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Research article

Influences of compatibilizer type and loading on properties of phenolic resin-crosslinked natural rubber composites filled with sepiolite

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Abstract. Natural rubber (NR) composites reinforced with sepiolite and crosslinked with phenolic resin were prepared. Effects of compatibilizer types and contents, namely 3-aminopropyl triethoxysilane (APTES) or epoxidized NR (ENR50), on curing, tensile, strain-induced crystallization, and stress relaxation were investigated. Compared to APTES, ENR50 provided a greater compatibilizing effect in the NR composites. The ENR50 introduced strong physical and chemical interactions between sepiolite and NR, while only physical interaction was present in the APTES compatibilized composites. Stronger interaction between rubber and sepiolite improved filler dispersion, swelling resistance, and tensile strength; and delayed stress relaxation of the composite. Increased addition of ENR50 improved the modulus and tensile strength, and the greatest tensile strength was achieved at 2 phr ENR50 with a 15% improvement over composite without compatibilizer. In the case of APTES, 2 phr level enhanced tensile strength, but a further increase in APTES content degraded tensile, swelling resistance, and stress relaxation responses, due to its plasticizing effect. Moreover, ENR50 enhanced the strain-induced crystallization and delayed stress relaxation of the composites more than APTES. Weaker interaction between rubber and filler in APTES filled composites was due to having only hydrogen bonds formed between rubber and filler, in addition to crosslinks.

Keywords: *natural rubber, compatibilizer, crosslinking, vulcanization, mechanical properties*

1. Introduction

Natural rubber (NR) based composites are among the major materials used to produce various engineering rubber products. However, NR has a poor resistance to oil and heat since it is a non-polar hydrocarbon with a high concentration of unsaturated double bonds that easily oxidize when exposed to heat, oxygen, ozone, or light [1]. The incorporation of fillers appears to be an effective method for improving the end-use properties of NR conveniently, effectively, and relatively inexpensively [2]. Reinforcing fillers are incorporated to improve the performance of rubber products, whereas non-reinforcing fillers are used to improve processability and decrease manufacturing costs. Carbon black and silica are the most often used reinforcing fillers in the rubber industry, helping achieve products with desired properties [3, 4]. Unfortunately, the production of carbon black or silica typically requires significant thermal energy, contributing to environmental problems [5]. Searching for an alternative reinforcing filler that provides a high level of reinforcement while having less of an impact on the environment remains a significant pursuit.

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NR composites with sepiolite filler have been developed [6–8]. Utilizing sepiolite as filler in rubber composites has attracted a lot of interest not only because it is uniquely needle-like with micropore channels, causing significant property improvements, but it is also inexpensive, nontoxic, naturally occurring, and widely accessible in large amounts [9, 10]. Sepiolite is classified as a phyllosilicate with the unit cell formula of $Si_{12}Mg_8O_{30}(OH, F)_4{\cdot}(H_2O)_4{\cdot}8H_2O$ [10]. It is a fibrous filler containing silanol groups (Si–OH) at the particle edges. Besides, it also has a high specific surface area (~200–300 m^2/g) and a high aspect ratio (length ~0.2–4 µm, thickness ~5–10 nm) [6, 8], allowing for effective adsorption and contact with the rubber matrix. Various studies have shown that sepiolite filler substantially improved mechanical properties, dynamic mechanical properties, and thermal properties of NR composites [6–8, 11–13]. It was discovered that the method of sepiolite incorporation into NR composites was critical for achieving good filler dispersion, which ultimately contributed to the great mechanical properties of the NR/sepiolite composites. For instance, Kumar *et al.* [6] focused on the tackiness of the composites made by brominated isobutylene-*co*-*p*-methylstyrene (BIMS) rubber and sepiolite. Using sepiolite at 8 phr could increase the tack strength up to 300% higher than the tack strength of neat BIMS rubber. Sepiolite as filler in NR was also studied [7]. The highest tensile strength obtained at 15 phr sepiolite contents was about 30% higher than the neat NR. The tensile strength values, however, decreased after 15 phr of the sepiolite content. Moreover, sepiolite was also extended to be used in rubber blends. The work reported by Mohanty *et al.* [8] focused on the sepiolite-filled natural rubber/butadiene rubber (NR/BR) blends. They tried to replace the use of silica and carbon black with sepiolite. Replacing silica by sepiolite increased the tensile strength and stress at 100, 200, and 300% strains, as well as the hardness of the compound. There was an almost 9% increase in the abrasion resistance when replacing 5 phr of carbon black with 2 phr of sepiolite. Since the nature of sepiolite filler does not swell in water, conventional mixing in an internal mixer was found to be an effective method for preparing NR composites [8, 14].

The choice of crosslinking system was also another factor affecting the final properties of the NR composites containing sepiolite filler. Among different crosslink systems, phenolic resin appeared to be a system of choice for preparing the NR composites filled with sepiolite. In addition to hydrogen bonding, the silanol groups (–SiOH) located at the edge of sepiolite particle chemically react with the hydroxyl groups (–OH) of this phenolic crosslinker, forming Si–O–C bonds between sepiolite and rubber chains, causing a drastic improvement of tensile strength [15]. Moreover, interactions between NR and sepiolite filler could be further improved by the incorporation of silane as a coupling agent. It has been found that with a 4% silane coupling agent, namely (bis-(triethoxysilylpropyl) tetrasulfide, TESPT) as compatibilizer in phenolic resin crosslinked NR composites filled with sepiolite, the tensile strength was about 14% greater than without compatibilizer [16]. Unfortunately, only one type of silane coupling agent is available in that study.

To date, the study on phenolic resin crosslinked NR/sepiolite composites is still limited. To gain the maximal property improvements for the phenolic resin crosslinked NR composites filled with sepiolite, further research into the effects of the type of compatibilizer on the properties of the NR composites is required. In this study, phenolic resin crosslinked NR composites filled with sepiolite were prepared. The influences of two alternative types of compatibilizer, namely 3-aminopropyl triethoxysilane (APTES) or epoxidized natural rubber (ENR50) at different doses on the properties of the composites were determined, as regards curing characteristics, tensile response, strain-induced crystallization, and stress relaxation. The interactions between rubber and filler induced by compatibilizer were assessed from swelling equilibrium, infrared spectroscopy, morphology, and dynamic mechanical properties.

