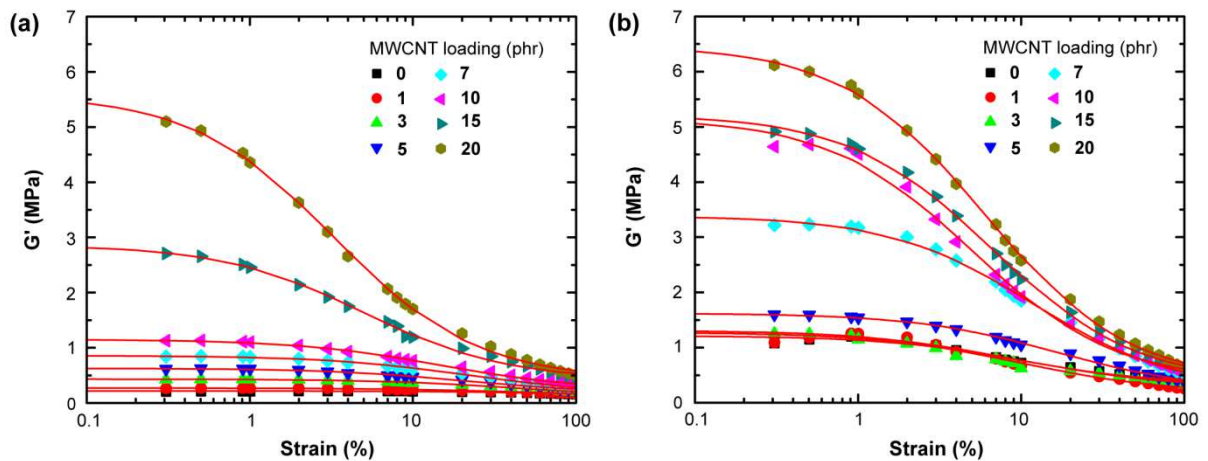


Fig. 7. Strain dependence of the shear modulus for (a) NR, and (b) MGNR, filled with various MWCNT loadings. The solid lines are fits based on the Maier-Göritz model (Eq. 5).

The Maier-Göritz model has been used to interpret the Payne effect, based on the polymer-filler interactions. During mixing the rubber chains are adsorbed onto the filler, first with so-called “stable bonds”. After formation of a stable bond on the filler surface, the remaining chain has less opportunity to contact and bond with the filler, so it is only able to form “unstable bonds” with very weak interactions [42-44]. Those bonds contribute to the

network density in a filled compound, which is directly related to storage modulus (G') and Payne effect [45, 46];

$$G' = Nk_B T \quad (3)$$

where N is the network density in the filled compound and k_B is the Boltzmann constant.

According to Maier and Göritz, the network density is given by [44];

$$N = N_c + N_{st} + N_l \quad (4)$$

where N is the total network density, N_c is the chemical network density, N_{st} is the network density caused by stable bonds at the filler surfaces and N_l is the density of unstable bonds between rubber and filler.

The relationship between storage modulus and strain (γ) is then as follows [45, 46]:

$$G'(\gamma) = G'_{st} + G'_l \frac{1}{(1+c\gamma)} \quad (5)$$

where G'_{st} is the storage modulus at large strain or deformation, G'_l is the amplitude of the Payne effect, and c is an experimentally determined parameter.

The Maier-Göritz model has been applied to experimental data with varied MWCNT loadings. The curve fits with Maier-Göritz model to our data are shown in Fig. 7, and the found model parameters are given in Table 1, showing that the storage modulus at high strain (G'_{st}) and the amplitude of Payne effect (G'_l) both increased with CNT content. The MGNR/MWCNT nanocomposites showed larger Payne effect than the NR/MWCNT nanocomposites. This suggests that polymer-filler and filler network interactions in the MGNR matrix were stronger than in the unmodified NR matrix. The large storage modulus difference as Payne effect in the MGNR/MWCNT nanocomposites was due to the comparatively large storage modulus of unfilled MGNR matrix relative to the NR matrix,

giving a large storage modulus to the MGNR/MWCNT nanocomposites. In addition, the large Payne effect of MGNR/MWCNT nanocomposites indicates strong interactions between MWCNT and MGNR, more networking of MWCNT filler in the nanocomposites, and better dispersion of CNTs in the matrix [45, 47]. Subramaniam et al. [4, 48] also found that the CNT nanocomposites with good dispersion and small agglomerates showed larger Payne effects when a modified CNT gave improved dispersion. The improved filler-filler network in MGNR/MWCNT nanocomposites, seen in the non-linear viscoelasticity assessment, is consistent with the low percolation threshold of MWCNT that also relates to electrical conductivity.

