

The Effect of Filler on Epoxidised Natural Rubber-Alumina Nanoparticles Composites

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Abstract

Epoxidised natural rubber (ENR)-alumina nanoparticles composites (ENRAN) were produced by melt compounding followed by sulphur curing. Alumina nanoparticles were introduced in 10, 20, 30, 40, 50 and 60 parts per hundred rubber (phr) in the compounding recipes to study the effect of filler loading to the cure characteristics and mechanical properties. The dispersion of the alumina nanoparticles was studied using scanning electron microscopy (SEM). The increase in alumina nanoparticles loading in ENR matrices were found to accelerate the curing process up to 40% compared to unfilled ENRs. The minimum torque (ML), maximum torque (MH) and torque difference (MH-ML) also increased due to the increasing crosslink density with the presence of alumina nanoparticles. The increase in alumina nanoparticles content in the ENR compound resulted in the decrease of the tensile strength, elongation at break (EB) and the impact strength but increase the hardness and tensile modulus compared to unfilled ENRs. The alumina particles were observed to be uniformly distributed in the matrices which contributed to the enhancement of MH, ML, tensile modulus and hardness of the ENRANs. When present in the matrix, the particles formed spheres of agglomerates thereby able to effect high filler-matrix interaction which also contribute to the increase in torque values.

Keywords: Epoxidised Natural Rubber, Alumina Nanoparticles, Cure, Mechanical, Fracture

1. Introduction

Much research has been carried out in the development of nano-filled composites through the incorporation of nano-scaled materials such as ceramics and carbon in polymer matrices. For instance organoclays [1], carbon nanotubes [2], alumina nanoparticles [3] and silica nanoparticles [4] have been added to polymers. Polymer nanocomposites exhibit unique properties even by the addition of low weight percent nanofillers (<5 wt%), that cannot be obtained from conventional or micro-scale fillers [5]. The incorporation of nanofillers enhances mechanical, electrical, optical and other properties of polymer composites without sacrificing too much of the good properties such as the toughness being traded for the stiffness as such found in the rubber filled carbon fibres [6]. Several polymers have been used for preparing polymer nanocomposites such as elastomers (natural rubber (NR), epoxidised natural rubber (ENR), styrene-butadiene rubber (SBR), chloroprene rubber (CR), ethylene propylene diene monomer rubber (EPDM) etc.), thermoplastics (nylon 6, 6, polypropylene (PP), polyethylene terephthalate (PET), polymethylmetacrylate (PMMA), polycarbonate etc.), and polymer blends.

The development of polymer-ceramic nanocomposites has created a number of technologies and opportunities that can be applied to ENR. In a previous research by Teh et al.[1], ENR was used as a compatibiliser in producing natural rubber-organoclays nanocomposites. Organoclays can be more easily dispersed in polar polymers compared to non-polar polymers such as NR [1]. ENR is miscible with more polar polymers [7] thereby offering unique properties such as good oil resistance, low gas permeability, higher wet grip, rolling resistance, and a high strength. The oil resistance of ENR 50 vulcanisate was reported to approach the characteristics of medium-acrylonitrile-content nitrile rubber and also surpasses that of CR [7]. The resistance to air permeability of ENR 50 has also been claimed to be comparable to butyl rubber and medium-acrylonitrile-content nitrile rubber [7]. Alumina has been recognised as a structural material with an extremely high melting point (2050 °C), high hardness, and capable to take on diverse shapes and functions [8]. The incorporation of nano-scaled alumina in PP has improved the mechanical properties of the polymer composites [9] and increased the wear resistance of PET filled alumina nanoparticles by nearly 2× over the unfilled polymer [10].

The ENR-alumina nanoparticles composites can be prepared using procedures as those used for NR. Rubber nanocomposites with an exfoliated morphology have been successfully prepared by several methods such as in situ polymerisation, solution blending, and direct melt compounding [11]. The solution method is widely used to prepare nanocomposites, which can be applied to ENR but this method is very inconvenient due to the use of organic solvents [12]. Hence, the melt compounding method using the internal mixer has been used to synthesise ENR-alumina nanoparticles composites.

