Effect of Nanosized Calcium Carbonate on the Mechanical Properties of Latex Films

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ABSTRACT: An acrylic dispersed nanosized calcium carbonate filler was added to a prevulcanized latex compound in different amounts. The effect of filler content on the curing time, modulus, tensile strength, elongation at break (Eb) before and after ageing, and the morphology of the films was investigated. Results showed that the curing time decreased with filler loading because of the increased interaction between the filler and rubber matrix, as reflected by the decrease in the apparent swelling index. Modulus at 100% elongation and modulus at 300% elongation increased with filler loading. Tensile strength and Eb increased up to 10 phr of filler loading and then decreased again. Aged films showed improved mechanical properties compared to those of unaged films. Micrographs showed that agglomeration occurred as the filler content was increased. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1550–1556, 2005

Key words: fillers; films; latices; swelling; morphology

INTRODUCTION

Fillers, especially mineral fillers, have been widely used in many industries, particularly in the rubber and latex industries, for decades. These fillers function as reinforcing agents, which increase certain mechanical properties, such as tensile strength, tear strength, and abrasion resistance.[1,2] Carbon blacks, kaolinite clays, silicas, and calcium carbonate are examples of fillers that impart certain reinforcing effects to rubbers and latex films. Extensive work has been done on the reinforcing effects of carbon blacks in the rubber industry[3,4] and silicas and kaolinite clays in the latex industry,[5–7] although there has been no published work to date on the use of nanosized calcium carbonate as a reinforcing agent in the latex industry.

In this study, acrylic dispersed nanosized calcium carbonate was used. The effect of addition of this nanosized calcium carbonate on the swelling index and tensile properties of prevulcanized natural rubber latex films before and after ageing was investigated.

EXPERIMENTAL

Materials and ingredients

Natural rubber latex (HA) was purchased from Kilang Hevea Bukit Perak (Kedah, Malaysia); nanosized calcium carbonate was supplied by NanoMaterials Technology Pte. Ltd. (Singapore). The specifications of the calcium carbonate are as shown in Table I. Other ingredients [sulfur, zinc oxide, potassium hydroxide, zinc diethyldithiocarbamate (ZDEC), and Vulcanox BKF] were supplied by M/S Bayer Ltd. (Mumbai, India).

Compounding and preparation of prevulcanized natural rubber latex films

The prevulcanized latex compound was prepared by compounding the ingredients shown in Table II in a reaction flask at 70 ± 1°C. A chloroform number test was used to determine the degree of vulcanization of the compound. Prevulcanization was stopped at chloroform number 3. The prevulcanized latex was then allowed to cool at room temperature for 3 days for maturation process to occur. Films were prepared by casting the prevulcanized latex onto glass substrates. Drying was done at room temperature for 4 days. The natural rubber latex films were next removed from the glass substrates and further dried for another 4 days at room temperature. The films were next aged in an oven at 70°C for 7 days.

Measurement of mechanical properties

The tensile properties of the films were determined using a tensometric testing machine according to ASTM D412-92 at 500 mm/min crosshead speed. The test was conducted at room temperature (25°C).

TABLE I
Specifications and Contents of Nanosized
Calcium Carbonate

Specification	Contents
Appearance	White dispersion
Specific gravity, dry basis	2.5–2.6
Particle size (avg), nm	40
Surface area (BET), m^2/gm	40
Whiteness, %	≥ 90
Particle shape	Cubic
pH	8.5–9.5
Moisture content, wt %	40–50
$CaCO_3$, dry basis (modified), wt %	≥ 97
MgO, wt %	≤ 0.6

Measurement of swelling index

Test pieces (30 × 5 × 2 mm) were soaked in toluene at 25°C for 54 h (equilibrium swelling). The swelling index of the films was calculated according to ASTM D3616-93. In this study, the swelling index is called the apparent swelling index (SI_{app}), attributed to the interaction between the curatives, filler particles, and rubber molecules.

Scanning electron micrography

Fractured tensile pieces were coated with chromium using an Emitech K575X sputter coater (Emitech, Houston, TX) for 30 s. The coated surfaces were next scanned using a Leo Supra 50VP ultrahigh field emission scanning electron microscope (FESEM; Hi-Tech Instruments Sdn. Bhd., Selangor, Malaysia).

