Effect of Flyash Content, Particle Size of Flyash, and Type of Silane Coupling Agents on the Properties of Recycled Poly(ethylene terephthalate)/Flyash Composites

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ABSTRACT: Recent time's polymer waste disposal is a challenging task as the quantity of polymer waste is increasing day by day. Here particulate composites have been developed from recycled poly(ethylene terephthalate) filled with flyash. Flyash of different particle sizes have been used, and effect of particle size and flyash content on the mechanical properties of composites has been analyzed. Tensile and flexural properties of the composites are found to increase with increase in filler content up to 15% and after that decreases due to the agglomeration of flyash particles. SEM studies also showed good dispersion at lower loadings. The use of silane coupling agents was found to increase the flyash/WPET interaction there by increase in mechanical properties is observed. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 201–208, 2011

Key words: recycled plastic; PET; flyash; composite

INTRODUCTION

Growing environmental awareness and reduction in available landfills capacity have prompted plastic recycling program in most developed countries. Only a few percentage of plastic waste is being recycled. Because the world wide conception of plastic is increasing sharply, recycling of plastic waste has to be increased, especially in rapidly developing countries like India and China. Utilization of recycled plastics for manufacture of composites has been studied by several authors.[1–4] Najafi et al.[4] analyzed the mechanical properties of wood plastic composites (WPCs) manufactured from sawdust and virgin and/or recycled plastics [high density polyethylene (HDPE) and polypropylene (PP)]. They found that the mechanical properties of specimens containing recycled plastics (HDPE and PP) were statistically similar and comparable with those of composites made from virgin plastics.

Poly(ethylene terephthalate) (PET) recycling has been main target of polymer recycling mainly because of its widespread use particularly in beverage industry. Chemical nature of PET permits a broad range of recycling options from mechanical recycling to chemical recycling.[5] Avila[6] reported dual analysis for recycled particulate composite based on recycled PET bottles and HDPE bottles. Thermomechanical recycling of plastic bottle was done and their use as composite material for engineering applications was studied. Pegoretti[7] prepared recycled PET and short glass fiber composites as well as reported the effect of hygrothermal aging on the molar mass and thermal properties of the composites. Avila[8] conducted mechanical analysis on recycled PET/HDPE composites by carrying out compression test and mechinability evaluation. The results showed good performance for both compression and mechinability. Abuisha et al.[9] developed a high-impact strength PET from virgin and recycled resins by blending with co-polyester thermo-mechanical elastomer. Addition of triphenyl phosphate (TPP) to polyester elastomer/PET blends encourages molecular weight buildup and improved impact strength and mechanical properties. Verney et al.[10] reported that weathering and recycling of PET causes degradation of polymer backbone and results in loss of polymer properties. To enhance the properties, PET was blended with polycarbonate (PC) and the blends showed better properties than neat PET. Pegoretti[11] developed nanocomposites by recycled PET and layered silicates (non-modified natural MMT clay and modified MMT). Atta[12] developed new epoxy resin based on recycled PET

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as organic coating. Lopez-Cuesta and Crespy[13] reported that mechanical properties and fire resistance of recycled PET was improved by using specific treatment of the waste material and incorporation of encapsulated red phosphorus in combination with co-additives.

Flyash is finely divided mineral residue resulting from combustion of coal in electric generating plants. They consist mostly of SiO_2, Al_2O_3, and Fe_2O_3 and are present in inorganic incombustible matter present in coal that has been fused during combustion to glassy amorphous structure. Flyash particles are generally spherical in shape and range in size from 0.5 to 100 μm. Flyash mostly used in cement industry could be used as filler in plastic products. Wong and Truss[14] reported that mechanical properties of flyash-filled polypropylene composite increased with increase in flyash content and the presence of compatibilizer increased the properties further. Addition of flyash filler in glass fiber reinforced polymer composites has also improved the performance of the composites.[15,16]

Coupling agents enhances the filler/matrix interfacial interaction, thereby increasing the mechanical properties. Thus, there will be efficient stress transfer in presence of coupling agents. Effect of surface coverage of silane treated $CaCO_3$ on the tensile properties of polypropylene composites were analyzed by Demjén and Pukánszky.[17] Amino functional silanes showed a strong reactive coupling effect leading to a maximum in tensile strength. Effect of silane and zirconate coupling agents on mechanical properties of mica/epoxy composites was studied by Bajaj et al.[18] They showed that the tensile modulus and flexural strength and modulus values were improved by the surface treatment of the coupling agents. Mathew et al.[19] reported that properties of silica-filled styrene-butadiene rubber composites were improved through plasma surface modification of silica. The filler dispersion, as revealed by scanning electron microscopy, was found to be greatly improved by the plasma as well as silane treatment.

