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Improve of rubber physical properties with addition of waste calcium carbonate

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Abstract
In the present study, the effects of waste calcium carbonate on properties of rubber were investigated. The rubber samples were prepared with weight percentage 15Wt% of waste calcium carbonate (four different samples), pressed in 4MPa and sintered at 1500C for 60 minutes. The properties such as hardness, elongation at rupture, tensile strength and 300% modulus were measured. The chemical analysis of calcium carbonate was investigated through X-Ray Fluorescence method (XRF) and sizing distribution of calcium carbonate were carried out through Laser Particle Size Analyzer device (LPSA). The results indicated that by increasing the waste calcium carbonate weight percentage up to 15Wt%, the physical properties of the rubbers improved. Also, more increasing the waste calcium carbonate led to decrease in favorable properties and standard.

Key words: rubber, waste calcium carbonate, additive, physical properties.

1. Introduction

Calcium carbonate (CaCO3) powder is a common filler in many industries, including in the rubber industry where it is used in the production of rubbers (Boynton 1980, Lefond 1983). Substituting a small percentage (3–5%) of the carbon black in a rubber with CaCO3 can decrease the rubber density and increase mechanical strength (by 40–45%), which increases its service life (Kauffman et al. 1974, Von Flotow & Etkin 1981, Bagghi & Sharma 1981, Gent 2001, Ai-lon 2012). Calcium carbonate is preferred over other fillers, such as barium sulfate (barite), aluminum silicate (kaolin), mica, pyrophyllite, silica, slate and magnesium silicate (talc) (Katz 1987), because it imparts softness, smoothness, resistance to abrasion, friction, erosion, and fire, and increases the flexibility and mechanical strength of the rubber (Poompradub 2010).Natural CaCO3 can be obtained from calcite and aragonite in mines. This CaCO3 can be found in limestone, spot disland, and other types of rock. Waste CaCO3 powder is produced as a by-product in stone sawing factories with a typfical particle size of 0.5–1µm (Strutz & Sweeney 1990). CaCO3 powder can also be produced by reaction of carbon dioxide with calcium hydroxide.

$Ca(OH)2 + CO2 \rightarrow CaCO3$

Table 1. Properties of calcium carbonate (Bagghi & Sharma 1981, Richard & Lewis 2004)

Chemical formula	CaCO3
Appearance	White solid
Crystalline structure	Hexagonal, Orthrombic
Refractive index	1.658
Molecular weight	100.09 gr
Specific gravity	2.7 g/cm3
Boiling point	899 °C
Melting point	825 °C

The precipitated CaCO3 has high purity (98–99%) and can be produced with a specific crystal morphology (Strutz & Sweeney 1990).
In this research, application of waste CaCO3 powder as a filler in rubber production was investigated.

2. Experimental

2.1. Sample Collection

Samples were collected from stone sawing factories around Neyriz, Iran. There are about 175 stone sawing factories in this region, and all of them produce CaCO3 powder. Each factory produces about 10 t (1 t = 1000 kg) of pure and micronized CaCO3 powder daily, which could be used as a fillers in many industries.

2.2. Sample characterization

The samples were dried before analysis. Particle size analysis (PSA) (SALD-2101, Shimadzu, Kyoto, Japan, ISO/IEC 17025 standard) was conducted at the Pharmacological School of Shiraz University (Shiraz, Iran), and included measurement of the number of particles, and the longitudinal and surface area equivalent diameters of the particles. X-ray fluorescence (XRF) (PW 1480, Philips, Amsterdam, Netherlands) was used to determine 32 elements in the samples. This analysis was conducted at Kansaran Binaloud Labratory (Tehran, Iran). After analysis, the CaCO3 powder was used as a filler in production of rubber at Dena Tire Manufacturing Company (Shiraz, Iran). After weighing the basic raw materials for rubber production (Table 2), the material was mixed in a mill for 6 min, and curing agents and accelerators were added during this time. The compound produced was extruded through two rollers on the mill. Various grades of rubber compounds were produced, and used to manufacturer parts. The vulcanization was carried out in a hydraulic press under a pressure of about 4 MPa, temperature of 150°C for 60 minutes. In the final stage, the rubbers were formed and reached their maximum values for dynamic-mechanical properties and tensile strength. The rubbers were tested for hardness, tensile resistance, percentage of elongation at rupture, and stress at 300% strain (300% modulus).

