Mechanical and morphology characteristics of natural rubber-styrene butadiene rubber (NR-SBR) blends in the presence of natural microbentonite

B Wirjosentono¹*, A H Siregar¹ and D A Nasution²

¹Department of Chemistry, Universitas Sumatera Utara, Medan, North Sumatra 20155, Indonesia
²School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Penang, Malaysia
*Email: basuki@usu.ac.id

Abstract. Natural rubber (NR) has been the world renewable natural elastomer produced mainly in South East Asia from the sap of rubber tree (*hevea brasiliensis*). However it only exported to manufacturing countries for production of various engineering and specialty rubber products. Blending of the natural rubber with synthetic rubber such as styrene butadiene rubber (SBR) is a mean to improve engineering specification of the NR, especially due to exposure of mineral oils during its service life. Whereas natural microbentonite functions not only as filler but also as coagulant breaker in both SIR-10 and SBR matrices, which improves miscibility of the blends.

In this work blending of Indonesian natural rubber (NR: SIR-10) with styrene butadiene rubber (SBR) were carried out in reflux reactor in xylene solution in the presence of various loading of natural microbentonite as fillers. Miscibility of the blends were measured from their mechanical properties as well as morphology of their fracture surfaces using electron microscopy (SEM). It was found that optimum loading of microbentonite in the NR/SBR (weight ratio: 50/50) blend was 3 per hundred rubber (phr), which showed good adhesion of the rubber matrices onto the filler surface and without any agglomeration.

1. Background

Blending natural rubber (NR) with styrene butadiene rubber (SBR) is intended to improve hardness and abrasion resistance of the NR, especially when the blend is being used as basic material for tyre. However compatibility of the blend is not sufficient without addition of other ingredients which is able to function as compatibiliser [1]. In industrial scale, blending of rubber blends is carried out using two-roll mill machine, in which the rubber matrices and all ingredients are in solid state at low temperature to inhibit any chemical interactions among the rubber matrices with the blending ingredients. Therefore, compatibility of the rubber blends can only be achieved by intensive deliberate blending procedures [2]. Mansila, et.al have compared compatibility properties of natural rubber/styrene butadiene rubber (NR/SBR) blends prepared using two-roll mill machine and by solution blending [3]. It was reported that in both cases there was no different on degree of entanglements of the rubber blends. However, further investigation on microstructure properties showed that the NR/SBR blends prepared using solution mixing showed more smooth fracture surfaces compared to those of prepared in two-roll mill machine [4].
In general, compatibility of polymer blends can be achieved not only by physical treatments, but also by physico-chemical modification using various additives: modifiers, coagents and fillers which functioned as compatibilisers. Wirjosentono et.al and Mahendra et.al have used miscible compounds containing polymer-reactive groups as modifiers and coagents, such as (meth)-acrylates, maleates and oleates, to achieve compatibility and miscibility of polymer blends and composites, [5-7]. Whereas a commercial cellulose microcrystal as filler has been utilized to improve compatibility of polystyrene composite, in which the cellulose particle surfaces might adsorb and functioned as solid phase breaker in the polymer matrices [8]. Wirjosentono et.al have also patented cyclic natural rubber (CNR)-based acrylate-grafted copolymers as adhesion promoter in the presence of cellulose nanocrystals for CNR-polypropylene surfaces [9]. Solid fillers, such as carbon black and clay not only function as reinforcements but also as compatibility improvers in rubber blends. Especially during solid blending of rubber compounds using two-roll mill, the presence of solid filler particles.

2. Experimental

2.1. Materials
Natural rubber (NR: SIR 10) was supplied from local rubber factory in North Sumatra, Indonesia. Styrene butadiene rubber (SBR, product no. Z106526), natural microbentonite product no. 285234, xylene reagent grade product no. 214736, were all ex. Sigma-Aldrich and were used directly without further treatment.

2.2. Preparations of NR/SBR blends
Natural rubber (NR: SIR 10) and styrene butadiene rubber (SBR), weight ratio: 50/50, were dissolved in xylene under stirring at room temperature (30°C), added with natural microbentonite, at various compositions. The mixtures were then refluxed in a reflux reactor under open nitrogen atmosphere for 3 hours. These were then dried in open air and under vacuum at 40°C, and compression moulded to tensile specimens according to ASTM D412-92.

2.3. Characterisations of NR/SBR blends
2.3.1. Mechanical testings. Tensile specimens of the rubber blends were tested according to ASTM D412-92, using Universal testing machine (Instron 3366) [10]. The testing parameters include: tensile speed 500 mm/minute and load cell of 10 kN, [11].

2.3.2. Morphology measurements. Morphology of gold coated fracture surface of the tensile specimens were then tested using Scanning electron microscopy (VPFESEM), model Zeiss Supra 35-VP, Carl Zeiss NTS GmbH, Oberkochen, Germany.

