



# Article Anti-Gnawing, Thermo-Mechanical and Rheological Properties of Polyvinyl Chloride: Effect of Capsicum Oleoresin and Denatonium Benzoate

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Abstract: Anti-rodent polymer composites were prepared using non-toxic substances denatonium benzoate (DB) and capsicum oleroresin (CO) mixed with polyvinyl chloride (PVC) matrix. DB is mixed in zinc stearate (ZnSt) called DB/ZnSt, and CO, providing burning sensation, is impregnated in mesoporous silica named SiCO. There are three sets of sample: Blank, composites Set I and Set II. Set I consists of DB/ZnSt at concentration of 1.96 wt% and SiCO at concentration of 12.16 wt%, 14.47 wt%, 18.75 wt% and 23.53 wt%. Set II comprises SiCO at the same amount of Set I. The antirodent composites studied are anti-gnawing, surface morphology, thermo-mechanical and rheological properties. Anti-rodent testing is analyzed by one-way blocked analysis of variance (ANOVA) and compared with Tukey test with a 95% level of significance, presenting good anti-gnawing efficiency. The best rat-proof sample is II.4, consisting of SiCO 23.53 wt%, which presents percentage of weight loss from gnawing at 1.68% compared to weight loss of neat PVC at 59.74%. The addition of SiCO at concentration ranging from 12.16 to 23.53 wt% reduces tensile strength around 25-50%, elongation at break strength around 2–23%, shear storage modulus (G') around 30%, shear loss modulus (G') shear viscosity ( $\eta$ ) and glass transition ( $T_g$ ) around 43% compared to Blank. The increase in SiCO concentration slightly improves the thermal stability of PVC composites around 3%, but the addition of DB/ZnSt at 1.96 wt% slightly reduces those properties.

**Keywords:** capsicum oleoresin (CO); denatonium benzoate (DB); polyvinyl chloride (PVC); anti-rodent polymer; design of experiment

# 1. Introduction

The damage of plastic products, especially electrical wire and cable, is often caused by rodents. This may cause outages or short circuits and fires and can stop production lines and break expensive machines [1,2]. Rodents prefer to gnaw elastomeric materials, especially flexible PVC, which is the main plastic for making insulation of electrical wire and cable [3]. They gnaw because all rodents have a single pair of incisors in the top and bottom jaws that are rootless and grow continuously throughout their lives [4,5]. If they allow their incisors to grow without restraint, they would not be able to gnaw their food and then would subsequently die. Therefore, they spend their lives gnawing and wearing their teeth down [6].



Citation: Techawinyutham, L.; Prasarnsri, A.; Siengchin, S.; Dangtungee, R.; Rangappa, S.M. Anti-Gnawing, Thermo-Mechanical and Rheological Properties of Polyvinyl Chloride: Effect of Capsicum Oleoresin and Denatonium Benzoate. *J. Compos. Sci.* 2022, *6*, 8. https://doi.org/10.3390/jcs6010008

Academic Editor: Francesco Tornabene

Received: 2 December 2021 Accepted: 20 December 2021 Published: 27 December 2021

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Today, methods for repelling rodents use chemical substances (rodenticides bait, rat poisons) [7,8], natural substances (peppermint oil, bay leaf, onions and chili) [9,10] and electronic control (e.g., ultrasonic, radio wave) [11,12], some of which can bring harm to humans, pets and the environment. This research uses non-lethal methods to prevent or deter rodent chewing on plastic products. The non-toxic chemical substances mixed in the PVC (polyvinyl chloride) compound are denatorium benzoate (DB) and capsicum oleoresin (CO). DB and CO provide an intensely bitter taste and burning sensation, respectively, resulting in a behavioral change of the rodents to stop chewing the plastic product. DB is the bitterest chemical compound known, it is also non-toxic, odorless, colorless and nonreactive [13–15]. It can be detected by humans at a concentration of 10 ppb, is discernibly bitter at 50 ppb and is unpleasantly bitter at 10 ppm [16,17]. CO is a dark reddish-brown liquid concentrate used as the alternative natural substance of capsaicin (CS), which is the main substance giving spicy taste and burning sensation for mammals in chili, because the cost of CS limits its usage [18-20]. The main component of CO is CS [21]. One ppm of CS provokes a perceptible warm sensation on the human tongue, and 10 ppm provokes a persistent burning sensation on the tongue [22].

