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ORIGINAL PAPER

Improving oxidation stability and mechanical properties of natural rubber vulcanizates filled with calcium carbonate modified by gallic acid

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Abstract A novel technique to modify the surface of calcium carbonate ($CaCO_3$) nanoparticles, used as an antioxidant and reinforcing filler, by gallic acid is disclosed. The new properties of the modified $CaCO_3$ could make it more useful and practical for the rubber industry. Thermal gravimetric (TGA), Fourier transform infrared spectroscopy, and transmission electron microscopy analyses showed that the gallic acid was bound onto the surface of $CaCO_3$. The gallic acid modified $CaCO_3$ exhibited a significant antioxidation property, as revealed by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) analysis. The mechanical properties of natural rubber vulcanizates filled with the gallic acid modified $CaCO_3$ showed an enhanced reinforcement with increasing loading levels, and increased resistance to ozonolysis over that seen with the unmodified $CaCO_3$ mixed with Irganox 1010 as the commercial antioxidant.

Keywords Polymer composites · Modification · Mechanical properties · Calcium carbonate · Natural rubber

Introduction

In general, rubber products require not only reinforcement but also antioxidation behavior to improve their mechanical properties and extend the usage period of the products [1]. The principle reinforcing substances currently used are carbon black, calcium carbonate ($CaCO_3$), and silica (SiO_2) [2, 3]. $CaCO_3$ has long been recognized

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as a versatile additive for use in a wide range of plastic and elastomeric applications. Its regular and controlled crystalline shape and ultrafine particle size together with the hydrophobic surface coating are combined to the benefit for both rubber processing and subsequent physical properties. However, the size of the (nano-) particles for reinforcing substances plays an important role in the strengthening and toughening of rubber composites [4–6]. Additionally, many kinds of rubber, such as natural rubber (NR), styrene butadiene rubber (SBR), butadiene rubber (BR) and so on, have unsaturated carbon–carbon double bonds in the chemical structure. These double bonds can easily enter into additional reactions with sunlight, oxygen, ozone, or long term heating to degrade the rubber. In order to prevent the rubber material from degradation or extend the service lifetime, many antioxidant additives, such as UV absorbers, antioxidants, and light stabilizers, are used. Antioxidants are compounds which scavenge and destroy oxy radicals before they have a chance to react with the rubber molecules. Aromatic amines are the most effective primary antioxidants but they are discoloring and can only be used where tan or darker colors are acceptable. The other class of primary antioxidants is the phenolic antioxidants, which are generally used in non-black loaded products where the discoloration brought about by the amine antioxidants cannot be tolerated. In protecting the rubber vulcanizate, phenols may produce colored reaction products (yellow, tan, or pink) but the discoloration is significantly less than that produced with amines. Consequently, phenols are generally called “nondiscoloring” [7].

In order to improve the role of $CaCO_3$, acting as a reinforcing filler and an antioxidant, the surface of $CaCO_3$ should be modified. A fairly large amount of research has been reported on the surface modifications to $CaCO_3$ [8–10] and the effects of different modified $CaCO_3$ preparations on the properties of rubber [11]. The most widely used methods for surface modification are surface grafting and coupling [12–18]. In addition, chemical decomposition is a relatively new method for modifying the surface of inorganic particles [19]. In this study, the novel technique, developed to improve the properties of NR, is the modification of the $CaCO_3$ reinforcing filler surface with gallic acid, a natural phenolic compound that has a potent antioxidant ability. This new gallic acid modified $CaCO_3$ combines the properties of a reinforcement filler with an antioxidant activity, and could be an advantage, in terms of the low cost and low energy consumption, during the rubber processing. The surface modification of $CaCO_3$ by gallic acid was confirmed by thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), and transmission electron microscopy (TEM). The antioxidation activity of modified $CaCO_3$ was determined by 2,2-diphenyl-1-picrylhydrazyl (DPPH) testing. Finally, the reinforcing effect and ozone resistance of modified $CaCO_3$ in NR vulcanizate were investigated.

