Sjournals
Scientific Journals
Scientific Journal of Environmental Sciences (2014) 3(3) 20-27
ISSN 2322-5017
doi: 10.14196/sjes.v3i3.1321

Contents lists available at Sjournals
Scientific Journal of Environmental Sciences
Journal homepage: www.Sjournals.com

Original article

Application of waste calcium carbonate in the tire industry

G.H. Ranjbar[a,]*, M.H. Azadi[b]
[a]*Department of Mining Engineering, Safashahr Branch, Islamic Azad University, Safashahr, Iran.*
[b]*Young Researchers club, Shiraz Branch, Islamic Azad University, Shiraz, Iran.*

**Corresponding author;* Department of Mining Engineering, Safashahr Branch, Islamic Azad University, Safashahr, Iran.

A R T I C L E I N F O

Article history,
Received 03 April 2014
Accepted 15 May 2014
Available online 29 May 2014

Keywords,
Waste powder
Calcium carbonate
Physical properties
Rubber filler
Particle size

A B S T R A C T

Calcium carbonate is used as inert filler in rubber industry in the production of tires. Calcium carbonate is abundant and inexpensive, so it is widely used for cost reduction. Too, calcium carbonate is known as non- reinforcing fillers in rubber industry. Waste CaCO3 powder is a by-product of sawing marble and could be used as a replacement for the CaCO3 fillers that are currently used in rubber production. In the present study, particle size, specific surface area, and physical properties such as tensile strength, 300% modulus, hardness and elongation at break were studied. The results were found that made ruubers from waste calcium carbonate was getting higher hardness, modulus, elongation at break than standard. Eventually, waste CaCO3 powder was suitable for use in the rubber industry.

1. Introduction

Fillers are compounding ingredients added to rubber compounds for the purpose of reinforcing them and/or cheapening their cost. Traditional fillers include carbon black, silica, calcium carbonate, calcium silicate and clay. In rubber industry, silica and carbon black are useful reinforcing fillers in order to improve the quality of rubber product in term of tensile strength, tear strength and abrasion. On the other hand, non-reinforcing filler calcium carbonate for example, acts only as diluent to reduce cost but does not affect strength. Therefore calcium carbonate and clay are classified as inert filler so it is widely used for cost reduction [1-6]. Calcium carbonate is better in resilience property than that of carbon black and silica [7]. There are two categories of calcium carbonates used for rubber - ground natural calcium carbonate (limestone) and precipitated calcium carbonate. Ground calcium carbonate filler has a low aspect ratio, low surface area, and low surface activity. Size classes are 3 - 12 and 0.7 – 2 micrometers. Wet-ground carbonate has better uniformity and finer particle size and is somewhat more expensive than dry-ground product. Precipitated calcium carbonate is used for applications requiring higher brightness, smaller particle size, greater surface area, lower abrasivity, and higher purity than ground natural products provide. Particle sizes are typically in the 0.07 - 0.7 micrometer median size range. Calcium carbonate is preferred over other fillers, such as barium sulfate (barite), aluminum silicate (kaolin), and mica, pyrophyllite, silica, slate and magnesium silicate (talc) [8]. Properties of calcium carbonate are shown in table 1. In this research, application of waste $CaCO_3$ powder as a filler in rubber production was investigated.

Table 1
Properties of calcium carbonate.

Chemical formula	**$CaCO_3$**
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

2. Experiments

2.1. Materials

1. Natural rubber - SMR 20
2. Activator - Zinc oxide:white seal
   - Stearic acid
3. Filler - Carbon black (N550) (Reinforcing filler)
   - Waste Calcium carbonate (Non-reinforcing filler)
4. Oil - Behran 840
5. Accelerator - MBTS
6. Vulcanizing agent - Sulfur

Natural rubber (NR): ribbed smoked sheets SMR-20 with specific gravity 0.913 ± 0.005 g/cm3, and low Tg = -75, supplied by Dena Tire Manufacturing Company, Shiraz, Iran.

Other standard rubber compounding ingredients such as stearic acid, zinc oxide and sulfur were of commercial grades and used without further purification.

