Utilization of Flyash as Filler for Unsaturated Polyester Resin

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ABSTRACT: Flyash is an inexpensive material that can reduce the overall cost of the composite if used as a filler for unsaturated polyester resin (PR). Flyash-filled unsaturated polyester resin (FPR) was cast into sheets. The tensile strength, flexural strength, and flexural modulus were determined. Calcium carbonate-filled polyester resin (CPR) and PR were also cast into sheets. The above-mentioned properties were determined and a comparison was made. The filler concentration was varied from 0 to 15 wt %. It was found that FPR was inferior to CPR and PR composites with respect to tensile and flexural strengths. But FPR was found to have a higher flexural modulus than those of CPR and PR. FPR with 10% flyash was found to have poor acid and solvent (benzene) resistances and good saltwater, alkali, weathering, and freeze–thaw resistances as seen from the mechanical properties. The possible ways of improving the strength of FPR are discussed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1385–1391, 1998

Key words: unsaturated polyester resin; flyash; filler; cost effective; effect of environment; mechanical properties

INTRODUCTION

Although composite materials are usually more expensive than most of the conventional building materials on a weight-to-weight basis, they may prove to be more economical in the long run, considering their prospects like low density, high strength-to-weight and modulus-to-weight ratios, corrosion resistance, low thermal expansion, excellent impact and damage tolerance characteristics, and the ability to tailor the mechanical, electrical, and thermal properties. Normally, thermosetting resins like polyester, epoxy, and phenolics are used as the polymeric binding matrix. Especially, the unsaturated polyester resins (although slightly inferior to epoxy resins in overall properties) are chosen first for making fiber-reinforced plastics (FRP) by any molder because of the ease of handling and fabrication and the low cost compared to other resins. About 85% of the FRP products (like boats, car and aircraft components, and chairs) are manufactured using polyester resins (PRs). Fillers are added to the PR system to improve the ease of handling, molding characteristics, and cured properties or to reduce the overall cost of the system. Almost any powdered material can be used as a filler, the common ones being obtained from natural deposits. Of the several hundred fillers used, those which find widespread use are the various grades of $CaCO_3$, quartz and silica flours, talc, and various clays.[1]

Flyash is a byproduct of the burning of pulverized coal in power plants. Most flyashes are collected from the flue gases of coal-fired power plants by either electrostatic or mechanical precipitators. Flyashes consist principally of the oxides of silicon and iron with varying amounts of

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constituents containing aluminum and some unburned carbon. The color of flyash may vary from light tan to brown and from gray to black. The particles are typically spherical and vary in size and density. Both the chemical and physical properties of the ash may differ widely between power plants and generating units.[2] There are two classifications for flyash in ASTM 618, namely, class F and class C produced from anthracite or bituminous coal and lignite or subbituminous coal, respectively.[3] Flyash, being a waste material, is dumped in heaps without finding a way for safe disposal. It represents an eco-enemy.

In the early 1950s, much work and research was being done on the use of flyash instead of cement and it became obvious that flyash did much more than replace cement and that it is a mineral admixture that imparts qualities into concrete which may not be attainable with any other material.[4] Dams have been built with concrete containing flyash. Some class C flyashes have been used in amounts of 50% or higher of the total cementitious material for building pavements exposed to freezing and thawing. Surveys made in 1979 of the American ready-mixed concrete industry showed that flyash was used in 37% of the ready-mixed concrete produced and the total amount of flyash used equals almost 10% of the total amount of portland cement used.[4] These reports[2,4] and others[5,6] showed that flyash can be used as a building material, as a binder in the place of cement and/or as an aggregate, as a substitute for sand, and as bricks. It has the potential for cutting costs because it is less expensive than is portland cement. As it is very cheap and plentifully available, flyash-filled thermosetting composite-based products must be more economical to produce than are the original thermosets. But, so far, not much work has been reported on the utilization of flyash as a filler for PRs. Hence, considering the large consumption of PR in making composite products (like storage tanks for industries boats) where even a 5 or 10% reduction in the cost would reduce the overall cost considerably, the authors thought that if flyash can be used as a filler it would be beneficial in two ways: One, it would reduce the overall cost of the composites and, two, it would be useful for the disposal for flyash, which is otherwise a hazard to the environment. However, the decision to use or not to use flyash should be based on the quality of the material available, on the ability to compensate for any deficiency of the composites produced, and on the cost reductions.

