Vol. **131** (2017) *ACTA PHYSICA POLONICA A* No. 1

Special Issue of the 6th International Congress & Exhibition (APMAS2016), Maslak, Istanbul, Turkey, June 1–3, 2016

ZnO Nanoparticles Bonded to SiO_2 Filler as a Curing Accelerator in Cold Vulcanizing Adhesives

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The aim of this study is to investigate the interaction of ZnO/SiO_2 particles between the chloroprene rubber and its effect on the cure characteristics and mechanical properties of the cold vulcanizing adhesives. Curing efficiency and mechanical properties of ZnO/SiO_2 filled adhesives were compared with SiO_2 filled adhesives. ZnO nanoparticles were bounded to SiO_2 spherical nanoparticles by hydrolysis and condensation process. The morphology and elemental content of ZnO/SiO_2 particles were investigated by scanning electron microscopy and energy dispersive spectroscopy. The ZnO/SiO_2 particles were then blended with chloroprene rubber as accelerator during the vulcanization process. Cure characteristics, which are scorch time (t_{s2}), cure time (t_{c90}), maximum torque (M_H) and minimum torque (M_L) of the rubber compounds were determined at 190 °C with a moving die rheometer. The fabric conveyor belt was used for measuring adhesive strength of the adhesives. The fabric conveyor belt was used for measuring adhesive strength of the adhesives. Application of the cold vulcanizing adhesives to the fabric conveyor belt was carried out at three different times (4, 8, and 24 h), 25 °C temperature and 0.3 kg/cm^2 pressure. The results showed that ZnO/SiO_2 particles provided a higher adhesive strength than silica in the 4, 8, and 24 h of adhesion. ZnO/SiO_2 filled rubber blends gained superior vulcanization characteristics by the increasing cure rate index with the reducing cure time and scorch time. It has been concluded that ZnO/SiO_2 particles can be used as a new curing accelerator and simultaneously reinforcing filler.

DOI: 10.12693/APhysPolA.131.200

PACS/topics: 81.20.–n

1. Introduction

Conveyor belts are used in mining, mechanical and plant engineering, and many other industries. They are necessary to transport heavy and bulky materials quickly and easily. They are made of fabric-rubber central core (carcass) and rubber covers. The covers protect the carcass from damage due to impacts, from chemicals, temperature and others [1]. Because of their widespread usage, conveyor belt damage is a major problem for many industries. There are three methods for conveyor belt repair: cold cure, hot vulcanization, and mechanical belt fastening. Hot vulcanizing method uses heat and pressure to cure new section of the belt. The method is not suitable for outer environment because it requires the use of a vulcanizing press. The cold cure method uses cold vulcanizing adhesives that are cured in the repair area. The cold vulcanizing adhesives can be used in a range of applications, including rubber-to-rubber bonds and rubber-to-metal bondings, as well as for cold splicing of fabric ply belts.

Cold vulcanization is a process used to vulcanize rubber compounds at room temperatures [2]. The adhesive used for cold bonding is a two-part bonding compound (cement and hardener). Hardener is a solution of highly efficient poly-/tri-/isocyanate. Cement based on chloroprene rubber contains several chemical additives. These additives consist of accelerators (to accelerate the vulcanization process), metal oxides (to assist in accelerating vulcanization and serve as vulcanizing agents), fillers (to serve as reinforcing/strengthening agents). Chloroprene rubber can be vulcanized by zinc oxide, either with or without sulfur [3]. Reinforcing fillers such as silica and carbon black have been used in rubber formulations to gain superior properties. Silica has strong filler-filler interactions due to a number of hydroxyl groups on the surface [4].

In this study, ZnO/SiO_2 particles were obtained by hydrolysis and condensation process. ZnO/SiO_2 particles were used by blending chloroprene rubber to prepare the cement of cold vulcanizing adhesive. Curing efficiency and mechanical properties of ZnO/SiO_2 filled adhesives were investigated and compare to those obtained by using SiO_2 filled adhesives.