Calcium carbonate was chosen as filler throughout this article, and its technical specifications are given in table 2.

MBTS and sulfur were the used accelerator and vulcanizing agent respectively.

Zinc oxide and stearic acid were the used as activator.

2.2. Preparation of rubber compounds and vulcanisates

All rubber (4 samples) compounds contained the same chemical composition. For each rubber compound, 15 parts per hundred of rubber (phr) of the waste calcium carbonate content was used. The ingredients used in each compound are listed in table 2.The mixing was carried out both in an internal mixer (model OOM laboratory mixer, 3 liter, Kobelco Co. Ltd., Japan) and a two-roll mill (model VW-007 20inc,Chingyang machinery Co. Ltd., China). All ingredients except sulphur were mixed with the rubber in the internal mixer with a fill factor of 0.7 at 80°C and a rotor speed of 50 rpm. After discharging, the compounds were further masticated in the two-roll mill for 6min. curing agents and accelerators were added during this time. Finally, the rubber compounds were taken out and sheeted through a two-roll mill. The rubber compounds were compression-moulded at 150°C using a hydraulic hot press (model HCFP100, Press sazan Co. Ltd., Iran), according to their respective cure time (t90) from the cure curves. In the final stage (curing or vulcanization), the rubbers were formed and reached their maximum values for dynamic-mechanical properties and tensile strength. The rubbers were tested for hardness (shore A), tensile strenght, percentage of elongation at break and stress at 300 % strain (300 % modulus). After analysis, the CaCO3 powder was used as a filler in production of rubber at Dena Tire Manufacturing Company (Shiraz, Iran).

Table 2
The ingredients of rubber compound formula.

Ingredients	**Recipe, Phr[a]**
Natural rubber (SMR-20)	110
Oil (Behran 840)	9
Stearic acid	4
Carbon black(N550)	28
Zinc oxide	3
Waste CaCO3 powder	15
MBTS	0.3
Sulfur	4

[a]**parts per hundred parts of rubber**

2.3. 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 break (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 3.

Table 3
Standard methods used for physical testing properties.

Properties	**Methods**
Tensile strength	ASTM D412-92 (die c)
Hardness	ASTM D2240 (Shore A)
Elongation at break	ASTM D1456
300% modulus	ASTM D412

2.4. Sample collection

Samples (calcium carbonate) were collected from stone sawing factories around Safashahr, Iran. There are about 100 stone sawing factories in this region, and all of them produce CaCO3 powder. Each factory produces about 10t (1t = 1000 kg) of pure and micronized CaCO3 powder daily, which could be used as a fillers in many industries.

3. Results and discussion

Specific surface area of calcium carbonate by Brunauer Emmett Teller (BET), average particle size and specific gravity were measured. The result was revealed in table 4.

The term BET was derived from the first initials of Burnauer, Emmett and Teller, method of measuring the surface area and porosity of solid material. Micromeritics ASAP 2010 Analyser (Accelerated Surface Area and Porosimetry System) provides versatility in gas selection and high vacuum for high-resolution low surface area measurements. Porosimetry is an important technique in the analysis of solids. It gives information about the surface area and porosity of solids and thus about the structure of the porous material and its surface architecture

& study of structural changes & determination of surface acidity of catalyst materials. The gas adsorption technique is performed by the addition of a known volume of gas (adsorbate), typically nitrogen, to a solid material in a sample vessel at cryogenic temperatures.

Table 4
Average particle size (µm), specific surface area (m2/g) and specific gravity (g/cm3) of calcium carbonate.

Filler	Average particle size (µm)	Specific surface area (m2/g)	Specific gravity (g/cm3)
Calcium carbonate	0.546 µm	3.8m2/g	2.60 g/cm3

3.1. Mechanical properties of compound rubber

The physical properties of rubber compounds prepared from waste calcium carbonate filler at 15 phr shuch as: hardness, tensile strength, percentage of elongation at break, and 300 % modulus were shown in table 5. These results correlate well with those for samples produced with the standard $CaCO_3$ filler used in the rubber industry, which are presented in the last line of the table 5.

