



Cure Characteristics and Physico-mechanical Properties of the Stearic Acid Surface of Modified Calcium Carbonate Reinforcement NR/SBR Compounds

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Abstract

Calcium carbonate is a cheap and readily available filler used in rubber industry. This material is not compatible with rubber matrix, so many researchers have tried to modify its surface with various materials in order to increase its hydrophobicity and improve compatibility with the rubber matrix. In this effort, surface modification of calcium carbonate was carried out by 1.5%, 3% and 4% stearic acid to achieve the technical knowledge of preparation method. The surface adjustments were investigated by Fourier transform infrared spectroscopy (FTIR), thermal analysis (TA), and scanning electron microscopy (SEM) and were compared with imported surface modified calcium carbonate (ISMCC) used in the rubber industry. Results showed surface modifications have been accomplished successfully. Furthermore, efficiencies of the prepared surface modified calcium carbonates (SMCCs) were investigated as fillers in the NR/SBR-based compounds. Cure characteristics and physico-mechanical properties of the compounds were considered and compared with reference compound that contained ISMCC. Using calcium carbonate modified by 3% stearic acid as a filler (SMCC(2)) not only preserved compound properties but also improved tensile properties, shortened the cure time and improved aging resistance in comparison with ISMCC.

Keywords: *Filler, Calcium carbonate, Stearic acid, Surface modification, NR/SBR.*

Introduction

The use of particulate fillers in rubber comes from early years of the rubber industry. Fillers

are added to rubber either to extend or cheapen the rubber compound or to add some desirable quality to the final compound and so increase

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serviceability of the end product [1]. Calcium carbonate is one of the most important non-black fillers used by volume and functionality for rubber compound. It is commercially available in large amounts at usable form and low cost [2]. It is known that hydrophilic character of calcium carbonate makes it difficult to disperse uniformly in polymeric matrix. Particulate calcium carbonate usually agglomerates, leading to the weakness of its interfacial interaction with polymer chain. In general, those zones of weaker cohesion are where flaws and other defects will be initiated upon stressing and cause failure of the rubber compound [3].

The affinity and activity of inorganic materials in relation to elastomers can be improved by certain surface modifications [4-6]. The surface of calcium carbonate is often rendered organophilic by a variety of surface modifiers such as silanes [7], phosphates [8], phosphonic acid [9], cationic polymer [10], palmitic acid [11] and stearic acid [12-16]. Among those mentioned, stearic acid is the most common surface modifier. This modification facilitates dispersion in the polymer nonpolar matrix as a consequence of reduction of the calcium carbonate surface energy and its polarity. The coated organic film represents the interface between the filler and the polymer matrix, and hence influences the wetting and adhesion

properties of two phases involved [17].

The aim of the present work is to modify the surface of calcium carbonate with stearic acid. Interaction between surface modified calcium carbonates (SMCCs) and NR/SBR based compound, according to cure characteristics and physico-mechanical properties for the vulcanizates were considered and compared with the compound that was contained imported surface modified calcium carbonate (ISMCC).

Experimental

Chemicals and reagents

Calcium carbonate with technical specification that is given in table 1, was obtained from Pars Jam, Iran. Meanland was supplied ISMCC. Stearic acid 95% was provided by Palmoleo Sdn., Bhd. Ethanol and acetone were purchased from Dr. Mojalali's Laboratories, Iran. SMR 20 (NR) with Mooney viscosity $M_L(1+100)@4$ oC of 52.5. SBR 1500 containing 23% styrene with Mooney viscosity $M_L(1+4)@100$ oC of 52 was obtained from Bandar Imam Petrochemical Company, Iran. CIIR was supplied by Exxon. Magnesium oxide 92% was provided by Sarbisheh Company, Iran. Carbon black N-660 was obtained from Iran Carbon Company. Behran Oil Company was supplied rubber process aromatic oil no. 290. Phenolic resin was purchased from Phenol Resin, Iran.