2. Experimental methods

2.1. Synthesis and characterization of ZnO/SiO_2 particles

ZnO/SiO_2 particles were synthesized by sol–gel procedure described in the literature [5]. 12 g of amorphous silica (SiO_2) powders were dispersed in 450 ml of ethanol

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by sonication for 10 min. Then the solution containing SiO_2 was heated to 65 °C. $Zn(CH_3COO)_2{\cdot}H_2O$ (21.95 g) and NaOH (2 g) were added simultaneously into the SiO_2 ethanol aqueous solution. The system was then continuously stirred for 20 min at 65 °C. After 20 min, ZnO/SiO_2 particles were filtered, washed four times with ethanol, and dried in air at room temperature.

The morphology of ZnO/SiO_2 particles was observed using a scanning electron microscope (SEM, Bruker, Germany). To analyze the Zn content of the ZnO/SiO_2 particles, elementary characterization was carried out using an energy-dispersive spectroscopy (EDS, Bruker, Germany).

2.2. Preparation and application of SiO_2 and ZnO/SiO_2 filled adhesives

Cold vulcanizing adhesives (CVA) are composed of two separate components which are mixed immediately before use. One of the components contains chloroprene based liquid rubber constituents, while the other component contains hardener. For the preparation of rubber compounds, blending of chloroprene rubber at different filler was carried out on a two roll mill. The curing formulation and filler content of composites are given in Table I. Composite of CVA–ZnO/SiO_2 were prepared in the same manner but using ZnO/SiO_2 as a filler instead of silica.

TABLE I

Formulation of rubber composites in phr (parts by weight per hundred parts of rubber by weight).

Materials	CVA-SiO_2	CVA-ZnO/SiO_2
chloroprene rubber	100	100
magnesium oxide	7	7
zinc oxide	3	3
filler	7	7
SiO_2	9	–
ZnO/SiO_2	–	9
accelerator	3.5	3.5

In splicing process of textile belts by cold vulcanization, cold vulcanized adhesive mixed with hardener by ratio 100:5 was applied on both test surfaces prepared for splicing. Test pieces, which were cut from the same area of the fabric conveyor belt, were used for measuring adhesive strength 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 h), temperature (25 °C) and pressure (0.3 kg/cm^2).

2.3. Cure characteristics, physical and mechanical properties of adhesives

The curing characteristics of the rubber compounds were determined using moving die rheometer (MDR, GOTECH 2000 A) at 190 °C according to ASTM D 1646 [6]. Obtained values of curing characteristic of rubber compound filled by ZnO/SiO_2 filler was compared with rubber compounds filled by SiO_2 filler. Measurements of adhesive strength of spliced fabric conveyor belt samples were carried out on the tensile testing machine (Devotrans DVT). The tension rate was 100 mm/min. 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 [7], at room temperature. Two measurements were carried out for each sample, and the average value was reported.

2.4. Swelling properties and cross-link density measurement

Swelling behavior of the cured rubber blends was determined by the change in mass using the modified method from Ahmed et al. [8]. Samples of rubber blend were weighed and inserted into the test tubes containing n-hexane solvent at constant temperature. The samples were periodically removed from the test tubes and blotted with filter paper to remove excess solvent from the surface of the samples. The swollen weight was immediately measured using an electrical balance. This procedure was continued until equilibrium, which took 15 days.

The mol.% uptake of the solvent (Q_t), swelling index (SI) and swelling coefficient (α) of the samples were calculated by the following equations [8, 9]:

$$Q_t\% = \frac{(W_2 - W_1)/W_1}{W_m} \times 100\%, \tag{1}$$

$$SI\% = (W_1 - W_2)/W_2 \times 100\%, \tag{2}$$

$$\alpha = \frac{W_2}{W_1}\rho_s^{-1}. \tag{3}$$

W_1 is the weight of the sample before swelling and W_2 is the weight of sample after swelling. W_m and ρ_s are molar mass and density of the solvent, respectively.

