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Research article

Curing, rheological, mechanical, and flame retardant properties of high thermal-resistant dibutyl phosphate-bound natural rubber

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Abstract. Dibutyl phosphate-bound natural rubber (DBNR) was prepared by reacting epoxidized natural rubber with 20 mol% (ENR-20) with dibutyl phosphate in a latex medium. Fourier transform infrared spectroscopy (FTIR) was used to confirm the molecular structures of ENR-20 and DBNR and to quantify the epoxide contents. The shear flows and thermal properties of DBNR were then characterized and compared with ENR-20 and natural rubber (NR). The DBNR exhibited the lowest viscosity curves, but it depicted the highest glass transition temperature (T_g) and residue from thermogravimetric evaluation, indicating higher thermal resistance. Subsequently, different NR/DBNR blend ratios were compounded, with and without flame resistance additives, compared with unmodified NR and chloroprene rubber (CR) compounds. We found that all natural rubber compounds exhibited reversion behavior due to the breakage of newly formed sulfidic bonds. However, chloroprene rubber showed marching cured curves, as evidenced by the increasing torque with prolonged testing time. Additionally, antimony trioxide retarded the curing reaction of NR, while tris(2-ethylhexyl) phosphate accelerated it. Therefore, the combination of these additives synergists with the intrinsic flame retardant properties of DBNR. The study revealed that the burning rate of NR/DBNR blends, exhibited very high flame resistance capability compared to gum NR and NR compounded with flame resistance additives.

Keywords: *natural rubber, dibutyl phosphate, flame retardant, antimony trioxide; tris(2-ethylhexyl) phosphate*

1. Introduction

Natural rubber (NR) stands as a green biopolymer derived from environmentally sustainable and renewable resources, primarily composed of cis-1,4-polyisoprene originating from *Hevea brasiliensis* trees [1]. Therefore, its composition, rich in carbon and hydrogen atoms, renders NR susceptible to easy ignition and rapid burning, posing significant fire hazards in various applications such as bedding, floor paneling, and interior elements in building and transportation. The predominant technique for rendering rubber flame-retardant involves integrating various additive-type flame retardants into the rubber matrix. These additives encompass halogenated compounds [2], metal hydroxides [3, 4], phosphorus-based flame retardants [5], intumescent agents [6], and nano-sized additives [7, 8]. Apart from the addition of flame retardant additives or fillers through mixing with rubber, blending rubber with polymeric materials possessing higher flame retardant properties, and chemically modifying the rubber molecules to integrate reactive flame retardants are the other two main approaches to enhance the flame retardancy of rubber [9]. Among these methods, the last method for integrating reactive flame retardants offers distinct advantages. This approach improves the

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flame retardant efficacy of rubber by inhibiting or suppressing the combustion process through chemical groups bound within the rubber molecular structures. Consequently, this enhances the flame retardant functionality within rubber products, extending their lifespan and bolstering resistance against volatilization, leaching processes, and solvent extraction as occurring in the additive-type flame retardants [8]. The reactive flame retardants, therefore, have the ability to maintain flame retardant efficacy while minimizing the potential loss of functional chemicals into the atmosphere and environment. It has been recognized that flame retardants offer specific advantages and some drawbacks. For instance, halogenated flame retardants display high efficiency in fire suppression but generate toxic combustion by-products and corrosive gases that pose significant environmental and health concerns [5]. On the contrary, inorganic options like magnesium hydroxide and aluminum hydroxide [4] are environmentally safer, yet they exhibit lower flame-retardant effectiveness. Nano-filler flame retardants excel in preserving the mechanical properties of rubber but fall short in fire suppression compared to halogen-based variants [5]. Consequently, there has been a growing emphasis on developing highly efficient halogen-free flame retardants (HFFR) [10, 11]. These newer flame retardants must maintain crucial mechanical, dynamic, and other pertinent properties of rubber products.

Organic phosphorus compounds are one of the effective and environmentally friendly halogen-free flame retardants. The phosphorus-based flame retardants can cause an increasing amount of carbonaceous or char residues during the burning process, reducing the volatilized decomposition products. Also, some phosphorus-based flame retardants can generate free radicals during the thermal decomposition process which can react with free radicals generated from polymer substrates during burning, causing a lack of fuel to propagate the flame [5]. Therefore, phosphorus compounds have considerably exhibited good flame retardant characteristics in many polymers, for instance, polyurethane elastomers [12], silicone rubber [13], ethylene propylene diene monomer (EPDM) rubbers [14], styrene butadiene rubber (SBR) [15], polyesters and epoxy resins [16], poly(vinyl chloride) (PVC), modified polyphenylene oxide (PPO), polycarbonate/acrylonitrile butadiene styrene terpolymer (ABS) [17], ethylene-vinyl-acetate (EVA) copolymer [18], nylon 6,6 [19], and polypropylene (PP) [20].

In natural rubber products, flame retardant additives containing phosphorus have also been utilized. These additives include antimony-containing polymer of bisphenol-A and triphenyl antimony dinitrate [21], bromo derivative of phosphorylated cashew nut shell [22, 23], and 2-ethyl hexyl diphenyl phosphate [22]. It is worth noting that antimony compounds may raise concerns regarding human health. Prolonged inhalation of antimony can lead to potential health issues such as pneumoconiosis, altered electrocardiograms, stomach pain, diarrhea, vomiting, and stomach ulcers. It has been observed that mixing 2-ethyl hexyl diphenyl phosphate with NR in concentrations ranging from 10 to 20 phr led to an increase flame retardancy [22]. Additionally, a double-shell co-microencapsulated mixture of ammonium polyphosphate and expandable graphite, used as an intumescent additive for flame retardant natural rubber composites [24], exhibited high flame retardant efficiency and environmental friendliness in NR composites. Furthermore, the melamine salt of pentaerythritol phosphate/graphite mixture, dispersed with graphite flakes, was found to enhance the thermal stability and flammability properties of NR [25].

It has been observed that using phosphorus-based flame retardants alone may not sufficiently enhance the flame retardancy of NR [5]. This limitation arises from the chemical composition of NR molecules, which lack a high oxygen content, making it challenging to transform into char. As a result, there is insufficient condensed and gaseous flame-retarding action during the burning process [26]. Consequently, ongoing efforts are dedicated to advancing phosphorus-based flame retardants to heighten their efficiency in NR. Strategies include their combination with other additives or high-flame-retardant polymers, or the modification of NR molecules to integrate superior flame-retardant capabilities.

One important approach to improve the efficiency by inhibiting or suppressing the combustible process of NR is to prepare reactive flame retardants by incorporating high flame retardant molecular segments into the NR molecules, as described in our previous work [5]. For instance, a reactive flame retardant was prepared by incorporating boric acid into natural rubber molecules via the hydroxyl groups of epoxidized natural rubber (ENR). In addition, a phosphorus-containing structure, poly(dimethyl-(methacryloyloxymethyl)phosphonate) (PDMMP), was grafted onto NR molecules to form a graft copolymer of natural rubber grafted with PDMMP (*i.e.*, NR-*g*-PDMMP). This modified NR was used as a flame retardant and showed high heat and flame resistance with an increased degradation temperature, level of limited oxygen index (LOI) and level of char residue, with a decreased burning rate [27]. Furthermore, two other types of phosphorus-containing NR grafted copolymers were prepared by grafting with poly(dimethyl(acryloyloxymethyl)phosphonate) (PDMAMP) to form NR-*g*-PDMAMP) and poly (dimethyl(methacryloyloxyethyl)phosphonate) (PDMMEP) to form NR-*g*-PDMMEP in a latex medium by photopolymerization. These also showed high thermal resistance [28]. Additionally, dibutyl phosphate (DBP) was fixed in the NR molecules by reacting with low molecular weight liquid natural rubber (ELNR). It was found that the phosphorus-modified natural rubber formulation decreases the flammability behaviors of the vulcanizates, but also decreases the mechanical properties because vulcanization is greatly affected by phosphorus units and the low molecular weight of ELNR [29].

