J. Rubb. Res., **13(2)**, 125–138

Effect of Filler on Physical Properties and Surface Morphology of Natural Rubber Latex Films

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The physical properties of unfilled and filled natural rubber latex (NRL) films were investigated. The presence of calcium carbonate in latex films, determined by ash content method that was lower than the amount of filler added to the compound, suggested that the filler tended to sediment. Images obtained from Field Emission Scanning Electron Microscope System (FESEM) on the filled latex film confirmed agglomerates in the latex films especially with higher filler loading and hence, influencing the appearance of the films whereby the dense colour was observed. The stress on the latex films due to the filler was investigated using Mooney Rivlin (C_1) stress-strain relaxation measurement method. The clear difference in the C_1 values obtained from the test sample before and after being stretched indicated possible breaking at the polymer-filler interphase, especially in natural rubber latex films with high filler loading. It was confirmed that the addition of calcium carbonate up to 20 parts per hundred rubber (p.p.h.r.) into compounded natural rubber latex produced films with some improvements in strength and stiffness. The improvement in strength, however, ceased and decreased on higher filler content and the elasticity of the film reduced drastically.

Keywords: physical properties; surface morphology; natural rubber latex films; calcium carbonate; tensile properties; C_1 parameter

Natural rubber latex (NRL) is a complex system containing rubber particles and various other natural substances like proteins, lipids and inorganic salts. When dried, the rubber particles in NR coalesced to form a relatively strong latex film, where the surface material of each rubber particle formed boundaries around the coalesced particles. In NRL, vulcanisation or crosslinking occurs between the rubbers of these particles converting, from temperature sensitive material to technologically useful elastic material. Fillers such as calcium carbonate, sodium fluorohectorite and kolonite clay are common bulk cheapeners reducing the cost of the latex products. Similar to natural surface materials, filler is expected to adhere to the rubber particles as other non-rubber materials when NRL films are formed. Cai *et al.*[1] demonstrated an improvement of tensile and tear strength of NRL films upon addition of filler and concluded that there is some physical reinforcing effect from filler-rubber interphase. Manroshan and Baharin[2] indicated that the reduction in swelling in filled vulcanised NRL films may be due to possible increase in the crosslink network

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due to polymer-filler interaction. In another study Varghese[3] suggested that intercalation occurred in filled vulcanised NRL films. Considering the expected structure of NRL films which is seen as coalesced rubber particles bordered by non-rubber materials, all these deductions are ambiguous.

Thus, to clarify some of the previous findings, FESEM micrographs of cross-sectional areas of filled vulcanised NRL were obtained to visualise the coalesced structure. By applying a stress strain measurement based on the Mooney Rivlin relationship[4,5], the effect of filler on the vulcanised rubber network could be gauged. This study confirmed the effect of calcium carbonate filler on the mechanical properties of NRL films and demonstrated the appearances of a cross-sectional area of filled NRL films.

MATERIALS

The ingredients for the latex mixture for the NRL films are as shown in *Table 1*. The NRL in this study was commercial grade 'Loprotex' obtained from Getah Indus (M) Sdn. Bhd. The aqueous dispersions of sulphur, zinc oxide, zinc diethyldithiocarbamate (ZDEC), zinc dibuthyldithiocarbamate (ZDBC), and Wingstay L® antioxidant were prepared by ball-milling for 72 hours respectively. Aqueous dispersion of grounded calcium carbonate (GCC) was from MG Chemical Sdn. Bhd. whilst Behn Meyer Sdn. Bhd. supplied the aqueous dispersion of precipitated calcium carbonate (PCC). For specific purpose of the study, different levels of sulphur were used (0 p.p.h.r., 0.5 p.p.h.r., 1.5 p.p.h.r. and 2.5 p.p.h.r.) to investigate the effect of filler at different levels of sulphur content and for each level of sulphur the concentrations of GCC and PCC were varied as shown at *Table 1*, to study the effect of the filler on NRL films properties.

Preparation of NRL films

The latex compounds were stirred for an hour and then left for 2 days under room temperature. After the standing period, either the required amount of GCC or PCC dispersion was added, prior to the film dipping process. The NRL preparation technique proposed by Pendle[6] was followed and the dipped vulcanised NRL films were kept in a desiccator at room temperature for drying until tested.

Particle Size Analysis

The diameter of the particles of NRL, PCC and GCC were measured using the Brookhaven Zeta-Plus Particle Sizing Analyzer in the range of 2 nm to 3 μm.

Field Emission Scanning Electron Microscope

Field Emission Scanning Electron Microscope (FESEM) was used to visualise the morphology of NRL films.

Ash Content Analysis

The ash content of NRL film was determined in accordance to the RRIM Training School Guide based on *ASTM D1278-91a (2007).*

Tensile Properties

Tensile strength, modulus (M300) and elongation at break of the NRL films were determined according to *ISO 37* using the 5565 Instron machine.

TABLE 1. COMPOUNDING FORMULATIONS OF NRL USED IN THE STUDY

Ingredients	part per hundred rubber (p.p.h.r.)
60% Loprotex NRL	100
20% Potassium hydroxide solution	0.25
20% Potassium laurate solution	0.25
50% Sulphur dispersion	0/0.5/1.0/2.5
50% ZDEC dispersion	0.75
50% ZDBC dispersion	0.5
50% Zinc Oxide dispersion	0.5
50% Wingstay L® dispersion	1.0
50% PCC or GCC dispersion	10/20/30/40

C_1 Measurement

The cross-sectional area of the test piece was calculated from the density, mass and length of the specimen. The sample was pulled at 3 mm/minute using the 5565 Instron machine and the gauge length of the strip was set for 100 mm. The best fitting procedure was used to pick out eight points equally spaced in 1/ (extension ratio).

