



EURASIA 2016 WASTE MANAGEMENT SYMPOSIUM

The Usability of Waste Marble Powder as Filler in Cold Vulcanizing Adhesives

Deniz Akin Sahbaz¹, Caglayan Acikgoz², O. Mete Kockar³

Abstract

The aim of this study is to investigate the usability of waste marble powder as filler in cold vulcanizing adhesives and its effect on the physical and mechanical properties of the cold vulcanizing adhesives. Experimental tests were performed to evaluate the possibility of using the waste marble powder as replacement of the conventional calcite powder in a formulation of cold vulcanizing cement. Cure characteristics, which are scorch time, cure time and minimum torque of the rubber compounds filled with marble powder and calcite were determined at 190°C with a Moving Die Rheometer. Measurements of adhesive strength and capability of elongation of spliced fabric conveyor belt samples were carried out on the tensile testing machine.

Inexpensive and eco-friendly filler, marble powder, has been successfully utilized for the process of cold vulcanizing adhesives. A favorability of adhesive strength and capability of elongation was obtained for the waste marble powder filled adhesives when compared to the calcite filled adhesives. Recycling of waste marble powder as filler appears to be a feasible solution not only to environmental problem, but also to the problem of economical processing of such adhesives.

Keywords: Cold vulcanizing adhesive, conveyor belt, filler, waste marble powder

1. INTRODUCTION

Turkey has approximately 42% of the total world marble reserves. Seven million tons of marble are produced in Turkey annually. Marble manufacturing industry produces high amount of waste. During the cutting process 20-30 % of the marble block turns into dust. Consequently, marble processing plants produce millions of tons waste materials each year in the world. Approximately 2.500.000 tons/year of marble sludge are generated as a by-product of marble production in Turkey [1]. Only in Afyonkarahisar, disposed waste marble is about 125.000 tons/year [2]. Many researchers recently were interested in studying the possibility of re-use of waste marble powder in useful industries such as cement and concrete production [3], wet end papermaking application [4], waste water treatment [5]-[6] and clay brick [7]. However, the utilization of marble powder is inadequate to consume all waste marble stocks.

In rubber industry, various types of fillers, such as carbon black, silica, calcium carbonate, talc and clay, have been very widely used. The fillers not only reduce the cost of the material but also improve the mechanical and dynamic properties of the compounds.

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For environmental protection, many researchers have studied the utilization of waste materials as fillers. A wide variety of waste materials have been studied, including chicken eggshell waste [8], oil palm ash [9], cuttlebone [10], rice husk derived silica [11], porous carbons derived from coconut shell and wood [12]. But, very limited information about the usage of waste marble powder as filler in rubber processing has been reported [11], [13]. The chemical composition of waste marble powder like the conventional fillers. It can be composed of inorganic compounds such as calcium and magnesium carbonates, and also silicates.

In recent years, in view of increasing requirements imposed on sealing and adhesive compositions in machine building and construction, interest in compositions based on rubbers capable of low-temperature vulcanization has arisen. Usually the cold self-vulcanizing patching compounds are composed of two separate components which are mixed immediately before use. One of the components usually contains chloroprene based liquid rubber constituents (such as zinc white, antioxidants, carbon black, fillers, plasticizers), while the other component contains hardener. The cold vulcanizing adhesive can use in all applications of bonding rubber to rubber, metal, wood and many other materials.

This study involved the preparation of cold vulcanizing adhesives, which contain marble powder as filler. Influences of marble powder loading compared with commercial calcite were investigated on vulcanization characteristics and mechanical properties.

2. MATERIALS AND METHODS

2.1. Materials

Marble powder was collected from the local marble cutting/processing industry. The marble powder was dried in an oven at 80°C for 24 h and then passed through sieve to obtain 90 µm before use.

Chloroprene rubber, magnesium oxide, zinc oxide, accelerator and other fillers were all obtained from Özerband Conveyor Belt Industry and Trade Inc., Turkey. The fabric conveyor belt were supplied from Billas Tire & Rubber Industry, Turkey. Hardener (HB Fuller, swift 9502) is purchased from Ağa Makina, Turkey.

2.2. Preparation of Cold Vulcanizing Adhesive

In the preparation of cold vulcanizing adhesive, chloroprene was used as elastomer for the rubber blend. The oxides of metals such as zinc and magnesium were used as vulcanization activator to adjust the vulcanization velocity. An ultra-accelerator was added into the rubber compound to increase the speed of vulcanization and to permit vulcanization to proceed at lower temperature and with greater efficiency. The mixing materials and sequences were kept constant for all mixes, except for the different types of filler, which were calcite and marble powder. However, the total amount of filler in each formulation was kept constant at 6 phr. The formulation of the mixes is given in Table 1.

