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The Effect of Grounded Calcium Carbonate on the Physical Properties of NR Vulcanised Latex Films

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The effect of filler loading on tensile strength, force at break, modulus, stress-strain relationship and surface morphology of natural rubber latex (NRL) films was studied. Grounded calcium carbonate (GCC) loaded into NRL latex compounds and the results obtained from latex films formed from these compounds, showed that their tensile strength and force at break improved initially but leveled and dropped when the GCC loading is more than 5% in NRL films. Disturbing the filler arrangement in the rubber matrix by scragging the test piece of filled NRL films changed the elastic constant value (C_1) of the filled test pieces with a large difference in highly filled films. Expected agglomeration of filler in gloves visualised via *the microscopy technique indicated disinclination of GCC to distribute well in NRL films. The discrepancy seen in SEM micrographs between differently filled films could be related to surface roughness of the NRL films. Among filled NRL films, the one containing 20% of GCC had the smoothest appearance in its surface morphology. Micrographs from FIB-SEM techniques show clear clustering of fillers at high dosages in the NRL films.*

Keywords: Natural rubber latex; filler; calcium carbonate

Compounded natural rubber latex (NRL), due to its dried film characteristics, is normally the preferred material for producing thin rubber products. Among the common products from NRL are latex gloves, balloons, condoms and catheters. The peculiarities seen in NRL films such as high elasticity and flexibility at low modulus compared to films made from dry bulk rubber, give an advantage to NRL in meeting the usage demands of these NRL products. Most products are to meet a set of minimum quality requirements based on their application to ensure safety in usage.

It is undeniable that a main contributor to the cost of producing NRL gloves is the bulk material in the gloves. The rubber content in NRL gloves of more than 95% is believed to be one of the reasons for the high strength superiority of NRL gloves. However, in recent years, due to the increased price of NRL, filler is added into latex to cheapen material cost. Surprisingly, these filled gloves meet the minimum requirements of current regulatory limits; hence, they are acceptable to consumers. With this attractive savings in cost, glove makers are pushing the limit of fillers in NRL gloves. Cai *et al*.[5] were among earlier workers reporting that ultrafine calcium carbonate could effectively improve tear strength, tensile strength and modulus of the NRL films. Improved modulus reflects

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an increase in stiffness of NRL films. It is thought that further stiffening an elastic thin product by incorporating high levels of a non-elastic material such as a filler, may render the product useless for its purpose. Therefore, this paper is intended to demonstrate this effect on NRL films.

EXPERIMENTAL

Formulation for preparation of NRL films in this study is given in *Table 1*. The other compound ingredients (in p.h.r.) include: 0.15 potassium laurate; 0.2 KOH; 0.7 sulphur; 0.4 ZDEC; 0.2 ZDBC; 0.5 ZnO; 1.0 wingstay L. Two different batches were prepared. For the first batch (A), compounding ingredients and grounded calcium carbonate (GCC) were mixed together into the latex and the compound was stirred at room temperature (25 ± 3ºC) for about 30 min and left to stand under room temperature for another 48 hours. The second batch (B) was prepared differently by adding GCC into the latex compound after the 48 h standing period.

Assuming that the amount of most of the non-rubber materials other than GCC in the latex compound was constant, NRL films with different loading of GCC were prepared from each of the latex compounds.

NRL films of required thickness were produced form these latex compounds, *via* a calcium nitrate coagulant dipping process technique using MRB's laboratory batch dipping machine.

Tensile properties of each NRL film were tested according to *ISO 37* at a rate of 500 mm/min crosshead speed using an Instron tensile machine. The test was conducted under room temperature (25 ± 3ºC).

Stress-strain properties of NRL films were determined *via* the Mooney Rivlin stress-strain relationship. Cross-sectional area of the test pieces was calculated from the density, mass and length of specimens. Gauge length of the strip was 100 mm and the sample was pulled at 3 mm/min using a 5565 Instron machine. The best fitting procedure was picked out of eight equally spaced points 1/(extension ratio).

The test pieces were subjected to cyclic pre-staining or scragging at 1000 mm/min for four times at 200% strain before carrying out C_1 measurements.

Samples for FIB-SEM analysis were immersed in Osmium tetra-oxide (OsO_4) solution for seven days and dried in vacuum at a reduced temperature prior to analysis. The latex film sample for visualisation was coated again with Osmium vapour under vacuum.

