

# Studies on Mechanical Properties of Fly Ash Filled PPO Composite with Coupling Agent

RSN Sahai, and Neha Pawar

**Abstract**—In this study, the effect of the coupling agent on fly ash filled polyphenylene oxide composites with different filler concentration (5 to 25% by weight) on the mechanical and rheological properties of the polyphenylene oxide composites (PPO) was investigated. The PPO Composites of fly ash were prepared by Haake Rheocord 9000 twin screw extruder machine. The standard test specimens were molded on compression moulding machine. Mechanical and rheological properties were determined using these test specimens. It was found that with the addition of fly ash as filler in PPO showed improvement in flexural strength and modulus with the increase in fly ash concentration, whereas tensile strength, melt flow index and impact strength are found to decrease with increase in fly ash concentration.

**Keywords**— Polyphenylene oxide (PPO), fly ash, Coupling agent, SEM.

## I. INTRODUCTION

**P**OLYPHENYLENE Oxide is widely used in the automotive industry and electrical industry. Fly ash is widely used as polymer filler as they are cheaper filler and save the final cost of the composite. Improvement in mechanical properties and thermal stability of the composites is achieved by use of fly ash in Polymer. In the present research work fly ash filled PPO composites of different concentrations were prepared using untreated and surface treated fly ash with coupling agents. Fly Ash filled PPO composites were compounded for various compositions and test samples were prepared using compression moulding process. These samples were tested for mechanical properties. There is a reduction in melt flow index, impact strength, tensile strength and elongation. The result shows enhancement in flexural strength and flexural modulus. Scanning electron microscopy was used to test the morphology of the samples which has shown proper distributions and adhesion of the filler and fly ash in PPO matrix when fly ash is treated with coupling agent. PPO forms one of group of rigid, heat-resistance, more-or-less self-

extinguishing polymer with a good electrical and chemical resistance, low water absorption and very good dimensional stability. This has led to a number of applications in television such as tuner strip, microwave insulation components and transformer housing. The excellent hydrolytic stability has also led to application in water distribution and water treatment application such as in pump, water meters, sprinklers system and hot water tanks. Fly ash, a waste product from the thermal power plants, possesses very good mechanical properties on account of the constituent phases contained in it like silica and alumina. Also fly ash consists of a mixture of solid and hollow spherical particles of varying sizes. These characteristics of fly ash qualify it as one of the good alternatives for use as filler in polymers. Utilization of fly ash (FA) as an additive component in polymer composites has received increased attention recently, particularly for price-driven/ high volume applications. This development has been brought about since incorporation of fly ash offers several advantages: it is the best way of disposing of fly ash, and as it is cheap and plentifully available, it decreases the overall cost of composites. Incorporation of fly ash in HDPE enhances both the thermal stability and the effective thermal conductivity of the composites. Deepthi<sup>1</sup> et al. have reported that fly ash cenospheres was used as reinforcing filler in HDPE to develop lightweight composites. In order to improve the interaction between the inorganic filler and the organic matrix, the cenospheres were surface treated with silane coupling agent and HDPE-g-dibutyl maleate was used as compatibilizer. The results reveal that, both surface modifications of cenospheres accompanied by compatibilization led to the substantial improvement in mechanical properties and thermal stability of the composites. Biglari<sup>2</sup> and Kole et.al ,have investigated the effective thermal conductivity and coefficient of thermal expansion (CTE) of composites synthesized with fly ash filler embedded in HDPE matrix. Incorporation of fly ash in HDPE enhances both the thermal stability and the effective thermal conductivity of the composites. CTE, however, significantly decreases as the FA content increases in HDPE. Effective thermal conductivity for HDPE containing 70-volume fraction (%) fly ash becomes almost twice than that for unfilled HDPE. Results on both the effective thermal conductivity and CTE of HDPE/FA composites have been discussed in light of various theoretical models.

