Effect of Coupling Agents on the Mechanical Properties of Fly Ash/Polyester Particulate Composites

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ABSTRACT: Fly ash (FA)/general purpose unsaturated polyester resin (GPR) particulate composites were made. The effect of the surface treatment of FA with two different silane coupling agents (CAs) on the mechanical properties, such as the tensile, flexural, compressive, and impact strengths and hardness, of FA–GPR composites were studied. The properties of FA–CA–GPR were also compared with that of GPR and $CaCO_3$–GPR. An enhancement in the tensile, flexural, compressive, and impact strengths and a decrease in the tensile and flexural moduli were observed when FA was surface treated with CA. Hardness also increases with CA-treated FA. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1755–1760, 2001

Key words: polyester resin; fly ash filler; coupling agents; mechanical properties

INTRODUCTION

Filling polymers with mineral dispersion has long been a practice in the plastic industry as a way to reduce overall production costs and enhance certain properties.[1] Generally, most mineral fillers used in thermoset and thermoplastic composites are ground into fine particles with relatively low aspect ratios. The low aspect ratios and relatively low price of the fillers are very attractive in a plastics market that grows more and more competitive.[1] Almost any powdered material can be used as filler, the common ones being obtained from natural deposits. Of the several hundred fillers used, those that find widespread use are various grades of calcium carbonate, quartz, mica,[2] silica flour, talc,[3] and various clays.[4]

The utilization of fly ash (FA) as an additive component in polymer composites has received increased attention recently, particularly for price-driven/high-volume applications.[5] This development has been brought about because the incorporation of FA offers several advantages; because it is the best way to dispose of FA, it decreases the overall cost of composites. FA is a waste material obtained in huge quantities from thermal power plants; it is a by-product of the burning of pulverized coal. It is a fine and powdery material. A microscopic view would reveal that the particles are essentially spherical.[6] FA has been used as a spherical filler[6] for the production of light-weight and high-strength concrete.[7] These fillers have been shown to increase the stiffness of the composites, but the strength, however, suffers a setback.[8] Srivastava and Shembekar[9] evaluated tensile and flexural properties of fly-ash-filled epoxy resin, and they reported that the loading of FA in epoxy–resin causes a decrease in the tensile and flexural properties of the composites.

A wide variety of fillers have been incorporated in pure polypropylene (PP) to impart flow and mechanical properties and to reduce costs.[10] Chand and Gautham[11] developed composites of FA and glass fiber with polyester resin and re-

ported their abrasive behavior and wear loss. Coutinho et.al.[12] prepared a composite of wood fiber and PP and found a decrease in mechanical properties. Many studies have been published concerning the processing conditions and properties of thermoplastics with wood fiber,[13–16] glass fiber,[17,18] mica,[19] and calcium carbonate.[20] Unfortunately, the better stiffness obtained through filling is often accompanied by drawbacks such as lower processibility and lower toughness. In our previous work,[5] similar type of results with FA/unsaturated polyester composite were reported.

To overcome these problems, a variety of methods have been adopted, including the choice of processing aid and modification of the filler surface. Based on the reasoning that a proper interlayer results in a balance between toughness and strength, the past decade has seen active efforts in developing new coupling agents (CAs) for the fillers.[21–23] The properties of a composite, such as strength and modulus, are important factors for producing high-quality composites. Many researchers have tried to improve the adhesion between filler and matrix resin by chemical reaction with CAs. Silane CAs are generally considered to be adhesion promoters between mineral fillers and organic matrix resins and, as such, provide improved mechanical strength and chemical resistance to the composites.[24]

In our previous article,[5] we reported that a 10% loading of FA caused smaller strength reductions of filled polyester resin, whereas loading beyond 10% caused a drastic deterioration of properties. So, in this article, the influence of silane-based CAs on the mechanical properties of FA /polyester resin with maximum of 40% loading are discussed.

