

EFFECT OF SHELLAC AS A RETARDER IN THE NATURAL RUBBER VULCANIZATION PROCESS

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Abstract

This research aims to improve the natural rubber compound (NR) for the complex rubber molding process using shellac flake from Lac as a retarder in the vulcanization process. To reduce some chemicals, steric acid which is a retarder in the vulcanization process was replaced by shellac to reduce the risk of health problems and to make the environmentally friendly. The effect of shellac on the mechanical and physical properties of rubber compounds was studied. Steric acid and shellac were mixed into five ratios as follows; 100:0, 75:25, 50:50, 25:75, and 0:100. (NR/shellac0, NR/shellac25, NR/shellac50, NR/shellac75 and NR/shellac100). Tensile strength, elongation at break, and modulus of elasticity were investigated using the Ultimate tensile test. It emerged that NR/shellac0 showed a higher modulus of elastic and maximum tensile strength than NR/shellac100 but NR/shellac0 exhibited lower viscosity, scorch time, and optimum time (t_{c90}) than NR/shellac100. When considering NR/Shellac25, NR/Shellac50, and NR/Shellac75, it was found that scorch time (t_{s2}), cure time (t_{c90}), molecular weight between crosslink, maximum tensile strength, and elongation at break increased with increasing shellac ratio. On the other hand, crosslink density and modulus of elasticity decreased with increasing shellac ratio. Shellac has a large structure with hydrogen bonding between the carbonyl group and hydroxyl group in their structure so it can interrupt the mixing of shellac and zinc oxide. Consequently, the combination of stearic acid/shellac with zinc oxide (ZnO) slows down the action of the sulfur in the curing process. Compatibility of other inorganic and organic substances including the rubber molecules in the crosslinking system slowly occurred so shellac could act as an inhibitor in the curing process. However, despite this delay, the compatibility of organic and inorganic substances together with rubber molecules in the cross-linking system remained, although at a slower rate.

Keywords: Cure time; Natural rubber; Retarder; Scorch time; Shellac; Vulcanization

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Introduction

Rubber materials became a necessary factor in industry and daily life. the reason for this dignity is the most fabulous discovery and development of vulcanization technology which means the changing of rubber material to a highly deformable chemically cross-linked elastic solid instead of its original state (which was sticky when warm and brittle when cold), the rubber industry since that time was established and appeared vast progressive development over more than 100 years ago (Bertow *et al.*, 2014). Utilization of natural rubber for the end products usually requires a modification of natural rubber molecules, such as the vulcanization process. The rubber vulcanization was produced by heating rubber with sulfur (Alam *et al.*, 2021). To accomplish vulcanization several requirements are needed for vulcanizing agents. Besides vulcanizing agents, some accelerators minimize the time required for vulcanization, also there are activators, antioxidants, fillers, and reinforcing agents. Moreover, the retarders represent the opposite work of accelerators, which help rubber resist reversion, especially in natural rubber compounds by increasing the scorch time to protect the products that may be exposed to high temperatures that lead to scorching, and more importantly the product service life when storing (Qiang *et al.*, 1988; Bahruddin *et al.*, 2015).

Stearic acid in rubber applications provides lubrication, increased viscosity, and a smoother finished product texture. The final thickness of the rubber is determined by the amount of stearic acid used. Zinc oxide in conjunction with stearic acid serves as a cure activator in the sulfur vulcanization system to increase the efficiency of the accelerators during the vulcanization process. The use of zinc oxide together with an accelerator has an affected on the speed and distribution of crosslinks formed (Chukwu *et al.*, 2019). They are used for low heat build-up, better modulus, and better abrasion resistance for tyre application.

Shellac is a biomaterial, a resin secreted by the female lac bug *Kerria lacca* on trees in India and Thailand. It consists of esters and polyesters of polyhydroxy acids. The main components of shellac are aleuritic and shellolic acid. Other components can be jalaric acid as shown in Figure 1 (Jasmina *et al.*, 2017). The color can vary between light yellow and dark red depending on the origin of the raw material. Shellac is used in the food industry as a coating for fruits as protection against dehydration and for the glossy and attractive aspect. Shellac can be added to the composition of food packaging materials for protection against bacteria

and as a water-repellent element. Nail polish, furniture, and wood varnish, (Bahruddin *et al.*, 2015) and the modern applications of shellac are 3D printing, smart sensors, Green electronics, stealth technology, and so on (Nandkishore *et al.*, 2022).