Table 5
Physical properties of compound rubber adding with filler (calcium carbonate) 15 phr.

Sample No.	Hardness (Shore A)	Tensile strength (MPa)	Elongation at break (%)	300% Modulus (MPa)
1	40	20	587	7.3
2	44	21.8	576	6.8
3	42	22.6	567	7.5
4	41	21.3	498	6.6
	40±5	15-30	350	> 4
Standard	ASTM	ASTM	ASTM	ASTM
	D-2240	D-412	D-1456	D-412

3.2. Characterization of the $CaCO_3$ powders Sizing

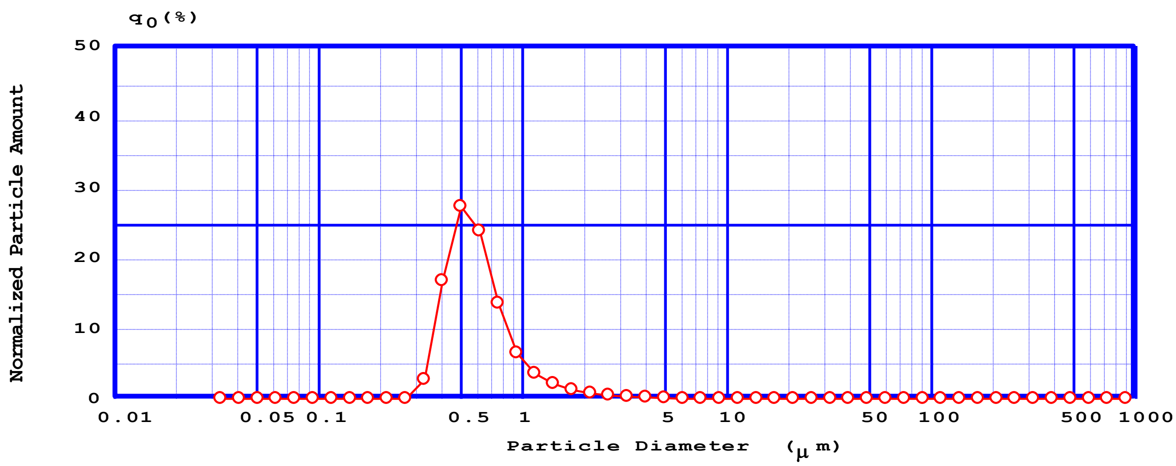
The samples were dried before analysis. Particle size analysis (PSA) (model SALD [Size Analyzer Laser - Diffraction] 2101, Shimadzu, Kyoto, Japan, ISO/IEC 17025 standard) was conducted at the Pharmacological School of Shiraz University (Shiraz, Iran), and included measurement of the number of particles.

All five $CaCO_3$ samples gave similar results for PSA. Therefore, the results for only one of these samples are presented in this section. The particle size distribution (Figure 1) showed that the mean particle size was 0.616 µm, the mode was 0.562 µm, and the median was 0.570µm. From the statistical point of view on the mass distribution percentage, it showed that the smallest particle size was 0.365µm and the biggest particle size was35.701µm.