EXPERIMENTAL

Materials

General purpose unsaturated polyester resin (GPR), 1% solution of methyl ethyl ketone peroxide (catalyst), 1% solution of cobalt–naphthenate (accelerator), and surface-modified calcium carbonate filler (120–150 μ, bulk density = 0.7289 g/cc) were obtained from Sakthi Fiber Glass Ltd., (Chennai, India). FA obtained from Ennore Thermal Power Plant (Chennai, India) was used as filler. CAs, AMP, and vinyltriethoxysilane (VES) were obtained from Sigma-Aldrich (St. Louis,

Table I   Characterization of FA

Parameter	Concentration (Average)
Moisture content (%)	6.7787
pH	8.6000
Bulk density (g/cc)	0.8487
Loss on ignition (%)	0.9566
Sulfate content (%)	0.3333
Chloride content (%)	0.3090
Iron content (%)	4.2000
Silica content (%)	92.4000
Aluminum content (%)	3.8000

MO). Methanol from Thomas Baker Ltd. (Mumbai, India) was also used in this investigation.

Characterization of FA

FA was characterized for the following properties: moisture content, loss on ignition, pH, bulk density, sulfate content, chloride content, iron content, silica content, and aluminum content.

The results are given in Table I. The particle size of the FA was determined by sieving through a suitable sieve (standard test sieve BSS 120, 150, 170, 240 μ). FA with particle sizes in the range of 120–150 μ was used in this study.

Treatment of FA with CAs

A 5% solution of AMP and VES in methanol was prepared. A 5% solution (11 mL) mixed with 112.5 g of dried FA in a closed container was shaken for 20 min in a mechanical shaker and kept as such for 20 min. This surface-treated FA contained 0.5% CA by weight. Similarly, 1.0 and 2.0% CA-loaded FA mixtures were prepared by taking 22 and 44 mL of CA solution with 112.5 g of FA.

Fabrication of Composite Sheets

For casting composites sheets, two aluminum sheets 3 mm in thickness and 30 × 30 cm were used. One side of both the aluminum sheets was coated with polyvinyl alcohol solution as a demolding agent and dried. A square aluminum frame of required thickness and 28 × 28 cm was placed on polyvinyl-alcohol-coated surface of one of the aluminum plates, the appropriately formulated resin (given in Table II) was poured inside the frame, and the second aluminum plate was placed above the frame in such a way that the polyvinyl-alcohol-coated surface was facing the

frame. Then, the two aluminum sheets were held tightly together by applying a 50-kg load externally. Then, the mold was allowed to stand for 12 h for complete curing. After that, the sample piece was taken out and cut to the required specimen size according to ASTM standards for tensile, flexural, compressive, impact, and hardness tests.

FA was dried at 120°C in a hot-air oven for 6 h before use to remove the moisture, and it was cooled in a desiccator, whereas calcium carbonate was used as provided. However, in either case, the filler was mixed with the resin–accelerator mixture at room temperature for 20 min with a mechanical stirrer to ensure complete wetting of the filler particles. Then, the required quantity of the catalyst was added, stirred again, and poured into the mold. At least six specimens of each type were made and subjected to testing to obtain the average value for tensile, flexural, compressive, impact, and hardness properties and to avoid possible errors obtained because of nonuniform distribution of the fillers.

Testing of Composites

The tensile (ASTM D638), compressive (ASTM D695), and flexural (ASTM D790) properties were studied with a universal testing machine (HTE-S-Series-H 50K-S model, Hounsfield Test Equipments Ltd., Salfords, Redhill, England, United

Table II   Various Formulations That Were Fabricated Into Particulate Composite Sheets

Serial Number	Code of Formulation	Fillers (%) FA/CaCO$_3$	CA (%)
1	GPR[a]	0	0
2	CaCO$_3$–GPR[a]	40	0
3	FA–GPR[a]		
	a	10	0
	b	20	0
	c	30	0
	d	40	0
4	FA–AMP–GPR[a]		
	a	40	0.5
	b	40	1.0
	c	40	2.0
5	FA–VES–GPR[a]		
	a	40	0.5
	b	40	1.0
	c	40	2.0

[a] Resin : accelerator : catalyst = 100 : 1 mL of 1% solution : 1 mL of 1% solution.

