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Effect of titanate coupling agent on the mechanical properties of flyash filled styrene butadiene

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Attempts have been made for utilization of flyash as a filler in elastomers as it is a waste product of thermal power stations, generated in huge quantities and has been posing problems of disposal. It is used as a filler for rubbers and plastics to a very small extent. It has been established that flyash does not at all contribute in enhancing mechanical properties of composites. The purpose of this work was to make meaningful utilization of flyash as a filler, by treating it with silane coupling agent LICA 01 i.e. neopentyl (diallyl)oxy, trineodecanonyl titanate. Composites of styrene butadiene rubber (SBR) containing treated and untreated flyash were made with varying proportions. A two-roll mill was used for dispersing the filler in the rubber and compression molding technique was used to cure the compounded material in sheet form. Tensile properties were measured on a computerized UTM using ASTM procedure. Comparison of properties of composites filled with treated and untreated flyash established that the treatment with flyash imparts better reinforcing properties. Tensile strength was improved by 13% while modulus at 400% and Young's modulus were improved by 198 and 17% respectively at the volume fraction (0.42).

Flyash an absolutely low cost inorganic waste product of thermal power stations is posing a menace and hence requires to be utilized for curbing environmental pollution. Attempts have been made to utilize flyash meaningfully for various purposes[1,2] viz. chemical field, agricultural field, cement and construction industries, but very few attempts have been made as a filler in elastomers and plastics[3,4] which could be the largest field for its large-scale utilization. As such flyash does not contribute to reinforcement in its untreated form. It was reasoned that promotion in adhesion between its surface with matrix material could bring about reinforcement.

Coupling agents which work as molecular bridges at the interface between two dissimilar substrates, such as inorganic fillers and an organic polymer matrix[5], were considered in the study.

Typically, silane – treated inorganic fillers are hydrophobic, orgnophilic and organofunctional. When incorporated into polymer systems, they often promote adhesion, catalyze, improve dispersion and rheology; improve impact strength, prevent embrittlement, improve mechanical properties etc. Reactivity of such coupling agents is possible with diverse substrates[3-11]. A study on the effect of treatment is carried out using flyash treated with 1% silane coupling agent. To ascertain the effect treatment of coupling agent on tensile properties of composites. It is observed that tensile strength was improved by 13% while modulus at 400% and Young's modulus were improved by 198 and 17% respectively at the volume fraction (0.42).

Experimental

Materials : The coupling agent [(LICA 01) : neopentyl (diallyl)oxy, trineodecanonyl titanate] was imported from Ken Rich Petrochemicals, Inc, USA. Flyash was procured from thermal power station, Deepnagar, Bhusawal (India). Other chemicals such as a stearic acid, zinc oxide, *N*-(1,3-dimethyl butyl)-*N*-phenyl-*p*-phenylene diamine (Antioxidant), tetramethyl thiuram disulphide (TMTD), zinc diethyl dithiocarbamate (ZDC) and sulphur) used were manufactured by Bayer India Ltd. Physical parameters of titanate coupling agent and constituents of flyash are reported as below :

Physical characterization of coupling agents (LICA 01) : Chemical name – neopentyl(diallyl)oxy, trineodecanonyl titanate; purity – 99%; physical form – liquid; color – brownish orange; sp. gr. – 1.02; flash point – 160; b.p. – 320°; viscosity – 850 cp; pH – 5; solubility – isopropyl alcohol, xylene, toluene, DOP, mineral oil, MEK.

Physical properties and of flyash : Colour – gray; particle shape – spherical; average particle size – 4–5 μM; bulk density – 0.8 g/cc; sp. gr. – 2.1–2.6; pH – 7.0–7.5.

Constituents of flyash : Silica (SiO_2) – 63.00; alumina

(Al_2O_3) – 29.00; magnesium oxide (MgO) – 3.50; potassium oxide (K_2O) – 0.30; calcium oxide (CaO) – 0.15; sodium oxide (Na_2O) – 0.15.

Characteristics of styrene-butadiene rubber : Trade name – Techlen SBR 1502; manufacture – IPCL, Baroda, India; volatile matter – 0.2%; polymerization system – cold emulsion polymerization; ash content – 0.3%; organic acid – 6.6%; mooney viscosity – 50; sp. gr. – 0.94.

