Effect of composition ratios and mixing steps on properties of BR/NR/NBR blends and blends foam

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Abstract. This research is aimed to prepare foam from BR/NR/NBR blends which should integrate key property of these three rubbers. BR possesses high abrasion resistance but low tensile strength while NR possesses high tensile strength [1]. The addition of NBR was advantage for non-polar solvent resistance [2]. The effect of the mixing steps of rubber with vulcanizing additives on vulcanization of rubber and on mechanical properties and foaming of BR/NR/NBR were reported. The ratios of BR/NR/NBR were various as 60/20/20, 40/40/20 and 20/60/20. The vulcanizing additives used for rubber compounding were 5 phr ZnO, 2 phr stearic acid, 1.5 phr MBTS and 2 phr sulfur. The first part of the work was to study the effect of mixing step on rubber blends. Compounding system I was carried out by masticated BR, NR and NBR on a two-roll mill after that vulcanizing agent was added consecutively obtaining BR/NR/NBR rubber compounds with various rubber compositions. Rubber compounds were then characterized and vulcanized in order to investigate vulcanizate properties. In System II, three rubbers were mixed separately with required vulcanizing additives on the two-roll mill, obtaining BR, NR and NBR compound containing the same content of vulcanizing agent. Then the compounds were blended to obtain compound blended for the same blend ratios in System I. The blended rubber compounds were then characterized and vulcanized for their properties. In term of rubber blend foaming these two mixing systems were also used to compound the rubbers by addition foaming agent into the compound during mastication or blending of rubber on the two-roll mill. The results showed that mixing step affected the properties of rubber compound and vulcanizate in rubber blend. As various rubbers were mixed in different step resulting in different viscosity and hence affect foaming of rubber and subsequently properties of rubber foam.

1. Introduction
Rubber foam, also known as cellular, sponge or expanded rubber, is mainly manufactured with foaming or blowing agent to produce air gap in rubber matrix. Rubber foams are well known for their endurance and shock absorber. In fact, rubber foam and rubber sponge can be used interchangeably. There are various applications of rubber foam including cushioning in automobile seat, shock absorber, furniture, wall insulation, shoes and heel for footwear and so on. Natural rubber not only shows distinctive features in high tensile and tear strength, high resilience [3] and good tacking properties, but also shows excellent dynamic properties with low hysteresis with high resistance to abrasion. Nonetheless, NR also has disadvantages which it could be easily deteriorated under oxygen, ozone and heat due to the unsaturation in the chains. In addition, NR is not resistant to petrol and organic solvent. Blending NR with other rubber or polymers can survive both processing and its disadvantage such as blending with...
EVA and crosslinking by irradiation [4] could improve foam processing and foam properties such as foam density and rebound resilience. High polar rubber such as NBR can be foam and applied mainly for gaskets, heat insulation, soundproof and vibration dampening applications. The advantages of nitrile rubber foam are smooth, even and soft outer skin. The surface of NBR foam offers flexible and resilience touch [5]. Butadiene rubber (BR) is the most elastic rubber and offers good abrasion and tear resistance as well as low heat buildup including low rolling resistance. In order to integrate properties of NR and NBR sponge and advantaged properties of BR, blend of BR/NR/NBR sponge will be studied in this part of the research. Sulfur curing system will be applied to the rubber blend. The solubility of the curatives into each rubber phase should affect curing and blowing of rubbers hence two compounding system will be compared.

2. Experimental

**Materials:** NR grade STR5L (standard Thai rubber) was purchased from PJ RUBBER Co., Ltd. Butadiene rubber, BR, grade 130B was kindly provided from UBE Chemicals, Thailand. Acrylonitrile butadiene rubber, NBR, grade 6240, with 34% acrylonitrile content, was purchased from LG Chem. Ltd., Korea. ZnO, stearic acid, MBT, OBSH and sulfur were kindly provided by Innovation group Thailand.

Preparation of rubber compound: System I, BR/NR/NBR with the ratio indicated in Table 1 were kneaded and masticated on a two-roll mill for 30 minutes. ZnO, stearic acid, MBT and OBHS were added respectively. After well dispersion, sulfur was added and mastication was carried on for 5 minutes obtaining BR/NR/NBR System I compound. In System II, each rubber was kneaded and masticated for 30 minutes before addition of additives written in Table 1. To prepared rubber blend, compound follow the composition stated in Table 1 was weighted to the required rubber ratio and mixed on the two-roll mill obtaining BR/NR/NBR System II compound. Rubber blend compound were then investigated for cure characteristic parameters using Moving Die Rheometer (MDR, Gotech model GT-M2000, Taiwan) at 170°C.