Table 2. Composition of the rubber mixture used for tire production

Material	Proportion (g)
Natural rubber (SMR 20)	100
Oil (Behran 840)	8
Stearic acid	2
Black N_550 (reinforcement)	30
ZnO2 powder (reinforcement –filler)	3.5
Waste CaCO3 powder (reinforcement –filler)	15
MBTS (accelerator)	0.4
Sulfur (curing agent)	3

3. Results and Discussion

3.1. Characterization of the CaCO3 powders

All four CaCO3 samples gave similar results for LPSA. Therefore, the results for only one of these samples are presented in this section. The particle size distribution (Figure 1) showed that the mean size was 0.597 µm (range 0.365–35.701µm), the mode was 0.562 µm, and the median was 0.561 µm. Based on the longitudinal equivalent diameter (Figure 2), the mean particle size was 0.761 µm (range 0.365–124.573 µm), the mode was 0.562 µm, and the median was 0.634 µm. Based on the surface area equivalent diameter (Figure 3), the mean particle size was 1.925 µm (range 0.365–188.947 µm), the mode was 0.562 µm, and the median was 1.281 µm.

3.2. Chemical Analyses

The XRF results (Table 3) showed that the samples contained 0.17 % (Al2O3 + Fe2O3) and 0.35 % MgO on average.

Table 3. XRF results for the CaCO3 powder samples.

Sample No.	CaO %	SiO_2 %	Fe_2O_3 %	MnO %	MgO %	Al_2O_3 %	K_2O %	Na_2O %	TiO_2 %	P_2O_5 %	L.O.I %
1	54.72	0.53	0.06	0.001	0.34	0.05	0.03	0.08	0.011	0.067	43.66
2	53.65	0.65	0.08	0.002	0.33	0.08	0.03	0.09	0.010	0.071	43.46
3	54.32	0.56	0.15	0.001	0.39	0.07	0.03	0.14	0.008	0.059	43.51
4	54.31	1.05	0.13	0.002	0.35	0.06	0.05	0.10	0.016	0.062	43.11

Sample No.	SO_3 %	Cl ppm	Ba ppm	Sr ppm	Cu ppm	Zn ppm	Pb ppm	Ni ppm	Cr ppm	V ppm	Ce ppm	La ppm
1	0.128	1162	3	246	6	21	8	31	9	7	1	62
2	0.183	435	6	223	3	117	1	27	4	10	41	50
3	0.528	398	9	254	3	21	7	32	7	11	3	1
4	0.135	399	8	206	6	22	1	32	7	9	2	1

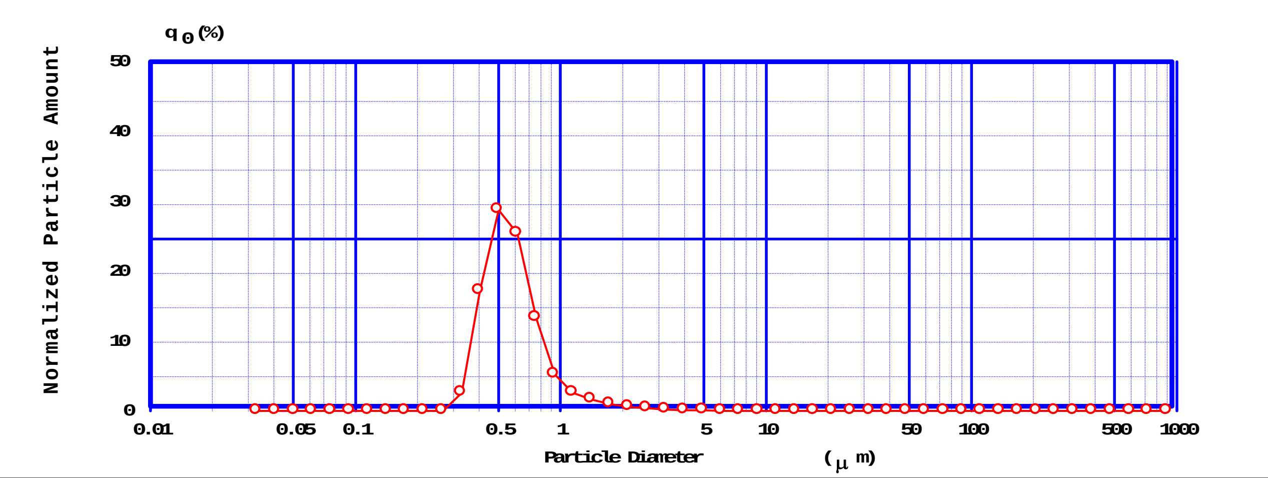
Table 3. XRF results for the CaCO3 powder samples (Continued).