Scragged C_1 Measurement

The samples were subjected to cyclic pre-straining or scragging at 1000 mm/minute for four times at 200% strain before carrying out the C_1 measurement.

RESULTS AND DISCUSSION

Particle Size

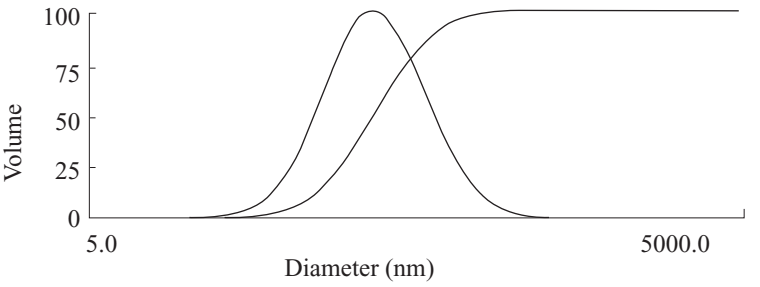
Comparative particle size analysis of GCC, PCC and NRL particles indicated that NRL particles were in a range of 272 to 793 nm in diameter whilst GCC particles were between 369 to 1609 nm in diameter and PCC particles were between 254 to 976 nm in diameter.

The wide particle size distribution of GCC suggested a tendency of the filler to agglomerate to form structures larger than latex rubber particles.

FESEM Micrographs of Vulcanised NRL Films

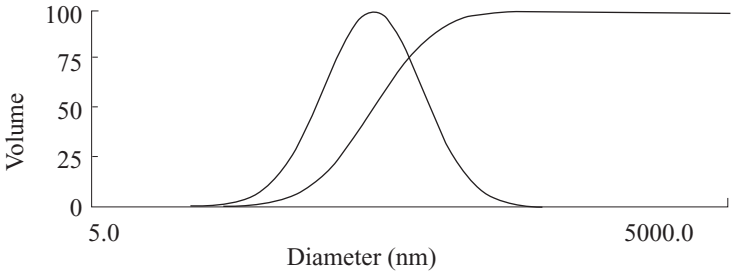
The micrographs of the vulcanised filled NRL films are given in *Figure 2*. The unfilled NRL film (micrograph A) confirmed the structure of NRL films as coalesced rubber particles seen as dark elliptical shaped areas. Micrograph B (i) and B (ii) with 10 p.p.h.r. PCC and 10 p.p.h.r. GCC in NRL films appeared similar to micrograph A, but with white small spots assigned to PCC and GCC agglomerates. The white dots of expected PCC and GCC in NRL films were seen to distribute better around the coalesced rubber particles in micrograph B than in micrograph C due to increase of filler content. Similar observations were seen in the other micrographs of NRL with higher filler contents (micrographs D and E) with more of the white spots or dots appearing with increased filler contents.

With the increase in the filler content, the NRL films tended to be darker which was very apparent in the finished films (*Figure 3*).



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
272.9	26	5	428.6	97	40	578.9	80	75
307.0	44	10	446.6	99	45	611.3	70	80
332.5	58	15	465.2	100	50	650.9	58	85
354.1	70	20	484.6	99	55	705.0	44	90
373.9	80	25	505.0	97	60	793.1		
392.5	87	30	527.1	93	65			
410.6	93	35	551.4	87	70			

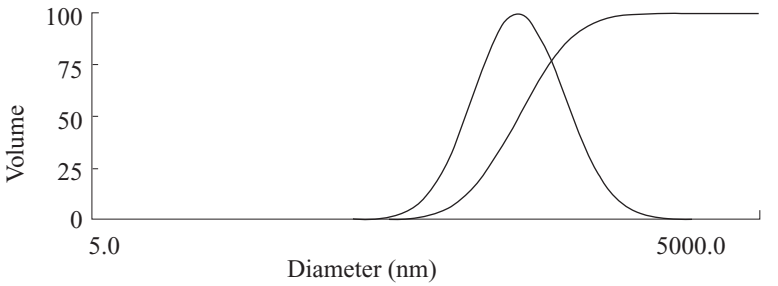
Particle diameter of NRL



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
369.5	26	5	688.6	97	40	1042.3	80	75
434.6	44	10	728.8	99	45	1123.6	70	80
485.2	58	15	771.0	100	50	1225.4	58	85
529.1	70	20	815.7	99	55	1367.9	44	90
570.4	80	25	863.4	97	60	1609.0	26	95
610.0	87	30	915.9	93	65			
649.1	93	35	974.6	87	70			

Particle diameter of GCC

Figure 1. Particle size distributions of NRL, GCC and PCC.



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
254.7	26	5	449.7	97	40	656.7	80	75
295.4	44	10	473.6	99	45	703.3	70	80
326.6	58	15	498.7	100	50	761.3	58	85
353.5	70	20	525.0	99	55	841.8	44	90
378.7	80	25	552.9	97	60	976.4	26	95
402.6	87	30	583.6	93	65			
426.1	93	35	617.7	87	70			

Particle diameter of PCC

Figure 1 (cont.). Particle size distributions of NRL, GCC and PCC.