2. Experimental

2.1. Materials

NR (Standard Thai Rubber, STR 5L), with a Mooney viscosity (ML 1+4 at 100 °C) of 75, was supplied by Chalong Concentrated Natural Rubber Latex Industry Co., Ltd., Songkhla, Thailand. Zinc oxide (ZnO) was produced by Global Chemical Co., Ltd., Samut Prakan, Thailand. Sepiolite clay was provided by Guangzhou Billion Peak Chemical Technology Co., Ltd., Guangzhou, China. It contains SiO_2 (55 wt%), Al_2O_3 (15 wt%) and Fe_2O_3 (3 wt%) with traces of water. Phenolic resin (HRJ-10518) was produced by Schenectady International Inc., New York, USA. Stannous chloride dihydrate ($SnCl_2{\cdot}2H_2O$) came

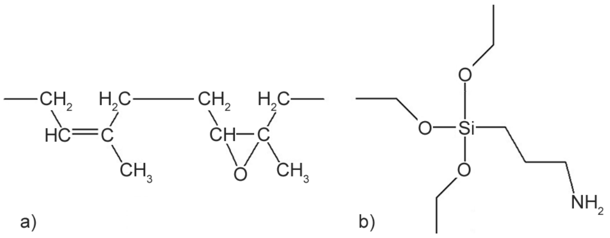

Figure 1. Chemical structures of a) ENR50, and b) APTES.

from KemAus, New South Wales, Australia. APTES was purchased from Evonik Industries, Essen, Germany; and ENR50 (with 50 mol% epoxide) with Mooney viscosity (ML 1+4 at 100 °C) of 80 was manufactured by Muang Mai Guthrie Public Co. Ltd., Surat Thani, Thailand. Both APTES and ENR50 were used as compatibilizers, and their chemical structures are shown in Figure 1. It was expected that additional interaction could be formed through the functional groups contained in the (Figure 1a) ENR (epoxide groups) and (Figure 1b) APTES ($–NH_2$) with the silanol groups ($–SiOH$) at the edge of the sepiolite particle.

2.2. Sample preparation

The NR and other chemicals were mixed in a small laboratory-size internal mixer (Plastograph EC, Brabender GmbH & Co., Duisburg, Germany) with 310 cm^3 mixing chamber at a fixed fill factor of 0.85. The initial mixing temperature was set at 50 °C with a rotor speed of 60 rpm. The sequence of chemical additions and mixing times are listed in Table 1. The total mixing time was fixed at 12 min for all rubber compounds. After leaving the rubber compounds at room temperature for 24 h, they were then hot pressed with a compression molding machine at 160 °C according to their respective curing times, determined by using a rheometer. The rubber composites containing ENR50 and APTES as compatibilizers were designated as ENR50 X and APTES X, respectively, where 'X' refers to the amount in phr. A baseline rubber composite free from compatibilizer was also prepared as a reference, and it was named a control.

Table 1. Formulation of phenolic resin crosslinked NR/sepiolite composites with alternative compatibilizers.

Role	Chemical	Quantity [phr]*	Mixing time [min]
Matrix	NR	100	2
Activator	ZnO	3	1
Filler	Sepiolite clay	30	5
Compatibilizer	Compatibilizer**	0, 2, 4 or 6	1
Catalyst	$SnCl_2·2H_2O$	1	1
Crosslink agent	HRJ-10518	10	2

*phr: parts per hundred parts of rubber
**ENR50 or APTES

2.3. Characterization

2.3.1. Curing characteristics

The curing characteristics of NR composites in the presence of the two alternative compatibilizers were determined at 160 °C using a rotorless type rheometer (Montech MDR 3000 BASIC, Buchen, Germany). The minimum torque (M_L), maximum torque (M_H), torque difference ($M_H - M_L$), scorch (t_1), curing times (t_{90}), and cure rate index (*CRI*) are reported.

2.3.2. Scanning electron microscopy

Dispersion and size of sepiolite filler inclusions in the rubber matrix were observed by scanning electron microscopy (SEM; FEI Quanta 400 FEG, the Netherlands). All the NR/sepiolite composites with or without compatibilizer were cryogenically fractured by using liquid nitrogen. The samples were sputter-coated with gold prior to the SEM examination.

2.3.3. Fourier transform infrared spectroscopy

Attenuated total reflectance – Fourier transform infrared (ATR-FTIR) spectroscopic analysis of the NR composites with and without compatibilizers was run using an INVENIO S (Bruker, Germany). Each spectrum was recorded with a resolution of 4 cm^{-1} from 4000 to 500 cm^{-1}.

2.3.4. Swelling equilibrium test

An equilibrium swelling test was performed to evaluate the swelling resistance and crosslink density for all composite samples. A sample of dimensions 10×10×2 mm was immersed in 30 mL of toluene at room temperature for 3 days. The swollen sample was removed and gently wiped with tissue paper to remove the excess solvent. The swollen sample was weighed before being dried in an oven at 70 °C to a constant weight. The percentage of swelling was calculated as Equation (1):

$$\text{Swelling degree [\%]} = \frac{M_s - M_0}{M_0} \cdot 100 \qquad (1)$$

where M_0 and M_s are, respectively, the initial and swollen weights.

The total crosslink density (CD) of each rubber composite was also estimated from the swelling using the Flory-Rehner relationship shown in Equation (2) [17]:

$$CD = -\frac{\ln(1 - V_\mathrm{r}) + V_\mathrm{r} + \chi V_\mathrm{r}^2}{2\rho V_\mathrm{s}\left(V_\mathrm{r}^{1/3} - 0.5V_\mathrm{r}\right)} \qquad (2)$$

where χ is the polymer-solvent interaction parameter, ρ is the rubber density, V_s is the molar volume of the solvent, and V_r is the volume fraction of rubber in the swollen mass, which can be estimated from Equation (3):

$$V_\mathrm{r} = \frac{\frac{M_\mathrm{d}}{\rho_\mathrm{r}}}{\frac{M_\mathrm{d}}{\rho_\mathrm{r}} + \frac{M_s - M_\mathrm{d}}{\rho_\mathrm{s}}} \qquad (3)$$

where M_d is the de-swollen weight, and ρ_r and ρ_s are, respectively, the densities of rubber and solvent.

2.3.5. Dynamic mechanical properties

The dynamic mechanical properties of NR composites containing different compatibilizers were determined by using a DMA 1 (Mettler Toledo, Switzerland). The tests were performed in tension mode at a heating rate of 2 °C/min and a frequency of 10 Hz over the temperature range from –80 to 80 °C. The damping factor (tan δ) is reported.

2.3.6. Tensile properties

The tensile properties of all composites were determined by using a universal testing equipment, LR5K Plus (Lloyd Instruments, West Sussex, UK). The samples were cut into dumbbell shapes with an overall test specimen length of 75 mm and were tested at 500 mm/min according to ISO 37 (type 2) [18].

