

Synthesis and Application of Multilayered Core Shell Particles for Toughening of Unsaturated Polyester Resin

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ABSTRACT: Toughening particles, comprising two radially alternating rubbery and glassy layers, were prepared by using sequential emulsion polymerization. The conditions which led to controlled particle size and morphology are discussed. A relatively new type of inert core shell particle [fly-ash (FA)] and surface-activated FA, by two different silane coupling agents, namely 3-aminopropyltrimethoxy silane (AMP) and vinyltriethoxysilane (VES)-based multilayered toughening particles, which radially comprise rubbery and glassy layers, were also prepared. The toughening particles were used with general purpose polyester resin (GPR) for making composite sheets. Formation of multiple layers in the core-shell particles and their morphology were confirmed by transmission electron microscopy (TEM). The mechanical properties such as tensile, flexural, impact, and hardness of the toughened GPR are discussed critically. The tensile fractured surfaces were studied by scanning electron microscopy (SEM). Thermal property such as thermogravi-

metric analysis (TGA) were also discussed. The composites were exposed to various adverse environmental conditions such as water, boiling water, salt water, acid, alkali, toluene, weather, and freezing–thawing for 30 days. The mechanical properties (viz. the tensile strength, tensile modulus, elongation at break, flexural strength, flexural modulus, impact strength and hardness of FA/GPR, FA.AMP core/GPR, and FA.VEScore/GPR) were studied before and after exposure to adverse environmental conditions. The results indicate that the mechanical properties of FA/GPR composite are improved by surface treatment of FA and their resistance to the various environmental stresses is also enhanced substantially on modification by toughening particles. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 511–528, 2004

Key words: multilayered core-shell particles; fly-ash; polyester; mechanical and thermal properties; morphology

INTRODUCTION

In general, thermosetting resins in the glassy state are undesirably brittle. General purpose unsaturated polyester resin (GPR) is a classic example of a brittle thermoset. Filling polymers with mineral dispersion has long been a practice in the plastic industry as a way to reduce overall production cost and enhance certain properties. Utilization of fly-ash (FA) as an additive component in polymer composites has received increased attention recently, particularly for price-driven/high-volume applications.¹ This development was brought about because the incorporation of FA offers several advantages and because it is the best way to dispose of FA. FA is a waste material obtained in huge quantities from thermal power plants; it is a byproduct of the burning of pulverized coal. It is a fine and powdery material. These fillers were shown to increase the stiffness of the composites, but the strength, however, suffers a setback.¹ Adhesion between the filler and matrix is of utmost impor-

tance for composite properties. High adhesion can be best acquired by binding the filler surface with polymer matrix by surface modification.¹ Covalent bonds are preferred, but ionic bonds, H-bonds, and other interactions may play an important role. This can be critical in the systems where toughened polymer matrix is based on block copolymers prepared by polymerization carried out on reactive end groups of an elastomeric prepolymer. Interactions between blocks of the copolymer may have different characters and may change during polymerization. As discussed in the previous articles,^{1–4} enhancing the inherent toughness of the polyester matrix is an important method of overcoming the decrease in impact properties on addition of FA to GPR. For several decades, efforts were made to improve the fracture resistance via rubber toughening.^{5,6} It has long been known that the fracture toughness of thermoplastics or thermosetting resins can be considerably improved with small rubber particles dispersed in polymer matrices. The earlier efforts focused on the use of thermoplastic additive and/or interpenetrating polymer network formation to produce composites consisting of both GPR and rubbery phases.⁷ Although toughening materials were commercialized, they were deficient in their morphology, and hence, the toughness of artefacts produced

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TABLE I
Name of the Chemicals Used

