

Research article

Characterization and properties of silica-filled natural rubber compounds using poly(vinyl propionate)-grafted natural rubber as compatibilizer

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Abstract. This work presents the use of natural rubber (NR) grafted with poly(vinyl propionate) (NR-g-PVP) as an alternative compatibilizer in silica-filled NR compounds. The effects of NR-g-PVP with 10, 20 and 30% grafting on the properties of NR compounds were studied and compared with a commercial coupling agent (bis[3-(triethoxysilyl)propyl] tetrasulfide, TESPT). NR-g-PVP was compatible with silica and NR. The NR-g-PVP reduced filler-filler interactions and increased filler-rubber interactions. The crosslink density decreased with the percentage of grafting due to the steric hindrance. The compatibilization affected the physical and mechanical properties. The interactions of NR-g-PVP with silica via hydrogen bonding and subsequent vulcanization prevented undesirable filler-filler interactions and reduced the absorption of accelerators or basic materials. It caused a good dispersion of silica in the NR matrix and improved physical and mechanical properties. A 10% grafting (G10) was suitable for the compatibilizer in a silica-filled NR compound, showing the largest improvements in tensile properties, tear strength, and hardness. However, TESPT provided better properties than G10.

Keywords: rubber, functional polymers, additive, blends, mechanical properties, reinforcement

1. Introduction

Natural rubber (NR) is harvested from the *Hevea brasiliensis* trees. It consists of many *cis*-1,4-polyisoprene units. It is widely used in the rubber industry, especially in tire manufacture. It has excellent properties, such as high elasticity, high elongation at break, good electrical insulation, and low heat build-up. However, there are some undesirable properties, such as poor weather and oil resistance, as well as poor flame resistance. Due to the undesirable properties and desired high-performance properties, raw natural rubber could not be directly used in rubber manufacture. Rubber compounding by adding various ingredients to the NR is a strategy to obtain high-performance NR and satisfy the end products. A general formulation for rubber compounding consists of

an activator, an accelerator, an antioxidant, a filler, and a curing agent. Among these ingredients, filler is an important material for rubber manufacture. It could lower the cost or improve the properties of the compound. Fillers are classified into two types: non-reinforcing fillers (*e.g.*, calcium carbonate, clay, and talcum) and reinforcing fillers (*e.g.*, carbon black and silica) [1]. Reinforcing fillers are important ingredients for tire manufacture. It plays an important role in enhancing mechanical properties. Carbon black was the first commercial reinforcing filler used in the tire industry until the development of other reinforcing fillers was revealed. In 1992, Michelin was the first to introduce silica into tire treads [2]. The incorporation of silica into the tire enhances the abrasion resistance, lowers rolling resistance, and improves

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the wet skid in comparison with carbon black [3]. The dispersion of silica in the NR matrix is unlike that of carbon black. Carbon black is easily and homogeneously dispersed, while silica is difficult to disperse due to its polarity. The polar silica is incompatible with non-polar NR. The surface of silica consists of several silanol groups (Si–OH). It exhibits a hydrophilic character and forms hydrogen bonds between the silica particles. This leads to strong filler-filler interactions, resulting in an aggregation and poor dispersion in the NR matrix [4]. These caused the deterioration of the mechanical properties of the NR compound. In addition, the acidic surface of silica causes an absorption of curatives and basic materials. Especially, the absorption of the accelerators by silica causes a delay in the vulcanization reaction, resulting in a low crosslink density [5]. The use of a silane coupling agent could solve these problems. The structure of the silane coupling agent consists of two structural parts. One part reacts with a silanol group of silica, and the other one reacts with NR. The bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT) is commonly used as a silane coupling agent in NR compounds [6–9]. Two reactions occur simultaneously during the mixing: a) the silanization reaction between the silanol group of silica and the alkoxy group of silane and b) the coupling reaction between sulfur in TESPT and NR molecules [4].

The incorporation of modified NR as a compatibilizer in silica-filled NR compounds is one of the successful approaches to improve the compatibility between silica and NR. It has been reported that incorporating epoxidized NR could improve the compatibility and mechanical properties of the NR compounds [10–12]. Katueangngan *et al.* [13] reported using hydroxyl telechelic natural rubber (HTNR) as a compatibilizer, affecting the cure characteristics of NR compounds. The addition of HTNR at 8% w/w of silica content decreased the cure time and increased the cure rate index, as well as increased the crosslink density of NR compounds. HTNR improved the tensile strength and elongation at break of the NR compound in comparison with the NR compound without a compatibilizer [14]. Borapak *et al.* [15] studied the incorporation of NR grafted with poly(2-hydroxyethyl acrylate) (NR-*g*-PHEA) with varying grafting percentages (6.5 to 14.5%) in NR compounds. The scorch time and cure time decreased with grafting percentages while the mechanical

properties of NR compounds improved. The 3 phr of NR-*g*-PHEA (14.5% grafting) showed the highest modulus, tensile strength, and reinforcing index [16]. Inphonlek *et al.* [17] synthesized and used poly (acrylic acid-*co*-acrylamide)-grafted deproteinized natural rubber ((PAA-*co*-PAM)-DPNR) as a compatibilizer in deproteinized natural rubber compounds. Tensile strength and elongation at break improved with the addition of (PAA-*co*-PAM)-DPNR containing 10 phr of monomer.