There are many works using CS and DB in plastic products for repelling rodents. Zhu [23] invented a rat-proof plastic drip irrigation tube/belt using synthetic CS as a rat-proof substance. The rat-proof tube/belt is non-toxic, does not pollute the environment and provides excellent anti-chewing deterrent against rodents. We et al. [24] invented anti-mouse cable and wire consisting of modified CS. CS covered acrylate for slow release, having a long-term repellent effect. Shumake et al. [25] studied the reduction of cable gnawing by northern pocket gophers by coated anti-gnawing substances on the cable. The repellent treatments consisted of 2.0% mass/mass levels of CS and DB. CS and DB appeared to be absolutely effective substances applied as a surface coating to cable to control gnawing damage by northern pocket gophers. Ichino [26] invented flexible PVC with DB against gnawing from rodents. DB acts as a repellent substance that at 2.5 wt% represents a practical maximum amount in PVC matrix. The rat-proof flexible PVC provided good effectiveness on the plastic. Techawinyutham et al. [27] studied SiCO/polylactic acid (PLA) composites, and results showed that the incorporation of SiCO (0.77, 1.54 and 3.08 wt%) slightly improved tensile strength but did not significantly affect tensile modulus and elongation.

The aim of this study is to create anti-rodent polymer composites and examine influence of anti-gnawing substances by means of the structure–property relationships such as rheological, mechanical and thermal properties. The concentration of anti-gnawing substances, SiCO and DB/ZnSt, was examined by the work of Techawinyutham et al. [28] with an anti-gnawing test of two weeks. This study focuses on the efficiency of anti-rodent substances (DB/ZnSt and SiCO) for three months in terms of percentage of weight loss using one-way ANOVA with block design analysis with a 95% level of significance of data. If the combination of DB/ZnSt and SiCO in PVC shows less gnawing damage than neat PVC, the composites can prevent rodents from severely damaging the essential plastic product made from flexible PVC such as electrical wire and cable.

#### 2. Materials and Methods

## 2.1. Materials

The CO was extracted from hot chili powder (Aro from Siam Makro Pub Co., Ltd., Bangkok, Thailand). Silica (CAS 112926-00-8) was in crystal form (22S Sipernat<sup>®</sup>, Evonik company, Essen, Germany). The particle size and surface area of silica were 14  $\mu$ m and 180 m<sup>2</sup>/g, respectively. DB (CAS 3734-33-6) in white crystalline pellets was purchased from Gratitude Infinite Pub Co., Ltd., Bangkok, Thailand. ZnSt (CAS 557-05-1) (Z784, Fisher Scientific International, Inc., Hampton, NH, USA) in white powder solid with melting temperature (T<sub>m</sub>) of 118–128 °C acted as a coating for anti-accumulation of DB, improving the distribution of DB in PVC matrix. PVC compound granulate (C2904NTA grade, Thai Plastic and Chemicals Pub co., Ltd., Rayong, Thailand) was selected as a polymer matrix

for the entire composites with a specific gravity of  $1.38 \text{ g/cm}^3$  (ASTM D792), elongation 279% and tensile strength of 17.3 MPa (JIS 3342).

# 2.2. Sample Preparation

## 2.2.1. CO Extraction

Dark reddish-brown liquid CO in Figure 1a was extracted from chili powder with a volatile solvent. Chili powder was soaked in acetone (chili powder: acetone = 5 g: 18 mL), then stirred at 1300 rpm for 7 h by an overhead stirrer (RW20 digital IKA Company, Freiburg im Breisgau, Germany). The mixture of CO was filtered by filter paper with 125 mm of diameter (Whatman<sup>TM</sup>, Maidstone, UK).



Figure 1. Pictures of; (a) CO; (b) SiCO; (c) DB/ZnSt.

#### 2.2.2. SiCO Preparation

Transformation of CO liquid to solid powder by using impregnation method is CO absorbed in the porous silica (SiCO) at a concentration of CO of 65 wt% and silica of 35 wt% as shown in Figure 1b. Firstly, silica was mixed with acetone then stirred at 50 °C for 5 min (RW20 digital IKA Company). Secondly, the CO was added to silica solution and stirred for 10 min. Finally, the SiCO was dried in an oven (Redline Model RF115 by Binder, Camarillo, CA, USA) at 60 °C for 2 h.

#### 2.2.3. DB/ZnSt Preparation

The small concentration of DB in the polymer matrix and large particle size of DB may lead to poor distribution and dispersion. Thus the process for reducing the size of DB and improving distribution and dispersing was needed. ZnSt was mixed with DB for anti-accumulation since the hydrophobic ZnSt particles covered the DB surface. The first procedure was mixing DB and ZnSt at weight ratio 1:1 in the high-speed mixer with agitator rotated at 3000 rpm and vibration of the chamber at 30 Hz for 5 min. The second process was decreasing particle size of DB/ZnSt using four hammer mills at high speed of 7000 rpm for 2 min, as presented in Figure 1c, with particle size of 3.49  $\pm$  1.27 µm.