2. Experimental

2.1. Materials

Table 1 shows the formulation used in this study. In these recipes, the contents of alumina nanoparticles were varied as 10, 20, 30, 40, 50 and 60 phr whereas rubber and other ingredients were kept constant. Epoxidised natural rubber was supplied by Malaysian Rubber Board under the trade name ENR 50 with 53% epoxidisation. The Mooney viscosities measured at ML (1 + 4) 100 °C was 85.5. Alumina nanoparticles were obtained from Nanostructured & Amorphous Materials Inc., USA with diameters ranging from 30-80 nm. Sulphur, zinc oxide, and stearic acid were purchased from System/Classic Chemicals Sdn Bhd, Tetramethylthiuram disulfide (TMTD) from Aldrich Chemistry and other chemicals such as N-cyclohexylbenthiazolyl sulphenamide (CBS) and N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) were supplied by Flexsys America, USA.

Table 1: Rubber compounding recipe.

Ingredients	Loadings (phr) ^a
ENR 50	100
Sulphur	1.6
Zinc oxide	2.0
Stearic acid	1.5
CBS ^b	1.9
TMTD ^c	0.9
6PPD ^d	2.0
Alumina	10, 20, 30, 40, 50, 60

^a Parts per hundred rubber^b N-cyclohexylbenthiazolyl sulphenamide^c Tetramethylthiuram disulfide^d N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine

2.2. Mixing & Cure Characteristic

The compounding process was performed according to ASTM D-3192 and carried out using a Haake internal mixer working at 90°C and a rotor speed of 60 rpm for 6 min. Firstly, ENR was masticated for 1 min before all ingredients were added except sulphur and mixed for another 4 min. Finally, sulphur was added and mixed for about 1 min before the mixture was dumped onto two roll mill.

From this stock, unvulcanised samples were cut to allow testing of curing characteristics in accordance to the Test Method ASTM D-2084 using Monsanto ODR 2000 Moving Die Rheometer (Alpha Technologies, Swindon, UK) at 150°C. Sheets with approximately 1mm and 3mm thickness were vulcanised using a semi efficient vulcanisation (EV) system in a hot press at 150°C at the respective cure times, t_{90} which derived from rheometer tests.

2.3. Mechanical Properties

Tensile properties of vulcanised samples were carried out according to BS 6746 using an Instron 4301 Universal Testing Machine at room temperature. It was performed at a cross-head speed of 500mm/min.

The test for hardness was carried out using the Shore type A Zwick/Roell Durometer according to ASTM D2240.

Samples prepared according to ASTM D 256 were tested for impact strength for unnotched Izod pendulum impact resistance using a CEAST impact tester. They were dipped into liquid nitrogen for 1 min before the samples were clamped to the machine and stroked by a pendulum at an energy level of 4 J. All tests were conducted at room temperature (25°C).

2.4. Swell Measurements

Cured test pieces of dimension 30 x 20 x 1 mm were swollen in toluene (solvent) for 24 hours at room temperature. Q (the weight of toluene absorbed per gram of rubber hydrocarbon) was determined according to the following expression [7]:

$$Q = \frac{W_s - W_{ds}}{W_d \times \frac{100}{W_t}} \quad (1)$$

where W_s is the swollen weight, W_{ds} is the deswollen weight, W_d is the dry weight and W_t is the formula weight.

2.5. Scanning Electron Microscopy (SEM)

The examination of the tensile fracture surfaces were carried out using a scanning electron microscope Model EVO 50 from ZEISS at magnifications of 500x and 5000x. For every samples, when taking