Properties of polymers could be improved by addition of fibrous or particulate fillers. The properties of these filled polymer composites depend on shape, size, distribution of the filler particles, and filler matrix adhesion. In this article, flyash filler of varying sizes have been used as reinforcement in waste PET polymeric materials. The effect of filler weight percentage on the composite properties has been analyzed. To improve the interaction between flyash particles and WPET, matrix coupling agents have been used. The effect of filler size, filler weight percentage, and silane coupling agent on tensile, flexural, and impact properties of the composites have been analyzed. The dispersion of filler in the matrix and filler/matrix interaction has been analyzed by scanning electron microscopy.

EXPERIMENTAL

Materials

Waste poly(ethylene terephthalate) was generated from crushing PET sheet followed by water wash. The grinded pellets were 8–9 mm in size. Flyash filler was obtained from Koradi thermal power plant, Nagpur, India and NTPC Farakka, west Bengal, India. The coupling agents 3-aminopropyltrimethoxysilane and vinyltrimethoxy silane were obtained from Aroma chemical agencies, India, to improve the interaction between polymer matrix and filler particles.

Preparation of the composites

Waste poly(ethylene tertephthalate) composites were prepared by varying the filler loading from 5% to 40% and varying flyash particle sizes (below 45 μm, 45–63 μm, and 63–90 μm). The coupling agents 3-aminopropyltrimethoxysilane and vinyltrimethoxy silane were used as coupling agent at different concentrations (0.5%, 1%, and 2%). For silane treatment, a dilute solution of amino/vinyl silane was prepared in isopropyl alcohol (weight of silane measured according to concentration of silane solution required) and mixed with preweighed quantity of flyash by stirring for 30 min. It was then dried in a hot air circulating oven at 80°C and used for the preparation of composites.

Before compounding, flyash was predried at temperature 80°C ± 5°C for 6 h in an air circulating oven. The preblend of WPET with varying concentrations of flyash (5–40%) were dry blended and the mixture was compounded using a co-rotating twin screw extruder with 16 mm diameter and 25 : 1 L/D ratio (M/S APV Baker, UK, Model MP19PC). The compounding condition for compounding WPET/flyash were (Zone 1, 100°C; Zone 2, 220°C; Zone 3, 240°C; Zone 4, 250°C; and Die (Zone 5), 260°C. The continuous feeding rate with torque 50–60 Nm was maintained. The RPM of the screw of the compounding extruder for all the experiments were maintained at 60 rpm. The extruded stands were passed through cold water at 25°C were then pelletized. Further this pellet was spread on the mold plates of the hydraulic compression molding machine (M/s Sterling Hydraulic Co., Mumbai) with a temperature profile of 260°C for 360 s at a pressure of 15 MPa. Breathing was carried out after 90 s with an interval of 1 min to remove moisture or air trapped in the material. The sheet was cooled to 40°C and cut into desired specimens for further

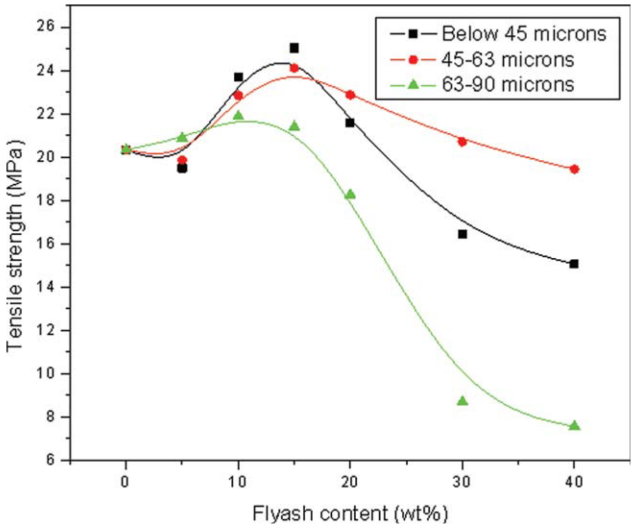


Figure 1 Variation of tensile strength value of WPET/flyash composites having flyash particles below 45 μm, 45–63 μm, and 63–90 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

testing as per ASTM standards. The thickness of the sheet was measured to be 1.6 mm.