This work presents the use of poly(vinyl propionate)-grafted natural rubber (NR-*g*-PVP) as an alternative compatibilizer in silica-filled NR compounds, comparing it with TESPT. We assumed that the addition of graft copolymer could improve the compatibility between silica and NR, giving better dispersion of silica in the NR matrix. The effects of the percentage of grafted PVP on cure characteristics, crosslink density, mechanical properties, physical properties, and morphology of the NR compounds were investigated. Viscoelastic behavior and thermal stability of the silica-filled NR compounds were also studied.

2. Experimental

2.1. Materials

Natural rubber (NR; Standard Thai Rubber 5L) was produced by Chalong Latex Industry Co., Ltd., Thailand. High ammonia-concentrated natural rubber latex (HA-NRL, 60% of dry rubber content) was produced by Jana Concentrated Latex Co., Thailand. Vinyl propionate (98%, VP), tetraethylene pentamine (98%, TEPA), and cumene hydroperoxide (80%, CHP) were supplied by Sigma-Aldrich. Potassium hydroxide (KOH) and methanol were supplied by Labscan Asia Co., Ltd. Potassium laurate (20%) was supplied by High Science Ltd., Part., Thailand. Silica (ULTRASIL[®] VN 3) with a Brunauer-Emmett-Teller (BET) surface area of 180 m²/g and bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT) were produced by Evonik Industries AG, Germany. Paraffinic oil, 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), diphenylguanidine (DPG), *N*-cyclohexyl-2-benzothiazole sulfonamide (CBS), and sulfur were purchased from KIJ Paiboon Chemical Ltd., Part., Thailand. Zinc oxide (ZnO) was manufactured by Global Chemical Co., Ltd., Thailand. Stearic acid was manufactured by Imperial Industrial Chemicals Co., Ltd., Thailand.

2.2. Synthesis of NR-g-PVP

NR-g-PVR was prepared and characterized according to our previous work [18]. In this study, the three weight percentages of VP were used at 10, 20, and 30 wt%. An amount of 200 g of distilled water and 10 g of potassium laurate (surfactant) were added to a three-necked round bottom flask containing 90 g of HA-NRL. The mixture was purged with nitrogen gas and heated to 50 °C before adding 1 phr of TEPA (initiator). The mixture of VP (10 g, monomer) and CHP (1 phr, initiator) was dropped into the reactor. The mixture was continuously stirred and left for 2 h under a nitrogen atmosphere. The pH of the mixture was kept at 10 during the reaction with 10 wt% of KOH solution. The obtained mixture was precipitated in cold methanol and dried in an oven at 60 °C for 24 h.

The chemical structure of the graft copolymer was verified by using a Fourier transform infrared (FTIR) spectrometer (PerkinElmer, Spotlight 200i, USA) and a proton nuclear magnetic resonance (¹H-NMR) spectrometer (500 MHz, Varian Unity Inova). For FTIR analysis, the data were recorded over the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹ in attenuated total reflectance (ATR) mode with 8 scans. Deuterated chloroform was used as the solvent in ¹H-NMR analysis.

2.3. Preparation of silica-filled NR compounds

The compounding formulations are listed in Table 1. The control formulation was a silica-filled NR compound without compatibilizer, while the NR-g-PVP formulation was a silica-filled NR compound with compatibilizer with varying %grafting (G10, G20 and G30). The last formulation was a silica-filled NR compound using TESPT as a coupling agent. The silica-filled NR compounds were prepared in two steps. The first step was done using an internal mixer (HAAKE™ Rheomix Lab Mixers, Rheomix 600 OS) with Banbury rotors. The net chamber volume is 625 cm³ at a fill factor of 70%. The mixing temperature was set at 90 °C with a rotor speed of 60 rpm. NR was masticated for 2 min before the addition of silica and NR-g-PVP. They were separately added into the masticated rubber. The first portion consisting of half of the combined silica and NR-g-PVP was added and mixed for 5 min. Then, the second

Table 1. Compounding formulations.

Material	Amount [phr]		
	Control	NR-g-PVP	TESPT
NR	100	100	100
Silica	30	30	30
NR-g-PVP (G10, G20 and G30)	–	2.5	–
TESPT	–	–	2.5
Paraffinic oil	8	8	8
ZnO	3	3	3
Stearic acid	1	1	1
TMQ	1	1	1
DPG	1	1	1
CBS	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5

portion was the remaining half of silica and NR-g-PVP, including paraffinic oil (processing oil), which were added and further mixed for 5 min. ZnO (activator), stearic acid (activator), and TMQ (antioxidant) were added and mixed for 3 min. Finally, the rubber compound was taken out from the internal mixer. The second step was performed by using a two-roll mill (Chareontut Co., Ltd., Thailand) at room temperature. DPG (accelerator), CBS (accelerator), and sulfur (curing agent) were added and further mixed for 5 min. Then, the compounds were taken out and left to cool down for 24 h before vulcanization. The compound sheets of 2 mm of thickness were prepared using a compression molding machine (SLLP50, Siamlab Engineering Co., Ltd., Thailand) at 170 °C with a pressure of 14 MPa. The compounds were vulcanized up to the optimum cure time (t_{90}). t_{90} is the time to reach 90% of maximum torque. It is determined from the cure curve from a moving die rheometer.

2.4. Compound characterizations

2.4.1. Cure characteristics

The cure characteristics of NR compounds were determined according to ASTM D5289. A sample was tested at 170 °C using a moving die rheometer (MDR, MonTech MDR3000 Basic, USA). The minimum torque (M_L), maximum torque (M_H), torque difference ($M_H - M_L$), scorch time (t_{s1}), and cure time (t_{90}) were reported. The cure rate index (CRI) was calculated according to Equation (1):

$$CRI = \frac{100}{t_{90} - t_{s1}} [\text{min}^{-1}] \quad (1)$$

2.4.2. Mooney viscosity

The Mooney viscosity of NR compounds was determined by using a Mooney viscometer (MonTech MV3000 Basic, USA) according to ASTM D1646. A sample was tested at 100 °C following preheating for 1 min and heating for 4 min with a large rotor.