Table 1. Formulation of the mixes

Materials	Compounds (phr)
Chloroprene Rubber	100
Magnesium oxide	7
Zinc oxide	3
Calcite or marble powder	6
Reinforcing fillers	16
Accelerator	3.5

The above-mentioned materials were blended in a laboratory sized mixing roll and formed into a sheet with a thickness of 1 mm, which was then dissolved in a solvent, forming a cement which is less viscous than the rubber mixtures.

2.3. Application of Adhesive

In splicing process of textile belts by cold vulcanization, cold vulcanized adhesive mixed with hardener by ratio 100:5 was applied both test surfaces prepared for splicing. Test pieces with width of 30 mm and length of 150 mm, which were cut from the same area of the fabric conveyor belt were used for measuring adhesive strength and elongation at break of the spliced area in a vulcanized fabric conveyor belt. Vulcanization processes of the cold vulcanizing adhesives were performed by adjustment of three parameters, that are: vulcanization time (4, 8 and 24 hours), temperature (25°C) and pressure (9 kg / 3000 mm²).

2.4. Cure Characteristics and Physical Properties

Curing speeds and optimal curing time of the rubber mixtures were determined using a Moving Die Rheometer (MDR, DEVOTRANS) according to ASTM D 1646. Samples of the respective compounds were tested at a vulcanization temperature of 190°C. The cure time t_{90} , scorch time t_{S2} , maximum torque and minimum torque, etc., were determined from the rheograph.

The cure rate index (CRI) of the sample was calculated from following equation [14]:

$$CRI = 100 / (\text{Cure time} - \text{Scorch time}) \quad (1)$$

The analysis of the density was carried out in analytical balance (Precisa, XB 220 A), with device for solid density, according to ASTM D 297 standard, at room temperature. Measurements of adhesive strength and elongation at break of spliced fabric conveyor belt samples were carried out on the tensile testing machine (Devotrans DVT). The tension rate was 100 mm/min.

3. RESULTS AND DISCUSSION

3.1. Rheological Characteristics

Figure 1 show the rheological curves of calcite and marble powder filled rubber blends. It is clear that the curing curves of all rubber blends are similar, suggesting that the marble powder is favorable as filler for the vulcanization process.

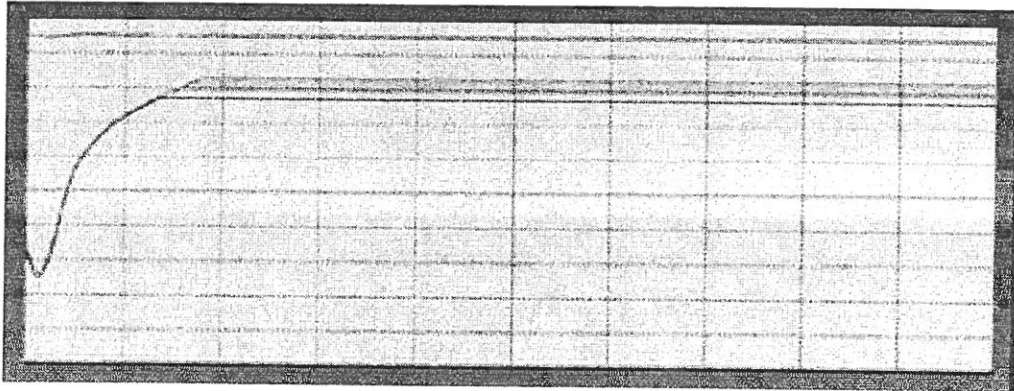


Figure 1. Curing curves of calcite and marble powder filled rubber blend compounds

Curing characteristics of chloroprene blend compounds are illustrated in Table 2. The minimum and maximum torque values are generally resulted from the degree of crosslink and strength of the filler particles within the rubber matrix [15]. The presence of the strong fillers such as marble powder in the rubber matrix decreases the mobility of chains of rubber and ultimately results in the higher values of maximum torque [11]. The difference between minimum and maximum torque, Δ Torque, is commonly supposed to be proportional to the crosslinking density [16].