Experimental

Materials

Nano-$CaCO_3$ (Calshitec Brillant-1500) was provided by the Shiraishi Calcium (Thailand) Co., Ltd. Gallic acid was purchased from Fluka. Sodium hydroxide and calcium chloride were obtained from Carlo Erba and Anular, respectively. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was purchased from Sigma. Methanol, benzene, and ethanol were obtained from Fisher Scientific Ltd., and were used as received. Standard Thai Rubber 5L (STR5L), manufactured by Thai Hua Chumporn Natural Rubber Co., Ltd. (Thailand), was used as a raw rubber. Active zinc oxide (ZnO), stearic acid, sulfur, and *n*-cyclohexyl-2-benzothiazyl sulfenamide (CBS), used as curing reagents, were purchased from PI Industry Limited. Irganox 1010, as a commercial antioxidant, was provided by Ciba Specialty Chemicals (Thailand) Co., Ltd.

Surface modification of $CaCO_3$ and characterization of modified calcium carbonate

1 mol of gallic acid was dissolved in 200 mL of 3% (w/v) sodium hydroxide solution and the solution maintained within a pH range of 8–9. Next, $CaCO_3$, dispersed in 500 mL of 0.5 M calcium chloride solution, was added and the suspension was stirred at room temperature for 1 h before being filtered and the modified $CaCO_3$ washed with distilled water. The final product was dried in an oven at 80 °C until at constant weight. TGA of the unmodified and modified $CaCO_3$ was performed (TG/DTA PerkinElmer Pyris, Seiko Instruments Inc., Japan) by heating up to 1000 °C at a rate of 10 °C/min under air. The infrared spectrograph of the modified $CaCO_3$ was obtained using a Fourier Transform Infrared Spectroscopy (Thermo-470, USA). The morphology of the modified $CaCO_3$ was observed by TEM (JEOL, Japan) at an accelerating voltage of 200 kV.

Antioxidation activity of modified $CaCO_3$

The antioxidation activity of the modified $CaCO_3$ was determined by using the stable DPPH radical [20, 21]. 1 mg of modified $CaCO_3$ was dissolved in 1 mL of methanol and 20 μL of this solution was dropped onto the thin layer chromatographic (TLC) plate. The solution of DPPH in methanol was then sprayed onto the TLC plate. For comparison, the same concentration of gallic acid in methanol solution was used as the control sample.

Preparation of NR composite and mechanical properties

The rubber compound was prepared by conventional mixing on a two-roll mill. The formulations of the different rubber compounds are presented in Table 1, and their vulcanization (curing) was performed by compression molding at 150 kg/m^2 and heating to 150 °C for 15 min. The thickness of the rubber vulcanizate was ca. 2 mm.

The tensile properties were measured by a Universal Testing Machine (LR 10 K PLUS, Fareham, UK) with a load cell of 5 kN in accordance to ASTM-D412 at room temperature and a crosshead speed of 500 mm/min. The average value of five measurements is reported. The hardness was measured using a Shore-type-A Lever Loader (REX GAUGE 2000 & OS-2 Stand) according to ASTM D 2240.

Table 1 The formulations, in parts by weight per hundred parts of rubber (phr), of NR vulcanizates

Sample code	NR-S	CM-10S	CM-20S	CM-40S	CM-60S	C-10S	C-20S	C-40S	C-60S
M-$CaCO_3^a$	–	10	20	40	60	–		–	–
$CaCO_3$	–	–	–	–	–	10	20	40	60
Irganox 1010	–	–	–	–	–	1	1	1	1

[a] Modified calcium carbonate

All formulation in addition were composed of NR (100 phr), sulfur (2 phr), stearic acid (2 phr), active zinc oxide (5 phr) and CBS (0.5 phr) and all were cured for 15 min at 150 °C

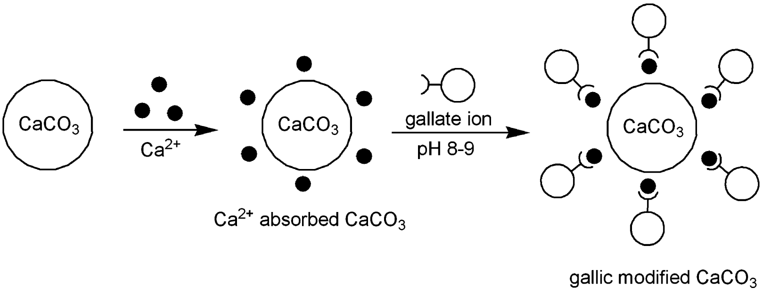
For testing the ozone resistance, NR samples were submitted to a deformation of 20% under stress using a sample holder and maintained for a 48 h period in a light and ozone-free atmosphere. The stretched sample was then exposed to an ozone atmosphere of 50 pphm (part per hundred million) at 40 °C for 48 h in an ozone cabinet (HAMPDEN, Northampton, England). The cracking traces on the rubber surfaces at a deformation of 20% stretch were examined by scanning with a CCD camera.