In this study, dibutyl phosphate was utilized to integrate phosphorus units into ENR molecules containing 20 mol% epoxide (ENR-20), resulting in the creation of dibutyl phosphate-bound natural rubber (DBNR) through a reaction in a latex medium. The modified NR was subsequently characterized and blended with unmodified NR (air dry sheet, ADS), both with and without two types of commercial flame retardant additives: antimony trioxide (Sb_2O_3) and tris(2-ethylhexyl) phosphate (TEHP). The flame retardancy of these formulations was assessed and compared with high flame retardant chloroprene rubber (CR). Additionally, investigations were conducted into curing, mechanical properties, and associated thermal characteristics.

2. Experimental

2.1. Materials

High ammonia (HA) latex concentrate was manufactured by Yala Latex Co., Ltd (Yala, Thailand). It contains approximately 60 wt% dry rubber content and has an average rubber particle size of about 0.61 µm. This HA latex concentrate was first epoxidized then used to prepare dibutyl phosphate-bound epoxidized natural rubber (DBNR). An air dry sheet (ADS) natural rubber was manufactured by Khuan Pan Tae Farmer Cooperative (Phattalung, Thailand) and used to blend with the DBNR. The goal was to prepare natural rubber blends with high heat resistance and flame retardant properties. The dibutyl phosphate used to modify epoxidized natural rubber (ENR) was manufactured by Sigma-Aldrich (Buchs, Switzerland). The hydrogen peroxide and formic acid used to perform epoxidation of the natural rubber molecules in the HA latex state were produced by Riedel-de Haën (Seelze, Germany). Teric N30 nonylphenol ethoxylate, a nonionic surfactant with a cloud point above 100 °C, was used to stabilize the epoxidized natural rubber (ENR) latex during performic epoxidation. This surfactant was manufactured by Indorama Ventures Oxides Australia Pty Limited (Brooklyn, VIC, Australia). Antimony trioxide (Sb_2O_3) and tris(2-ethylhexyl) phosphate (TEHP) were used as additional flame retardants in the natural rubber compounds. These chemicals were manufactured by Sigma-Aldrich (Buchs, Switzerland). Antimony trioxide (Sb_2O_3) is in powdered form with an average particle size of about 5 µm and a melting temperature of approximately 655 °C. Conversely, tris(2-ethylhexyl) phosphate (TEHP) exists in a liquid state with a viscosity at 20 °C of approximately 13–15 mPa·s, a density at 20 °C of 0.92 g/mL, and a boiling point of about 215 °C. Neoprene or polychloroprene rubber used for a comparison of flame retardant capability was manufactured by DuPont Performance Elastomers (Wilmington, USA). It is a G-type neoprene with a Mooney viscosity (ML 1 + 4, 100 °C) in the range of 42–54. Other chemicals used in the rubber compound formulations were obtained commercially and used as received. These include zinc oxide (ZnO) and stearic acid cure activators in NR, manufactured by Global Chemical Co., Ltd. (Samut Prakarn, Thailand) and Imperial Chemical Co., Ltd. (Pathum Thani, Thailand), respectively. In this work, ZnO was also used as a curing agent for neoprene rubber. Magnesium oxide (MgO), also used for the curing of neoprene rubber, was manufactured by Honeywell Fluka TM (Charlotte, USA). *N*-tert-butyl-2-benzothiazolesulfenamide (TBBS) cure accelerator in NR was manufactured by Thermo Fisher Scientific Chemicals, Inc. (Ward Hill, USA). Additionally, the sulfur curing agent was produced by Mahachai Chemicals Co., Ltd. (Samut Sakorn, Thailand). Wingstay L, a polymeric sterically hindered phenol antioxidant, was manufactured by North Wanxing Chemical Co., Ltd. (Beijing, China). Finally, Deoflow S processing aid was manufactured by DOG Deutsche Oelfabrik

(Hamburg, Germany). It's noted that Deoflow S is a calcium salt of saturated fatty acids and amide-esters, acting as a zinc-free and water-free lubricant and dispersing agent in rubber compounds.

2.2. Preparation of epoxidized natural rubber

Epoxidized natural rubber was prepared by performic epoxidation according to the procedure and characterization described elsewhere [30]. The HA latex was first diluted to 20% dry rubber content (DRC) and then measured for a quantity of 1.5 M, referring to the molecular weight of the repeating unit of natural rubber. Subsequently, the Terric N30 non-ionic surfactant (10 wt%) was introduced at a concentration of 15 g/L, while maintaining continuous stirring at 100 rpm for at least 30 min at 50 °C to thoroughly mix all ingredients. Formic acid (1.0 M) and then hydrogen peroxide (2.4 M) were then added dropwise into the solution mixture. After that, the reaction was allowed to proceed and the latex sample was collected at reaction times of 0.5, 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, and 22 h. The sampled latex was coagulated by adding an excess amount of methanol and fabricated into a thin film. It was then washed with clean water several times to remove any remaining unreacted chemicals. The rubber sample was eventually dried in a hot air oven for about 24 h before being cooled down to room temperature. Fourier transform infrared spectroscopy (FTIR) was used to characterize the molecular structure of the obtained ENR. The level of epoxide content of ENR at each reaction time was estimated based on the methodology described by Davey and Loadman [31].

2.3. Preparation of dibutyl phosphate-bound natural rubber

Epoxidized natural rubber with 20 mol% epoxide was first prepared by specifying the reaction time of epoxidation at 1.15 h based on the result in experimental Section 2.2. After reaching an epoxide content of about 20 mol%, the temperature of the reaction mixture was cooled down from 50 to 30 °C with continuous stirring at 100 rpm. After that, dibutyl phthalate was added dropwise into the ENR latex at a concentration ratio of [DBP]/[epoxidized units] = 1. Then, the reaction was allowed to proceed for about 2 h before being coagulated with an excess amount of methanol and fabricated into a thin sheet of dibutyl phosphate-bound epoxidized natural rubber (DBNR). The sheet was washed several times with clean water and dried at 50 °C in a hot air oven. Fourier-transform infrared spectroscopy, thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA) were then used to characterize the dry DBNR.