Ash Content

In order to estimate the inorganic filler in the NRL films, the ash content analysis of each film was carried out. The ash content of unfilled NRL represented the inorganic non-rubbers including natural occurring minerals and added chemicals. Addition of filler to the compounded NRL increases the ash content in the films. However, the ash content measured was lower between 25 to 30 percent than the p.p.h.r. filler added to the NRL mixture before the preparation of the dipped films. Hence, the expected sedimentation of the filler had occurred, reducing the amount of filler pick up and remained in each NRL film.

Tensile Properties

In a rubber product, the physical behaviour is normally used to estimate the application capability of the intended products. Thus, in the present study, the tensile properties in particular, the strength before rupture and stiffness values of the NRL films were compared (*Figure 5*).

The NRL films without sulphur crosslinks were not as strong for any practical purposes as the NRL films with sulphur. For these films, the addition of filler worsens the strength of these films. Therefore, the results indicated that filler alone cannot improve the strength of NRL films. The filler only stiffens the NRL films as given by the increase in modulus values of filler with increase in filler content.

Increasing the sulphur content in NRL improved the strength properties (TS) of the films peaking circa 1.0 p.p.h.r. As indicated by Chong[7], the addition of sulphur as the crosslinking agent in NRL compounds improved the TS but beyond a maximum value it subsequently decreased due to the formation of too many crosslinks which

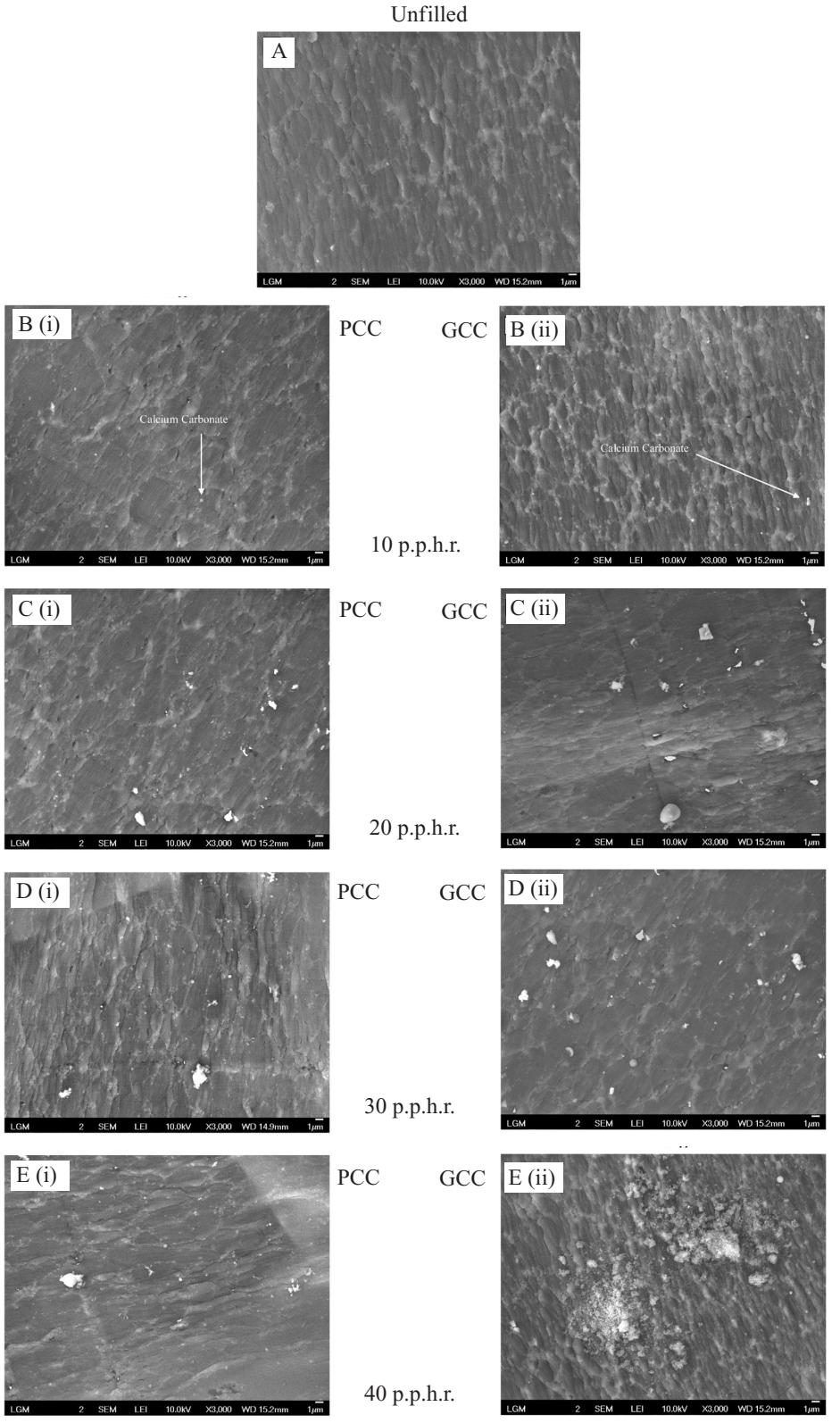


Figure 2. The micrographs of the distributions of GCC and PCC filler on NRL surface morphology.