In the vulcanization of rubber, filler generally plays a vital role in accelerating the rate of cure process [17]. Also, as shown in Table 2, there is very little variation of CRI with change of filler type at same amount of filler loading. The values of CRI indicate the cure process becomes a little faster in presence marble powder as filler instead of calcite.

Table 2. Curing characteristics of chloroprene blend compounds

Curing characteristics	Calcite filled rubber blends	Marble powder filled rubber blends
Minimum torque (lb.in)	1.742	1.827
Maximum torque (lb.in)	5.581	5.607
Δ Torque (lb.in)	3.839	3.78
Cure time t_{90} (min)	1.30	1.32
Scorch time (min)	0.52	0.52
Cure rate index (min^{-1})	128.2	125.0

Consequently, the cure characteristics given in Table 2 illustrates no considerable outcome on the loading of marble powder instead of calcite in chloroprene blends.

3.2. Physical Properties

Densities of calcite and marble powder filled chloroprene rubber samples were 1.324 g/cm^3 and 1.347 g/cm^3 , respectively. Comparing the calcite filled rubber to marble powder filled rubber, the slightly smaller density of the calcite filled rubber could be attributed to volume change due to the chemical reactions between rubber and fillers.

This study investigated how the waste marble powder affect the mechanical properties of cold vulcanizing adhesives. The mechanical properties of the adhesives involve adhesive strength and elongation at break. Figure 1 shows the variation of maximum strength values of cold vulcanizing adhesives with adhesion time. Marble powder can provide a higher adhesive strength than calcite for cold vulcanizing adhesives in the 4 hours of adhesion. However, marble powder filled adhesives have slightly lower adhesive strength values in the 8 and 24 hours of adhesion.

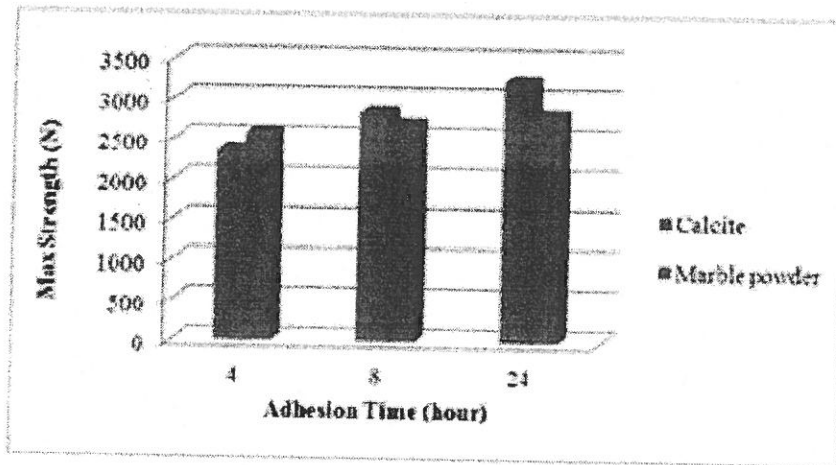


Figure 2. Variation of maximum strength values of spliced conveyor belt with adhesion time (Pressure $9 \text{ kg} / 3000 \text{ mm}^2$; Temperature: 25°C)

Table 3 shows the variation in elongation at break of spliced conveyor belt with adhesion time. The marble powder filled adhesives show a 16% increase in elongation at break compared to the calcite filled adhesives in the 4 hours of adhesion. Also, the both adhesives show lower values of elongation at break in the 8 and 24 hours of adhesion. The values decreased with the adhesion time for the both adhesives because the cross-links restrict the free motion of molecules [18].

Table 3. Variation in elongation at break of spliced conveyor belt with adhesion time (Pressure $9 \text{ kg} / 3000 \text{ mm}^2$; Temperature: 25°C)

Adhesion Time (hour)	Elongation at Break, E_b (%)	
	Calcite Filled Adhesives	Marble Powder Filled Adhesives
4	498	579
8	498	498
24	497	497

4. CONCLUSIONS

In summary, the present study mainly deals attention on the utilization of waste marble powder as new type of filler for rubber compounds. In formulation of cold vulcanizing adhesives, marble powder was used instead of calcite as a filler. The mechanical properties of the marble powder filled adhesives were comparable with those of commercial calcite filled adhesives. Marble powder filled adhesives have the better performance as compared to calcite filled adhesives in the 4 hours of adhesion. However, marble powder filled adhesives have slightly lower adhesive strength values in the 8 and 24 hours. But, we prefer marble powder filled adhesive which is economic material and is also useful for decreasing the waste products from the environmental issues.