2.3.7. Microstructural properties

Changes in crystallite size and crystallinity during stretching were monitored using wide-angle X-ray scattering (WAXS) measurements at the Siam Photon Laboratory, Synchrotron Light Research Institute, Nakhon Ratchasima, Thailand. The test was performed under crosshead speed of 500 mm/min. The SAXSIT software was utilized to process the data. The crystallinity [%] corresponding to the (200) and (120) planes during stretching was estimated using Equation (4) [19].

$$\text{Crystallinity [\%]} = \frac{A_\mathrm{c}}{A_\mathrm{c} + A_\mathrm{a}} \cdot 100 \qquad (4)$$

where A_c is the area below the (200) and (120) crystalline peaks, and A_a is the area for the amorphous halo.

The average crystallite size corresponding to (120) plane was determined using the Scherrer equation (Equation (5)) [20]:

$$\text{Crystallite size} = \frac{K\lambda}{\beta \cos\theta} \qquad (5)$$

where K is equal to 0.64, λ is the wavelength, β is the half-width at half height of the diffraction peak fitted with a Lorentzian function, and θ is the Bragg angle.

2.3.8. Stress relaxation test

The stress relaxation responses of the composites under isothermal conditions were determined by using a temperature-scanning stress relaxation TSSR meter (Brabender, Duisburg, Germany). The dumbbell-shaped specimens (ISO 527, type 5A) [21] were placed in the heating chamber with an initial temperature of 23 °C and stretched to 50% for 2 h. The short-time relaxations during isothermal conditions were recorded.

3. Results and discussion

3.1. Curing characteristics

Figure 2 shows a typical relationship between torque and time during vulcanization for the rubber composites containing different compatibilizer types and loadings. The curing parameters M_L, M_H, and $M_\mathrm{H} - M_\mathrm{L}$ are summarized in Table 2. It was found that the curing characteristics of the NR composites depended drastically on the type and content of the compatibilizer. The M_L, initial compound viscosity, increased with the dose level of the compatibilizer. Incorporation of the compatibilizer reduced the size of sepiolite filler domains and caused a more uniform dispersion of filler throughout the NR matrix, as will be discussed later. Improvements in both size and dispersion of filler increased the contact area between rubber and filler, retarding the mobility of rubber chains and increasing the M_L. The M_H and $M_\mathrm{H} - M_\mathrm{L}$ indicating the stiffness and crosslink density of the vulcanizates containing ENR50 and APTES showed different trends. Compared to the control sample, increased incorporation of ENR50 increased both M_H and $M_\mathrm{H} - M_\mathrm{L}$ whereas they decreased when APTES was incorporated. This difference might be explained by the difference in chemical

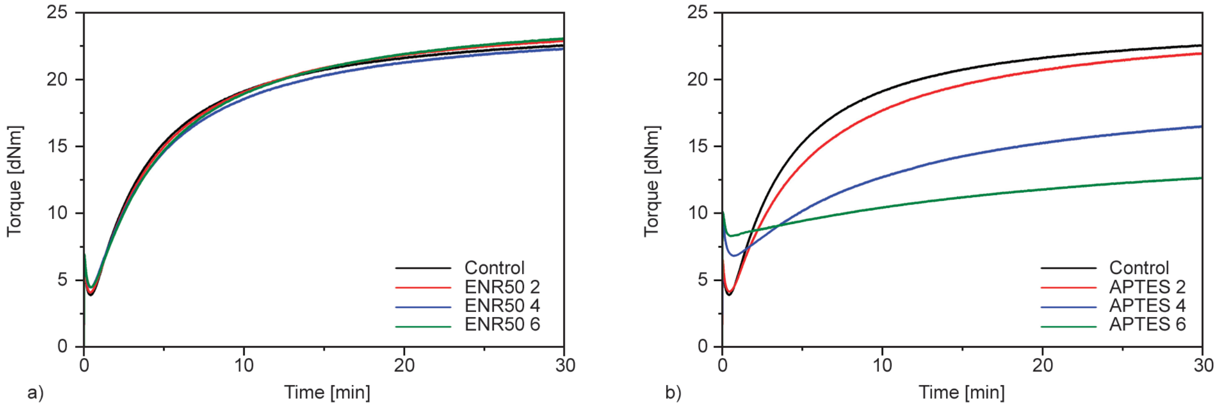

Figure 2. Curing characteristics of NR composites compatibilized with a) ENR50, and b) APTES.

Table 2. Minimum torque (M_L), maximum torque (M_H), and torque difference ($M_H – M_L$), scorch (t_1), curing times (t_{90}) and cure rate index (CRI) of the NR composites compatibilized with ENR50 or alternatively APTES.

Sample	M_L [dN·m]	M_H [dN·m]	$M_H – M_L$ [dN·m]	t_1 [min]	t_{90} [min]	*CRI* [min^{-1}]
Control	3.87	23.60	19.73	0.86	20.29	5.15
ENR50 2	4.09	24.55	20.46	0.87	25.22	4.11
ENR50 4	4.15	24.19	20.04	0.88	28.23	3.66
ENR50 6	4.48	24.91	20.43	0.95	27.79	3.76
Control	3.87	23.60	19.73	0.86	20.29	5.15
APTES 2	4.15	21.95	17.80	0.97	17.41	6.08
APTES 4	6.82	16.50	9.68	2.07	21.75	5.08
APTES 6	8.30	12.64	4.34	4.46	22.91	5.42

structures of the compatibilizers. In the case of phenolic resin crosslinked diene rubber, it is well-accepted that the presence of an acidic catalyst ($SnCl_2·2H_2O$) causes the ether bridge and hydroxymethyl end groups in the phenolic resin to break down, creating active benzylic cations. These cations are subsequently crosslinked to the rubber chains via chroman ring and/or methylene bridge linkages [22, 23]. When ENR was added, the epoxide groups in the ENR were opened and changed into hydroxyl groups during heating [24]. This phenomenon may increase the acidic conditions during vulcanization at an elevated temperature, synergistically improving the dissociation of phenolic resin.