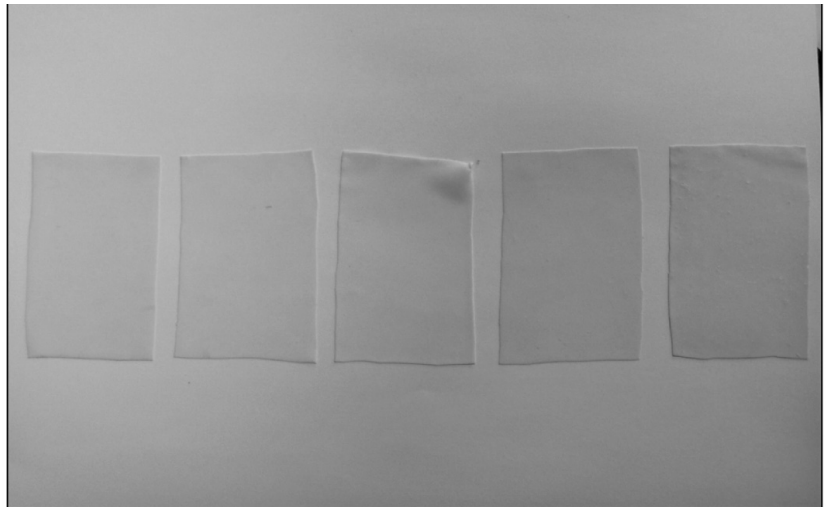


Figure 3. The appearance of NRL films due to the added filler, (From left: 0 p.p.h.r., 10 p.p.h.r., 20 p.p.h.r., 30 p.p.h.r., and 40 p.p.h.r.)

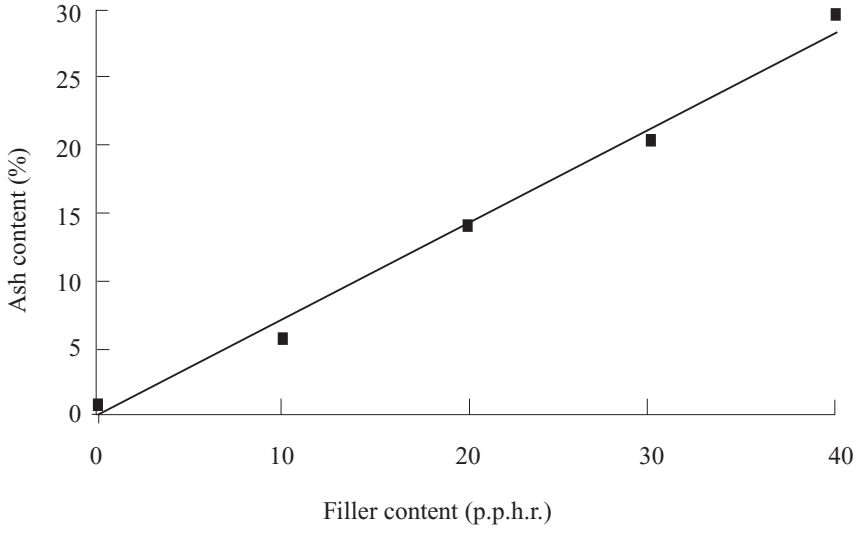


Figure 4. Ash content analysis of NRL films with varying filler concentration.