Surface morphology of films was determined using a scanning electron microscope (SEM, JEOL Ltd. Japan; Model SMI 3050 SE). All SEM images were taken using a

TABLE 1. NR LATEX FILM FORMULATION

	Weight (%)					
NR Latex	100	95	90	80	70	60
GCC	-	5	10	20	30	40

secondary electron detector at an acceleration voltage of 3000V with a magnification of 18,000 ×.

FIB-SEM of latex/filler was performed using Focused Ion Beam System JFIB-2300S at an accelerating voltage of 3000V, whereby the Ga-ion was charged at about 50 pA for the incising process. The image scale was set at 7.5 μm with a magnification of 36,000 ×. A thin carbon layer was deposited onto the incising surface to prevent samples from curving during the slicing process. FIB-SEM images were taken after every 100 nm slit.

RESULTS AND DISCUSSION

Results from physical properties (tensile strength and force at break) of NRL films were graphed to compare whether the addition of filler affected properties of the NRL films. It can be seen from *Figure 1*, that tensile strength of NRL films prepared from batch A, improved initially but dropped after amount of GCC at 5%. A similar trend was observed for aged test samples. In batch A, the GCC was expected to be involved in the sulphur crosslinking formation in the NRL compound during the 48 h standing period. However, this involvement did not help in improving the tensile strength value of these NRL films. It can be seen from the graph that strength values, in fact, decreased with increase of GCC contents in NRL films. The effect of film thickness on the tensile strength value is arguable, hence, force at break values (FaB) were plotted against the GCC content (*Figure 2*) and again it is confirmed that strength properties of filled NRL films did not improve significantly. GCC content stiffens the NRL films with an increase of modulus values (*Figure 3*).

The results of NRL films from batch B where the GCC was added after the latex maturation period (as it minimised the effect of GCC in crosslink formation within NRL films) were somewhat similar to NRL films of batch A. Strength values did not improve much (*Figures 4, 5* and *6*) and like previous results, strength reduced with higher filler content.

The strength study clearly indicates that GCC is not a strength inducer in NRL films and the addition is merely as a cheapener. The initial increase in strength properties at low filler content may be due to the slight stiffening effect attributed by GCC at low levels, but at high levels, GCC may introduce more stress points throughout the NRL films, causing strength to fail earlier.

The pick-up of materials during glove dipping processing is another important factor as this will certainly affect thickness of the glove. NRL films having 20% GCC gave comparable tensile strength values compared to unfilled NRL films, while NRL films with a much higher GCC content, as expected, did not fare very well compared to unfilled NRL films (*Figure 7*). A similar observation was made in the FaB values (*Figure 8*) but, with the thinnest samples (A) giving lowest overall FaB values. This illustrates that thickness of NRL films is a vital factor in filled NRL films, because it is possible for a very thin unfilled NRL film to show similar strength properties in comparison with a highly filled NRL film.

Fillers such as GCC stiffen NRL films, and this is one property that the GCC filler consistently improved in all NRL films. Modulus values, indicating the stiffness of the NRL films increased with filler loading (*Figure 9*). GCC is in fact, a reasonably hard non-elastic material, therefore, it is expected that such a material will stiffen NRL films. It is observed from this study that the stiffening effect gave a temporary small increase in low filled NRL films and the improvement diminished upon 10% of GCC in NRL films.