Navin Chand<sup>3</sup> et al. studied fly ash cenospheres filled high density polyethylene composites. The surface of

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cenospheres was modified using silane treatment and incorporating them in a versatile thermoplastic high density polyethylene. The silane treatment resulted in considerable improvement in the impact strength and density of the composites which ultimately translated into better wear performance of composites even in severe abrasive conditions. A. C. Miller<sup>4</sup> et.al. Studied effect of silane coupling agent adsorbate structure on adhesion performance with a polymeric matrix. The effect of the silane coupling agent adsorbate structure on adhesion performance is investigated. Glass beads are treated with two different sets of silanes where each set contains the same organo-functional group, but a different number of alkoxy groups, viz. one, two, or three. Adhesion strength measurements were obtained from tests in which single, silane-treated glass beads were imbedded into rectangular poly (vinyl butyral) specimens that were then subjected to an applied tensile stress until failure occurred at one of the poles of the sphere. The results indicate that the mono-alkoxy silanes have the least effect on adhesion, the consequence of poor attachment of the silane to the mineral surface, while the di- and tri-alkoxy silanes produce a marked increase in adhesion strength due to the increased stability of their bonds to the glass surface and their ability to form more extensive interphases with the polymer. C.M. Vaz et.al studied the Use of coupling agents to enhance the interfacial interactions in starch-EVOH/hydroxylapatite composites. Different zirconate, titanate and silane coupling agents were selected in an effort to improve the mechanical properties of starch and ethylene-vinyl alcohol copolymer (EVOH)/hydroxylapatite (HA) composites, through the enhancement of the filler particles- polymer matrix interactions and the promotion of the interfacial adhesion between these two phases. The mechanical performance was assessed by tensile tests and discussed on the basis of the respective interfacial morphology (evaluated by scanning electron microscopy). The main relevant parameters were found to be the surface properties and reactivity of the filler (non-sintered HA) and the chemical nature (pH and type of metallic centre) of the added coupling agent. Significant improvements in the stiffness were achieved (about 30% increase in the modulus) when using the acidic zirconate coupling agents. The acidic zirconate combined the capability of crosslinking the polymer matrix with the establishment of donor-acceptor interactions and hydrogen bonding between it and the ceramic particles, leading its very good interfacial adhesion.

REN Hui<sup>6</sup> et.al, studied the reinforcement of styrene-butadiene rubber with silica modified by silane coupling agents. The properties of styrene-butadiene rubber (SBR) reinforced by modified silica was investigated according to national standards. Silica was modified by silane coupling agents KH-570, KH-590, and KH-792. The optimized geometries of molecular modified silica reinforced SBR were obtained by using B3LYP calculation of density functional theory with the 6-31+G basis sets. The natural bond orbital analyses were carried out. The Si—O bond length of silica modified by KH-792 was the shortest and the electronegative

of O was the highest. It indicated that the connection between silica and KH-792 was the tightest. Higher tensile strength and elongation of reinforced SBR was obtained by silica modified with the KH-792. It was caused by large delocalization of lone pair electrons of the two N atoms in KH-792. The S—C bond length in silica modified by KH-590 was longer than the ordinary S—C bond length. Then the sulfur free radical ( $\cdot\text{S}\cdot$ ) was produced more easily in vulcanization. The degree of crosslink was increased by the cross-linkage of the rubber molecule and the sulfur free radical. That was why the highest stress and tear strength of reinforced SBR was produced when silane coupling agent KH-590 was used. K. Agarwala<sup>7</sup>, et.al. studied the Microstructural and Thermophysical properties of polymer nanocomposite based on polyphenyleneoxide and Ferrimagnetic iron oxide. Nanocomposites of polyphenyleneoxide (PPO) filled with nanoparticles of organically modified  $\gamma\text{-Fe}_2\text{O}_3$ , in varied concentration from 0 to 20 wt. %, were prepared. Thermal stability of these nanocomposites was evaluated by thermo-gravimetric analysis (TGA) and their dimensional stability was measured at sub-ambient as well as at elevated temperatures by thermo-mechanical analysis (TMA). The glass transition temperature ( $T_g$ ) of the nanocomposites, measured by c (DSC), was found to decrease with increasing weight fraction of  $\gamma\text{-Fe}_2\text{O}_3$ . Phase morphology of the nanocomposites was analyzed by scanning electron microscope (SEM). The distribution of  $\gamma\text{-Fe}_2\text{O}_3$  in PPO matrix was studied by determining the iron using an X-ray energy dispersive spectroscope (EDX) attached to the SEM. These analyses reveal that the nanoparticles of  $\gamma\text{-Fe}_2\text{O}_3$  with an average diameter of 20 nm were dispersed uniformly in the PPO matrix and also that there was very good matrix-filler adhesion. A detailed morphological study using a Gatan hot stage attachment with the SEM showed that there was no change in the surface morphology from ambient to high temperature up to 280 °C, beyond which segregation of the nanoparticles took place. Measurements by vibrational sample magnetometer (VSM) showed that the degree of saturation magnetization increased with increasing filler concentration from 0% to 10 wt. % of  $\gamma\text{-Fe}_2\text{O}_3$ . The magnetic nanocomposites, in general, also showed very good mechanical strength and high temperature resistance. C.P. Tsuia<sup>8</sup> et.al.studied the Prediction for debonding damage process of glass beads-reinforced modified polyphenylene oxide under simple shear. A three-dimensional finite element cell modeling technique has been applied to predict the particle-matrix debonding process of particulate polymer composite (PPC) subject to simple shear loading. The particle-matrix debonding in PPC has been simulated by using two different debonding criteria: stress-based and strain-based. The stress-based debonding criterion uses the hydrostatic tensile stress as a critical stress while the strain-based one uses the equivalent plastic strain at failure as a critical factor for element failure. In this analysis, glass beads-reinforced polyphenylene oxide (GB/PPO) has been used for verification of the predicted results. As compared with the results from scanning electron microscopy (SEM)