2.4.3. Swelling test

The swelling of NR compounds was tested according to ISO 1817. The dimensions of the samples were 10×10×2 mm (width × length × thickness). They were weighed and swollen in toluene at room temperature for 72 h. The swollen samples were taken out from the toluene, and the surfaces were wiped with a tissue before being weighed. The swelling of the compound was calculated according to Equation (2):

$$\text{Swelling} = \frac{w_s - w_i}{w_i} \cdot 100 [\%] \quad (2)$$

where w_i and w_s are the initial weight and the weight of the swollen sample in grams, respectively.

2.4.4. Mechanical properties

The tensile properties were tested according to ISO 37 Type II. Six specimens per formulation were cut into a dumbbell shape and tested using a universal testing machine (LLOYD Instruments, Ametek Inc., USA) at a crosshead speed of 500 mm/min with a 1 kN load cell. The 300% modulus, 500% modulus, tensile strength, and elongation at break were determined. The average values and their standard deviations (*SD*) are reported. Tear resistance was investigated according to ISO 34 using a universal testing machine (LLOYD Instruments, Ametek Inc., USA). Six specimens were cut with type C die and tested at a crosshead speed of 500 mm/min with a 1 kN load cell. The average tear strength with *SD* is reported.

2.4.5. Physical properties

The hardness of NR compounds was determined according to ASTM D2240 type A. The measurement was performed using a hardness tester (Bareiss, BS61 II). The average of measurement at 5 different points of each specimen is reported with *SD*.

2.4.6. Viscoelastic behavior

The viscoelasticity of NR compounds was tested using a dynamic mechanical analyzer (DMA8000,

PerkinElmer, USA). The dimensions of the specimens were 12×35×2 mm (width × length × thickness). The test was performed in tension mode at 0.2% strain control and a frequency of 1 Hz. The operating temperature was in the range of –90 to 160 °C at a heating rate of 2 °C/min.

2.4.7. Thermogravimetric analysis

The thermal stability of NR compounds was analyzed by using a thermogravimetric analyzer (TGA8000, PerkinElmer, USA). The test was performed from 30 to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.4.8. Morphological analysis

The phase morphologies of NR compounds were studied using a scanning electron microscope (FEI Quanta 400, FEI company, Oregon, USA). The specimens were frozen in liquid nitrogen and quickly fractured to create cross-section surfaces. These surfaces were coated with gold before imaging.

3. Results and discussion

3.1. Characterization of NR-g-PVP

NR-g-PVP was synthesized by emulsion polymerization in the presence of redox initiators. The ¹H-NMR spectra of NR and NR-g-PVP are presented in Figure 1. NR showed the characteristic peak belonging to the CH proton at 5.10 ppm. The graft copolymer showed a new peak at 3.75 ppm, corresponding to the CH proton close to the ester group. The calculation of weight percentages of PVP grafted onto the NR was described in our previous work [18]. The use of 10, 20, and 30 wt% of VP provided the 9.2, 17.6, and 26.4 wt% grafting levels on the

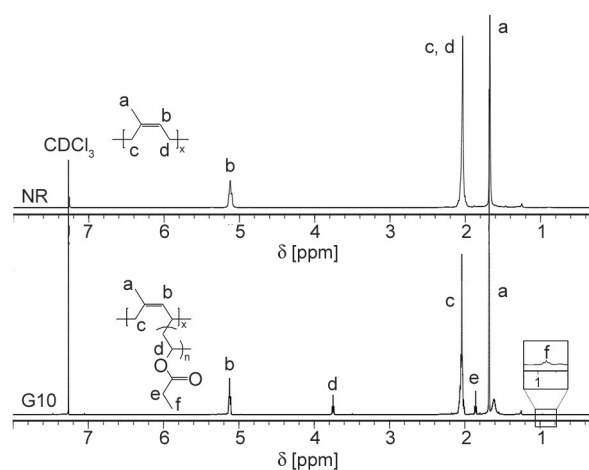


Figure 1. ¹H-NMR spectra of NR and NR grafted with 9.2 wt% of PVP (G10).

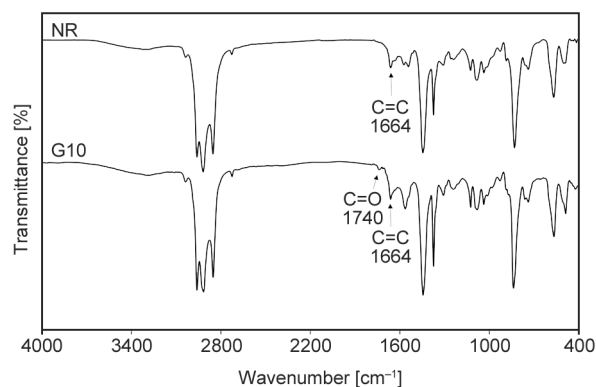


Figure 2. FTIR spectra of NR and NR-g-PVP with 10% grafting (G10).

NR. These graft copolymers were named G10, G20, and G30, respectively.