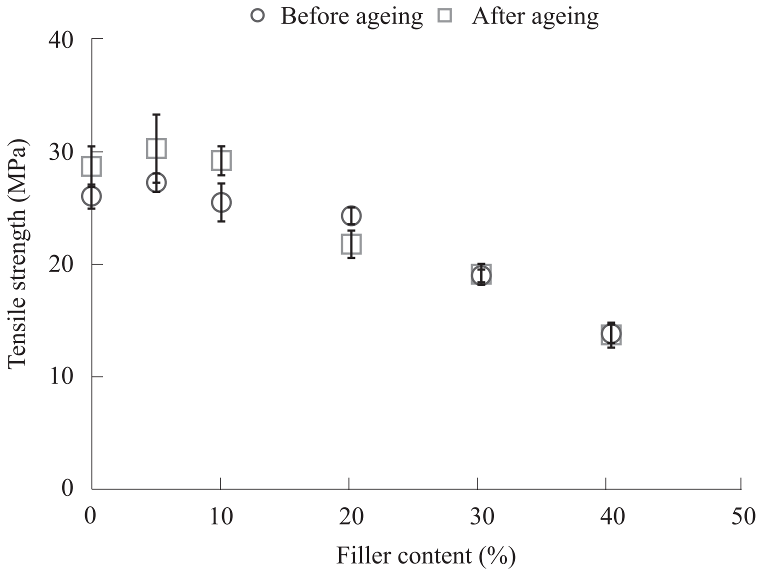

Figure 1. Effect of filler content on the tensile strength of NRL films (batch A).

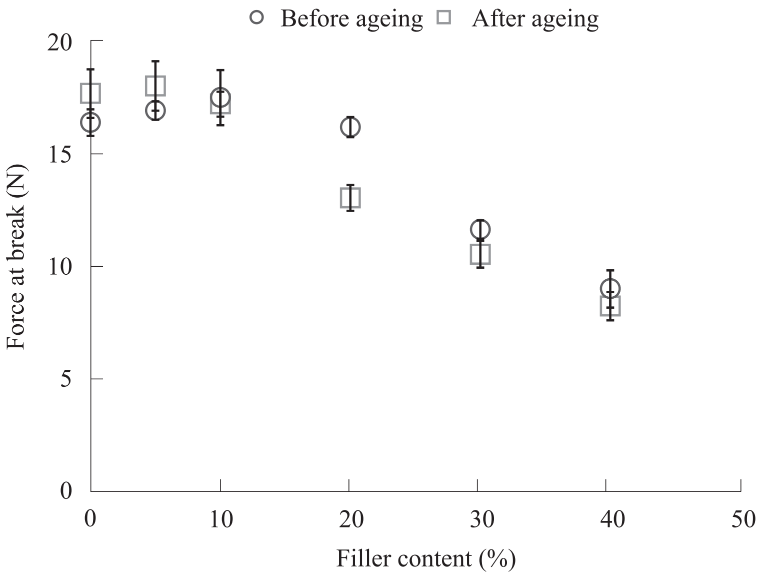

Figure 2. Effect of filler content on the force at break of NRL films (batch A).

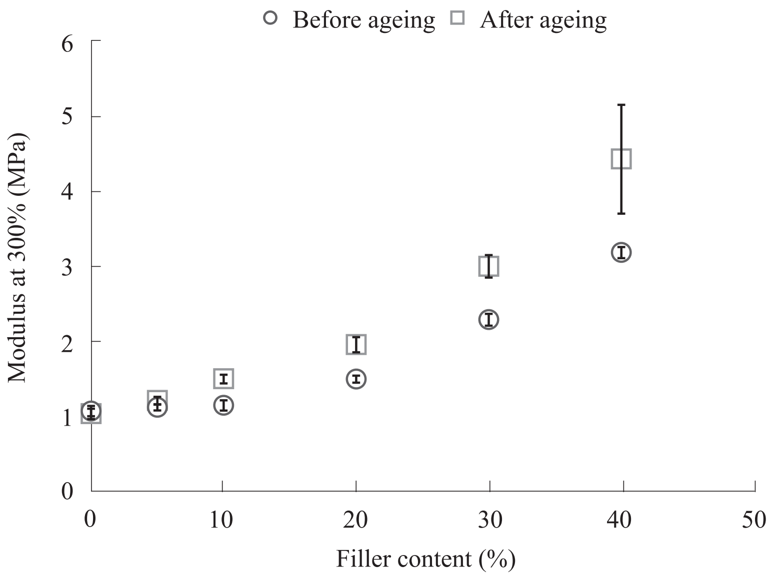

Figure 3. Effect of filler content on the modulus at 300% of NRL films (batch A).

