

Effect of Carbon Nanotube-Silane Addition on Mechanical Properties of Chloroprene Rubber-filled Carbon Black

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ABSTRACT

Chloroprene-filled CNT rubber has been investigated for the electromagnetic shielding application. Nevertheless, there are continuous studies to overcome CNTs agglomeration, materials loss and air contamination issues generated during conventional melt compounding process. Thus, the current study proposes the usage of polar and low molecular weight ethanol solvent as dispersant for CNT fillers and silane-based Si-69 as coupling agent. Si-69 is a widely used fillers' coupling agent because of its reliable performance in the industrial-scaled rubber compounding process. This study is to investigate the effect of carbon nanotube (CNT)-Silane addition as secondary fillers on tensile strength, elastic modulus and cure characteristics of chloroprene rubber (CR)-filled carbon black (CB) compound. The CR-filled CB was prepared by internal mixing, followed by roll-mill process in which CNT-Silane dispersion was added. For comparison, the samples of CR-filled CB without CNTs addition and with as-received CNTs addition were prepared and characterized. The CR composite added with CNT-Silane dispersion displayed tensile strength and elastic modulus (at 300% elongation) of 23 MPa and 18 MPa respectively, which are 4% higher than the CR composite added with as-received CNTs. The findings were supported by the FESEM micrograph of tensile fracture samples that showed the CNT-Silane addition produced better CNTs dispersion in the CR-filled CB compound. Furthermore, the usage of

CNT-Silane improved the CR-filled CB compound processibility by reducing the minimum (ML) and maximum torque (MH) values from 0.34 and 1.11 N.m in as-received CNT samples to 0.32 and 1.04 N.m respectively in CNT-silane samples.

Keywords: *Flexible electronics, electromagnetic interference (EMI), synthetic rubber, carbon nanotube, silane coupling agent*

Introduction

Recent flexible and stretchable electronics applications create high demands for flexible and durable materials [1]. Chloroprene-filled CNT rubber has been investigated for the electromagnetic shielding application [2]. Nevertheless, there are continuous studies to overcome CNTs agglomeration generated by conventional melt compounding technique. Furthermore, CNT powder becomes airborne quite easily during pouring and compounding process in the industrial-scaled internal mixer. This airborne problem contributes to raw materials loss and air contamination issues.

Several studies had reported the latex mixing method, where CNTs is mixed with rubber in latex form [3,4]. Although promising results were reported, the scientific method is not feasible and incurs high manufacturing cost. Solvent dispersion technique is a promising approach to resolve the CNTs mixing problem [4]. However, the studies used hazardous tetrahydrofuran and toluene which require laborious drying process to remove the nonpolar high molecular weight organic solvents from CNTs. It is also reported that uncommon dispersing or coupling agent such as 1-decyl 3-methyl imidazolium chloride was used for CNTs [5], which again requires a cleaning process to remove the corrosive halide species.

Thus, the current study proposes the usage of polar and low molecular weight ethanol solvent as a dispersant for CNT fillers and silane-based Si-69 as a coupling agent. Si-69 is a widely used fillers' coupling agent because of its reliable performance in the industrial-scaled rubber compounding process [6]. The current paper will report the effect of CNT-Silane filler dispersion addition on the tensile strength and elastic modulus of the CR-filled CB+CNT compound. Microstructural tensile fracture sample and cure characteristics of the compound according to ASTM D6204 standard is also presented to support the mechanical findings.

Methodology

CR master batch with the formulation as stated in Table 1 was prepared using an internal mixer (Yi Tzung) operating at 60 °C, rotor speed of 900 rpm and mixing time of 8 mins. Subsequently, the CR match batch was divided into three smaller portions and then was calendered separately with different formulations (refer Table 2) using two-roll mill (model: MT2-2, Yi Tzung) at a rotor speed of 19.3 rpm (front) and 22.5 rpm (back) and mixing time of 5 min. All chemicals used in the formulations are from industrial grade.