2.4. Preparation of rubber compounds

Dibutyl phosphate-bound epoxidized natural rubber (DBNR) was compounded by blending with unmodified NR (ADS) at various blend ratios of NR/DBNR of 60/40, 70/30 and 80/20 wt% with and without flame retardants: antimony trioxide and tris(2-ethylhexyl) phosphate, as compounding formulations shown in Table 1. Furthermore, natural rubber was also compounded with and without flame retardants for comparison purposes according to F_1 to F_3 in Table 1. The mixing was performed in a Brabender Plasticorder with Mixer 50 EHT model 835205 (Brabender GmbH & Co. KG, Duisburg, Germany), equipped with tangential rotors at 60 °C with a rotor speed of 60 rpm, as per the mixing schedule indicated in Table 1. In the compounding procedure, the NR or its blend with DBNR was first masticated for about 3 min for neat NR compound and 5 min for NR/DBNR blends. Then, the Deoflow S processing aid was incorporated and mixing continued for about 2 min. It is noted that Deoflow S acts as a lubricant and dispersing agent to improve the dispersion of compounding ingredients, reduce compound viscosity, and enhance the flow properties of the compound without significantly influencing vulcanization characteristics. After that, stearic acid and zinc oxide activators were sequentially added, with each continuing to mix for 1 min. The flame retardants (antimony trioxide and tris(2-ethylhexyl) phosphate) were then incorporated and mixed for about 3 min each. Then, Wingstay L antioxidant, TBBS accelerator and sulfur were finally sequentially added, with each continuing to mix for 1 min.

The rubber compound was then dumped from the mixing chamber and sheeted out using a two-roll mill and then conditioned at room temperature for at least 24 h. The curing characteristics of the rubber compounds were then tested using an oscillating disk rheometer (ODR), model ODR2000 by Alpha Technologies (Hudson, USA) at 160 °C and 1° arc. The rubber vulcanizate sheets were then fabricated for further testing and characterization by a compression molding machine, Chaicharoen Karnchang Ltd (Bangkok, Thailand) at 160 °C with the corresponding cure time based on the ODR test under a compression

Table 1. Compounding formulations and mixing schedule of natural rubber (NR) and NR/DBNR blends.

Ingredients	Quantity [phr]									Mixing time [min]
	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	F_9	
NR	100	100	100	60	60	70	70	80	80	3
DBNR	–	–	–	40	40	30	30	20	20	2
Deoflow S	15	15	15	15	15	15	15	15	15	2
Stearic acid	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	1
ZnO	5	5	5	5	5	5	5	5	5	1
Sb_2O_3	–	15	15	–	15	–	15	–	15	3
TEHP	–	–	25	–	25	–	25	–	25	3
Wingstay L	1	1	1	1	1	1	1	1	1	1
TBBS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1
Sulfur	2	2	2	2	2	2	2	2	2	1

Table 2. Compounding formulations and mixing schedule of chloroprene rubber.

Ingredients	Quantity [phr]			Mixing time [mim]
	F_{10}	F_{11}	F_{12}	
CR	100	100	100	8
Stearic acid	1	1	1	1
TMTD	0.5	0.5	0.5	1
Sulfur	0.5	0.5	0.5	1
Wingstay L	1	1	1	1
MgO	4	4	4	1
ZnO	5	5	5	1
Sb_2O_3	–	15	15	3
TEHP	–	–	25	3

pressure of about 4.83 MPa. For the compounding of chloroprene rubber, different chemical ingredients and mixing schedules were used, as indicated in Table 2. In such a case, tetramethylthiuram disulfide (TMTD) was used as a curing accelerator along with the curing agents sulfur and magnesium oxide (MgO). However, the curing and fabrication of rubber sheets from the neoprene compounds were performed in the same manner as described for the NR compounds.

2.5. Fourier transform infrared spectroscopy

The chemical structure of synthesized epoxidized natural rubber (ENR) and dibutyl phosphate-bound natural rubber (DBNR) was characterized by using a FTIR Spectrometer, model 1600 by Perkin-Elmer (Shelton, USA), in the wavenumber range of 4000–500 cm^{-1} and at a resolution of 4 cm^{-1}.

2.6. Rheological properties

Shear flow properties of ENR-20, DBNR and unmodified NR (ADS) were characterized by a capillary rheometer, model RH7 by Rosand Precision Limited (Stourbridge, UK), with a capillary die diameter of 2 mm and length of 32 mm and 180° entry angle. The test was performed at 160 °C in the shear rate range of 10–2000 s^{-1}. The results were reported in terms of the relationship between apparent shear stress and apparent shear rate (flow curve) and apparent shear viscosity and apparent shear rate (viscosity curve).

2.7. Thermal properties

Thermal properties of DBNR and unmodified NR (ADS) before compounding were characterized by two different approaches: dynamic mechanical analysis and thermogravimetric analysis. The results were compared with the thermal properties of ENR-20, the based material for synthesizing DBNR. In DMA, a dynamic mechanical analyzer, model DMA7 by Perkin-Elmer (Shelton, USA), was exploited in the temperature range of –80 to 30 °C to observe the damping properties in terms of $\tan\delta$ along with the glass transition temperature (T_g) of each raw rubber. On the other hand, the TGA was performed using a thermogravimetric analyzer, model TGA–50 by Shimadzu (Tokyo, Japan). The test was performed in the temperature range from room temperature to 800 °C with a heating rate of 10 °C/min under a nitrogen atmosphere.

2.8. Mechanical properties

Tensile properties of rubber vulcanizates were tested by a universal testing machine, model H 10KS, Hounsfield Test Equipment Co., Ltd, (Surrey, UK) using die Type C and test conditions according to ASTM D412.

2.9. Flame retardant properties

The evaluation of flame retardant properties in terms of burning rate was performed according to the guidelines in ISO 3582. In the burning rate, test specimens with dimensions of 50×150×13 mm were preconditioned in a desiccator at 25 °C with 65% humidity for a minimum of 24 h before testing. The specimens were then secured horizontally within gauze, clamped in a holder for the test. The ignition source, a gas burner, was applied to the top of the specimen for 60 s. After this period, the gas burner was turned off, allowing the specimen to burn until either extinguishment occurred or the flame reached a specific benchmark. Burning rate measurements were obtained by recording the time taken to burn from the top to the specified benchmark over a length of 125 mm, or until extinguishment. Consequently, the burning rate was calculated by establishing the ratio between the length burned (mm) and the time taken for the flame to reach the benchmark, as defined in the Equation (1) [9]:

$$\text{Burning rate}\,[\text{mm/s}] = \frac{L_\text{b}}{t_\text{b}} \qquad (1)$$

where L_b and t_b represent the length of burning [mm] and the time at which the flame reached the benchmark or distinguished [s], respectively.

3. Results and discussion

3.1. Chemical modification of NR molecules to create DBNR

Figure 1 displays the FTIR spectrum of epoxidized natural rubber containing 20 mol% epoxide (ENR-20). It can be seen that the absorption peaks at wavenumbers 2965 and 2920 cm^{-1} are clearly visible. They are associated with C–H stretching vibrations of CH_3 and CH_2, respectively. Furthermore, the peaks at 1450 and 1650 cm^{-1} were observed due to the presence of CH_2 scissoring vibration and the C=C stretching vibration, respectively [32]. In addition, the characteristic peaks of epoxide groups in ENR manifest additional signals at 870 and 1250 cm^{-1}, corresponding respectively to the oxirane ring and the stretching vibration of C–O–C bonds. Moreover, a faint absorption at 1065 and 1710 cm^{-1} were detected in the FTIR spectrum, attributed to the presence of tetrahydrofuran rings [33] and carbonyl groups, a secondary product resulting from the epoxide ring-opening reaction during ENR preparation.