## 2.2.4. Anti-Rodent Sample Preparation

PVC compound pellets and anti-gnawing substances were subsequently mixed in an internal mixer (MX75, Chareon Tut co., Ltd., Samut Prakan, Thailand) at various contents following Table 1 at a rotational speed of 40 rpm at 160 °C for 10 min. The concentration of anti-gnawing substances, SiCO and DB/ZnSt, combined with PVC matrix determined by work of L. Techawinyutham et al. [28]. The anti-rodent composites were subsequently compressed by compression molding machine (QC-601T, Comtech company, Taipei, Taiwan) at 170 °C, with preheat and a compression process time of 10 min at a pressure of 2500 psi. Then, the samples were cut for anti-gnawing, morphology, thermo-mechanical and rheological test.

Sam	ples	B/ZnSt (wt%)	SiCO (wt%)	
	I.1	1.96	12.16	
0.11	I.2	1.96	14.47	
Set I	I.3	1.96	18.75	
	I.4	1.96	23.53	
Set II	II.1	-	12.16	
	II.2	-	14.47	
	II.3	-	18.75	
	П.4	-	23.53	

Table 1. Content of anti-rodent samples.

# 2.3. Experimental Design and Anti-Gnawing Test Procedures

In the anti-gnawing study, female rats (Rattus norvegicus, Wistar, 6 wk) were used since they are less aggressive and more commonly housed in a group and for a longer period than male rats [29,30]. However, there was no scientific report about the gender effect on gnawing behavior. There were two rats in cage 1 and cage 2. For cage 3, there was a rat as displayed in Figure 2. The samples can be divided into 3 sets; Blank, Set I and Set II. The sample shape was rectangular ( $15 \text{ mm} \times 100 \text{ mm} \times 2.8 \text{ mm}$ ) and made a small hole at the top of the samples for hanging in the cage as shown in Figure 3. Each set of samples were hung on the lid of the cage for a month, after that the samples will be subsequently replaced with the new set of samples as shown in Table 2. The weight of the samples and the appearance was recorded at the end of each month. There were 8 pieces of Blank and 2 pieces of each concentration for composite Set I and Set II.



Figure 2. Experiment; (a) 2 rats for cage 1 and cage 2; (b) a rat in cage 3.



Figure 3. Pictures of; (a) specimens for anti-rodent testing; (b) testing environment.

Table 2. Experimental design of gnawing test.

Testing Period Animal Cage	1st Month	2nd Month	3rd Month
Cage 1	Blank	Set I	Set II
Cage 2	Set I	Set II	Blank
Cage 3	Set II	Blank	Set I

#### Statistical Analysis

The obtained data in term of percentage of weight loss of the samples were analyzed using one-way blocked analysis of variance (ANOVA) and means were compared with Tukey test by Minitab Statistical Software 17 (Minitab Inc., State College, PA, USA) with a 95% level of significance. ANOVA can help to present the influence of anti-rodent substance concentration, number of rats and period of time on the percentage of weight loss; therefore, the optimum concentration of the substances can be predicted.

### 2.4. Fourier-Transform Infrared Spectroscopy (FT-IR)

PVC compound and the PVC composites were loaded in FT-IR spectroscopy in attenuated total reflection (ATR) accessory for reflection mode using a Thermo Scientific Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific Inc.) with a scan range from 400 to 4000 cm<sup>-1</sup>.

## 2.5. Morphology

The scanning electron microscope (SEM) micrographs backscattered electron (BSE) mode of the surface structure of PVC and PVC composites were obtained by using a low-vacuum operated at 20 kV at a magnification of 250× (non-sputter coated). The samples were laid on a graphite conductive coating film. The SEM and energy dispersive spectroscopy (EDS) results were obtained from SEM instrument, a Hitachi, model SU3500 (Japan). For high magnification at 1000x of surface morphology of PVC, I.4, and II.4, the samples were coated with a platinum layer in argon gas at a power of 10 mA for 1 min using an MC1000 ion sputter coater machine (Hitachi, Tokyo, Japan) SEM sputter coater before taking the SEM image.

#### 2.6. Tensile Response

Tensile test was determined on the universal testing machine (Cometech QC-506M1-204, Taichung City, Taiwan) according to ASTM D638. The tensile test was performed at room temperature with crosshead speed of 50 mm/min and gauge length of 25 mm. The dimension of the specimens followed ASTM D638 IV with a thickness of 3 mm. At least five experiments were performed for each sample and the average values were considered and discussed.

# 2.7. Thermal Properties Analysis

## 2.7.1. Differential Scanning Calorimetry (DSC)

DSC measurements (DSC 3—Mettler Toledo CO. Ltd., Greifensee, Switzerland) were carried out to analyze the thermal properties of Blank and PVC composites. A small piece of samples ( $5.0 \pm 1 \text{ mg}$ ) were scanned in the range of -65– $180 \degree$ C at a heating rate and cooling rate of 20 °C/min with the isothermal period for 2 min. N2 environment at a constant flow rate of 50 mL/min was used. Thermal enthalpy of the samples was characterized by glass transition temperature ( $T_g$ ).