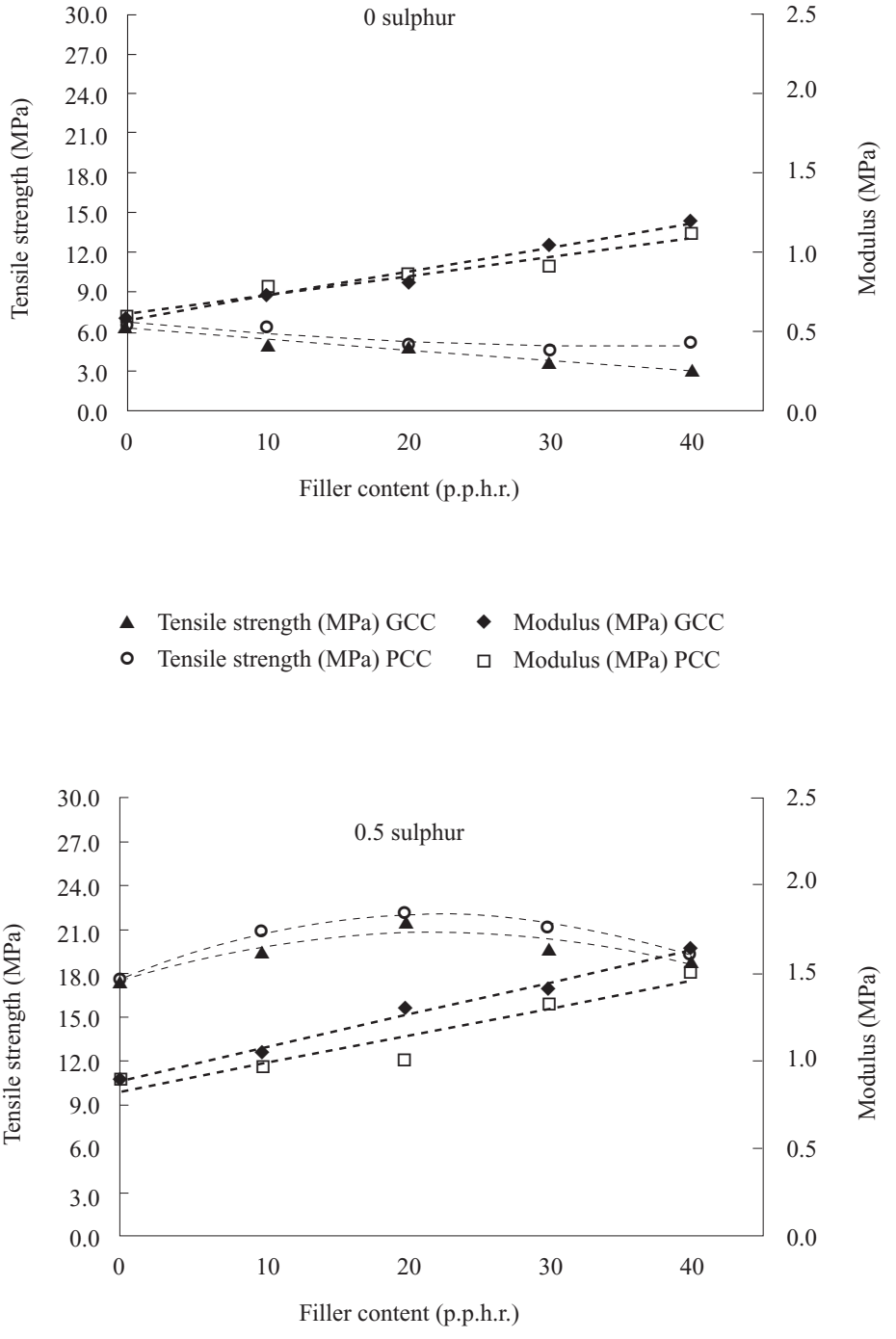


Figure 5. Tensile strength and modulus of NRL films on varying filler content at different levels of sulphur content.

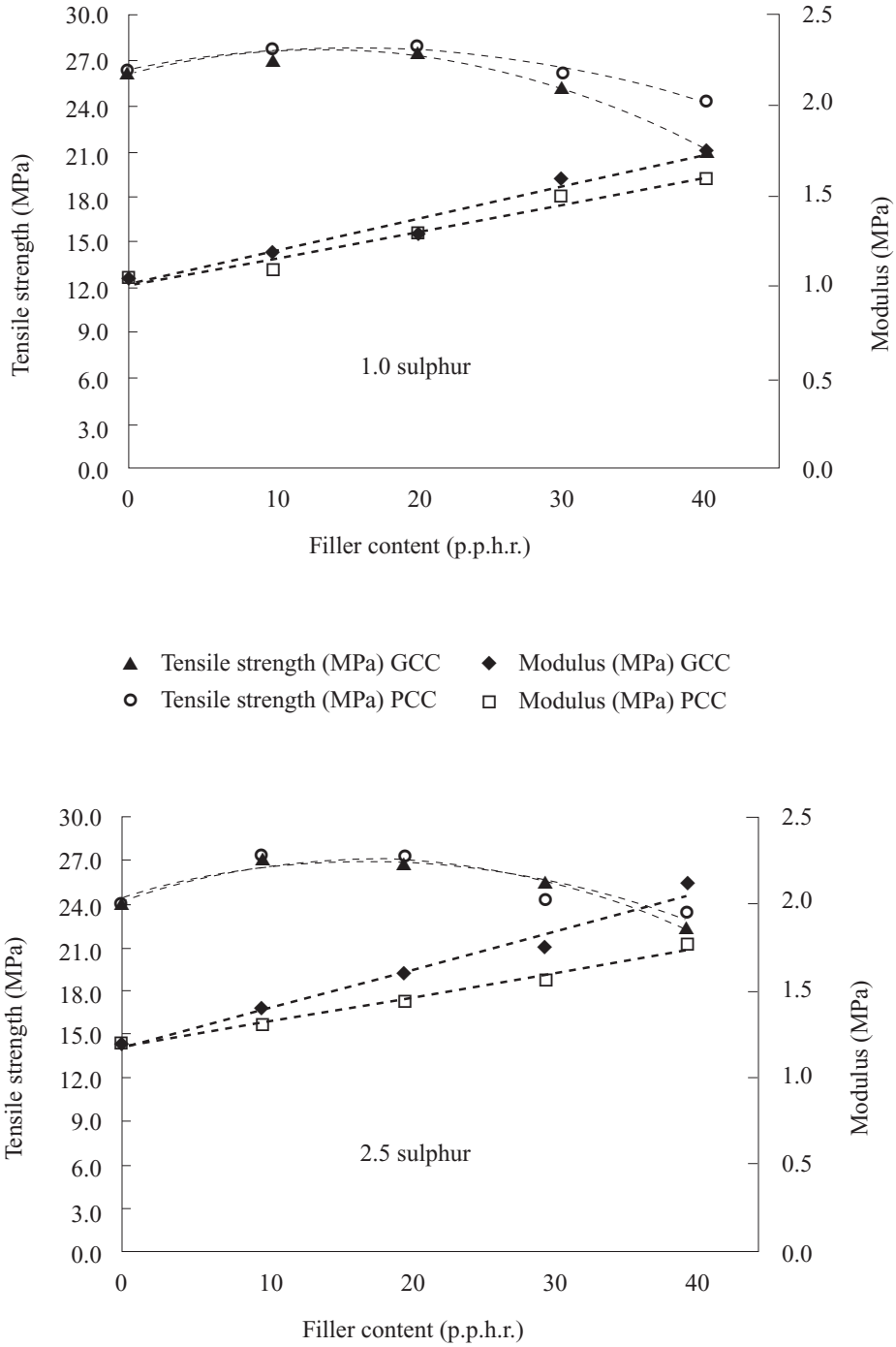


Figure 5 (cont.). Tensile strength and modulus of NRL films on varying filler content at different levels of sulphur content.