Table III   Tensile and Flexural Properties of FA–GPR Composites

Type of Composite	Composition (%)		Tensile Strength (N/mm^2)	Flexural Strength (N/mm^2)
	FA	Resin		
GPR	0	100	13.22	58.916
FA–GPR	10	90	9.33	37.300
FA–GPR	20	80	8.73	28.059
FA–GPR	30	70	8.02	22.372
FA–GPR	40	60	7.43	19.845

Kingdom). The impact strength (ASTM D265) of all the particulate composites were measured with a impact tester (Type 1997, S.N 117, International Engineering Industries, Bombay, India). The hardness (ASTM D2240) of the composites were studied with a tree durometer/shore "D" hardness tester (Blue Star Engineer's pvt. Ltd., Bombay, India).

RESULTS AND DISCUSSION

Effect of CAs on the Tensile and Flexural Properties of the Composites

The interface between the filler particle and the matrix has a great influence on the mechanical properties of a composite. The mechanical properties can, therefore, give indirect information about interfacial behavior. In this study, the mechanical properties of composites with various FA–GPR contents were analyzed in Table III. Table IV shows the tensile properties of the FA–CA–GPR composites. The content of CA varied between 0.5 and 2.0 wt %. The incorporation of CA resulted in significant improvements in the tensile strengths of FA–CA–GPR composites. These results agree well with rubber–wood/HDPE composites.[25] The tensile modulus of GPR was found to increase and the percentage elongation at break to decrease when filled with FA or CaCO$_3$. With FA–CA–GPR, the increase in modulus and decrease in elongation were only moderate (Table IV). The flexural properties of GPR, FA–GPR, and FA–CA–GPR are given in Table V. The flexural strength of 40% fly-ash-filled GPR was about 66% less than that of GPR. However, when FA–GPR was treated with 2% silane CA, the flexural strength was only 36% lower than that of GPR. A similar type of decrease was reported by other

Table IV Tensile Properties of Fabricated Composites

Type of Composite	Composition (%)			Tensile Strength (N/mm^2)	Tensile Modulus (N/mm^2)	Tensile Elongation (%)
	Resin	FA/CaCO$_3$	CA			
GPR	100	0	0	13.220	766.66	4.0
CaCO$_3$–GPR	60	40	0	10.413	626.66	2.6
FA–GPR	60	40	0	7.043	590.00	2.1
FA–AMP–GPR	60	40	0.5	8.100	466.60	2.6
	60	40	1.0	9.900	443.30	2.9
	60	40	2.0	10.830	358.78	3.2
FA–VES–GPR	60	40	0.5	7.600	458.82	2.7
	60	40	1.0	9.400	410.34	3.0
	60	40	2.0	10.800	332.58	3.2

authors for filled systems.[12,26] For instance, Bajaj et al.[3] reported that the flexural strength of surface-treated mica/epoxy samples showed significant improvements in flexural strength over the untreated mica/epoxy composites. The strength of the composite decreased with increasing filler content even though initially there was an increase of up to 10% of the mica content. When the concentration of CA was increased from 0.5 to 2.0% by weight, flexural strength was also found to increase. The flexural modulus of GPR increased three times when filled with 40% FA. However, FA–CA–GPR had a flexural modulus only about twice that of GPR. The surface modification of FA with CA decreased the flexural modulus. This is in agreement with the general trend that elongation decreases with increasing filler content.[1,2] According to surface-wetting theory,[27] the adhesive strength of the FA–GPR composite without CAs is low, although its adhesive work is high. This is because the surface energy of FA particles does not match that of the polyester resin (adhesive), so the interaction is weak. However, in the presence of CA, the bonding (adhesive strength), being higher than the elasticity between the FA and polyester matrix, may be increased, leading to increased elongation and decreased modulus. After processing with silane CA, the tensile and flexural strength of FA–GPR increases because FA particles are wetted better by the resin in the presence of CA (because of reduced surface energy). Moreover, the CA forms stronger chemical bonds with the FA and the polyester matrix. The adhesion-promoting ability of CAs, according to the chemical bonding theory,[28] produces a molecular bridge between the filler and the organic matrix that results in covalent bonds between inorganic mineral filler and the organic polymer matrix and contributes to improved adhesion and bulk properties of the composites. The increase in the tensile and flexural strengths of FA-filled GPR by the inclusion of