The estimation of epoxide content in ENR molecules relied on absorbance ratios between specific absorption peaks at wavelengths 870 cm^{-1} (a_{870}) and 835 cm^{-1} (a_{835}). The 835 cm^{-1} peak represents the =C–H out-of-plane bending vibration of isoprene units [34]. This facilitated the calculation of the absorbance ratio using the Equation (2) [31]:

$$\text{Absorbance ratio} = \frac{a_{870}}{a_{870} + a_{835}} \qquad (2)$$

Figure 2 depicts the relationship between the content of epoxide groups in ENR molecules and the reaction time. Evidently, the epoxide content exhibited rapid initial increases within the first three hours of the reaction, followed by a gradual ascent until reaching the final state of reaction. In Figure 2, it is clear that achieving the desired 20 mol% epoxide content necessitated a reaction time of 1:15 h.

Figure 3 shows the FTIR spectrum of dibutyl phosphate-bound natural rubber (DBNR). It can be seen that the spectrum shows an absorption band appearing at a wavenumber of about 1100 cm^{-1}, which can be assigned to the stretching vibration of the P=O bond [35]. In addition, the absorption band positioned between 1100–950 cm^{-1}, marked at 1078 cm^{-1}

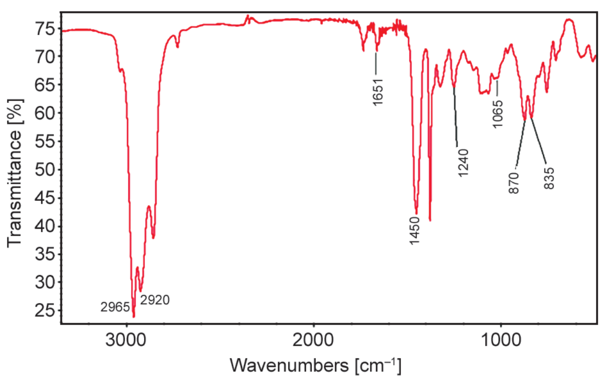

Figure 1. FTIR spectrum of ENR with 20 mol% epoxide (a reaction time of 1:15 h).

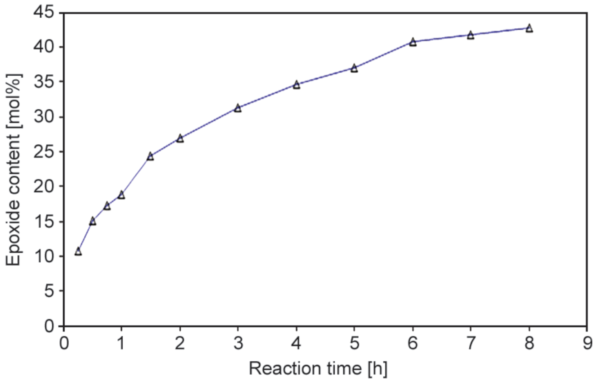

Figure 2. Relationship between content of epoxide groups in ENR molecules as a function of reaction time.

in Figure 4, originates from the P–O stretching vibrations in the dibutyl phosphate molecules bound to natural rubber [36]. Furthermore, the wavenumber range of 980-1100 cm^{-1} also signifies the presence of the –C–O stretching vibration [37] in DBNR molecules. This range overlaps with the P–O stretching vibration, evident from the broad absorption peak observed within these wavenumber ranges (Figure 3). Moreover, the broad absorption shoulder band in the region of 3200–3600 cm^{-1} can be assigned to the O–H stretching vibration present in the opened rings of ENR molecules [38]. In addition, the strong absorption band at 1725 cm^{-1} can be attributed to the stretching vibration of carbonyl groups based on the reaction of epoxide groups and the acid functional groups present in the reaction media [39].

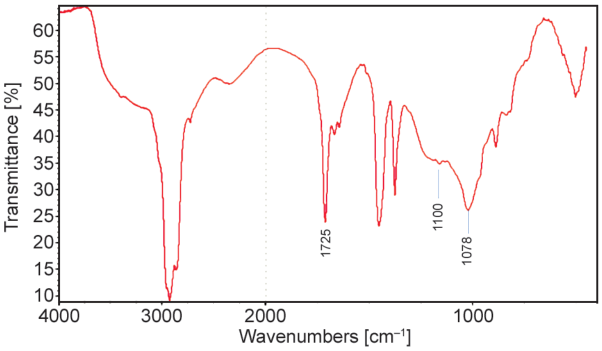

Figure 3. FTIR spectrum of dibutyl phosphate-bound natural rubber.