Results and discussion

Surface modification of $CaCO_3$

Due to the poor solubility of $CaCO_3$ in aqueous systems, the novel technique to modify the $CaCO_3$ surface by gallic acid was to introduce calcium ions (Ca^{2+}) onto the $CaCO_3$ surface in order to make the active site and ease the further reaction with the gallic acid (modifier). The mechanism of modification is proposed in Scheme 1. First, calcium ions generated by the $CaCl_2$ solution are absorbed onto the surface of $CaCO_3$ via an electrostatic interaction with the counter carbonate ion. The gallate ions generated in situ by the reaction between NaOH and gallic acid, within the pH range of 8–9, were then absorbed on the $CaCO_3$ particle via the electrostatic interaction with the Ca^{2+} seeding added previously. Finally, the desired product, gallic acid modified $CaCO_3$, was obtained and then characterized by using TGA, FTIR, and TEM analysis in order to confirm that the process of modification on the surface of $CaCO_3$ was successful.

A comparison of the TGA thermograms obtained from the unmodified and gallic acid modified $CaCO_3$ is shown in Fig. 1. Within the TGA curve of gallic acid modified $CaCO_3$, four main peaks were detected: the first and second peaks at 100 and 230–260 °C correspond to moisture ($\sim$5% by weight) and carbon dioxide being liberated upon heating, respectively, while the third peak at 300–500 °C probably corresponds to the further loss of either the hydroxyls or the residual decomposition of gallic acid [22]. Finally, the fourth peak at 600–770 °C ($\sim$30% weight loss) is due to the decomposition of $CaCO_3$ to calcium oxide and carbon dioxide. The approximate amount of gallic acid bound onto the surface of $CaCO_3$ particles was estimated to be about 25% by weight.



Scheme 1 The routes for synthesis of gallic acid surface modified $CaCO_3$

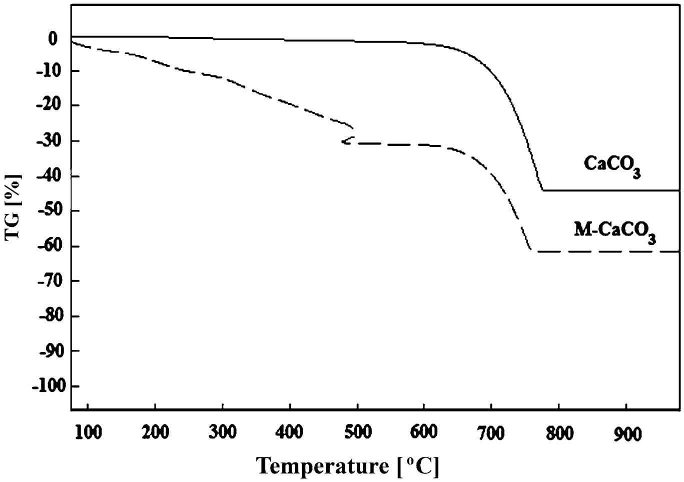


Fig. 1 Representative (TGA) thermal analysis curves of unmodified $CaCO_3$ ($CaCO_3$) and gallic acid modified $CaCO_3$ (M-$CaCO_3$)

From the FTIR spectrum of unmodified $CaCO_3$ (Fig. 2), the absorption peaks that appeared at 712.9, 874.9, 1506.1, 1794.4, and 2512.3 cm^{-1} are the characteristic absorption peaks of calcite $CaCO_3$ [23]. After the surface modification of $CaCO_3$ by gallic acid, the absorption peaks of gallic acid appeared at 1282.63 and 1303.06 cm^{-1} for C=C stretching and 1592.18 cm^{-1} for C=O stretching.

Representative TEM micrographs of unmodified and modified $CaCO_3$ show that the unmodified $CaCO_3$ was dispersed with some aggregates in benzene/ethanol solution and that the particles were in the size range of 100–200 nm (Fig. 3). The modified $CaCO_3$ particle size was larger with a much more aggregated structure, caused by the intermolecular interactions due to H-bonding of the modifiers. It is clearly seen that the gallic acid modifier formed a thin layer on the $CaCO_3$ surface (e.g. arrow in Fig. 3b), an observation which supports the notion that the $CaCO_3$ surface was successfully modified.