Sample No.	W Ppm	Mo ppm	Ga ppm	Nb ppm	Zr ppm	Y ppm	Rb ppm	Co ppm	As ppm	U ppm	Th ppm
1	1	1	4	5	43	2	12	4	10	1	3
2	1	2	2	13	37	1	15	1	23	1	9
3	1	1	4	2	44	2	13	6	34	1	2
4	1	1	5	5	39	2	18	11	23	1	6

SHIMADZU SALD-2101 (SALD-2101-WEA1:V1.20)

(File Name) sample 3
(Sample ID) (Sample #)
(Date) 06/02/15 (Time) 21:59:41

R Index=1.60-0.10i | Median D : 0.561 | Modal D : 0.562 | Mean V : 0.597 | Std Dev : 0.166 | 10.0%D : 0.408 | 50.0%D : 0.561 | 90.0%D : 0.930 | S Level : 0 | D Func :None | D Shift : 0



	Diam x(μm)	Cum Q_0(%)	Diff q_0 (%)		Diam x(μm)	Cum Q_0(%)	Diff q_0 (%)		Diam x(μm)	Cum Q_0(%)	Diff q_0 (%)
1	1000.000	100.000	0.000	18	28.988	99.998	0.002	35	0.840	87.614	13.417
2	811.975	100.000	0.000	19	23.538	99.997	0.003	36	0.682	74.197	25.403
3	659.303	100.000	0.000	20	19.112	99.994	0.005	37	0.554	48.794	28.853
4	535.337	100.000	0.000	21	15.518	99.989	0.007	38	0.450	19.942	17.242
5	434.680	100.000	0.000	22	12.601	99.982	0.011	39	0.365	2.699	2.699
6	352.949	100.000	0.000	23	10.231	99.971	0.021	40	0.297	0.000	0.000
7	286.586	100.000	0.000	24	8.308	99.950	0.037	41	0.241	0.000	0.000
8	232.700	100.000	0.000	25	6.746	99.913	0.059	42	0.196	0.000	0.000
9	188.947	100.000	0.000	26	5.477	99.854	0.097	43	0.159	0.000	0.000
10	153.420	100.000	0.000	27	4.447	99.757	0.160	44	0.129	0.000	0.000
11	124.573	100.000	0.000	28	3.611	99.597	0.257	45	0.105	0.000	0.000
12	101.150	100.000	0.000	29	2.932	99.340	0.401	46	0.085	0.000	0.000
13	82.131	100.000	0.000	30	2.381	98.939	0.636	47	0.069	0.000	0.000
14	66.689	100.000	0.000	31	1.933	98.303	1.049	48	0.056	0.000	0.000
15	54.149	100.000	0.000	32	1.570	97.254	1.727	49	0.046	0.000	0.000
16	43.968	100.000	0.000	33	1.275	95.527	2.621	50	0.037	0.000	0.000
17	35.701	100.000	0.002	34	1.035	92.906	5.292	51	0.030	0.000	0.000

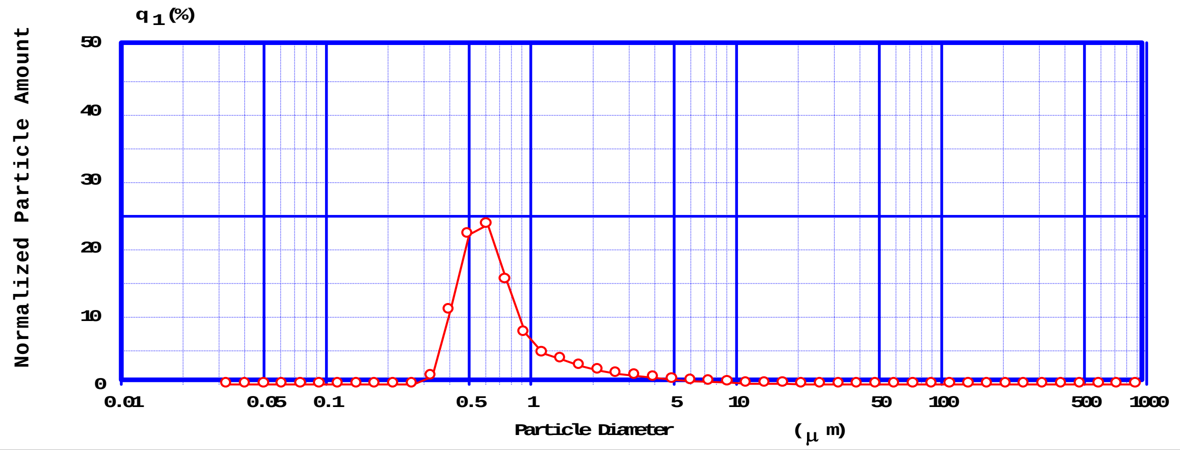
Sampling Mode : Manual Refractive Index : 1.60-0.10i
Signal Accumulation Count : 1 Interval (sec) : ___ Signal Averaging Count : 64
Max of Absorbance Range : 0.200 Min of Absorbance Range : 0.010
Ultrasonic Dispersion Time (sec) : ___ Waiting Time After Ultrasonic Dispersion(sec) : ___