Particle size analysis :

Surface area is a major parameter in connection with filler-matrix interaction for reinforcing purposes. The finer the particle size, the higher is the surface area and higher the reinforcement. The details regarding particle size distribution of the flyash used in the study are given in Fig. 1. The data was used to find out the mean particle size, which was found to be 2 µm. The analysis is done on Shimadzu SALD-2001 instrument by a Shimadzu (Asia Pacific) Pvt. Ltd., Singapore.

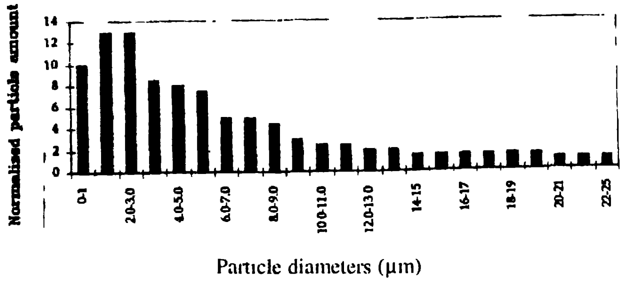

Fig. 1. Particle size distribution of flyash.

Treatment of flyash by titanate coupling agent :

The coupling agent (1 g) was mixed[3–13] with ethylalcohol (100 ml) to make a solution for applying to filler (100 g) i.e. one gram of coupling agent was used per 100 g of flyash. The filler (flyash) was mixed with the solution of coupling agent in ethylene alcohol with stirring to ensure uniform distribution of the coupling agent, mixing was continued for 30 min. The treated filler (flyash) was then dried at 100°C in an oven for about 5 h to allow complete evaporation of the alcohol.

Preparation of composites :

The compounding of the rubber was carried out on laboratory scale two roll mill. The rubber was first masticated for 5 min. Additives were added as : SBR – 100; stearic acid – 3.0; zinc oxide – 3.0; antioxidant [*N*-(1,3-dimethylbutyl)-*N*-phenyl-*p*-phenylenediamine) – 1.0; accelerator (I) [tetramethyl thiuram disulphide (TMTD)] – 0.50; accelerator (II) [zinc diethyl dithiocarbamate (ZDC)] – 0.50; sulphur – 1.50; treated filler – variable; curing time – 30 min; curing temp. – 150°C. After the addition of all of the additives, the compounding was continued for 30 min for homogeneous mixing. This compounded matter was then vulcanized using sulfur system by press curing method (compression molding machine) at 150°C for 30 min in chrome plated mould having cavity dimensions (15 cm × 15 cm × 0.3 cm). The curing characteristics were determined using a multichannel DTA. The curing time was determined by subjecting compounds to DTA at 150°C, for various intervals and observing the thermograms[4,10].

Scanning electron microscopy (SEM) :

SEM was carried out by Leica Cambridge (Stereoscan 440) scanning electron microscope (Cambridge, UK). Polymer specimens were coated with gold (50 µm thick) in an automatic sputter coater (Polaron Equipment Ltd., Scanning electron microscope coating unit E 5000, UK). Acceleration potential was 20 kV. Photographs of representative areas of the sample were taken at different 500 and 1000X magnifications.

Measurement of mechanical properties :

Mechanical properties such as tensile strength, modulus at 100%, 200% were determined by subjecting dumbbell shaped specimens (in confirmation with ASTM D-412) to a universal testing machine (R & D Equipment, Mumbai, India). The sheets from which specimen were cut had been conditioned for 24 h prior to subjecting to universal testing machine (100 kg load cell), at a crosshead speed of 50 cm/min. Hardness was measured on Durometer (Blue-Steel, India) on shore-A scale.

Results and discussion

Comparison between treated and untreated flyash – filled SBR composites are made by testing the composites for mechanical properties viz. tensile strength, moduli at 100%, 400%, Young modulus and the hardness.

Treated flyash composites showed improvement in mechanical properties and the mechanism of adhesion due to coupling agent is proposed for flyash as a filler. Plates 3 and 4 pertain to SEM of SBR composites of untreated and treated flyash while Plates 1 and 2 show SEM of treated and untreated flyash. It is clear from photographs that the distribution of treated flyash in rubber matrix is quite homogeneous.

Tensile strength :

The dependence of the tensile strength on volume fraction of flyash is represented in Fig. 2. It is seen that on increasing the volume fraction of (both treated and untreated) flyash, the tensile strength increases up to a certain value because the filler has reinforcing ability. Both the treated as

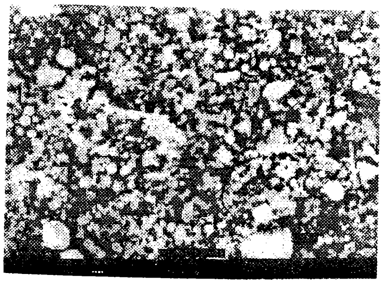

Plate 1. SEM of untreated flyash – 75 μ.