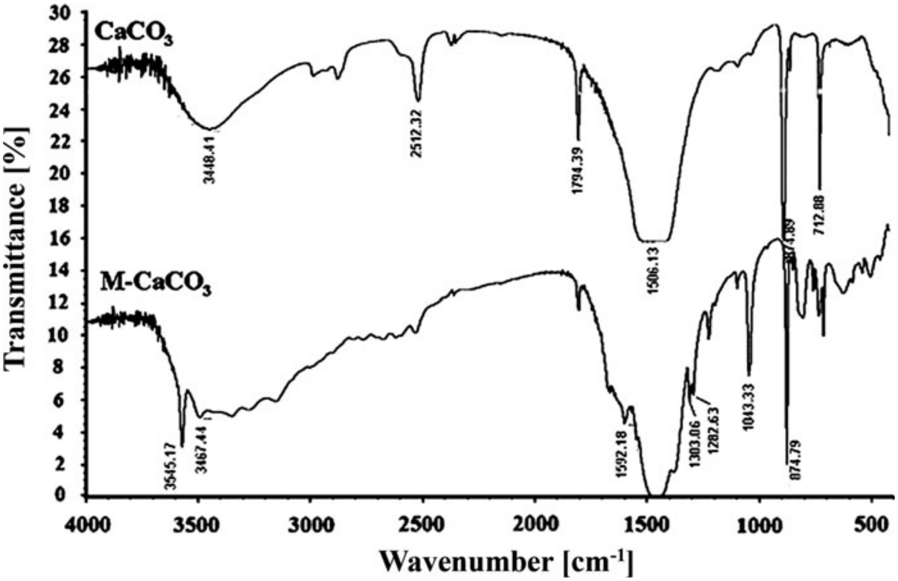


Fig. 2 Representative Fourier transformed infrared spectra of unmodified $CaCO_3$ ($CaCO_3$) and gallic acid modified $CaCO_3$ (M-$CaCO_3$)

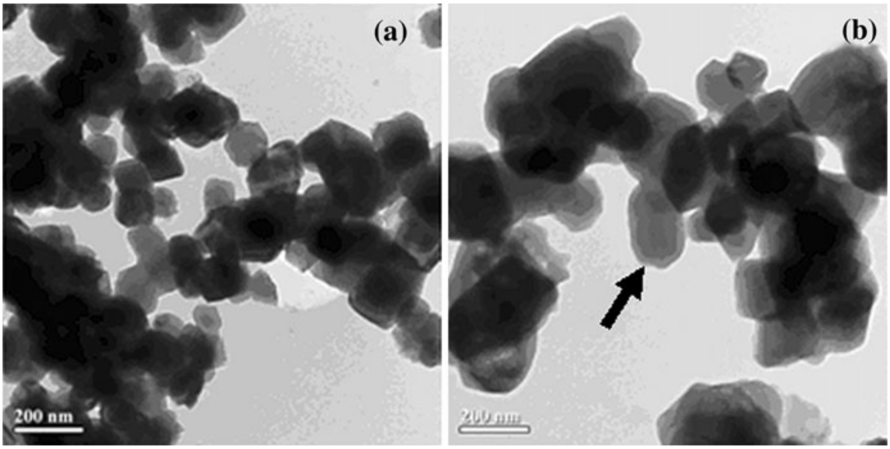
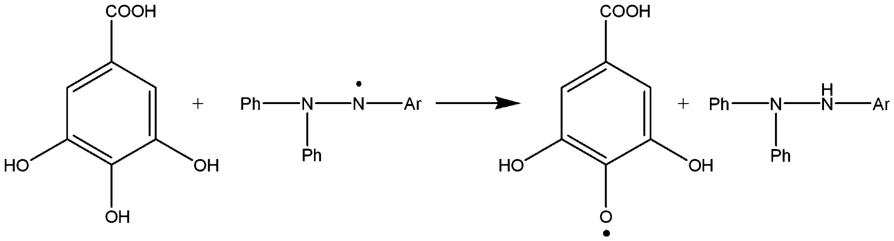