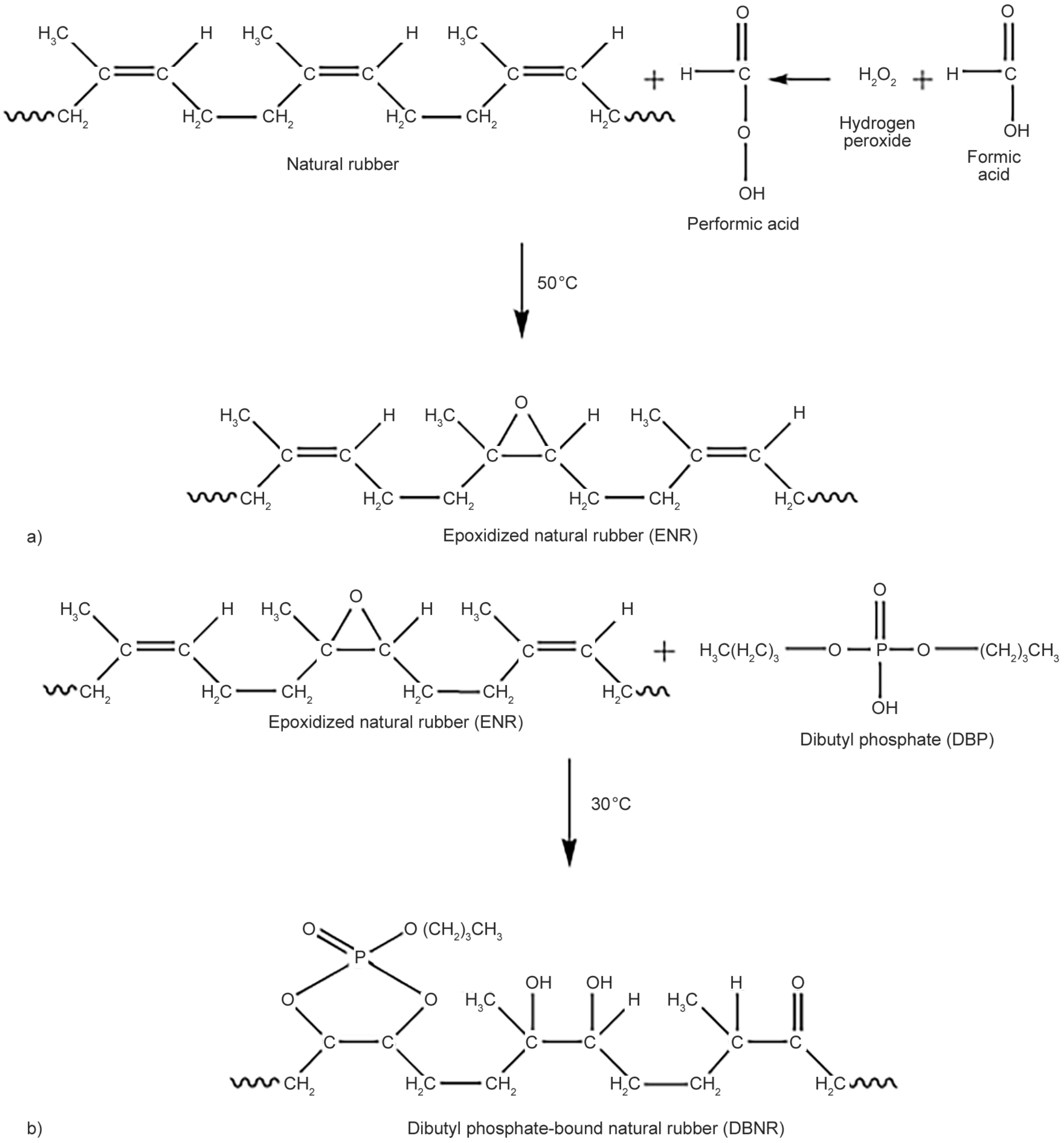

Figure 4. Reaction schemes for preparation of ENR-20 shown in scheme I (a), and dibutyl phosphate-bound natural rubber shown in scheme II (b).

Therefore, a reaction mechanism for the preparation of ENR-20 and DBNR has been proposed as described in the reaction schemes in Figure 4. This starts with the synthesis of epoxidized natural rubber with an epoxide content of 20 mol% (ENR-20) by proceeding with performic epoxidation for 1 h and 15 min (Figure 3), as shown in reaction scheme I in Figure 4a. After that, the temperature was decreased from 50 to 30 °C, then dibutyl phthalate with a concentration ratio of [DBP]/[epoxidized units] = 1 was gradually added into the ENR-20 latex, thereafter the reaction proceeded for about 2 h. It was found that the ENR-20 reacts with DBP and forms DBNR, as demonstrated in the proposed reaction scheme II in Figure 4b.

3.2. Shear flow properties

Figure 5 demonstrates the shear flow properties of unmodified NR (ADS), ENR-20, and DBNR, in terms of the relationship between apparent shear stress and apparent shear rate (flow curve), as well as apparent shear viscosity and apparent shear rate (viscosity curve). It is evident that the apparent shear stress of all materials increased, while the apparent shear viscosity decreased with the increase in apparent shear rate. This indicates shear thinning behavior in all the molten rubbery materials. Additionally, the lowest flow and viscosity curves were observed in DBNR, while the highest were noted in NR. The flow and viscosity curves of ENR-20 are positioned between those of DBNR and NR. This may be attributed to the fact that unmodified rubber molecules, without any chemical treatment, have a high molecular weight, leading to higher shear flow properties due to high chain entanglement, which retards and inhibits the flow of material. On the other hand, ENR-20 and DBNR, having undergone chemical treatment, experience chain breakage, resulting in a lower molecular weight. Although ENR-20 and DBNR contain polar functional groups that should foster high chemical interactions between their molecules, thereby increasing flow resistance, the influence of molecular weight predominates, overshadowing this chemical interaction. The lower flow and viscosity curves of DBNR offer benefits for ease of processing, including improved flow during the mixing and fabricating of the material.

3.3. Thermal properties of NR(ADS), ENR-20, and DBNR

Figure 6 presents the tan δ as a function of temperature for unmodified natural rubber, epoxidized natural rubber with 20% epoxidation, and dibutyl phosphate-bound natural rubber. The tan δ curve represents the ratio between the loss modulus, which indicates energy dissipation or damping, and the storage modulus, representing stored energy. In Figure 6, the tan δ peaks for unmodified NR, ENR-20, and DBNR are observed at approximately –57.5, –34.0, and –3.9 °C, respectively, indicating their respective glass transition temperatures (T_g). Notably, DBNR shows the highest T_g at approximately –3.9 °C, indicating a deviation from typical rubbery behavior at room temperature. This makes the compounding and fabrication of rubber products from DBNR challenging. Consequently, blends of DBNR with unmodified NR have been explored to enhance flame retardancy. Additionally, Figure 6 illustrates that the area under the tan δ-temperature curves decreases in the order of NR > ENR-20 > DBNR. Since this area quantifies the energy dissipated through molecular motions and internal friction, it reveals a decreasing trend in damping capacities in the same order. In particular, the heavily modified DBNR exhibits a significantly reduced damping capacity compared to unmodified NR. To harness the potential of DBNR for flame

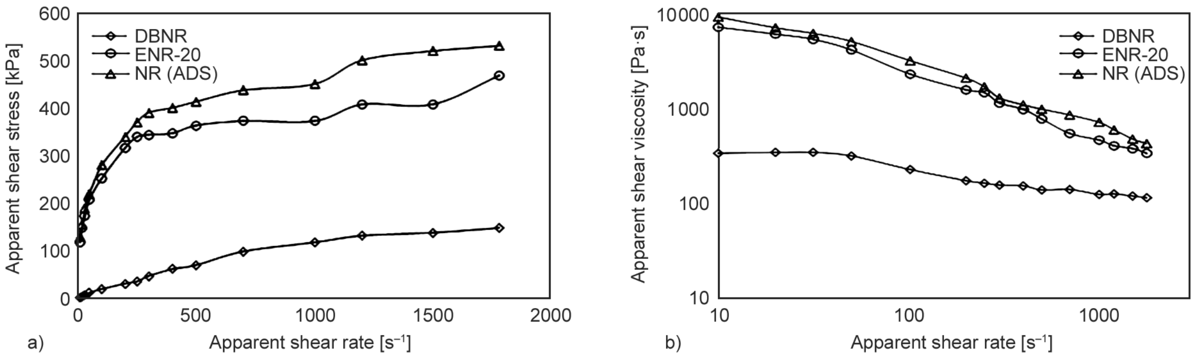

Figure 5. Relationship between apparent shear stress (a) and apparent shear viscosity (b) as a function of apparent shear rate of unmodified NR(ADS), ENR-20 and DBNR tested at 160 °C.

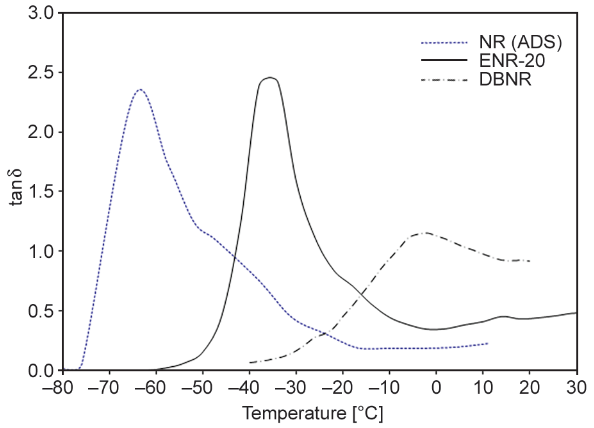

Figure 6. Tan δ as a function of temperature of unmodified NR (ADS), ENR-20 and DBNR.

retardant rubber applications, while addressing other compromised properties, investigations into blending it with other rubbery materials were conducted.