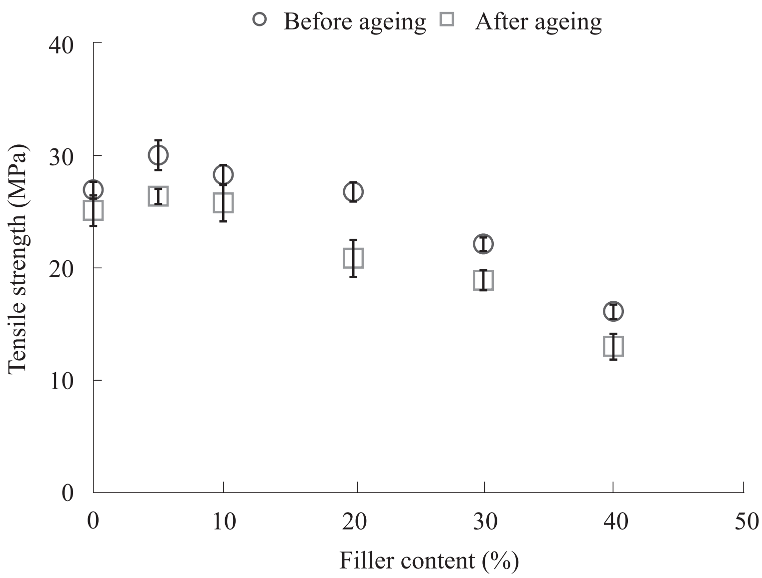

Figure 4. Effect of filler content on the tensile strength of NRL films (batch B).

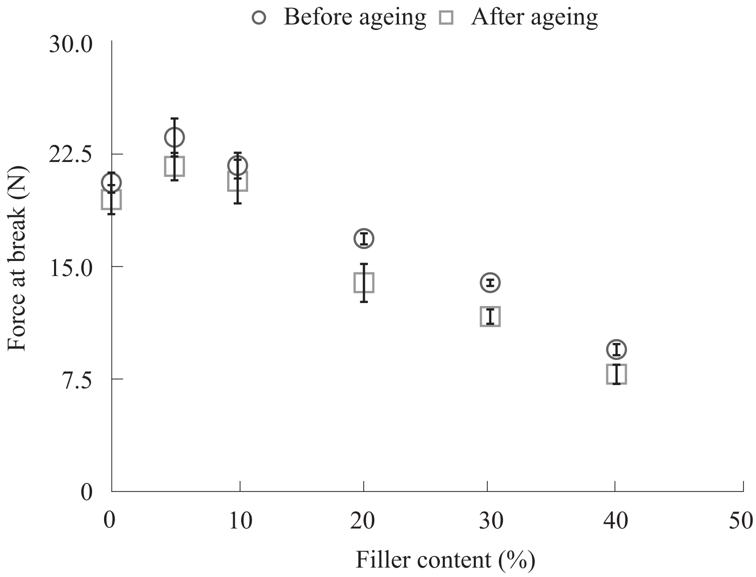

Figure 5. Effect of filler content on the force at break of NRL films (batch B).

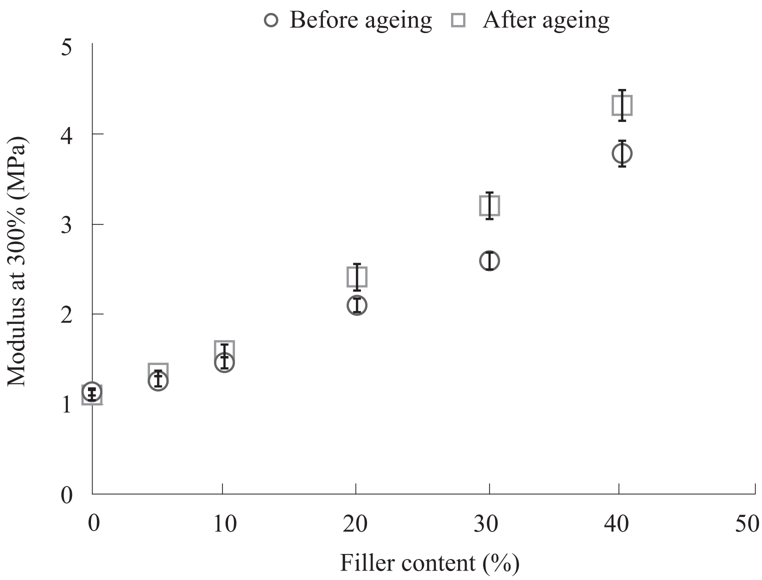

Figure 6. Effect of filler content on the modulus at 300% of NRL films (batch B).