Fig. 3 Representative TEM photographs of **a** unmodified $CaCO_3$ ($CaCO_3$) and **b** gallic acid modified $CaCO_3$ (M-$CaCO_3$)

Antioxidant activity of modified $CaCO_3$

The antioxidant activity of the gallic acid modified $CaCO_3$ was determined by the radical scavenging activity method using DPPH. After spraying DPPH solution onto the TLC plate, sufficient time was allowed (about 10 s) for the DPPH to react not only with the modified $CaCO_3$ but also with the gallic acid as the reference. The



Scheme 2 DPPH radical scavenging mechanism of gallic acid

color of DPPH turned from purple to yellow, indicating that the odd electron of the DPPH radical had paired with hydrogen from a free radical scavenging antioxidant to form the reduced DPPH-H (Scheme 2) [24–27]. Accordingly, the gallic acid modified $CaCO_3$ had an antioxidant activity, as expected from its phenolic group.

Mechanical properties of modified $CaCO_3$ filled NR vulcanizates

The reinforcement of modified $CaCO_3$ was investigated in terms of moduli. The mechanical properties of NR vulcanizates filled with unmodified or modified $CaCO_3$ are shown in Fig. 4. For the tensile properties, the moduli of NR vulcanizates (Fig. 4a, b) increased with increasing filler contents (0–60 phr) for both unmodified and modified $CaCO_3$ compared to the NR vulcanizate without any reinforcing filler, presumably due to the reinforcement effect of the $CaCO_3$. For each level of filler content, the moduli of NR vulcanizates filled with the gallic acid modified $CaCO_3$ tended to be similar to that filled with unmodified $CaCO_3$, and so the gallic acid coating on the $CaCO_3$ surface does not inhibit the reinforcement effect of $CaCO_3$.

With respect to the tensile strength (T_B) of the NR vulcanizates, a biphasic response was seen with the T_B increasing as the unmodified $CaCO_3$ filling was increased up to a maximum value of 23.16 ± 0.07 MPa at a filler content of 40 phr. Thereafter, increasing the unmodified $CaCO_3$ contents further, up to 60 phr, the highest ratio tested, caused a decrease in the T_B of the NR vulcanizate (Fig. 4c). The addition of the modified $CaCO_3$ in place of the unmodified $CaCO_3$ differed in that the maximum T_B attained was 13.3% lower, at 20.06 ± 0.02 MPa, but was obtained with half the filler concentration (20 phr). Thereafter, the T_B decreased more markedly with increasing modified $CaCO_3$ contents (20–60 phr) than that seen with increasing levels of unmodified $CaCO_3$ contents.

The elongation at break (E_B) of NR vulcanizates (Fig. 4d) showed a triphasic response, initially decreasing with increasing unmodified $CaCO_3$ contents to a minimum value (620 ± 19%) at a $CaCO_3$ content of 20 phr, and then slightly increasing up to the maximum observed E_B (674 ± 12%) at a $CaCO_3$ content of 40 phr. Thereafter, the E_B declined with increasing unmodified $CaCO_3$ contents from 40 to 60 phr. The induced increase in E_B was more marked with the gallic acid modified $CaCO_3$ than that with the unmodified $CaCO_3$ addition, attaining a 5.8% higher maximum E_B value (713 ± 16%) at half the required filler content (20 phr).