Mechanical properties

Tensile specimen according to ASTM D638M-91 was compression molded from pelletized samples. The tensile strength and elongation of all the samples were measured using universal tensile tester LR 50K (M/S Lloyd Instrument Company, UK) at a cross-head speed of 50 mm/min. The results reported are average values of at least five specimens.

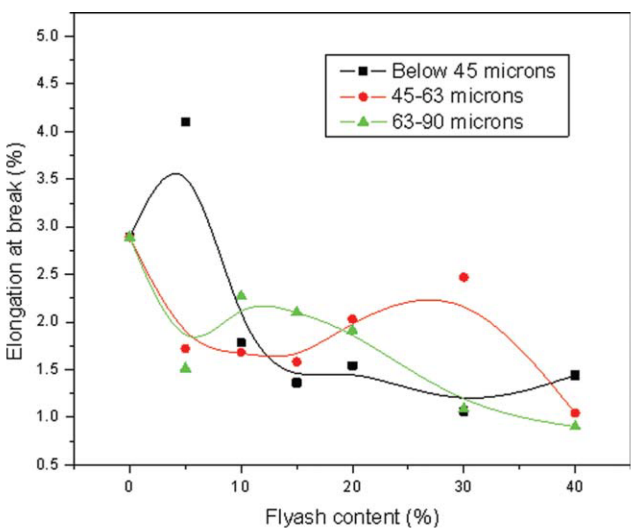


Figure 2 Variation of elongation value of WPET/flyash composites having flyash particles below 45 μm, 45–63 μm, and 63–90 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

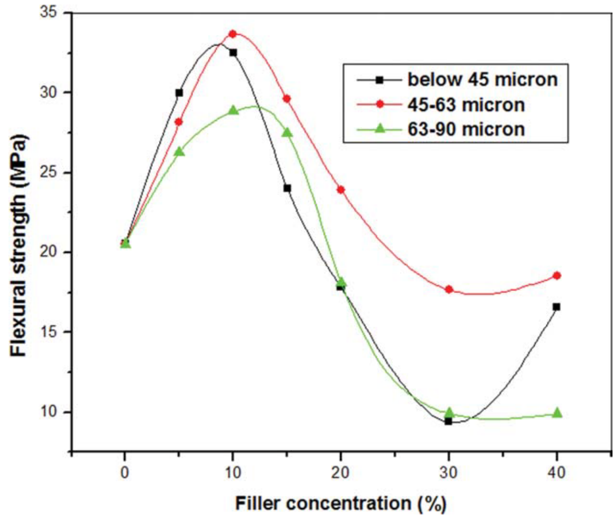


Figure 3 Effect of flyash loading and particle size of flyash on the flexural strength of WPET/flyash composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For flexural testing rectangular bars of dimensions 80 × 25 × 1.6 (length × breadth × thickness) were cut from compression molding sheet. Flexural strength and modulus were measured using universal tensile tester LR 50K (M/S Lloyd Instrument Company, UK) according to ASTM D790 M-92. Jaw speed of 0.8 mm/min was maintained for three point bending strength and span was 60 mm. Average values of five results are reported.

Impact strength was determined as per ASTM D1709 using Avery Denison's pendulum type Impact tester model 6709 with pendulum type ram of maximum capacity 2.7 and 15 J with a striking velocity of 3.46 m/s and 5 J striker. Average value of five results is reported.

