Thermal aging and chemical resistance evaluation of carbon black filled natural rubber blending: effect of the composition of acrylo nitrile and styrene butadiene rubber

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Abstract. Natural rubber (NR) has excellent tensile and abrasion properties, but its thermal and chemical resistance needs to be improved. The present study investigates the effect of acrylonitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR) composition in NR compounding filled carbon black (CB). The effect of chemical and heat resistance was examined by varying the addition of SBR/NBR (phr/phr) as follows 40/0; 35/5; 30/0; 25/15; and 20/20 into 60 phr (part hundred rubber) NR filled by 50 phr CB respectively. Compared with NR composites, SBR/NBR addition improved the hardness and density slightly. While tensile strength, modulus, abrasion resistance, and compression set decreased significantly. The volume, hardness, and physical properties were measured before and after 28 days of immersion in acidic, alkalis, and salty solutions. It was found that the higher loading SBR/NBR enhances chemical resistance. The hydrochloric and sulphuric acid immersion influenced the physical changes more vigorously. The thermal aging evaluation was observed by measuring the hardness and tensile strength at hot air circulation of 70°C for 24; 48 and 72 hours. The higher SBR/NBR loading could minimize the changes in hardness and tensile strength. To sum up, SBR/NBR addition improves the chemical and heat resistance on ternary blends.

1. Introduction
The demand for rubber and derivative rubber products for transportation, industrial machinery, mining applications, oil gas exploration, etc has increased. Thus, many new nano-composites as popular advanced engineering materials have been developed to supply that demand. Due to the high price and less efficient nano-composites of polymer and fillers such as silica, carbon black, clay, and montmorillonite, new polymeric materials have been focused on mixing binary or ternary blends [1,2]. This method reduces production costs with low investment and a highly efficient process. The combination of some polymers may produce new polymeric materials with desired physical, mechanical, tensile, and other properties. Generally, the blending of rubber-rubber is preferable for commercial industrial production rather than rubber-plastic blends. Binary or ternary rubber blends
have a high processing ability and a fine dispersion due to the crystalline structure and phase of each component are nearly similar [3,4]. However, the specified desired properties of the blends depend on the mixture ratio, polarity of polymers, composition of each polymer, miscibility, and the homogeneity of the polymers [5,6].

Natural Rubber (NR) has been the most well-known base polymer for polymeric materials for some advantages including good compression set, abrasion resistance, and tensile properties [7,8]. In addition, the availability of NR is higher than synthetic rubber (petroleum-based polymer). Thus, the production cost of NR-based products could be more profitable and efficient. Based on the chemical structure of NR that has double bond carbon (cis, 1-4 isoprene), some negative aspects may affect the physical and mechanical properties of NR [9]. For instance, the resistance of NR to oil, gas, ozone, oxygen, solvent, acidic solution, base solution, heating, and other chemicals is relatively lower compared to other synthetic rubber [10]. Therefore some efforts have been researched like chemical modification (epoxidation, chlorination, hydrogenation, grafting, de-hydrogenation, Etc) [11]. Due to the high price and complex technology of chemical modification, blending NR with other synthetic rubber was chosen to design polymeric material based natural rubber [1].

Since massive demand for coal as energy globally has risen, some coal exploration as open-pit mining has been developed in many areas. The issue of coal derivative products as new alternative energy becomes a trigger to increase the total coal production. Consequently, the demand for rubber products related to coal machinery, conveyor belt, idler roller belt, bucket elevator, and other open-pit mining equipment has doubled [12]. Rubber products for this application need special requirements particularly high chemical resistance, for instance, from acid water used during transporting the coal from the open-pit until the processing unit [12,13]. In addition, the products also shall have excellent physi-mechanical and thermal aging properties. Therefore, this research focuses on designing the ternary natural rubber blends that could comply with the rubber products’ requirement standard.