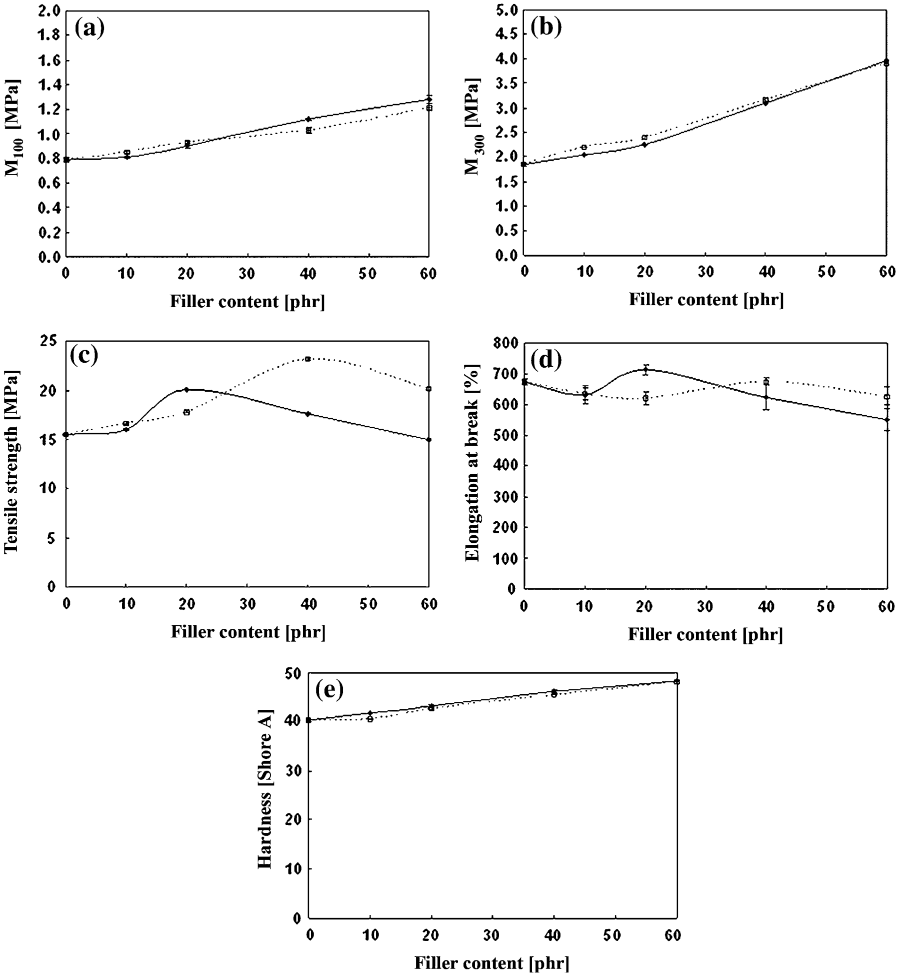


Fig. 4 Effect of filler content on mechanical properties of NR vulcanizates: *open square* unmodified $CaCO_3$, *filled diamond* gallic acid modified $CaCO_3$: **a** modulus at 100% elongation; **b** modulus at 300% elongation; **c** tensile strength; **d** elongation at break; **e** hardness

Thereafter, the E_B value declined slightly at a constant rate with increasing modified $CaCO_3$ contents.

According to these results, the values of T_B and E_B of modified $CaCO_3$ filled NR samples were lower than those of unmodified $CaCO_3$ filled NR ones, except for the inclusion of modified $CaCO_3$ at 20 phr where they were higher. The difference in the tensile properties between the unmodified $CaCO_3$ and the modified $CaCO_3$ filled NR vulcanizates may be due to the different surface properties of $CaCO_3$ [2]. When the inorganic particles are introduced into the rubbery matrix, they decrease the effective load-bearing cross-sectional area, which would reduce the tensile strength of the composites as the inorganic particle content was increased [28]. On the other hand, the aggregation of inorganic particles in the rubbery matrix reduces the contact area and creates physical defects in the rubber composites, all of which will decrease the effective interfacial interaction, and the T_B of rubber composites. This is in agreement with the TEM photographs (Fig. 3), which showed that the modified $CaCO_3$ was more aggregated than the unmodified $CaCO_3$. Finally, the hardness of composite materials (Fig. 4e) increased with increasing filler content for both $CaCO_3$ and the gallic acid modified $CaCO_3$. Additionally, the hardness of the modified $CaCO_3$ filled NR samples was comparable with that of unmodified $CaCO_3$ filled ones.

Morphology of modified $CaCO_3$ filled NR vulcanizates

The SEM photographs (Fig. 5) of the rubber composite materials clearly supported the above notion as to why similar mechanical properties for both $CaCO_3$ and gallic acid modified $CaCO_3$ filled NR vulcanizates were obtained. The white spots represent the filler particle and the black-toned color represents the NR matrix. The particles of either unmodified or modified $CaCO_3$ were dispersed homogeneously in the NR matrix, even at relatively high filler contents, although some aggregates were clearly observed in the modified $CaCO_3$ filled NR samples. Although the roughness of the rubber surface increased with increasing filler content, however, the compatibility between $CaCO_3$ (both unmodified and modified $CaCO_3$) and NR matrix could be obtained. Accordingly, it is inferred that the gallic acid did not affect the mechanical properties of NR vulcanizates.