The use of composite materials in engineering is becoming increasingly important. Therefore, studies on the mechanical properties of FRP composites are very important. Many studies have been published concerning the mechanical properties of the polymer composites with a variety of fillers. The dynamic mechanical properties of composites from sawdust-filled PR was studied by Marcovich et al.[7] Maldas et al.[8] compared the properties of composites with organic and inorganic fillers in polymeric resins. Raj et al.[9] studied the effect of wood-based (cellulosic) fillers in polymeric materials. Kaolin has been used as a filler for PR and the properties of the composites were studied.[10] The mechanical properties of silver powder-filled polypropylene was studied by Wu et al.[11] Doului et al.[12] studied the effects of $CaCO_3$ filler on the properties of a polyurethane matrix. Liu et al.[13] studied the mechanical properties of talc-filled polypropylene. So, considering the importance of the mechanical properties of the composites, in the present study, the authors have restricted their interest only to the mechanical properties of FPR. Keeping in view the fact that the composite products during their end use may be exposed continuously to different environmental conditions, the authors thought that it would be useful if studies were carried out on the effect of environmental stress like chemical contact, exposure to weather, and freeze–thaw (periodic exposure to very low temperature and high-temperature alternatively) on the mechanical properties of FPR.

EXPERIMENTAL

A commercially available PR (isoresin) having better chemical resistance than that of general purpose PR, mixed with an inhibitor, and dissolved in styrene was used as the polymeric matrix. Methyl ethyl ketoperoxide (catalyst), cobalt naphthenate (accelerator), and surface-modified $CaCO_3$ (filler, 4 μm, density 0.7139) were also used. All the above were obtained from Sakthi Fiber Glass Ltd. (Chennai, India). Flyash obtained from the Neyveli Lignite Corp. Neyveli (India) was used as another filler.

Characterization of Flyash

The loss on ignition (a measure of the quantity of the organic matter present) of the flyash was determined by heating 5 g of the flyash in a muffle furnace at 450°C for 24 h, which was then cooled in a desiccator and weighed. The difference in weight before and after heating was taken as the loss on ignition (it was found to be 12.5%). The moisture content of the flyash was determined by heating 5 g of the flyash in an electric oven at 120°C for 24 h, which was then cooled in a desiccator and weighed. The difference in weight with the sample before heating was taken as the moisture content of the flyash (3%). The particle size of the flyash was determined by sieving through a suitable sieve (ASTM E11/61 and mesh number 200). Flyash having a size greater than 75 μm was discarded. The density of the flyash was found to be 0.8421.

Fabrication

For casting, two aluminum sheets of 3-mm thickness having dimensions of 30 $\times$ 30 cm were used. One side of the aluminum sheet was coated with wax and a mylar sheet placed over the wax. These two aluminum sheets were placed one over the other in such a way that the mylar sheets lie inside and face one another. In between the aluminum sheets, rubber seals of the required thickness (depending on the thickness of the final sample piece) were placed; then, the aluminum sheets were held tightly together by C cramps on three sides and one side was kept open for pouring the resin into the mold. An isophthalic resin with 2% catalyst (MEK peroxide) and 2% accelerator (cobalt naphthenate) was poured into the mold and filled. The mold was allowed to stand for 5 h for curing. After that, the sample piece was taken out and cut to the required specimen size according to ISO standards for tensile, flexural, and Izod impact tests. In a similar way, FPR and calcium carbonate-filled PR (CPR) were cast into sheets and the test specimens were cut. The flyash was dried at 120°C in an air oven for 24 h before use to remove the moisture, while the $CaCO_3$ was used as such. In either case, the fillers were mixed with the raw resin the previous day, allowed to stand overnight, and then mixed thoroughly for 4 h at room temperature with a mechanical stirrer to ensure complete wetting of the filler particles. At least four specimens of each type were made and subjected to testing (the results show the average value for impact, tensile, and flexural tests) to avoid possible errors obtained due to nonuniform distribution of the filler, etc. The variation of the results between the replicate samples was ranged from 1–5%.