Previous studies reported that ternary blends of NR/BR/SBR of 25/25/50 phr reinforced SiO$_2$ nanoparticles successfully improved the processing ability and mechanical properties by adding an optimum number of SiO$_2$ [11]. Burgaz, Gencoglu, and Goksuzoglu [10] found that optimum carbon black filled in ternary blends of NR/BR and NR/BR/SBR improve compression set, tensile strength and stress relaxation, and thermo-mechanical properties. Besides, Abdelsalam, Araby, El-Sabbagh, Abdelmoneim, and Hassan [5] stated that optimum carbon black filler in ternary blends of 30/30/40 phr of NR/SBR/NBR could increase the compatibility between CB and the polymer matrix. Commercial carbon black has been used as a reinforcing filler for polymer matrix since it is very fine dispersed and contributes massive enhancement on tensile and physic mechanical properties for organic polymers [5,8,14]. Based on those findings, carbon black was chosen as a reinforcing filler for ternary blends in this research.

To improve the chemical resistance of natural rubber-based polymeric materials, some additives were added such as nano alumina to against hydrochloric acid aqueous and sodium hydroxide; barium sulfate against hydrochloric acid aqueous; ZnO against acidic and base solution. Bach, Vu, and Vu [11] used carbon fillers, graphite, shungite filler, and silicon carbide to enhance rubber composites’ chemical resistance in the oil pump impellers. The acrylonitrile-butadiene rubber (NBR) has been used widely in rubber composites for oil gas application since it has a good oil abrasion and chemical resistance [3,16,18]. Styrene-butadiene rubber is also commonly mixed with organic polymer because it has better abrasion resistance, crack initiation resistance, high filler loading capacity, and lower heat build-up behavior [2,4,19].

Previous research reported that binary blending of SBR and NR results in rubber that has excellent tensile strength, elastic modulus, and wear resistance with the good processing-ability and cure rate index [8,11]; the binary blending of NBR and SBR also could improve some mechanical and oil resistance [2,4]. However, research on ternary blends of NR, SBR, and NBR with predominantly NR filled carbon black is very limited. There is still a lack of information of processing-ability in which
NR is more dominant than SBR/NBR filled carbon black using homogenizer UB 4000. The scientific findings on the NBR addition effect against acidic and base solutions on NR/SBR polymer are very limited. To the best of our knowledge, no systematic work has been reported about the effect of SBR/NBR addition into dominated NR-filled carbon black polymeric materials on physico-mechanical thermal aging and chemical resistance particularly the resistance to the acidic and base solution of ternary natural rubber blends. The result of this research would be valuable in formulating natural rubber products for open pit mining application such as conveyor belt, idler roller, rubber pad, seal, and other rubber spare parts.

2. Experimental method

2.1. Materials

Natural rubber Standard Indonesian Rubber (SIR-10) was bought from Felda Indorubber crumb rubber factory in South Sumatera, Indonesia. The specifications of SIR 10 are as follows: Volatile Matter 0.003%; PRI (Plasticity Retention Index) 68% and Mooney viscosity (ML1+4 of 82 at 102°C). Styrene-Butadiene Rubber (SBR) Bayer M Ltd Type 1502 has specifications as follows: density of 0.945; styrene content 23% weight; Mooney viscosity (ML1+4) of 54 at 102°C. Acrylonitrile Butadiene Rubber (NBR) Bayer M Ltd has specifications as follows: acrylonitrile content 32%; density of 1.17; Mooney viscosity (ML1+4 of 47 at 102°C).

Filler: carbon black high abrasion furnace as N330 that has 28-36 nm particle size and 70-99 m²/g surface area. Main accelerator TMTD and secondary DPG. Compatibilizer used in this ternary blend was Ultra-blend 4000 (UB4000). Plasticizers and softeners: aromatic oil, Stearic Acid, paraffin wax (Oleo-chemicals Industry, PT Sumi Asih). Activators: ZnO (NC 105 Global Chemical Co, Ltd). Other standard chemicals for rubber compounding include age resister, sulfur curative agent, coumarone resin, 6PPD (Brataco Chemical), and other chemicals.