#### 2.7.2. Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) TGA instrument was Mettler Toledo TGA/DSC 3+ HT/1600 with identification 360 and the main sensor (TGA/HT DSC HSS2). The sample weight of PVC and all composites was 16  $\pm$  2 mg. The testing temperature range was 40–600 °C with isothermal for 3 min at 40 °C. The testing occurred under a nitrogen atmosphere with a constant flow rate of 50 mL/min at a constant heating rate of 10 °C/min for investigating degradation temperature and thermal stability of PVC and all PVC composites.

#### 2.8. Dynamic Rheology

The rheological properties of the molten Blank and the PVC composites were analyzed using a rheometer (KNX2112, Malvern, UK) with parallel plates geometry with a diameter

of 25 mm. The specimens were cut into a circle shape with a diameter of 25 mm and thickness of 3 mm. The measurements were performed in the dynamic oscillatory mode at 170 °C. The strain value was set at 0.1% to linear viscoelastic region (LVR) of PVC. The shear modulus of each sample was measured under frequency sweep which was taken in range from 0.1 to 1000 Hz with a constant strain at 0.1% with preheating time for 5 min. Shear viscosity ( $\eta$ ) of Blank and PVC composites was investigated under dynamic strain sweep (0.01–500%) at 170 °C with preheating time for 5 min.

#### 2.9. Accelerated Weathering

Accelerated weathering is a weathering testing to measure future properties of materials under adverse environmental conditions (ultraviolet radiation, extreme temperature, and humidity conditions). PVC, I.4 and II.4 were aged according to ASTM G155-13 cycle 1 in accelerated weathering tester machine (Q-Sun Xe-3, Q-Lab Corp., Westlake, PA, USA). One side of those samples was exposed to artificial light of xenon lamp with irradiance of  $0.35 \text{ W/m}^2$  and UV sensor of 340 nm at a temperature of 63 °C for 102 min in the controlled humidity of 30% in an accelerated weathering chamber. For the second step, the samples were exposed to light irradiation and water spray with irradiance of  $0.35 \text{ W/m}^2$  and UV sensor of 340 nm for 18 min. The samples were removed at 300 h and 600 h from accelerated weathering chamber.

#### 3. Results and Discussion

3.1. Characterization

#### 3.1.1. Morphology Response of DB/ZnSt

SEM micrographs at  $100 \times$  magnifications and EDS mapping of DB/ZnSt particles are displayed in Figure 4a,b respectively. SEM image of DB/ZnSt particles was scanned for identifying chemical composition mapping by EDS technique. EDS mapping used for ensuring that DB was covered with ZnSt particles. It showed that DB was mixed in ZnSt homogeneously and DB also was covered with ZnSt particle for preventing agglomeration of DB and improving dispersion of DB in PVC matrix.



**Figure 4.** (a) Scanned region in the SEM micrographs of DB/ZnSt particles; (b) elemental mapping of the scanned area; (c) EDAX spectra of DB/ZnSt particles.4c.

3.1.2. Morphology Response of PVC and PVC Composites

SEM micrographs at  $100 \times$  magnifications of PVC compound and PVC composite surface are presented in Figure 5 (Also Refer: Figure S1). The fillers showed good distribution in PVC matrix. The increase in anti-gnawing substances (SiCO and DB/ZnSt) caused the



holes on the sample surface to be larger, due to high substance particles causing weak interaction between the PVC matrix and the substances.

Figure 5. SEM micrographs of (a) PVC; (b) I.1; (c) I.2; (d) I.3; (e) I.4; (f) II.1; (g) II.2; (h) II.3; (i) II.4.

Comparing PVC composites Set I and Set II, EDS mapping showed that PVC composites Set I had greater and bigger holes than PVC composites set II. It may be DB/ZnSt had poor adhesion with PVC as shown in Figure 5b–i. The surface of PVC composite samples had higher and larger holes compared to PVC because of the existence of SiCO and DB/ZnSt. From Figure 6, the surface roughness of composite Set I (consisting of DB/ZnSt) was higher than composite Set II because anti-gnawing substances reduced the adhesion between the fillers and PVC matrix, especially DB/ZnSt due to good lubricating property of ZnSt and oily property of CO.



Figure 6. SEM micrographs with magnification 1000× of (a) PVC; (b) I.1; (c) II.4.

3.1.3. Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR-ATR was used to investigate the difference in structure of PVC and PVC composites as shown in Figure 7. The band of PVC was described in Table 3. FTIR spectrums of PVC composites were slightly different from Blank because of overlapping bands of PVC, DB and SiCO [31]. FT-IR bands of I.4 consisted of phenylic residues as 1536 cm<sup>-1</sup> referring to DB and Si–O–Si bonding as 1103 cm<sup>-1</sup> and 472 cm<sup>-1</sup> referring to silica (SiCO) [32–35].