Mechanical Testing

The impact tests were carried out according to ISO 180 specifications using an unnotched specimen of a rectangular shape with a length of 65 mm, breadth of 12.7 mm, and thickness of 6 mm, the energy of the pendulum being 7.5 kJ. The tensile strength was measured using a universal testing machine (Instron Model 430 and capacity 5 KN). It was carried out as per ISO-527. The specimen used was dumbbell-shaped, with a total length of 220 mm, breadth of 25 mm, and thickness of 4 mm with a span length of 50 mm and breadth of 10 mm. Flexural strength was determined by a three-point bending method. The test was carried out as per ISO 178 (span length was 50 mm; total length, 80 mm; breadth, 10 mm; thickness, 4 mm; and speed, 2 mm/min).

Environmental Tests

Flyash-filled PRs were cast with 10% flyash to study the effect of environmental stress on the strength of the filled and neat resins. For a comparative study, a cast PR without fillers was also subjected to the environmental stress tests.

Acid Resistance

The specimens for tensile and flexural tests were cut from the cast samples according to standards ISO-527 and ISO-180, respectively. The specimens were kept immersed in a 15% nitric acid solution for 30 days, dried, and then tested.

Alkali Resistance

In a similar way, tensile and flexural test specimens were kept immersed in a 15% NaOH solution for 30 days and then tested.

Weathering Resistance

Tensile and flexural test specimens were cut according to standard specifications and left exposed to the atmosphere throughout the day and night for 30 days and then tested.

Table I Tensile Strength of PR, CPR, and FPR Composites

Sample No.	Filler Content (%)	Tensile Strength (MPa)		Elongation at Break (mm)	
		CPR	FPR	CPR	FPR
1	0	51.2	51.2	180	180
2	5	49.3	37.5	140	110
3	10	44.8	35.6	115	96
4	15	41.2	30.0	112	85

Freeze–Thaw Resistance

The test specimens (cut from the cast sheets with and without flyash as per specifications) were kept in the night at 0°C and during the daytime at room temperature. This is called one freeze–thaw cycle. The specimens were subjected to 30 such cycles before being tested.

Solvent Resistance

The samples were immersed in benzene for 30 days and taken out, thoroughly cleaned, and tested for tensile and flexural strength.

Water Absorption

The samples were weighed and immersed in water for 30 days, wiped well to remove water on the surface of the sample, and weighed. The difference in weight gives the water absorption.

RESULTS AND DISCUSSION

The loss on ignition and the moisture content of the flyash were found to be 12.5 and 3%, respectively. Flyash having a particle size to 75 μm was used. Coarser particles were discarded. The tensile strengths of PR, CPR, and FPR are given in Table I as a function of the filler content. It is obvious that in the range of the filler content studied the tensile strength of CPR did not decrease considerably. But, with the flyash-filled composites, the strength decreased to a considerable extent even with 5% addition of flyash. There is not much difference in strength when the resin is filled with 10% flyash. This much filler may not be sufficient to decrease the strength drastically, but with 15% flyash, the strength decreased sharply. This may be due to the difference in particle size. With the flyash particles being much larger (75 μm) compared to those of $CaCO_3$ (4 μm), the distribution of flyash particles in the cured composites may not be as uniform in FPR as in $CaCO_3$. Also, since $CaCO_3$ was already surface-modified with a suitable (stearic acid) coupling agent, there may be improved bonding between the matrix and the filler and, hence, a higher strength. A similar trend was observed with respect to the flexural strength of the PR, CPR, and FPR (Table II). The flexural modulus increased with both CPR and FPR composites compared to PR (Table II), as expected, although the moduli of the CPR composites were slightly lower than those of the FPR composites. Because for the same weight load the volumetric fraction of a substance will be always smaller if the particle size is large (because of smaller total surface area) and bigger if the particle size is small (because of larger total surface area), flyash particles having a larger particle size (75 μm) than that of $CaCO_3$ (4 μm) have a smaller volumetric fraction. Hence, with the same quantity of the resin, flyash will be wetted more readily than will $CaCO_3$. Marcovich et al.[7] reported a similar increase in the flexural modulus with sawdust and $CaCO_3$-filled composites compared to neat polymer resin.