Figure 1. Distribution of the particle sizes based on the numbers of particles

SHIMADZU SALD-2101 (SALD-2101-WEA1:V1.20)

(File Name) sample 3	
(Sample ID)	(Sample #)
(Date) 06/02/15	(Time) 21:59:41

R Index=1.60-0.10i	Median D : 0.634	Mean V : 0.761	10.0%D : 0.430	S Level : 0
	Modal D : 0.562	Std Dev : 0.278	50.0%D : 0.634	D Func :None
			90.0%D : 1.747	D Shift : 0



	Diam x(μm)	Cum Q1(%)	Diff q1(%)		Diam x(μm)	Cum Q1(%)	Diff q1(%)		Diam x(μm)	Cum Q1(%)	Diff q1(%)
1	1000.000	100.000	0.000	18	28.988	99.890	0.063	35	0.840	72.708	15.309
2	811.975	100.000	0.000	19	23.538	99.827	0.090	36	0.682	57.399	23.361
3	659.303	100.000	0.000	20	19.112	99.737	0.120	37	0.554	34.038	21.930
4	535.337	100.000	0.000	21	15.518	99.617	0.147	38	0.450	12.108	10.899
5	434.680	100.000	0.000	22	12.601	99.470	0.191	39	0.365	1.209	1.209
6	352.949	100.000	0.000	23	10.231	99.279	0.293	40	0.297	0.000	0.000
7	286.586	100.000	0.000	24	8.308	98.986	0.419	41	0.241	0.000	0.000
8	232.700	100.000	0.000	25	6.746	98.567	0.549	42	0.196	0.000	0.000
9	188.947	100.000	0.000	26	5.477	98.017	0.726	43	0.159	0.000	0.000
10	153.420	100.000	0.000	27	4.447	97.292	0.972	44	0.129	0.000	0.000
11	124.573	100.000	0.001	28	3.611	96.319	1.271	45	0.105	0.000	0.000
12	101.150	99.999	0.003	29	2.932	95.048	1.613	46	0.085	0.000	0.000
13	82.131	99.996	0.006	30	2.381	93.435	2.069	47	0.069	0.000	0.000
14	66.689	99.990	0.011	31	1.933	91.366	2.770	48	0.056	0.000	0.000
15	54.149	99.979	0.018	32	1.570	88.597	3.707	49	0.046	0.000	0.000
16	43.968	99.961	0.028	33	1.275	84.889	4.603	50	0.037	0.000	0.000
17	35.701	99.932	0.042	34	1.035	80.286	7.578	51	0.030	0.000	0.000