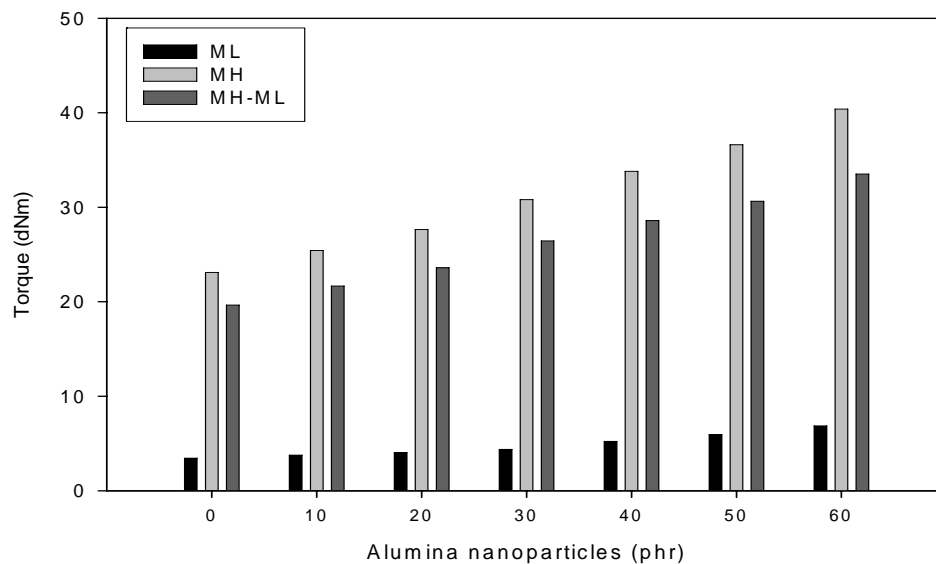
micrographs a minimum of three frames at each magnifications were taken to ensure a high confidence level in the analysis. The objectives were to get ideas on the fracture mode and to investigate the filler dispersion and particles shape, qualitatively. The fractographs were captured under variable pressure using secondary electron operated at 20 kV.

3. Results and Discussion

3.1. Curing Characteristics

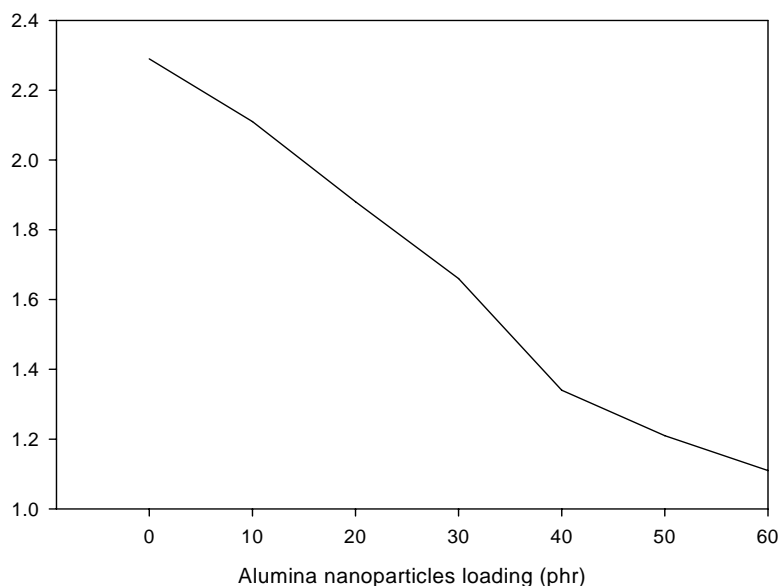
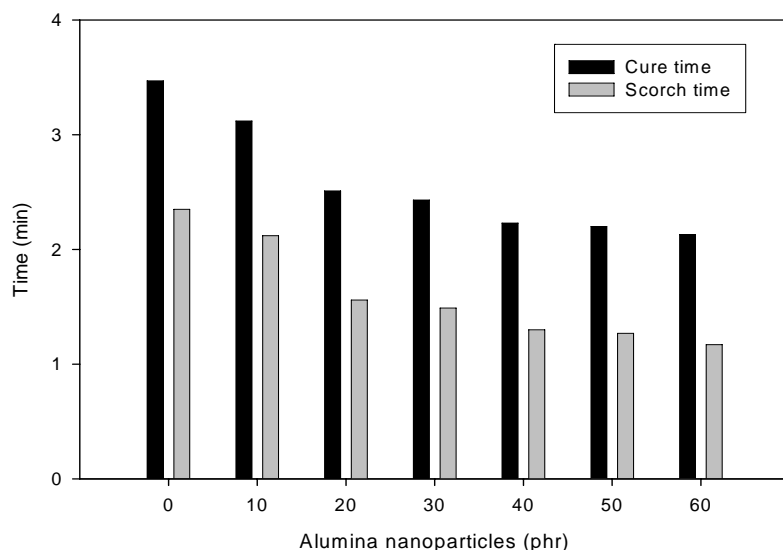
Figure 1, Figure 2 and Figure 3 depict the cure characteristics of ENRANs. It can be deduced from Figure 1 that the incorporation of alumina nanoparticles has increased the MH and ML as well as MH-ML in composites. The increment of torque values has suggested that there are good interactions between ENR and filler surfaces [11]. This can be most attributed by high compatibility between alumina nanoparticles and ENR matrix which results in some reinforcements in the composites [13].