The elongation of the composites (FPR and CPR) decreased significantly compared with that of the original polymer (Table I) and it continued to decrease with increase of the filler content both in CPR and FPR (Fig. 1), showing that the brittleness of the composite increases with flyash content (or, in other words, the toughness is decreased with increasing flyash content).

The impact strengths of all the composites were found to be smaller than that of the neat resin matrix (Table III), and with increasing filler content, the impact strength decreased. The above observations show that FPR composites are very

Table II Flexural Properties of PR, CPR, and FPR Composites

Sample No.	Filler Content (%)	Flexural Strength (N/mm^2)		Flexural Modulus (kg/mm^2)	
		CPR	FPR	CPR	FPR
1	0	113.8	113.8	2514	2514
2	5	106.6	74.5	3031	3075
3	10	82.43	71.4	3052	3173
4	15	80.0	62.7	3086	3237

much inferior in mechanical properties compared to the PR and CPR composites. The reason must be poor adhesion or bonding at the interface between the polymer matrix (organic) and the flyash (inorganic particles) due to the incompatibility between the organic and inorganic phases. So, if the flyash particles are treated with some silane or chrome coupling agents (which react with the polymeric as well as with the inorganic phase and, hence, improve the bonding between the two[14]), then there may be some improvement in the mechanical properties of the FPR composites. The incorporation of various additives/coupling agents in these systems helps to promote the adhesion at the polymer–filler interface and, hence, the stress transfer between the fiber and the polymer improves the degree of the filler dispersion, increases the fiber loading in the composite, and improves the processability and moldability.[14] Several authors have made attempts to improve the mechanical and other properties of composites by modifying the surface of the filler or fiber with suitable coupling agents. For example, a number of attempts have been made to improve the adhesion of cellulosic fillers to the polymer matrix by modifying the surface of the fiber or matrix.[9] Chemical modification of the surface of organic fibers with different silane coupling agents and isocyanate has been reported by Raj et al.[9,15] Clemons et al.[16] and others[17] modified milled aspen fibers with maleic anhydride. Wu et al.[11] reported that the surface treatment of silver powder with a titanate coupling agent marginally improved the mechanical properties of polypropylene. The tensile strength of polypropylene was improved to a maximum with talc which was surface-modified with a series of modifiers.[13]

Table III Impact Strength of PR, CPR, and FPR Composites

Sample No.	Filler Content (%)	Impact Strength (J/m)	
		CPR	FPR
1	0	112.6	112.6
2	5	108.6	55.2
3	10	85.5	27.4
4	15	80.0	19.3

Resistance to Environmental Stress

While in service, the composites may be in contact with seawater (e.g., FRP boats used in the sea) or exposed to weather or aggressive chemical environments continuously. So, the authors tested the ability of the flyash-filled composites to withstand these aggressive environments. Since the strength of the 15% flyash-filled composite was found to be too low compared to that of the 10% filled composite, the latter composition was used to make specimens and subjected to environmental stress. The results are presented in Tables IV and V.

Acid Resistance

The unfilled PR was found to be unaffected by the acid as seen from the tensile and flexural strengths and flexural modulus (Tables IV and V), whereas the FPR composite showed poor acid resistance (Tables IV and V) as indicated by the 15% decrease in the tensile strength and 30% decrease in the flexural strength. Being a mixture of inorganic oxide (SiO_2, Fe_2O_3, Al_2O_3), the flyash should have been attacked readily by the acid and converted to soluble salts, leaving behind voids leading to the decreased strength and flexural modulus.