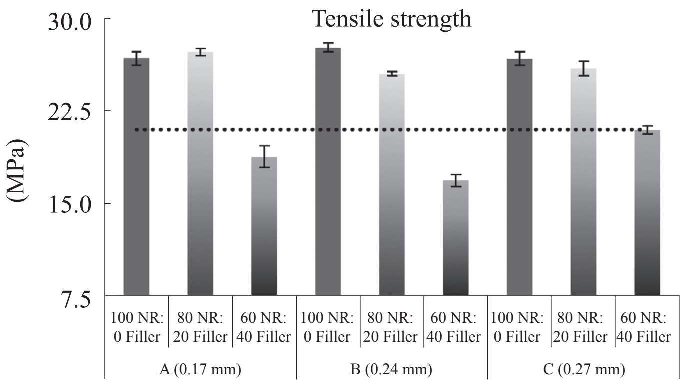

Figure 7. Effect of filler content on tensile strength with different thickness of NRL films.

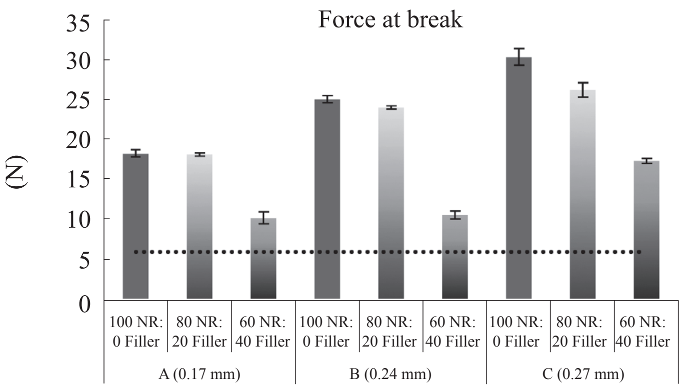

Figure 8. Effect of filler content on the force at break (N) with different thickness of NRL films.

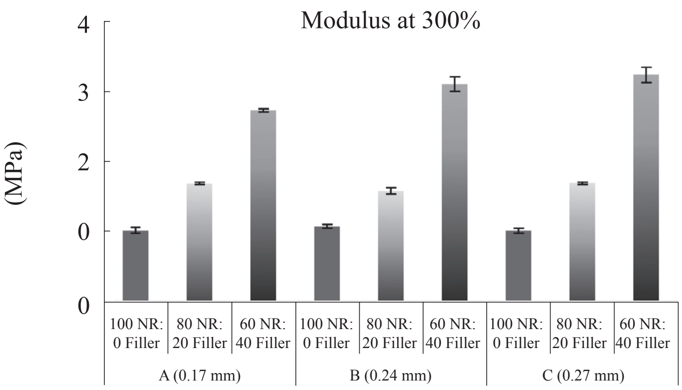

Figure 9. Effect of filler content on the modulus at 300% with different thickness of NRL films.

According to Cai *et al.*[5], particle diameter of ultrafine calcium carbonate is the main factor for its reinforcing ability at filler contents below a 15% level. The smaller the particle diameter, the better the diffusion efficacy, together with its matching effect where the free volume of rubber tends to be stronger and its role as an impurity weaker as well as its ability to inhibit higher expansion of the micro crack. In addition, with the micronisation of particles, the filler particles became aggregates of a limited amount of atoms, which exhibited a special surface effect. The smaller the particle, the greater the specific surface area became. With the surface effect tending to be stronger, the contact area between filler and rubber particles increased, ensuring the formation of physical tangles. At the same time, the ability to inhibit the movement of macromolecules as well as carrying efficiency increased, resulting in a good reinforcing effect. However, when the amount of reinforcing agent exceeded a critical value, contact of rubber particles with reinforcing agent particles tended to be saturated. If the amount of reinforcing agent continued to increase, the aggregates became larger and the distance between the rubber particles increased, which broke down the monolithic construction of the material, causing poorer reinforcing effect.

A stress-strain experiment was conducted on the filled NRL to elucidate the theory above. In the experiment, the test piece is stretched at a very slow rate and the Mooney-Rivlin elastic contact C_1 was obtained. C_1 is an estimate of the apparent physical crosslinking in NR vulcanisates.