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

(File Name) A1-1
(Sample ID) (Sample #)
(Date) 12/04/28 (Time) 12:29:34

R Index=1.70-0.20i	Median D : 0.570	Mean V : 0.616	10.0%D : 0.409	S Level : 0
	Modal D : 0.562	Std Dev : 0.180	50.0%D : 0.570	D Func :None
			90.0%D : 1.010	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	0.001	35	0.840	84.137	13.537
2	811.975	100.000	0.000	19	23.538	99.997	0.003	36	0.682	70.599	23.815
3	659.303	100.000	0.000	20	19.112	99.994	0.005	37	0.554	46.784	27.231
4	535.337	100.000	0.000	21	15.518	99.989	0.008	38	0.450	19.553	16.780
5	434.680	100.000	0.000	22	12.601	99.981	0.014	39	0.365	2.773	2.773
6	352.949	100.000	0.000	23	10.231	99.967	0.028	40	0.297	0.000	0.000
7	286.586	100.000	0.000	24	8.308	99.940	0.052	41	0.241	0.000	0.000
8	232.700	100.000	0.000	25	6.746	99.888	0.087	42	0.196	0.000	0.000
9	188.947	100.000	0.000	26	5.477	99.801	0.145	43	0.159	0.000	0.000
10	153.420	100.000	0.000	27	4.447	99.656	0.237	44	0.129	0.000	0.000
11	124.573	100.000	0.000	28	3.611	99.419	0.358	45	0.105	0.000	0.000
12	101.150	100.000	0.000	29	2.932	99.061	0.515	46	0.085	0.000	0.000
13	82.131	100.000	0.000	30	2.381	98.546	0.787	47	0.069	0.000	0.000
14	66.689	100.000	0.000	31	1.933	97.760	1.314	48	0.056	0.000	0.000
15	54.149	100.000	0.000	32	1.570	96.446	2.212	49	0.046	0.000	0.000
16	43.968	100.000	0.000	33	1.275	94.234	3.580	50	0.037	0.000	0.000
17	35.701	100.000	0.002	34	1.035	90.653	6.517	51	0.030	0.000	0.000

Sampling Mode : Manual Refractive Index : 1.70-0.20i
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) : ___

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

3.3. XRF Analysis

X-ray fluorescence (XRF) (model PW 1480, Philips, Amsterdam, Netherlands) analysis was carried out in the X-Ray Laboratory of Kansaran Binaloud of Geosciences (Tehran, Iran) for qualitative determination of calcium carbonate samples for elements(32 elements). The results are reported in three different concentration groups, i.e. major (>1%), minor (100 ppm-1%), traces (<100 ppm).

The sample was placed into a disposable cup. The X-ray source was a palladium tube using a 45kV accelerating voltage. One set of spectra was the result of analysis with a titanium target. In the titanium secondary target analysis, the source was pointed at the target and the target element was excited and fluoresced. Then the target fluorescence was used to excite the sample. The titanium target increased the sensitivity for the light elements. This was utilized for the analysis and detection of the following elements (Sulfur, Silicon, Potassium, and Calcium). The second sets of spectra were analyzed with a Collimator. A collimator was placed between the source and sample to reduce signal (background). This technique was also used to determine remaining elements (Bromine, Iron, Zinc, and Chlorine). The elements contained in the sample are thereby excited to emit the elementspecific X-ray fluorescence radiation. A liquid nitrogen cooled light element detector (LED) Si(Li) measured the fluorescent and scattered x-rays from the sample as a multichannel analyzer and software assigned each pulse an energy value, thus producing the spectrum. The XRF results (table 6) showed that the samples contained 0.808 % Al2O3 + Fe2O3 and 0.78 % MgO on average.

Table 6
XRF results for the CaCO3 powder samples.

Sample No.	CaO %	SiO2 %	Fe2O3 %	MnO %	MgO %	Al2O3 %	K2O %	Na2O %	TiO2 %	P2O5 %	L.O.I %
1	53.68	0.47	0.11	0.001	0.86	0.16	0.01	0.12	0.016	0.029	43.86
2	54.53	0.25	0.02	0.001	0.74	0.03	0.01	0.08	0.011	0.068	43.85
3	54.43	0.31	0.07	0.001	0.71	0.15	0.01	0.07	0.016	0.001	43.64
4	54.51	0.30	0.07	0.001	0.80	0.17	0.01	0.10	0.019	0.055	43.70

Sample No.	SO3 %	Cl ppm	Ba ppm	Sr ppm	Cu ppm	Zn ppm	Pb ppm	Ni ppm	Cr ppm	Co ppm	V ppm	Ce ppm	La ppm
1	0.001	7131	137	198	26	16	5	11	5	6	17	18	8
2	0.001	3160	141	151	26	20	6	3	4	4	14	13	6
3	0.001	2535	102	160	28	21	6	12	5	2	14	16	5
4	0.001	2597	159	180	31	22	8	8	4	2	14	15	7