RESULTS AND DISCUSSION

Effect of filler on curing of latex compound

Figure 1 shows the effect of acrylic dispersed calcium carbonate on the optimum prevulcanization time for the prevulcanized natural rubber latex compound. The optimum prevulcanization time was taken as the time to obtain number 3 in the chloroform number test. It could be seen that the optimum prevulcanization time decreases with increasing filler loading. According to Arora et al.,[8] carboxyl-containing functional monomers, such as acrylic or methacrylic acid, function to provide sites for crosslinking by further reaction with other species in the latex. This suggests that the acrylic dispersion increases the rate of prevulcanization of the latex compound by providing sites for interaction between the filler, curatives, and the latex particles in the compound, thus decreasing the time to reach prevulcanization, as shown in Figure 1.

Effect of filler on the swelling index

Figure 2 shows the effect of the filler loading on the apparent swelling index (SI_{app}) of the aged and un-

aged prevulcanized latex films. The SI_{app} decreased as the filler loading was increased for both aged and unaged films. In unfilled rubber systems, the decrease in swelling index is caused by the crosslinking between the curatives and the rubber molecules. In this study, the decrease in swelling index is attributed to the interaction between the filler particles, curatives, and the rubber molecules. As the filler loading increases, the carboxyl-containing acrylic dispersion, which provides sites for crosslinking as explained by Arora et al.[8] (Fig. 1), also increases, causing further reduction in SI_{app}.

Aged films, however, have lower SI_{app} values compared to those of unaged films. This is probably caused by vulcanization of the curatives present in the films, given that slightly excessive crosslinking also has a favorable effect on the resistance to swelling, as reported by Hofmann.[9]

Effect of filler on modulus

Figures 3 and 4 show the effect of filler loading on the modulus at 100% elongation (M_{100}) and modulus at 300% elongation (M_{300}), before and after ageing. The increase in M_{100} and M_{300}, as shown in Figures 3 and 4, is proportional to the increase in filler loading. The increase in modulus with filler loading is explained by the stiffening effect caused by the interaction between the filler and rubber particles, as shown in Figure 2.

Aged films showed higher M_{100} and M_{300} values compared to those of unaged films, a phenomenon attributed to the heating of the films, which caused enhanced stiffening as a result of the interaction of the curatives with the filler particles and the rubber molecules.

Effect of filler on tensile strength

Figure 5 show the relationship between the filler loading and the tensile strength of the prevulcanized latex films, before and after being subjected to