Name of the chemical	Name of the company
General purpose unsaturated polyester resin, methyl ethyl ketone peroxide (1% solution in dibutyl phthalate), cobalt naphthenate (1% solution in dibutyl phthalate)	Naphtha Resins and Chemicals Ltd., Mumbai, India
Fly-ash	Ennore Thermal Power Plant, Chennai, India
Acetone, methanol	Thomas Baker, Chennai, India
Styrene, aerosol OT, dibutyltindilaurate, anhydrous CaCl ₂ , furfural, ethylene glycol dimethacrylate	E-Merck, Germany
Hydroquinone, <i>n</i> -butylacrylate	Sisco-Research Laboratory Limited, Chennai, India
Toluene, sodium chloride, sodium hydroxide	Priya Research Laboratory, Chennai, India
Hydrochloric acid, sulphuric acid, ethylacrylate, methylmethacrylate, Magnesium sulphate	Central Drug House Ltd., Mumbai, India
AMP, VES	Oscar Chemicals, Mumbai, India Sigma Aldrich, USA

from them was very strongly dependent upon the molding condition. There was, therefore, great scope for improvement and, in particular, a need to develop rubber toughened (RT) GPR materials, the toughness of which could be more reproducibly controlled and would be less susceptible to the processing regime. During the last two decades, these improvements were achieved by blending the matrix GPR with separately prepared toughening particles.⁸

Emulsion polymerization is used to prepare the toughening particles which typically comprise two radially alternating rubbery and glassy layers, the outer layers always being of glassy polymer. The particles are crosslinked during their formation to ensure that they retain their morphology and size during blending with GPR and a subsequent molding of the blends. This route to RTGPR has the distinct advantage of allowing independent control of the properties of the matrix GPR, the composition, morphology, size of the dispersed rubbery phase and glassy phase, and the level of inclusion of the toughening particles.

Multilayered core-shell particles have glassy polymer as core, over which are deposited alternate layers of rubbery and glassy polymers. When these particles are used as filler in brittle polymers, there is substantial decrease in the brittleness of these polymers.⁹⁻¹³ This article is aimed at elucidating the preparation and properties of two layer toughening particles based on the different core shells such as poly(methyl methacrylate) (PMMA), FA, and surface-treated FA. The re-

sults of its mechanical, thermal, morphological, and environmental stress crack resistances are discussed critically.

EXPERIMENTAL

Purification of monomers

The acrylic monomers (viz. methyl methacrylate, *n*-butyl acrylate, styrene, ethylacrylate, acrylonitrile, and ethylene glycoldimethacrylate) (Table I) used in the present study were purified as follows to remove the inhibitor. About 200 ml of the monomer and 100 ml of 10% solution of NaOH were taken in a separating funnel, shaken well for about 5 min, and allowed to stand for the aqueous and organic layers to get separated thoroughly. The lower aqueous layer was decanted and discarded and the above procedure was repeated three times. Finally, the monomer was washed thoroughly with water, allowed to stand over anhydrous CaCl₂ overnight, and distilled under reduced pressure. The collected monomers were stored in the refrigerator for further use.

The two layer toughening particles which are represented schematically in Figure 1 were prepared by sequential emulsion polymerization in which seed particles were first formed and the glassy and rubbery layers were deposited in subsequent stages. The base comonomer formulations used for the formation of the rubbery and glassy layers were butylacrylate-styrene (BA-Sty; 78.2:21.8 mol %) and methyl methacrylate ethylacrylate (MMA-EA; 94.4:5.1 mol%), respectively (Tables II and III).

The polymerizations were performed at 70°C under nitrogen atmosphere in a three-necked round-bottomed flask. Distilled deionized water (DDI) and Aerosol OT (AOT) were taken in a round-bottomed flask. The solution containing MMA and ethylene-glycoldimethacrylate (EGDMA) was added dropwise over a period of 10–15 min. The temperature was maintained at 70°C. Two percent solution of potassium persulfate (KPS) solution was added after 10 min. The reaction mixture was stirred continuously.

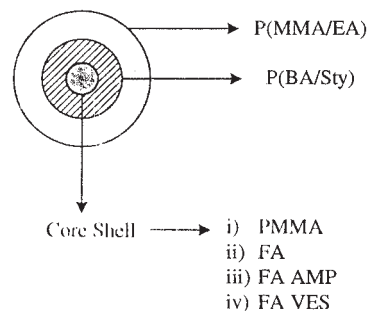


Figure 1 Schematic representation of two layer toughening particles.