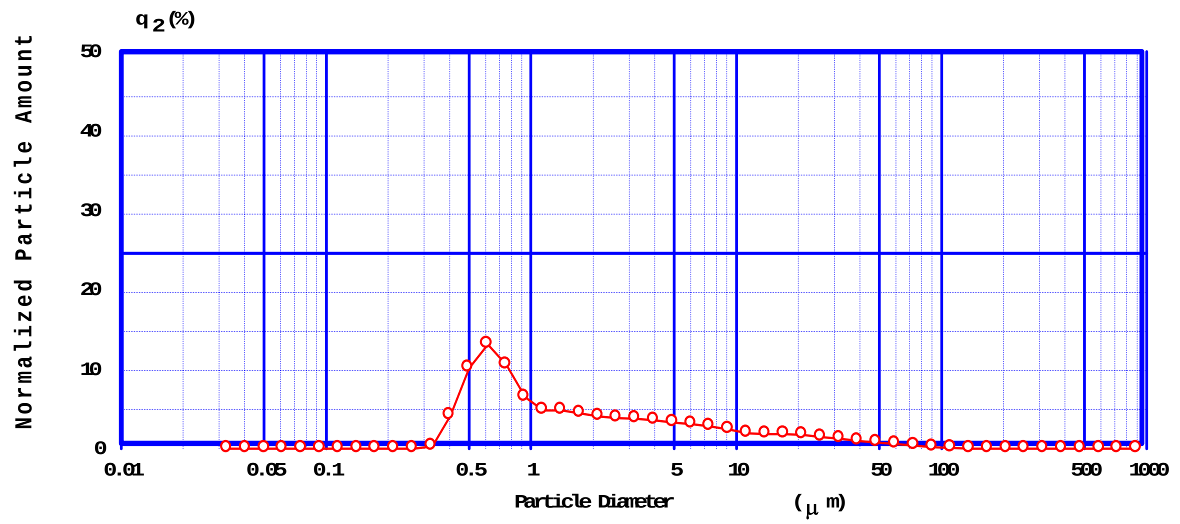
Sampling Mode : Manual Refractive Index : 1.60-0.10i
Signal Accumulation Count : 1 Interval (sec) : ___ Signal Averaging Count : 64
Max of Absorbance Range : 0.200 Min of Absorbance Range : 0.010
Ultrasonic Dispersion Time (sec) : ___ Waiting Time After Ultrasonic Dispersion(sec) : ___

Figure 2. Distribution of the particles size based on longitude equivalent diameter

SHIMADZU SALD-2101 (SALD-2101-WEA1:V1.20)

(File Name) sample 3
(Sample ID) (Sample #)
(Date) 06/02/15 (Time) 21:59:41

R Index=1.60-0.10i	Median D : 1.281	Mean V : 1.925	10.0%D : 0.511	S Level : 0
	Modal D : 0.562	Std Dev : 0.571	50.0%D : 1.281	D Func :None
			90.0%D : 15.009	D Shift : 0



	Diam x(μm)	Cum Q_2(%)	Diff q_2(%)		Diam x(μm)	Cum Q_2(%)	Diff q_2(%)		Diam x(μm)	Cum Q_2(%)	Diff q_2(%)
1	1000.000	100.000	0.000	18	28.988	95.488	1.507	35	0.840	38.417	10.603
2	811.975	100.000	0.000	19	23.538	93.982	1.765	36	0.682	27.814	13.135
3	659.303	100.000	0.000	20	19.112	92.216	1.911	37	0.554	14.679	10.213
4	535.337	100.000	0.000	21	15.518	90.306	1.897	38	0.450	4.466	4.170
5	434.680	100.000	0.000	22	12.601	88.408	2.008	39	0.365	0.296	0.296
6	352.949	100.000	0.000	23	10.231	86.400	2.492	40	0.297	0.000	0.000
7	286.586	100.000	0.000	24	8.308	83.908	2.893	41	0.241	0.000	0.000
8	232.700	100.000	0.000	25	6.746	81.015	3.089	42	0.196	0.000	0.000
9	188.947	100.000	0.003	26	5.477	77.926	3.306	43	0.159	0.000	0.000
10	153.420	99.997	0.028	27	4.447	74.621	3.594	44	0.129	0.000	0.000
11	124.573	99.969	0.104	28	3.611	71.027	3.819	45	0.105	0.000	0.000
12	101.150	99.865	0.232	29	2.932	67.208	3.938	46	0.085	0.000	0.000
13	82.131	99.633	0.407	30	2.381	63.269	4.094	47	0.069	0.000	0.000
14	66.689	99.226	0.613	31	1.933	59.175	4.451	48	0.056	0.000	0.000
15	54.149	98.613	0.830	32	1.570	54.724	4.840	49	0.046	0.000	0.000
16	43.968	97.783	1.040	33	1.275	49.884	4.906	50	0.037	0.000	0.000
17	35.701	96.743	1.255	34	1.035	44.978	6.561	51	0.030	0.000	0.000

Sampling Mode : Manual Refractive Index : 1.60-0.10i
Signal Accumulation Count : 1 Interval (sec) : ___ Signal Averaging Count : 64
Max of Absorbance Range : 0.200 Min of Absorbance Range : 0.010
Ultrasonic Dispersion Time (sec) : ___ Waiting Time After Ultrasonic Dispersion(sec) : ___