Table 1: Formulations of master batch

Chemicals	Loading(phr)
Chloroprene (CR)	100
Zinc oxide (ZnO)	5
Stearic Acid (ST Acid)	0.5
Nocrac AD-F	2
Coumarone Resin (G90)	8
Carbon Black (N550)	40

Table 2 shows 1 phr CNTs was added as second fillers for CNT and CNT-Silane samples. During roll-mill, as-received CNTs was added in dry form for CNT samples, whereas, CNTs was added in dispersion form for CNT-Silane samples. CNT-Silane dispersion was prepared with the ultrasonication of 1.25 g Si-69 silane coupling agent in the 100 mL ethanol solution (95%). Then, as-received CNTs was mixed into the Si-69 solution. Additional 100 mL ethanol solution was then added, followed by further agitation by ultrasonication for 60 min. As a control, CR compound samples without CNTs (which is an established formulation) were also prepared.

Table 2: Second formulations added during roll mill

Chemicals	Loading (phr) for		
	CNT	CNT-Silane [#]	Control
Carbon Nanotubes (CNTs)	1	1 [#]	0
Magnesium Oxide (MGO)	4	4	0
Ethylene Thiourea (ETU-80)	0.7	0.7	0.7
N-Cyclohexyl-2-Benzothiazole Sulphenamide (CBS)	0.75	0.75	0.75

[#]amount of added CNT (in dispersion form) was controlled at 1 phr dry weight of CNTs. Silane and ethanol solutions were not included in phr calculation.

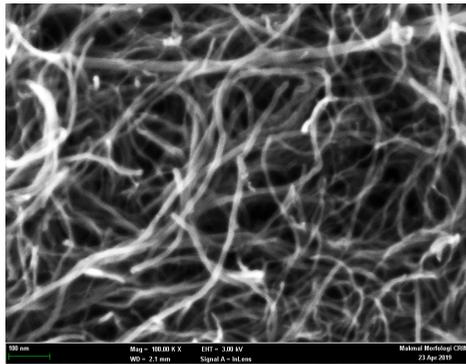
Sheet samples (sample size = 4) for the tensile test were prepared by hot press process of each calendared CR rubber compound in the respective sheet-shaped cavity steel molds, at 160 °C and pressure of 110 kg-force for 10 min. Tensile tests were performed on the samples according to JIS K 6251 standard using Tensometer (model: UR-2060, U-CAN DYNATEX) to obtain the average and standard error of tensile strength and elastic modulus. Surface of tensile fracture samples were observed using Field-emission Scanning Electron Microscope (FESEM, 3 kV accelerating voltage, secondary electron emission mode, Merlin compact-60-25, Carl Zeiss).

Lastly, cure characteristics of the fresh calendared CR compounds were characterized using rheometer (UR-2010, U-CAN DYNATEX) according to ASTM D6204 standard.

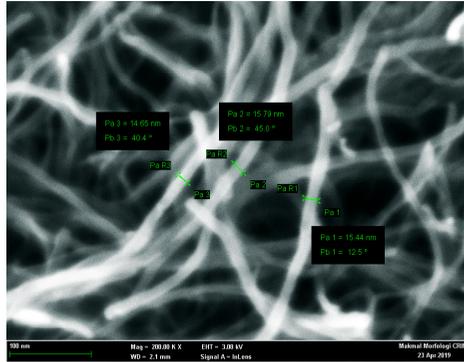
Result and Discussion

Microstructure of CNT

Figure 1 shows the as-received CNTs used as fillers for CNT and CNT-Silane samples had a diameter range between 14 to 16 nm. Physical entanglement between CNTs were clearly shown, which explains the presence of CNTs agglomeration before the CNTs were added during the CR compounding.