TABLE II
Formulation for Prevulcanized Natural
Rubber Latex Compound

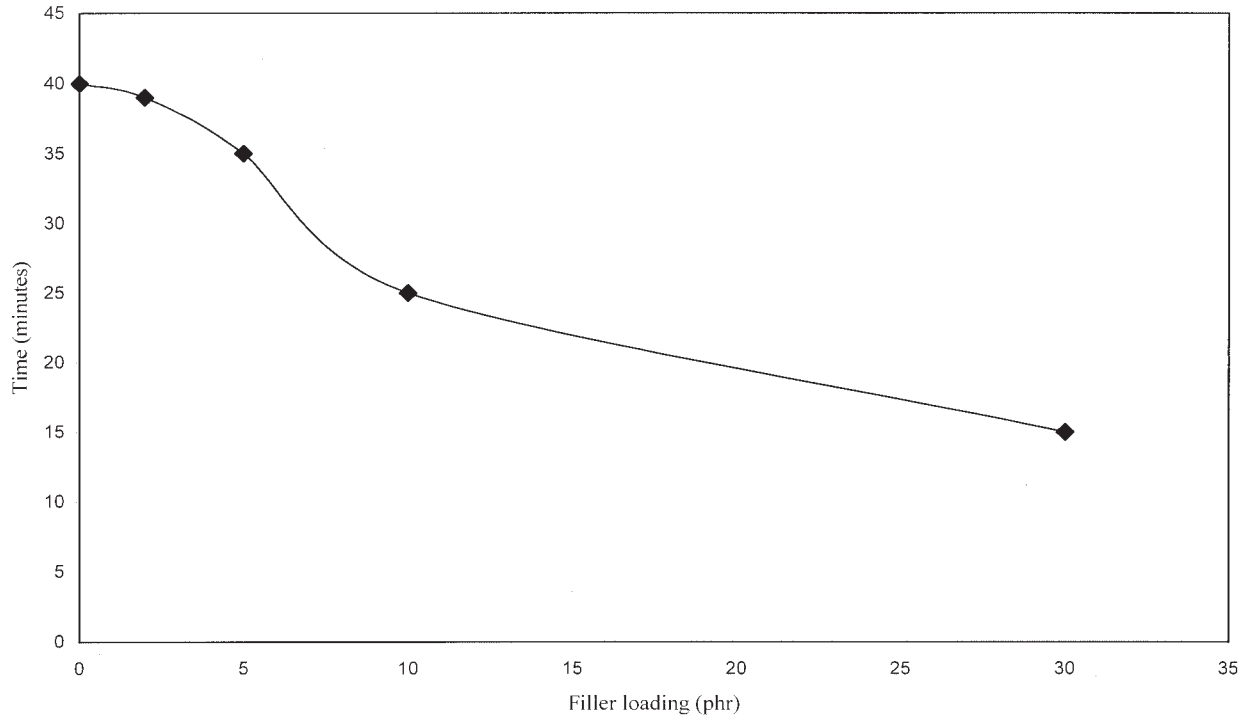| Ingredient	Parts by mass	
	Dry	Wet
60% HA Latex	100	166.7
10% Potassium hydroxide	0.5	5
50% Sulfur	1.5	3
50% Zinc diethyldithiocarbamate	1	2
25% Zinc oxide	2	8
50% Vulcanox BKF	1	2
10% Nanosized $CaCO_3$	0, 2, 5, 10, 30	0, 20, 50, 100, 300

Figure 1   Effect of filler loading on the optimum prevulcanization time of prevulcanized natural rubber latex compound.

ageing. From the results obtained, the tensile strength increased with filler loading, reaching a maximum value at 10 phr, which then decreased again for both aged and unaged films. The improve-

ment in tensile strength at 10 phr of the latex films suggests that there is positive interaction between the acrylic dispersion and the calcium carbonate particles of the filler with the rubber matrix, thus
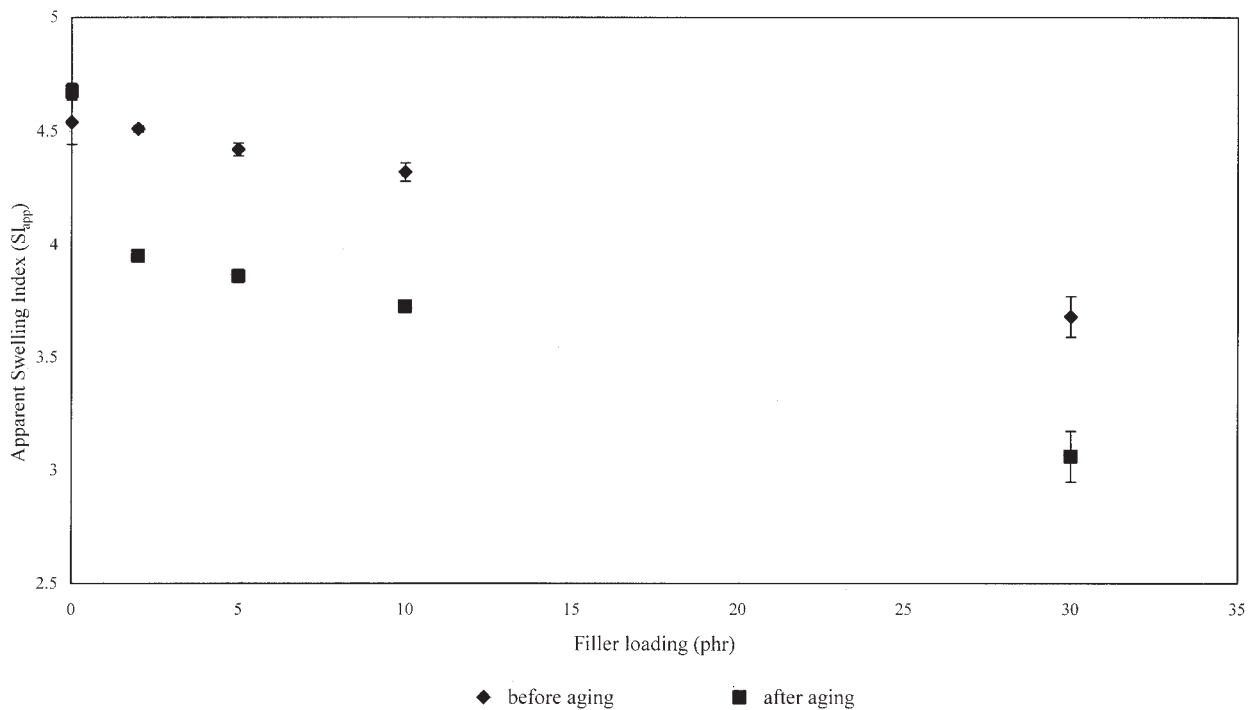

