Rubber blend · styrene butadiene rubber · nitrile rubber · acrylonitrile-styrene-butadiene rubber · oil resistance · mechanical properties

Compounds and vulcanisates of acrylonitrile-styrene-butadiene rubber (NSBR) were prepared, and their properties were compared with those of conventional blends between styrene butadiene rubber (SBR) and acrylonitrile-butadiene rubber (NBR). Results reveal discrepancy in cure behaviour of NSBR from SBR/NBR blends to some extent, i.e., the NSBR yields inferior crosslink density to the SBR/NBR blends, and thus the hardness. By contrast, the cured NSBR specimens offer superior tensile strength and processability. Payne effect as an indication of filler network formation magnitude is slightly greater in the NSBR system. In summary, it is possible to substitute the SBR/NBR blends with single NSBR eliminating the complexity in blending process while giving advantageous processability and tensile strength.

Eigenschaftsvergleich von Nitriß-Styrol-Butadienkautschuk mit Verschnitten aus Styrol-Butadien Kautschuk und Nitrilkautschuk

Kautschukverschnitte · Styrol-Butadien Kautschuk · Nitrilkautschuk · SBR/NBR Verschnitte · Ölbeständigkeit · mechanische Eigenschaften


Figures and Tables: By a kind approval of the authors.

Comparison on Properties of Acrylonitrile Styrene Butadiene Rubber (NSBR) and Styrene Butadiene Rubber (SBR) / Nitrile Rubber (NBR) Blends

The main purpose of blending two or more rubbers together is typically to combine inherent properties of the individual components to a single material. Such enhanced properties include mechanical properties and processability, and in some circumstances the product cost could be diminished [1-4]. In practice, a physical blending is the most widely used technique for preparing rubber blends because of its ease of operation with cost effectiveness [1]. However, the blending technique is still restricted by a difficulty in mixing process particularly in the blends of polarity and viscosity mismatching systems.

Styrene butadiene rubber (SBR) is one of the most useful synthetic rubbers, particularly in tyre industry, because of its good resistances to abrasion and crack (or cut) growth [5]. However, its oil resistance is considerably poor. Conversely, acrylonitrile-butadiene rubber (NBR) is a polar elastomer possessing high resistance to non-polar substances such as hydrocarbons oils and solvents, but its mechanical properties are considerably superior compared with those of SBR. Therefore, blending of these two polymers is possible to combine the individual properties to a single material. Notably, because of the difference in polarity between SBR and NBR, the thermodynamic incompatibility with poor batch-to-batch consistency is resulted, leading to poor mechanical properties [6]. Typically, the control of state-of-mix and/or the incorporation of compatibiliser are used to overcome such problem. The production of a copolymer, namely, acrylonitrile-styrene-butadiene rubber (NSBR) is therefore an alternative to the SBR/NBR blends because the NSBR integrates advantages of SBR in terms of processability and abrasion resistance, and of NBR in views of oil resistance. The present work aims to investigate the potential use of NSBR to substitute conventional SBR/NBR blends by comparing properties of NSBR copolymer with those of SBR/NBR blends. By this means, a general guideline for selecting the appropriate materials having a balance of processability, resistances to abrasion, crack growth, and hydrocarbon oil could be drawn.

Experimental

Materials

All materials used in this work were used as-received. Styrene butadiene rubber (SBR 1502; styrene content of 23.5%) and acrylonitrile–butadiene rubber (NBR: N230; acrylonitrile content of 35%) as raw rubbers were manufactured by Bangkok Synthetics Co., Ltd. (Rayong, Thailand) and Japan Synthetic Rubber Co., Ltd. (Tokyo, Japan), respectively. Acrylonitrile-styrene-butadiene rubber (NSBR: Sabor™ DT100; acrylonitrile content and styrene content of 30% and 5%, respectively) was produced by Lion Copolymer, LLC. (Baton Rouge, USA). Carbon Black (N550) as reinforcing filler was supplied by Thai Carbon Product Co., Ltd. (Bangkok, Thailand). Stearic acid as cure activator was purchased from Petch Thai Chemical Co., Ltd. (Bangkok, Thailand). Zinc oxide (ZnO) as cure activator and sulphur (S8) as vulcanising agent were

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supplied by Chemmin Co. Ltd., (Samuth-prakarn, Thailand). N-t-butyl-2-benzo-thiazolesulfenamide (TBBS) as cure accelerator was purchased from Kitpiboon chemical Ltd., Part. (Bangkok, Thailand).