As a result, more of the active benzylic cations formed, causing greater crosslinking of the rubber chains. Thus, the stiffness and crosslink density were continuously improved with the additional level of compatibilizer. In contrast, the increased addition of APTES reduced the M_H and $M_H – M_L$. Such reduction was probably due to the presence of an amine group in the APTES, which is considered alkaline, hindering phenolic resin dissociation by absorption of some of the acidic catalysts ($SnCl_2·2H_2O$). Consequently, the amount of benzylic cations formed during vulcanization was reduced. This would surely limit crosslink reactions between NR chains, leading to reduced M_H and $M_H – M_L$. The t_1 and t_{90} tended to increase with the incorporation of compatibilizers. However, the prolonged t_1 and t_{90} can be explained by different reasons depending on the type of compatibilizers. The addition of ENR50 increased the rubber portion and sites for crosslink reaction due to a portion of the ENR structure being the NR. Thus, more times are required for completing vulcanization. In contrast, longer t_1 and t_{90} in the APTES were probably due to interfering with the vulcanization reaction induced by amine functional groups contained in this compatibilizer. The CRIs of all the NR composites compatibilized with ENR50 or APTES were changed slightly depending on the type of compatibilizers.

3.2. Scanning electron microscopy

The effects of compatibilizer type on filler dispersion in the NR matrix were determined by SEM imaging. Figure 3 shows micrographs of representative NR/sepiolite composites with the two alternative types of compatibilizer at 2 phr. An image of the NR/sepiolite composite without compatibilizer is also included for comparison.

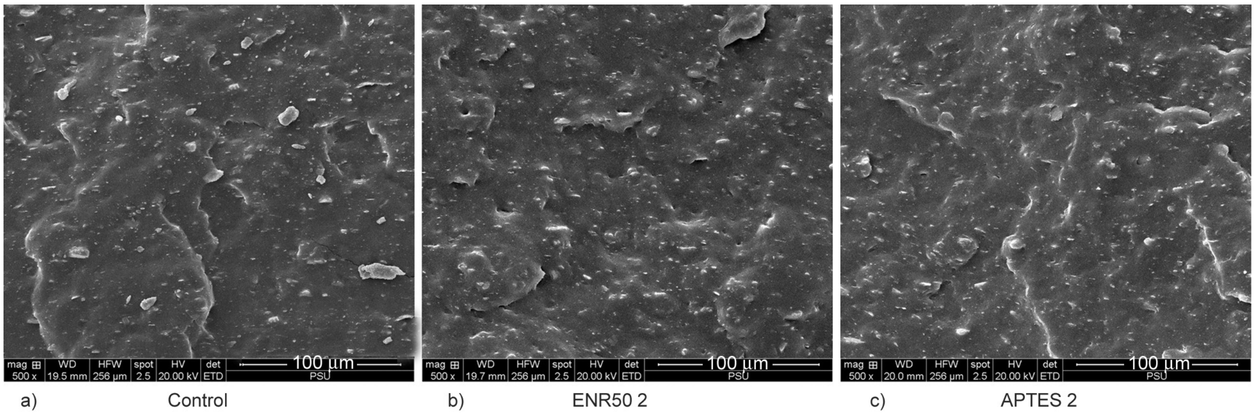

Figure 3. SEM micrographs of the filled NR composites: a) control sample without compatibilizer, b) ENR50 as compatibilizer, and c) APTES as compatibilizer.

Compared to the sample without compatibilizer (Figure 3a), the incorporation of compatibilizer significantly reduced the size of sepiolite filler domains (lighter dispersed particles) in the rubber matrix. The size of filler domains was reduced from about 5.29±3.06 µm to about 2.16±1.62 and 3.39±2.41 µm in the ENR50 and APTES compatibilized composites (Figure 3b and Figure 3c), respectively. The dispersion of the filler also became more uniform when a compatibilizer was added. Such improvement would result in an increased viscosity, as mentioned earlier. However, the composite with ENR50 as a compatibilizer showed smaller-sized sepiolite domains with more uniform dispersion when compared to the APTES compatibilized case. This was tentatively attributed to the greater chemical interactions between ENR50 and sepiolite filler, which will be discussed in the next section.

3.3. Fourier transform infrared spectroscopy

Figure 4a shows the FTIR spectra of uncompatibilized phenolic resin crosslinked NR composite filled with sepiolite filler (Control sample), and representative ENR50 and APTES compatibilized NR composites at 4 phr. To clearly observe the changes in FTIR spectra, the peaks in 4000–3000 cm^{-1} regions are magnified in Figure 4b. For the control sample, the peak at 3693 cm^{-1} is due to the OH stretching of sepiolite filler. When the compatibilizer was added, the characteristic peak intensities of the NR composites changed, depending on the type of compatibilizer. Addition of ENR50 as compatibilizer reduced peak intensities corresponding to the free OH of sepiolite, OH groups of phenolic resin, and hydrogen bonding between sepiolite and phenolic resin at 3693 and 3600–3100 cm^{-1}, respectively. A reduction of FTIR peak intensity suggests a decrease in the corresponding

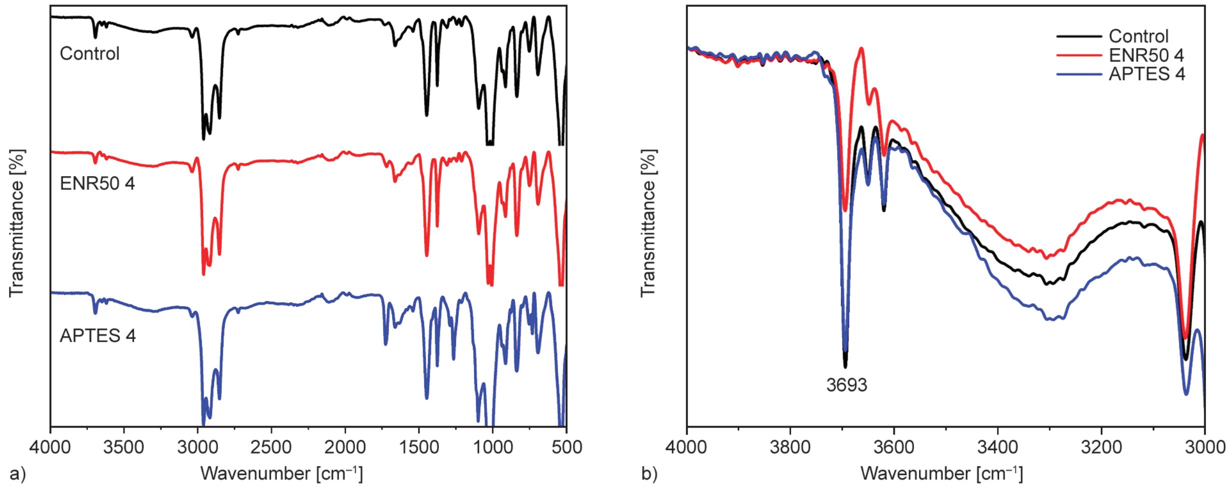

Figure 4. FTIR spectra of phenolic resin-crosslinked NR/sepiolite composites with and without compatibilizers over the ranges a) 4000–500 cm^{-1}, and b) 4000–3000 cm^{-1}.