Plots of C_1 against filler content for test samples from batches A and B are given in *Figures 10* and *11*. It is interesting to note that the elastic constant of unscragged NRL films increased with the filler loading for both batches A and B. This explains the apparent increase in physical crosslinks with increased filler. On the other hand, when the NRL films were scragged, the C_1 values seemingly diverged from the unscragged C_1 values and the reinforcing effect diminished giving much lower C_1 values.

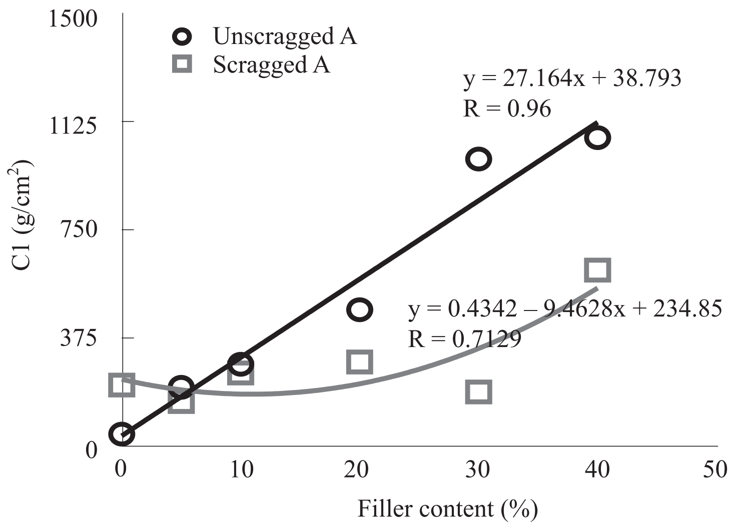

Figure 10. The effect of filler content (%) on stress-strain behaviour using Mooney Rivlin Plot (batch A).

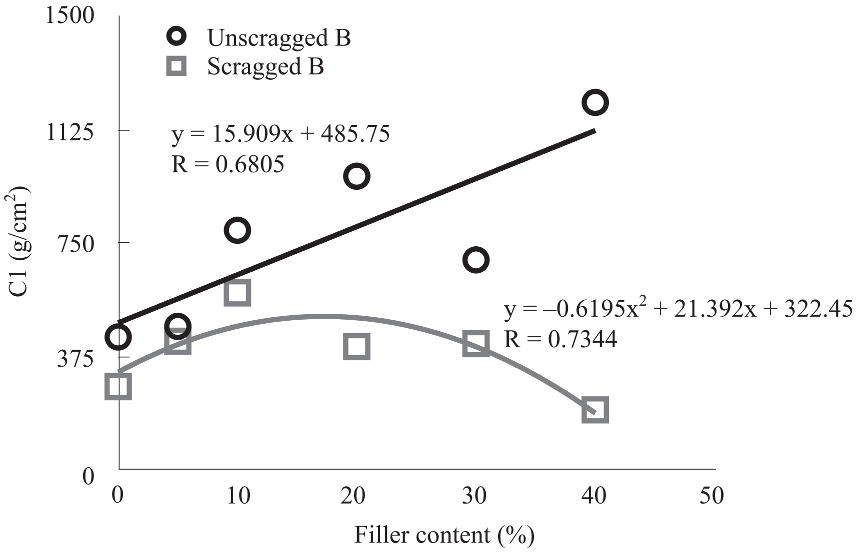

Figure 11. The effect of filler content (%) on stress-strain behaviour using Mooney Rivlin Plot (Batch B).

Surface of latex films prepared by incorporating the GCC filler were observed by SEM as showed in *Figure 12*. The difference in micrographs could be seen on the surface roughness. It was observed that the film containing 20% GCC showed a smoother surface compared with other films prepared. This could be related to better interfacial adhesion between the filler and rubber phase.

Figure 13 showed the two-dimensional SEM image upon etching with the Ga-ion beam. The dark domains represent rubber matrix, while the bright domains represent aggregates containing GCC particles. It was found that the amount of aggregates intensified throughout the rubber matrix with higher content of GCC. It was postulated that low dispersibility of GCC during latex compound had create incompatibility, thus affect the interactions between the GCC and the rubber particles. The morphology observed was consistent with the decrement in the mechanical properties of the NRL film prepared.