Ozone resistance of modified $CaCO_3$ filled NR vulcanizates

The protection of rubber articles from ozone aging is of considerable interest to the industry since reaction of ozone with unsaturated elastomers results in decomposition and chain scission of the polymer [29, 30]. Chemicals are added to rubber products to impart effective resistance to ozone aging under both static and dynamic service conditions of the rubber articles. The effect of unmodified and modified $CaCO_3$ contents on the ozone resistance of the NR vulcanizates is shown in Fig. 6. Due to the presence of carbon–carbon double bonds in the backbone structure, NR is susceptible to degradation by ozone attack to form ozonides, which cause brittleness and the formation of macroscopic cracks on the surface of the rubber samples [31]. The cracking traces from ozonolysis were clearly observed on the surface of the NR vulcanizate after exposure to 50 pphm of ozone. In the modified $CaCO_3$ filled NR sample, a decrease in ozone cracking traces on the sample surface was obtained. The size of cracking traces of surface of NR vulcanizate filled with the unmodified $CaCO_3$ and the commercial antioxidant (Irganox 1010) was larger than that of the NR vulcanizates filled with the modified $CaCO_3$. Several theories of antiozonant protection of rubber have been proposed. They include the scavenger, protective film, relinking and self-healing film theories. The scavenger model proposes that the antiozonants diffuse to the rubber surface and react with ozone at a faster rate than ozone reacted with the backbone carbon–carbon double bonds of unsaturated elastomers [32, 33]. For the protective film theory, the antiozonant/ozone reaction products forming a thin film on the rubber surface can protect the rubber product