The FTIR spectrum of NR-g-PVP is shown in Figure 2. The characteristic absorption bands observed at 1664 and 1740 cm^{-1} corresponded to the stretching vibrations of C=C and C=O, respectively. Both $^1\text{H-NMR}$ and FTIR data confirmed success in grafting PVP onto NR.

3.2. Cure characteristics and Mooney viscosity

The data obtained from MDR provided information on the cure characteristics of the NR compound before, during, and after curing. The cure curves of silica-filled NR compounds are presented in Figure 3. All the curves showed the reversion type of cure behavior. This was due to the decomposition of

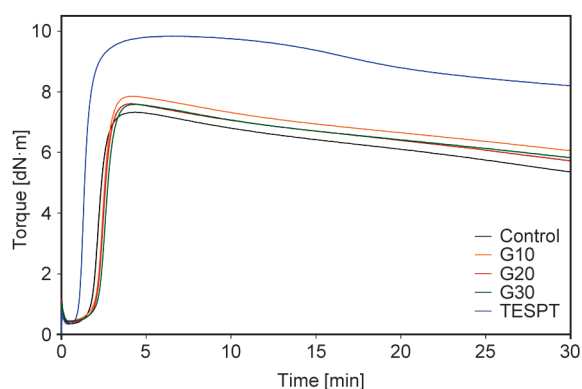


Figure 3. Cure curves of silica-filled NR compounds.

polysulfidic linkages and the degradation of rubber chains with prolonged vulcanization and/or high temperatures, usually observed in isoprene rubber. These mechanisms cause a decrease in torque and a loss of crosslink density [19]. M_L is the minimum torque taken at the lowest point of the cure curve. It indicates the viscosity of an unvulcanized material. It seemed that the M_L of the NR compounds increased with the addition of NR-g-PVP (0.41–0.45 $\text{dN}\cdot\text{m}$) in comparison to the NR compounds without a compatibilizer (0.36 $\text{dN}\cdot\text{m}$), while the M_L of NR compound with TESPT (0.34 $\text{dN}\cdot\text{m}$) was not significantly changed (Table 2). This was due to the addition of graft copolymer into the NR compound. Generally, the viscosity relates to molecular weight. The number average molecular weight of NR-g-PVP was approximately 250 000 g/mol [18]. Thus, this component caused the increase in M_L of the NR compounds. A similar increase in M_L after adding graft copolymer in deproteinized NR compounds has been reported [17].

M_H is the maximum torque, indicating the stiffness of the fully vulcanized material. In this state, the molecular movement of polymer chains is restricted because of the full crosslinking. It is known that crosslinking increases the stiffness of a material. The crosslinking in NR compounds with NR-g-PVP occurred through interactions between NR-g-PVP and silica via hydrogen bonding as well as vulcanization, while the crosslinking in the NR compound with TESPT occurred through silanization (reaction between TESPT and silica) and vulcanization (Figure 4). The higher M_H of the NR compound with TESPT indicated that it had higher stiffness in comparison with NR compounds with NR-g-PVP (Table 2).

The crosslink density can be assessed from torque difference [15, 20]. A sample with higher crosslink density gives a higher $M_H - M_L$. Sulfur is a curing agent for vulcanized rubber. NR compound with TESPT had two different sources of sulfur: one from a material in the recipe (Table 1) and the other one

Table 2. Cure properties and Mooney viscosity of silica-filled NR compounds.

Sample	M_L [$\text{dN}\cdot\text{m}$]	M_H [$\text{dN}\cdot\text{m}$]	$M_H - M_L$ [$\text{dN}\cdot\text{m}$]	t_{s1} [min]	t_{90} [min]	CRI [min^{-1}]	ML[1+4] at 100 °C [MU]
Control	0.36	7.33	6.97	1.84	2.78	106	19±0.1
G10	0.45	7.86	7.41	2.09	2.97	114	22±0.1
G20	0.41	7.61	7.20	2.12	2.99	115	23±0.1
G30	0.44	7.59	7.15	2.24	3.16	109	23±0.2
TESPT	0.34	9.84	9.50	1.08	2.13	95	22±0.1