Table V Flexural and Compressive Properties of Fabricated Composites

Type of Composite	Composition (%)			Flexural Strength (N/mm^2)	Flexural Modulus (N/mm^2)	Compressive Strength (N/mm^2)
	Resin	FA/CaCO$_3$	CA			
GPR	100	0	0	58.916	577.14	4228.4
CaCO$_3$–GPR	60	40	0	36.663	740.34	3245.08
FA–GPR	60	40	0	19.845	1505.77	2976.00
FA–AMP–GPR	60	40	0.5	23.840	1340.40	3086.46
	60	40	1.0	29.450	1220.60	3341.00
	60	40	2.0	36.430	1084.80	3746.44
FA–VES–GPR	60	40	0.5	22.645	1440.63	3014.35
	60	40	1.0	28.474	1325.45	3174.26
	60	40	2.0	35.334	1275.36	3446.36

Table VI   Impact Strength and Hardness of Fabricated Composites

Type of Composite	Composition (%)			Impact Strength (J/m)	Hardness (Dimensionless)
	Resin	FA/CaCO$_3$	CA		
GPR	100	0	0	33.33	85
CaCO$_3$–GPR	60	40	0	11.11	88
FA–GPR	60	40	0	8.88	87
FA–AMP–GPR	60	40	0.5	9.44	90
	60	40	1.0	9.99	92
	60	40	2.0	10.60	96
FA–VES–GPR	60	40	0.5	9.00	88
	60	40	1.0	9.90	90
	60	40	2.0	10.02	92

CA makes this composite more or less equivalent to conventional CaCO$_3$-filled GPR as seen in Tables IV and V.

Effect of CAs on the Compressive Strength of the Composite

When the FA–GPR was subjected to compressive loading, the material failed at lower loads compared to GPR, which indicates a drastic decrease in compressive strength. However, when FA was treated with CA, the FA–CA–GPR had an increased compressive strength, showing its ability to take up more compressive load and its resistance to crack propagation in the presence of the CAs. The results are given in Table V. The compressive strength of FA–CA–GPR was also similar to that of CaCO$_3$-filled GPR.

Effect of CAs on the Impact Strength of the Composite

The impact strength of GPR and the FA–GPR and FA–CA–GPR composites are presented in Table VI. The impact strength of FA–GPR particulate composites was inferior to that of GPR. When filled with increasing FA, the impact strength decreased. This was because of poor interfacial adhesion between the inorganic filler and the organic matrix. The composites made with surface-modified FA had improved impact strength. This observation was quite expected for filled composites and has been commonly observed.[29] In the presence of the CA, there was excellent interfacial bonding between the matrix and the filler, which may facilitate a better transfer of stress. As impact strength is a measure of the energy needed to break a material, the results show that more energy was required to break the surface-modified FA filled composites. However, this was lower than that of the CaCO$_3$-filled GPR, probably because of the bigger particle size of FA than that of CaCO$_3$.

Effect of CAs on Hardness of the Composite

The durometer hardness values of the various composites made in this study are given in Table VI. The values indicate that the mineral-filled composites were harder than the unfilled composites. The surface modification further increased the hardness. This observation is in agreement with the fact that the hardness is a measure of resistance to penetration. This resistance to the penetration of GPR increased when filled with the mineral FA, and still more resistance was offered by the material when the surface of the filler was modified with CAs for improved compatibility between the filler and the matrix.

CONCLUSIONS

Through careful analysis of properties, the following conclusions were drawn for the FA– AMP–GPR, FA–VES–GPR, and FA–GPR composites:

1. Treatment with silane CA mainly resulted in an increase in the tensile, flexural, compressive, and impact strengths and the hardness of the composites.
2. The mechanical properties were enhanced when the content of both CA was increased from 0.5 to 2.0%.