Band of II.4 also showed Si–O–Si bonding at bands of 1103 and 472 cm<sup>-1</sup> referring to silica. Additionally, other peaks of SiCO and peak of DB was overlapped by peaks of PVC compound. The bands of carbonyl group and Si–O–Si bonding were slightly shifted to higher wavenumber probably because of an increase in those group structures due to addition in SiCO.



Figure 7. ATR-FTIR spectrums of PVC, I.4, and II.4 before and after aging in weathering.

Description of Vibrations	Wavenumbers (cm <sup>-1</sup> )
C-H stretching	2850–2958
C=O stretching vibration	1722–1725
C-H bending	1421–1424
C-H rocking	1257–1260
trans C-H wagging	961
-C-C- stretch	870–873
C-Cl stretching	750-850
cis C-H wagging	615

Table 3. Vibrational modes and wavenumbers observed in PVC compound [36-40].

The degradation of chemical structures of PVC and PVC composites after aging in weathering machine were analyzed by ATR-FTIR in Figure 7. Comparing FT-IR curve of non-aging sample and aging sample, it can be clearly seen the change of spectra. The longer weathering time decreased intensities of the distinctive IR bands of Blank, I.4 and II.4 as similar to work of Matuana et al. [41] Gallouze et al. [42]. Moreover, it can be observed that the shift of FTIR spectrum to lower wavenumber referred to a decrease in that bonding as degradation of those structures. It was because the significant levels of chemical degradation action of "photolysis" and "hydrolysis" caused random main chain scission [42–45]. It also shifted bands of the ester carbonyl group C=O (1716–1724 cm<sup>-1</sup>) to lower wavenumber [45].

PVC degradation firstly induced the oxidation of these polyenes providing conjugated double bonds and the carbonyl groups [46]. The decrease in absorption band means that the PVC chains were maybe cut and the atoms decreased especially in polyene and the carbonyl groups by water, temperature and UV irradiation during weathering test [47]. The concentration of SiCO and DB also decreased with increasing aging time; moreover, the anti-rodent substances seemed to increase the degradation of PVC structures. It is likely because the large difference in swelling and shrinkage between the fillers and PVC matrix from moisture and high temperature during aging leading to cracking and stress formation at the particle/matrix interface [48,49]. From FTIR result, it can be suggested that the PVC composites are suitable to be used at aging time lower than 620 h.

#### 3.2. Anti-Rodent Testing

ANOVA was used to evaluate the significance of concentration of substances, number of rats and period of testing time on anti-rodent test in term of percentage of weight loss. The result showed that model summary of one-way blocked ANOVA provided a coefficient of determination (R-squared) 80.53% and the probability of residual plot at *p* value > 0.235 as shown in Figure S2. The analysis of variance for the percentage of weight loss was presented in Table 4.

Source	DF	Adj SS	Adj MS	F-Value	<i>p</i> -Value
Sample	8	37,715	4714.3	23.58	0.000
Cage	2	9426	4713.2	23.57	0.000
Month	2	1639	819.3	4.10	0.022
Error	59	11,796	199.9		
Lack-of-Fit	14	7072	505.2		
Pure Error	45	4723	105.0	4.81	0.000
Total	71	60,575			

Table 4. Analysis of variance for the percentage of weight loss.

The results showed that the most gnawed sample was Blank. The minimum average of weight loss occurred at II.4. Tukey pairwise comparisons of samples, cage and period of time on sample weight loss with 95% confidence showed in Tables 5–7 respectively. It is

reported that Blank cannot prevent rodent, but the best rat-proof sample was II.4 which showed mean of weight loss at 1.68%. The other samples were not different significantly on the anti-gnawing test. From Figure 8, it can be clearly seen that the increase in SiCO concentration caused reduction in the sample weight loss. Table 5 shows that there was no significant difference in weight loss in the Set I because of the existence of DB/ZnSt giving bitter taste. The percentage of weight loss of II.4 is slightly lower than I.4. It may be some degradation of low thermal stability DB. From the results, it can be concluded that SiCO and DB can protect the polymer from gnawing by rodent.

Setting	Ν	Mean of Weight Loss (%)	Grouping
Blank	24	59.74	А
II.1	6	32.48	В
II.2	6	26.52	В, С
I.1	6	13.09	В, С
II.3	6	12.65	В, С
I.2	6	10.92	В, С
I.3	6	8.70	В, С
I.4	6	7.01	В, С
II.4	6	1.68	С

Table 5. Grouping information of samples using the Tukey method and 95% confidence.

Table 6. Grouping information of cage using the Tukey method and 95% confidence.

Cage	Ν	Mean of Weight Loss (%)	Grouping
C3	24	35.28	А
C2	24	12.73	В
C1	24	9.59	В

Table 7. Grouping information of period of time using the Tukey method and 95% confidence.

Month	Ν	Mean of Weight Loss (%)	Grouping
1	24	25.9047	А
2	24	16.4909	А, В
3	24	15.2018	В



Figure 8. Effect of substances concentration, number of rats and time on percentage of weight loss.