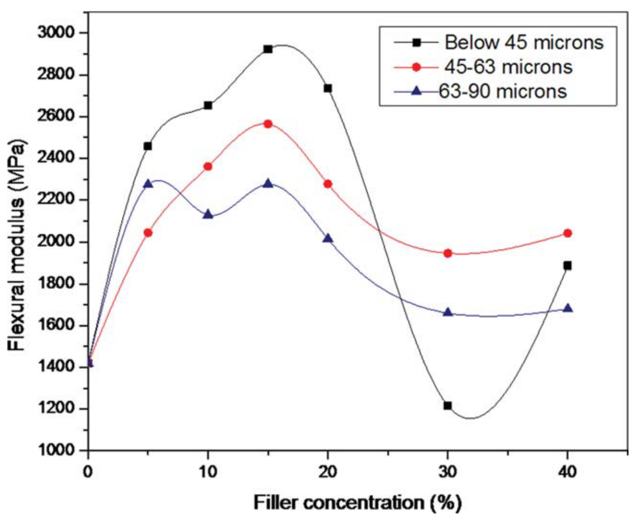


Figure 4 Effect of flyash loading and particle size of flyash on the flexural modulus of WPET/flyash composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

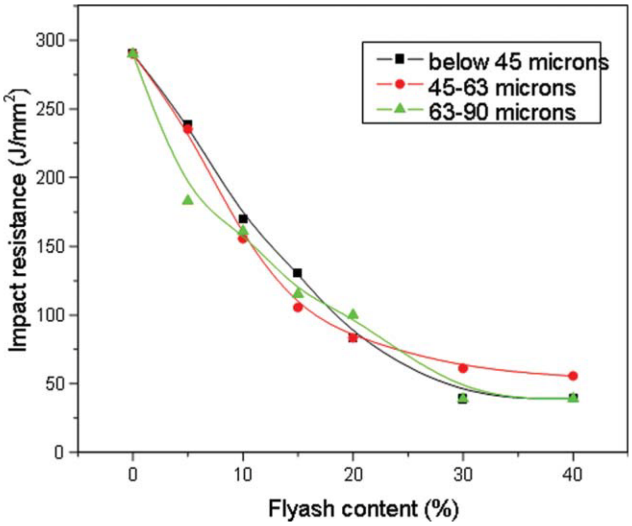


Figure 5 The effect of filler content on impact strength of flyash/WPET composites having flyash particles below 45 μm, 45–63 μm, and 63–90 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scanning electron microscope

SEM was carried out on a JEOL, JSM-6380 scanning electron microscope operated at 15 kV to characterize the microstructure of the composite and to evaluate the microparticle dispersion in polymer matrix. The cryogenic fracture surface was used to take SEM.

RESULTS AND DISCUSSIONS

Effect of concentration and size of flyash particles on mechanical properties of WPET/flyash composites

Figures 1 and 2 show the variation of tensile strength and elongation value of WPET filled flyash particles having particles below 45 μm, 45–63 μm, and 63–90 μm. The figure shows that tensile strength is not much affected by 5% flyash content. At higher loadings, tensile strength increases with increase in flyash content and attains a maximum at 15% flyash content. Smaller particles are found to have more increase in tensile strength with increase in flyash content compared with larger ones (63–90 μm). For smaller particles, as particle size decreases, interfacial area/unit volume is increased, and hence, tensile strength is increased. The stress transfer will be more efficient in smaller particles filled composites compared with larger ones. As the filler content increases from 15%, the tensile strength value decreases. This is because of the particle agglomeration at higher filler contents. Particle agglomeration tends to reduce the strength of a material because