Table 1. Technical specifications of calcium carbonate.

Specific gravity	2.8
Oil absorption	25 ml/100 g
Particle size	8-10 μm
Surface area	1.1 m^2/g

Methods

Fourier transform infrared analysis (FTIR) was carried out by ATR cell FTIR Spectrum GX, Perkin-Elmer. The conditions were same for each set of the samples. Thermal analysis (TA) was performed by TA 1500, Scinco. Samples were heated in nitrogen atmosphere to 800 °C from room temperature at the heating rate of 20 °C/min. Scanning electron microscopy (SEM) was carried out by LMU, Tescan. Cure characteristics were measured at 180 °C with MDR 900, Hiwa Company according to ASTM D 5289. Mooney viscosity was determined by Hiwa 400, according to ISO 289. Compounds were cured in a laboratory press PTP 600, PGH Company at 180 °C and 220 KN. The swelling test was taken according to ASTM D 471. Hardness was measured by Hardnessmeter 49038 Shore A, Bareiss, according to ASTM D 2240. Tensile tests were performed on dumb-bell shaped specimens by M-350-5019, Testometric Company, according to ASTM D 412. Thermo-oxidative aging of vulcanized blends were studied according to ASTM D 573 and carried out in a laboratory type oven Elektro-mag Company with sensitivity of ± 1 °C. Compounds were prepared in an internal mixer Wellshayang, 2 L.

Surface modification of calcium carbonate by stearic acid

The procedure published by Mihajlovic et al. [18] was changed and was used for surface

modification. In experiments, 10 g of calcium carbonate was stirred in 100 mL warm distilled water (70 °C), and then 0.15 g of dissolved stearic acid in hot water was added to the suspension and stirred for 10 min. The suspension was filtered and was washed by ethanol, acetone and water. Obtained powder was dried at 110 °C and SMCC(1) was prepared. The same procedure was repeated by using 0.3 and 0.4 g of stearic acid to prepare SMCC (2) and SMCC (3) respectively. Modification of calcium carbonate was investigated by FTIR, TA and SEM techniques.

Compounds preparation

Compounds were prepared in an internal mixer Wellshayang 2 L to get homogenous mixtures and to minimize the influence of mixing conditions. The components were added to the mixer respectively in 20 minutes as follows in additional times:

- 0 min: NR (mastication)
- 1.5 min: SBR (blending of NR and SBR)
- 3 min: CIIR
- 6 min: carbon black and other chemicals
- 10 min: oil
- 20 min: discharge

Compounds formulation is shown in Table 2. Two surface modified samples SMCC (1) and SMCC (2) showed more similar characteristics to ISMCC according to FTIR, TA and SEM results, so SMCC(3) was not used for preparation of the compounds.

Table 2. Compounds formulation.

Compound name	C ₁	C ₂	C ₃	C ₄
Ingredients				
NR	20	20	20	20
SBR	15	15	15	15
CIIR	66	66	66	66
MgO	0.155	0.155	0.155	0.155
C-N 660	57	57	57	57
ISMCC^a	51	-	-	-
Calcium carbonate	-	51	-	-
SMCC(1)^b	-	-	51	-
SMCC(2)^c	-	-	-	51
Stearic acid	2.032	2.032	2.032	2.032
Phenolic resin	1.02	1.02	1.02	1.02
Aromatic oil	20.4	20.4	20.4	20.4

^aISMCC: Imported surface modified calcium carbonate

^bSMCC(1): Calcium carbonate+1.5% stearic acid

^cSMCC(2): Calcium carbonate+3% stearic acid

Results and discussion

Characterization tests FTIR spectra

Chemical structures of calcium carbonate and stearic acid are shown in Figure 1.

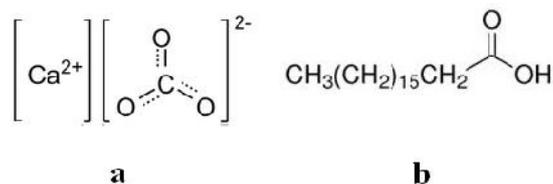


Figure 1. Chemical structures, a: Calcium carbonate, b: Stearic acid.

