Failure Mode of Epoxidised Natural Rubber - Microalumina Particle Composite (ENRAM) Using Electron Microscopy

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Abstract. ENRAM at 50% ENR epoxidation at 5phr microalumina was evaluated for failure morphology in the tensile mode (tensile strength of) 19.9MPa at magnifications of 25x-3300x. The sample morphology before fracture showed uA particles with jagged edges due to agglomeration of finer particles. The mean particle size measured was 45μm. After fracture, the features observed on the fracture surfaces were i. ENR matrix ii. microalumina dispersed on the surfaces after being dislodged and iii. voids in the matrix. There was no matrix breakage observed, but predominantly pull-out of the microalumina agglomerated flakes leaving voids of 30μm-100μm. These values commiserated with the particle size range of the starting alumina particles. The voids showed an unusual surface with villi-like protrusions. The ENRAM particle pull-out failure can be explained by the failure model theory put forward by [1], where particle pull-out happened when the villi-microalumina agglomerated flakes adhesion was overcome. We would expect this mechanism to predominate as the particle sizes are greater than 10 μm, the critical size for pull-out to happen.

1. Introduction

Natural rubber is derived mainly from Hevea brasiliensis, a type of plant originated from the Amazonian Basin. On its own, rubber has high tensile strength. However, natural rubber tends to degrade when exposed to elevated temperature, ozone, and oxygen, due to its unsaturated nature as a polymer [2]. To improve natural rubber, epoxidation was conducted on NR to make it more resistant to ageing. As a result of the presence of epoxy ring in the NR molecular structure, epoxidised natural rubber (ENR) has excellent damping characteristic in increasing order of epoxidation [3].

Particulate alumina used as filler in rubber is nothing new. Addition of particle ranging from micro to nano size have been proven to improve mechanical property of polymer [4,5], [1,6–10] used ENR together with alumina nanoparticle. Meanwhile in [11,12] NR was used with micro sized alumina particle. Another combination is nanoalumina with NR as exampled in [13], [14] used alumina with NR with ENR as the compatibiliser. Various studies [15,16] have shown that smaller filler particle size resulted in composite with better mechanical properties. However, since nano sized alumina particle is significantly more expensive than its micro sized counterpart, the use of alumina microparticle as the filler will result in a material that will cost less to produce. Consequently, the cost of the total system will be driven down. Therefore, the effect of using a micro-sized alumina filler with ENR as its matrix on the characteristic of the tensile fracture surface of said composite (ENRAM) is the focus of this study as there is not enough body of work that can explain the fracture behaviour of this particular composite.
2. Experimental study

2.1 Materials

Table 1 shows the ingredients of the material used in this study. The epoxidised natural rubber (ENR) was supplied by Felda Rubber Industries Sdn Bhd. The ENR was bought under the trade name EKOPRENA 50 with mean epoxidation level of 49.5%. The Mooney viscosity measured at ML (1+4 @100°C) was 90. Alumina microparticle was obtained from Finetech Chemical Sdn. Bhd.

Table 1. Formulation of samples

| Ingredients   | LOADINGS (phr)a |
|---------------|-----------------|
| ENR 50        | 100             |
| Sulphur       | 1.6             |
| Zinc oxide    | 2.0             |
| Stearic acid  | 1.5             |
| CBSb          | 1.9             |
| TMTDc         | 0.9             |
| 6PDDd         | 2.0             |
| Alumina       | 5               |

Note:
aParts per hundred rubber, bN-cyclohexylbenthiazyl sulphenamide cTetramethyldiuram disulphide, dN-(1,3-Dimethylbutyl)-N’-phenyl-p-phenylenediamine

2.2 ENRAM composite preparation

The ingredients were compounded together in an external mixer according to ASTM D-3192 at 90°C and a rotor speed of 60rpm for 6 min. All the ingredients were mixed for 4 minutes except for sulphur after the ENR was masticated for 1 minute. At about 1 minute before the mixture was dumped and cooled down to room temperature, sulphur was added. To cure the stock, a semi efficient vulcanization (EV) system was used. The material was pressed in a hot press at 150°C for about 3 minutes in a 300 mm x 300 mm x 1 mm mould.