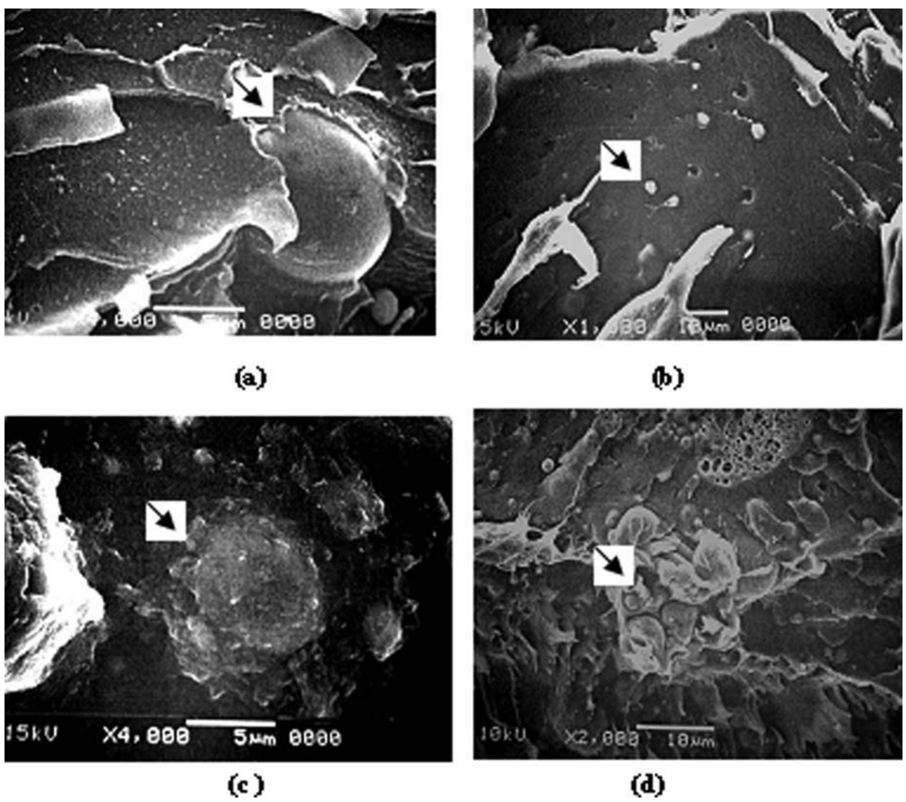


Figure 6 (a–d) Scanning electron micrograms of flyash-filled (size below 45 μm) WPET composites at different flyash contents (The arrow shows the flyash particles and the agglomerates.).

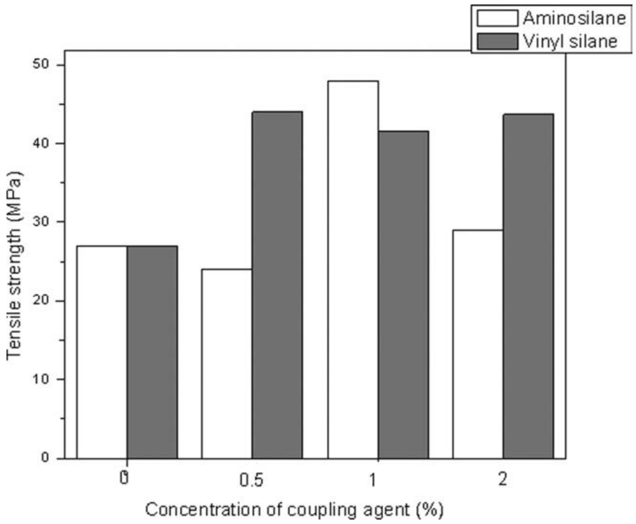


Figure 7 Effect of vinyl silane and aminosilane coupling agent concentrations on tensile strength of flyash-filled WPET composites.

the agglomerates are weak point in material and break easily when a stress is applied to them. These points then acts as stress concentrator. Agglomerations resulting from larger sized filler particles will produce weaker materials than composites having well dispersion of small sized particles. The elongation at break value is found to decrease with increase in flyash content for all the composites. Rate of decrease of elongation is more for smaller particles compared with those of higher particle size. The poor interfacial interaction in the composite and amorphous (glassy) nature of the flyash makes the WPET/flyash composite a brittle material.

Figures 3 and 4 show variation of flexural strength and modulus of PET flyash composite with filler content and particle size. Just like tensile properties, flexural modulus increases up to 15% loading for all particle sizes and then decreases. Rate of increase is more for smaller particle size than larger ones. Because smaller particles have higher surface area than larger ones, these particles can have higher interaction with matrix at lower concentration of filler. Agglomeration if present, the apparent volume occupied by the filler is increased and agglomeration results in bigger particles by which void space is generated, which can be responsible for strain propagation. Figure 5 shows the effect of filler content on impact strength of flyash filled WPET. The impact strength of WPET is found to have a sharp decrease with flyash filler irrespective of the size. About 20% decrease in impact strength is observed by incorporating 5% filler. Decrease in impact strength with filler loading may be partly due to the brittle nature of flyash filler. The filler/matrix interaction is also not so efficient that the impact stress is transferred to the filler particles. When an impact load is applied, the flyash particles could be pulled out of the matrix at some weak points and crack propagation and composite failure occurs.

Scanning electron micrographs of flyash filled (size below 45 μm) WPET composites at different flyash contents are shown in Figure 6(a–d). The figure shows that flyash particles are encapsulated in PET matrix resulting in smooth composite surface. Filler dispersion is good at lower filler loading. At higher loadings, particle agglomerations start. Agglomerates are clear in Figure 6(d). At 40% loading, number of agglomerates is more than individual filler particles.