2.2. Rubber Compounding

The formulation of rubber mastication was listed in Table 1. NR was masticated firstly for about 3-5 minutes, then SBR and NBR were mixed with NR for about 12-15 minutes. Some chemicals for rubber compounding were mixed as follows: 5 phr UB 4000; 50 phr Carbon Black; 5 phr ZnO; 1 phr Stearic acid; 3 phr paraffin wax; 2 phr sulfur; 3 phr BHT, and other 0.5 phr resin. The sample formulated in Table 1 were compounded based on the standard procedure ASTM D3182. The rubber mastication and compounding were prepared using an open two-roll mill of 220mm diameter, 560mm length at a speed of 10 r/min and friction ratio of 1:1.15. During the process, the temperature of rolls controlled periodically at less than 50°C to prevent pre-heated and pre-vulcanization of the rubber compound. After a sulfur curative agent was mixed, the sample for testing was pressed and heated using specific molding at 150°C within optimum cure time (t90) about 16-20 minutes. Three replication of each formula were tested.

| Sample Formulation | NR (phr) | SBR (phr) | NBR (phr) |
|--------------------|----------|-----------|-----------|
| NR/SBR/NBR_{(100/0/0)} | 100 | 0 | 0 |
| NR/SBR/NBR_{(60/40/0)} | 60 | 40 | 0 |
| NR/SBR/NBR_{(60/35/5)} | 60 | 35 | 5 |
| NR/SBR/NBR_{(60/30/10)} | 60 | 30 | 10 |
| NR/SBR/NBR_{(60/25/15)} | 60 | 25 | 15 |
| NR/SBR/NBR_{(60/20/20)} | 60 | 20 | 20 |
2.3. Testing procedures
Physico-mechanical properties were tested one day after heating and pressing at 25-30°C room temperature. Tensile properties such as tensile strength and modulus were measured based on the ISO 37. Universal Testing Machine - Instron 3366 at a crosshead speed of 500mm/min using a dumb-bell shaped cutter sample was used to measure tensile strength and modulus.

The density of ternary rubber blends was conducted based on the ASTM D395 at 25-30°C room temperature. Hardness (International Rubber Hardness Degree/IRHD) was measured based on ASTM D2240 using a Wallace dead load. Hardness was measured by preparing a 6 mm thickness of samples and counted after 5 seconds of loading.

The compression set of the ternary blends was measured at 25% deflection, 70°C for 22 hours based on ASTM D395. The compression set was subjected to examine the extent by which the samples fail to return to its original shape and thickness. The value was calculated between the differences of original thickness and recovered thickness.

Abrasion resistance was tested using Wallace Croydon Akron Abrasion tester following BS 903, Pt.A.9 Method C. The diameter was 15 cm of abrading wheel and 1-inch thickness was placed at an angle 15° to the abrading wheel. A load of 4.5 kg was placed on the disc with 12.7 mm in thickness and 6.35 cm in diameter that has a hole in the center, the result was calculated as volume loss per 1000 revolutions.

To evaluate the chemical resistance of ternary blends of NR/SBR/NR to hydrolysis, degradation, oxidation, and specific hardening or surface attack, in this research, some chemical solution was employed such as 3.5% NaCl; buffer pH 2; buffer pH 4; 10% HCl; 5% H2SO4; 10% Detergent; 10% NH4OH; and 10% NaOH at room temperature. Chemical resistance was measured following the ISO/TR 7620. The test samples with 2 mm in thickness were completely immersed in the chemical solution in a close vessel to avoid evaporation. The samples were immersed at 25-30°C room temperature for 28 days. The volume and hardness of the fresh samples and after immersed samples were measured. The change of hardness was evaluated by subtracting the hardness after immersion with the fresh samples. The percentage change of volume (%V) was calculated based on the different mass of samples in the air after immersion from the initial mass of samples in air and the immersion chemical solution density. Analytical balance 0.0001g was used to weigh the samples.

The thermo-oxidative aging evaluation was tested according to the ASTM D473. The same fresh and aged samples were measured before and after the aging process using Aging Chamber Oven Model VAT, 60, ASLI (China). The vulcanized ternary blends of NR/SBR/NBR were aged using hot air circulation at a test frame of 5 rpm; setting the temperature at 70°C for 24 hours and 72 hours. Hardness and tensile strength were measured before and after aging. The difference of its value was analyzed as the aging resistance of ternary blends of NR/SBR/NBR. The test was conducted in triplicate for each formulation, the average value was reported in this paper.