In this research, shellac has been applied in the vulcanization of rubber because shellac has a complex composition comprised of some naturally occurring acids, esters, and alcohols (Yates *et al.*, 1960). On the other hand, stearic acid, which stands as the primary cure activator, originates from bio-based fats; however, its production involves a hazardous chemical process. Shellac represents the group that can be formed crosslink as Figure 2 (Limmatvapirat *et al.*, 2007). Therefore, the large structure of shellac may suppress the sulfur crosslink system in natural rubber so the vulcanizing time will be decreased. This work is focused on the vulcanization process, especially in scorch time and curing time. To reduce the problem of premature process in the rubber industry, this behavior makes

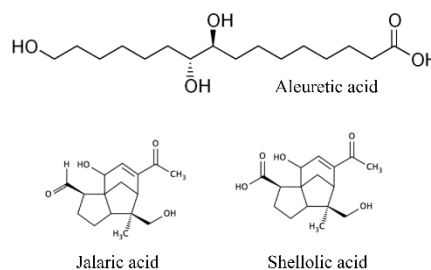


Figure 1. The main component of shellac; according to Jasmina *et al.* (2017)

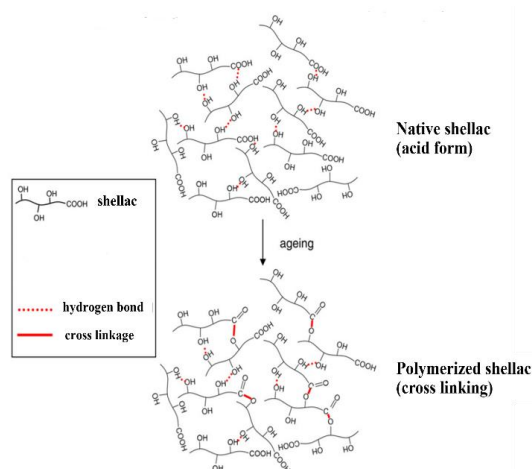


Figure 2. Schematic description of aging of shellac; adapted from Limmatvapirat *et al.* (2007)

sure of preventing premature vulcanization upon processing.

Materials and Methods

Materials

Chemical contents used in the formulation of natural rubber compounds are shown in Table 1. The natural rubber sheet was supported by the National Metal and Materials Technology Center (MTEC) and chemicals including Sulfur (S; vulcanizing agent), N-cyclohexyl-2-benzothiazole sulfonamide (CBS; accelerator) Zinc oxide (ZnO; activator), and Steric acid (activator) were supplied by Lucky Four Co., Ltd. Shellac flake was supplied by The Northern Siam Seedlac Co., Ltd.

Table 1. Compounding formulation (phr) of Natural rubber (NR)/Steric acid/shellac

Sample code	Content (phr)
NR/Shellac0	100/2.5/0
NR/Shellac25	100/1.875/0.625
NR/Shellac50	100/1.25/1.25
NR/Shellac75	100/0.625/1.875
NR/Shellac100	100/0/2.5

Natural Rubber Sheet Preparation

Natural rubber compound (NRC) was mixed with natural rubber sheet, ZnO, stearic acid/shellac, CBS, and sulfur. The compounding formulation is shown in Table 1. NRC was made using a two-roll mill (YFM model YFTR-8) at room temperature and a maximum roll speed was kept at 20 rpm to prevent increasing temperature compound. A natural rubber sheet (NRS) was made using compression molding at 150°C then a sheet of 2 mm thicknesses was de-molded and rest 8 h under an air atmosphere.

The other ingredients in the natural rubber compound were fixed at phr contents: ZnO 5.0, CBS 2.5, and sulfur 2.0.

Characterization of NRS

Viscosity and Vulcanizing Characteristics

The viscosities of the natural rubber compound were determined at 100°C for 8 min (ISO 289-1) using a Mooney viscometer (GOTECH/MV-3000AU).

The vulcanizing characteristics of the compounds were determined at 150°C for 20 min (ISO 6502-1999) using a Moving Die Rheometer (Instron CEAST 9340).

Crosslink Density and Swelling Measurement (Kongpun and Furukawa, 2014)

Crosslink density and molecular weight between crosslinking points were calculated from the Flory-Rehner equation and were measured as Equation 1.

$$\nu_c = \frac{-1}{V_s} \frac{V_p + XV_p^2 + I(1-V_p)}{d_p(V_p^{\frac{1}{3}} - V_p/2)} = \frac{1}{M_c} \quad (1)$$

where ν_c is the crosslink density; V_s is the molar volume of the solvent (toluene: $1.068 \times 10^2 \text{ cm}^3/\text{mol}$); V_p is the volume fraction of NRS in the swollen state, which is equal to $V_p = 1/(1+Q)^{12}$; χ is the solvent interaction parameter (In this case, $\chi = 0.5353$); d_p is the density of the NRC; a ; is the molecular weight between crosslinking points.