To confirm that stearic acid was successfully coated on the surface of calcium carbonate, the samples were characterized by FTIR, and results are shown in Figure 2. Characteristic absorption peaks of calcium carbonate (a) are at 1405, 858 and 765 cm^{-1} [19]. In pure stearic acid spectrum (b), there is an absorption peak at the wave number of 3000 cm^{-1} due to stretch vibration of O-H group which is usually overlapped with the absorption band of aliphatic C-H vibrations at 2918 cm^{-1} and 2849 cm^{-1} . The peak at 1702 cm^{-1} represents

characteristic absorption peak for the stretching vibration of carbonyl group. The peak at 1463 cm^{-1} indicates the -CH₂ bending peak and 1432 cm^{-1} represents C-H bending and 1160 cm^{-1} shows the C-H stretches. After modification (c,d,e), shape of the peak at 1405 cm^{-1} was changed and the peak at the band of 1087-1089 cm^{-1} is appeared for different SMCCs due to the existence of C-H stretches. This peak is also seen for ISMCC (f). These evidences can be demonstrated modification of the samples.

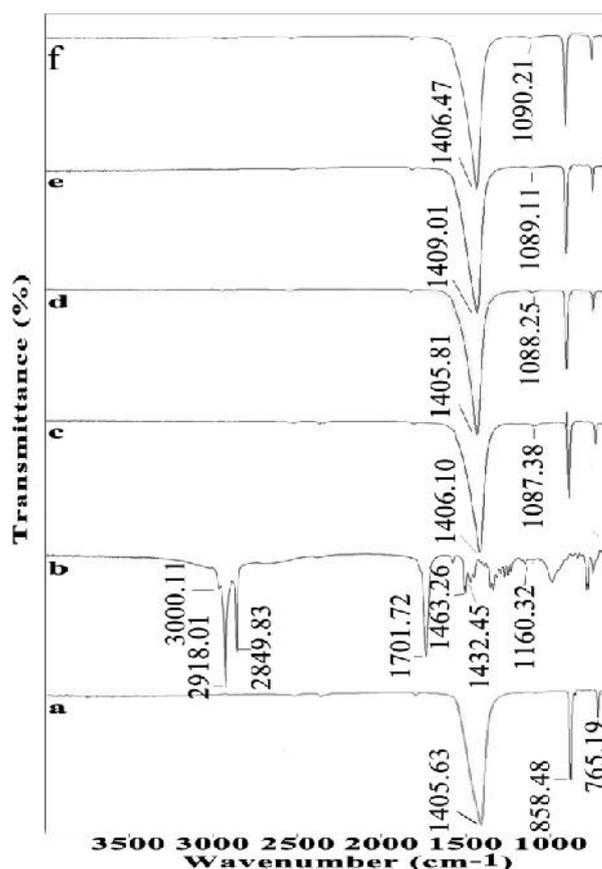
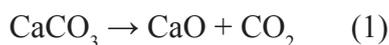


Figure 2. FTIR Spectra, a: Calcium carbonate, b: Stearic acid, c: SMCC(1) d: SMCC(2), e: SMCC(3), f: ISMCC.

Thermal analysis

Thermal Analysis (TA) of the samples are shown in Figure 3. In Thermal gravimetry analysis (TGA), calcium carbonate (a) has 44% weight loss in the temperature range 500-800 °C due to removal of carbon dioxide according to the reaction 1.



Thermal degradation of stearic acid (b) is seen in temperature range 200-400 °C. Three modified samples show 1.35% (c) 2.134% (d) and 3.71% (e) weight losses respectively in

this temperature range. ISMCC (f) also has 2.03% weight loss.