3. Results and discussion

3.1. Physico-mechanical properties
Compared to single blends of NR with 50 phr of carbon black filler, the addition of SBR/NBR improved the hardness and density significantly. Both SBR and NBR had higher hardness than NR, thus the higher loading of NR might increase the hardness of ternary blends as listed in table 2. Along with the increased hardness, the carbon black filler, the ternary blends’ density was slightly higher than NR composites. As depicted in table 2, at the same number of carbon black filler, the NBR addition improved hardness and density less significantly. In agreement with previous research, the higher loading of carbon black improved the hardness and density of NR/BR [2,5,19]. It is found that the SBR/NBR addition did not affect the hardness and density significantly [4]. In confirmation of previous research, the hardness value is mainly determined by reinforcing the mix in rubber composites [5,6,10].
The remarkable enhancement of the tensile strength and modulus was caused by the less interaction between NBR, SBR, NR during the mastication process and less fine dispersion of carbon black within the rubber matrixes. During mastication, NR was more dominant than SBR and NR. It is predicted that an excessive 60 phr of NR based on rubber polymer might cause the mastication inhomogeneous. Similar results of NR and BR’s blending were less finely masticated [5], thus homogenizer UB4000 was added.

Table 2. The Effect of SBR/NBR loadings on physico-mechanical of NR/SBR/NBR ternary blends.

| Samples formulation | Composition NR/SBR/NBR ternary blends |
|---------------------|----------------------------------------|
|                     | 100/0/0 | 60/40/0 | 60/35/5 | 60/30/10 | 60/25/15 | 60/20/20 |
| Hardness (IRHD)      | 64      | 70      | 71      | 71       | 73       | 74       |
| Density (g/cm³)      | 1,137   | 1,229   | 1,235   | 1,235    | 1,238    | 1,241    |
| Tensile Strength (MPa)| 17.8    | 15.1    | 14.1    | 14.1     | 14.1     | 13.9     |
| Modulus at 100% elongation (MPa) | 7.4  | 5.7     | 5.2     | 5.2      | 5.1      | 5.1      |
| Modulus at 300% elongation (MPa) | 9.1   | 6.3     | 5.7     | 5.7      | 5.5      | 5.4      |
| Abrasion resistance (DIN.mm³) | 75     | 71      | 65      | 65       | 64       | 63       |
| Compression set 25% defl, 28°C, 72 hours (%) | 6.8 | 7.2     | 7.1     | 7.2      | 7.3      | 7.3      |

Similarly, the modulus trend at 100% and 300% elongation also significantly decreased due to the high loading of SBR/NBR. Similarly, it is reported that the reactivity of surface interaction caused this decrease in modulus, the weaker SBR/NBR/NR interaction with carbon black, aggregation between NR/SBR/NBR - carbon black, and filler dispersion in the rubber matrix [5,10]. Based on table 2, the formulation of 60/30/10 phr of ternary blends might result in optimum and stable modulus and tensile strength. It implies that 50 phr of carbon black filler had better interaction with the portion of 60/30/20 ternary blends of NR/SBR/NBR.

The affinity of carbon black filler and ternary blends may carbon black and rubber matrixes’ interaction by weakening hydrogen bonds and van der walls interaction among them. The improvement of modulus, tensile strength property may be due to the fine dispersion of CB in the ternary blends using homogenizer UB4000 [1]. In addition, rubber filler interaction between CB and NR/SBR/NBR associated with the contact of the surface of filler resulted in a more effective constraint of the motion of rubber chains with improved interfacial bonding between CB and NR/SBR/NBR [2,5]. The loading of SBR/NBR may increase, but at the optimum number of NR, the tensile strength and modulus would remain stable at 60/30/10 phr. It is also reported that an excessive number of NBR and CB led to agglomeration and aggregation of filler - filler or filler-rubber matrix, so the ternary rubber blends phase was at a weak point and decreased the tensile properties [4,10]. However, to ensure this phenomenon and study the morphology of this ternary blends in this research, further observation using SEM might be necessary.