SUMMARY

The application of GCC affects the properties of NRL films. The tensile strength and force at break values improved at low levels of GCC but dropped when GCC loading is more than 5% in NRL films. The elastic constant of unscragged NRL films increased with filler loading. Scragging disturbed the filler arrangement and the reinforcement mechanism diminished. SEM technique allows visualisation of surface smoothness of NRL films due to filler addition. However, this observation is inconsistent as only the film with 20% GCC appeared to be smooth as seen in the SEM micrograph, while FIB-SEM provides a better relationship

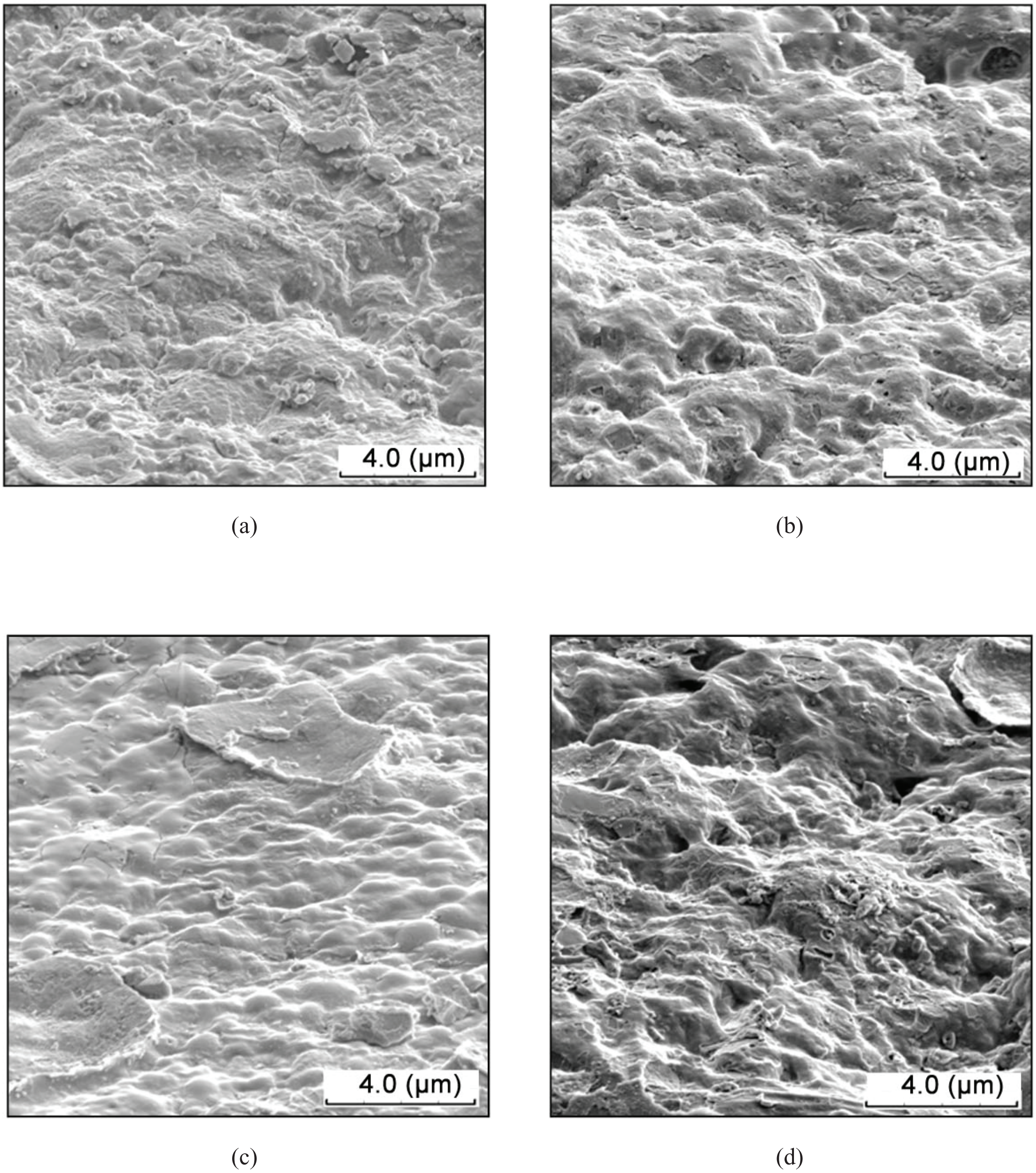

Figure 12. SEM micrograph of latex films containing GCC at (a) 5%, (b) 10%, (c) 20% and (d) 40%.