Table 1. Model parameters in the Maier-Göritz model from fits to experimental data on the variously filled composites.

MWCNT (phr)	G'_{st} (MPa)		G'_1 (MPa)		c	
	NR	MGNR	NR	MGNR	NR	MGNR
0	0.10	0.19	0.11	0.94	0.02	0.09
1	0.10	0.19	0.17	1.09	0.02	0.10
3	0.11	0.22	0.32	0.98	0.02	0.13
5	0.17	0.33	0.46	1.40	0.05	0.06
7	0.17	0.35	0.70	3.12	0.05	0.09
10	0.23	0.39	0.91	4.77	0.07	0.20
15	0.42	0.43	2.44	4.85	0.20	0.15
20	0.43	0.44	5.16	6.05	0.31	0.17

3.5 Dynamic mechanical properties and mechanical percolation

The variations of storage modulus and $\tan \delta$ across the NR/MWCNT and MGNR/MWCNT nanocomposites are shown in Fig. S6. The storage modulus consistently increased with MWCNT content, due to both the hydrodynamic effect and the immobilized rubber on filler surfaces. In rubbery state the storage modulus of MGNR/MWCNT nanocomposites is higher than that of NR/MWCNT nanocomposites. This is attributed to

better MWCNT dispersion, enhanced interfacial interactions, and improved filler networking in the MGNR matrix, as observed earlier.

The $\tan \delta$ peak generally identifies the T_g of a polymer. The shifting of T_g to higher temperature generally indicates that the mobility of rubber molecules is restricted by filler surfaces. However, for the NR nanocomposites of this study it was found that the T_g shifted to a lower temperature as MWCNT loading increased. Decreasing T_g upon adding fillers is caused by the low absorption of molecular chains on CNT surfaces [26, 49]. In contrast, T_g for MGNR nanocomposites was almost constant when MWCNT loading was varied. The remaining T_g as that of unfilled MGNR also indicates some interactions between filler and matrix. Moreover, it is interesting to note that, at the same concentration, the unfilled MGNR and its nanocomposite exhibited lower $\tan \delta$ peaks than the corresponding NR nanocomposites, indicating improved dynamic properties with less heat buildup and damping in the MGNR composites [50].

The storage modulus at 25°C and low strain amplitude from DMA analysis can be used to assess mechanical percolation by using the excess modulus (e), defined as $(E-E_0)/E_0$ where E and E_0 are the initial moduli of filled and unfilled rubber [22], respectively. A log-log plot of the excess modulus as function of the volume fraction (ϕ) of filler is shown in Fig. 8. The switch points of two line segments can be used to estimate the mechanical percolation thresholds for both NR and MGNR nanocomposites. The NR/MWCNT nanocomposites had percolation threshold around filler volume fraction 0.047, which corresponds to 10 phr. With the modified NR the percolation threshold shifted to 0.025 (~5 phr), indicating that CNT can form filler networks at a comparatively low loading level in the MGNR matrix. It well-known that uniform dispersion of filler in a polymer matrix gives high interfacial area and short inter-particle distances, which facilitate forming a connected network at a low filler loading [51].