Effect of coupling agent on properties of flyash/WPET composites

Ishida[20] has reviewed microstructure of coupling agents and their functions in composites, coatings, and adhesive joints. They reported that the surface characteristics, including acidity, topology, and homogeneity were found to influence the structure of the coupling agent. Silanes tend to be ordered in the interphase and the degree of organization depends largely on the organofunctionality. The coupling

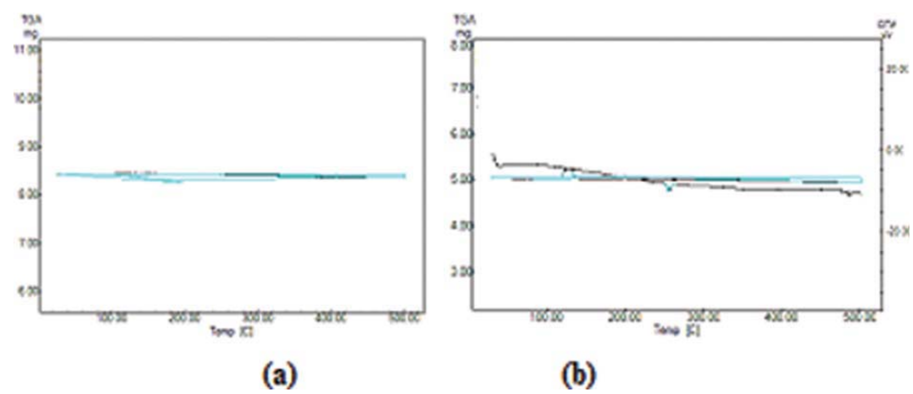


Figure 8 Thermograms of untreated flyash and silanized (2% vinyl silane treated) flyash. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

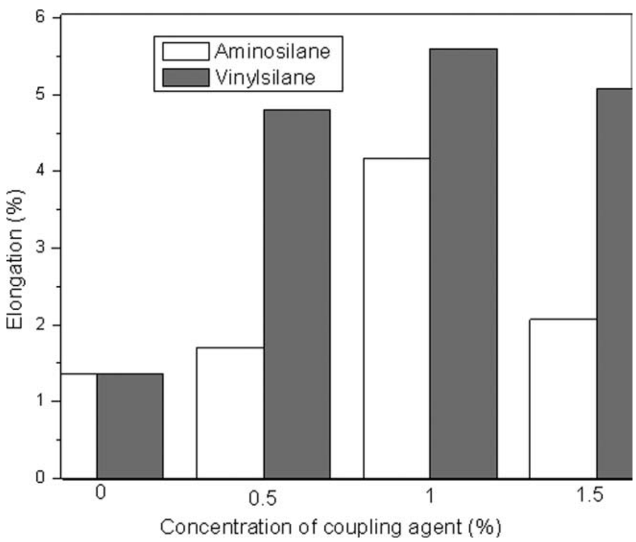


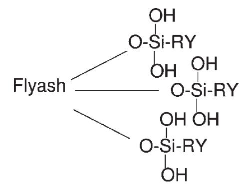
Figure 9 Percentage elongation of WPET/flyash composites in presence of coupling agents.

agent/matrix interface is a diffuse boundary where intermixing takes place due to penetration of the matrix resin into the chemisorbed silane layers and the migration of the physisorbed silane molecules into the matrix phase. With proper selection of the organofunctionality and the curing conditions, silanes can chemically react with the matrix to form copolymers.

Effect of vinyl silane and aminosilane coupling agent concentrations on tensile strength of flyash-filled WPET is shown in Figure 7. Both the coupling agents increase the tensile strength of composites. To explain the mechanism of action silanes can be represented by YR-Si$(OR_2)_3$, where R is an aliphatic linkage, that serves to attach functional organic groups to silicon. OR_2 is hydrolyzable alkoxy group. In presence of moisture, silanes are hydrolyzed to form silanols.

$$YR_1Si(OR_2)^3 \xrightarrow{H_2O} YR_1Si(OH)_3$$

The hydrolyzed silanol forms strong covalent bonds or H-bonds with flyash. The individual coupling agent molecules attached to flyash forms a continuous link. Thermograms of the silanized flyash confirm the silane coating on the treated flyash (Fig. 8). The hydrophilic polymer chain of polymerized silane can adhere to PET matrix mainly because of wander walls type attractive force. Silane coupling agent forms a bridge at the interface. Thus, the activated surface of flyash is shown schematically below.