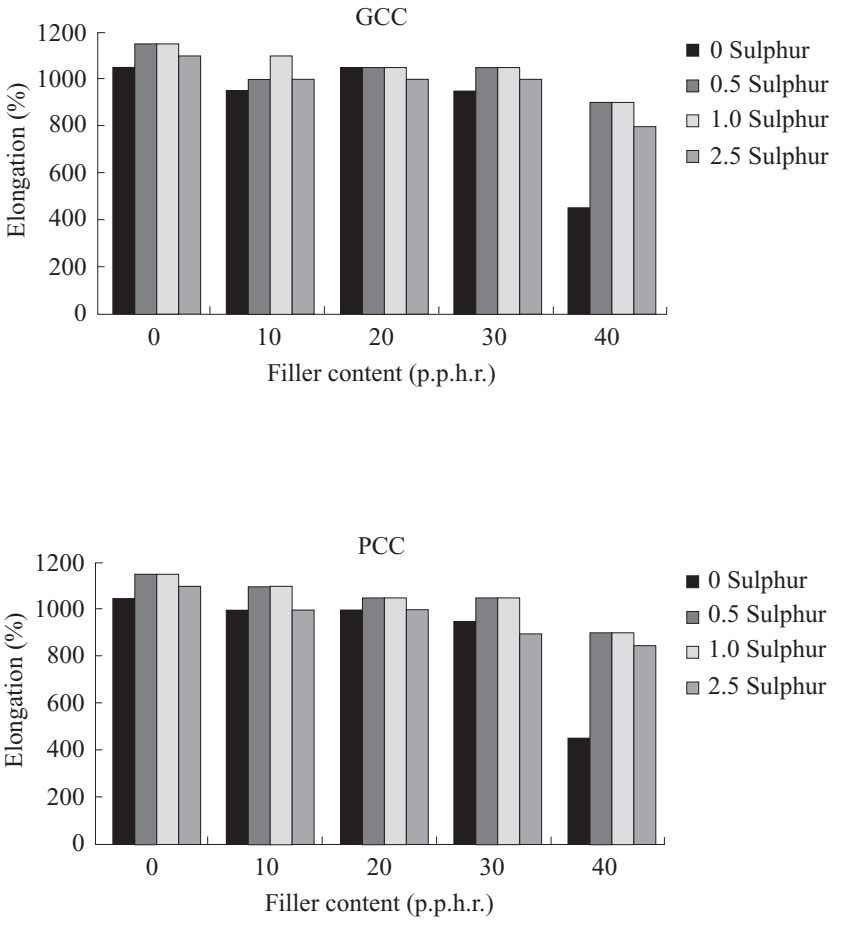


Figure 6. Elongation at break of NRL films on varying filler concentration

affected the degree of crystallisation of rubber during stretching.

For sulphur vulcanised NRL, the addition of calcium carbonate as filler either as the coarse GCC or the finer PCC into the NRL mixture up to 20 p.p.h.r. improved the TS of the films. The actual cause for this behaviour in NRL films is still not clear. However, the reduction in TS above 20 p.p.h.r. filler may be due to the formation of large calcium carbonate clusters in the films as shown before in the micrographs in *Figure 2*. The presence of calcium carbonate clusters may induce localised stress especially at weak areas thus, resulting in flaws in the NRL films. A similar trend was observed in both GCC and PCC loaded NRL films, although at different levels of sulphur content.

The highest elongation at break (EB) was demonstrated by 0.5 p.p.h.r. sulphur level of unfilled NRL films. Reduction in EB at higher sulphur levels related to the increase in modulus as stiffer materials are not expected to elongate as much as soft material.