3. A decrease in the tensile and flexural moduli of FA–CA–GPR was observed when FA was surface treated with silane CAs.

4. When FA loaded with 2% CA was used for making composites, it originated properties comparable to those of $CaCO_3$-filled GPR.

5. Among the two silane CAs, AMP was found to be better than VES in modifying the FA–GPR composite.

These results reveal that FA can be used as filler in GPR as well as the conventional $CaCO_3$ filler if it is surface treated with 2% silane CA.

REFERENCES

1. Katz, H. S.; Mileswski, J. V. Handbook of Fillers and Reinforcement for Plastics; Van Nostrand Reinhold: New York, 1978.
2. Morrell, S. H. Plast Rubb Proc Appl 1981, 1, 179.
3. Bajaj, P.; Jha, N. K.; Anandakumar, R. J Appl Polym Sci 1992, 44, 1921.
4. Richardson, M. O. W. Polymer Engineering. Composites; Applied Science Publications: London, 1977.
5. Saroja devi, M.; Murugesan, V.; Rengaraj, K.; Anand, P.J Appl Polym Sci 1998, 69, 1385.
6. Albinger, J. M. In Concrete Construction; Applied Science Publications: London, 1982, p 417.
7. Lin, W.; Wenyou, X. In Industrial Congress, International Academic Publications: Beijing, 1990.
8. Chand, N.; Khare, N. Ind J Eng Mater Sci 1999, 6, 342.
9. Srivastava, V. K.; Shembekar, P. S. J Mater Sci 1990, 25, 3513.
10. Kokta, B. V.; Raj, R. G.; Daneaut, C. Polym Plast Technol Eng 1989, 28, 247.
11. Chand, N.; Gautham, K. K. Res Ind 1993, 38, 181.
12. Coutinho, F. M. B.; Costa, T. H. S.; Carvalho, D. J Appl Polym Sci 1997, 65, 1227.
13. Woodhams, R. T.; Thomas, G., Rodgers, D. K. Polym Eng Sci 1984, 24, 1167.
14. Kokta, B. V.; Chen, R.; Daneault, C.; Valada, J. L. Polym Compos 1983, 4, 229.
15. Klason, C.; Kubat, J.; Stromvall, H. E. Int J Polym Mater 1984, 10, 159.
16. Raj, R. G.; Kokta, B. V.; Daneault, C. J Appl Polym Sci 1989, 37, 1089.
17. Curtis, P. T.; Bader, M. G.; Bailey, J. E. J Mater Sci 1978, 13, 377.
18. Czarnecki, L.; White, J. L. J Appl Polym Sci 1980, 25, 1217.
19. Tausz, S. E.; Chaffey, C. E. J Appl Polym Sci 1982, 27, 4493.
20. Bigg, D. M.; Preston, J. R. Polym Eng Sci 1976, 16, 706.
21. Jeffery, G. H.; Bassett, J.; Mendham, J.; Denney, R. C. Vogel's Textbook of Quantitative Analysis; The English Language Book Society: London, United Kingdom, 1989.
22. Arroyo, M.; Perez, F.; Vigo, J. P. J Appl Polym Sci 1986, 32, 5105.
23. Stamhuis, J. E. Polym Compos 1988, 9, 72.
24. Pluddemann, E. P. Silane Coupling Agents, 2nd ed.; Plenum: New York, 1991.
25. Rozman, H. D.; Kon, B. K.; Abusaman, A.; Kumar, R. N.; Ishak, Z. A. M. J Appl Polym Sci 1998, 69, 1993.
26. Ahmed, Z.; Sarwar, M. I.; Mark, J. E. J Appl Polym Sci 1998, 70, 297.
27. Pluddemann, E. P. Molecular Characterization of Composite Interface; Plenum: New York, 1982.
28. Pluddemann, E. P. Interface in Polymer Matrix Composite; Academic: New York, 1974.
29. Tjong, S. C.; Xu, Y.; Meng, Y. Z. J Appl Polym Sci 1999, 72, 1647.