The gel fraction (g) of the NRS was determined from the original weight and the weight of the dried NRS after swelling to an equilibrium state in toluene at 60°C, using the following formula: $g = W_b/W$, where W_b is the weight of the sample that was dried after equilibrium swelling and W is the original weight. The degree of swelling of the NRS was determined from the weights before and after equilibrium swelling with toluene. The degree of swelling (q) was calculated in Equations (2) and (3).

$$q = 1+Q \quad (2)$$

$$Q = \left[\frac{(W_a - W_b)/d_s}{W_b/d_p} \right] \quad (3)$$

where Q , W_a , d_s , and d_p are the volume ratio of solvent in the swollen state to gel in the unswollen state, the weight of a sample swollen to the equilibrium state, the density of solvent, and the density of a sample, respectively.

Tensile test

The tensile test was performed using the Instron type tensile tester (Instron3366) at ambient temperature according to ASTM D412 Die C.

Fourier Transfer Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FTIR) measurements were carried out using PerkinElmer Spectrum (Perkin Elmer Inc., Waltham, MA, USA) in the ATR mode at the wavelength range between 3,600 and 500 cm^{-1} .

The sensitivity, the resolution, and the number of scans were 4 cm^{-1} and 32 times, respectively.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were performed to determine the thermal behavior of NRCs. Thermograms of NRCs were recorded with DSC (DSC 3+, Mettler-Toledo) at a heating rate of $10^\circ\text{C}/\text{min}$ from -85°C to 200°C under a nitrogen atmosphere.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) investigations were performed with Mettler-Toledo model TGA/DSC 3+ as the following conditions: samples of about 10 mg were heated at a heating rate of $10^\circ\text{C}/\text{min}$, first in a nitrogen atmosphere from ambient temperature (30°C) to 600°C

Results and Discussion

Tables 2 and 3 show the relationship between viscosity and vulcanizing characteristics with various shellac contents. Additional shellac in the natural rubber vulcanization process affected the properties of a rubber compound that is, the scorch time t_{s2} increased from 2.55 to 4.59 besides the Mooney viscosity and crosslink density decreased from 21.72 to 18.01 and 3.29 to 2.80 (mol/cm^3)* 10^{19} .

Table 4 shows crosslink density and molecular weight between crosslinks and Table 5 shows the mechanical properties of NR with various blend ratios of steric acid/shellac. Crosslink density was calculated using Flory-Rehner's equation. Crosslink density increased whereas molecular weight

Table 2. Relationship between the Mooney Viscosity with the addition ratio of shellac

Sample	Steric acid/Shellac ratio	Mooney Viscosity (ML 1 + 4 (100°C))
NR/Shellac0	100/0	21.72
NR/Shellac25	75/25	21.42
NR/Shellac50	50/50	20.42
NR/Shellac75	25/75	20.03
NR/Shellac100	0/100	18.01

Table 3. Relationship between the cure time (T_{c90}) and scorch time (T_{s2}) with an additional ratio of shellac

Sample	Scorch time; t_{s2} (min)	Cure time; t_{c90} (min)
NR/Shellac0	2.55	4.33
NR/Shellac25	2.59	5.01
NR/Shellac50	3.05	5.22
NR/Shellac75	3.08	5.37
NR/Shellac100	4.59	7.01

Table 4. Crosslink density and molecular weight between crosslink of NR with various blend ratios of steric acid/shellac

Sample	Crosslink density (mol/cm^3)* 10^{19}	Molecular weight (g/mol)* 10^{18}
NR/Shellac0	3.29	3.04
NR/Shellac25	3.27	3.06
NR/Shellac50	2.98	3.39
NR/Shellac75	2.92	3.43
NR/Shellac100	2.80	3.57

Table 5. Mechanical properties of NR with various blend ratios of steric acid/shellac

Sample	Tensile strength (MPa)	Elongation at break (%)
NR/Shellac0	29.53	857.32
NR/Shellac25	29.02	859.32
NR/Shellac50	28.84	892.36
NR/Shellac75	28.61	937.22
NR/Shellac100	25.65	942.90

between crosslinks decreased with increasing shellac content. This result indicates that the formation of shellac in NR was suppressed by the large structure of shellac. When considering the molecular weight between crosslinks, the molecular weight between crosslinks increased because the large structure of shellac slowly reacted with ZnO.