Figure 1: Torque maximum (MH), torque minimum (ML) and torque difference (MH-ML) for different alumina nanoparticles loading (phr) in ENR matrix.



The MH can be regarded as a measure of the composites modulus [1]. The significantly increased values in MH (refer to Figure 1) with filler loading are indirect hint for improved interaction behaviour and good interfacial adhesion between matrix and filler. This claim is in line with Ciprari [14] which mentioned that for strongly binding polymers to filler surfaces there will be an area of high density and thus, high modulus forms next to the surface. Thus if all areas of the filler surfaces are capable of adsorption (high interaction), the segments of polymer chains will be absorbed on the surfaces and form a flat (dense) layer close to the filler surfaces. This area will have combination properties of fillers (high modulus) and matrix [14].

The ML is related to the viscosity of nanocomposites [1]. The incorporation of alumina nanoparticles moderately increased the ML and thus viscosity of the ENRANs compounds (Figure 1).

Figure 2: The weight of absorbed toluene per gram of rubber, Q for different phr of alumina loading.**Figure 3:** The scorch time and cure time for different alumina nanoparticles loading of ENR/alumina nanoparticles composites.

The addition of fillers of a smaller size tends to impose extra resistance to flow due to higher restriction to molecular motion of the macromolecules; hence higher viscosity [16].

The MH-ML shows a similar trend with maximum torque. The MH-ML is a measure of the dynamic shear modulus, which indirectly relates to the crosslink density of the nanocomposites [7, 17]. The increment of MH-ML values may suggest that alumina nanoparticles also act as crosslinking agent in the matrices. It was proved by swelling measurement through an expression in Eq. (1). Figure 2 shows the relationship between the weights of toluene uptake per gram of rubber, Q against filler loading. It can be seen that the Q value decreased with increasing amount of alumina nanoparticles in composites. It can be reasonably assumed that the increasing of crosslink which resembles a three dimensional network in the composites have lessened the capability of the composites to absorb toluene since there are less open chains in the composites for the toluene to penetrate. This supports the argument that alumina nanoparticles have help for better crosslinking.

The presence of alumina nanoparticles has accelerate curing process with a significant decrease in scorch, t_2 and cure time, t_{90} (refer Figure 3). This may due to the effect of filler's surface area whereby, the smaller the particle sizes, the larger the surface area available for reaction; hence, greater interaction between matrix and the filler particles. This claim is in agreement with Ishak & Bakar [16] which reported that fillers play an important role in accelerating vulcanisation process.

3.2. Mechanical Properties

Table 2 summarises the tensile properties, hardness and impact strength of ENR filled and unfilled alumina nanoparticles. Tensile strength and EB decreases as the alumina loading increases. This result shows different trend if compared to previous research by Arroyo et al. [11]; since this present work involves with high filler loading. In a research of low filler loading conducted by Ash et al. [18]; incorporation of 5% wt alumina nanoparticles into a polymethylmethacrylate (PMMA) matrix has increased the average value of strain-to-failure up to 600%. Normally (in the case of conventional composites) tensile strength will increase with increasing filler loading until maximum point is reached; whereby the filler particles are no longer adequately separated or wetted by rubber phase [16].

In present work, reduction in tensile strength may occur due to the agglomeration of filler particles or simply the result of physical contact between adjacent agglomerates [16]. The agglomerate is a domain that can act like a foreign body in composites. Since there was a high amount of agglomerates in higher filler loading composites, these agglomerates (refer to Figure 5) act as obstacles to chains movement and initiate failure under stress. This explain why EB (refer to Table 2) showed the same trend with tensile strength; which decreases with increasing amount of filler loading. Agglomerates will become stress concentrator and building up stresses in composites quicker than usual and caused earlier rupture if compared to unfilled samples. However, a different explanation was given by Ismail & Chia [7] who claimed that poor tensile strength may be attributed to the geometry of fillers. Strength of the composites with irregularly shaped fillers decreased due to the inability of the fillers to support stresses transferred from the polymer matrices [17]. Since, the alumina nanoparticles had form sphere-like agglomerates (refer to Figure 4) in ENR matrices, this claim cannot be apply as a cause of decreasing tensile strength in present study.