based in situ simple shear test of GB/PPO composite, the model with the stress-based criterion is much more appropriate for simulation of the shear damage process. The importance of selecting an appropriate debonding criterion for achieving correct simulation results could be revealed. The essential information like the threshold strain for initiation of shear damage could then be acquired from the model with the verified stress-based debonding criterion. P. A. Mahanwar<sup>9</sup> et al. have reported Mechanical Properties of Fly Ash Filled High Density Polyethylene and found increase in mechanical properties. U. Atikler<sup>10</sup> et al. studied Mechanical and morphological properties of recycled high-density polyethylene, filled with calcium carbonate and fly ash and investigated the effect of filler loading and treatment of FA with silane coupling agent on mechanical and morphological properties. It was found that silane treatment indicated significant improvement the mechanical properties of the HDPE-FA composites. Iftakhar Ahmad<sup>11</sup> and Prakash A. Mahanwar reported tensile and flexural strengths and moduli were found to increase with fly ash addition. Tensile elongation drastically reduced at fly ash concentration greater than 10%. With increasing fly ash concentration impact resistance decreased up to about 15% fly ash concentration and then did not reduce significantly on further addition.

The present study deals with Fly Ash filled PPO composite with and without coupling agent.

## II. EXPERIMENTAL

### A. Materials

Polyphenylene Oxide of grade Noryl n110 grade is obtained from general electrical, USA. Fly Ash of size 120 $\mu$  was obtained from DIRK, Mumbai Group under the brand name of Pozzocrete. Phenyltriethoxysilane was obtained from Spectrochem Pvt. Ltd and N-(2-Aminoethyl)-3-Aminopropyltrimethoxysilane was obtained from aldrich chemistry, dow corning coporation, USA.

### B. Compounding of filler and polymers

Preheating of fillers enhances faster mixing, makes compounding easier and lowers energy consumption. It reduced equipment wear, and improves product quality in filled thermoplastics. Fly ash was preheated in an oven at the temperature of the 100°C for a 1 hour. It removes the residual moisture from the fly ash. Silane was added with stirring to yield a 2% final concentration. Five minutes were allowed for hydrolysis and silanol formation. Large objects, e.g. glass plates, were dipped into the solution, agitated gently, and removed after 1-2 minutes. They were rinsed free of excess materials by dipping briefly in ethanol. Particles, e.g. fillers and supports, were salivated by stirring them in solution for 2 – 3 minutes and then cure of the mixture was done at 100°C for 1 hour. Mixing was done in tumbler mixer at the different proportion of PPO and fly ash (coupling agent treated and untreated) for 5 minutes.

### C. Preparation of The Polymer Composites

The predried raw materials are dry blended in the require ratio(5,10,15,20,25 wt % of fly ash) in twin screw extruder which is counter rotating with 16mm diameter and having L/D ratio of 25:1. The temperature profile for the melt blending was kept as Zone1-200 °C, Zone 2-240°C, Zone 3-260°C, Die-270°C.