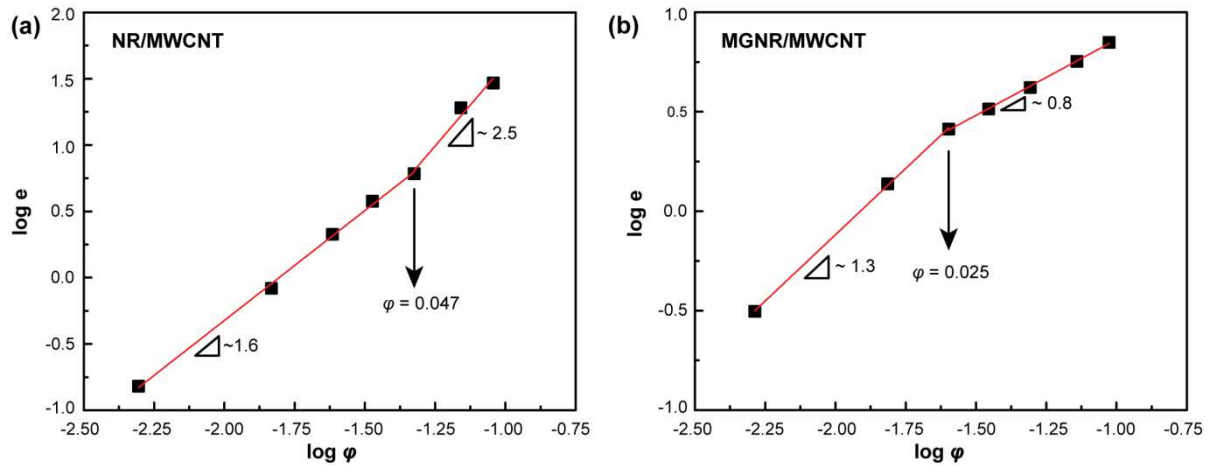


Fig. 8. Log-log plots of the excess modulus (e) as function of filler volume fraction for the two types of matrices tested.

Huber and Vilgis [52] proposed that below the percolation threshold the excess modulus should scale proportionally (slope = 1) with the volume fraction of carbon black in filled rubber. However, in this study the exponent at low filler content is greater than 1, which might be due to the high aspect ratio and reinforcement effects of carbon nanotubes in rubber. Above the percolation threshold the NR nanocomposites show a straight line in the log-log plots, with slope/exponent 2.5, whereas the MGNR nanocomposites give exponent 0.8. According to the Huber and Vilgis approach, this exponent n depends on the fractal dimension, d_f , of the filled materials by the equation $n = 2 / (3 - d_f)$. The application of this equation results in $d_f = 2.2$, which is close to the theoretical d_f for diffusion-limited aggregation (DLA) ($d_f = 2.5$). Therefore, this suggests a cluster–cluster aggregation (CCA) mechanism. In the case of MGNR/MWCNT nanocomposites, the exponent $n = 0.8$ approaches the nearly vanishing fractal dimension $d_f = 0.5$, indicating reduced size of the filler clusters. Similar observations were reported for natural rubber/expanded organo-montmorillonite nanocomposites [43].

Moreover, the low mechanical percolation threshold of MGNR/MWCNT is also confirmed by a plot of Young's modulus against the volume fraction of filler, shown in Fig.

9a. Above the percolation limit, a power-law for jammed systems was employed to estimate the mechanical percolation threshold [53, 54];

$$E = E_1 + A(\varphi - \varphi_p)^n \text{ for } \varphi > \varphi_p \quad (6)$$

where φ is the volume fraction of MWCNT, φ_p is the percolation threshold volume fraction of MWCNT, and E_1 is the elastic modulus of the composite for $\varphi = \varphi_p$. As shown in Fig. 9a, the best fit to Young's modulus data with Eq. 6 yields $\varphi_p = 0.050$ (~10 phr) for NR/MWCNT and $\varphi_p = 0.021$ (~5 phr) for MGNR/MWCNT. The φ_p estimates from Eq. 6 match the earlier switch point estimates well, as shown in Fig. 8. The exponent n found from Eq. 6 is quite low compared to other reported composites [53]. However, low n values have also been reported elsewhere. The mechanical percolation threshold is greater than the electrical percolation threshold because the electrons can tunnel quantum mechanically between conductive filler particles when the distance between them is less than 10 nm [55, 56], whereas stress transfer between two filler particles requires an inter-particle distance below 10 nm to modify the mechanical properties. Therefore, larger mechanical than electrical percolation thresholds have been generally observed for polymer composites [23, 57].