functional groups, in the composite [25]. Thus, it is reasonable to conclude that the amounts of free OH of sepiolite, OH of phenolic resin, and bonding between sepiolite and phenolic resin were reduced, possibly due to other competing interactions between sepiolite and ENR50. In contrast, the peak intensities assigned to OH of sepiolite were not reduced in the case of APTES compatibilized NR composites, implying that chemical bonding did not occur. Note here that the characteristic peak of amine in APTES located at 3383 cm^{-1} [26] overlaps with the peaks in the range of 3600–3100 cm^{-1}. The peak intensity in this range of APTES-compatibilized NR composites was found to increase and became broad, suggesting that hydrogen bonds formed between APTES and sepiolite filler. The distinct changes in peak intensity of ENR50 and APTES compatibilized composites were attributed to differences in the extent of interactions between the compatibilizer and the sepiolite filler, as proposed in Figure 5.

ENR50 possibly induced a greater extent of matrix-filler interactions with sepiolite filler by additional hydrogen bonding and chemical linkages between –OH groups of sepiolite and –OH groups of ENR50. During mixing and vulcanization, epoxide rings in the ENR50 tend to open due to the presence of acidic conditions at such elevated temperatures, resulting in the formation of hydroxyl groups (–OH) [24, 27]. These hydroxyl groups further reacted with the hydroxyl groups on the sepiolite surfaces in the presence of acid catalyst and heat, forming ether bonds via condensation (see Figure 5a), similar to the reactions in ENR compatibilized silica-filled NR [28]. The ENR50 may easily physically or chemically interact with NR because dominantly ENR consists of cis-1,4-polyisoprene, as does NR [29, 30]. Conversely, only hydrogen bonds can be formed between amine groups (–NH$_2$) of APTES and the –OH groups of sepiolite filler (see Figure 5b), so that no reduction of peak intensity corresponding to OH in sepiolite and phenolic resin was detected (see Figure 4b). These interactions between sepiolite filler and compatibilizer are expected to provide some benefits to the composites.

3.4. Swelling equilibrium

Equilibrium swelling test is a method to assess the extent of interfacial interactions between filler and rubber matrix in a composite [31, 32]. Effects of compatibilizer type and loading on swelling and total

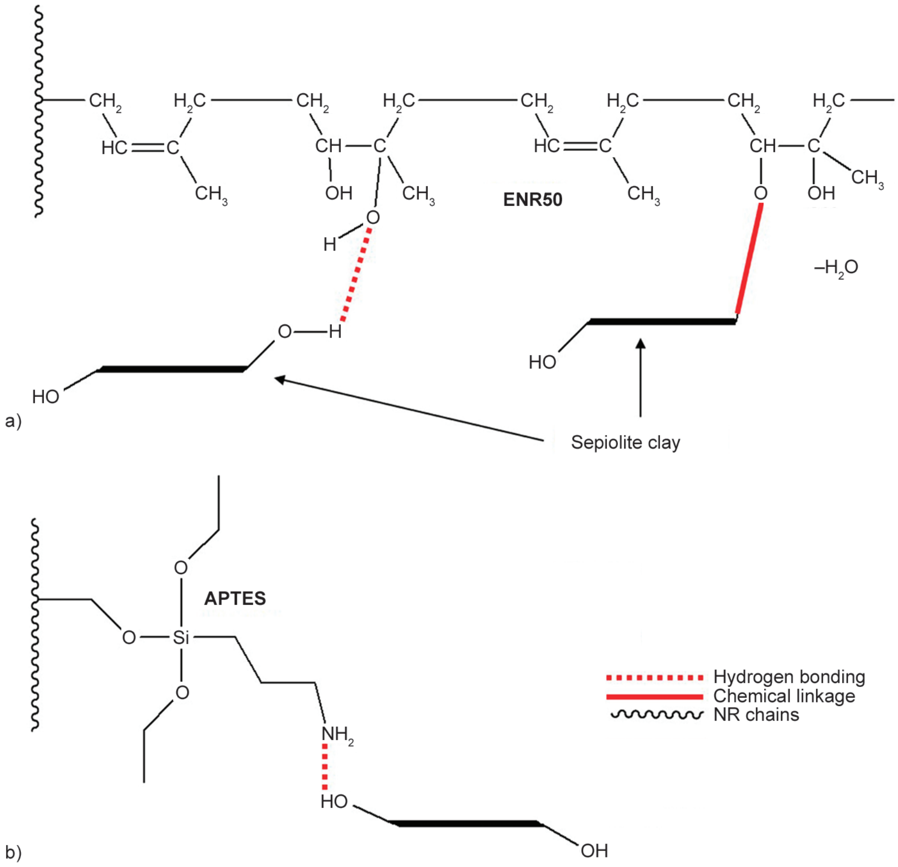

Figure 5. Possible interactions between a) sepiolite clay and ENR50, and b) sepiolite clay and APTES.

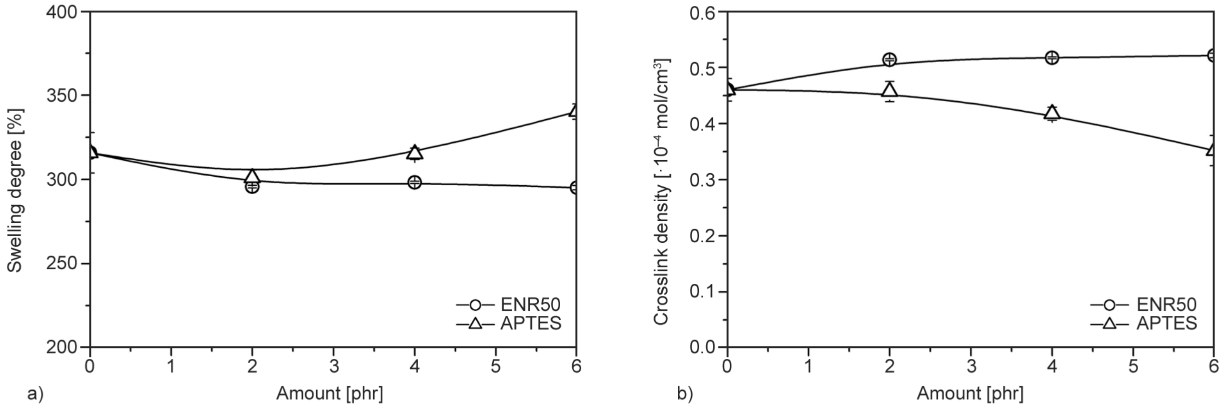

Figure 6. a) Degree of swelling, and b) crosslink density of NR composites compatibilized with ENR50 or with APTES.

crosslink density (*CD*) of the NR/ sepiolite composites are shown in Figure 6. ENR50 as a compatibilizer decreased swelling of the sepiolite filled NR composites (Figure 6a). The decrease of swelling was more pronounced with increased ENR50 loading, so the swelling resistance of NR composites improved with the ENR50 dose.