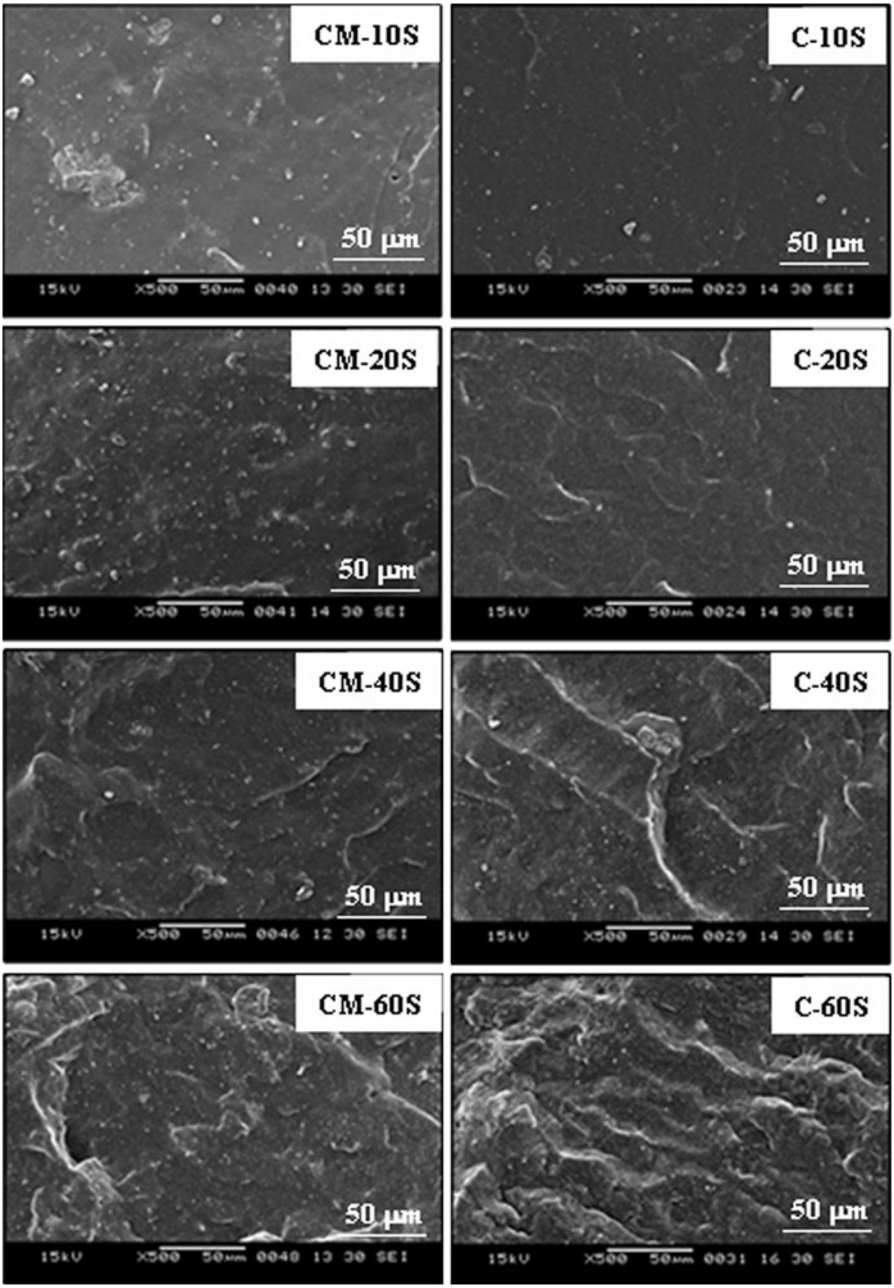


Fig. 5 Representative SEM photographs of NR vulcanizates filled with and without modified $CaCO_3$

[34, 35]. The relinking model has the antiozonant preventing polymer chain scission or causing bond recombination [36, 37]. The reaction of the antiozonant with the ozonized rubber or zwitterion (carbonyl oxide) could form a self-healing film on the

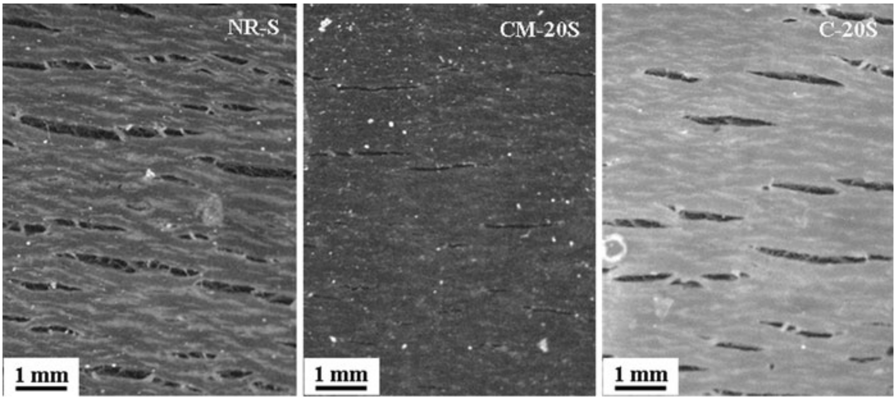


Fig. 6 Representative photographs of the stretched surface of NR vulcanizates after exposure to air with 50 pphm ozone at 40 °C for 48 h

rubber surface [38]. Based on our results, one possible mechanism which can describe the antiozonant function is that the antiozonant, hence gallic acid modified $CaCO_3$, could migrate to the surface of rubber, react directly with ozone (hence scavenging oxy radicals prior to reaction with double bond of rubber) and finally reduce the crack propagation rate. This result is in agreement with Scheme 2. However, there are other reactions such as a chain termination after oxy radicals reacted with rubber. Accordingly, the gallic acid modified $CaCO_3$ enhanced the resistance to ozonolysis of NR vulcanizates and can be used as the antioxidant to replace Irganox 1010 in NR vulcanizates.

Conclusions

Gallic acid surface modified $CaCO_3$ was successfully prepared by first introducing the Ca^{2+} ions onto the $CaCO_3$ surface. The possible mechanism of modification of $CaCO_3$ by gallic acid was proposed. The surface characterization of modified $CaCO_3$ determined by TGA and FTIR confirmed that the gallic acid as modifier had bound onto the surface of $CaCO_3$ to achieve good surface properties. According to TEM observations, the size of modified $CaCO_3$ became larger with a much more aggregated structure compared with the unmodified $CaCO_3$. The gallic acid modified $CaCO_3$ had an antioxidant activity, as evaluated by DPPH testing. The moduli and ozone resistance of the NR vulcanizates could be enhanced by increasing the modified $CaCO_3$ loading. Accordingly, compared with the unmodified $CaCO_3$, the gallic acid modified $CaCO_3$ greatly improved the antioxidation and reinforcing properties of NR vulcanizates and so has potential practical applications in rubber technology.

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