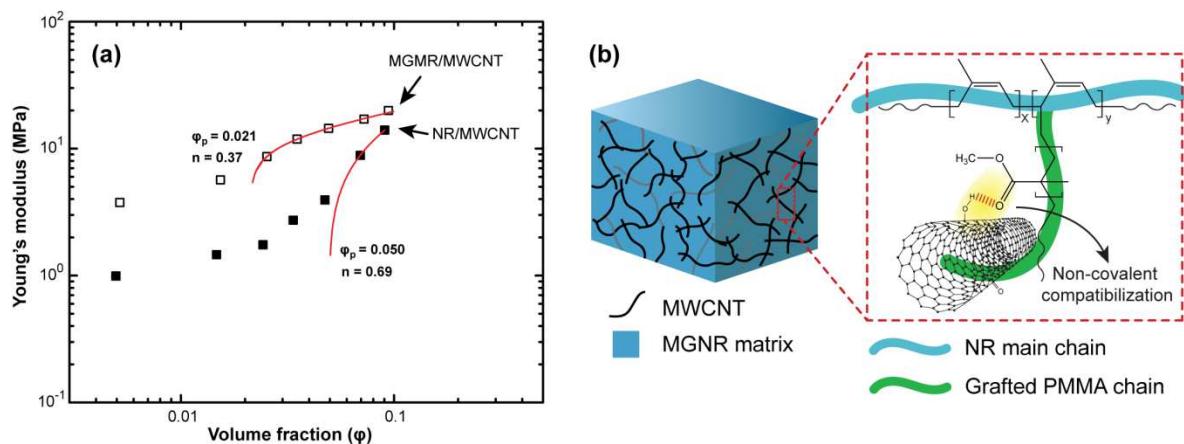


Fig. 9. (a) Initial modulus or Young's modulus as function of volume fraction of MWCNT in NR and MGNR. (b) Schematic representation of uniform dispersion and formation of MWCNT network in MGNR composites assisted by non-covalent compatibilization.

Taking into account all the results above, a matching microstructure of reinforced MGNR/MWCNT nanocomposites is proposed in Fig. 9b. To functionalize NR latex via emulsion polymerization, PMMA chains were successfully grafted onto NR. After melt mixing with MWCNT, the nanotubes allowed the grafted PMMA in MGNR to be absorbed and attached on the filler surfaces by polar interactions, which effectively entangled and anchored the filler particles, resulting in a uniform dispersion of MWCNT in MGNR matrix and improved stress transfer between these phases. As a consequence, the mechanical and electrical properties of nanocomposites were greatly improved. At the same time, the MGNR had better compatibility with MWCNT filler than NR had, leading to the formation of conductive network at a comparatively low loading level. Thus, modification of rubber with vinyl monomer can be used to develop conductive elastomer/MWCNT composites with highly enhanced electrical and mechanical properties.

4. Conclusion

The objective of this work was to study the effects of functionalizing NR with PMMA for non-covalent compatibilization with MWCNT filler. The PMMA grafted on NR improved filler dispersion in the NR matrix, which improved mechanical reinforcement and reduced the percolation threshold. The tensile strength of MWCNT/MGNR nanocomposites was two-fold that of NR/MWCNT nanocomposites. Moreover, the percolation threshold was dramatically reduced, and electrical conductivity was clearly improved by grafting PMMA onto NR. This is attributed to the affinity of CNT to the grafted PMMA, improving filler dispersion and networking in the modified MGNR matrix.

Declaration of competing interest

The authors declare no conflict of interest.

Acknowledgement

This research was supported by the Natural Rubber Innovation Research Institute, Prince of Songkla University (Grant No. SAT590823S). Also, thanks to the PSU research and development office (RDO), Prince of Songkla University and Assoc. Prof. Dr. Seppo Karrila for assistance with manuscript preparation.

Appendix A. Supplementary material

Supplementary data to this article can be found online at

References

- [1] H. Pang, L. Xu, D.-X. Yan, Z.-M. Li, Conductive polymer composites with segregated structures, *Prog. Polym. Sci.* 39 (2014) 1908-1933.
- [2] M.J. Yee, N.M. Mubarak, E.C. Abdullah, M. Khalid, R. Walvekar, R.R. Karri, S. Nizamuddin, A. Numan, Carbon nanomaterials based films for strain sensing application—A review, *Nano-Struct. Nano-Objects* 18 (2019) 100312.
- [3] A.R. Chowdhury, J. Jaksik, I. Hussain, R. Longoria, O. Faruque, F. Cesano, D. Scarano, J. Parsons, M.J. Uddin, Multicomponent nanostructured materials and interfaces for efficient piezoelectricity, *Nano-Struct. Nano-Objects* 17 (2019) 148-184.
- [4] K. Subramaniam, A. Das, D. Steinhauser, M. Klüppel, G. Heinrich, Effect of ionic liquid on dielectric, mechanical and dynamic mechanical properties of multi-walled carbon nanotubes/polychloroprene rubber composites, *Eur. Polym. J.* 47 (2011) 2234-2243.
- [5] T. Fujigaya, N. Nakashima, Non-covalent polymer wrapping of carbon nanotubes and the role of wrapped polymers as functional dispersants, *Sci. Technol. Adv. Mat.* 16 (2015) 024802.
- [6] M. Konni, A.S. Dadhich, S.B. Mukkamala, Evaluation of surface changes at the interface between TiO₂ nanoparticles and COOH-MWCNTs on hydrogen adsorption capability, *Nano-Struct. Nano-Objects* 18 (2019) 100304.
- [7] M.R.R. Hamester, C. Dalmolin, D. Becker, Role of π - π interactions and chain flexibility in dispersion and dynamic-mechanical properties of nanocomposites with multiple wall carbon nanotubes, *J. Appl. Polym. Sci.* 136 (2019) 48195.
- [8] G.Y. Jiang, S.Q. Song, Y.H. Zhai, C. Feng, Y. Zhang, Improving the filler dispersion of polychloroprene/carboxylated multi-walled carbon nanotubes composites by non-covalent functionalization of carboxylated ionic liquid, *Compos. Sci. Technol.* 123 (2016) 171-178.
- [9] S. Salaeh, T. Banda, V. Pongdong, S. Wießner, A. Das, A. Thitithammawong, Compatibilization of poly(vinylidene fluoride)/natural rubber blend by poly(methyl methacrylate) modified natural rubber, *Eur. Polym. J.* 107 (2018) 132-142.