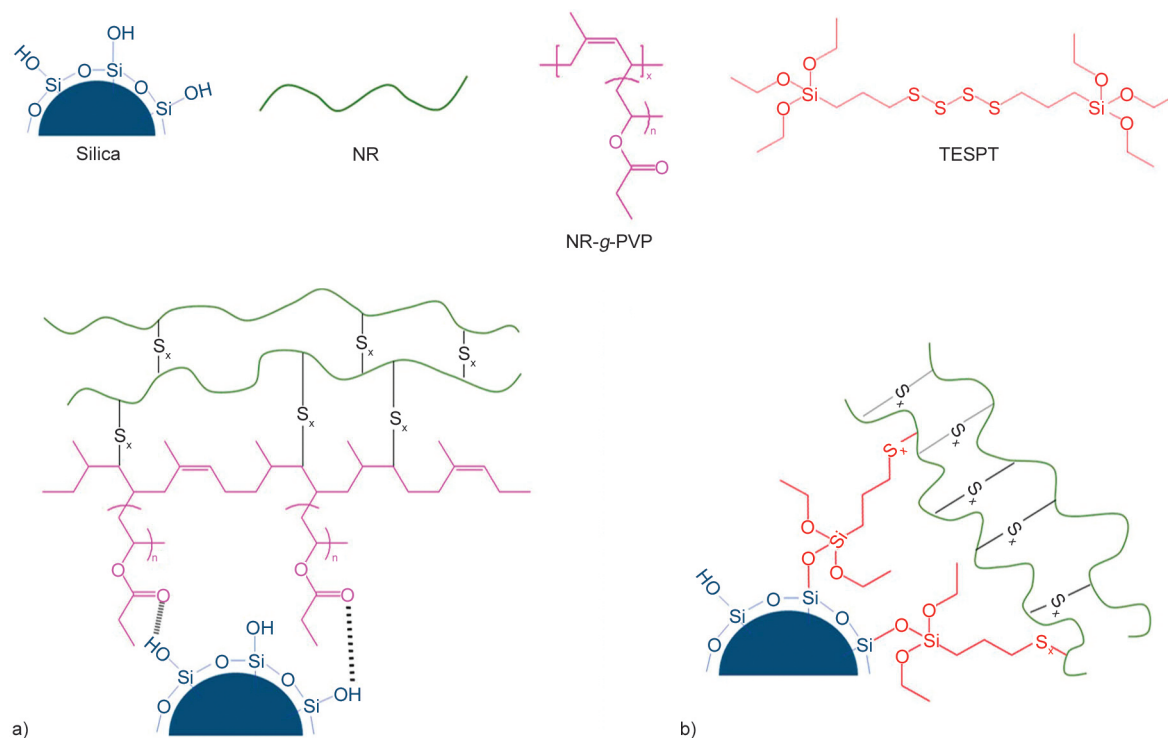


Figure 4. Proposed interactions between a) silica and NR-g-PVP, and b) silica and TESPT.

from the dissociation of TESPT (Figure 4). Thus, the higher sulfur content in the NR compound with TESPT provided a higher crosslink density. The addition of NR-g-PVP increased the t_{s1} and t_{90} of NR compounds in comparison with control. In addition, these tended to increase with the % grafting. This could be explained by steric hindrance. The general structure of a graft copolymer consists of a linear backbone and randomly distributed branches. The large NR-g-PVP molecules with long-chain branches caused steric hindrance, limiting the interactions between NR-g-PVP and silanol groups on the silica surfaces, resulting in remaining unreacted silanol groups. These silanol groups could absorb the accelerators through either hydrogen bonding or van der Waals forces, leading to an increase in t_{s1} and t_{90} . A high percentage of grafting of PVP onto NR provided more steric hindrance and more undesirable interactions between the remaining silanol groups on the silica surfaces and accelerators, resulting in retarding the vulcanization. Therefore, NR compounds with G30 showed the highest t_{s1} and t_{90} . In the case of the NR compound with TESPT, it was effective in interacting with silanol groups on silica surfaces due to a smaller molecule resulting in a reduction of the absorption of accelerators on silica, leading to a reduction of t_{s1} and t_{90} . The rate of vulcanization could be inspected from *CRI*. An increase in *CRI*

was observed for the NR compounds with NR-g-PVP. This was attributed to the several active sites on NR molecules contributed by NR-g-PVP, resulting in an acceleration in the vulcanization rate [21]. The Mooney viscosity of all NR compounds was increased by NR-g-PVP. This was attributed to the good filler-rubber interactions between the graft copolymer and silanol groups on the silica surfaces through hydrogen bonding [16]. An increase in the Mooney viscosity of NR compound with TESPT was due to the interactions of TESPT and silanol groups through a silanization reaction.

A swelling test could also indicate the crosslink density in NR compounds [8, 13]. NR compound is immersed in a solvent. Theoretically, the solvent molecules are difficult to penetrate in a crosslinked rubber with a high crosslink density. Thus, a high crosslink density provides low swelling. The reduced swelling of NR compounds with NR-g-PVP indicated a higher crosslink density in comparison with the control (Figure 5). This agrees with the results on crosslink density obtained from a torque difference determined by MDR. However, the NR compound with TESPT showed the lowest swelling compared to the NR compounds with NR-g-PVP. As previously described, a large molecule with long-chain branches limited the interactions between NR-g-PVP and silica. Thus, the remaining silanol groups were

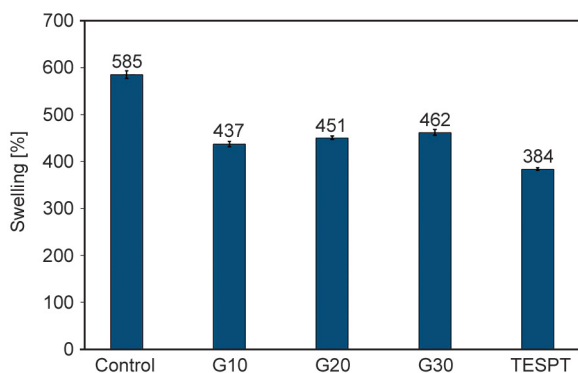


Figure 5. Swelling of silica-filled NR compounds in toluene.

able to absorb the accelerators, resulting in a lower crosslink density. The small molecule of TESPT was more efficient in interacting with silica, resulting in fewer remaining silanol groups that could absorb the accelerators. Thus, the highest crosslink density provided the least swelling. Although TESPT has a small molecular size, it has been reported that only 25% of silanol groups were able to react with silane due to limited accessibility [22]. The presence of bulky groups (triethoxysilylpropyl groups) at both chain ends also caused steric hindrance [23]. These observations suggested that the steric hindrance affected the crosslink density.