2.3 Tensile testing

A sheet of the material was taken as a sample for tensile testing. 5 dumbbell shaped samples were taken along one of the sides of the sheet. Another 5 samples were taken from another side perpendicular to the first side. The tensile testing was run per ISO 37 standards at the Science & Technology Research Institute for Defence in Kajang on Hounsfield Testing Machine; model H25KS/06 with QMat 5.16 software. The nominal rate of traverse is 200 mm/min. The gauge length was determined to be 20 mm as indicated in the standard.

2.4 Scanning electron microscopy

Scanning electron microscope was used to view the characteristic of the raw material and to view the fracture surface of the composites. Two fracture surfaces from each direction of the sample which had undergone tensile testing were put under the microscope. The microscope used was JEOL JSM-7001F, a thermal Field Emission Scanning Electron Microscope (FESEM). The samples were coated with a thin layer (25 nm) of platinum-gold. The sample was scanned using EDS mapping technic to determine the location of different elements to help determine the location of the alumina microparticles and other substances.
3. Results and discussion

3.1 Tensile test

Tensile testing of the samples showed that the average value of tensile strength for the composite is 18.43 MPa in the first test direction and 21.36 MPa in the second one. The total average of the tensile strength of the composite is 19.9 MPa. This value is slightly higher than that reported in [8], which form the basis of this research. In the research, nano sized alumina was used as the filler. However, further study needs to be done before any conclusion can be made regarding effect of filler size on tensile strength of ENR – alumina composites.

3.2 Al₂O₃ microparticle FESEM microscopy

On 100x magnification, the alumina microparticle demonstrated wide polydispersity with diameters ranging from around 50 to 150 μm of nearly spherical individuals (Figure 1a). Upon closer inspection at 650x magnification, each particle was found to be an agglomerate of much smaller alumina particle (Figure 1b). The shape of the alumina particle was thin pieces instead of spherical. Two main shapes of particle were found out, rectangular (Figure 1c) and circular (Figure 1d) flake where diameter ranges from 4 to 6 μm with thickness around 0.3 μm.

![Figure 1](image)

Figure 1. a) Magnification: 100x. b) Magnification: 650x. c) Magnification: 7500x. d) Magnification: 15000x.

3.3 ENRAM FESEM microscopy

For the study of fracture surface of the composites after tensile testing, random selection of fracture surface was then prepared as explained in the experimental method. Upon inspection at 200x magnification, the fracture surface exhibit areas of rough surface of the ENR-50 matrix (Figure 2a). Alumina filler can also be seen dispersed on the fracture surface. Based on the previous study in [8] it is found out that the rough surfaces were indicator of shear yielding.

As mentioned before, apart from rough surface, holes were another feature of the fracture surface similar to phenomenon observed in [6]. The micrograph in Figure 2a shows the matrix, ENR-50, with holes with varied sizes from around 30 to 100 μm. Upon closer inspection at 900x magnification, villus-like features can be seen on the surface inside the hole (Figure 2b). These villi are made of the ENR-50 matrix. A further inspection on the previous site at 2300x magnification reveals that some alumina particle was removed from the main agglomerate and sticks to the matrix (Figure 2c).