- [10] L.L. Xu, C. Huang, M.C. Luo, W. Qu, H. Liu, Z.W. Gu, L.M. Jing, G.S. Huang, J. Zheng, A rheological study on non-rubber component networks in natural rubber, *RSC Adv.* 5 (2015) 91742-91750.
- [11] K.A.M. dos Santos, P.A.Z. Suarez, J.C. Rubim, Photo-degradation of synthetic and natural polyisoprenes at specific UV radiations, *Polym. Degrad. Stabil.* 90 (2005) 34-43.
- [12] T. Kochthongrasamee, P. Prasassarakich, S. Kiatkamjornwong, Effects of redox initiator on graft copolymerization of methyl methacrylate onto natural rubber, *J. Appl. Polym. Sci.* 101 (2006) 2587-2601.
- [13] S.Z. Szilasi, R. Huszank, D. Szikra, T. Vaczi, I. Rajta, I. Nagy, Chemical changes in PMMA as a function of depth due to proton beam irradiation, *Mater. Chem. Phys.* 130 (2011) 702-707.
- [14] R.S. Thomaz, R.M. Papaléo, Ion Beam Modification of Poly(methyl methacrylate) (PMMA), in: V. Kumar, B. Chaudhary, V. Sharma, K. Verma (Eds.), *Radiation Effects in Polymeric Materials*, Springer International Publishing, Cham, 2019, pp. 113-139 (Chapter 4).
- [15] P.C. de Oliveira, A.M. de Oliveira, A. Garcia, J.C. de Souza Barboza, C.A. de Carvalho Zavaglia, A.M. dos Santos, Modification of natural rubber: A study by ^1H NMR to assess the degree of graftization of polyDMAEMA or polyMMA onto rubber particles under latex form in the presence of a redox couple initiator, *Eur. Polym. J.* 41 (2005) 1883-1892.
- [16] P. Song, Z. Xu, Y. Wu, Q. Cheng, Q. Guo, H. Wang, Super-tough artificial nacre based on graphene oxide via synergistic interface interactions of π - π stacking and hydrogen bonding, *Carbon* 111 (2017) 807-812.
- [17] Y. Chen, W. Wei, Y. Zhu, J. Luo, X. Liu, Noncovalent functionalization of carbon nanotubes via co-deposition of tannic acid and polyethyleneimine for reinforcement and conductivity improvement in epoxy composite, *Compos. Sci. Technol.* 170 (2019) 25-33.
- [18] G. Sui, W.H. Zhong, X.P. Yang, Y.H. Yu, Curing kinetics and mechanical behavior of natural rubber reinforced with pretreated carbon nanotubes, *Mat. Sci. Eng. A-Struct.* 485 (2008) 524-531.
- [19] Y. Luo, P. Zhao, Q. Yang, D. He, L. Kong, Z. Peng, Fabrication of conductive elastic nanocomposites via framing intact interconnected graphene networks, *Compos. Sci. Technol.* 100 (2014) 143-151.
- [20] D. Ponnamma, R. Ramachandran, S. Hussain, R. Rajaraman, G. Amarendra, K.T. Varughese, S. Thomas, Free-volume correlation with mechanical and dielectric properties of natural rubber/multi walled carbon nanotubes composites, *Compos. Part A-Appl. S.* 77 (2015) 164-171.
- [21] R. Ravindren, S. Mondal, K. Nath, N.C. Das, Investigation of electrical conductivity and electromagnetic interference shielding effectiveness of preferentially distributed conductive filler in highly flexible polymer blends nanocomposites, *Compos. Part A-Appl. S.* 118 (2019) 75-89.
- [22] A. Ivanoska-Dacikj, G. Bogoeva-Gaceva, S. Rooj, S. Wießner, G. Heinrich, Fine tuning of the dynamic mechanical properties of natural rubber/carbon nanotube nanocomposites by organically modified montmorillonite: A first step in obtaining high-performance damping material suitable for seismic application, *Appl. Clay Sci.* 118 (2015) 99-106.
- [23] S. Rooj, A. Das, K.W. Stöckelhuber, S. Wießner, D. Fischer, U. Reuter, G. Heinrich, 'Expanded organoclay' assisted dispersion and simultaneous structural alterations of