Differential Thermal Gravimetry (DTG) analysis results for the samples is shown the thermal degradation peak of stearic acid (b) in the temperature range of 200-400 °C which is also observed for SMCCs and ISMCC. Differences among the decomposition behavior of the samples before 500 °C can be confirmed the modification of calcium carbonate. SMCC (1) and SMCC (2) showed more similar behavior to ISMCC.

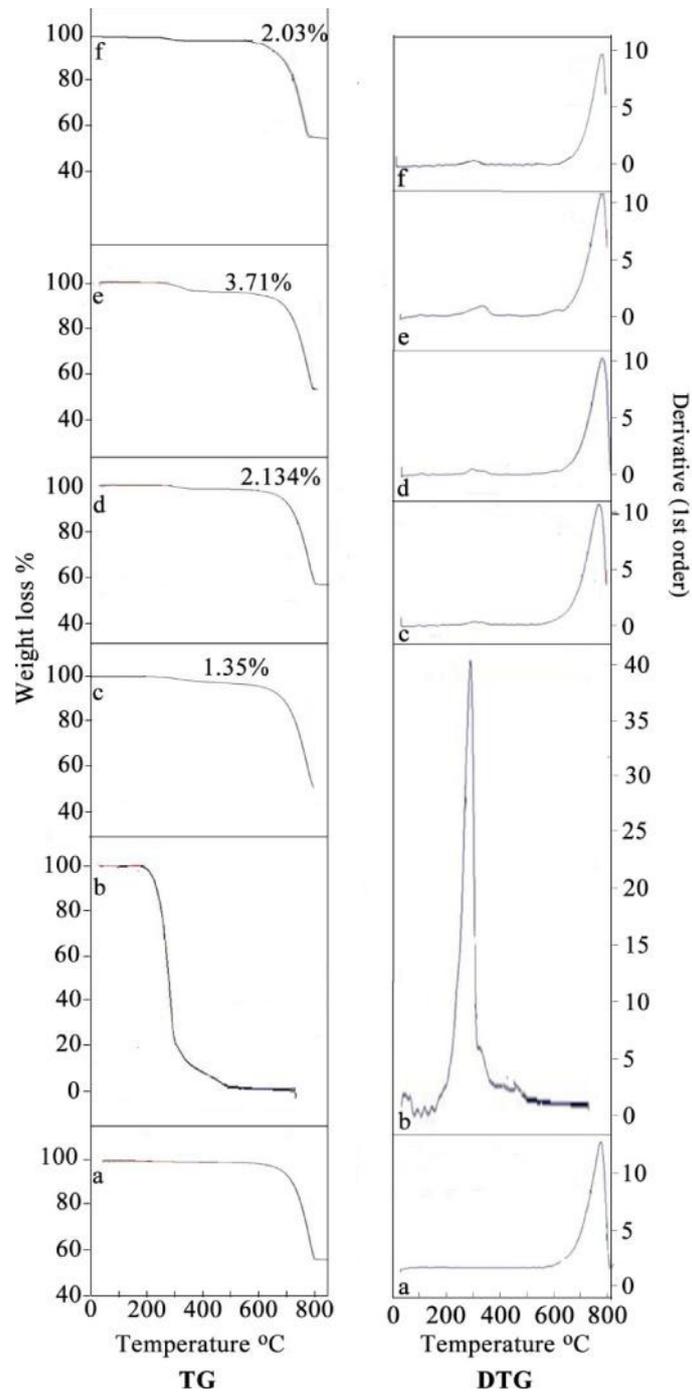


Figure 3. TG/DTG diagrams, a: Calcium carbonate, b: Stearic acid, c: SMCC(1) d: SMCC(2), e: SMCC(3), f: ISMCC.

Scanning electron microscopy (SEM) images Morphologies of the samples are shown in Figure 4. Approximately larger particles are seen after modification. SMCC (1) and SMCC

(2) are represented more similar morphology with ISMCC, while higher degree of aggregation is observed by SMCC (3).