Figure 7 displays TGA thermograms of unmodified NR (ADS), ENR-20, and DBNR. It is evident that a significant single-stage weight loss occurs in the temperature range of 310 to 460 °C. This loss is attributed to the degradation of functional groups in the rubber molecules, along with their hydrocarbon contents. The chemical modification of NR molecules, by incorporating polar functional groups in ENR-20 and DBNR, results in notable changes in degradation behaviors. These changes include a delay in the onset of degradation by about 20 °C, from approximately 310 °C in ADS to 330 °C for both ENR-20 and DBNR.

Furthermore, there are significant differences in weight loss observed among the materials. Specifically, NR exhibits the highest weight loss at 94.6 wt%, while ENR-20 and DBNR show lower percent weight losses at 79.9 and 76.7 wt%, respectively. This suggests that DBNR possesses the highest heat resistance, followed by ENR-20. On the other hand, NR demonstrates the poorest thermal stability, with the lowest residue of about 5 wt%.

3.4. Curing properties of NR, NR/DBNR blends and chloroprene rubber.

Figure 8 shows cure curves of gum NR compound and its compounds with antimony trioxide and a combination of antimony trioxide and tris(2-ethylhexyl) phosphate. It is evident that all NR compounds exhibit reversion cure behavior, potentially due to the deterioration of newly formed linkages characterized by low bonding energy, notably polysulfidic (–C–S_x–C–) and some disulfidic (–C–S–S–C–) bonds [40]. These particular linkages prove vulnerable to elevated temperatures and high shear forces. In addition, the NR compound with a combination of antimony trioxide and TEHP exhibits the highest trend of reversion due to the effect of TEHP that causes early activation of the curing reaction of NR molecules by lowering the scorch and cure times along with the highest cure rate index, as demonstrated in Table 3. Furthermore, the incorporation of solely antimony trioxide into the NR compound leads to rising minimum, maximum torques and torque differences (Table 3) higher than the gum NR vulcanizate. This may be due to the flow resistance of Sb_2O_3 particulates with a very high melting temperature (655 °C) during the curing test. On the other hand, the combination of Sb_2O_3 and TEHP in the NR compound causes a decline in these torque values due to the plasticizing and lubricant effects resulting from the addition of the TEHP liquid into the NR compounds. Moreover, the incorporation of Sb_2O_3 in the NR compound causes a lower scorch time and cure rate index with a similar value of cure time.

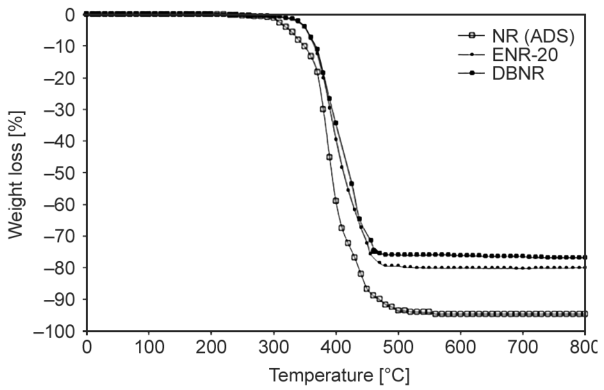

Figure 7. TGA Thermograms of unmodified NR (ADS), ENR-20 and DBNR under nitrogen atmosphere.

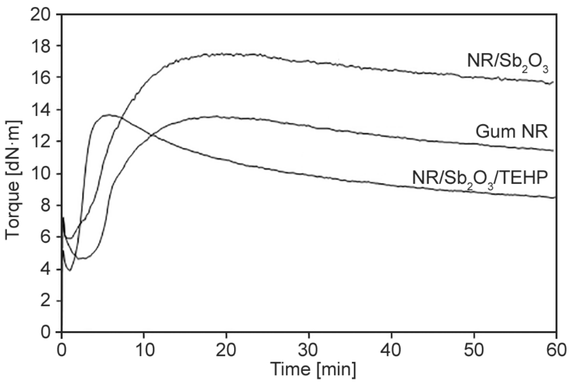

Figure 8. Cure curves of gum NR and its compounds with antimony trioxide and a combination of antimony trioxide and tris (2-ethylhexyl) phosphate.

Table 3. Curing properties in terms of minimum (M_L), maximum (M_H) and torque difference ($M_H - M_L$) along with cure time (T_{c90}) and scorch times (T_{s1}) and cure rate index (CRI) of DBNR/NR and CR with and without flame retardants.

Materials	Minimum torque [dN·m]	Maximum torque [dN·m]	Torque difference [dN·m]	Scorch time [min]	Cure time [min]	Cure rate index
Gum NR	4.63	13.52	8.89	5.22	11.85	15.08
NR/Sb_2O_3	5.91	17.49	11.58	3.52	11.81	12.08
NR/Sb_2O_3/TEHP	3.91	13.67	9.76	2.02	3.71	59.17
NR/DBNR = 60/40	2.14	6.74	4.60	6.01	10.59	21.83
NR/DBNR = 70/30	7.12	12.61	5.49	2.51	5.62	32.15
NR/DBNR = 80/20	3.86	15.32	11.46	2.02	4.68	37.59
NR/DBNR = 60/40FR	2.15	6.10	3.95	2.34	4.41	48.31
NR/DBNR = 70/30FR	3.69	8.84	5.15	2.52	4.67	46.51
NR/DBNR = 80/20FR	3.84	9.57	5.73	3.08	5.88	34.36
Gum CR	7.98	21.79	13.81	6.72	45.37	2.58
CR/Sb_2O_3	9.64	22.22	12.58	4.32	46.16	2.39
CR/Sb_2O_3/TEHP	3.42	27.52	24.12	2.35	32.52	3.31

Figure 9 depicts cure curves of rubber compounds consisting of NR/DBNR blends with different blend ratios, both without and with flame retardants, a combination of Sb_2O_3 and TEHP. It is clearly seen that all NR/DBNR blend compounds exhibit reversion cure behavior, as described in Figure 8. Additionally, the NR/DBNR blends with a higher proportion of NR show higher maximum torque and torque difference (Table 3) owing to the higher shear stress and shear viscosity of NR compared to DBNR (Figure 5). Moreover, a clear decreasing trend in scorch and cure times is observed with an increasing cure rate index in NR/DBNR blends without flame retardant (Figure 9a). This is attributed to the rising unsaturation for the crosslinking reaction due to increased NR contents. When comparing the rubber compound with and without flame retardant, it is notable that the NR/DBNR blend without flame retardant, at a given blend ratio, exhibits significantly higher maximum torque and torque difference (Table 3). This difference is attributed to the addition of flame retardants, particularly tris(2-ethylhexyl) phosphate, which induces a lubricating effect in the rubber compounds. Therefore, a stronger NR/DBNR blend material exhibiting a higher maximum torque, alongside an increased crosslink density, as indicated by its augmented torque difference, was attained in the blend without additional flame retardant additives. Furthermore, an inverse trend in the scorch and cure times is observed in rubber compounds with increasing NR proportion due to the retardation of the curing reaction caused by the flame retardant additives, particularly antimony trioxide. It is noted that in Figure 8, TEHP caused an acceleration of the curing reaction, but the retardation was caused by the Sb_2O_3. In this case, the influence of the Sb_2O_3 in crosslinking may overshadow the influence of TEHP.