Figure 3 shows FT-IR spectra of NR with various blend ratios of stearic acid/shellac. An important peak is at $2,917\text{ cm}^{-1}$ (C-H stretching) and $1,540\text{ cm}^{-1}$ (COO-). When the amount of shellac increased to 100%, bonding of COO- in NR at $1,540\text{ cm}^{-1}$ increased intensity peak. However, the functional group at $1,017\text{ cm}^{-1}$ was found. It seems that the peak at $1,540\text{ cm}^{-1}$ exhibited symmetric and asymmetric stretching of the carboxyl group (COO-). When deprotonation of the carboxyl group in shellac occurred. This reaction caused a decrease in the C-O stretching band at $1,017\text{ cm}^{-1}$ (Brajniov *et al.*, 2018). Therefore, when the $1,540\text{ cm}^{-1}$ peak increased, the $1,017\text{ cm}^{-1}$ peak decreased. These results indicated that the tendency for hydrogen bonding or crosslinking of carbonyl groups (C=O) and hydroxyl groups (-OH) in the structure of shellac was increased.

Figure 4 shows the DSC thermograms of each ratio of stearic acid/shellac blended with NR. The glass transition temperature (T_g) of NR with various ratios of stearic acid/shellac showed similar values of T_g that are approximately -61.57°C to -60.79°C . The endothermic peaks due to the melting of stearic acid of NR/Shellac0, NR/Shellac25, and NR/Shellac50 were about $82-85^\circ\text{C}$. On the other hand, T_m did not occur in NR/Shellac75 and NR/Shellac100 because of the lower stearic acid content than in NR/Shellac0, NR/Shellac25, and NR/Shellac50. It seems that shellac can be disturbed reaction of stearic acid, in conjunction with some metallic oxides, notably zinc oxide, from the activating system during sulfur vulcanization. The essence of activating the vulcanization process was that sulfur acting on its own was a very slow process. Consequently, the essence of activating the vulcanization process was to increase the efficiency of crosslink formation. Thus, the t_{s2} and t_{c90} were increased with decreasing stearic acid contents.

Figure 5 is a collection of TGA curves for five samples (NR with various ratios of stearic acid/shellac). The regions of decomposition of NR/Shellac0, NR/Shellac25, NR/Shellac50, NR/Shellac75, and NR/Shellac100 were 385.90°C , 386.86°C , 384.44°C , 385.35°C and 384.41°C , respectively. The decomposition temperatures of all samples were not separated but overlapped. This may suggest that shellac did not affect the decomposition of the rubber compound.

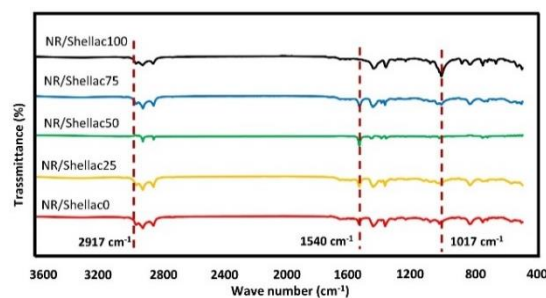


Figure 3. FT-IR spectra of NR/Shellac0, NR/Shellac25, NR/Shellac50, NR/Shellac75 and NR/Shellac100

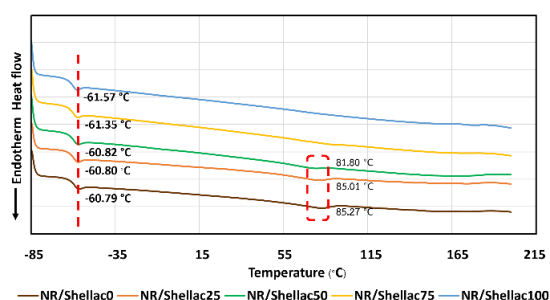


Figure 4. DSC thermograms of NR/Shellac0, NR/Shellac25, NR/Shellac50, NR/Shellac75 and NR/Shellac100

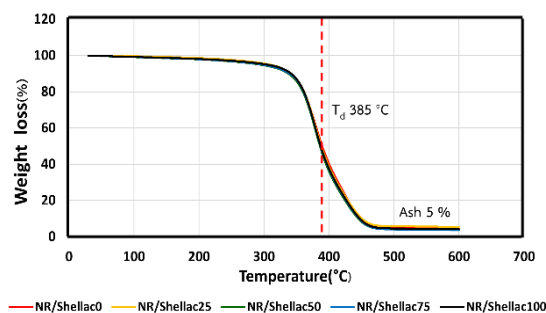


Figure 5. TGA curves of NR/Shellac0, NR/Shellac25, NR/Shellac50, NR/Shellac75 and NR/Shellac100

Conclusions

Shellac is a new retarder in the natural rubber vulcanization process and prevents premature vulcanization during the process especially when using molds that contain grooves or holes and through storing periods. Retarders have an important rule because these retarders work on

what is called the scorch time of compounds that keep goods from undesirable vulcanizing processes by storing them in addition to increasing the shelf time of products.

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