In aminosilane the Y unit is $-NH_2$ group, which can react with $-OH$ groups of other molecules of silane or PET matrix. In vinylsilane, Y group is vinyl group. It is reported that the presence of hydrophilic aminogroup in silane coupling agent can react with resin matrix and make strong interface.[21]

In aminosilane treated composites, tensile strength increases with silane concentration up to 1% and then decreases. For vinyl silane treated composites shows a different trend. Here a sharp increase in tensile strength is obtained in presence of 0.5% vinyl silane, after that increasing concentration of silane does not affect much on the tensile strength of the composites. Figure 9 shows percentage elongation of WPET/flyash composites. It is seen that elongation value increases with addition of flyash treated with coupling agent. Elongation value is found to be maximum for 1% aminosilane treated composite and after that, at 2% concentration, the elongation value is decreased. The elongation value is found to be higher for vinyl silane treated composites than aminosilane treated one. Here the elongation value increases linearly with increase in concentration of

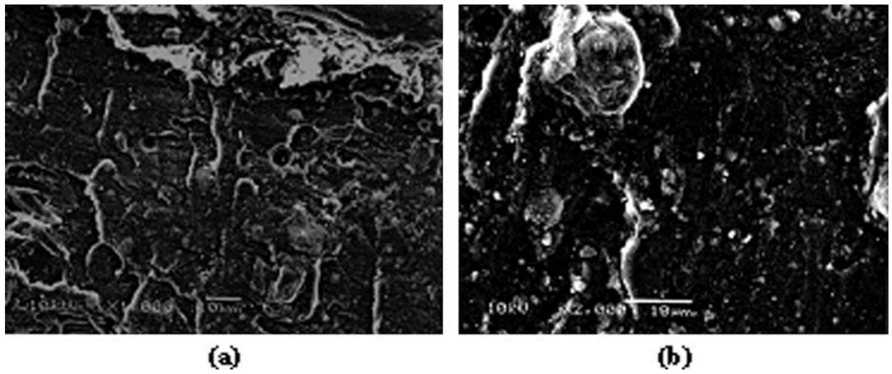


Figure 10 Scanning electron micrographs of WPET filled with vinyl silane treated flyash.

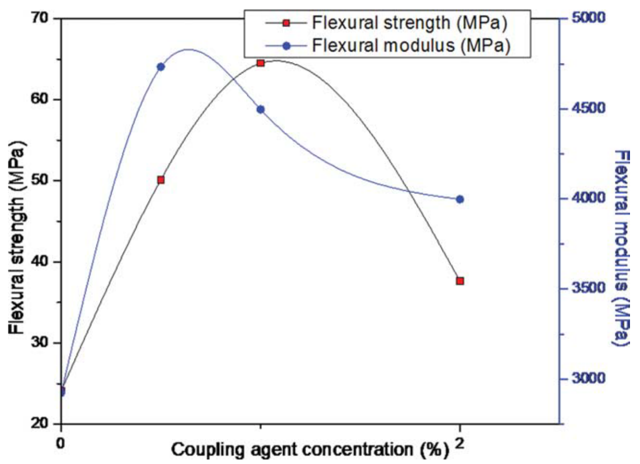


Figure 11 Variation of flexural strength and modulus of WPET/flyash composites with concentration of aminosilane coupling agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vinyl silane coupling agent up to 1% concentration and after that a slight decrease is observed. Effect of surface coverage of silane treated $CaCO_3$ on the tensile properties of polypropylene composites were analyzed by Demjén and Pukánszky.[17] Amino functional silanes showed a strong reactive coupling effect leading to a maximum in tensile strength.

Figure 10 shows scanning electron micrographs of WPET filled with vinyl silane treated flyash. Incorporating coupling agent enhances the dispersion of filler particles in polymer matrix. When comparing with Figure 6, we can see that agglomeration is lower in the presence of coupling agents. In untreated composites [Fig. 6(b)], holes generated by pulling out of the filler particles from WPET matrix is present. The silane coupling agent binds the filler and WPET matrix together. Hence, due to high filler/matrix interactions the holes generated by pulling out the filler particles is absent in presence of vinyl silane coupling agents.