♦ before aging   ■ after aging

Figure 2   Effect of filler loading on the apparent swelling index (SI_{app}) of prevulcanized natural rubber latex films before and after ageing.
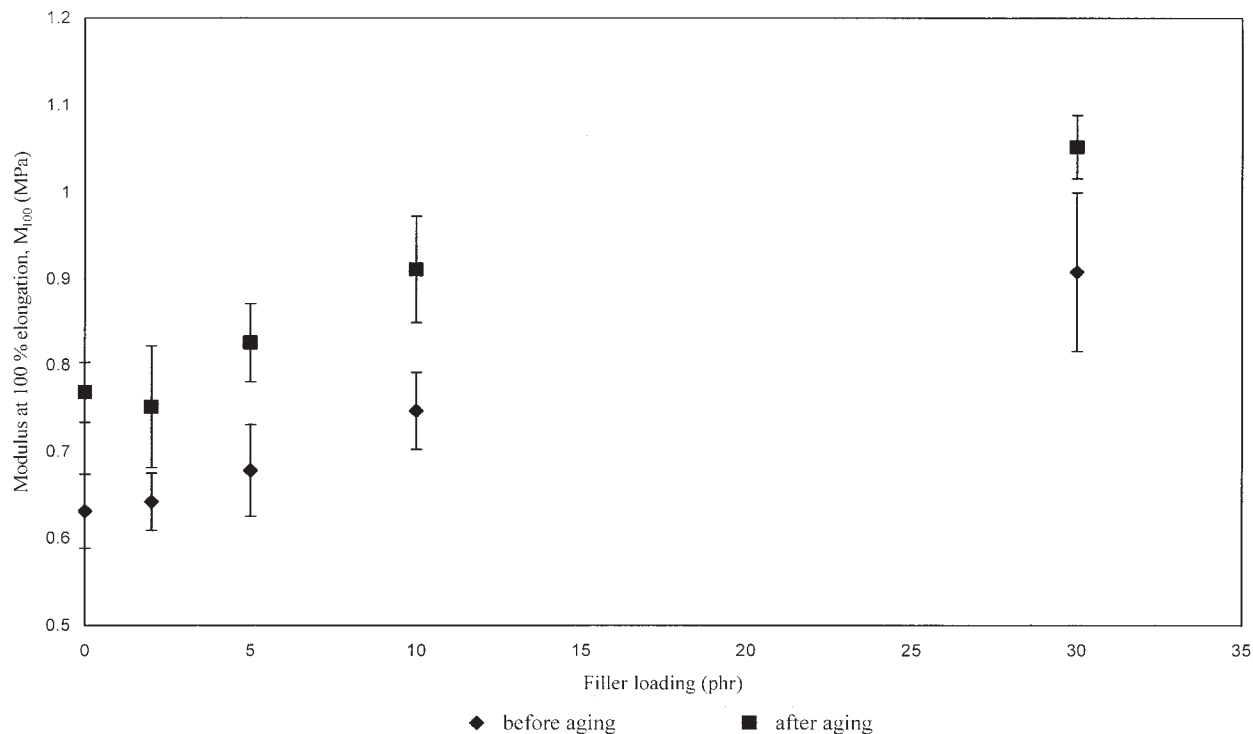
Figure 3 Effect of filler loading on the modulus at 100% elongation (M_{100}) of prevulcanized natural rubber latex films before and after ageing.