The influence of the number of rats on weight loss was investigated. Cage 3 (individual rat) showed the highest weight loss since individual rat had more aggressive behavior

and/or stress than social rat. The social rat had relations with their members [29,50]. This led the individual rat to bite something for stress relaxation, because gnawing behavior of rat comes from stress or loneliness [51–54]. Table 6 presents cage 1 and 2 consisting of two rats that were not significantly different.

The period of time for anti-gnawing testing affected the percentage of weight loss. Table 7 shows that weight loss at the first month and the last month was clearly different. The weight loss of the 1st month showed the maximum value at around 26%, since at the beginning of the test, the rats were excited with the samples; however, after that they felt less interested. Therefore, the minimum weight loss was shown at the last month in the sample.

#### 3.3. Tensile Properties

Tensile test was used for determining tensile strength, tensile modulus and elongation at break of Blank and all PVC composites as presented in Table 8 and Figure 9. The addition of anti-gnawing substances: SiCO and DB/ZnSt obviously decreased in tensile strength of the composites compared to Blank. Tensile strength of the composites Set I did not differ significantly to composites Set II since small amount of DB/ZnSt did not have an effect on tensile strength. It can be concluded that only SiCO had an influence on tensile strength. The tensile strength reduced with increasing content of SiCO in the PVC matrix especially for I.3, I.4, II.3 and II.4. It is because the high concentration of stresses around the filler particles and the aggregation of SiCO particles in PVC matrix contributed to decrease in the contact area between PVC and SiCO as well as created physical defect in the PVC composites, as can be clearly seen in SEM micrographs displaying voids on the sample surface [55,56]. It caused no stress transferred from PVC matrix to the particles [55–57]. Similarly, A. Zhu et al. [57] found that tensile strength decreased with addition content of silica in PVC up to 4 wt% and J. E. Crespo et al. [55] reported that an increase in filler content in PVC led to tensile strength decrease. Moreover, capsicum oil acting as plasticizer in the PVC matrix reduced tensile strength as similar to work of N. Gil et al. [58] since the polymer chains can move freely with high mobility [55,59].

Code	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Modulus (MPa)
PVC	$16.42 \pm 1.1$	$522.15\pm74.1$	$10.76\pm0.5$
I.1	$12.23\pm1.0$	$531.21\pm82.9$	$9.61\pm0.3$
I.2	$12.03\pm0.5$	$514.56 \pm 42.1$	$9.66\pm0.9$
I.3	$10.65\pm0.4$	$459.46 \pm 47.0$	$9.72\pm0.6$
I.4	$8.09\pm0.8$	$321.49\pm62.5$	$9.38\pm0.5$
II.1	$13.13\pm0.8$	$508.79 \pm 64.4$	$8.95\pm0.5$
II.2	$12.51\pm0.5$	$489.58\pm34.0$	$9.25\pm0.3$
II.3	$11.03\pm0.5$	$441.64\pm43.5$	$9.58\pm0.5$
II.4	$8.41\pm0.6$	$318.60\pm51.8$	$9.61\pm0.4$

Table 8. Tensile strength, tensile modulus and elongation at break of PVC and all PVC composites.

Elongation at break of Blank did not differ significantly to PVC composites except I.4 and II.4 because of high amount of SiCO. Normally, silica decreased elongation at break but the addition of SiCO in PVC matrix below 18.75 wt% did not reduce the elongation, due to capsicum oil improving chain mobility of PVC [55,59]. The elongation was not affected by DB/ZnSt. The addition of SiCO at 23.53 wt% (I.4 and II.4) resulted in a reduction of elongation at break due to high concentration of silica causing weak interaction between fillers and polymer matrix. The addition content of silica in PVC matrix decreased in elongation similar to work of Ł. Klapiszewski et al. [60] because poor stress transferred from PVC matrix to fillers [55–58].



Figure 9. Stress-strain curves of PVC compound and PVC composites.

The addition of anti-rodent substances caused slight decrease in tensile modulus compared to Blank. The small amount of DB/ZnSt in PVC matrix did not reduce tensile modulus. The capsicum oil in SiCO had a negative effect on the rigidity of PVC which led to the modulus being decreased with increasing plasticizer content as similar behavior to work of Crespo et al. [55] and Gil et al. [58]; however, the increase in SiCO concentration in this work did not affect the modulus. This may be because of the higher amount of silica improving tensile modulus and the resistance to deformation of the composites. This was similar to work of Ł. Klapiszewski et al. [60] and M. Fasihi et al. [61] because of strong stiffness of silica particles. It can be summarized that SiCO had a minimal effect on reducing tensile modulus.