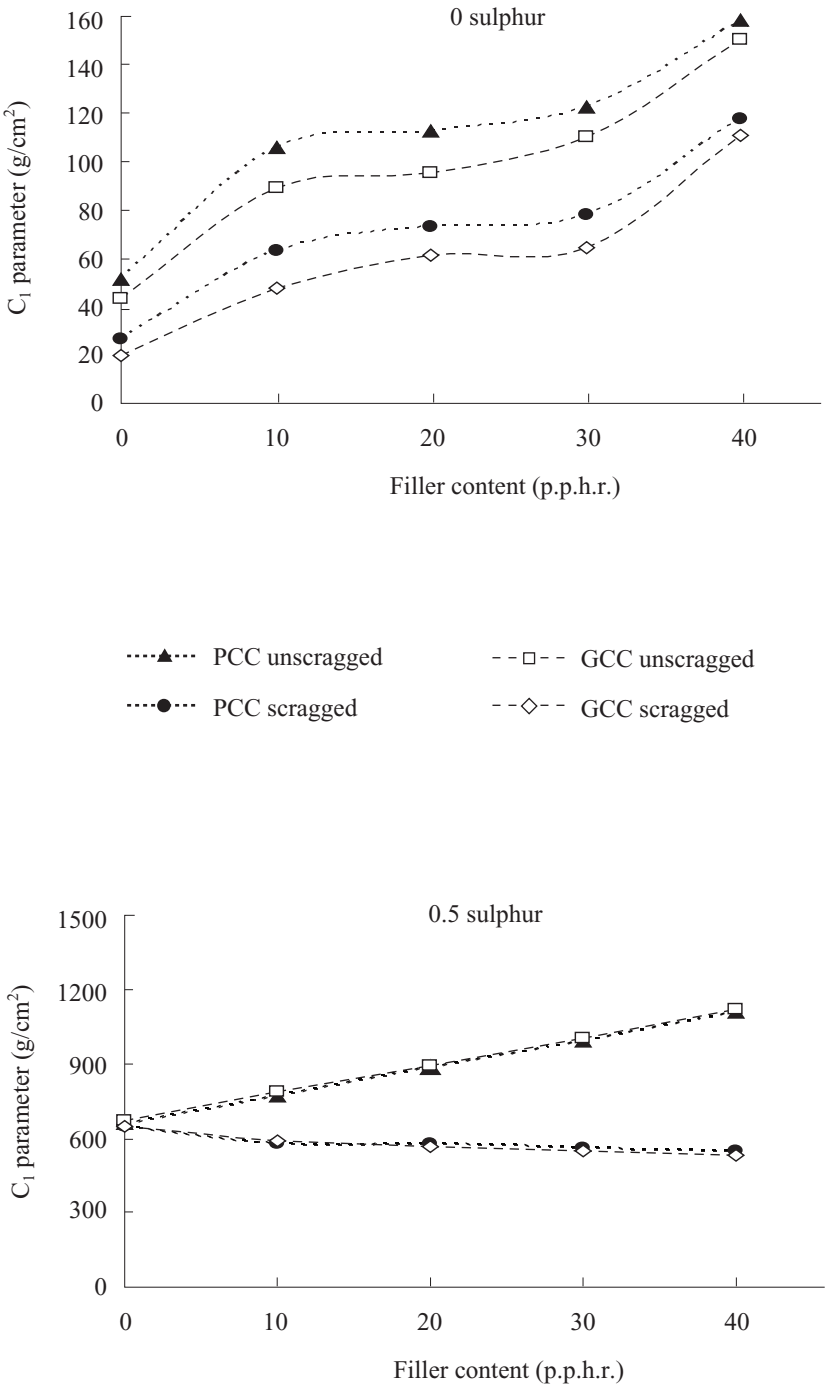


Figure 7. C_1 parameter of NRL films on varying filler content at different levels of sulphur content.