giving extra reinforcement to the samples while calcium carbonate is being embedded in the rubber matrix. According to Blackley,[1] it is generally agreed that a prerequisite for reinforcement of a rubber vulcanizate by a particular filler is that there should be strong adhesive interaction between the
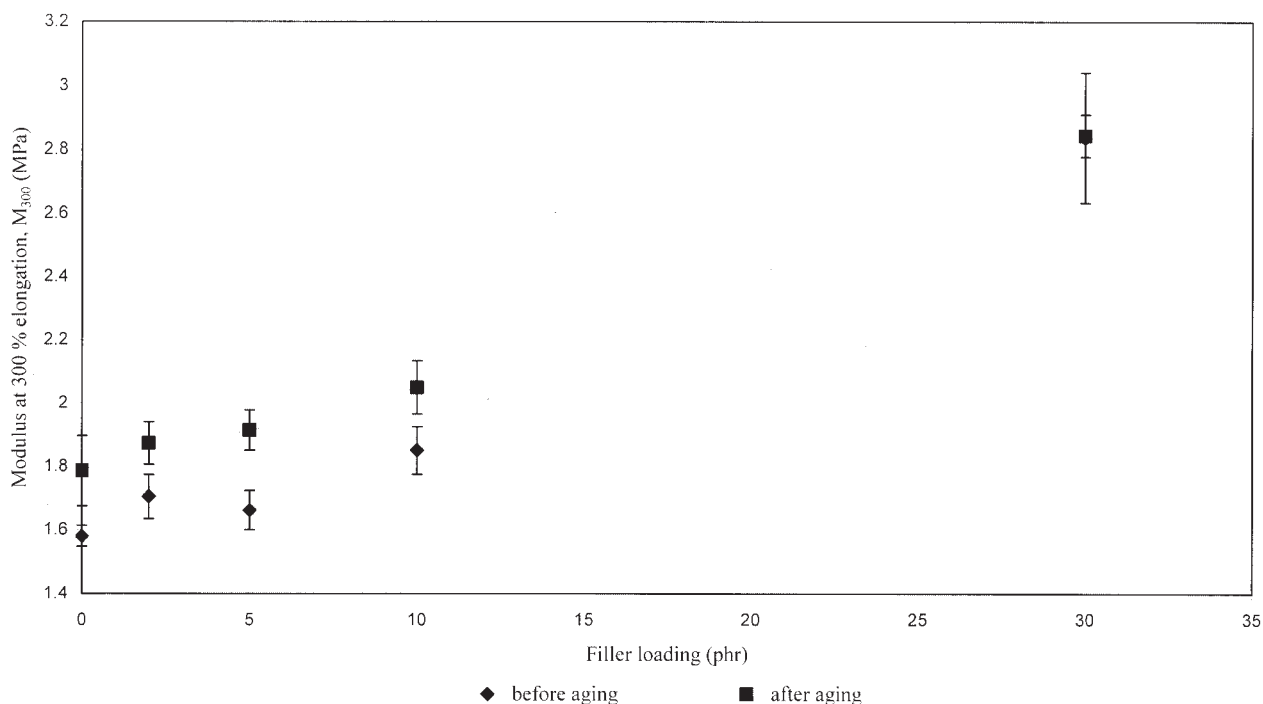