**Rubber preparation**

The rubber blends were prepared at 5 different SBR/NBR composition ratios of 100/0, 75/25, 50/50, 25/75 and 0/100. The compounding ingredients, as shown in Table 1, were prepared with a laboratory-size internal mixer (Haake Rheomix90, Germany) equipped with cam-type rotors. The rubber compounds were prepared based on a fill factor of 0.75 with a two-stage mixing technique at set temperature and rotor speed of 50 °C and 50 rpm, respectively. In the first mixing stage, the ZnO, stearic acid and carbon black were incorporated sequentially into raw rubber with total mixing time of 12 minutes. In the second stage, the rubber mix prepared from the first mixing stage was masticated for 2 minutes at 50 °C, and then the sulphur and TBBS were incorporated into the rubber mix, and allowed 5 minutes to achieve good distribution and dispersion of all ingredients.

**Characterisation**

Cure behaviour was monitored with the use of rubber process analyser (RPA; Alpha Technology, USA). Cure characteristics of rubber compounds, including scorch time (ts2), cure time (tc90), minimum torque (ML) and maximum torque (MH), were investigated at 155 °C. Torque difference (MH – ML) was taken as an indication of the crosslink densities of the vulcanisates [7]. In order to prepare vulcanised specimens (aka. vulcanisates), the uncured compounds were compression moulded using a hydraulic hot-press under pressure of 16 MPa at 155 °C for the optimum cure time (tc90) as predetermined from the RPA. Apart from cure characteristics, the rheological behaviour of rubber compounds was determined by RPA with strain sweep tests at temperature and frequency of 100 °C and 0.99 rad/s, respectively.

Hardness of vulcanisates was measured using a durometer with Shore A scale (Cogenix Wallace, UK) as per ASTM D2240. Tensile properties were determined using a universal testing machine (Instron 5566, USA) according to ASTM D 412, Die C. Dynamic mechanical test of vulcanisates was carried out by dynamic mechanical analyser (Gabo, Eplexor 25N, Germany) in tension mode. Temperature was scanned from -60 to 80 °C at 2 °C/min under static strain, dynamic strain and frequency of 1%, 0.1% and 10 Hz, respectively. The tanδ at 60 °C was used to represent the magnitude of rolling resistance of vulcanised rubber [5, 7]. Glass transition temperature (Tg) was determined from the temperature at the damping peaks [8].

Measurement of oil resistance in this work was based on changes in tensile properties, according to ASTM D471. The specimens were immersed in hydraulic oil at room temperature for 7 days. Relative tensile properties as calculated from Equation (1) were used as an indication of oil resistance [9].

\[
\text{Relative tensile strength} = \frac{\sigma_{0-2}}{\sigma_{0-1}}
\]

where \(\sigma_{0-1}\) and \(\sigma_{0-2}\) are the tensile strength before and after oil immersion, respectively. Bound rubber content is known to be a measure of the filler-rubber interaction [10]. As the filled compound is extracted with good solvent, the gel-like rubber bound to the filler surfaces will not be soluble while the rest will go into solution. In this work, the determination of bound, impenetrable (and therefore in-
are shown in Table 2. Evidently, in SBR/NBR blends, scorch time and cure time are shortened as NBR content increases. Similar findings were reported elsewhere [1, 2]. The results might be explained by the polarity of the bulk, depending strongly on NBR content. Such polarity might affect the decomposition of TBBS to form ammonium mercaptide, which functions as actual cure accelerator [13]. Compared with the blend systems, the NSBR offers similar tendency of scorch safety and short cure time to the 25/75 SBR/NBR blend, which is due probably to the corresponding acrylonitrile content in NSBR. Also, the minimum torque (ML) of NSBR is slightly lower than SBR/NBR rubber blend systems, indicating the superior processability of the NSBR to the blend systems. The maximum torque (MH) and torque difference (MH-ML) of SBR/NBR blends somewhat decrease with increasing SBR content. However, the NSBR system shows slightly smaller magnitude of crosslink density, compared with the blend systems, as evidenced by its somewhat lower values of MH-ML.