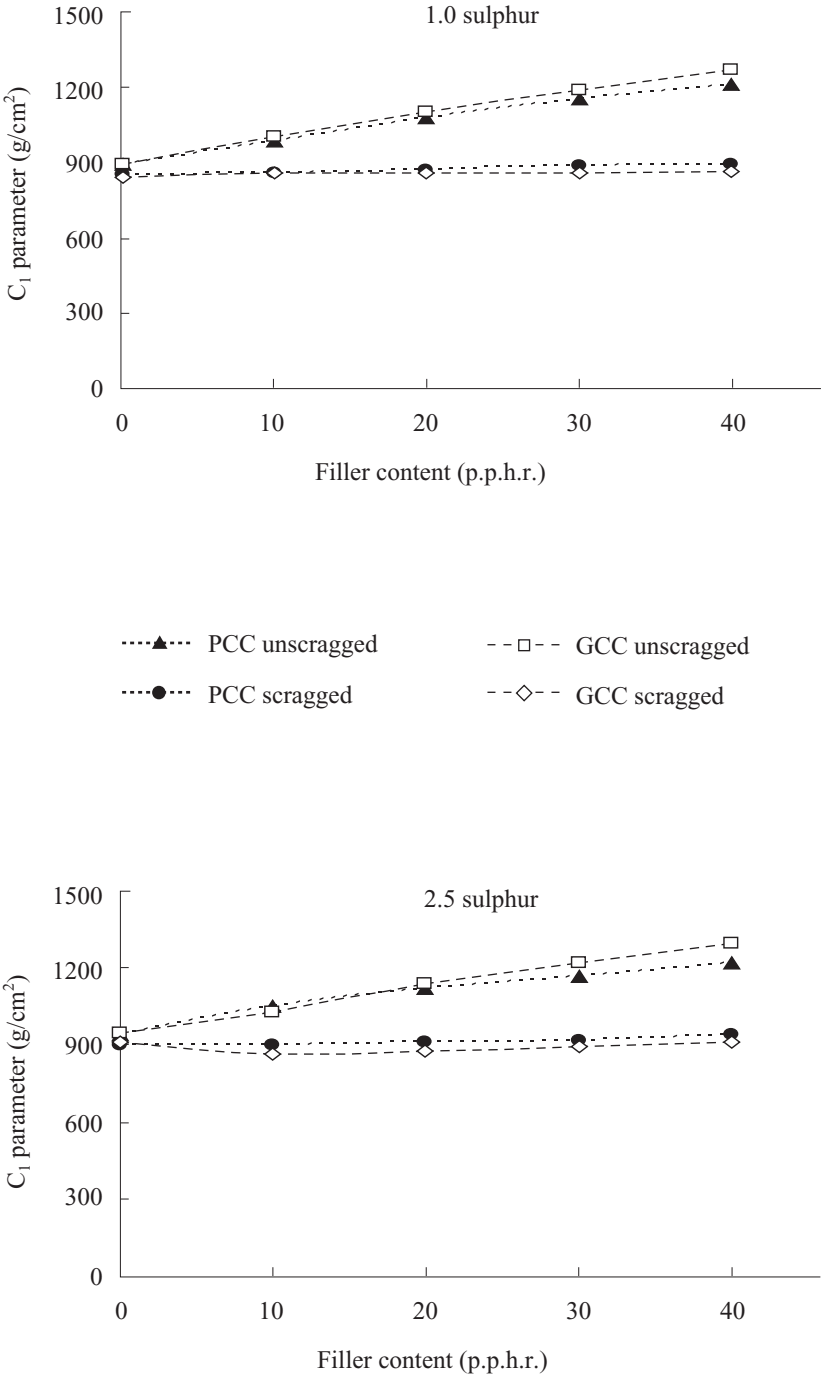


Figure 7 (cont.). C_1 parameter of NRL films on varying filler content at different levels of sulphur content.

Mooney Rivlin Relation of Filled NRL Films

The Mooney Rivlin constant, C_1, is typically associated with the sheer modulus of the network and provides a practical estimate to the physically effective crosslink density. The details of the C_1 constant were described elsewhere[4,5,8,9]. *Figure 8* shows the C_1 before and after scragging of unfilled and filled as well as without sulphur and different levels of sulphur in NRL films. Without sulphur, the C_1 was low but increased with the filler loading even after scragging, ruling out the possibility of the filler improving the crosslinking. In these films, there were no sulphur crosslinks due to the absence of sulphur. In the presence of sulphur, the C_1 values of the films were higher than those without sulphur films. Likewise, the C_1 value increased with filler content. However, the C_1 value dropped to a value equivalent to the C_1 of unfilled films after scragging. This was because scragging broke up the rubber-filler interphase and this was another indication that the filler did not improve the crosslinking. It only increased the stiffness of the films. The C_1 parameter was also markedly dependent on the amount of the sulphur levels. It is expected that a high level of sulphur introduces a high level of croslinks formation between the rubber chains, hence reducing the relaxation in the regime. By comparing the unscragged and scragged data, a consistent effect of scragging of filled films was demonstrated, but for unfilled films, there was no effect of scragging.

The results above confirmed that calcium carbonate filler either coarse (GCC) or fine (PCC) was not a factor for crosslinking formation. Apparent improvement such as the strength values may be due to the stiffening effect of the filler. The temporary apparent reinforcement of filler was realised after the films were scragged, whereby, scragging or pre-straining of filled NRL films broke the links of the rubber-filler interphase and filler-filler interphase. The improvement in the strength properties failed when more areas of localised stress occurred in the films due to filler agglomerates at high filler levels.

CONCLUSION

The concentration of filler loading influenced the physical properties and appearance of the films with noticeable change in filled latex films. The tensile strength of the films improved until about 20 p.p.h.r. and then reduced when more areas of localised stress occurred in the films due to filler agglomerates. The Mooney Rivlin relationship of filled NRL confirmed that the apparent improvement in the crosslink density (C_1 constant) of filled NRL films may not necessarily be due to formation of crosslinks.

ACKNOWLEDGEMENTS

The authors would like to thank the Directorate of the Malaysian Rubber Board for their permission to publish this paper. We are also grateful to Suhaimi Mohamed from the Materials Characterisation Unit for his technical assistance during the study.

Date of receipt: July 2009
Date of acceptance: November 2009

REFERENCES

1. CAI, H.H., LI, S.D., TIAN, G.R., WANG, H.B. AND WANG, J.H, (2003) Reinforcement of Natural Rubber Latex Film by Ultrafine Calcium Carbonate. *J. appl. Polym. Sci.*, **87** p. 982–985.

2. MANROSHAN, S. AND BAHARIN A., (2005) Effect of Nanosized Calcium Carbonate on the Mechanical Properties

of Latex Films. *J. appl. Polym. Sci*., **96**, p. 1550–1556.

3. VARGHESE, S. (2004) Natural Rubber Latex Nanocomposites. *Inter. Latex Conf., Akron, Ohio*.

4. CAMPBELL, D.S. AND CHAPMAN, A.V. (1990) Relationships between Structure and Performance of Vulcanisates. *J. nat. Rubb. Res*., **5(4)**, p. 246–258.

5. CAMPBELL, D.S., CHAPMAN, A.V., GODCHILD, I.R. AND FULTON, W.S. (1992) Experimental Determination of the Mooney-Rivlin Constant for Natural Rubber Vulcanisates. *J. nat. Rubb. Res*., Vol. **7(3)**, p. 168–180.

6. PENDLE, T.D. (1995) Dipping with Natural Rubber Latex. *NR Technology, Kuala Lumpur, Rubber Research Institute of Malaysia*.

7. CHONG K.L. (1977) The Chemistry of Sulphur Vulcanisation of Natural Rubber Latex, PhD Thesis, London School of Polymer Technology, The North London Polytechnic.

8. FARIDAH HANIM, A.H. (2001) Plasticiser Transportation Studies in Polar and Non-Polar Rubbers, PhD Thesis, London School of Polymer Technology, The North London Polytechnic.

9. FARIDAH HANIM, A.H., TINKER, A.J. AND FARID, A.S. (2004) Determination of Crosslink Densities of Filled Rubbers by Cyclic Pre-straining. *J. nat. Rubb. Res*., **7(4)**, p. 248–264.