In the case of APTES, solvent penetration slightly decreased on addition of 2 phr compatibilizer, but then increased with further addition of APTES. Many studies have shown that the swelling resistance of NR composites improved only when strong interactions between filler and rubber matrix exist [7, 33, 34]. The strong filler-rubber interactions hindered the rubber chain movements, making it more difficult for toluene to pass through the rubber matrix. The data obtained from the equilibrium swelling test were further used for estimating total crosslink density (*CD*) by applying the Flory-Rehner equation [17] and the results are included in Figure 6b. Clearly, the *CD* of the NR composites compatibilized with ENR50 increased with dose of compatibilizer, while it was clearly reduced by an addition of APTES exceeding 2 phr. Thus, a reduction of swelling degree and an increased *CD* in the ENR50 compatibilized composites clearly proved strong interfacial interactions between sepiolite filler and ENR50 matrix. However, hydrogen bonding between APTES and sepiolite may occur, but it may not be strong enough to withstand the penetration of the solvent. As a result, a reduction of swelling resistance and crosslink density was found in the APTES compatibilized NR/sepiolite composites.

3.5. Dynamic mechanical properties

To verify the strong interfacial interactions between the NR matrix and sepiolite filler through the compatibilizer, the changes in the damping factor (tan δ) were examined by using Dynamic mechanical analysis (DMA) [35]. Figure 7 shows tan δ as a function of temperature for the NR composites containing different compatibilizer types and doses. It is seen that all composites displayed a single tanδ peak around –50 to –56 °C, at the glass transition temperature (T_g) of the NR matrix [36]. The addition of compatibilizers greatly affected the characteristics of the tan δ peaks, depending on both the type and the content of the compatibilizer. The T_g and tan δ

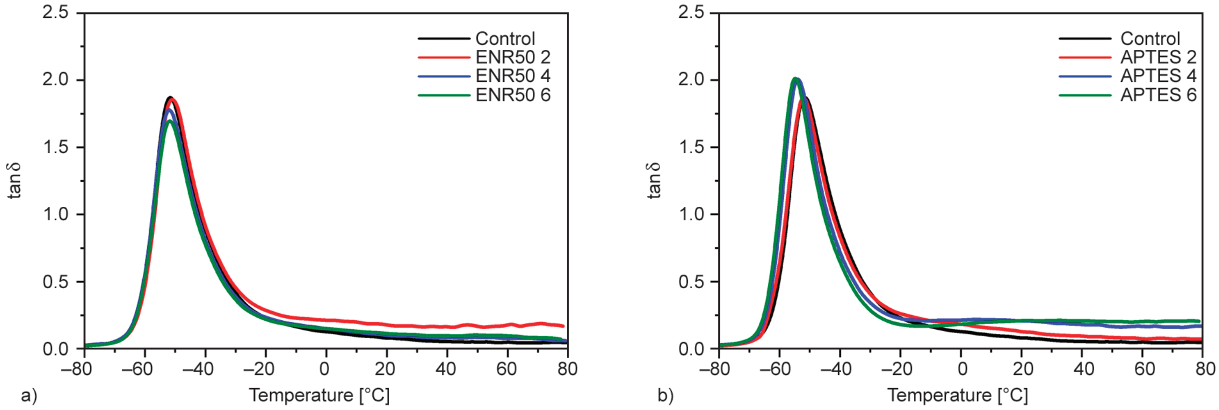

Figure 7. tan δ responses to temperature of the NR composites compatibilized with a) ENR50, and b) APTES.

Table 3. Glass transition temperature (T_g) and tan δ peak height for the various samples.

Sample	T_g [°C]	tan δ peak height
Control	-50.95	1.90
ENR50 2	–51.50	1.90
ENR50 4	–52.07	1.83
ENR50 6	–51.02	1.72
Control	–50.95	1.90
APTES 2	–52.85	1.92
APTES 4	–54.68	2.08
APTES 6	–55.91	2.05

peak heights are listed in Table 3. From Figure 7 and Table 3, increased ENR50 content did not alter the T_g but decreased the height of the tan δ peak for the NR composites. This reduction was more pronounced upon increasing the ENR50 dose. Lowering of the tan δ peak height is a general phenomenon observed when the interfacial contacts between the polymer matrix and the filler are strong [35, 37]. The interactions between rubber and filler restrict segmental polymer chain mobility, decreasing tan δ peak height. Thus, this corroborates that the addition of ENR50 as a compatibilizer induced strong interactions between rubber and filler. A reduction of tan δ peak height due to better rubber-filler interactions has also been noted in other compatibilized rubber composites [38].

Considering the composites compatibilized with APTES, increasing the compatibilizer dose decreased T_g toward a lower temperature and increased the height of the tan δ peak. A reduction of T_g upon the addition of APTES was tentatively attributed to the plasticizing effect of APTES, increasing the flexibility of polymer chains to retain rubbery behavior at a lower temperature [39]. As a result, flowability increased, giving rise to increased energy losses within the material during viscous deformation. Therefore, tan δ peak height increased.

3.6. Tensile properties

Influences of compatibilizer type and content on the tensile properties of NR/sepiolite composites are displayed in Figure 8. Interestingly, an increased dose of ENR50 compatibilizer increased the stress at various strains, whereas only a small amount of APTES addition benefited the NR/sepiolite composites. The raw outputs of the tensile properties are summarized in Table 4. From Figure 8a and Table 4, the moduli at 100% and 300% strains and tensile strength of the NR composites compatibilized with ENR50 increased with compatibilizer dose, compared to composite without compatibilizer. The improvement of 300% modulus was up to 51% at 6 phr compatibilizer. The highest tensile strength was found at 2 phr compatibilizer, and it was about 15% above the control sample. This is comparable to that with a 6% silane coupling agent compatibilized sepiolite-filled NR composite, giving about 13% over that of a non-silanized composite [16]. However, the lower cost of ENR is a great advantage of it as a compatibilizer.