However, a loading of less than 10 phr of alumina nanoparticles in ENR matrices might generate the same result as achieved by other researchers [11, 15]; which tensile strength increases with increasing filler loading.

The modulus at 100% and 300% elongation increases with increasing filler loading if compared to the tensile strength and EB. The increase of tensile modulus may be attributed to the higher crosslink density and good distribution of fillers in ENR matrices. These results are in agreement with cure characteristics obtained (refer to Figure 1). The presence of polar group in ENRs (epoxide groups) may contribute to electrostatic adsorption between ENR particles and alumina nanoparticles. This phenomenon is driven by different charges acting on matrix or fillers surfaces; which depend on filler's type, pH value or inter-medium [15]. This mechanism will strengthen the polymer-ceramic interface. It will hold them together and increase their resistance to deformation. This helps in increment of the composites modulus. The uniformity of fillers distribution has efficiently hinders the chains movement during deformation. This mechanism will increase the stiffness of the composites as well as tensile modulus [19].

Table 2: Mechanical properties of ENR filled various loading of alumina nanoparticles.

Properties	Alumina Nanoparticles (phr)						
	0	10	20	30	40	50	60
Tensile strength (MPa)	20.93	17.35	17.16	16.45	16.36	15.71	14.80
Tensile modulus (MPa)							
100% Elongation	0.63	0.74	0.75	0.97	0.99	1.15	1.34
300% Elongation	2.68	2.94	3.70	4.16	4.26	4.96	5.44
Elongation at break, EB (%)	625	557	540	540	525	521	495
Hardness (Shore A)	11.7	12.5	13.63	14.43	15.73	17.13	18.93
Impact Strength (J/m)	239.75	215.55	175.24	172.39	168.74	168.48	153.95

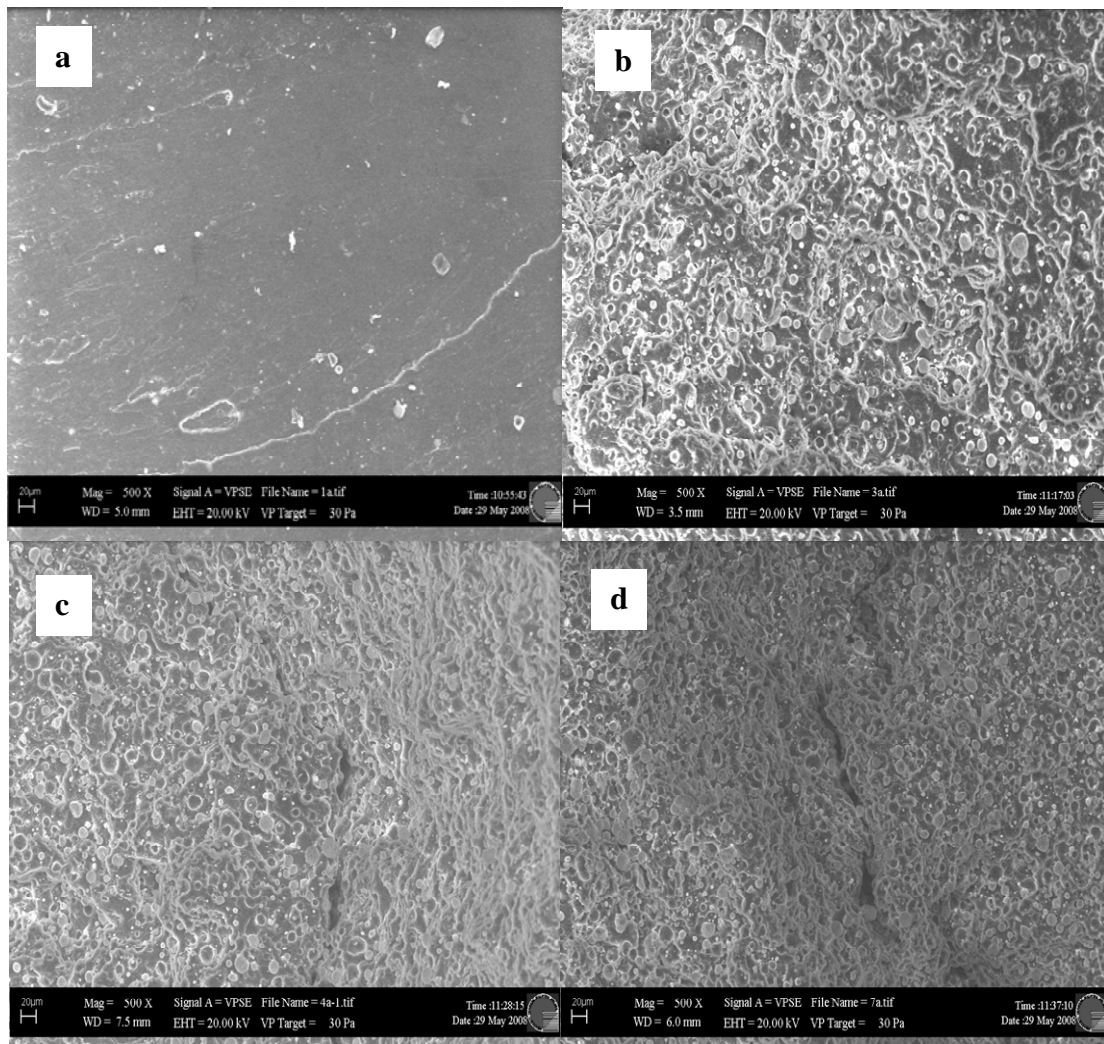
The tensile properties are in agreement with the results obtained from the analysis of the hardness and impact strength. The increase in hardness is related with high tensile modulus and the increasing amount of hard alumina nanoparticles in the ENR matrices. On the other hand, as can be suggested from the impact test, the elastic behavior of the matrix proportionately varies with the addition of the alumina nanoparticles. As the loading of alumina fillers increases, the ability of the composites to absorb impact energy decreases since there are less ratio of the rubber matrix to fillers. This result in decreasing impact strength which explained the capability of the composites to withstand energy before fracture.