The physical cross-link density (v) of the vulcanized rubber blends was calculated using the Flory–Rehner equation using the volume fraction (v_r) of the swollen rubber network in the solvent at equilibrium state according to the following equation [10, 11]:

$$v = \frac{-\left[\ln(1 - v_r) + v_r + x v_r^2\right]}{\rho_r V_s\left(\sqrt[3]{v_r}\right)}. \tag{4}$$

x is the interaction parameter between the polymer and solvent, V_s is the molar volume of the swelling solvent. The V_s is 130.3 cm^3/mol. The interaction parameter (x) of chloroprene rubber with n-hexane is 0.48 for emulsion chloroprene rubber. The v_r is obtained by the following equation [11, 12]:

$$v_r = \frac{W_{rf}/\rho_r}{W_{rf}/\rho_r + W_{sf}/\rho_s}. \tag{5}$$

W_{rf} and W_{sf} are the weight fractions of polymer and solvent, respectively, in the swollen material. Densities of n-hexane (ρ_s) and rubber (ρ_r) are 0.663 and 0.9598 g/cm^3, respectively.

3. Results and discussion

3.1. Characterization of ZnO/SiO_2 particles

Figure 1 displays the SEM micrographs of ZnO/SiO_2 particles, taken at $10^2\times$ magnification. The spherical

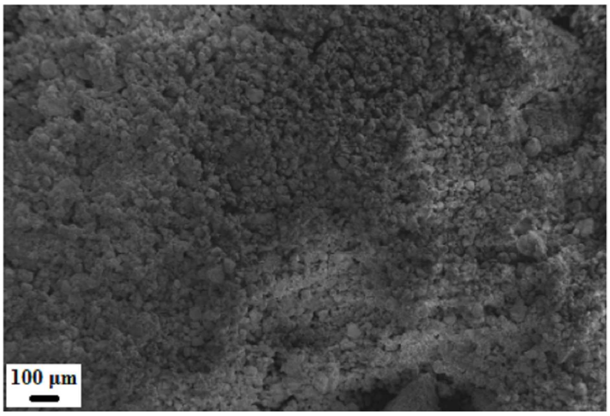

Fig. 1. SEM micrograph of ZnO/SiO_2 particles.

shaped particles with clumped distributions are visible through the SEM analysis.

Elemental analysis by EDS in point mode was conducted at the surface of ZnO/SiO_2 particles. As shown in Fig. 2, the elements like carbon, oxygen, zinc and silicon are detected. The mass fraction of Zn was 8.22%, which illustrated that zinc nanoparticles actually existed on the surface of silica (Table II).

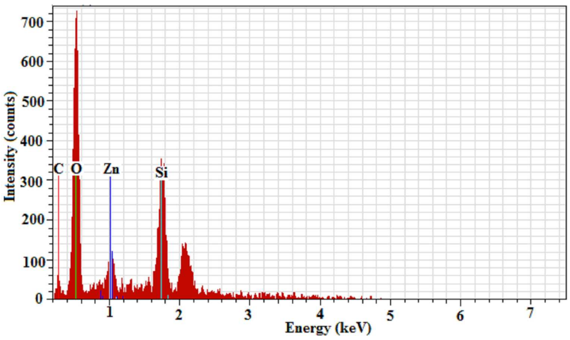

Fig. 2. EDS patterns of ZnO/SiO_2 particles.