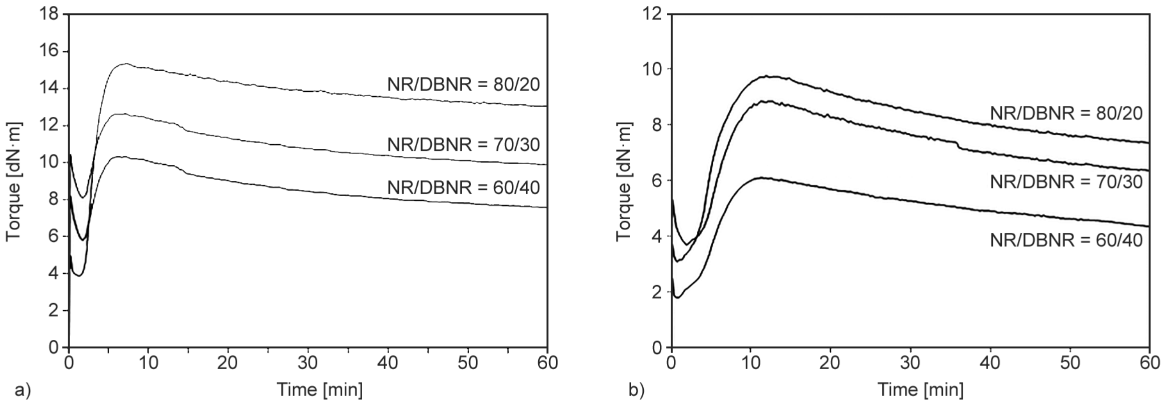

Figure 9. Cure curves of NR/DBNR blend compounds with different blend ratios without (a); and with a combination of antimony trioxide and tris(2-ethylhexyl) phosphate) (b).

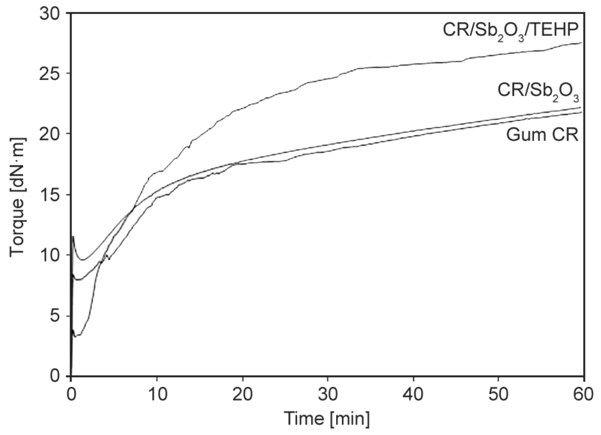

Figure 10. Cure curves of chloroprene rubber without and with flame retardants (antimony trioxide and tris (2-ethylhexyl) phosphate).

For a comparison of the flame retardant capability, chloroprene rubber (CR) was also prepared and characterized for its curing properties, as shown in Figure 10. It is clearly seen that CR exhibits distinct curing characteristics, displaying marching cure behaviors. Additionally, the inclusion of antimony trioxide and the combination of antimony trioxide with tris(2-ethylhexyl) phosphate led to a higher trend in maximum torque, while simultaneously reducing scorch and cure times (as shown in Table 3). It is noted that the CR compounds exhibit a much longer cure time compared to NR and NR/DBNR blend compounds. However, the addition of antimony trioxide and tris(2-ethylhexyl) phosphate accelerated the curing reaction in CR due to a decreasing trend in scorch and cure times.

3.5. Tensile properties

Figure 11 shows the tensile strength and elongation at break of NR/DBNR blends without and with a combination of antimony trioxide and tris(2-ethylhexyl) phosphate flame retardants. It is clearly seen that at a given NR/DBNR ratio, higher tensile strength and elongation at break are observed in the NR/DBNR blends without the addition of flame retardants. In addition, both properties increased with increasing NR proportions. This is due to the molecular characteristics of DBNR, which has very low viscosity and flow curves as compared with the neat NR (Figure 5). Even though the tris(2-ethylhexyl) phosphate activated the curing reaction of NR and caused a larger torque difference than the gum NR, the influence of the retardation by antimony trioxide and the molecular characteristics of DBNR resulted in an overall lower tensile strength and elongation at break of the blend with a combination of antimony trioxide and tris(2-ethylhexyl) phosphate.

Figure 12 depicts the tensile strength and elongation at break of natural rubber and chloroprene rubber vulcanizates with and without flame retardants. It is evident that NR vulcanizates (Figure 12a) exhibited higher strength than CR vulcanizates (Figure 12b). Additionally, the incorporation of flame retardants led to a decreasing trend in tensile strength for both rubber compounds. Furthermore, incorporating flame retardant additives had a small effect on the elongation at break of NR vulcanizates, but an improvement in elongation at break is observed in chloroprene rubber compounded with antimony trioxide and tris(2-ethylhexyl) phosphate. Additionally, a similar decreasing trend in elongation at break was observed in both rubber vulcanizates.

3.6. Flame retardancy

Figure 13 shows the burning rate of gum NR and NR compounded with antimony trioxide, as well as a combination of antimony trioxide and tris(2-ethylhexyl) phosphate. It can be observed that the gum NR vulcanizate depicts a burning rate of about 0.85 mm/sec, which is similar to the previous finding [4]. This is attributed to the intrinsic burning behavior

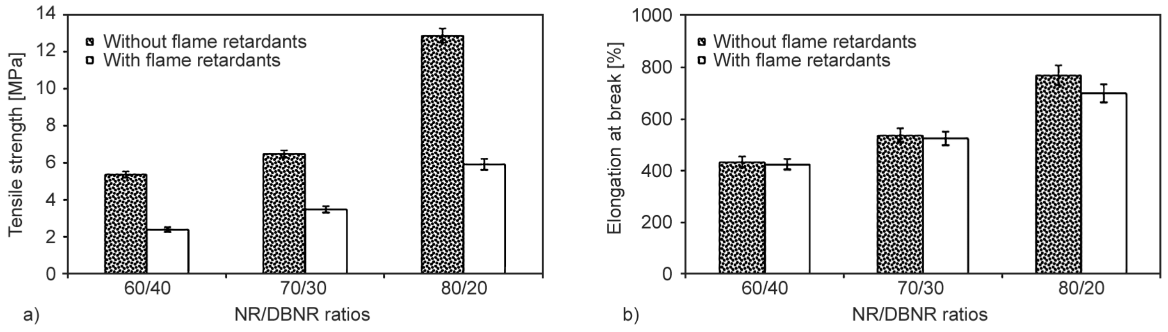

Figure 11. Tensile strength (a); and elongation at break (b) of NR/DBNR blends with and without flame retardants (antimony trioxide and tris (2-ethylhexyl) phosphate)).