From the micrograph, it can be concluded that these villi were mere remnants of the interface between the matrix and alumina. The interface failed during tensile loading that resulted in particle pull out. This means that the ENR-50 matrix fully enveloped and wetted the alumina particle upon curing. These are strengthened by the fact that these features exhibit large surface area instead of a simple smooth surface.
Another interesting feature on the fracture surface can be seen in Figure 3a and 3b at 1200x and 3300x magnification respectively. The ENR-50 matrix can be seen in the background with alumina agglomerate sticking out of the matrix. The alumina agglomerate appears to be inside a void in the matrix. The size of the agglomerate is measured at about 30µm. It can be seen clearly that some matrix still bonds to the particle agglomerate. As such, the conclusion is that the agglomerate was pulled out from the other side of the ENR-50 matrix during tensile loading. The presence of ENR-50 residue further confirms that the alumina agglomerates were properly wetted during mixing and curing process. Apart from that we can see clearly from the formed void around the agglomerate that it is almost dislodged from the matrix because of debonding during the application of uniaxial force. This phenomenon of debonding and crack progression was studied by [17] by observing ongoing tensile loading of polymer composite under microscope. The model of debonding and crack progression for this study will be presented in the next part of the paper based on another study by [18] on failure of particulate polymer.

Figure 4a shows an alumina agglomerate protruding out of the ENR matrix at 750x magnification. However, unlike Figure 3, the size of the particle is much bigger (70 µm), so there is little matrix residue seen left on the outermost surface of the agglomerate. Upon closer inspection, a crack line can be seen across the agglomerate vertically. This is also another example of particle pullout but at a larger scale than observed on Figure 3.

In Figure 4b, a larger agglomerate of filler around 100 µm can be seen at 500x magnification embedded in the ENR matrix. The agglomerate appears to be flat and does not protrude out from the matrix. The agglomerate surface also appears to be on the same plane as the fracture surface of the matrix. However, there is still ENR-50 matrix residue left on the surface of the agglomerate. It can be proposed that this phenomenon happens because the agglomerate have a flat surface and the debonding happened at said surface.

From observed fractographs, particle pullout and void were the dominant mechanism of failure found in this study. This may be explained by the size of the particle agglomerate (30 µm – 100 µm) which is greater than the 10 µm critical limit for particle pullout to happen in this type of composites as discovered in [1].
3.4 Failure modes of particulate composite

From the SEM micrograph of the fracture surface of the material, two main modes of failure can be found out, which are the yielding of the ENR matrix and the pulling out of the alumina microparticle agglomerate. All the mechanism that leads to failure can be visualised in Figure 5. When no force is acting on the composites, the particle agglomerate is embedded within the matrix as shown in Figure 5a. Once uniaxial tension is applied, when the composites is approaching failure, voids begin to develop. If a void happens to occur on a site where particle agglomerate is present, the whole particle agglomerate may still stay whole and attached to only one side of the void as shown in figure 5b. Upon failure, the situation will develop into complete pull-out of the particle agglomerate from the matrix. Figure 5c shows the example from the specimen that corresponds to a specific type of failure modes. The propagation of crack seems to agree with the visual representation of void formation in [8,18] and similar to how microdamage evolve in [19], with the different being that the model in that study was intended for a solid particle instead of agglomerates in this study and the previous two.

![Figure 5](image)

Figure 5. Fracture surface model of failure during the progression of crack. a) Alumina agglomerate as filler in ENR-50 matrix. b) Tensile loading along the horizontal axis. c) Features of the fracture surface. Adapted from [18]

4. Conclusion

Failure mechanism of ENR – alumina micro particle was studied by subjecting it to tensile failure. Then, the fracture surface was studied using FESEM. Among the features observed on the fracture surface were the ENR matrix, voids and pulled out particles. Crack propagating on the interfacial boundary of matrix and filler will result in particle pullout and voids due to adhesion force between the agglomerate and the matrix being overcame by the tensile force. The size of the void ranges from 30 to 100 µm, which match the observed size of the raw and pulled out microalumina particle agglomerates. It was also observed that the particle agglomerates were properly wetted by the matrix, suggested by matrix residue on pulled out particle agglomerate and the villi inside the void left by it. This type of failure mechanism predominates due to the critical diameter for the agglomerate (10µm) have been surpassed for agglomerate pull out to happen.
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