Figure 4 Effect of filler loading on the modulus at 300% elongation (M_{300}) of prevulcanized natural rubber latex films before and after ageing.
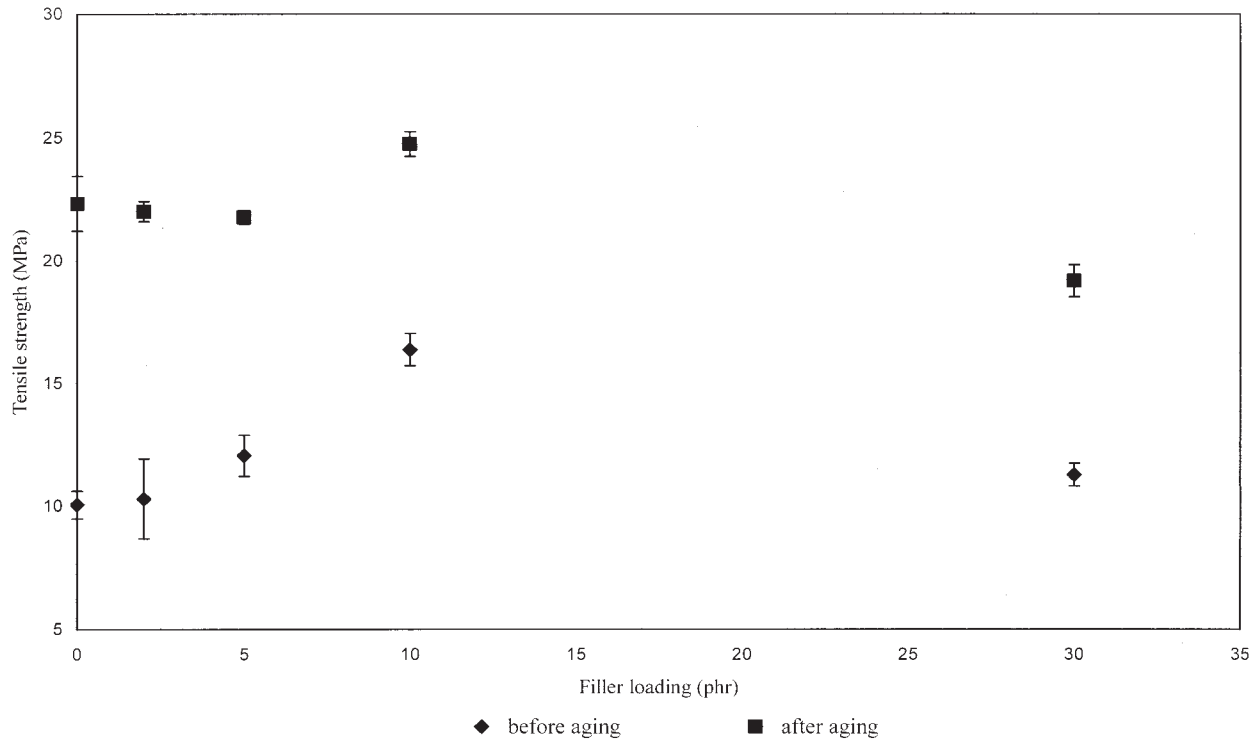
Figure 5 Relationship between filler loading and tensile strength of prevulcanized natural rubber latex films before and after ageing.

surface of the filler particles and the rubber matrix in which they are embedded.

At 30 phr of filler loading, the tensile strength decreased but the crosslink density (in reference to swell-ing index), M_{100}, and M_{300} showed an increase, as seen in Figures 2, 3, and 4, respectively. In their study on the characteristics of experimental *cis*-1,4 polyisoprene latices, Preiss et al.[10] reported that the decrease in
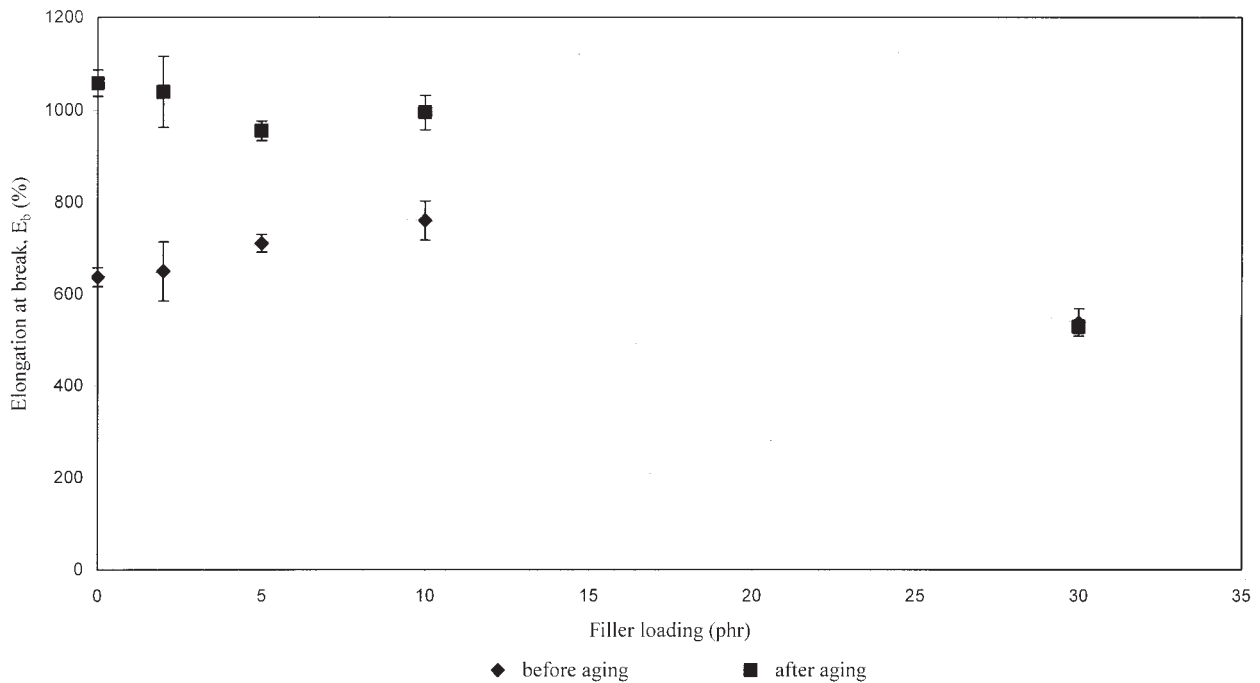