Figure 3. Distribution of the particles size based on surface area equivalent diameter

The results from characterization of the four waste CaCO3 powder samples are summarized in Table 4. The mean numbers of particle size (selected sample) was 0.597µm, the mean longitudinal equivalent diameter was 0.761µm, and mean surface area equivalent diameter was 0.974 µm. When sieved through a 325 mesh sieve (45 µm), the average percentage of the CaCO3 that remained on the sieve was 0.356 %. The average purity of the powders was 98.50 %, and they were all white. These results indicate the powders are suitable for use as fillers in production of rubbers and other rubber parts.

Table 4. Characterization of the CaCO3 powders.

Sample No.	Mean numbers of particles µm	Mean longitudinal diameter of particles µm	Mean specific area diameter of particles µm	Percentage remaining on 325 mesh sieve (45 µm) %	$CacO_3$ + $MgcO_3$ %	MgO %	Fe_2O_3 + Al_2O_3 %
1 (selected sample)	**0.597**	**0.761**	**0.974**	**0.356**	**97.259**	**0.34**	**0.11**
2	0.585	0.609	1.815	0.471	98.950	0.33	0.16
3	0.558	0.616	1.651	0.411	98.619	0.39	0.22
4	0.581	0.682	1.730	0.839	99.03	0.35	0.19

3.3. Testing of the tire product (Mechanical Properties)

The tensile properties were determined using an Instron universal testing machine (model Shimadzu xlv12, Shimadzu Co. Ltd., Kyoto, Japan) with a crosshead speed of 350 mm/min., and 1-kN load cell. The specimens were stamp-cut from a 2-mm-thick compression-moulded sheet (ASTM D412-92). 300% modulus (ASTM D412) and elongation at rupture (ASTM D1456) was also determined.

The sample hardness was determined using a shore A durometer (model DIA 7021, Shindong Co. Ltd., Japan) in accordance with ASTM D2240. It was determined at three different positions on the specimens (about 6-mm thick) and the median value was indicated. Each mechanical property test was repeated five times and an average value was used in the data analysis. Physical testing procedures were suitably followed the standard test methods which can be ASTM shown in table 5.

Table 5. Physical and mechanical testing of four rubber samples produced with the waste CaCO3 powders

Sample No.	Hardness	Tensile strength Kg/Cm^2 (MPa)	Elongation at rupture %	300 % modulus Kg/Cm^2 (MPa)
1	43	230(23)	588	70(7)
2	42	227(22.7)	582	71(7.1)
3	41	216(21.6)	583	69(6.9)
4	45	222(22.2)	590	70(7)
Standard	40±5 **ASTM D-2240**	150-300 **ASTM D-412**	350 **ASTM D-1456**	> 40 **ASTM D-412**

4. Conclusions

Waste calcium carbonate from marble sawing was analyzed by XRF and DLS. The results showed it was similar to the fillers currently used in the rubber industry. Tires produced with this waste powder had similar properties to those produced with the standard filler. Therefore, the waste powder could be used as an inexpensive replacement filler.

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Supporting Information

Table S1. Specifications for micronized calcium carbonate used in the rubber industry

Filler	Mean particle size µm	Distribution of particles size µm	Particle shape	Specific gravity g/cm^3	Specific surface area (BET) m^2/g	Humidity %	CacO$_3$ %	MgO %	Fe$_2$O$_3$ + Al$_2$O$_3$ %
Natural CaCO$_3$	3-120	0.1-600	Cubic	2.7	0.3-2	≤ 0.5	≥ 94.5	≤ 0.7	≤ 0.3
Precipitated CaCO$_3$	0.07-1	0.1-2	Cubic spherical	2.6	11-26	≤ 0.5	≥ 94.5	≤ 0.7	≤ 0.3

Table S2. Specifications for nanosize calcium carbonate used in the rubber industry (NPCC-GBT/9590-2004/Chinese Standard)

Filler	Mean particle size µm	Specific surface area (BET) m^2/g	Particle shape	Specific gravity g/cm^3	Filler brightness %	Humidity %	Color of CacO$_3$	CacO$_3$ %	MgO %	Al$_2$O$_3$ + Fe$_2$O$_3$ %
CaCO$_3$	15- 40	40	Cubic	2.7	≥ 88	≤ 0.5	White powder	≥ 94.5	≤ 0.7	≤ 0.3