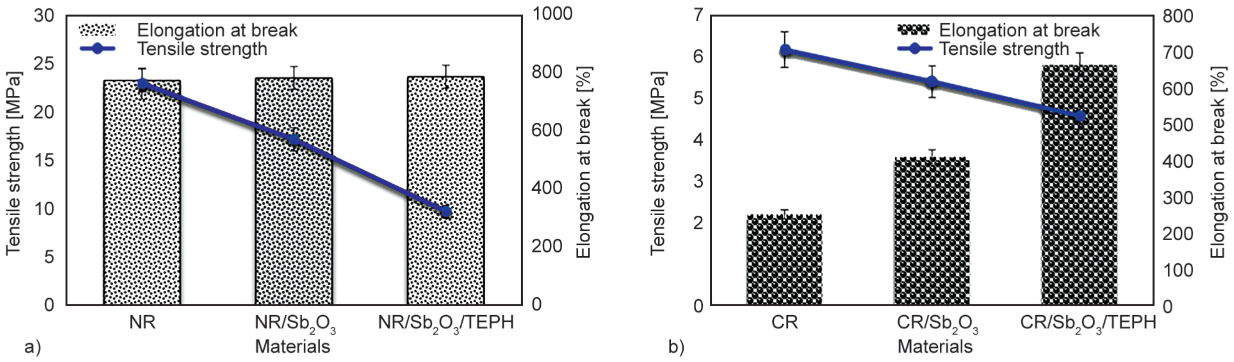

Figure 12. Tensile strength and elongation at break of natural rubber (a), and chloroprene (b) vulcanizates with and without flame retardants.

of hydrocarbon contents in NR molecules. However, the incorporation of antimony trioxide caused a significant decrease in the burning rate of the rubber sample, leading to a higher flame retardant capacity of NR/Sb_2O_3 compound. The combination of antimony trioxide and tris(2-ethylhexyl) phosphate exhibits a synergistic effect in further reducing the burning rate and enhancing the flame retardancy of the rubber specimen. Consequently, these two flame retardant additives were incorporated into the NR/DBNR blends to further enhance the flame retardancy of the NR samples, as illustrated in Figure 14.

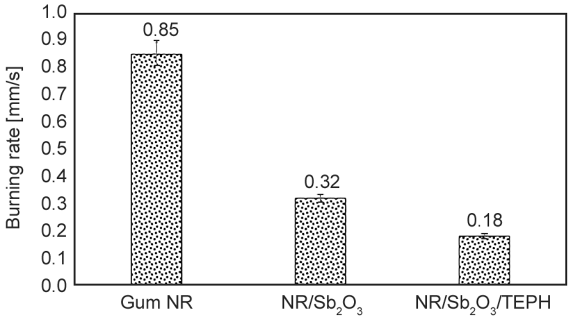

Figure 13. Burning rate of gum NR, and NR compounded with antimony trioxide and a combination of antimony trioxide and tris(2-ethylhexyl) phosphate).

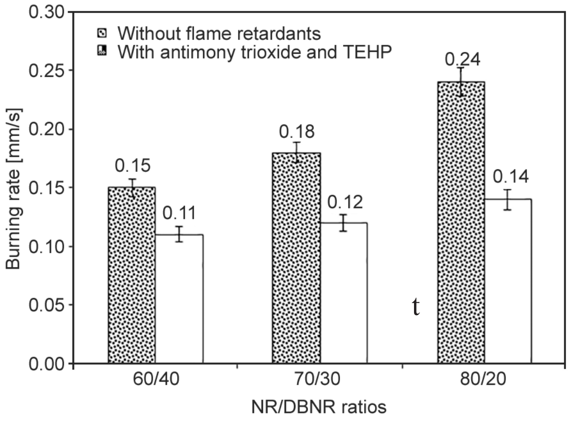

Figure 14. Burning rate of NR/DBNR blends with and without flame retardants (antimony trioxide and tris(2-ethylhexyl) phosphate)).

In Figure 14, it is evident that the burning rates for all rubber compounds are significantly lower compared to the gum NR compound in Figure 13. Furthermore, the burning rate shows an increase with higher DBNR contents in NR/DBNR blends, indicating the flame-retarding ability of DBNR containing phosphorous contents in its molecules. The addition of a combination of antimony trioxide and tris(2-ethylhexyl) phosphate in the NR/DBNR blend results in a notable decrease in the burning rate. This can be attributed to the synergistic effect of flame retardant additives (antimony trioxide and tris(2-ethylhexyl) phosphate) and the intrinsic flame retardance of DBNR due to dibutyl phosphate-bound natural rubber molecules.

This observation suggests a distinctive combustion characteristic for neat DBNR, with a flame propagation duration of only 58 s (Table 4), demonstrating its intrinsic high flame retardance with halogen-free characteristics. Table 4 further illustrates the flame propagation duration before extinguishment for chloroprene rubber and its compounds with flame resistance additives. Notably, CR compounds exhibit

Table 4. Characteristics of combustion for neat DBNR and chloroprene rubber compounded with and without flame retardant.

Materials	Time for flame propagate before extinguished [s]
Neat DBNR	58
Gum CR	45
CR/Sb_2O_3	16
CR/Sb_2O_3/TEHP	10

a very short time before the flame is extinguished. However, it's important to consider that these are halogenated rubbers, raising environmental and safety concerns.

4. Conclusions

The high ammonia (HA) latex concentrate natural rubber latex was diluted from 60 to 20% DRC for performic epoxidation to produce epoxidized natural rubber with 20 mol% epoxide. Subsequently, ENR-20 was further functionalized to dibutyl phosphate-bound natural rubber (DBNR) through a reaction with dibutyl phosphate in a latex state. FTIR was used to verify molecular characteristics of ENR-20 and DBNR and to quantify the epoxide contents in ENR molecules. The raw DBNR, ENR-20, and unmodified natural rubber (ADS) were then characterized for their rheological properties in terms of shear flow properties. Additionally, thermal properties were assessed through dynamic mechanical analysis and thermogravimetric analysis. It was found that DBNR exhibited the lowest flow curve, viscosity curve, and area under the tan δ-temperature curve, with the order of NR > ENR-20 > DBNR. Furthermore, DBNR exhibited the highest T_g at about –3.9 °C, compared to -57.5 and -34.0 °C for NR and ENR-20, respectively. Also, the DBNR also showed the largest residue from burning in a TGA test, indicating higher thermal resistance. Following this, NR/DBNR blends with different blend ratios were compounded, both with and without flame resistance additives, a combination of antimony trioxide and tris(2-ethylhexyl) phosphate. Unmodified natural rubber (ADS) and chloroprene rubber (CR) were also compounded, without and with flame resistance additives, for comparison purposes. All natural rubber and NR/DBNR blend compounds exhibited reversion behavior due to the breakage of newly formed sulfidic bonds. Nevertheless, chloroprene rubber exhibited marching cured curves with a rising torque over time. It was also observed that antimony trioxide retarded the curing reaction of NR, while cure acceleration was found in NR compounded with tris(2-ethylhexyl) phosphate. Therefore, the combination of antimony trioxide and tris(2-ethylhexyl) phosphate was used in NR/DBNR compounds, synergizing with the intrinsic flame retardant properties of DBNR. It was found that the NR/DBNR blends exhibited significantly lower burning rates (*i.e.*, higher flame retardance) than gum NR vulcanizate. The addition of flame resistance additives further enhanced flame retardancy by lowering their burning rate. Therefore, these types of NR compounds can possibly be used to prepare high flame and heat-resistant rubber articles with halogen-free additives in various applications. Exchanging some portions of NR with DBNR can prove beneficial, as it reduces or eliminates the need for additional flame retardant additives while achieving the desired level of flame retardancy. However, it's important to note that using DBNR alone may not be suitable for certain rubber product applications due to its high T_g and low damping properties, as indicated by the DMA test results.

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