Studies on the Effect of Titanate Coupling Agent (2.0%) on the Mechanical Properties of Flyash-Filled Polybutadiene Rubber

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ABSTRACT: Flyash, a waste product of thermal power stations, generated in huge quantities, has been posing problems of disposal. Attempts have been made for its utilization as a filler in elastomers and plastics; however, it has been established that untreated 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 a titanate coupling agent and to use it as a filler in PBR. The properties under consideration were tensile strength, modulus at 100 and 400%, Young's modulus, hardness, etc. Composites were made with varying proportion of untreated and treated flyash. A two-roll mill was used for dispersing the filler in the rubber, and a compression-molding technique was used to cure the compound in sheet form. Tensile properties were measured on a computerized UTM using an ASTM procedure. Comparison of properties of composites filled with treated and untreated flyash established that treatment of flyash imparts better reinforcing properties. Tensile strength was improved by 50%, while modulus at 400% was improved by 400%. Similarly, Young's modulus also was improved by 209%. The Titanate-coupling agent used here has promoted adhesion between flyash and the PBR. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1293–1298, 2004

Key words: polybutadiene; composites; mechanical properties

INTRODUCTION

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 that 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, titanate-treated inorganic fillers are hydrophobic, organophilic 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 was carried out earlier using flyash treated with a 1% titanate coupling agent.[10,11] The results of the study were encouraging, and hence this work was undertaken to ascertain the effect treatment of 2.0% coupling agent on tensile properties of the composites.

EXPERIMENTAL

Materials

The Titanate 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).

PBR, a *cis*-1, 4-polybutadiene rubber, was manufactured by Indian Petrochemical Corporation limited (IPCL), Baroda, 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 dithio-

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TABLE I
Physical Characterization of Titanate Coupling Agents (LICA 01)

Chemical name	Neopentyl (diallyl) oxy, trineodecanonyl titanate
Typical purity	99%
Physical form	Liquid
Color	Brownish orange
Specific gravity	1.02
Flash point	160
Boiling point	320
Viscosity	850 cp
pH	5
Solubility	Isopropyl alcohol, xylem, Toluene, DOP, Mineral oil, MEK
Density	Heavier

TABLE II
Constituents of Flyash

Compounds	Percentage
Silica (SiO_2)	63.00
Alumina (Al_2O_3)	29.00
Magnesium oxide (MgO)	03.50
Potassium oxide (K_2O)	0.30
Calcium oxide (CaO)	0.15
Sodium oxide (Na_2O)	0.15

carbamate (ZDC), and Sulphur] were manufactured by Bayer India Ltd. Physical parameters of a titanate coupling agent, constituents of flyash, and characteristics of polybutadiene are reported in Tables I, II, and III, respectively.

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 the surface area and the higher the reinforcement. The details regarding particle size distribution of the flyash used in the study are given in Figure 1. The data were used to find out the mean particle size, which turned out to be 2 μm. The analysis is done on a Shimadzu SALD-2001 instrument.

Treatment on flyash by titanate coupling agent

Two percent solution of the titanate coupling agent (LICA 01) in isopropyl alcohol was used for applying to 100 g of filler,[5–14] that is, 2 g of the coupling agent was used per 100 g of flyash. The filler (flyash) was mixed with the solution of the coupling agent in isopropyl 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 ethanol.

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 sequentially, as given in Table IV. After the addition of all of the additives, the compounding was continued for 30 min so that additives got mixed homogeneously. This compounded matter was then vulcanized using a sulfur system by a press-curing method (compression molding machine) at 150°C for 30 min in a chrome-plated mold having cavity dimensions of 15 × 15 × 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.[7]

Scanning electron microscopy (SEM)

SEM was carried out by a Leica Cambridge (Stereoscan 440) scanning electron microscope (Cam-