**Preparation of rubber foam:** Various BR/NR/NBR blends foam was produced in a compression moulding machine at 170°C under the pressure of 1500 psi for 16 min. The rubber sponge obtained was then cut into specimen for various tests. Scanning electron microscopy, Hitashi, TM3030, was used to take rubber cell foam micrographs. The dumbbell-shaped specimens were tensile tested according to ASTM D412 using Instron universal testing machine Model Instron 596, with the extension rate of 500 mm/min. Compression set was performed by applied compression force on to specimens to its 50 % height for 22 h. After determined time, the specimens were left to relax for 30 min then the height of the rubber foam were recorded. Compression set was determined using equation 1:

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%\text{Compression set} = CRI = \frac{100}{t_{c2} - t_{c90}} \quad \text{equation 1}
\]

| Ratios of BR/NR/NBR (by weight) | BR | NR | NBR | ZnO | Stearic acid | MBT | OBSH | Sulfur |
|---------------------------------|----|----|-----|-----|--------------|-----|------|--------|
| 60/20/20                        | 60 | 20 | 20  | 5   | 2            | 1.5 | 10   | 2      |
| 40/40/20                        | 40 | 40 | 20  | 5   | 2            | 1.5 | 10   | 2      |
| 20/60/20                        | 20 | 60 | 20  | 5   | 2            | 1.5 | 10   | 2      |

3. Results and discussion

Mechanical properties of rubber blend prepared via System I and System II are presented in Figure 1. (a)-(b). It was reported by Noordemeer [6] that MBT has preference to be soluble in NBR to BR and EPDM meanwhile sulfur prefer to dissolve in nonpolar rubber to polar rubber. At high NR content, i.e. 60 % by weight, curing rate in NR phase occurred in System I was less than that in System II and resulting in lower tensile strength. Among these 3 three rubbers BR possess lowest curing rate and this
causes the lowered curing rate of rubber blend with high BR content in System II. Tensile strength and elongation at break of the rubber blends were increased with NR content as vulcanized NR generally possesses high tensile strength due to its stress induced crystallization.

**Figure 1.** Maximum cure rate (a), tensile strength at 300 % strain (b) and elongation at break (c) vulcanized rubber blends.

**Figure 2** Morphology and cell size distribution of BR/NR/NBR foam prepared via System I, (a)-(f) compared via System II (a’)-(f’).

The morphology of BR/NR/NBR blends foams and cell size distributions are shown in Figure 2 (a)-(f) and cells size distribution are shown in Figure (a’)-(f’). For rubber blend foam prepared via System I with various BR and NR as shown in Figure 2 (a)-(c). Cell size of rubber foam was found increased with the content of NR. This was due to the Mooney viscosity of NR compound was 13 Mooney units whereas BR and NBR compounds were found 25 and 40 Mooney unit respectively. High NR content, 60
% by weight, lead to flow ability of rubber compound during compression moulding. During melt, blowing agent was thermally decomposed and produced N$_2$ gas [7] then crosslinking rubber was expended. BR/NR/NBR with low Mooney viscosity would be easily expanded resulting in larger cell foam as seen in Figure 2 (c). For rubber blend foam compounded via System II, rubber cell size at high NR compound content, i.e. 60%, shows the smallest cell size. As mentioned earlier that rubber blend with the ratio of 20/60/20 in System II exhibited maximum cure rate compared with the other ratios due to the high NR content and curatives has already dispersed in NR compound before blending of the rubber compounds and this cause highest delta toque (i.e. crosslink density) consequently less expansion of the cell foam was performed. Tensile stress at 300 % strain and compression set of the foams were elucidated in Figure 3 (a)-(b). It has been known that BR and NBR vulcanizates performed less elastomeric behaviour than NR [8] and this was responsible for compression set of BR/NR/ENR foam.

![Figure 3](a) Tensile stress at 300 % strain and (b) compression set of BR/NR/NBR foam prepared from System I compared with System II.

4. Conclusions
Ternary rubber blend of BR/NR/NBR were prepared via 2 compounding method named as System I and System II and foaming of the blends were also prepared. The morphology of the foam showed that blends ratio and step of mixing affected cure characteristic, mechanical properties of rubber blends. Mechanical properties of rubber blend prepared via system I are higher than that prepared via system II. The highest delta torque of compound prepared via System II was the highest and this resulted in the smallest cell size of the foam consequently low compression set. It was clear that the mixing step affected the properties of rubber compound and vulcanize in rubber blend. As various rubbers were mixed in different step resulting in different viscosity and hence affect foaming of rubber and subsequently properties of rubber foam.

5. References
[1] Ismail M-N, El-Sabbagh S. H., and Yehia A.A. 1999 Elastomer and plastics. 31 255-270.
[2] Matador Rubber 2007 Education and Culture Lifelong Learning Program Leonardo Da Vinci.
[3] Salleh S, Ahmad Z and Ismail H 2016 Procedia chemistry 19 346-350.
[4] Salmazo LO, Lopez-Gil A, Ariff Z.M, Job A.E and Rodriguez-Perez M.A 2016 Industrial Crops and Products 89 339-349.
[5] Zhao X, Niu K, Xu Y, Peng Z, Jia L, Hui D and Zhang L 2016 Composites Part B 107 106-112.
[6] Guo R, Talma A.G, Datta R.N, Dierkes W.K and Noodermeer J.W.M 2008 European Polymer Jornal 44 3890-3893.
[7] Lopattananon N, Wangpradit N, Nakason C and Kaesaman A 2014 Journal of Rubber Research 17 80-95.
[8] V Raji V, Ramakrishnan S, Sukumar R, Brahmakumar M and Ravindratha Menon AR 2015 Society of Chemical Industry 10 4956.

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