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BIOGRAPHY



Deniz AKIN ŞAHBAZ works as a research assistant at Afyon Kocatepe University Chemical Engineering Department.

Akin Şahbaz received his BSc in Chemical Engineering in 2009 from Kocaeli University, Kocaeli, Turkey, and his MSc in Chemical Engineering in 2012 from Afyon Kocatepe University, Afyonkarahisar, Turkey. She is PhD student on Cold Vulcanizing Adhesives at Bilecik Şeyh Edebali University Chemical Engineering Department.

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Program

Day 01

08:30-14:00 HALL 1

MESE HALL

Opening Program

08:30	Registration
Opening Ceremony	
09:30	<i>Prof. Dr. Gülede Engin</i> Head of Environmental Engineering Department
09:40	<i>Prof. Dr. Ahmet Demir</i> Dean of Civil Engineering Faculty
09:50	<i>Prof. Dr. İsmail Yüksek</i> Rector of Yıldız Technical University
10:00	Coffee Break
Opening Panel : Prof. Dr. Gülede Engin	
10:40	Evaluation of Research Activities Dealing With Solid Waste Management in Mediterranean Sea Basin Countries <i>B. Topkaya</i>
11:20	The Business of Waste Management: Opportunities for (Informal & Formal) Private Sector <i>C. Visvanathan</i>
12:00	Overall Assessment on Solid Waste Management of Istanbul and Turkey <i>S. Yildiz</i>
12:40	Lunch

HALL 1

HALL 2

Session 1: WASTE MINIMIZATION AND RECYCLING		Session 1: LANDFILLING		Session 1: HAZARDOUS & INDUSTRIAL WASTE MANAGEMENT	
Session Chair: Prof. Dr. Jonathan Wong		Session Chair: Prof. Dr. C. Visvanathan		Session Chair: Prof. Dr. Ilirjan Malollari	
14:00	The Usability of Waste Marble Powder as Filler in Cold Vulcanizing Adhesives <i>D. A. Sahbaz, C. Akkoç, O. M. Kocakar</i>	14:00	Keynote - Recent Insights Regarding the Design and Construction of Modern MSW Landfill Barrier Systems <i>R. K. Rowe</i>	14:00	Energy Recovery in a Kraft Pulp Mill Wastewater Treatment Plant <i>A.C.P. Lopes, C.M. Silva, A.P. Rosa, F. Rodrigues</i>
14:20	Evaluation of Waste PET Bottles in the Manufacturing of Water Reducible Acrylic Modified Alkyd Resins <i>N. Akgun, O. N. Buyukyongu, I. Acar, G. Guclu</i>	14:20	Accelerated Landfill Bio-stabilization by Means of Aeration and Moisturization <i>M. Rizkowsk, R. Stegmann</i>	14:20	CO ₂ Capture Analysis of Tobacco Biochar-AIC3 Composite <i>N. Soyler, S. Ceylan, Y. Topcu</i>
14:40	Production of Eco-friendly Handmade Paper from The Waste Paper Generated in Municipalities of Dhaka City, Bangladesh <i>M. Alam, S.Y. Rikta, M.D.T. Hasnine, F. Ahmed, A.K.I. Kamal</i>	14:40	Bioreactor Landfill for Sustainable Disposal of MSW: A Case Study <i>Asif A. Siddiqui</i>	14:40	Comparison Between Batch and Continuous Reactor Systems for Biosorption of Neodymium (Nd) Using Microalgae <i>M.A. Kucuker, J.B. Nadal, K. Kuchta</i>
15:00	Impact of Recycling Processes on Polymers Quality - Enhance Usability and Market <i>L. Plening, K. Kuchta</i>	15:00	Fuzzy Approach to Predict Methane Production in Bioreactor Landfills <i>M. Di Addato, B. Ruggen</i>	15:00	Copper Removal from Ammoniacal Spent Etchant using Magnetic Nanoparticles <i>O.A. Yassin, G.G. Heciosmanoglu, S. Genc, E.T. Oner, Z.S. Cans</i>
15:20	Recycling Glass Wastes: Application of the Fine Fraction in Autoclaved Aerated Concrete <i>C. Straub, M.V.A. Florea, H.J.H. Brouwers</i>	15:20	Operating Landfills as Bioreactor by Recirculating Leachate <i>C. Yaman, Y. Kucukaya, B. Pala, G. Delice</i>	15:20	Adsorption of Copper in Waste Printed Circuit Boards with Modified Biosorbents <i>E. Yapiç, Z. Gunkaya, A. Ozkan, M. Banar</i>
15:40	Use of Alkaline By-products (girts, dregs and lime mud) Generated in Kraft Pulping Process as Intermediate Layer of Sanitary Landfill <i>R.M.P. Farage, C. M. Silva, A.A.P. Rezende, A.T.d. Matos, M.T. Borges, U.C. Cinque, M.B. Gouvea, E.N. Santos</i>	16:00	Coffee Break	15:40	Assessing Environmental Impacts of a University Building Through Life Cycle Assessment Methodology <i>Z. Gunkaya, A. Ozkan, M. Banar</i>
16:00	Coffee Break	16:00	Coffee Break	16:00	Coffee Break