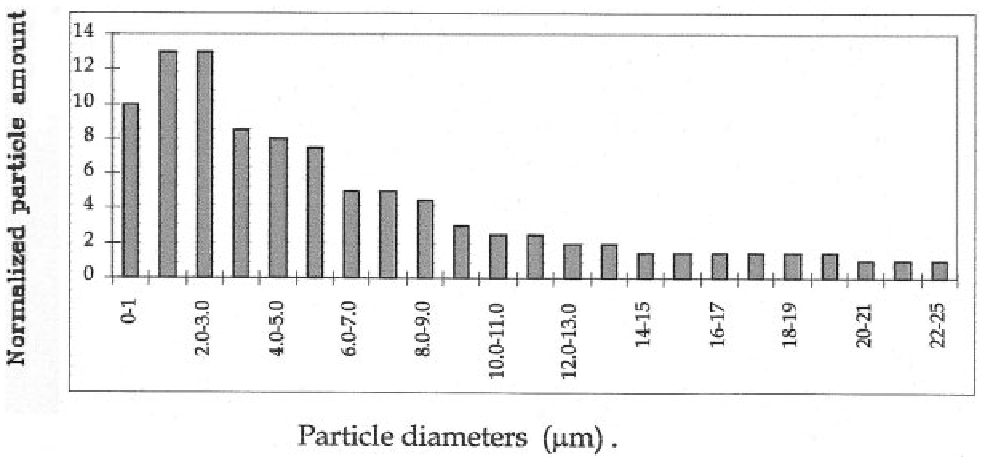


Figure 1 Particle size distribution of flyash.

TABLE III
General Characteristics of Polybutadiene Rubber

Trade name	Cisamer 1220
Manufacturer	IPCL Baroda, India
Appearance	Light Amber/Bale.
Polymerization system	Solution
Microstructure	98% *cis*
Specific gravity	0.91
Mooney viscosity	43 ML_{1+4} 100°C
Ash content	0.1%

bridge, 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 magnifications.

Measurement of mechanical properties

Mechanical properties such as tensile strength and modulus at 100 and 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 specimens were cut had been conditioned for 24 h prior to subjecting to tensile testing with a 100-kg load cell, at a crosshead speed of 50 cm/min. Hardness was measured on a Durometer (Blue-Steel, India) on shore-A scale.

RESULTS AND DISCUSSION

Comparison between treated and untreated flyash-filled PBR composites is made by testing the composites for mechanical properties viz. tensile strength, moduli at 100 and 400%, and hardness.

Treated flyash composites showed improvement in mechanical properties, and the mechanism of adhesion due to the coupling agent is proposed for flyash as a filler. Figures 2 and 3 pertain to SEM of PBR composites of untreated and treated flyash. It is clear from the photographs that the treatment caused a favorable effect as the distribution of treated flyash in the rubber matrix (observed in Fig. 3) is quite homogeneous.

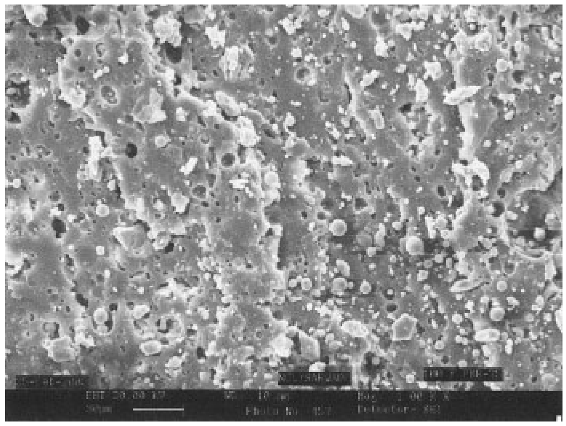


Figure 2 SEM of untreated flyash-filled PBR at volume fraction (0.48).

Tensile strength

The dependence of the tensile strength on the volume fraction of flyash is represented in Figure 4. It is seen that upon increasing the volume fraction of (both treated and untreated) flyash, the tensile strength increases up to a certain value because the filler has some reinforcing ability. However, treatment improved the reinforcement, to the extent of 40% approximately. After attaining the maximum tensile strength (corresponding to 0.51 volume fraction) the decline started. This decline is obviously because of the dewetting effect, coming into play when inadequate ma-

TABLE IV
Compounding Recipe

Component	Proportion
PBR	100
Stearic acid	2.0
Zinc oxide	3.0
Antioxidant (*N* - (1,3-dimethyl butyl)-*N*-phenyl-*p*-phenylene diamine)	1.0
Accelerator (1) [Tetramethyl thiuram disulphide (TMTD)]	0.5
Accelerator (II) [(Zinc diethyl dithiocarbamate (ZDC)]	0.5
Sulphur	1.5
Filler (treated/untreated)	Variable
Curing time	30 min
Curing temp.	150°C