TABLE II

Contents of different elements (in wt% and at%) in the ZnO/SiO_2 particles

Element	[wt%]	[at.%]
carbon	3.32	5.63
oxygen	50.17	63.98
zinc	8.22	2.56
silicon	38.29	27.82

3.2. Rheological characteristics

The cure characteristics of the rubber compounds are elucidated in terms of maximum torque (M_H), minimum torque (M_L), torque difference (ΔM), optimum cure time (t_{c90}), scorch time (t_{s2}) and cure rate index (CRI). The cure rate index, which is a measure of cure reaction rate, was calculated from the following equation [13]:

$$CRI = 100\% / (t_{c90} - t_{s2}) . \tag{6}$$

Cure parameters of chloroprene blend compounds are displayed in Table III. The results show that the scorch time and cure time of the ZnO/SiO_2 filled rubber blends are lower than the SiO_2 filled rubber blends. ZnO/SiO_2 filled compounds have significantly faster cure rate index in comparison with the SiO_2 filled compounds. The silanol groups on silica surface could cross-link with chlorine atom of chloroprene rubber [14]. The reductions of both t_{s2} and t_{c90} found in this study show that the chemical interaction between chloroprene rubber and silica increased in the presence of ZnO particles, bonded to surface of SiO_2 filler.

The maximum torque value of SiO_2 filled rubber compound is higher than value of ZnO/SiO_2 filled rubber compound. The higher values of maximum torque show higher stiffness at the end of the vulcanization [15]. The lower M_L value for SiO_2 filled rubber blends indicates the better processability of this formulation compared to ZnO/SiO_2 filled rubber blends [16].

TABLE III

Curing characteristics of of SiO_2 and ZnO/SiO_2 filled chloroprene blends.

Curing characteristic	SiO_2	ZnO/SiO_2
minimum torque [lb.in]	0.560	1.115
maximum torque [lb.in]	5.403	3.987
Δ torque [lb.in]	4.843	2.872
cure time [min]	4:03	1:04
scorch time [min]	0:56	0:38
cure rate index [min^{-1}]	32.05	230.41

3.3. Physical and mechanical properties

Figure 3 shows the variation of maximum strength values of cold vulcanizing adhesives with adhesion time. ZnO/SiO_2 filler provided a higher adhesive strength than silica for cold vulcanizing adhesives in the 4, 8, and 24 h of adhesion. As ZnO/SiO_2 particles could act as a curing accelerator for chloroprene rubber, loading of ZnO/SiO_2 particles instead of SiO_2 in adhesive compound results in both faster adhesion and increases adhesive strength.

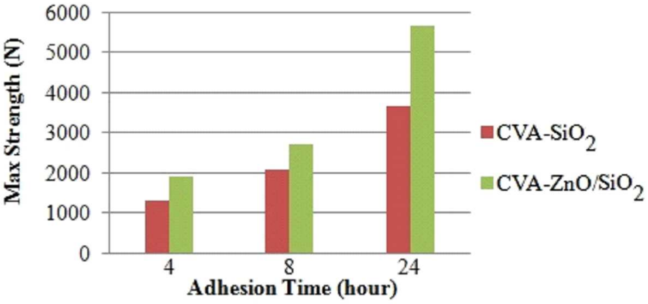

Fig. 3. Variation of maximum strength values of spliced conveyor belt with adhesion time (pressure: 0.3 kg/cm^2; temperature: 25 °C).

Densities of SiO_2 and ZnO/SiO_2 filled chloroprene rubber blends were 1.059 g/cm^3 and 1.130 g/cm^3, respectively. Rubber density depends upon the kind of rubber which is used for blends. The change in density may be due to the chemical reaction between rubber and curing agents.

3.4. Swelling properties and cross-link density

Table IV shows the swelling and cross-link parameters of SiO_2 and ZnO/SiO_2 filled rubber blends. The swelling index and coefficient values of ZnO/SiO_2 filled rubber blend are lower than the values of SiO_2 filled rubber blend due to the increases in cross-link density and the decreases in polymer–solvent interaction. The swelling is directly correlated to the cross-link density of a network chain [12]. The less solvent uptake into the ZnO/SiO_2 filled rubber blends compared to the SiO_2 filled rubber blends are due to the higher crosslink density of ZnO/SiO_2 filled rubber blends.

TABLE IV

Swelling and cross-link parameters of SiO_2 and ZnO/SiO_2 filled rubber blends.