(a)



(b)

Figure 1: FESEM micrograph of as-received CNT fillers at magnification of: (a) 100,000 \times , and (b) 200,000 \times

Tensile Test

Tensile strength (TS) with standard error bar plots in Figure 2 show that Si-69 treatment on CNT filler able to negate the deteriorating effect of CNT addition as fillers in the CR-filled carbon black (CB) compound. TS of samples filled with CNT-Silane is comparable to the control samples (with no CNT content) and was 3% higher than the CNT samples (with as-received CNTs). The low TS of the CNT samples were caused by the formation of CNTs agglomerations in the CR-filled CB compound, resulted in an earlier failure. This agglomeration problem was resolved with the usage of CNTs treated with Si-69, in which the latter assisted CNT fillers dispersion through calendaring process with CR-filled CB. It is believed a better dispersion of CNT-Silane provide more uniform tensile stress distribution throughout the CR tensile samples, reducing stress concentration at particular weak regions. Furthermore, the Si-69 addition strengthened the interaction between CNT-Silane fillers and CR matrix. Nevertheless, CNT-Silane fillers did not perform well as reinforcement agent for CR compound, thus the TS did not improve significantly in comparison with control samples. It appears that the presence of silane provided lubrication effect to the CR compound which permitted polymer chain slippage toward tensile fracture.

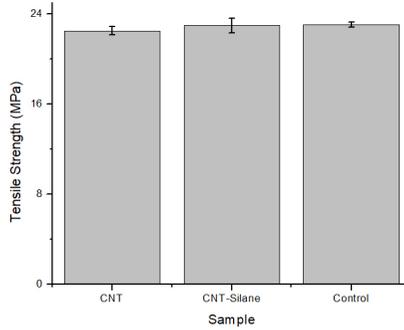


Figure 2: Tensile strength of CR compound samples

It appears that the addition of CNT-Silane fillers improved the stiffness characteristic by enhancing the tensile modulus at 300% of elongation (refer Figure 3). The Si-69 addition strengthened the interaction between CNT-Silane fillers and CR matrix, thus increased the resistance toward the tensile elongation [7]. This can be the reason for the enhanced stiffness value.

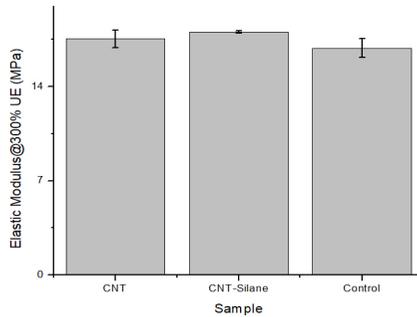


Figure 3: Elastic modulus (at 300% elongation) of CR compound samples

Microstructural Surface of Tensile Fracture

FESEM micrograph in Figure 4 shows the ductile fracture surface due to the observed apparent shear yielding mechanism. The fracture surface appeared rough and many cavities were observed in the rubber matrix with uniform distribution [8]. CNT-Silane exhibited smoother fracture surface, thus verify the argument that silane acted as lubrication which triggered shear slippage fracture.