3.3. Morphology

The dispersibility of silica in NR compounds was investigated by SEM. The filler dispersion plays a major role in determining the properties of rubber compounds [24]. Aggregation of silica was observed in the compound without a compatibilizer, caused by strong filler-filler interactions (Figure 6a). This is the fact that the surface of silica consists of silanol groups, which are highly polar in character. These could generate strong hydrogen bonding between the silica particles, leading to an aggregation. The incorporation of NR-g-PVP caused the formation of the interactions between NR-g-PVP and silica via hydrogen bonding before bonding with the rubber chains through vulcanization, as proposed in Figure 4. It behaved as a bridge preventing the aggregation of silica. It not only decreased the filler-filler interactions but also increased the filler-rubber interactions, leading to a good dispersion of silica in the NR matrix (Figure 6b–6d). These results indicated that the NR-g-PVP enhanced the compatibility of silica and NR. The good dispersion of silica in NR compound with TESPT was also observed in Figure 6e. The interactions between TESPT and silica through silanization

reactions and the subsequent coupling reactions between TESPT and NR also decreased the filler-filler interactions and increased the filler-rubber interactions. Generally, the silanization proceeds by primary and secondary reactions that occur during mixing. Primary and secondary silanization reactions proceed during mixing. Primary silanization reaction occurs either by direct condensation reaction between a silanol group on the silica surface and the first out of three ethoxy groups in the TESPT molecule or by hydrolysis of the alkoxy groups of TESPT to form reactive hydroxyl groups before the condensation reaction. The secondary reaction occurs between adjacent TESPT molecules on the silica surface [9, 25].

3.4. Mechanical and physical properties

The stress-strain curves of silica-filled NR compounds are presented in Figure 7. The addition of NR-g-PVP with 10% grafting slightly improved the 500% modulus, tensile strength and elongation at break of the NR compound (Table 3). This was due to the improvement of filler-rubber interactions [16, 26]. It is known that a good dispersion of filler strongly relates to the mechanical properties of the composite. NR-g-PVP decreased the filler-filler interactions and increased the filler-rubber interactions, as a good dispersion of silica was observed in SEM images. However, a high percentage of grafting tended to decrease the tensile properties. This was attributed to the higher density of long-chain branches increasing steric hindrance that limited the interactions between NR-g-PVP and silanol groups on the silica surfaces, as mentioned earlier. The lower crosslink density was caused by more undesirable interactions between silica and accelerators, leading to the deterioration of tensile properties. TESPT provided greater filler-rubber interactions and higher crosslink density. This caused an increase in tensile properties.

The tear strength of NR compounds with NR-g-PVP had a trend similar to the tensile properties (Figure 8). The highest tear strength was observed for the NR compound with TESPT owing to its highest crosslink density [27]. A significant improvement in hardness was found for the NR compound with NR-g-PVP at 10% grafting and with TESPT (Table 3). This was attributed to the good dispersion of silica in the NR matrix and the rigidity of silica particles reducing the flexibility and elasticity of NR

chains [17, 28]. These observations suggested that the dispersion of silica in the NR matrix was strongly

related to the physical and mechanical properties of the composite.