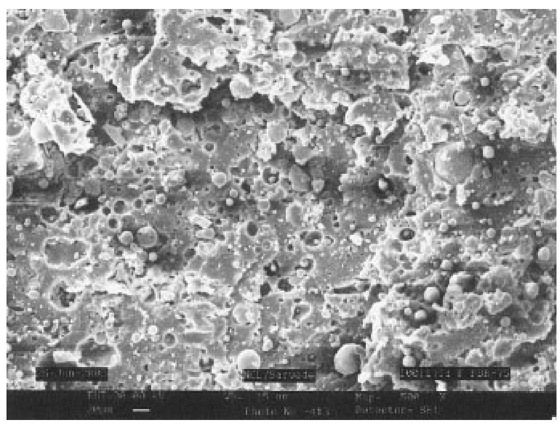


Figure 3 SEM of LICA 01 treated flyash-filled PBR at volume fraction (0.54).

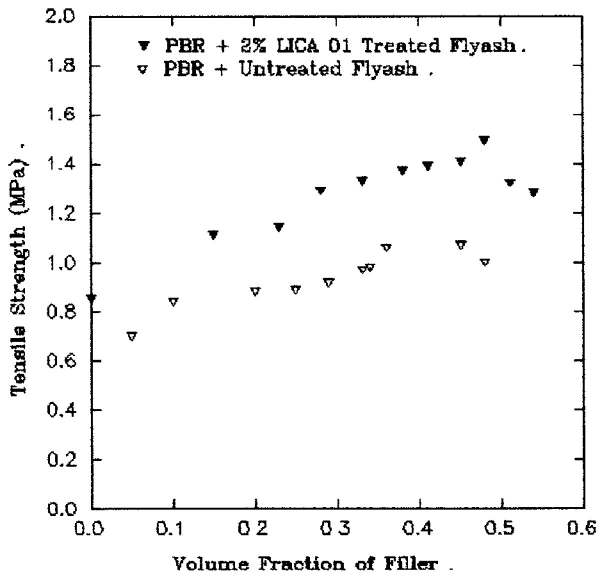


Figure 4 Tensile strength as a function of volume f raction of treated and untreated flyash–PBR composites.

trix material is available to hold the filler phase, which is in excess. The peak values of tensile strength of the composites correspond to 1.49 and 1.07 MPa for treated and untreated flyash, respectively.

Modulus at 100% and 400% elongations

The dependence of modulus at 100 and 400% elongation with the volume fraction of treated and untreated flyash–PBR composites is depicted in Figures 5 and 6, respectively. It is seen that in both cases the moduli increases initially, attains a maximum value for particular value of concentration of fillers, then decreases.

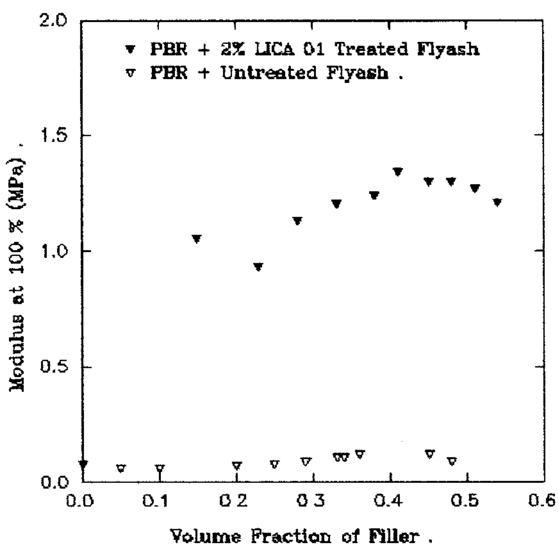


Figure 5 Modulus at 100% as a function of volume fraction of treated and untreated flyash–PBR composites.

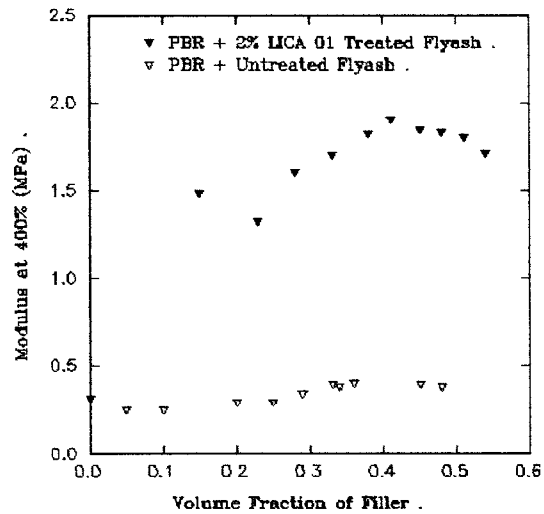


Figure 6 Modulus at 400% as a function of volume fraction of treated and untreated flyash–PBR composites.