- multiwall carbon nanotube (MWCNT) clusters in natural rubber, *Compos. Sci. Technol.* 107 (2015) 36-43.
- [24] J. Chen, X. Cui, Y. Zhu, W. Jiang, K. Sui, Design of superior conductive polymer composite with precisely controlling carbon nanotubes at the interface of a co-continuous polymer blend via a balance of π - π interactions and dipole-dipole interactions, *Carbon* 114 (2017) 441-448.
- [25] J.-C. Hsu, W. Cao, F. Yang, T.-J. Yang, S. Lee, Absorption behavior of poly(methyl methacrylate)-multiwalled carbon nanotube composites: effects of UV irradiation, *Phys. Chem. Chem. Phys.* 19 (2017) 7359-7369.
- [26] A. Das, K.W. Stöckelhuber, R. Jurk, J. Fritzsche, M. Klüppel, G. Heinrich, Coupling activity of ionic liquids between diene elastomers and multi-walled carbon nanotubes, *Carbon* 47 (2009) 3313-3321.
- [27] M.A. Pantoja-Castro, J.F. Perez-Robles, H. Gonzalez-Rodriguez, Y. Vorobiev-Vasilievitch, H.V. Martinez-Tejada, C. Velasco-Santos, Synthesis and investigation of PMMA films with homogeneously dispersed multiwalled carbon nanotubes, *Mater. Chem. Phys.* 140 (2013) 458-464.
- [28] C.-Q. Li, J.-W. Zha, Z.-J. Li, D.-L. Zhang, S.-J. Wang, Z.-M. Dang, Towards balanced mechanical and electrical properties of thermoplastic vulcanizates composites via unique synergistic effects of single-walled carbon nanotubes and graphene, *Compos. Sci. Technol.* 157 (2018) 134-143.
- [29] C. McClory, T. McNally, M. Baxendale, P. Pötschke, W. Blau, M. Ruether, Electrical and rheological percolation of PMMA/MWCNT nanocomposites as a function of CNT geometry and functionality, *Eur. Polym. J.* 46 (2010) 854-868.
- [30] S. Thomas, S.C. George, S. Thomas, Evaluation of mechanical, thermal, electrical, and transport properties of MWCNT-filled NR/NBR blend composites, *Polym. Eng. Sci.* 58 (2018) 961-972.
- [31] N. Wang, S. Pandit, L. Ye, M. Edwards, V.R.S.S. Mokkalapati, M. Murugesan, V. Kuzmenko, C. Zhao, F. Westerlund, I. Mijakovic, J. Liu, Efficient surface modification of carbon nanotubes for fabricating high performance CNT based hybrid nanostructures, *Carbon* 111 (2017) 402-410.
- [32] S. Roy, T. Das, C.Y. Yue, X. Hu, Improved Polymer Encapsulation on Multiwalled Carbon Nanotubes by Selective Plasma Induced Controlled Polymer Grafting, *ACS Appl. Mater. Inter.* 6 (2014) 664-670.
- [33] H. Zhang, J. Chen, X. Cui, Y. Hu, L. Lei, Y. Zhu, W. Jiang, Thermal annealing induced enhancement of electrical properties of a co-continuous polymer blend filled with carbon nanotubes, *Compos. Sci. Technol.* 167 (2018) 522-528.
- [34] T. McNally, P. Pötschke, P. Halley, M. Murphy, D. Martin, S.E.J. Bell, G.P. Brennan, D. Bein, P. Lemoine, J.P. Quinn, Polyethylene multiwalled carbon nanotube composites, *Polymer* 46 (2005) 8222-8232.
- [35] K. Song, Interphase characterization in rubber nanocomposites, in: S. Thomas, H.J. Maria (Eds.), *Progress in Rubber Nanocomposites*, Woodhead Publishing, Kidlington, 2017, pp. 115-152 (Chapter 4).
- [36] X.H. Liu, J. Kruckel, G.Q. Zheng, D.W. Schubert, Electrical conductivity behaviour of sheared poly(methyl methacrylate)/carbon black composites, *Compos. Sci. Technol.* 100 (2014) 99-104.
- [37] M. Knite, A. Linarts, Polymer/Nanographite Composites for Mechanical Impact Sensing, in: K.K. Sadasivuni, D. Ponnamma, J. Kim, S. Thomas (Eds.), *Graphene-Based Polymer Nanocomposites in Electronics*, Springer, Heidelberg, 2015, pp. 223-252 (Chapter 9).