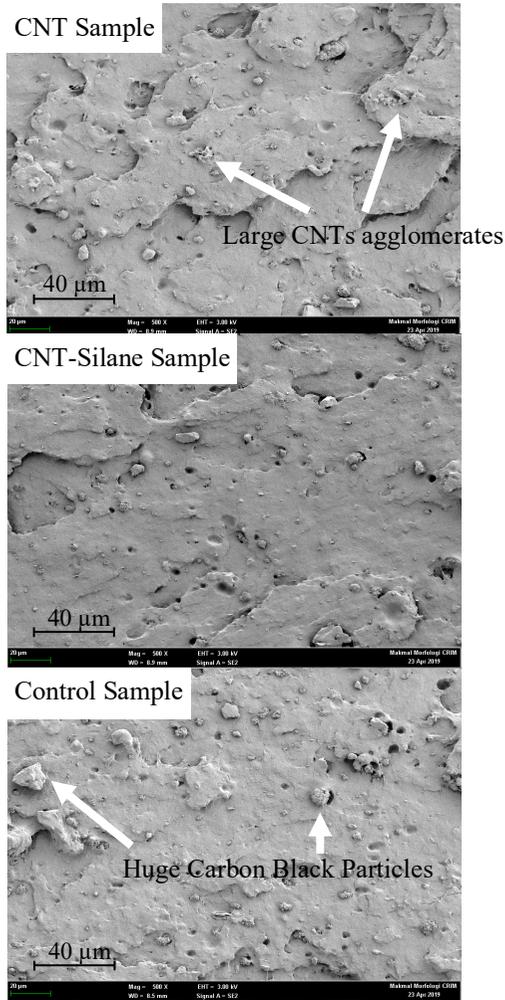


Figure 4: Low magnification FESEM micrographs of the surface of tensile fracture samples

FESEM micrograph in Figure 5 shows large CNT fillers agglomerates were found in the CNT tensile sample. CNT fillers agglomerates appeared in smaller size and dispersed widely in the CNT-Silane sample. The microstructural difference in the CNT fillers agglomerates size and distribution indicates an improved CNT fillers dispersion in the CR-filled CB compound. This microstructural finding verified the current tensile strength and elastic modulus findings.

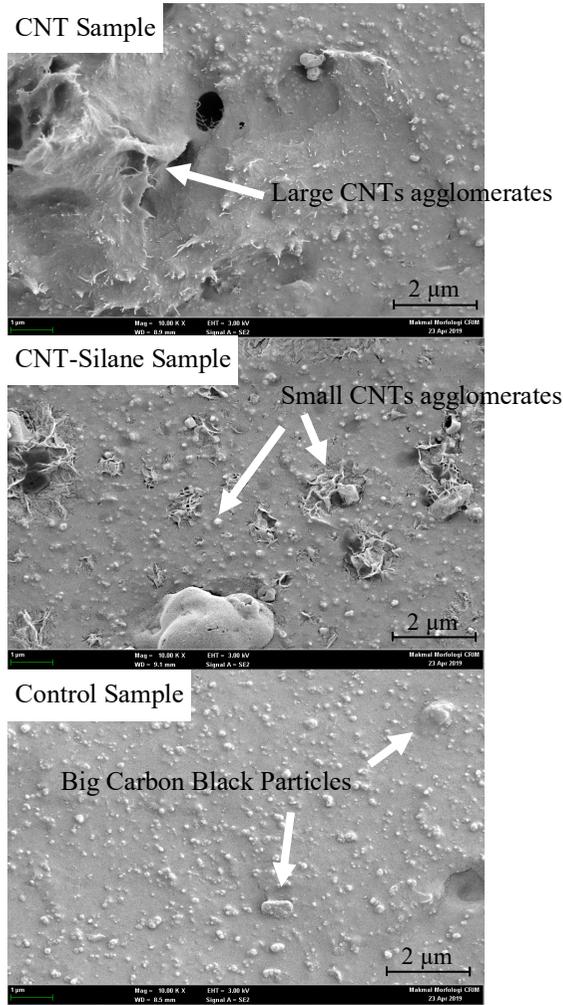


Figure 5: High magnification FESEM micrographs of the surface of tensile fracture samples

Cure Characteristics

Rheological data (refer Table 3) explains the cure characteristics of the as-cast samples, in terms of scorch time (TS2), cure time (TC90) and maximum torque (MH). The CNT sample experienced a shorter TS2 as compared to the control sample. However, with the substitution of CNT fillers with CNT-silane fillers, the TS2 of CNT-Silane sample was extended to 3 min 17 seconds, though 5 seconds shorter than the control sample. It is understood

that during the scorch delay period, the majority of the accelerators' chemical reactions took place [9].