The peak values of the moduli of both types of composites lie at 0.45 volume fractions (treated and untreated). The modulus of treated flyash is about 4.87 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, afterwards, the rate of increment for composites filled with treated flyash was substantially higher.

Young's modulus

Young's modulus as a function of volume fraction of filler for treated and untreated flyash-filled PBR composites is represented in Figure 7.

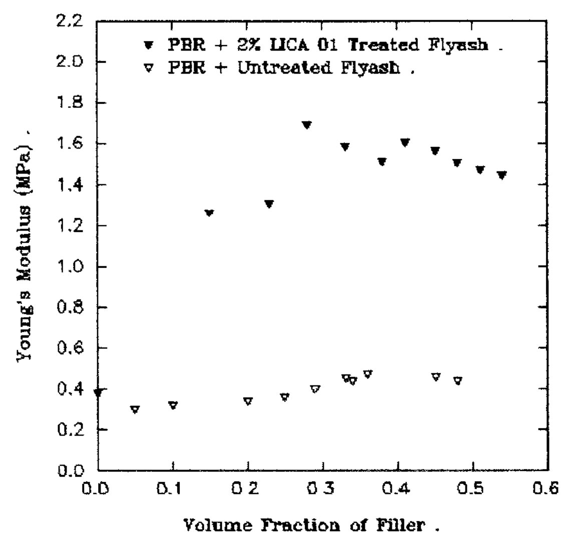
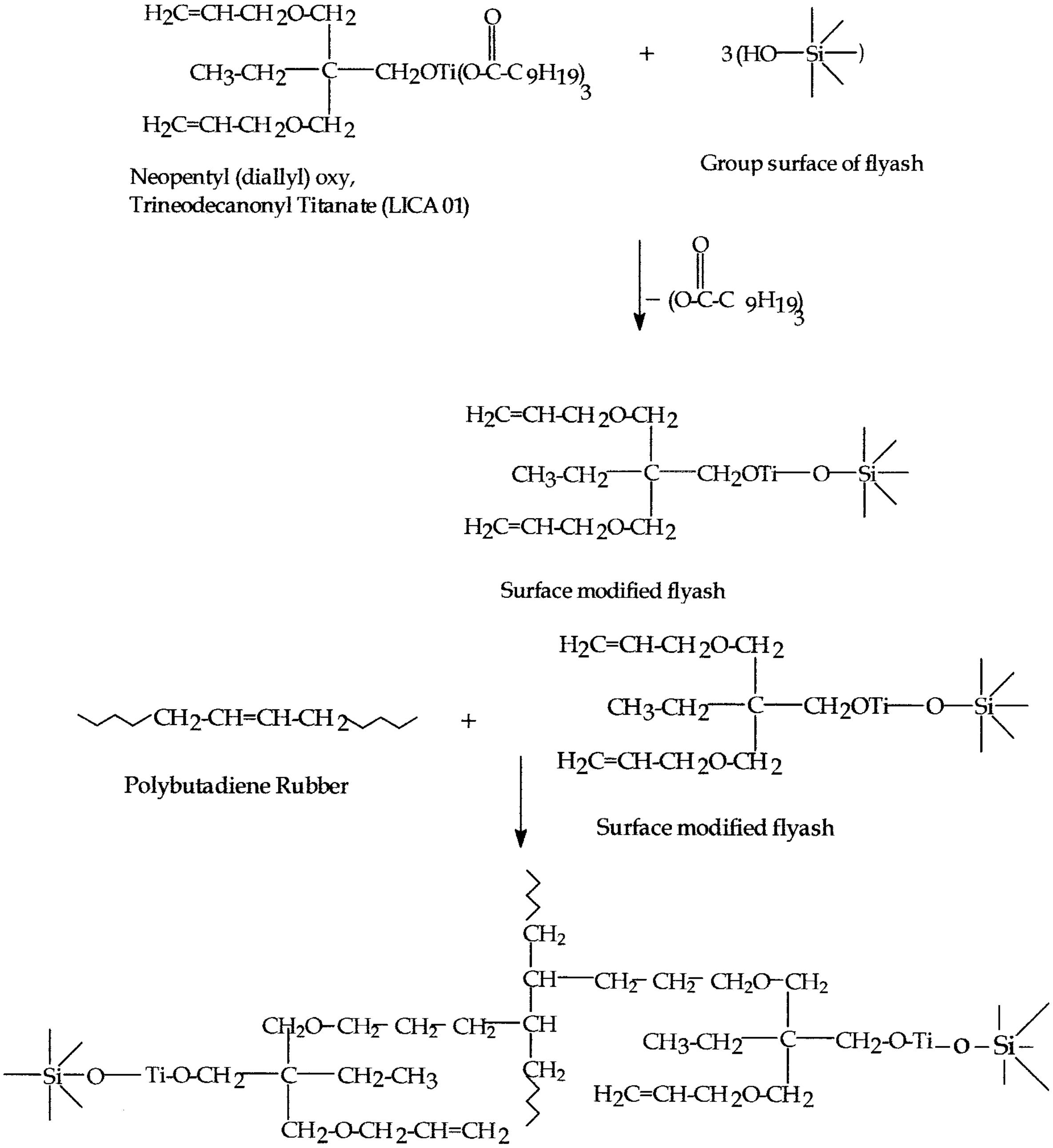


