Mechanical, thermal and adhesion characteristics of natural rubber/epoxidised natural rubber (NR/ENR 25) blends containing natural microbentonite

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Abstract. Blending of natural rubber (NR) with epoxidised natural rubber (ENR 25) improved engineering characteristics of the blends, especially on their toughness, resistant to mineral oil, as well as their adhesion on hydrophilic surfaces, such as metals and concretes. Addition of natural microbentonite was expected not only to improve the blend’s compatibility, but also to enhance their thermal characteristics and adhesion properties on hydrophilic surfaces. In this works Indonesian natural rubbers (SIR-10) have been blended with epoxidised natural rubber (ENR-25) in a reflux rector in xylene solution with addition of various loading of natural microbentonite as fillers. Mechanical properties of the blends were characterized using tensile tests (tensile strength, elongation at break, and Young’s modulus), whereas their thermal properties were measured using differential scanning calorimetry (DSC). Furthermore, to estimate their adhesion properties on hydrophilic surfaces, the blends were immersed in water, and their water uptake were measured gravimetrically, as well as changes on their mechanical properties. It was found that optimum composition of natural microbentonite in the blend with highest tensile strength and Young’s modulus was obtained when loading of the filler was 4 phr. When compared to that without filler, DSC thermogram of the optimum blend showed better thermal properties (lower heat release decreased from 903.10 J/g to 420.17 J/g) although the decomposition temperatures did not change considerably (407.8° to 408.09°C). Whereas the later also exhibited higher water uptake (0.05 to 0.34 %) and still with acceptable mechanical properties as adhesive materials.

1. Background
As semisynthetic elastomer based on natural rubber, epoxidised natural rubbers were usually named as: ENR 10, ENR 25, and ENR 50, according to their degree of epoxidation: 10, 25, and 50 %, respectively. Due to their content of oxirene rings, the semisynthetic elastomer possesses higher polarity, hardness and tensile strength, but lower elongation at break, when compared to those of natural rubber. Here, Indonesian natural rubber SIR 10 (NR) has been blended with epoxidised natural rubber (ENR 25) and filled with natural microbentonite (NMB), not only to improve oil resistant of the NR-ENR 25 blends, but also their adhesion on polar surfaces, as well as their thermal stability, [1]. Addition of clay fillers in rubber blends has been reported to function, firstly as reinforcements, in which the filler particles were able to fill molecular bundle gaps and hence improve mechanical
properties of the rubber blends, [2]. Secondly, as thermal stabilizer, the clay fillers being possessed hydrous silicates structure, formed char that covered and protected the rubber matrices during heating and combustion, [3,4]. Especially as nanosize fillers, the clay fillers were more effective (even under 5 phr loading) as reinforcements although without good adhesion with the hydrophobic rubber matrices, [5]. When loading of the fillers became saturated, in which no more spaces to fill, the excess filler particles tended to agglomerise, forced by their polar-polar interactions to form bigger and low surface area particles and hence lowered surface adhesion with the rubber matrices, [6].

Improved adhesion of polymer matrices on surface of particles or substrates can be achieved by addition of coagents and modifiers, which were able to act as adhesion bridges by reducing surface energy differences between interphase with the rubber matrices, [7,8]. Characteristics of interphases between two surfaces were important to let good adhesion of both surfaces. Physically the interphase materials were able to diffuse into both front molecular layers of both interacting surfaces, [9]. And chemically the interphase materials, which were also called as adhesion promoters, possessed reactive groups that able to graft on one or both of the interacting molecular surfaces, [10]. Adhesion promoters based on cyclic natural rubber-grafted maleic coagents, filled with nanocellulose and blended with polypropylene have been patented by Wirjosentono et.al, [11]. In this works, Indonesian natural rubber of SIR 10 (NR) has been blended with epoxidised natural rubber (ENR 25) and filled with various loadings of natural microbentonite (NMB). The blending were carried out in reflux reactor in xylene solution as have been reported by previous researchers, [12,13]. Another section of your paper.

2. Experimental

2.1. Materials
Natural rubber: Standard Indonesian Rubber grade-10 (NR: SIR-10) was supplied by a rubber company in Sumatera Utara, Indonesia. Epoxidised natural rubber: degree of epoxidation 25% (ENR 25), xylene, natural microbentonite (particle size < 15 μm) were all ex. Sigma-Aldrich Chemicals and were used directly without further purification.

2.2. Preparations of NR-ENR blends containing natural microbentonite
NR and ENR 25 (constant weight ratio: 50/50) were dissolved in xylene homogenously at 30°C under intensive stirring with additions of various loadings of natural nanobentonite (NMB). The solution mixtures were then refluxed in a reactor for 30 minutes, casted on a glass plates, dried in open air at 30°C and under vacuum at 40°C to constant weight, [12,13].

2.3. Characteristics of NR/ENR blends

2.3.1. Mechanical properties. The casted and dried plates of rubber blends were dumle cut to tensile specimens according to ASTM D412-92; The tensile tests were carried out using Universal Testing Machine, Instron 3366, at a crosshead speed of 500 mm/min with 10 kN load, for tensile strength, elongation and Young’s modulus measurements.

2.3.2. Thermal analysis. Thermal analysis of the rubber blend samples were carried out using differential scanning calorimeter technique (DSC Mettler-Toledo), heating range 30o – 500oC and heating rate 10oC/min.

2.3.3. Water uptake tests. Tensile specimens of rubber blends were immersed in distilled water for upto 30 days and then their mechanical properties (tensile strength, elongation at break, and Young’s modulus) were tested.
3. Results and discussions

3.1. Mechanical properties

Results of mechanical properties of NR-ENR 25 (ratio: 50/50) blends in the presence of various loading of natural microbentonite fillers were shown in Table 1.