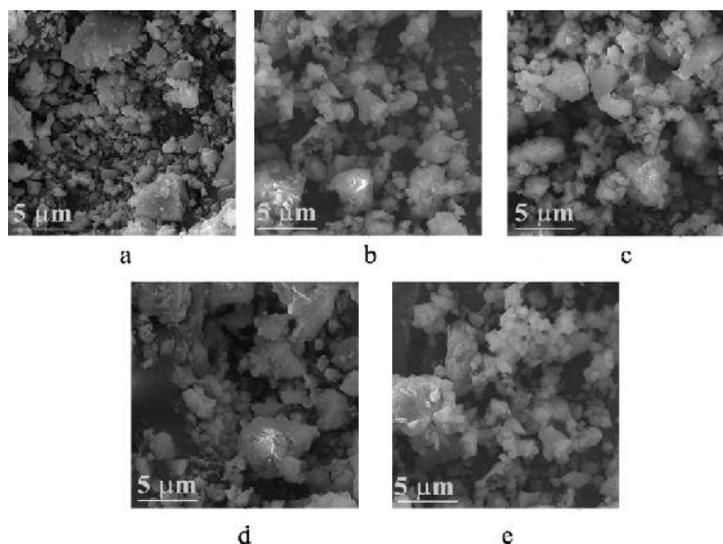


Figure 4. SEM images, a: Calcium carbonate, b: SMCC(1) c: SMCC(2), d: SMCC(3), e: ISMCC.

Cure characteristics

Cure characteristics of the compounds were tested and are summarized in Table 3. Torque changes after curing of the compounds (M_H - M_L) represents creation of the cross-links and state of the interactions between the components in the mixture. This parameter was increased after modification of calcium carbonate, which may show a better distribution of filler in the rubber matrix and improvement of the reinforcement effects.

Scorch time (T_{s_2}), the time required for the beginning of the cross linking process, decreased after modification of calcium

carbonate. It would have resulted by earlier start of vulcanization process due to the distribution of the filler and better dispensation of heat within the compound.

T_{c90} , the time to reach 90% of the maximum torque, was decreased by using the SMCCs. It might be showed the faster vulcanization process due to the better distribution of the filler that may also spread the curing agent repartition.

According to the results, preparation of C_3 and C_4 are more economically efficient in comparison with C_1 because of shorter curing time.

Table 3. Cure characteristics of the compounds.

Compound name	C_1^a	C_2^b	C_3^c	C_4^d
Rheological properties				
M_H - M_L (dN.m)	3.311	2.759	3.035	3.311
T_{s_2} (s)	290	393	278	242
T_{c90} (s)	570	523	436	504

^a- Compound which contains ISMCC

^b- Compound which contains calcium carbonate

^c- Compound which contains SMCC(1)

^d- Compound which contains SMCC(2)

Mooney viscosity

Viscosity of the rubber compound plays vital role in deciding its processing behavior. The

Mooney viscosities of the compounds were tested and are summarized in Table 4.

Table 4. Mooney viscosity of the compounds.

Compound name	C ₁ ^a	C ₂ ^b	C ₃ ^c	C ₄ ^d
Mooney viscosity				
M ₁ (1+4) (Mooney)	33.65	37.58	37.53	39.06

^a- Compound which contains ISMCC

^b- Compound which contains calcium carbonate

^c- Compound which contains SMCC(1)

^d- Compound which contains SMCC(2)

As it is shown, the Mooney viscosity for the samples didn't have significant changes after modification. This might be caused by uniform distribution of the molecular weight in the blend. The Mooney viscosity was a bit higher for C₃ and C₄ in comparison with C₁ but it stayed on acceptable range for the selected compound.

Swelling

The swelling test was taken by using toluene

as solvent at 25 °C for 166 h and the percent change in mass was calculated by equation 1 and is shown in table 5.

$$\% \Delta M = \frac{M_2 - M_1}{M_1} \times 100 \quad (1)$$

where:

ΔM = Change in mass (%)

M₁ = Initial mass of specimen (g)

M₂ = Mass of specimen after immersion (g)

Table 5. Swelling test of the compounds.