### D. Compression Molding

Compression moulding was done in to make a sheet of composite which is (180x180x2). For compression moulding Teflon sheets were used. The material was placed in between two Teflon sheets in mould and mould is closed. Degassing is done to remove all entrapped gasses and volatile. 15 minutes were allowed for heating the top and bottom platen which were kept at 290°C. Mold was cooled by cooling channels where water flows from inlet and comes out from an outlet. Mold was allowed to cool till the temperature of the mold reaches room temperature. The specimens were cut for the tensile molding as per the ASTM D1238, for the flexural test as per the ASTM D790M -92 and for the impact testing as per the ASTM D256.

## III. RESULTS AND DISCUSSION

### A. Melt Flow Index

Fig.1 shows the variation in Melt flow index of treated and untreated Fly Ash filled PPO composite. It is seen that, melt flow index decreases with increasing concentration of fly ash. The decrease in melt flow index is seen due to agglomeration of particles, thereby lowering the total surface area available for the interaction with the matrix. The phenomenon of agglomeration is depicted by sinusoidal behavior of change of melt flow index of fly ash filled PPO composite. The variation in melt flow index of Phenyltriethoxysilane coupling agent treated fly ash filled PPO composite shows that there is a decrease in melt flow index of coupling agent treated composite as compare to untreated fly Ash filled PPO composite. This may be due to restriction to flow of polymer chain as adhesion restricts the free chain movement of polymer. It proves the better adhesion between the polymer and filler. At 20% loading of fly ash M.F.I. is almost equal to the M.F.I. of untreated Fly Ash and PPO thereafter, which may be due to chain slippage at higher concentration.

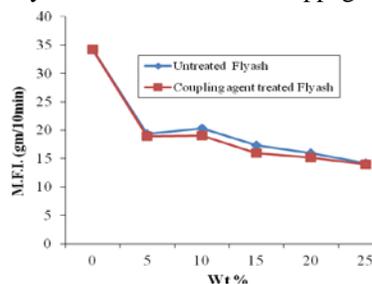


Fig. 1 values M.F.I of fly ash filled PPO composite

### B. Impact Strength

Table I indicates the values of impact strength of fly ash and PPO composite. It is seen that impact strength decreases, with increasing concentration of Fly Ash. The trend in impact strength supports the phenomenon of agglomeration of particles. Another reason of decrease in impact strength may be due to reduction of elasticity of material due to filler addition and thereby reducing the deformability of matrix and in turn the ductility in the skin area, so that the composite tend to form a weak structure. An increase in concentration of filler reduces the ability of matrix to absorb energy and thereby reducing the toughness, and impact strength.

It is seen that the impact strength of virgin polymer decreases by 47% at 5% loading of fly ash, whereas at 15% loading of fly ash is decreases by 63%. At higher loading that is at 25% loading of filler 70% reduction in impact strength is seen. Silane coupling agent treated fly ash shows some improvements in impact strength as compare to untreated fly ash filled PPO composite.

TABLE I  
VARIATION IN IMPACT PROPERTIES OF FLY ASH FILLED PPO COMPOSITE

Wt (%)	Impact strength of Untreated Fly Ash filled PPO (J/m)	Impact strength of Coupling agent treated Fly Ash filled PPO (J/m)
0	74.44	74.44
5	35.00	48.17
10	33.33	41.00
15	27.77	40.00
20	25.00	32.12
25	22.00	32.86

### C. Flexural properties

Fig.2 represents the variation in flexural strength of untreated and coupling agent treated fly ash filled polyphenylene oxide composite. It is seen that flexural strength increase with increasing concentration of fly ash. It is due to good dispersion of filler into polymer matrix and hence there is increase in the total area for deformation stress. As we increase the concentration of filler till 10% the rate of flexural strength increases. The rate of change of flexural strength remains constant. At higher concentration rate of flexural strength decrease. It is may be due to, at higher concentration, dispersion of filler is poor which is at 25% of fly ash, thereby reduction in effective total surface area for responding the applied stress and, hence the rate of flexural strength decreases.