## 3.4. Thermal Analysis

## 3.4.1. Differential Scanning Calorimetry (DSC)

The influence of anti-gnawing substance in PVC matrix on thermal properties was investigated by DSC. The 2nd heating curve is displayed in Figure 10. The 2nd heating curve of Blank and PVC composites did not clearly show crystallization temperature (T<sub>c</sub>) and melting temperature (T<sub>m</sub>), similar to work of Jia et al. [62]. T<sub>g</sub> of the PVC composites was slightly lower than PVC because of SiCO. The increase in SiCO concentration dropped  $T_g$  of PVC composites since capsicum oil acted as plasticizer [63]. The shifting of  $T_g$  to lower temperature because of CO acting as plasticizer was similar to work of C. Bueno-Ferrer [64] and P. G. Nihul [65]. CO corresponds to increase in disorder, free volume of the macromolecules and chain mobility of PVC [62]. It was also probably because agglomeration of SiCO particles dropped the interaction between PVC chains and the fillers [66]. However, work of M. Mohagheghian [67] and S. Lavina [68] reported that the additional amount of silica particles in PVC matrix increased in Tg of the composites and reduction in chain the mobility of polymer [67]. It can be concluded that CO had higher influence on Tg than silica. DB in composite Set I provided higher Tg than composite Set II since some degradation of DB in the PVC matrix obstructed the movement of PVC chain [67]. The small endothermic peak occurring in Blank around 110 °C and in the composites ranging from 75 to 85 °C was a change in heat capacity probably due to degradation of the additive in the flexible PVC [69]. At low thermal decomposition, the addition of capsicum oil in SiCO slightly decreased thermal stability of the composites.



Figure 10. DSC 2nd heating curve of PVC compound and PVC composites.

3.4.2. Thermogravimetric Analysis (TGA)

Thermal stability of PVC and all composites were analyzed by TGA and DTG presented in Figures 11 and 12 respectively. All TG curves indicated two major steps of weight loss which displayed similar degradation trend as similar work of Al-Sagheer et al. [16], Klapiszewski et al. [60] and Ari et al. [70] The first step of weight loss occurring in the temperature ranging in 250-350 °C as presented in Table 9 was attributed to the PVC dehydrochlorination process corresponding to the HCl elimination reaction followed by the formation of conjugated structure polyene sequences or the polyene linkages [16,60,70,71]. The second step of weight loss, occurring in a higher temperature in range of 350–500  $^{\circ}$ C, corresponds to thermal degradation of carbon chain of conjugated structure polyene [16,70]. The thermal degradation of the composites Set I shifted to lower temperature; however, for the composites Set II the thermal degradation shifted to higher temperature compared to PVC compound. This is because the composites Set I consisted of low thermal stability of DB/ZnSt that initiated the dehydrochlorination of PVC. For the PVC composites, the increase in content of SiCO led to improving of thermal degradation of PVC because of high thermal stability of silica particles. Silica can improve thermal stability of PVC as similar to work of Mohagheghian et al. [67] and Al-Sagheer and Z. Ahmad [16] since the polymer chains were restricted and absorbed in the thermally stable silica network. Moreover, silica required higher heat to be decomposed into ash than the polymer matrix [67]. Mohammad et al. [58] reported that plasticizer in PVC accelerated the degradation of PVC; however, in this work, CO absorbed in nanoporous silica did not decrease thermal stability of PVC matrix. Greater content of SiCO increased residual weight due to the residual of silica retained [16]. The residual weight of the PVC composites Set I higher than PVC and composite Set II due to char of DB. It can be concluded that DB/ZnSt produced poor effect on thermal stability of PVC; however, the addition of SiCO particles in PVC matrix improved thermal stability of the PVC.



Figure 11. TGA of PVC and PVC composites.



**Figure 12.** DTG of PVC and PVC composites.

Table 9. Thermal characteristics of PVC and PVC composites.

Sample	T <sub>onset1</sub> (°C)	T <sub>onset2</sub> (°C)	T <sub>1%</sub> (°C)	T <sub>5%</sub> (°C)	T <sub>50%</sub> (°C)	T <sub>max1</sub> (°C)	T <sub>max2</sub> (°C)	Ash Content (%wt)
PVC	293.59	432.53	257.87	283.57	326.55	313.66	443.34	28.66
I.1	272.11	433.69	239.77	267.40	324.59	294.80	455.28	29.34
I.2	273.70	430.22	243.04	268.46	328.22	297.45	457.16	29.43
I.3	275.25	440.48	240.91	268.85	331.45	298.30	458.72	30.50
I.4	277.18	449.96	234.40	271.01	339.35	299.96	457.17	31.22
II.1	291.49	454.29	260.14	284.82	337.02	315.70	457.09	25.56
II.2	290.81	446.31	256.56	285.67	340.25	315.37	459.66	26.67
II.3	290.09	442.24	252.82	286.00	340.78	314.22	454.68	27.42
II.4	288.93	430.87	242.22	283.07	348.68	314.02	453.14	27.85