The elongation at break of the composite improved slightly with the dose of ENR50. Slight decreases in tensile strength and elongation at break were noted at a high loading of compatibilizer, probably due to an excessive crosslink density. The chain length between two adjacent linkages is shortened when the crosslink density is relatively high, restricting the movement of the polymer chains during stretching, and this lowers the tensile strength and extensibility [40]. The improved tensile properties are tentatively attributed to chemical and physical interactions between sepiolite filler and NR matrix, induced by ENR50 as previously proposed in Figure 5. Without

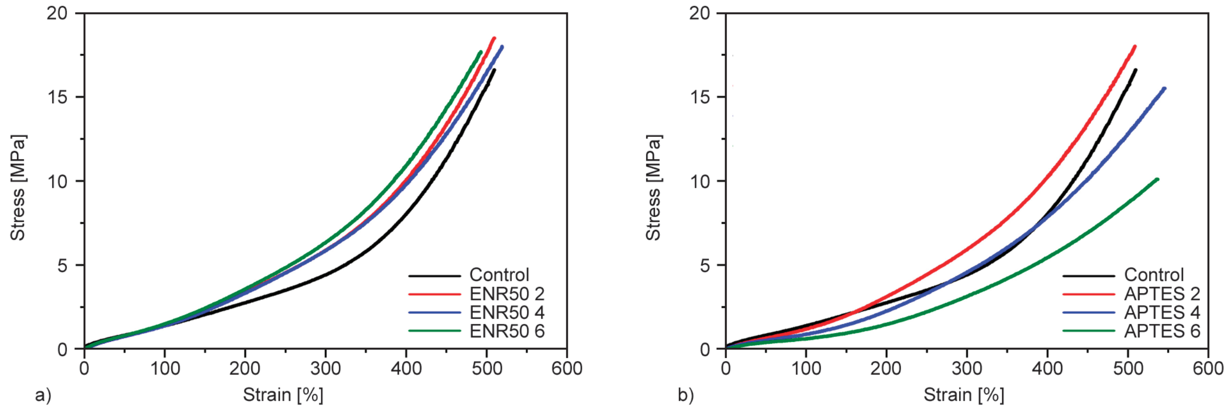

Figure 8. Representative stress-strain curves of NR composites compatibilized with a) ENR50, and b) APTES.

Table 4. 100 and 300% moduli (100%M and 300%M), tensile strength (*TS*), and elongation at break (*EB*) of NR composites compatibilized with ENR50 or with APTES.

Sample	100%M [MPa]	300%M [MPa]	*TS* [MPa]	*EB* [%]
Control	1.40±0.02	4.42±0.02	16.21±0.51	508±2
ENR50 2	1.46±0.05	5.87±0.23 (+33%)	18.61±1.06 (+15%)	510±26
ENR50 4	1.42±0.14	5.93±0.55 (+34%)	18.07±1.51 (+11%)	519±31
ENR50 6	1.58±0.16	6.67±0.64 (+51%)	17.57±0.82 (+8%)	496±28
Control	1.40±0.02	4.42±0.02	16.21±0.51	508±2
APTES 2	1.19±0.16	5.81±0.69 (+31%)	17.98±0.72 (+11%)	523±35
APTES 4	0.86±0.08	4.40±0.58 (+0%)	14.91±0.78 (–8%)	545±40
APTES 6	0.62±0.02	3.15±0.12 (–29%)	10.01±0.67 (–38%)	531±18

a strong interaction, such improvement should not be there.

In the case of APTES compatibilized NR composites (Figure 8b), improved tensile properties were seen only at 2 phr APTES dose level. The tensile strength was improved by about 11% from the reference composite, due to hydrogen bonds between APTES and sepiolite. Further addition of APTES decreased 100 and 300% moduli and tensile strength, while it increased elongation at break due to a plasticizing effect. Increased APTES concentrations caused oligomerization, forming a thick silane layer on the surface of the filler.

3.7. Microstructural properties

Figure 9 shows the development of crystallinity during stretching in the NR composites with and without compatibilizers. Note here that the crystallinity of APTES 6 is not included because the sample failed before strain-induced crystallization started. The crystallinities of all samples increased with strain, which increased the chain orientation of NR [41]. The crystallinity level at a given strain in NR composite depended on compatibilizer type and loading. Compared to the control sample, the addition of ENR50 seemed more advantageous than the use of APTES. ENR50 gave the earlier onset of strain-induced crystallization in NR composites, with the onset strain changing from about 200 to 125%, suggesting that ENR50 contributed to chain orientation (see Figure 9a). Moreover, increased ENR50 content raised the crystallinity in NR at various strains. It is believed that the crystallinity during stretching is generated by the highly stretched short chain segments between crosslinks. These shorter chains are fully stretched, oriented and become nucleation sites for strain-induced crystallization [42]. Interactions between sepiolite and rubber chains induced by the ENR50 resulted in an overall increase in crosslink density, as previously discussed, see Figure 6. An increase in crosslink density (ν) is accompanied by a decrease in molecular weight between crosslinks (M_c), according to the equation: $\nu = 1/2M_c$ [43], increasing the number of fully stretched short chains for strain-induced crystallization. The greatest crystallinity improvement was found in the composites compatibilized with 2 phr ENR50. A reduction of crystallinity after 2 phr was probably due to an excessive crosslink density that hindered crystallization [20, 44, 45].

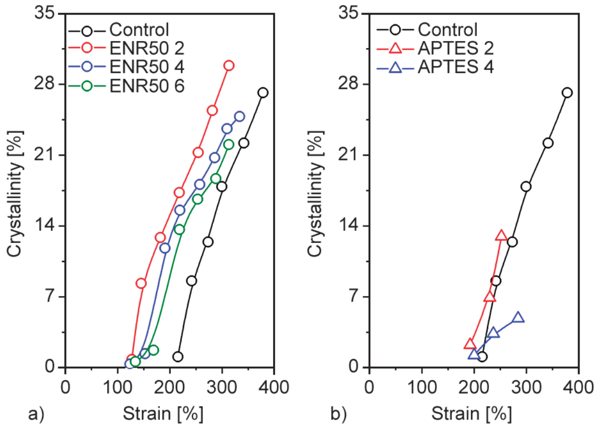

Figure 9. Crystallinity versus strain for the NR composites compatibilized with a) ENR50, and b) APTES.