Flexural strength of Phenyltriethoxysilane coupling agent treated fly ash filled PPO composite shows that the flexural strength increases as the percent loading of Fly Ash increases, rate of increase of flexural strength is constant. But at 10% loading of Fly Ash it is slightly more. There is an improvement in flexural strength when Fly Ash is treated with Phenyltriethoxysilane coupling agent, this may be due to increase in adhesion.

Fig.3 indicates the variation in flexural modulus of untreated and coupling agent treated Phenyltriethoxysilane coupling agent treated Fly Ash filled polyphenylene oxide. It is seen that the flexural modulus of composite increase as the

concentration of the filler increases in composite, where as there is an improvement in flexural modulus when Fly Ash is treated with a coupling agent. The rate of increment in flexural modulus is almost same but at 10% loading of Fly Ash it is high. The increase in flexural modulus is may be due to proper adhesion between polymer and filler, which improved the strength of the polymer chains.

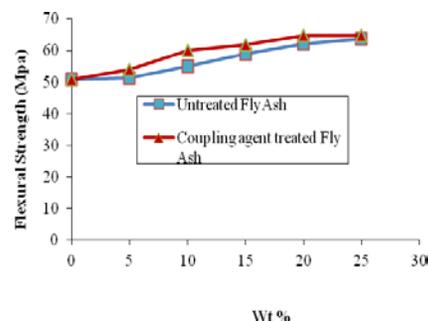


Fig.2 Variation in flexural strength of fly ash filled PPO composites

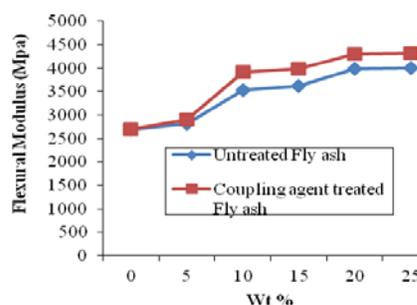


Fig. 3 variation in Flexural modulus of Fly Ash filled PPO composite

### D. Tensile Properties

Fig.4 shows the variation in tensile strength of untreated and coupling agent treated Fly Ash filled PPO composite. It is seen that tensile strength decreases at 5% loading of Fly Ash. The rate of change of tensile strength remains constant almost, but at 20% lading it decreases to a lower value. It indicates that agglomeration of particle was more at 20% loading and it affected the tensile strength of the composite. Tensile strength of strength of Phenyltriethoxysilane coupling agent treated Fly Ash filled PPO composite shows that there is an improvement in tensile strength when Fly Ash is treated with a coupling agent. It is seen that the tensile strength is increases at 10% loading of Fly Ash, the increment may be due to the platy structure of the Fly Ash providing good reinforcement at 10% Fly Ash which is treated with silane coupling agent.

Fig.5 represents the variation in elongation at break of untreated and coupling agent treated Fly Ash filled PPO composite. It is seen that the elongation at break decreases drastically to a lower value when a PPO is filled with Fly Ash, thereafter the decrease rate of elongation at break is constant, may be due to interference is created through the physical interaction and immobilization of the polymer matrix by the presence of mechanical restraints. So as the

filler concentration increases the elongation gets reduced. This decrease in elongation is attributed to restriction of polymer chain movements. Tensile stresses more likely at low volume fractions, and it is possible that these stresses may generate interface cracking. In the flakes, the possibility of a tensile stress near the periphery of the flakes is low. Elongation at break of Phenyltriethoxysilane coupling agent treated Fly Ash filled PPO composite reveals that elongation at break increases when Fly Ash is treated with silane coupling agent, indicating good dispersion of filler into the matrix as silane improves the adhesion between filler and matrix. The improvement is seen more when PPO is filled with treated Fly Ash, thereafter the decrease rate of elongation at break is constant.