The compression set is the important key parameter in deflection and compressive loads of rubber parts such as rubber pad, damper, idler roller, seal Etc. Compression stress increased with increasing filler content [2,3,19] while the compression set determined the ability of rubber vulcanizates to retain its elastic properties after prolonged compressive loads at certain temperatures [10,20]. The small compression set refers to the elasticity and the ability to maintain original thickness and low damping properties while a large compression set indicates lower stiffness but higher damping properties. The compression set is closely related to the Payne effect, the viscosity of NR/SBR/NBR, and the sulphuric vulcanization system [2,11,13]. It is shown that the compression set of ternary blends increased with the increase of NBR addition until it reached about 7.3%. Compared to NR composites, ternary blends has a high compression set that represents the material blend of NR, SBR, NBR which
needs to be improved. In other words, the rigid carbon black fillers in an appropriate amount of SBR/NR, affinity and polarity of SBR/NR with carbon black might restrict the chain mobility of the network of ternary elastomeric rubber blends. Table 2 shows that the lowest compression set was NR composites. It could be explained that the chemical bonds and physical interaction of CB filler rubber were strong enough, so the compression set results to show less permanent deformation [4,19]. The most elastic blends were NR composites, whereas the higher NBR the less elastic NR/SBR/NBR ternary blends are. As similarly reported by previous research, this more permanent deformation of NR/SBR/NBR was due to its relatively higher rigid styrene and acrylonitrile content [2,5].

The abrasion resistance or the volume loss due to mechanical rubbing and erosive action is a major requirement for tire, rubber pad, rail pad, etc. Similar to the decreasing value of tensile strength, the abrasion resistance also experiences a decrease of about 4-12 DIN.mm³ by the increasing SBR/NBR in ternary blends. The blends have less crosslink density that leads to allowing erosion due to low stiffness [5,14,17]. Even though NBR and SBR have good abrasion resistance as reported by Pashaei, Hosseinzadeh, and Syed [4], table 2 shows different results that the addition of SBR and NBR decreased abrasion resistance. This is because the ternary blends of NBR and SBR were not as homogenous as NBR composites filled carbon black. This phenomenon is also found in research by Susanto and Marlina [8] who blend SBR and NR filled carbon black; Bach, Vu and Vu [11] who blend NR/NBR filled silica. The higher SBR/NBR (20/20 phr) addition influences the abrasion resistance value less significantly. Some papers also reported a similar finding. For instance, acrylonitrile does not directly affect the bonding interaction between filler rubber while NR/BR does due to the less dispersion and affinity of carbon black among the three different ternary polarities of ternary blends (NR, SBR, NBR) [4,5,19]. Consequently, it could not contribute strongly to resist friction and decrease the lost volume.

3.2. Chemical resistance
Chemical resistance of ternary blends of NR/SBR/NBR was evaluated to measure the ability to resist the chemical attack with fewer physical appearance changes, surface, volume, and hardness over a period of time. In a chemical environment such as a chemical solution, polymeric materials can react chemically, absorb, dissolve, crack, stress, and plasticize, diffuse solvent into the inner surface [7, 8, 15]. Based on the ISO/TR 7620:2005 (E), the good resistance of ternary blends is showed by the minimum changes of volume and hardness after chemical solution immersion for 28 days at temperature 25-30°C. Table 3 shows the comparative acids, alkalis, and salty resistance of ternary blends NR/SBR/NBR. As listed in table 3, the changes in hardness and volume of ternary blends became smaller because the higher SBR/NBR addition shows that SBR/NBR contributes positively. The complex structure of NR, SBR, and NBR filled carbon black might resist chemical attack stronger than NR filled carbon black composites.

In systematic comparison in table 3, NR filled carbon black composites without SBR/NBR exhibited a minor effect deterioration after 28 days of alkalis and acidic solution. In comparison, the SBR/NBR addition into ternary blends contributed positively to the chemical resistance. Previous research mentioned that the effect of styrene and acrylonitrile enhances acidic resistance [15]. As listed in table 3, the higher NBR added means the lower decrease in hardness value and the less swelling effect. It is clearly shown that each formulation did not affect the increasing volume after immersion. The same results were reported that the adsorption effect on the inner surface of ternary blends was minimized due to the formation of the new surface crust [15]. Compared to oil and organic solvent immersion, the effect on physical properties changing would be more rigorous than a chemical solution since the differences in vapor pressure, chemical properties, and diffusion transport enable to accelerate swelling or shrinkage effect [8,19].