3.3. Morphology of Fracture Surfaces and Filler Dispersion

Figure 4 and Figure 5 display SEM micrographs taken from the tensile fracture surfaces for unfilled and filled ENR at magnification of 500x and 5000x, respectively. The dark phase represents the ENR matrix and the bright phase corresponds to the alumina particles. Fractographs in Figure 4 show alumina nanoparticles have uniformly distributed in the composites but poorly dispersed. There are fillers that form clusters (agglomerates) or aggregates (further examination under transmission electron microscope (TEM) in future study) with size larger or smaller than original size of starting alumina nanoparticles (30-80nm) presence in the composites.

Considering the tensile mechanical data in Table 2 and having a look at the fracture surfaces in Figure 4, it seems that the rougher the fracture surface is the better the mechanical properties of the related composite [1]. Most of the fracture surfaces show spherical shaped dimples from pull out alumina fillers except for fractograph of unfilled ENR (refer to Figure 4 (a) and Figure 5 (a)). Fractograph of unfilled ENR (refer Figure 5 (a)) shows characteristic of ductile fracture under uniaxial tensile loads. When less than 20 phr alumina is added to ENR matrix the surface roughness increases with the increasing alumina loading. There is no obvious phase separation observed, implying good miscibility between ENR and alumina at this point. This is an indicator of better alumina-ENR adhesion. Fractograph in Figure 5 (b) for 10 phr filler loading shows similar contrast which represents a good adhesion between filler and matrix. It proves that dispersed alumina nanoparticles in low filler loading were fully encapsulated in the matrix even in the event of tensile pull out. However, the increasing surface roughness was not in line with decreasing tensile strength obtained. This is due to agglomerations effect that occurred during compounding. Agglomerates acted as foreign body and initiated cracks in the composites under stress (refer to Figure 5(b)). The agglomerates reduced the tensile strength and EB of ENRANs.