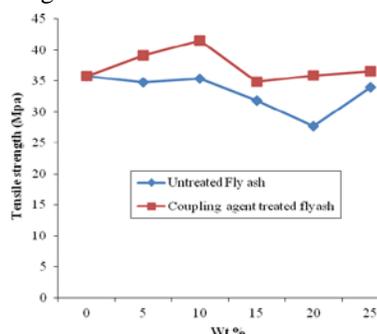


Fig. 4 variation in Tensile strength of Fly Ash filled PPO composite

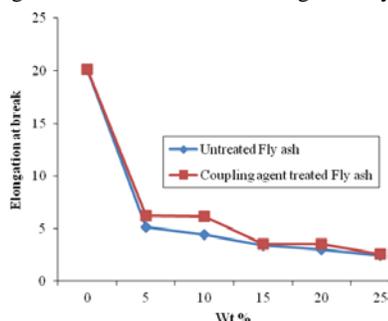


Fig. 5 variation in Elongation at break of Fly Ash filled PPO composite

#### E. Microstructure Characterizations

SEM is used to study the morphology of PPO Fly Ash composite with and without coupling agent. Fig. 6 and Fig. 7 shows the SEM images of PPO with 10 percentage concentration of Fly Ash respectively. The interaction between the filler and the matrix gets increases due to good dispersion of the filler particles into the blend matrix when coupling agents is used.

Fig. 8 and Fig. 9 depicts the presence of visible dots in the composite where the Fly Ash is filled without treatment of coupling agents indicates the immiscibility of the filler and matrix. When coupling agents were added into the PPO the composite displays the significantly finer morphology. The filler particles are sufficiently small to enable good distribution in the matrix. A plain morphology was observed when PPO is without filler.

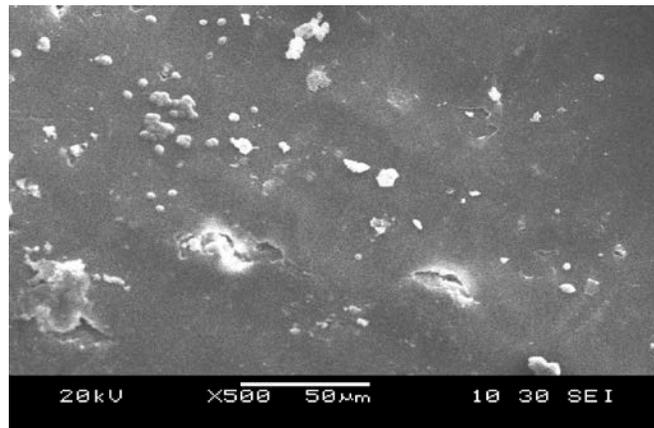


Fig. 6 Untreated Fly Ash with PPO (PPO-FI-2)

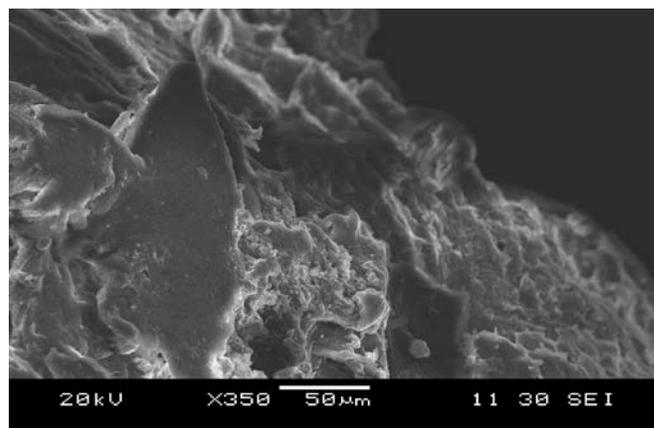


Fig. 7 Treated Fly Ash with PPO (PPO-FI-CA-2)

#### IV. CONCLUSION

➤ M.F.I, Impact strength, Tensile strength and Elongation at break of the composite decreases with increase in increasing concentration of Fly Ash for treated and untreated filler filled PPO composites. This is primarily because of interfacial stresses developed between filler and matrix at the time of curing and stressing of composite leads to micro-cracks reducing its tensile properties. This happens also because of weak filler matrix adhesion.

➤ Flexural strength and flexural modulus of the Fly Ash filled composite increases as filler loading is increases. At 10% of Fly Ash loading the Flexural strength and flexural modulus is higher.

➤ Coupling agent such as N- ( Phenyltriethoxysilane for fly ash were found to be good coupling agent for the fly ash PPO composite. Addition of fly ash as filler into the Polyphenylene oxide with coupling agent increased the mechanical properties such as tensile strength, Impact strength, elongation at break, flexural strength and flexural modulus as compare to untreated filler filled PPO composite.

➤ SEM images showed good dispersion of fly ash filler into the PPO matrix when they are treated with coupling agent.

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