Immersion of the ternary blends in buffer pH2 solution caused a decreased hardness more significantly than the pH4 solution. Whereas, the volume did not significantly increase due to the adsorption effect on the surface. It is highlighted that 10% of HCl immersion caused an extreme
increase in hardness at +15 IRHD on NR composites. The ternary blends with SBR/NBR also exhibit an increase in hardness for only +6-10 IRHD. This result agrees with the impermeable film on NR composite’s surface of the formation of the impermeable film on the surface of NR composite during the chlorination process; hydrochloric acid would cause NR to crust formations of chlorinated rubber membrane with a certain thickness and increasing hardness by Hadi and Kadhim [15]. However, for some time until the membrane dissolves, hydrochloric acid will crack and damage the inner membrane.

Conversely, sulfuric acid destroys the surface of NR composites more strongly than ternary blends. In addition, sulfuric acid immersion contributes to the decreasing in each formulation’s hardness more vigorously than other acidic solutions such as buffer pH 2 and pH 4. As reported by Kashani, Ngo, Hemachandra and Hajimohammadi [21], sulfuric acid is very corrosive to tires (natural rubber composites) and may destroy the double back bonds of isoprene.

Table 3. The Effect of SBR/NBR loading on the chemical resistance of NR/SBR/NBR ternary blends.

| Samples Formulation | Change In | H2O Buffer | Buffer | 10% HCl | 5% H2SO4 | 10% NH4OH | 10% NaOH | 10% Detergent | 3.5% NaCl |
|---------------------|-----------|------------|--------|---------|----------|-----------|----------|---------------|----------|
| NR/SBR/NBR (100/0/0) | Volume (%) | 0 | 13 | 0.13 | 15 | 0.17 | 31 | 0.16 | 18 | 0.02 | 22 |
|                       | Hardness IRHD | 0 | -4 | -4 | +15 | -8 | -5 | -8 | 0 | -2 |
| NR/SBR/NBR (60/40/0) | Volume (%) | 0 | 12 | 0.12 | 13 | 0.15 | 28 | 0.12 | 12 | 0 | 0.1 |
|                       | Hardness IRHD | 0 | -2 | -2 | +10 | -5 | -1 | -2 | 0 | -1 |
| NR/SBR/NBR (60/35/5) | Volume (%) | 0 | 08 | 0.08 | 08 | 0.08 | 19 | 0.08 | 07 | 0.02 | 0.03 |
|                       | Hardness IRHD | 0 | -2 | -1 | +9 | -4 | -1 | -2 | 0 | -1 |
| NR/SBR/NBR (60/30/10) | Volume (%) | 0 | 05 | 0.05 | 06 | 0.08 | 17 | 0.08 | 06 | 0.01 | 0.03 |
|                       | Hardness IRHD | 0 | -2 | -1 | +8 | -4 | -1 | -2 | 0 | -1 |
| NR/SBR/NBR (60/25/15) | Volume (%) | 0 | 02 | 0.02 | 03 | 0.07 | 18 | 0.01 | 03 | 0 | 0.02 |
|                       | Hardness IRHD | 0 | -1 | -1 | +6 | -4 | -1 | -1 | 0 | 0 |
| NR/SBR/NBR (60/20/20) | Volume (%) | 0 | 02 | 0.02 | 05 | 0.17 | 01 | 0.01 | 03 | 0 | 0.02 |
|                       | Hardness IRHD | 0 | -1 | -1 | +6 | -3 | -1 | -1 | 0 | 0 |

The resistance of NR composites in alkalis solution was weaker than ternary blends. The high loading of SBR/NBR in NR composites could minimize the hardness and volume changes. Compared to the acidic solution, the changes were relatively smaller than both HCl and H2SO4 immersion effects. Similarly, the immersion detergent and NaCl solution did not have any significant effect on physical properties changes. Looking at Table 3, the addition of SBR/NBR could positively impact acidic, alkali, and salty resistance. The effect of good compatibility of acrylonitrile, styrene, and isoprene groups filled by carbon black in ternary blends rubber. As explained in the effect of SBR/NBR on physico-mechanical properties, the chemical resistance characteristics might be enhanced by forming more cross-link bonding and complex structure of matrix polymer. This similar clarification has also reported the contribution of styrene groups on chemical resistance [21].
3.3. Thermal ageing properties

In this work, chemical immersion evaluation and thermal aging properties become key parameters on rubber product evaluation. As designated for rubber products in coal open pit mining usage, acid mine water and sun-light, oxygen, ozone exposure, air oxidation, and heating from the friction and conduction of the machine may reduce the shelf life and shorten the usage period [12, 13].