3. Results and Discussions

3.1. Mechanical properties
Table 1 showed mechanical properties of NR/SBR blends in the presence of various loading, (per hundred rubber: phr), of natural microbentonite (NMB), in which weight ratios of NR/SBR were maintained constant (50/50). It was clear that tensile strength of the blends were increased when loading of NMB were increased, (to 3 phr), which due to reinforcement effects of the NMB fillers, in which the NMB fillers were able to fill molecular gaps within the rubber blends. However, further increased of the NMB loading, (up to 7 phr), affected decreased of the tensile strength, because of agglomeration of the NMB fillers after saturated loading [12]. This phenomena will be further analysed in next discussion on morphology characteristics of the blends. Regarding their elongation at breaks, they constantly decreased as the NMB loading were increased. The presence of NMB fillers even at low loading (≤ 3 phr, before agglomeration of the filler taken place) also decreased flexibility of the blends. This was
because that the presence of phenyl groups in SBR and NMB filler inhibited molecular rotations and flexibility of the rubber matrices. However in this stage, the elongation decrease still could be overcome by increase of tensile strength, which hence their Young’s modulus also increase (0.023 – 0.041 MPa). Whereas when the NMB loading were increased upto 7 phr, decreased of the elongation at break were higher than those of tensile strength, which then decreased their Young’s modulus, (0.041 – 0.029 MPa). Therefore, optimum loading of NMB fillers was found, i.e. with maximum tensile strength, (24.25 MPa), and maximum Young’s modulus, (0.041 MPa), when the NMB loading was 3 phr.

Table 1. Mechanical properties (tensile strength and elongation at break) of NR/SBR (ratio: 50/50) blends in the presence of various loading (per hundred rubber: phr), of natural microbentonite fillers

| Blend’s sample       | Natural microbentonite (phr) | Tensile strength (MPa) | Elongation at break (%) | Young’s modulus (MPa) |
|----------------------|-----------------------------|------------------------|-------------------------|----------------------|
| NR/SBR               | 0                           | 14.65                  | 648                     | 0.023                |
| NR/SBR/NMB1          | 1                           | 18.86                  | 620                     | 0.030                |
| NR/SBR/NMB3          | 3                           | 24.45                  | 598                     | 0.041                |
| NR/SBR/NMB5          | 5                           | 20.34                  | 550                     | 0.037                |
| NR/SBR/NMB7          | 7                           | 15.20                  | 520                     | 0.029                |

3.2. Morphology measurements

Morphology measurements of the fracture surfaces of NMB-filled NR-SBR blends were carried out using scanning electron microscopy (SEM), and the results were shown in Figures 1a-1c.
Figure 1. SEM micrographs of fracture surface of NR-SBR blends containing various loading of natural microbentonite (NMB), (a) without NMB, (b) containing NMB 3 phr, (c) containing NMB 5 phr.

It was shown that, fracture surface of NR-SBR blend without NMB, Figure 1a, indicated fracture of the rubber blend only without the presence of NMB fillers. Interestingly, fracture surface of NR-SBR blend containing 3 phr of NMB filler, exhibited the presence of NMB fillers covered with rubber matrices, due to good adhesion between the rubber matrices on the NMB filler surfaces, which in turn improved mechanical properties (tensile strength and Young’s modulus). When the NMB loading were increased upto 7 phr the farcture surfaces, Figure 1c, showed bigger size of agglomerated NM fillers as well as pores due to pulled out of the agglomerated filler during tensile testing, due to low surface area and low adhesion with the rubber matrices [13].

4. Conclusions
Low loading of NMB fillers functioned as reinforcement but the higher loading exhibited agglomerations and lower adhesion in NR-SBR blends. Therefore, optimum loading of NMB fillers was found when the NMB loading was 3 phr.
Morphology measurements of fracture surfaces of the blends supported the optimum mechanical properties, which showed the presence of NMB fillers covered with rubber matrices when the NMB loading was optimum, and indicated agglomeration and pulled out pores of the fillers.

Acknowledgements
The authors would like to thank to Directorate of Research and Public Services, Ministry of Research and Technology/National Research and Innovation Agency of Republic of Indonesia, for supporting this works through scheme of Basic Research (PD-DRPM-Kemenristek/BRIN), year 2021 (contract number: 4860/UN5.1.R/PPM/2021).

References
[1] Ismail H, Shaari S M and Othman N 2011 Polymer Testing 30 784
[2] Mansilla M A, Marzocca A J, Macchi C and Somoza A 2015 European Polymer Journal 69 50
[3] Mansilla M A, Valentin J L, Lopez-Manchado M A, Gonzalez-Jimenez A 2016 Marzocca A J European Polymer Journal 81 365
[4] Mansilla M A, Marzocca A J, Macchi C and Somoza A 2017 Polymer Testing 63 150
[5] Wirjosentono B, Tamrin T, Mahendra I P, Nasution D A, Ismail H, Sukatik S and Mendez J A 2018 IOP Conf. Series: Journal of Physics: Conf. Series 1120
[6] Mahendra I P, Wirjosentono B, Tamrin T, Ismail H, Mendez J A and Causin V 2019 *Journal of Polymer Research* **26** 215

[7] Wirjosentono B, Tamrin T, Siregar A H, Nasution T I, Dalimunthe K Z and Nasution D A 2018 *IOP Conf. Series: Journal of Physics: Conf. Series* **1116**

[8] Wirjosentono B, Tamrin T, Siregar A H, Sukatik S and Nasution D A 2019 *IOP Conf. Series: Materials Science and Engineering IOP Conf. Series: Materials Science and Engineering* **578**

[9] Wirjosentono B, Tamrin T, Ismail H and Mahendra I P 2020 *Paten Indonesia*

[10] Jovanovic S, Samarzija-Jovanovic S, Markovic G, Jovanovic V, Adamovic T and Marinovic-Cincovic M 2016 *M Composite Part B* **98** 126

[11] Mohan T P, Kuriakose J and Kanny K 2011 *Journal of Industrial and Engineering Chemistry* **17** 264

[12] Bhadran B, Vijayan D, George N, Chandra C S J, Begum P M S and Joseph, R 2018 *Applied Clay Science* **165** 91

[13] Sadek E M, El-Nashar D E and Ahmed S M 2018 *Egyption Journl of Petroleum* **27** 1177