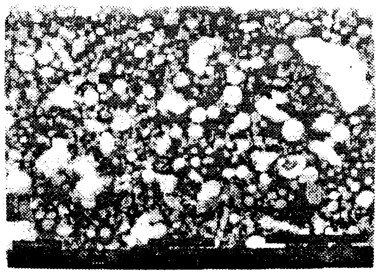

Plate 2. SEM of treated (LICA 01) flyash microsize – 75 μ.

Plate 3. SEM of untreated flyash filled - SBR at volume fraction (0.50).

Plate 4. SEM of LICA 01 treated flyash filled – SBR at volume fraction (0.55).

well as untreated showed this ability. The treatment proved to improve substantially the extent of reinforcement. After attaining, the maximum (about 0.52 and 0.45 volume fraction for treated and untreated) the decline started. This decline is because of dewetting effect, which has resulted from inadequate matrix material to hold filler particle. The peak values of tensile strength of the composites correspond to 1.80 MPa and 1.60 MPa. For treated and untreated flyash respectively. It is note worthy that the tensile strength of flyash treated SBR composites is higher than that of untreated flyash – SBR composites.

Modulus at 100% and 400% elongations :

The dependence of modulus at 100%, 400% elongation with volume fraction of treated and untreated flyash – SBR composites show that in both the cases moduli increases initially, attains a maximum value for particular value of concentration of fillers and it decreases. The peak values of moduli of both the composites lie at 0.55 and 0.45 volume fractions of flyash treated and untreated. The modulus of treated flyash is about 7.20 times higher than that of untreated flyash. The initial rate of increment in the property with increasing volume fraction of the filler was similar in both the cases, however, after volume fraction 0.40 the rate of increment for composites filled with treated flyash was substantially high.

Young's modulus :

The peak value for Young's modulus as a function of volume fraction composites is obtained to be 1.85 MPa at 0.42 volume fraction and that for untreated is 1.59 MPa at 0.42 volume fraction, i.e. it shows 1.16 times higher than untreated flyash composites.

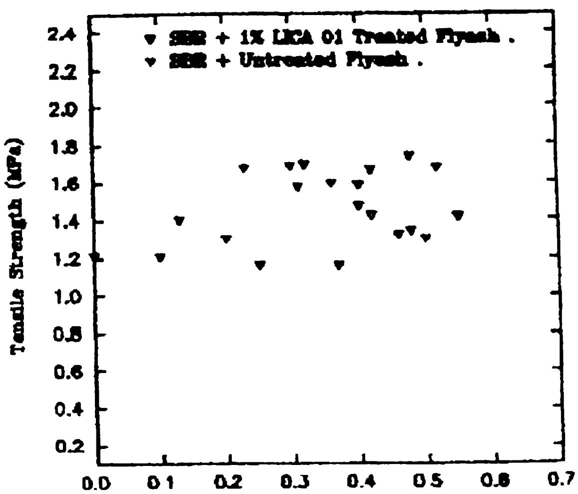

Fig. 2. Tensile strength as a function of treated and untreated flyash - SBR composites.

SEM of composites :

The SEM photomicrographs of treated and untreated flyash filler are shown in Plates 1 and 2. It is clear from these photographs that treated flyash exhibit uniform, spherical shape and fine discrete particulate nature while untreated flyash shows tendency to form agglomerates. Titanate coupling agent helps in proper dispersion of flyash particles as evident from Plate 2 and is responsible for higher strength of composites due to its homogeneous dispersion in the composites. SEM of flyash – filled vulcanizates are shown in Plates 3 and 4. Untreated composite fracture shows non-adhesive appearance and formation of agglomerates while treated composites show a very uniform distribution, regular, adhesive appearance causing further enhancement in polymer-filler attachment.

Hardness :

The dependence of the hardness on concentration of treated and untreated filler in SBR shows that, hardness of both the treated and untreated flyash – SBR composite increased linearly on increasing the concentrations of fillers, however with a constant rate of increment.

Conclusions :

Higher values of tensile properties are obtained in the case of composites, filled with treated flyash indicating the involvement of silane coupling agent in the composites.

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