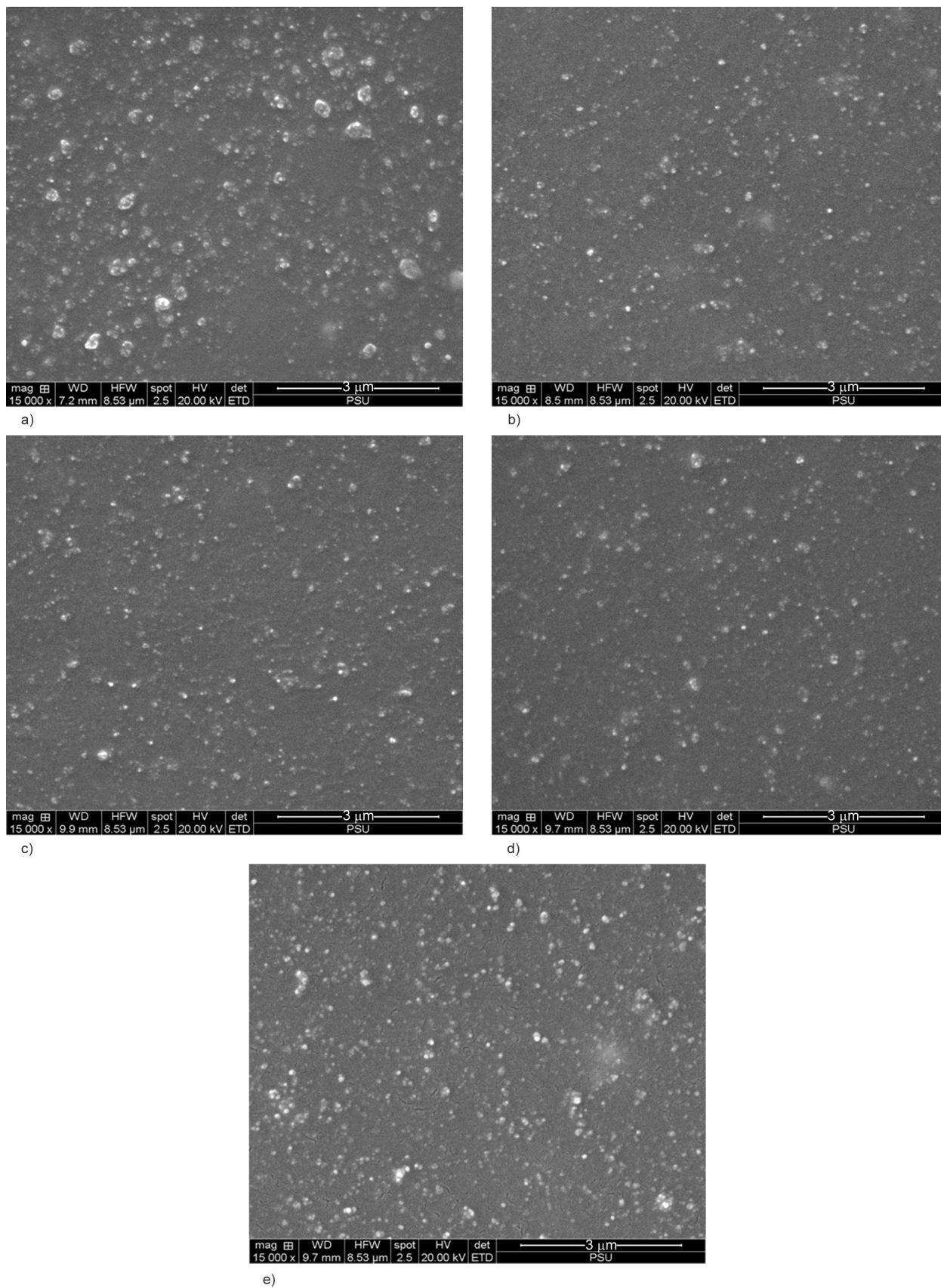


Figure 6. SEM images of silica-filled NR compounds: a) Control, b) G10, c) G20, d) G30, and e) TESPT.

Table 3. Tensile properties and hardness of silica-filled NR compounds.

Sample	300% Modulus [MPa]	500% Modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]	Hardness [Shore A]
Control	3.4±0.4	10.3±1.6	15.9±0.7	600±31	39±0.6
G10	3.9±0.5	12.2±1.5	20.9±0.5	625±32	41±0.3
G20	3.3±0.1	10.6±0.4	16.2±0.3	589±16	40±0.6
G30	3.1±0.1	9.3±0.7	15.9±0.7	620±19	40±0.5
TESPT	7.2±0.9	20.1±2.2	23.8±1.2	547±26	42±0.6

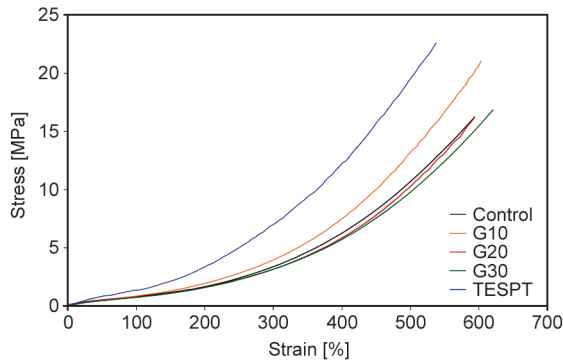


Figure 7. Stress-strain curves of silica-filled NR compounds.

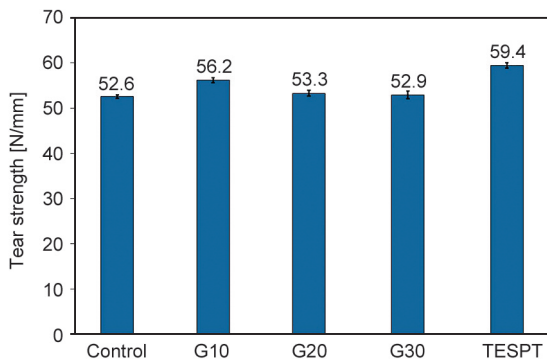


Figure 8. Tear strength of the silica-filled NR compounds.

3.5. Dynamic mechanical thermal analysis

The viscoelastic behaviors of silica-filled NR compounds were investigated by DMA. The storage modulus (E') and loss tangent ($\tan \delta$) as a function of

temperature are presented in Figure 9. Generally, E' measures the elastic response of a material, and it relates to the stiffness. An increase of E' was seen in NR compounds with 10% grafting and with TESPT (Figure 9a). The improved stiffness resulted from the strong filler-rubber interactions. A weaker silica-rubber interaction caused a reduction of E' in NR compounds with 20 and 30% grafting. A sudden drop of E' appeared around -45 to -43 °C, which is the glass transition region, and the onset temperature is defined as the glass transition temperature (T_g). The T_g of the NR compound without compatibilizer was approximately -45 °C (Figure 9b). It was found that the addition of NR-g-PVP did not significantly change the T_g of NR compounds (Table 4). In addition, the $\tan \delta$ values at -10 , 0 and 60 °C relate to the tire performance for ice traction, wet traction and rolling resistance, respectively. A higher $\tan \delta$ is desired at low temperature, while a lower $\tan \delta$ is desired at high temperature. It seemed that the addition of NR-g-PVP and TESPT in silica-filled NR compounds was insignificantly changed of $\tan \delta$ at -10 °C in comparison with the control. This indicated that there was no improvement in ice traction. Similarly, there was no significant change of $\tan \delta$ at 0 °C in the silica-filled NR compounds with NR-g-PVP and TESPT in comparison with the control. It suggested that they did not improve the wet traction.