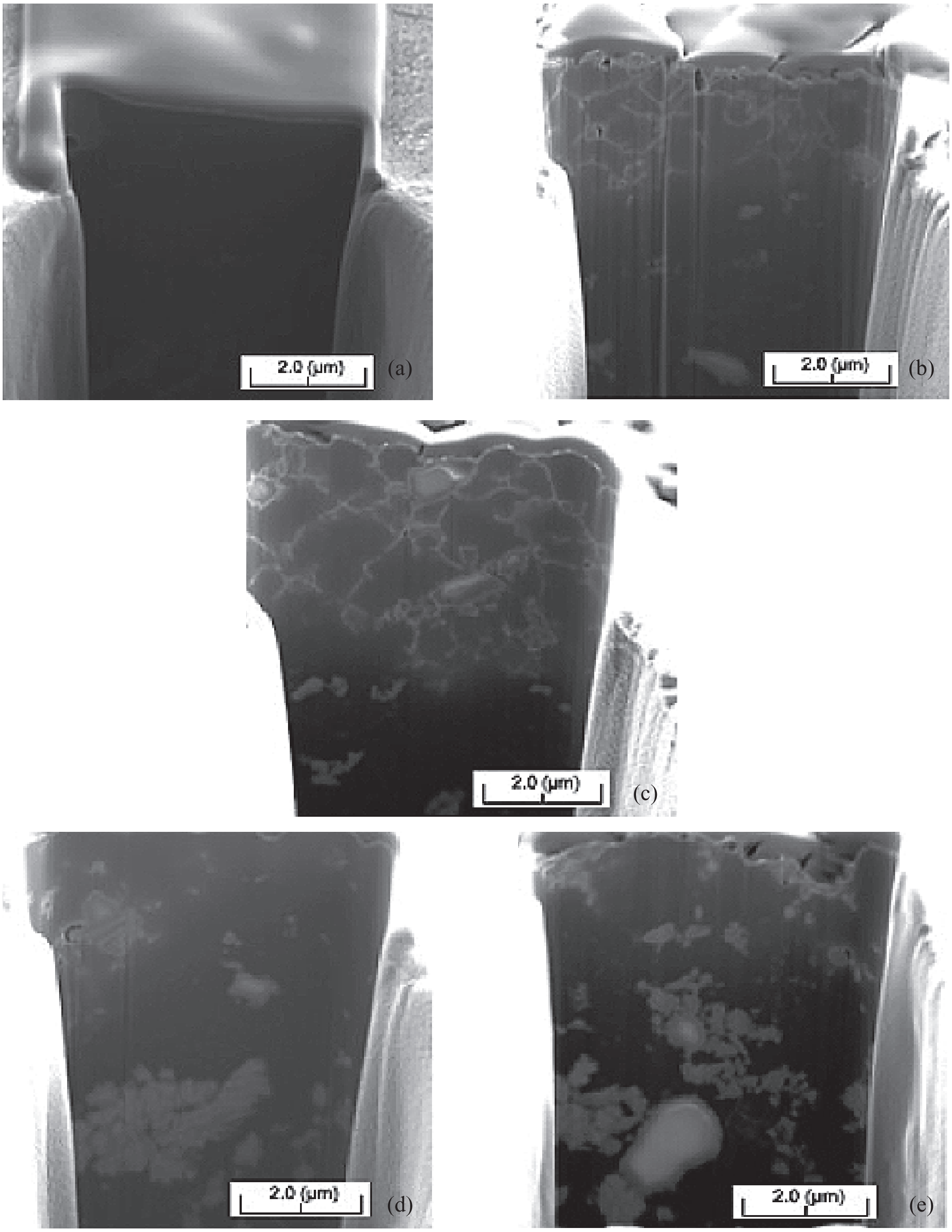

Figure 13. FIB-SEM images latex films at varied GCC content;
(a) no filler, (b) 5%, (c) 10%, (d) 20% and (e) 40% taken in the etching process.

between differently filled NRL films with more spots due to filler clustering as observed with increased GCC levels in the NRL films.

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