As mentioned before, since the ternary blends were mainly dominated by NR that was susceptible to thermal and air oxidation due to the attack on carbon-carbon double bonds of n-isoprene, the SBR and NBR were added to the blends properly. Similar findings were also reported by Liu, Li, Xu and Zhang [22] that NBR enhances the thermal degradation properties of composites.

Figure 1 shows surface hardness changes due to thermal aging at 24 and 72 hours. The graph shows that hardness increased insignificantly as a function of SBR/NBR content as expected. By comparing before and after age 24, 72 hours, it is noticeable that the addition of SBR/NBR contributed positively to the heat resistance of the ternary blends. The NR composites experienced serious damage on the surface, the hardness became remarkably higher by the more extended aging and after 72 hours, the surface became mushy. Previous research mentioned that overheating for a long time could destroy the molecular chain of (n 1,4 cis-isoprene) and influence the movement and mobility of the filler and break the bonding filler- rubber and rubber-rubber [11,19,20]. The main-chain scission polymer backbone or sulfidic cross-linked during the ageing period which led to cleavage of the networking structure and change rubber properties [18]. On the other hand, compared to NR composites without SBR/NBR, the graph shows that the hardness of NR/SBR/NBR ternary blends before and after 24 hours of aging did not change significantly (the increasing hardness is about 3-5 IRHD). It is showed that the higher loading of SBR/NBR, the smaller hardness changes of ternary blends. Higher SBR / NBR can withstand heating longer and prevent surface thermal-oxidative degradation. Similar findings stated that SBR and or NBR might contribute to span the overheating that leads to inhibit overheating and over vulcanization so that the stiffening effect that destroys the surface of ternary blends might be hindered [1,11,20,22].

Tensile strength values decreased by the longer aging time at 70°C approximately 3-7 MPa for each composition. Figure 2 depicts the remarkably decreasing tensile strength after 24 and 72 hours of NR composites without SBR/NBR addition. Meanwhile, in the ternary blends when SBR and SBR/NBR were blended with NR, the changes of tensile strength could be minimized by the more extended periods. Similarly to the hardness changes, the aging may deteriorate the tensile strength of the ternary
blends. The decrease in the tensile strength value due to the longer aging period is less significant with the higher the SBR / NBR loading. This is in agreement with research findings by Zainal, Santiagoo, Ayob, Ghani, Mustafa, and Othman [20] on the improvement of thermal properties on the blending of propylene and acrylonitrile butadiene rubber using carbon black bagasse. Besides that deterioration factor as explained in hardness change, tensile strength dropped due to the over vulcanization. Over a long time, it may lead to serious cross-link density that exceeds a critical point. Consequently, the chain segment becomes less effective, less mobile, and distracts the normal orientation of the network chain and stress concentration, so that the tensile strength was dropped [1,2,18].

![Figure 2. Thermal aging profile: tensile strength changes of NR/SBR/NBR ternary blends.](image)

Another aspect that may exacerbate the thermal aging effect was evaporation. The number of volatile matter compounded in this research such as aromatic oil, paraffin wax, and other chemicals might evaporate and migrate from inner to its surface of the polymer thus it weakened the tensile strength. Theoretically, less finely carbon black dispersion within polymeric ternary blends influences the surface damage so that the optimum amount of filler should be dispersed properly [5,10]. The processing-ability also affects the homogeneous polymer matrix and the tensile and thermal oxidative degradation of the ternary blends.