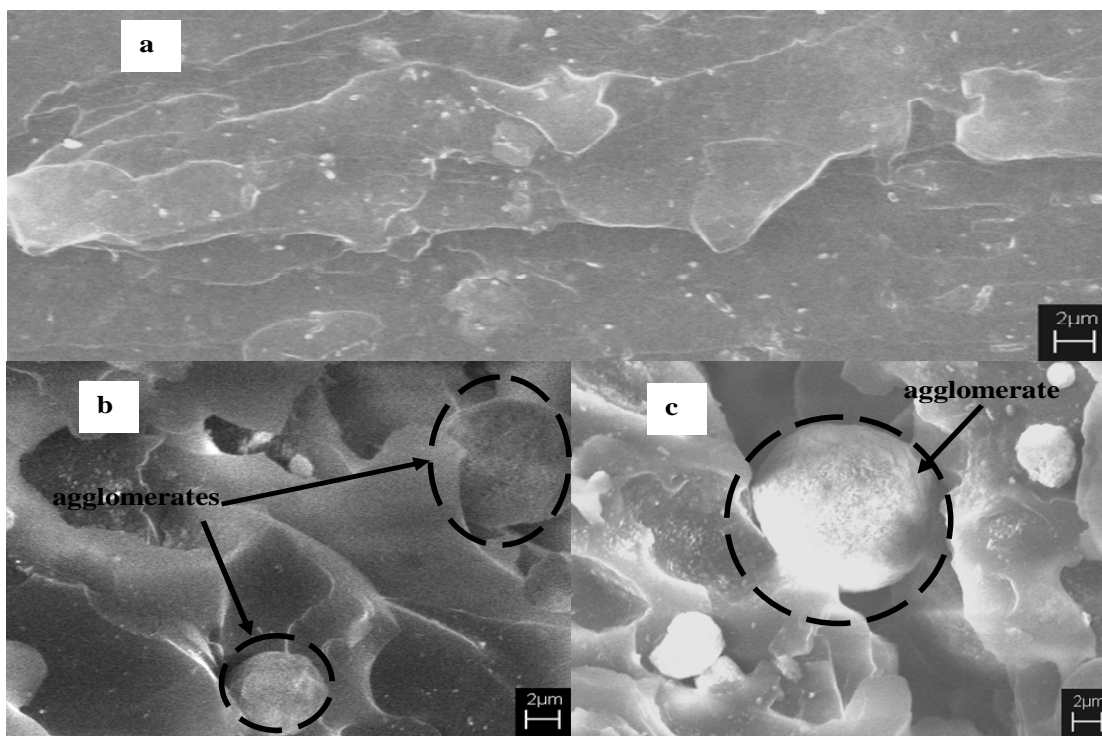
Figure 4: SEM fractographs using secondary electron at 500x magnification for (a) 0 phr (b) 20phr (c) 30 phr (d) 60 phr of alumina nanoparticles loading in ENR.



From the fractographs in Figure 4, surface roughness decreases with further increasing filler loading from 30 phr to 60 phr. It can be observed that the density of agglomerates increases as the alumina content was further loaded (refer to Figure 4). This may be due to the worsening wettability of matrix onto filler surface when ratio of fillers to ENR matrix is too high, hence premature or brittle type fracture [1]. It can be observed in Figure 5(c) where unwetted alumina agglomerate was solely present in between crack surfaces of high filler loading composite (60 phr). Composites with low filler loading show higher tensile strength if compared to composites with higher filler loading since there were less agglomerates and better wettability in the composites.

Although the size of agglomerates were big but sphere-like agglomerate has lessen their effect as stress concentrator in ENRANs. So, it did not show pronounced effect on tensile properties since it enhanced the tensile modulus. However, high amount of hard alumina nanoparticles dispersed in ENR matrices significantly increases the hardness and decreases the impact strength of the composites.

Figure 5: Fractographs under 5000x magnification. (a) unfilled ENR; ductile fracture. (b) 10 phr alumina loading; show similar contrast. (c) 60 phr alumina loading; show alumina agglomerates which act as foreign body and initiate crack during tensile deformation.



4. Conclusions

The incorporation of alumina nanoparticles in ENR accelerated curing process and improved curing characteristics. Adding high amounts of alumina nanoparticles did not cause pronounced effect to the tensile properties. The tensile strength and elongation at break decreased with increasing alumina content in composites but increased the tensile modulus. The presence of alumina nanoparticles in ENR matrix has reduced the impact strength and improved hardness of ENRANs up to 60% than unfilled ENRs. Morphology of fracture surfaces shows that tensile properties are not only affected by crosslink density but also better distribution, agglomeration and wettability. The presence of uniformly distributed alumina nanoparticles have efficiently hinder the polymer chains movement during deformation and contribute to the high stiffness of the composites.

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