Table IV Tensile and Flexural Strengths of PR and FPR Composites Before and After Exposure to Environmental Stress

Sample No.	Name of Test	Tensile Strength (MPa)		Flexural Strength (N/mm^2)	
		PR	FPR	PR	FPR[a]
1	Before exposure to environmental stress	51.2	35.6	113.8	71.4
2	Acid resistance	52.7	30.6	112.2	49.5
3	Alkali resistance	51.41	34.5	110.0	69.7
4	Saltwater resistance	49.0	34.5	107.5	72.2
5	Solvent resistance	39.3	21.5	96.4	35.1
6	Weathering resistance	48.6	34.5	103.3	68.9
7	Freeze–thaw resistance	48.1	37.3	108.3	76.0

Flyash content = 10%.

Alkali Resistance

Unlike acid, alkali does not seem to attack the PR as well as the FPR composites, as is evident from the flexural and tensile strengths (Tables IV and V).

Solvent Resistance

The flexural strength of the PR decreased only a little (about 6%) on immersion in benzene, whereas that of the FPR composite was decreased drastically (about 50%). This observation is also confirmed by the nude eye observation of the flyash-filled composite dipped in benzene for 30 days. The composite became fragile visibly after immersion in benzene with the formation of some scaly material on its surface, probably through reaction with the organic material present in the flyash (the loss on ignition of flyash, which is a measure of the quantity of the organic matter present, was found to be 12.5%). A similar trend was observed in the tensile strength and flexural modulus.

Table V Flexural Modulus of PR and FPR Composites Before and After Exposure to Environmental Stress

Sample No.	Name of Test	Flexural Modulus (N/mm^2)	
		PR	FPR[a]
1	Before exposure to the environmental stress	2514	3173
2	Acid resistance	2482	2840
3	Alkali resistance	2405	3270
4	Solvent resistance	1726	1571
5	Saltwater resistance	2499	3158
6	Weathering resistance	2410	3080
7	Freeze–thaw resistance	2510	3173

[a] Flyash content = 10%.

Saltwater Resistance

The tensile strength, flexural strength, and flexural modulus of FPR as well as of PR were not much affected by immersion in salt water, showing good resistance to this environment (Tables IV and V).

Weathering Resistance

The flexural strength, tensile strength, and flexural modulus of the FPR composites and PR were not much influenced after exposure to weather for 30 days (3% decrease in tensile strength and flexural strength for FPR and 5 and 9% decrease in tensile strength and flexural strength, respectively, for PR), showing that FPR composites have excellent weathering resistance (Tables IV and V).

Freeze–Thaw Resistance

The freeze–thaw resistance of the FPR and PR were found to be excellent as the mechanical properties were not deteriorating (6 and 4% decrease in tensile strength and flexural strength, respectively, of PR and no decrease in strength with

FPR) after being subjected to 30 freeze–thaw cycles (Tables IV and V).

CONCLUSIONS

The tensile and flexural strengths of the FPR composites were found to be inferior to those of the PR and CPR composites, whereas the flexural modulus of the FPR composite increased on addition of flyash. FPR composites having 10% flyash content were found to have better mechanical properties compared to those with 5 and 15% flyash content. The FPR composites (10% flyash content) were found to have poor acid and solvent resistance but good alkali, salt water, weathering, and freeze–thaw resistance. So, for general purpose applications (where the reduction in strength is not a matter), PR can be filled up to 10% flyash. If the surface of flyash can be modified with coupling agents which will improve the adhesion between the flyash and polymer matrix, the strength may further be increased. Under such circumstances, even higher amounts of flyash may be loaded in the PR resin. Further study is going on in our laboratory on the effect of the modification of the surface of flyash with coupling agents on the properties of flyash-filled composites.

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