Figure 6 Effect of filler loading on the elongation at break of prevulcanized natural rubber latex films before and after ageing.
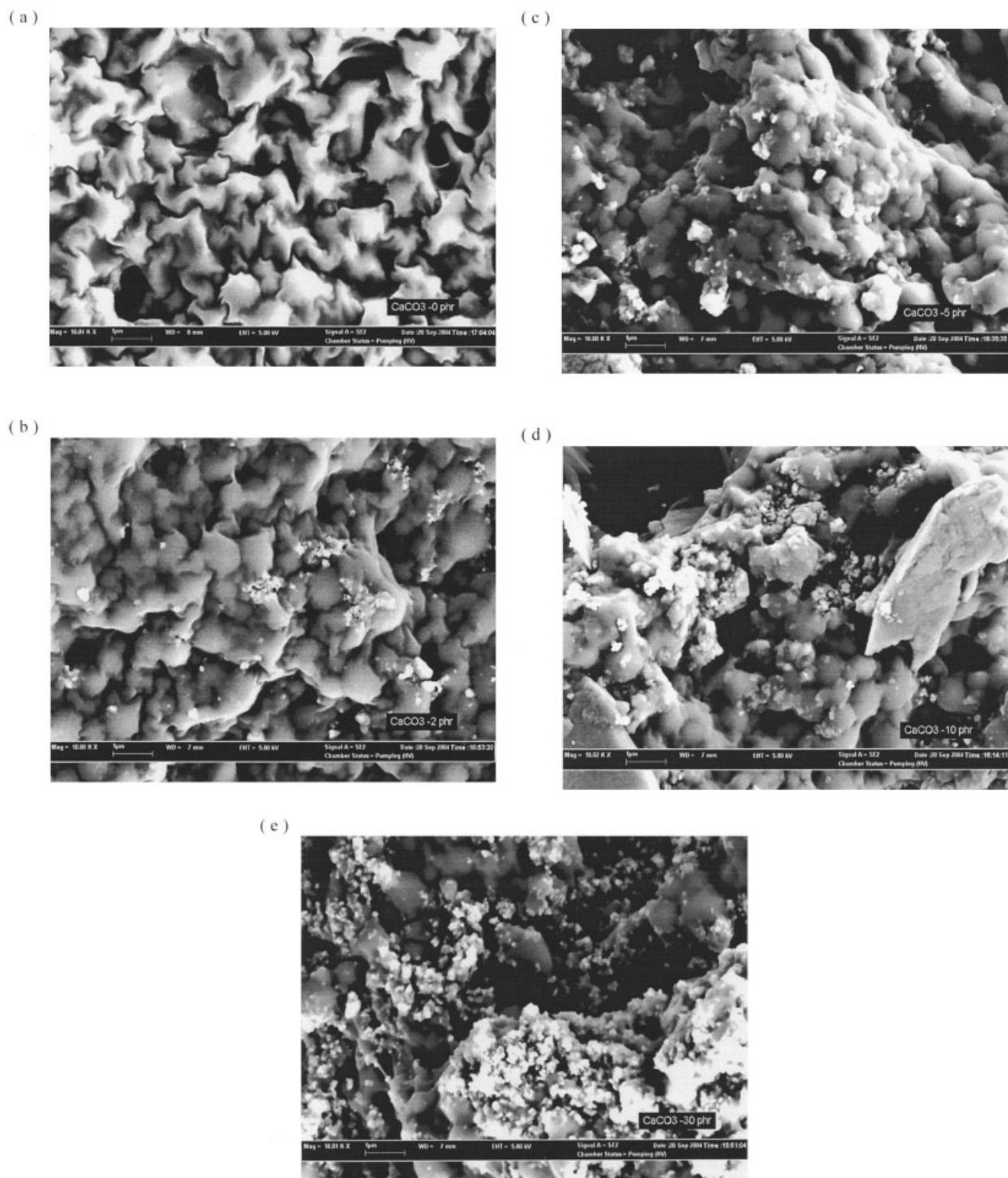
Figure 7 Morphology of fractured surface of tensile pieces with (a) 0 phr, (b) 2 phr, (c) 5 phr, (d) 10 phr, and (e) 30 phr of filler loading.