Figure 7 Young's modulus as a function of volume fraction of treated and untreated flyash–PBR composites.

The peak value for treated flyash composites is obtained to be 1.60 MPa at 0.42 volume fraction, while that for untreated is 0.45 MPa at a 0.33 volume fraction. This showed that the treatment not only enhanced the magnitude of Young's modulus but also allowed more filler to be accommodated in the composites, thereby making possible a reduction in the cost.

Mechanism of PBR–filler interaction

A mechanism of PBR–filler (flyash) interaction due to the incorporation of LICA 01 has the following two steps:[3–14] Step I—reaction between titanate coupling agent and a flyash (Surface); Step II—reaction between surface-modified flyash and unsaturation in PBR.



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Thus, a single molecule of LICA 01 can couple free radically with one olefinic unit of the elastomer molecule and also two —OH groups of filler, resulting in an increased elastomer–filler interaction.

Hardness

Figure 8 shows the dependence of the hardness on the concentration of the treated and untreated filler in PBR. It is seen that hardness of both the treated and

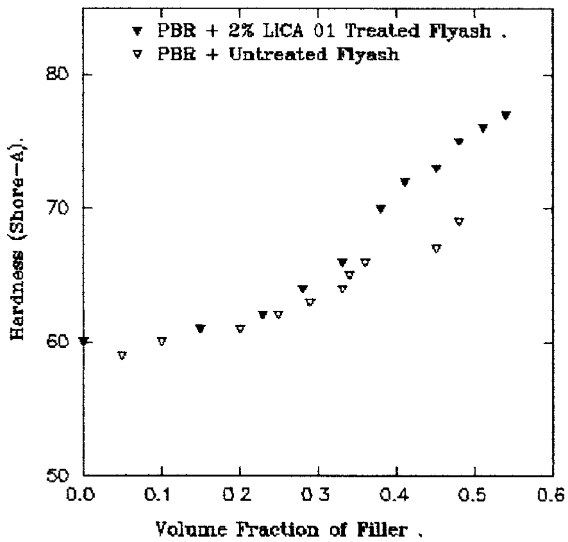

Figure 8 Hardness as a function of volume fraction of treated and untreated flyash–PBR composites.

untreated flyash–PBR composite increased linearly upon increasing the concentrations of fillers; however, with a constant rate of increment.

CONCLUSIONS

The treatment of flyash with coupling agent [Neopentyl (diallyl) oxy, Trineodecanonyl Titanate] has effected enhanced magnitudes of tensile strength modulus at 100 and 400% elongation and Young's modulus. The enhancement was prominent in modulus 400% and Young's modulusm, which showed that matrix filler adhesion was improved as a result of the treatment. Further, the treatment of filler resulted in incorporating the filler in composites to a higher extent without compromising quality. This will definitely be useful in cost reduction.

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