It has been reported that the storage modulus (G') of rubber compounds is controlled mainly by following effects: (i) hydrodynamic effect of rigid filler in rubber matrix; (ii) crosslink network connecting the polymer molecules; (iii) chemical and physical interactions of rubber-filler and filler-filler [14]. Since the filler-filler-interaction is strain-dependent, the filler transient network could be destroyed at sufficiently high strain. Such strain is considerably smaller than the strain required for disrupting the polymer-polymer network, i.e., well below 100% strain [14]. The decrease in G' with increased strain is sometimes known as “Payne effect” which is used as a measure of filler transient network magnitude in rubber compounds [14–17].

Referred to Figure 1, the magnitude of discrepancy in G' at low (i.e., 0.56% strain) and high strains (i.e., 100% strain), is considered as the Payne effect magnitude. Evidently, the magnitude of Payne effect is highest in the NSBR system. In SBR/NBR blends, the Payne effect is more pronounced with increasing SBR content, implying the high magnitude of transient filler network formation. Additionally, the magnitude of Payne effect of the blends is found to be greater than that of filled SBR and filled NBR, demonstrating the “synergistic effect” in SBR/NBR blends. Not only the Payne effect, but also the mechanical properties exhibit the synergistic effect, which is advan-

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**Table 2**

<table>
<thead>
<tr>
<th>Sample codename</th>
<th>% Bound rubber</th>
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<tr>
<td>SON100</td>
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</tr>
<tr>
<td>S25N75</td>
<td>40</td>
</tr>
<tr>
<td>S50N50</td>
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<tr>
<td>S100NO</td>
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</tr>
<tr>
<td>NSBR</td>
<td>20</td>
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**Bound rubber of SBR/NBR blend and NSBR compounds filled with 50 phr carbon black**

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**Extractable rubber**

1. **Bound rubber**
2. **Carbon black**
3. **Connecting filament**
4. **Occluded rubber**

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**Schematic representation of bound rubber and occluded rubber in rubber compound filled with carbon black [modified on Leblanc's work as reported in ref 19]**

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soluble) rubber content based on the gravimetric method was conducted with toluene as good solvent for SBR, and acetone as good solvent for NBR and NSBR [11]. Small pieces of approximately 1.5 g of uncured specimens were immersed in 80 mL of solvent for a total of 7 days at room temperature, and then filtered out. The residues after extraction were dried in hot-air oven for 24 hours at 80°C. In the case of SBR/NBR blends, the uncured rubbers were immersed in 80 mL of toluene during 7 days. Thereafter the materials were immersed in acetone for 7 days, to remove non-bound NBR portion being insoluble in toluene. Subsequently, the rubber specimens were dried at 80 °C for 24 hours. The percentages of bound rubber contents were calculated from Equation (2) [8, 12].

\[
\%\text{ Bound rubber content (BRC)} = \frac{W_f - W_m}{W_f - W_m} \times 100
\]

(Equation 2)

where \(W_f\) is the weight of filler–rubber gel, \(W\) is the weight of the test specimens. The \(m_f\) and \(m_p\) are the weights of filler and polymer in the rubber compound, respectively.

**Results and Discussion**

Cure characteristics of rubber compounds...
tageous for the blend systems over the single SBR and NBR systems. Detail of mechanical properties will be given later.

Figure 2 shows the results of bound rubber content (BRC) in SBR/NBR blends and NSBR systems. The error bars indicate the standard deviations of the measurements for 3 specimens in each rubber system. In SBR/NBR blends, with the use of toluene as solvent, the unexpected synergistic effect is observed, and the greatest BRC is noticeable at the SBR/NBR blend ratio of 25/75. The high BRC values found in SBR/NBR blends might partly be caused by the inclusion of unbound NBR portion in the blends which is insoluble in toluene. To support the proposed explanation, further experiment was performed by immersing the rubber compounds in toluene and acetone sequentially. By this means, the unbound NBR would dissolve in acetone as its good solvent. Results obtained are shown in Figure 2 where the synergistic effect disappears. The BRC values of SBR/NBR blends are in between the single SBR and NBR systems. In NSBR copolymer, the relatively high BRC is observed, compared with SBR/NBR blends. This suggests the greater magnitude of rubber-carbon black interaction in NSBR copolymer.

Referred to results of Payne effect and BRC, the NSBR compound exhibits relatively high magnitude of the Payne effect, implying the high amount of tri-dimensional filler transient network of carbon black in rubber compounds. Such network might be composed of plenty of voids between black agglomerates in which some portion of rubber could reside in the voids as illustrated in Figure 3 [18, 19]. The occluded rubber in such voids leads to the high BRC found in NSBR system.