## 3.5. Rheological Behavior

The dynamic rheological behavior of Blank and all composites were determined by oscillary rheometer. G and G'' as a function of frequency for PVC and the PVC composites plotted on log-log scale compound are shown in Figure 13a,b respectively. G' of PVC and PVC composites was lower than G''. The highest shear storage modulus was PVC for all frequencies. The addition in SiCO led to increasing in G' and G'' at low frequency. For the composites Set I consisting of DB/ZnSt caused G' and G'' slightly lower than composites Set II because ZnSt acting as plasticizer improved chain mobility reduced G' and G'' of the composites [72]. This was similar to research of Liang et al. [72] and Sugimoto et al. [73]; moreover, they reported that G' reduced with increasing plasticizer concentration. The increase in the amount of SiCO improved G' and G'' as similar behavior to work by Al-Oweini et al. [33] and Kamibayashi et al. [74] since silica particle obstructed polymer chain mobility [70]. Although silica improved G' and G'' of PVC matrix, there was CO in porous of silica acting as a plasticizer. It caused G' and G'' of the PVC composites lower than those of PVC.





**Figure 13.** (a) G'; (b) G'' of PVC and the PVC composites.

The shear viscosity as a function of shear rate of Blank and all PVC composites are displayed in Figure 14. PVC showed the highest shear viscosity. The PVC composites Set II had higher shear viscosity than Set I since ZnSt in DB/ZnSt in composites Set I acts as a lubricant. The melt viscosity of all PVC composites and PVC did not observe a Newtonian plateau viscosity; however, they exhibited shear thinning profile at all shear rates. The higher shear rate, the more shear-thinning behavior. The increase in SiCO concentration reduced shear viscosity because capsicum oil acted as plasticizer and improved chain mobility of PVC since it decreased polymer concentration in the continuous phase [72]. The addition of silica concentration increased shear viscosity since the high surface area of silica particles improved interaction between PVC and silica which led to restricting polymer chain mobility [70]. However, the viscosity of the composites did not improve as regularly as was found in the work of Kamibayashi et al. [74] and Otsubo [75]. CO had a higher influence on shear viscosity than silica. It can be concluded that the shear viscosity of the PVC matrix decreased with increasing SiCO concentration.



Figure 14. Shear viscosity of PVC and the PVC composites.

## 4. Conclusions

The influence of DB/ZnSt and SiCO composited with PVC on anti-gnawing, morphology, thermo-mechanical and rheological properties were studied. Anti-rodent substances were a good distribution in PVC matrix; however, the addition in substances increased the hole on the PVC surface and reduced interaction between the fillers and PVC matrix. Anti-gnawing data were analyzed by one-way block design of ANOVA. The statistical model shows that it fits a set of observations. SiCO and DB/ZnSt can protect the polymer from the rodent. The results suggested that II.4 consisting of SiCO at 23.53 wt% was the best anti-rodent composite with good mechanical and thermal properties. The addition of SiCO and DB/ZnSt decreased tensile strength. For the highest SiCO concentration, elongation at break reduced since a high amount of SiCO decreased compatibility between PVC matrix and the substances. However, the tensile modulus did not change significantly with an increasing amount of SiCO. T<sub>g</sub>, G', G'' and  $\eta$  decreased with increasing SiCO concentration since capsicum oil improves the flexibility of PVC. Thermal stability of PVC reduced with addition DB, but it improved with an increasing amount of SiCO.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10 .3390/jcs6010008/s1, Figure S1: EDS mapping micrographs, Figure S2: Probability plot of percentage of weight loss, Figure S3: Samples after anti-gnawing test for one month, Figure S4: DSC cooling curve of PVC compound and PVC composites.

**Author Contributions:** Conceptualization, R.D. and L.T.; methodology, L.T. and A.P.; formal analysis, investigation, writing—original draft preparation, L.T.; writing—review and editing, S.M.R.; visualization, supervision, S.S. and R.D. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by King Mongkut's University of Technology North Bangkok (KMUTNB) with Contract no KMUTNB-65-BASIC-01.

**Institutional Review Board Statement:** The study was conducted according to the guidelines of the Declaration of Helsinki, and approved by the Institutional Review Board (or Ethics Committee) of Mahidol University (protocol code of MUSC59-011-344 and date of approval of 21 December 2016).

Acknowledgments: The author gratefully thanks Natural Composites Research Lab (NCR) (Materials and Production Engineering, KMUTNB) for financial and instrument, Center of Innovation in Design and Engineering for Manufacturing (CoI-DEM), KMUTNB for supporting TGA machine and World Pigment Industries Co.,Ltd. (Bangkok, Thailand) for supporting silica and ZnSt. We would like to thank COAX Group Corporation Ltd., Bangkok, Thailand for supporting SEM machine and EDS analytical system and Tepmanas Bupha-Intr for helping anti-gnawing testing. Protocal no. MUSC59-011-344 is approved from Faculty of Science, Mahidol University.

Conflicts of Interest: The authors declare no conflict of interest.

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