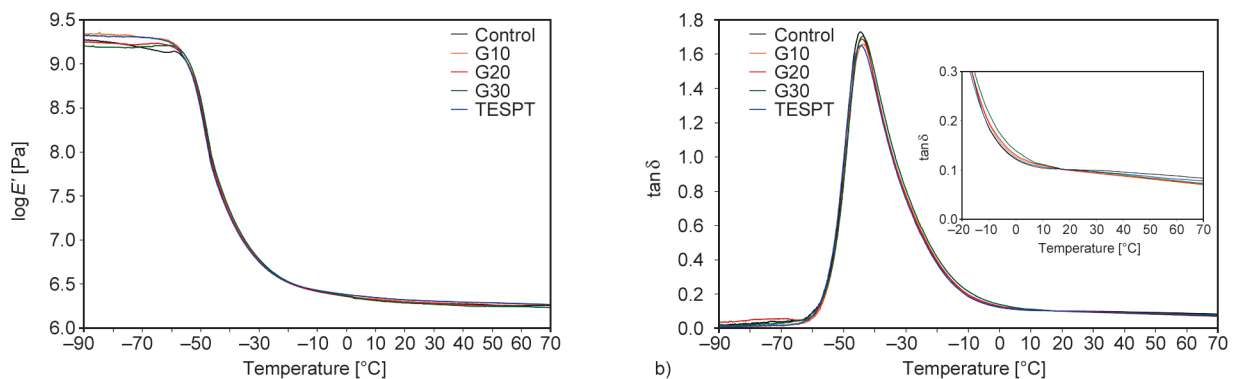


Figure 9. DMA curves of the silica-filled NR compounds: a) storage modulus and b) $\tan \delta$.

Table 4. Glass transition temperatures, thermal decomposition temperatures, and residual weights of silica-filled NR compounds.

Sample	T_g [°C]	T_5 [°C]	T_{max} [°C]	Residual weight [%]
Control	–45	222	382	20
G10	–43	223	387	20
G20	–44	222	386	21
G30	–44	223	386	21
TESPT	–45	220	385	22

The rolling resistance was evaluated at 60 °C. A reduction of hysteresis leads to a lower rolling resistance. In this case, a reduction of $\tan \delta$ at 60 °C was negligible both in silica-filled NR compounds with NR-*g*-PVP and TESPT in comparison with the control. This indicated that neither NR-*g*-PVP nor TESPT improved the rolling resistance of silica-filled NR compounds.

3.6. Thermal stability

The thermal stability of silica-filled NR compounds was analyzed by TGA. The degradation temperature is defined as the temperature at 5% weight loss (T_5) obtained from a TGA curve, while the maximum weight loss temperature (T_{max}) was taken from the derivative thermogravimetry (DTG) curve. The addition of NR-*g*-PVP and TESPT did not affect the T_5 (Table 4). All the NR compounds exhibited similar degradation steps (Figure 10a). A minor degradation was observed around 200–300 °C. This was probably due to the volatilization of processing oil (paraffinic oil) [29]. The major degradation temperature started around 300 °C. This was attributed to the decomposition of rubber chains [30]. The change of T_{max} of the NR compounds (385–387 °C) was

negligible in comparison with the control (382 °C) (Figure 10b).

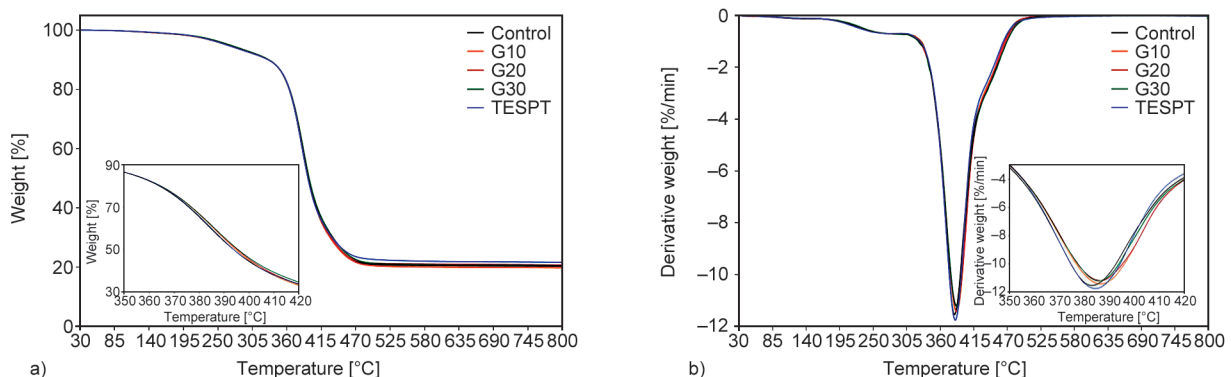
These results indicated that there was no improvement in thermal stability.

4. Conclusions

The use of NR-*g*-PVP as an alternative compatibilizer in silica-filled natural rubber compounds successfully improved the compatibility between silica and NR. The interactions between NR-*g*-PVP and silica decreased the filler-filler interactions and increased the filler-rubber interactions. This was attributed to preventing/reducing the absorption of the accelerators and thereby increasing the crosslink density. A good dispersion of filler and a higher crosslink density played important roles in determining the properties of silica-filled NR compounds. The %grafting of PVP onto NR in the graft copolymer affected cure properties, crosslink density, and mechanical properties of the NR compounds. A higher %grafting provided excessive steric hindrance retarding the vulcanization, lowering crosslink density, and deteriorating mechanical properties. G10 was suitable as a compatibilizer in silica-filled NR compounds. However, TESPT was a more effective coupling agent than the NR-*g*-PVP. The high molecular weight of NR is one of the main reasons for steric hindrance. This will probably decrease by using the NR with low molecular weight. A hybrid compatibilizer system (TESPT and NR-*g*-PVP) is interesting to develop in silica-filled natural rubber compounds in future work.

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**Figure 10.** a) TGA curves and b) DTG curves of the silica-filled NR compounds.

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