Figure 4 reveals hardness results of rubber vulcanisates in which the relatively high hardness is found in the blend systems in conjunction with the synergistic effect. Among the blend systems, the NBR-rich system demonstrates relatively low hardness despite its relatively high crosslink density as determined from cure torque difference (MH-ML) as illustrated in Table 2. It is proposed that the apparent results of hardness in SBR/NBR blends might be governed dominantly by the magnitude of filler transient network formation as evidenced from the results of Payne effect (see Figure 1). Despite the high magnitude of Payne effect in NSBR system, the hardness of NSBR is in between that of filled SBR and filled NBR systems, and evidently lower than that of the SBR/NBR blends. The hardness result appears to be in line with the result of crosslink density where the NSBR possesses lower crosslink density (as determined from torque difference illustrated in Table 2). In other words, the hardness of NSBR is dominated by crosslink density over the filler network formation. Additionally, it is known that the hardness could be used to predict modulus especially at small deformation of vulcanisates in many circumstances, i.e., the greater the hardness, the higher the low-strain modulus [13]. Figure 5 reveals the results of modulus at 100% strain (M100) of vulcanisates in which the synergistic effect is also noticed in a similar fashion to those of hardness. Thus similar explanation could be applied. Figure 6 shows a comparison of tensile strength in vulcanisates of SBR/NBR blends and NSBR copolymer. Since the NSBR vulcanisate possesses relatively poor filler dispersion degree (as implied by the high magnitude of Payne effect) in association with low crosslink density magnitude, the relatively low ultimate tensile strength was initially anticipated. Evidently, the highest tensile strength is observed in the NSBR system followed by filled NBR and filled SBR systems, respectively. In addition, the strength of SBR/NBR blends is inferior to the neat and NSBR systems, implying “antagonistic effect” which is believed to be the result of poor interfacial adhesion (via polarity mismatching) between NBR and SBR phases in blends [20]. Similar result trend is also found in elongation at break, as illust-
rated in Figure 7. Comparison of oil resistance of NSBR and SBR/NBR blends is exhibited in Figure 8. According to previous work, the relative tensile properties could be used an indication of for oil resistance in rubber vulcanisates [9]. Expectedly, the NBR single system offers highest oil resistance while the NSBR and NBR-rich blends give comparable oil resistance. This means the NSBR is practically advantageous due to its compromise in its mechanical strength, flexibility and oil resistance. Furthermore, the NSBR system requires no complex blending procedure for controlling consistent phase morphology in rubber matrix, leading to a significant reduction in production cost and time. Among SBR/NBR blends, the oil resistance increases with increasing NBR content in blends, which is not unusual. This is because the NBR contains acrylonitrile group as a polar group which is known to yield high resistance to hydrocarbon oil. Figure 9 exhibits the plots of loss factor (tan delta) against temperature of SBR/NBR and NSBR vulcanisates. The glass transition temperature (Tg) as determined from the temperature at the damping peak of NSBR is close to that of the filled NBR and the NBR-rich blend (S25N75). The results suggest comparable service temperature range of NSBR, NBR and S25N75. However, the inferiority of S25N75 to NSBR and NBR is its complexity in preparation as well as its presence of discrete phase (as evidenced by its 2 tan delta peaks) leading to its poor mechanical properties. Compared with NBR, the NSBR is more practical in its balance of mechanical strength, flexibility and oil resistance. In some applications such as industrial rollers where magnitude of rolling resistance is concerned, the value of tan delta at 60 °C is capable of predicting the rolling resistance of rubber [5, 7]. It is apparent from Figure 10 that the tan delta values at the temperature range of 40-80 °C of NBR and NSBR are comparable, and significantly higher than that of SBR single system. As one can expect, in SBR/NBR blends, the tan delta appears to increase with increasing NBR content, due mainly to the dilution effect. The fraction of SBR having low tan delta is substituted by that of NBR possessing high tan delta. This might be considered as a main disadvantage of NBR-rich blends and NSBR which could practically be alleviated by the adjustment of crosslink density.
Conclusions
The property comparison of filled NSBR copolymer and SBR/NBR blends was conducted, and the following conclusions could be drawn:

- The NSBR system and SBR/NBR blends offer comparable or slight discrepancies in cure characteristics, depending on the NBR content in blends.

- Main advantages of NSBR are its superiority in processability, tensile strength, flexibility and oil resistance with the expenses of inferiority in hardness, modulus and hysteresis. The crosslink density of NSBR is slightly lower than that in NBR-rich blends.

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References

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