Session 2: BIOLOGICAL METHODS FOR WASTE DISPOSAL

Session Chair: Prof. Dr. R. Kerry Rowe

Session 2: WASTE TO ENERGY

Session Chair: Prof. Dr. Baris Celi

Session 2: HAZARDOUS & INDUSTRIAL WASTE MANAGEMENT

Session Chair: Prof. Dr. Ilirjan Malollari

16:20	Keynote: Decentralised Composting for Food Waste Management: Problem and Solution <i>J. W.C. Wong</i>	16:20	Analyses of Regional Biogas Potentials in Turkey <i>J.D. Gramke, F.C. Ertem, R. Kitter, F. Gokgoz, P. Neubauer, W. Sinner</i>	16:20	Bottom Ash Treatment - "State-of-the-art" in Germany <i>V. Enzner, K. Kuchta</i>
16:40	Benefits of Compost Application Regarding Mitigation of Greenhouse Gas Emissions in Arid Climates <i>T. Agacayak, O. Larsen, F. Buks, M. Kaupenjohann, V. S. Rotter</i>	16:40	Development of Methodology for Monitoring of the Process Stability at Biogas Plant Using Near-Infrared Spectroscopy <i>I. Alamanluk, A. Nsair, K. Kuchta</i>	16:40	Metal Species in Chelate-treated Municipal Solid Waste Incineration Fly Ash Particles Estimated by Micro-scale Elemental Correlation Analysis <i>H. Kitamura, F. Takahashi</i>
17:00	Composting of Strawberry Harvest Residues with Poultry and Dairy Manures <i>K. Ekinçi, B.S. Kumbul, F. Sevik, K. Suluk, H. Kacar, H. Tunca, N. Turemis</i>	17:00	Development of Velocity Sensor to Optimize the Energy Yield in a Biogas Plant <i>A. Nsair, O. Bade, K. Kuchta</i>	17:00	Paint Sludge from Automotive Industries: Recycling as Construction Material <i>G. Sahoglu, M. K. Sahoglu</i>
17:20	Effect of Aeration Rate on the Respiration Activity of the Fresh Organic Fraction of Municipal Solid Wastes <i>A. C. Evangelou, V.T. Chintzos, D.P. Kamilis</i>	17:20	Critical Limitations for Successful Landfill Gas to Energy Projects <i>O. Sevimoglu, I. Sel</i>	17:20	Waste Management Strategy Through Mine Production Scheduling <i>Y. A. Sari, M. Kumral</i>
17:40	Biomass Yield and Phosphate Fertilizer Production from BNR Sludge <i>B. Ozdemir, B. Kurtulus</i>	17:40	The Biogas Potential for Separately Collected Biodegradable Waste at Source: A Study for Istanbul City <i>K. Sezer, M. Gencosmanoglu, F. Hosoglu, V. Balahori, S. Yildiz</i>	17:40	Physico-Mechanical Characterization of Steel Slags Produced by the Facilities in Southern of Turkey and Usability as Coarse Aggregate in Different Pavement Layer According to Turkish HTS <i>I. Gokalp, V.E. Uz, M. Saitan, B. Ergin</i>
18:00		18:00	A Novel Membrane Technology for Selective Hydrogen Sulfide Removal From Biogas <i>E. Tishun, A. Bayraktar, E. Sahinkaya, B. Celi</i>	18:00	An Evaluation of Performance and Operating Cost by Chemical Coagulation and Electrocoagulation Processes for Treatment of Metalworking Wastewaters <i>M. Koby, E. Demirbas</i>
19:00	GALA DINNER (BOSPHORUS TOUR)				