- [38] H. Liu, Q. Li, S. Zhang, R. Yin, X. Liu, Y. He, K. Dai, C. Shan, J. Guo, C. Liu, C. Shen, X. Wang, N. Wang, Z. Wang, R. Wei, Z. Guo, Electrically conductive polymer composites for smart flexible strain sensors: a critical review, *J. Mater. Chem. C* 6 (2018) 12121-12141.
- [39] N. George, B. Venugopal, H. John, A. Mathiazhagan, R. Joseph, Nanosilica decorated multiwalled carbon nanotubes (CS hybrids) in natural rubber latex, *Polymer* 161 (2019) 170-180.
- [40] L. Bokobza, Rubber Nanocomposites: New Developments, New Opportunities, in: J. Karger-Kocsis, S. Fakirov (Eds.), *Nano- and Micro- Mechanics of Polymer Blends and Composites*, Hanser, Munich, 2009, pp. 141-165 (Chapter 4).
- [41] J.C. Majesté, Rheology and Processing of Polymer Nanocomposites: Theory, Practice, and New Challenges, in: S. Thomas, R. Muller, J. Abraham (Eds.), *Rheology and Processing of Polymer Nanocomposites*, Wiley, New Jersey, 2016, pp. 69-134 (Chapter 3).
- [42] A.P. Meera, S. Said, Y. Grohens, S. Thomas, Nonlinear Viscoelastic Behavior of Silica-Filled Natural Rubber Nanocomposites, *J. Phys. Chem. C* 113 (2009) 17997-18002.
- [43] S. Rooj, A. Das, K.W. Stöckelhuber, D.Y. Wang, V. Galiatsatos, G. Heinrich, Understanding the reinforcing behavior of expanded clay particles in natural rubber compounds, *Soft Matter* 9 (2013) 3798-3808.
- [44] A.K. Zachariah, A.K. Chandra, P.K. Mohammed, J. Parameswaranpillai, S. Thomas, Experiments and modeling of non-linear viscoelastic responses in natural rubber and chlorobutyl rubber nanocomposites, *Appl. Clay Sci.* 123 (2016) 1-10.
- [45] D. Ponnamma, S.H. Sung, J.S. Hong, K.H. Ahn, K.T. Varughese, S. Thomas, Influence of non-covalent functionalization of carbon nanotubes on the rheological behavior of natural rubber latex nanocomposites, *Eur. Polym. J.* 53 (2014) 147-159.
- [46] K.K. Sadasivuni, Y. Grohens, Nonlinear Viscoelasticity of Two Dimensional Filler Reinforced Rubber Nanocomposites, in: D. Ponnamma, S. Thomas (Eds.), *Non-Linear Viscoelasticity of Rubber Composites and Nanocomposites: Influence of Filler Geometry and Size in Different Length Scales*, Springer, Heidelberg, 2014, pp. 43-57 (Chapter 3).
- [47] K. Subramaniam, A. Das, G. Heinrich, Development of conducting polychloroprene rubber using imidazolium based ionic liquid modified multi-walled carbon nanotubes, *Compos. Sci. Technol.* 71 (2011) 1441-1449.
- [48] K. Subramaniam, A. Das, F. Simon, G. Heinrich, Networking of ionic liquid modified CNTs in SSBR, *Eur. Polym. J.* 49 (2013) 345-352.
- [49] M. Poikelispää, A. Das, W. Dierkes, J. Vuorinen, The effect of partial replacement of carbon black by carbon nanotubes on the properties of natural rubber/butadiene rubber compound, *J. Appl. Polym. Sci.* 130 (2013) 3153-3160.
- [50] A. Malas, C.K. Das, A. Das, G. Heinrich, Development of expanded graphite filled natural rubber vulcanizates in presence and absence of carbon black: Mechanical, thermal and morphological properties, *Mater. Des.* 39 (2012) 410-417.
- [51] M.-R. Pourhossaini, M. Razzaghi-Kashani, Effect of silica particle size on chain dynamics and frictional properties of styrene butadiene rubber nano and micro composites, *Polymer* 55 (2014) 2279-2284.
- [52] G. Huber, T. Vilgis, Universal Properties of Filled Rubbers: Mechanisms for Reinforcement on Different Length Scales, *Kaut. Gummi Kunstst.* 52 (1999) 102-107.
- [53] G. Ramorino, F. Bignotti, S. Pandini, T. Riccò, Mechanical reinforcement in natural rubber/organoclay nanocomposites, *Compos. Sci. Technol.* 69 (2009) 1206-1211.