4. Conclusion
SBR/NR addition into NR polymeric materials reinforced carbon black was successfully blended by using UB4000 as a homogenizer. The increased values of hardness, density, and compression set were more significant than NR composites in the same number of 50 phr carbon black. Furthermore, with the addition of NBR which was higher than the SBR in the ternary NR mixture, the parameter value experienced a slight increase. Conversely, the NBR addition negatively affects tensile strength, modulus 100% and 300% elongation, and abrasion resistance of the ternary blends. Agglomeration and less fine carbon black dispersion due to NBR/SBR might reduce the chemical bonding of filler-rubber and rubber-rubber within the ternary blends. The nitrile and styrene groups are more rigid than isoprene, influencing the tensile and physical properties. It is found that NBR/SBR also enhanced the chemical resistance of the ternary blends. In the systematic evaluation by observing the changes of hardness and volume using chemical solutions within 28 days, Changes in hardness and volume can be categorized as not having a significant effect as a substitute for 5% H2SO4 and 10%
HCl solutions. Thermo-oxidative aging at 70°C temperature influenced the increasing hardness and decreasing tensile strength of the ternary blends by the more extended period time. The SBR/NBR loading could minimize the hardness and tensile changes. Compared to NR filled carbon black composites, ternary blends had higher heat resistance. It is suggested to study the processing-ability and morphology of the ternary blends for further research.

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References
[1] Jovanović S., Samaržija-Jovanović S, Marković G, Jovanović V, Adamović T and. Marinović-Cincović M 2016 Composites Part B: Engineering 98 126-33
[2] Xue X, Yin Q, Jia H, Zhang X, Wen, Ji Q and Xu Z 2017 App. Surface Sci. 423 584-91
[3] Mao N D, Thanh T D, Thuong N T, Grillet A C, Kim N H and Lee J H 2016 Composites Part B: Engineering 93 280-8
[4] Pashaei S, Hosseinzadeh S and Syed A A 2017 Polymer Composites 38(4) 727-35
[5] Abdelsalam A. A, Araby S., El-Sabbagh S H, Abdelmoneim A and Hassan M A 2019 J. Thermoplastic Composite Mat 0892705719844556
[6] Husnán M H, Ismail and Shuib R 2018 Mat. Sci. and Eng. 309 012028
[7] Chauhan N. P, Meghwal K, Gholipurmalekabadi M and. Mozafari M, in Polyaniine blends, composites, and nanocomposites 2018 (Elsevier,) pp 149-74
[8] Susanto T and Marlina P 2019 Jurnal Dinamika Penelitian Industri 30(2)
[9] Susanto T presented at the MATEC Web of Conf. 2018 (unpublished)
[10] Burgaz E, Gencoglu O and Goksuzoglu M 2019 Res. on Eng. Struc. and Mat. 5(3) 233
[11] Bach Q V, Vu C M and Vu H T 2019 Silicon, 1-11
[12] Bugaric U, Tanasijević M, Polovina D, Ignjatović D and Jovančić P 2014 Technical Gazette 21(5) 925-32
[13] Yang G 2014 Sensors & Transducers 181(10) 210
[14] Wisojodharmo L, Fidyaningisih R, Fitriani D, Arti D and Susanto H 2017 MS&E 223(1) 012013
[15] Hadi F and Kadhim R, presented at the IOP Conference Series: Mat. Sci. and Eng, 2020 (unpublished)
[16] Abdul Rashid E S, Muhd Julkapi N B and. Abdul H Y W 2018 J. Appl. Polymer Sci. 135(32) 46594
[17] Bhawal P., Das T K, Ganguly S, Mondal S and Das N C 2019 Polymer Bull. 76(4) 1877-97
[18] Saha T and Bhowmick A K 2019 Rubber Chem. and Tech. 92(2) 263-85
[19] Liu P, Zhang X, Jia H, Yin Q, Wang J, Yin B and Xu Z 2017 Composites Part B: Engineering 130 257-66
[20] Zainal M, Santiagoo R, Ayob A, Ghani A A, Mustafa W A and Othman N S 2019 J. Thermoplastic Comp. Mat. 0892705719832072
[21] Kashani A, Ngo T D, Hemachandra P and Hajimohommadi A 2018 Constr. and Build. Mat. 171 467-73
[22] Liu J, Li X, Xu L and Zhang P 2016 Polymer testing 54 59-66