	SiO_2	ZnO/SiO_2
swelling index SI [%]	22.80	17.17
swelling coefficient (α)	0.344	0.259
mol % uptake of the solvent (q_t)	0.265	0.199
crosslink density [10^4 mol cm^{-3}]	53.30	73.41

4. Conclusion

The present study aimed at improving the efficiency of the cold vulcanizing adhesives using ZnO/SiO_2 particles, which simultaneously behave as curing agent and rubber reinforcing. The ZnO/SiO_2 particles were incorporated in the rubber matrixes. The mechanical properties, vulcanization behaviour and cross-link density of the compounds were evaluated. ZnO/SiO_2 filled rubber blends demonstrated better curing efficiency and improved adhesive strength properties in adhesives, compared to those obtained by using of SiO_2 filler. ZnO/SiO_2 particles also introduced greater cross-link density in the rubber vulcanizate in comparison to SiO_2. Curing characteristics showed that the ZnO/SiO_2 particles accelerate the vulcanization process with the reducing cure time and scorch time. From this study, it is concluded that ZnO nanoparticles bonded to SiO_2 filler will play an important role as a new curing accelerator in rubber industry.

Acknowledgments

This study has been supported by Scientific Project 2015-01.BŞEÜ.03-03 from Bilecik Seyh Edebali University, Turkey. The authors would like to thank BILLAS Tire & Rubber Industry and Trade Inc. and OZERBAND Conveyor Belt Industry and Trade Inc., Turkey for assisting this research.

References

[1] M. Barburski, *J. Industr. Text.* **45**, 1322 (2016).

[2] A. Whelan, *Polymer Technology Dictionary*, Springer Science & Business Media, London 1994.

[3] C. Chandrasekaran, *Rubber Seals for Fluid and Hydraulic Systems*, William Andrew, Burlington 2009.

[4] I.M. Ulfah, R. Fidyaningsih, S. Rahayu, D.A. Fitriani, D.A. Saputra, D.A. Winarto, L.A. Wisojodharmo, *Proced. Chem.* **16**, 258 (2015).

[5] A. Susanna, L. Armelao, E. Callone, S. Dirč, M. D'Arienzo, B. Di Credico, L. Giannini, T. Hanel, F. Morazzoni, R. Scotti, *Chem. Eng. J.* **275**, 245 (2015).

[6] ASTM D1646:2015, *Standard Test Methods for Rubber — Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer)*, West Conshohocken (PA) 2015.

[7] ASTM D297:2015, *Standard Test Methods for Rubber Products — Chemical Analysis*, West Conshohocken, (PA) 2015.

[8] K. Ahmed, S.S. Nizami, N.Z. Raza, K. Shirin, *Adv. Mater. Phys. Chem.* **2**, 90 (2012).

[9] K. Ahmed, S.S. Nizami, N.Z. Riza, *J. Adv. Res.* **5**, 165 (2014).

[10] J. Wu, W. Xing, G. Huang, H. Li, M. Tang, S. Wu, Y. Liu, *Polymer* **54**, 3314 (2013).

[11] S.S. Choi, E. Kim, *Polym. Test.* **42**, 62 (2015).

[12] B. Alcock, T.A. Peters, R.H. Gaarder, J.K. Jørgensen, *Polym. Test.* **47**, 22 (2015).

[13] S. Ngamsurat, K. Boonkerd, U. Leela-Adisorn, P. Potiyaraj, *En. Proced.* **9**, 452 (2011).

[14] P. Sae-oui, C. Sirisinha, U. Thepsuwan, K. Hatthapanit, *Europ. Polym. J.* **43**, 185 (2007).

[15] S. Domčeková, D. Ondrušová, Z. Mičicová, M. Pajtášová, R. Moravčík, L. Buňová, *Proced. Eng.* **136**, 245 (2016).

[16] S.Z. Salleh, M.Z. Ahmad, H. Ismail, *Proced. Chem.* **19**, 346 (2016).