Sample No.	W Ppm	Mo ppm	Nb ppm	Zr Ppm	Y ppm	Rb Ppm	V ppm	As ppm	U ppm	Th ppm
1	1	1	11	18	5	13	17	14	1	1
2	1	1	8	13	6	11	14	14	1	1
3	1	1	3	21	6	10	14	13	1	1
4	1	1	10	22	7	12	14	10	1	1

The results from characterization of the four waste CaCO3 powder samples are summarized in table 7. The mean particle size ranged from 0.558–2.079 µm, the mean surface area equivalent diameter was 1.860 µm. When sieved through a 325 mesh sieve (45µm), the average percentage of the CaCO3 that remained on the sieve was 0.012 %., and average of humidity was 0.145%. The average purity of the powders was 98.96 %, and they were all white. These results indicate the powders are suitable for use as filler in production of rubbers and other rubber parts.

Table 7
Characterization of the CaCO3 powders.

Sample No.	Mean particle Size (µm)	Percentage remaining on 325 mesh sieve (45 µm)%	Mean specific area diameter of particles (µm)	Color of powder	Humidity	CaCO3 %
1	0.616-2.079	0.005	2.079	white	0.18	98.90
2	0.604-1.981	0.004	1.981	white	0.17	99.01
3	0.581-1.730	0.039	1.730	white	0.10	98.96
4	0.558-1.651	0.035	1.651	white	0.13	98.98

4. Conclusion

Waste calcium carbonate from marble sawing was analyzed by XRF and DLS. Waste CaCO3 powder is a by-product of sawing marble and could be used as a replacement for the CaCO3 fillers that are currently used in rubber production. In the present study, particle size, specific surface area, and physical properties such as tensile strength, 300% modulus, hardness and elongation at break were studied. The results were found that made ruubers from waste calcium carbonate was getting higher hardness, modulus, elongation at break than standard. Eventually, waste CaCO3 powder was suitable for use in the rubber industry.

Acknowledgment

The authors would like to thank Islamic Azad University of Safashahr, Iran and Dena Tire Manufacturing Company, Shiraz, Iran.

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	Specificgravity (g/cm3)	Specific surface area (BET) m2/g	Humidity %	CaCO3 %
Natural CaCO3	3-120	0.1-600	Cubic	2.7	0.3-2	≤ 0.5	94.5≥
Precipitated CaCO3	0.07-1	0.1-2	Cubic spherical	2.6	11-26	≤ 0.5	94.5≥

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(m2/g	Particle shape	Specificgravity (g/cm3)	Filler brightness %	Humidity %	Color of CacO3	CaCO3 %
CaCO3	15- 40	40	Cubic	2.7	88≥	≤ 0.5	White powder	94.5≥

This article was with patronage Islamic Azad University of Safashahr, Iran.

References

Arayapranee, W., Rempel, G.L., 2008. A comparison of the properties of rice husk ash, silica,and calcium carbonate filled 75:25 NR/EPDM blends", J. Appl. Polym. Sci., 110 (02), 1165-1174.

Bagghi, A.K., Sharma, B.G., 1981. Reinforcement and physical properties of filled rubber system. Indian J. Technol., 19, 368-372.

Baker, C.S.L., 1978. Properties of natural rubber with some highly reinforcing carbon blacks. NR Technol., 8, 24-32.

Brentin, R., Sarnacke, P., 2011. Rubber compounds (A market opportunity study). pp.36-37, September.

Edwards, D.C., 1990. Review polymer-filler interactions in rubber reinforcement. J. Mater. Sci., 25, 4175-4185.

Moonchai, D., Moryadee, N., Poosodsang, N., 2012. Comparative properties of natural rubber vulcanisates filled with defatted rice bran, clay and calcium carbonate. Maejo Int. J. Sci. Technol., 6(02), 249-258.

Sobhy, M.S., El-Nashar, D.E., Maziad, N.A., 2003. Cure characteristics and physicomechanical properties of calcium carbonate reinforcement rubber composites. Egypt. J. Sol., 26 (02), 241-257.

Vichitcholchai, N., Na-Ranong, N., Noisuwan, W., Arayapranee, W., 2012. Using rice husk ash as filler in rubber industry. Rubber Thai J., 1, 48-55,