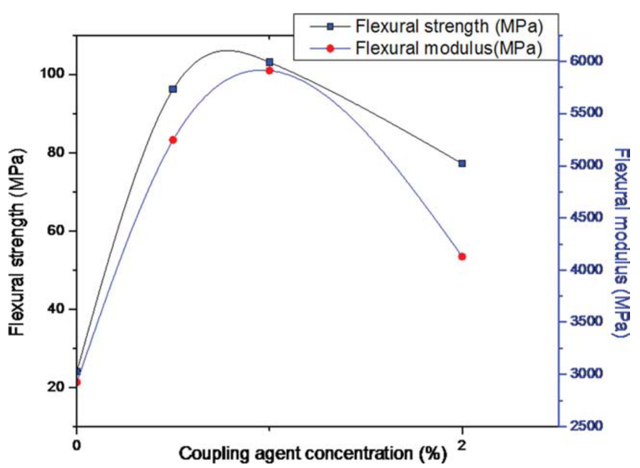


Figure 12 Variation of flexural strength and modulus of WPET/flyash composites with concentration of vinylsilane coupling agent.

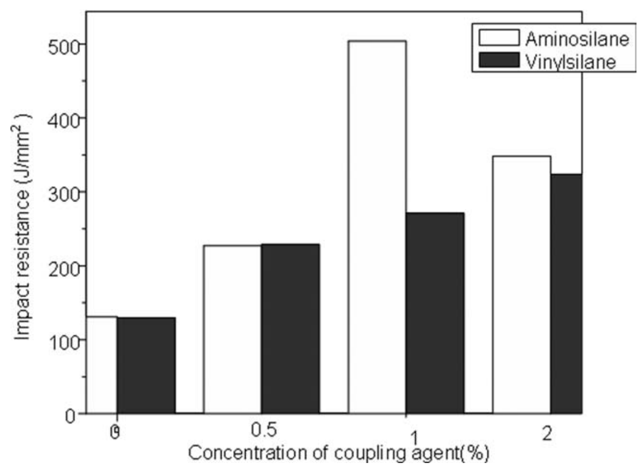


Figure 13 The effect of coupling agent concentration on impact resistance of WPET/flyash composites.

Flexural properties of WPET/flyash composites at different coupling agent concentrations are given in Figures 11 and 12. Both aminosilane and vinyl silane coupling agents increase the flexural strength and modulus of WPET/flyash composites. Both the silane treatments increase the flexural strength up to 1% concentration and after that a decrease in flexural strength is obtained at higher concentration of coupling agent. Rate of increase is higher for vinyl silane treated composites compared with aminosilane treated one.

Figure 13 shows the effect of coupling agent concentration on impact resistance of WPET/flyash composites. It is clear that impact resistance increased by the addition of both the coupling agents. At 1% concentration, aminosilane treated composite show highest impact strength with a 280% increase compared with untreated composites. The improved interfacial interaction in the treated composites increased the stress transfer in the composites. Hence, the impact resistance is higher in silane treated composites. Even though the impact strength of the composite is decreased with increase in flyash content, use of silane coupling agent could improve the toughness of the composite material.

CONCLUSIONS

Flyash is found to be a good filler for waste PET polymer matrix. Smaller flyash particles are found to impact higher tensile strength with increase in flyash content compared with larger ones. The tensile and flexural strength increases up to 15% loading for all particle sizes and then decreases due to filler agglomerations at higher filler contents. The impact strength of WPET is found to have a sharp decrease with flyash filler irrespective of the size. The elongation value of the composites also showed that the brittle of the WPET is increased by addition of flyash particles. Agglomeration of fillers at higher filler contents is clear from SEM photos.

Both the amino silane and vinyl silane coupling agents increase the tensile strength and flexural strength of composites because of the improved interfacial interaction. It is seen that elongation value increases drastically with addition of flyash treated with coupling agent. Agglomeration is lower in the presence of coupling agents. Impact resistance of low-impact flyash/WPET composites could be improved by silane coupling agents. Scanning electron micrographs of silane treated and untreated composites shows that flyash WPET interaction is improved by silane coupling agent.

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