Compound name	C ₁ ^a	C ₂ ^b	C ₃ ^c	C ₄ ^d
Change in mass by swelling (%)	32	35	38	27

^a- Compound which contains ISMCC

^b- Compound which contains calcium carbonate

^c- Compound which contains SMCC(1)

^d- Compound which contains SMCC(2)

The influence of using SMCC(2) on change in mass by swelling is considerable. This value is proportional to the rubber-filler interaction and was shown the improved interaction.

Physico-mechanical properties

The compounds physico-mechanical properties

before and after aging are presented in Table 6. Thermo-oxidative aging of vulcanized blends were studied by aging for 96 hours at 100 °C. The properties of the compounds were measured after 24 hours of aging test. Percentage of retention in properties of the specimens was calculated by equation 2.

$$\% \text{ Retention} = \frac{\text{Value after aging}}{\text{Value before aging}} \times 100 \quad (2)$$

Table 6. Physico-mechanical properties of the compounds.

Property		Compound name			
		C ₁ ^a	C ₂ ^b	C ₃ ^c	C ₄ ^d
Hardness	Before aging (Shore A)	53.2	47.2	46.4	53.4
	After aging (Shore A)	52.1	45.4	44.6	52.4
	Retention (%)	97.9	96.2	96.1	98.1
Tensile strength	Before aging (MPa)	5.36	5.25	4.91	5.66
	After aging (MPa)	4.85	4.35	4.01	5.23
	Retention (%)	90.48	82.85	81.67	92.40
Elongation at break	Before aging (%)	396.87	411.82	376.23	375.37
	After aging (%)	320.21	326.77	290.55	309.67
	Retention (%)	80.68	79.34	77.22	82.49
Modulus 100%	Before aging (MPa)	1.52	1.56	1.48	1.83
	After aging (MPa)	1.29	1.31	1.17	1.61
	Retention (%)	84.87	83.97	79.05	87.97
Modulus 300%	Before aging (MPa)	4.06	4.06	4.07	4.99
	After aging (MPa)	3.52	3.49	3.38	4.59
	Retention (%)	86.69	85.96	83.04	91.98

^a- Compound which contains ISMCC

^b- Compound which contains calcium carbonate

^c- Compound which contains SMCC(1)

^d- Compound which contains SMCC(2)

Hardness may be defined as the resistance to indentation under conditions that do not puncture the rubber. This property was increased after modification in C4 and its value is close to C1. This behavior confirmed the improvement of the filler reinforcement effect. Tensile strength of rubber compound (its resistance to rupture under tension) was not changed significantly. Fillers with strong chain attachments through active sites provide the most resistant to chain extension and separation required for elongation. This case caused decrease in elongation after modification in C4. The force required to stretch a defined specimen of rubber to a given percent of elongation is measured as modulus. Modulus 100% and modulus 300% were increased for the compound C4.

Higher surface activities effectively increased the surface area exposed to the elastomer and increased the modulus. Result showed that the physico-mechanical properties depend on the aging and the values decreased. Higher retained values are also noticed that SMCC (2) improves the aging resistance.

Conclusion

Based on the results obtained from this work, the following conclusion can be drawn:

1. The surface of calcium carbonate was successfully modified by stearic acid and the modification was confirmed by FTIR spectra, TG/DTG analyses and SEM images.
2. Curing of the compounds by using the prepared SMCCs were more economically

efficient in comparison with ISMCC because of the shorter curing time due to the better hydrophobicity and better dispensation of heat within the compound.

3. Modification of the calcium carbonate by 3% stearic acid was improved the tensile properties because of the higher surface activity.

4. ISMCC could be successfully substituted by SMCC (2) in the compound formulation.

5- SMCC (2) was improved the aging resistant.

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