Table 3: Rheological data displayed according to ASTM D6204 terminology

Sample	Time (min: second)		Torque (N.m)			Cure Rate Index (min ⁻¹)
	TS2	TC90	ML	MH	MH – ML	
CNT	3:09	7:35	0.34	1.11	0.77	17.45
CNT-Silane	3:17	7:53	0.32	1.04	0.72	17.93
Control	3:22	7:53	0.32	1.03	0.72	19:26

TC90 is the time required to reach 90% of a complete cure, and this is normally the state of cure at which most of their physical properties reach the optimum levels [9]. Similar to the TS2 data, the CNT sample has a lower TC90 than the control sample. It is believed that the addition of CNTs had increased the thermal conductivity of CNT sample, and improved heat transmission in the blended compounds. The previous study claimed that the improved thermal conductivity due to CNT addition results in an increase in the rate of vulcanization [3]. However, we also believed that the presence of CNT agglomerates (as shown by Figure 5) could have increased the CB fillers connectivity in the CR-filled CB+CNT compound. As a result, the combination of both higher heat transmission and fillers connectivity may contribute to the shorter time for the full cure of CNT sample.

Interestingly, TC90 of CNT-Silane sample reached 7 min 53 seconds, on par with the control sample. The microstructural images (as in Figure 5) showed that the CNT-Silane fillers were dispersed more uniformly in CNT-Silane sample than the untreated CNT fillers in the CNT sample. The CNT-Silane dispersion resulted in a greater distance between fillers (CNT-Silane and carbon black particles). Thus, this factor diminished the efficiency of heat transmission through the inter-fillers network and indirectly extended the TS2 and TC90. This explains the TS2 and TC90 of CNT-Silane sample were longer than the CNT sample.

TS2 and TC90 data were used to calculate the cure rate index (see Equation 1), in which the latter represents the vulcanization rate of the vulcanizates.

$$Cure\ rate\ index\ (CRI) = 100/(TC90-TS2) \tag{1}$$

CRI of the three samples (refer Table 3) arranged from the highest to the lowest as follow: Control, CNT-Silane and CNT samples. The finding shows that CNT-Silane addition improved the vulcanization rate of CR-filled

CB+CNT by ~3%. However, more study is needed to improve the CRI, as it is still 8% lower than the CRI of the control sample.

It is also shown that Si-69 acted as lubricant, causing a decrease of the minimum (ML) and maximum torque (MH) values of the CNT-Silane sample. Its ML and MH were comparatively lower than the CNT sample and on par with the values of the control sample. ML is a measure of the stiffness of the unvulcanised sample taken at the lowest point of the cure curve [9]. Whereas, MH represents the stiffness of the fully vulcanized sample at vulcanization temperature [10]. Hence, the findings suggest the substitution of as-received CNT with the CNT-Silane increase the processability of CR-filled CB+CNT compound.

It is believed longer TS2 and TC90, as well as lower ML and MH of CR-filled CB, added with CNT-Silane enabled a better dispersion of the secondary fillers (CNTs) during the calendaring process of CR-filled CB+CNT. Again, the cure characteristics findings could explain the good CNT-Silane fillers dispersion as observed in the tensile fracture sample (as shown by Figure 5).

Conclusion

Substitution of as-received CNT with the CNT-silane as the secondary fillers improved the tensile strength and elastic modulus of cured of the CR-filled CB samples by 4%. The substitution to CNT-silane increased both mechanical characteristics of the CR-filled CB from 22.5 MPa and 17.6 MPa to 23.0 MPa and 18.1 MPa respectively. The usage of CNT-Silane also increased the cure rate index (CRI) of the CR vulcanizates from 17.45 to 17.93 min⁻¹. CNT-Silane also improved the compound processability, where there were decreases of minimum (ML) and maximum torque (MH) values from 0.34 and 1.11 N.m in as-received CNT samples to 0.32 and 1.04 N.m respectively in CNT-silane samples. Future work study needs to investigate the effect of direct mixing of Si-69 or other types of silane coupling agent into the CR-filled CB+CNT compound. The study could cut-down the number of compound processing steps to increase the feasibility of the rubber nano composite compounding process for industry application.

Acknowledgement

The authors wish to thank Sunrich Integrated (SRIT) for providing raw materials, sample preparation and characterization facilities. Special thanks also to Tony Chew (SRIT) for useful discussions. This manuscript is an extended version of manuscript presented in MERD'19.

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