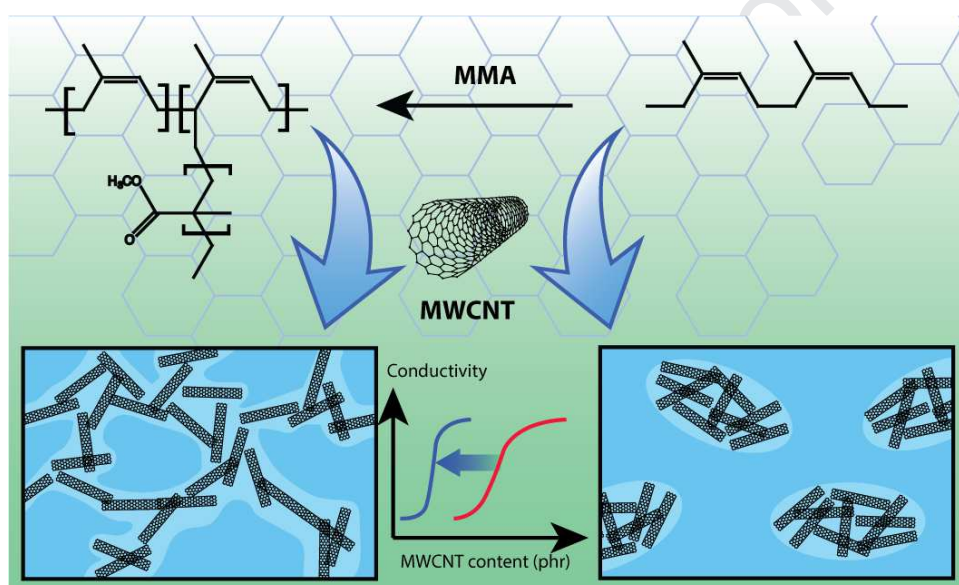
- [54] S.M. Liff, N. Kumar, G.H. McKinley, High-performance elastomeric nanocomposites via solvent-exchange processing, *Nat. Mater.* 6 (2006) 76.
- [55] J.-F. Zou, Z.-Z. Yu, Y.-X. Pan, X.-P. Fang, Y.-C. Ou, Conductive mechanism of polymer/graphite conducting composites with low percolation threshold, *J Polym. Sci. Pol. Phys.* 40 (2002) 954-963.
- [56] S. Belaïd, G. Boiteux, P. Cassagnau, Rheological and electrical properties of EVA copolymer filled with bamboo charcoal, *Rheol. Acta* 52 (2013) 75-84.
- [57] A. Noël, J. Faucheu, J.-M. Chenal, J.-P. Viricelle, E. Bourgeat-Lami, Electrical and mechanical percolation in graphene-latex nanocomposites, *Polymer* 55 (2014) 5140-5145.

Journal Pre-proof

Highlights

- Uniform dispersion of multi-walled carbon nanotube in natural rubber matrix were observed.
- Enhancement of electrical conductivity assisted by non-covalent compatibilization.
- The flexible and stretchable methyl methacrylate functionalized natural rubber with highly conductive.
- Good carbon nanotube networking of natural rubber composites were observed.
- Future advance natural rubber nanocomposite for electrical device and smart polymer materials.

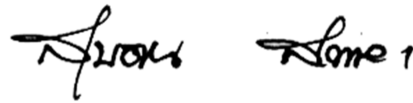
Graphical abstract



Conflict of Interest Form

The authors declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Pattani, Thailand (19/01/2020)

Two handwritten signatures in black ink, one on the left and one on the right, both appearing to be cursive and somewhat stylized.

Dr. Subhan Salaeh