In the case of APTES compatibilized composites (see Figure 9b), a 2 phr compatibilizer level slightly increased crystallinity, also slightly improving swelling resistance and increasing crosslink density as previously discussed, see Figure 6. However, the plasticizing effect of APTES at higher doses may prevent strain-induced crystallization by increased chain mobility, reducing the chances of chain orientation for crystallization.

Considering the crystallite sizes in NR composites shown in Figure 10, a reduction of crystallite size with strain was noted in all cases due to an increased

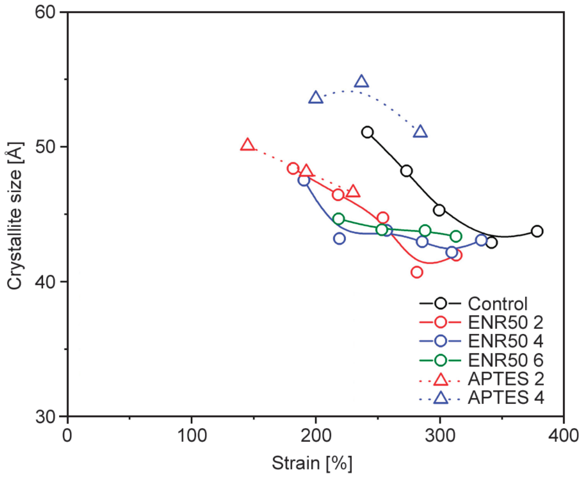

Figure 10. Crystallite size *versus* strain for the NR composites compatibilized with ENR50 or APTES.

number of crystallites with increasing strain. A large number of crystals formed during stretching competed with each other for crystallite growth, reducing the size of crystals [44]. Strong interactions between filler and rubber chains seen with ENR50 and 2 phr APTES facilitated crystallization and reduced the size of crystallites. On the other hand, poor interaction between filler and rubber in the case of 4 phr APTES lowered the overall crystallinity, producing larger crystallites. The less crosslinked rubber samples had bigger crystallites in lesser numbers, with less chance of competitive growth of crystallites.

3.8. Stress relaxation

To further investigate the effects of compatibilizers on stress relaxation behavior during isothermal relaxation, temperature scanning stress relaxation tests were run. Figure 11 shows normalized stress during isothermal relaxation of the NR composites compatibilized with ENR50 or APTES. The result for composite without compatibilizer is also included for comparison. The stress in all composite samples decreased with relaxation time as the polymer chains were sliding by each other [46]. Strong interactions between rubber chains and filler particles in a rubber composite are known to slow down the rate of stress relaxation [15, 47]. The negative slopes of stress relaxation decreased when a compatibilizer was added to the composites, depending on type and dose level. Increasing ENR50 decreased the negative slope for the composite, corroborating comparatively strong interactions between rubber and filler (see Figure 11a). The smallest stress relaxation rate was for the case with 2 phr ENR50. This appears to be the dose level of ENR50 compatibilizer in the NR composites filled with sepiolite filler that gives the greatest filler–rubber interactions. In contrast, 2 phr APTES slightly reduced the rate of stress relaxation, and the rate of stress relaxation increased again at larger APTES doses due to its plasticizing effect (see Figure 11b). The plasticizer increased the mobility of rubber chains, reducing the energy required for molecular motion and increasing the ability of macromolecules to slip over each other [48]. In addition, a lower crosslink density in the APTES compatibilized samples (see Figure 6) would also contribute to the mobility of the rubber molecules.

4. Conclusions

NR composites filled with sepiolite and crosslinked with phenolic resin were prepared with two alternative compatibilizers, namely ENR50 and APTES. Effects of compatibilizer type and dose on curing, tensile response, strain-induced crystallization, and stress relaxation were investigated. The results clearly revealed that ENR50, as a compatibilizer, provided

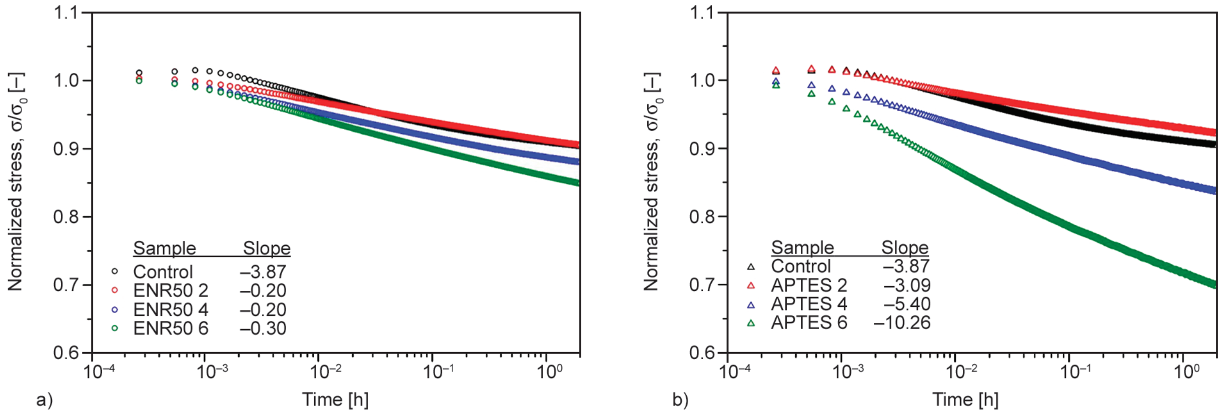

Figure 11. Normalized stress during isothermal relaxation of the NR composites compatibilized with a) ENR50 and b) APTES.

great improvements in various properties. Based on FTIR and DMA tests, ENR50 could induce strong physical and chemical interactions between sepiolite filler and NR matrix, enhancing the swelling resistance of the composites. In contrast, only physical interactions were found in the APTES compatibilized composites. Compared to APTES, ENR50 decreased the size of sepiolite domains and improved filler dispersion in the rubber matrix. Initially, the dose of ENR50 improved the modulus and tensile strength of the composites, but the greatest tensile strength was achieved at 2 phr ENR50 for a 15% improvement over the composite without compatibilizer. In the case of APTES, a dose level of 2 phr was found to enhance tensile strength, but a further increase in APTES dose degraded the tensile response due to a plasticizing effect. Moreover, ENR50 enhanced strain-induced crystallization and delayed stress relaxation of the composites when compared to cases with APTES. The application of ENR50 as a compatibilizer in the phenolic resin crosslinked NR/sepiolite composites was found to be a great choice. Aside from enhancing various composite properties, ENR50 also has a great cost advantage as a compatibilizer.

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