Table 1. Mechanical properties of NR-ENR 25 (ratio: 50/50) blends in the presence of various loading of natural microbentonite fillers

| Blend’s sample | Microbentonite (phr) | Tensile strength (MPa) | Elongation at break (%) | Young’s modulus (MPa) |
|----------------|-----------------------|------------------------|-------------------------|-----------------------|
| NR-ENR 25      | 0                     | 19.05                  | 548                     | 0.035                 |
| NR-ENR 25-NMB2 | 2                     | 23.36                  | 560                     | 0.042                 |
| NR-ENR 25-NMB4 | 4                     | 26.32                  | 579                     | 0.045                 |
| NR-ENR 25-NMB6 | 6                     | 24.33                  | 570                     | 0.042                 |
| NR-ENR 25-NMB8 | 8                     | 22.30                  | 550                     | 0.040                 |

The results exhibited that tensile strength of the rubber blends were increased (19.05 -26.32 MPa) when the NMB loading were increased upto 4 phr, however further increase on the NMB loading (upto 8 phr) affected decrease back on tensile strength (26.32 – 22.30 MPa). These were due to that at low loading, the NMB fillers were able to fill molecular bundle gaps and functioned as reinforcements in the NR-ENR 25 blends, [1]. Whereas further increase on the NMB loading, the filler particles became saturated and the excess agglomerated due to their high polar-polar adhesion and formed bigger size particles, which possesses lower surface area as well as lower adhesion with the rubber matrices. These phenomena also caused increased of elongations at break (548 – 579 %) and Young’s modulus (0.035 – 0.045 MPa) when the NMB loading were increased to 4 phr. And also the decrease of elongations at break (579 – 550 %), and Young’s modulus (0.045 – 0.040 MPa) when the NMB loadings were decrease to 8 phr.

3.2. Thermal properties

Results of investigation of thermal properties of (NR-ENR 25) blends were shown in Figure 1 and those of NR-enr 25 blend containing 4 phr of NMB filler were in Figure 2, whereas Table 2 summarized the thermal data in both Figures 1 and 2. Both DSC thermograms of Figures 1 and 2 exhibited 2 peaks, consisted of endothermic and exothermic processes.

![Figure 1. Results of DSC analysis of NR-ENR 25 blend without NMB filler (NR-ENR 25)](image-url)
The endothermic peaks of both in Figures 1 and 2 did not show any significant differences on their peak temperatures (159.00°C and 159.30°C) and on their heat consumed (-72.25 and -70.06 J/g). Both endothermic peaks indicated similar evaporation processes of volatile products in the NR-ENR 25 blends without effect of NMB loading (4 phr). The exothermic peaks in both Figures 1 and 2 also did not show any significant temperature differences (407.81°C and 408.09°C). However, exothermic peak in Figure 1 (that of NR-ENR 25 blend without NMB filler, heat release 903.10 J/g) exhibited higher heat release when compared to that of in Figure 2 (that of NR-ENR 25 blend containing 4 phr NMB fillers, heat release 420.17 J/g). These evidences revealed that the presence of NMB fillers (4 phr) functioned as thermal stabilizer for NR-ENR 25 blend, due to hydrous silicates contents in the NMB fillers, which able to form char during decomposition of the rubber blends, [5,6].

3.3. Water uptake behaviours
Data of water uptake in Table 2 showed that the presence of NMB filler (4 phr) increased water uptake of NR-ENR 25 blends (0.05 – 0.34 % after 30 days immersion in distilled water. This due to that the NMB fillers absorbed more water in the rubber blends through their hydrous silicates structures. Consequently, due to absorption of water, before and after water uptakes, tensile strengths as well as elongation at breaks of both (NR-ENR 25) and (NR-ENR 25-NMB4) were slightly decreased, (tensile strength: 19.05 – 17.08 and 26.32 – 23.54, respectively, and elongation at breaks: 548 – 490 % and 579 – 515 %, respectively). Interestingly, the water uptake treatment did not considerable change Young’s modulus of the rubber blends, (0.035 – 0.035 MPa, and 0.045 – 0.046 MPa, respectively).
Table 3. Water absorption and mechanical properties of NR/ENR 25 (ratio: 50/50) blends before and after water uptake for 30 days

| Blend’s sample | Water uptake (%) before | Tensile strength (MPa) after | Elongation at break (%) before | Young’s modulus (MPa) after |
|---------------|------------------------|----------------------------|-------------------------------|---------------------------|
| NR-ENR 25     | 0.05                   | 19.05                      | 17.08                         | 548                       | 490                       | 0.035                   | 0.035                    |
| NR-ENR 25-NMB4| 0.34                   | 26.32                      | 23.54                         | 579                       | 515                       | 0.045                   | 0.046                    |

4. Conclusions
Increase of NMB loading (upto 4 phr) affected increases however further increase (upto 8 phr) affected decrease of mechanical properties (tensile strength, elongation at breaks, and Young’s modulus) of NR-ENR 25 blends. The presence of NMB fillers (4 phr) functioned as thermal stabilizer for NR-ENR 25 blend, due to hydrous silicates contents in the NMB fillers. Consequently, due to absorption of water, tensile strengths as well as elongation at breaks of both (NR-ENR 25) and (NR-ENR 25-NMB4) were slightly decreased, but did not considerable change their Young’s modulus. Therefore the later can be further studied as rubber blend compounds using standard fillers and vulcanizing systems and utilized as adhesives on hydrophilic (metal, concrete, and woods) surfaces.

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