tensile properties with increasing crosslink density is a consequence of the decreasing ability of the latex particles to coalesce and integrate fully as the concentration of crosslinks in the particles increases. In this

study, the decrease in tensile properties at 30 phr of filler loading is attributed to an increase of filler to filler interaction compared to the filler to rubber interaction, which is needed to reinforce the rubber net-

work. As the filler content continues to increase above a critical level, the contact of rubber molecules with reinforcing agent particles tends to be saturated, the aggregates become larger, and the distance between the rubber particles increased, thus breaking down the monolithic construction of the material and finally diminishing the reinforcement effect, as reported by Cai et al.[11] in their study on the reinforcement of natural rubber latex film by ultrafine calcium carbonate.

Aged films have higher tensile strength than that of unaged films. The effect of applying heat to the room-temperature–cured prevulcanized latex films further increases the mechanical properties because the interactions between the curatives, filler, and rubber particles are increased, as evident from the apparent swelling index results, thus conferring to aged films higher tensile strength than that of unaged films.

Effect of filler on elongation at break

Figure 6 shows the effect of filler loading on the elongation at break (Eb) of the prevulcanized latex films before and after ageing. The results obtained showed the same trend as observed in Figure 5, with the Eb reaching a maximum at 10 phr of filler loading and then decreasing with further filler loading. Eb for aged films was higher than that of unaged films but showed a similar trend as that observed for unaged films with increasing filler loading. A valid explanation could not be provided at this moment because this is unusual for aged films to have higher Eb than that of unaged films, given that the aged films have been known to have higher crosslinking, as evidenced from Figure 2.

Effect of filler on morphology of films

Figure 7 shows the micrographs of fractured surfaces of tensile pieces with different filler loadings. As observed, it seemed that the size of the filler particles increases with filler loading, which suggests that agglomeration of the fillers took place in the films. Large agglomerates formed when the filler content was increased up to 30 phr, as shown in Figure 7(e). This results in a decrease in tensile strength and elongation at break of films, as shown in Figures 5 and 6. Improvements in tensile strength (Fig. 5) and Eb (Fig. 6) were observed, even though minor agglomerations were seen in films with 10 phr of filler loading because the fillers were well distributed in the samples.

CONCLUSIONS

The use of nanosized calcium carbonate fillers in a latex compound affects the prevulcanization time of the compound because the optimum prevulcanization time decreased with filler loading. The reduction of optimum curing time was a result of the increased interaction between the filler and rubber matrix, as reflected by the decrease in SI_{app}. The M_{100} and M_{300} values increased as a result of increased filler content. The tensile strength and Eb, however, increased up to 10 phr of filler loading before decreasing. FESEM micrographs showed that agglomeration of the fillers occurred as more filler was incorporated into the films. Aged films showed higher M_{100}, M_{300}, tensile strength, and Eb values, compared to those of unaged films, which is a result of enhanced interaction between the curatives with the fillers and the rubber molecules as heat was applied to the films.

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