TABLE II
Characterization of FA

Parameter	Concentration (Average)
Moisture content (%)	6.80
PH	8.60
Bulk density (g/mL)	0.90
Loss on ignition (%)	0.96
Sulphate content (%)	0.33
Chloride content (%)	0.31
Iron content (%)	4.20
Silica content (%)	92.40
Alumina content (%)	3.80

Aliquot samples of 5 ml of the emulsion were removed every 10 min, coagulated, and filtered. The obtained polymer was washed with water, dried, and weighed. From the weight of the polymer obtained, % conversion was calculated. It was found that about 98% conversion was achieved after 2 h of reaction time. So, the reaction was stopped after 2 h by cooling the reaction mixture down to room temperature. PMMA emulsion was thus obtained. To this emulsion, a mixture of BA and styrene (Sty) was added along with EGDMA as crosslinker and 2% KPS solution as initiator and the reaction for the deposition of rubbery layer was started by heating to 70°C. The reaction time for near complete conversion was optimized to be 2 h. Hence, the reaction mixture was subjected to heating and stirring simultaneously for about 2 h. The system was then allowed to attain room temperature. Then, to this solution, the emulsion mixture of MMA and EA along with initiator and crosslinking agent was added for the deposition of glassy layer. The solution was stirred and maintained at 70°C for 2 h.

After the deposition of both rubbery and glassy layers was completed, the emulsion was coagulated by adding 5% solution of MgSO₄. The coagulated particles were filtered and washed with water to remove MgSO₄. Finally, the particles were filtered and washed with methanol to remove unreacted monomers. The particles thus obtained were dried in a

vacuum oven at 70°C. These particles were added to GPR in varying amounts as toughening agent and cast into sheets (Table IV).

Synthesis of fly-ash-based core shell particles

FA was sieved and dried in a hot-air oven for 6 h and cooled to room temperature. The required amount of FA was then used as core for the synthesis of multilayered core-shell particles. The formulations for the formation of FA-based multilayered core-shell particles are given in Table III. Adopting the same procedure as in the previous section, the rubbery and glassy layers were deposited on FA particles as core. The prepared multilayered core-shell particles with FA as core were added to GPR and cast into sheets (Table IV).

Synthesis of surface-treated fly-ash-based multilayered core-shell particles

A 5% solution of 3-aminopropyltrimethoxysilane (AMP) and vinyltriethoxysilane (VES) in methanol was prepared. Eleven milliliters of 5% solution 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 contains 0.5%, by weight of coupling agent. Similarly 1.0 and 2.0% of coupling agent loaded FA were prepared by taking 22 and 44 ml of coupling agent solution with 112.5 g of FA. This surface-treated FA was used as core over which rubbery and glassy layers were deposited by emulsion polymerization by using the procedure described above (Table III). These multilayered core-shell particles with surface-treated FA as core were added to GPR and particulate composite sheets were made (Table IV).

Fabrication of composite sheet

For casting, two iron sheets of 6 mm thickness having dimensions of 30 × 30 cm were used. One side of each of the iron sheets was coated with Teflon and high

TABLE III
The Recipe for the Synthesis of Multilayered Core Shell Particles

Sample no.	Reagents	PMMA core	FA ^a core	Rubbery layer	Glassy layer
1	MMA (mol)	0.5465	—	—	0.3764
2	DDI (mol)	6.9440	6.944	6.944	6.944
3	KPS (mol)	0.0007	0.0007	0.0007	0.0007
4	EGDMA (mol)	0.02	0.02	0.02	0.02
5	AOT ^b	0.68	0.68	0.68	0.68
6	BA (mol)	—	—	6.944	—
7	Styrene (mol)	—	—	0.1812	—
8	Ethylacrylate (mol)	—	—	—	0.037
9	FA ^b	—	80	—	—

^a FA untreated, FA surface treated.

^b Weight in grams.

TABLE IV
Composition and Notations for PMMA, FA, and Surface-Treated FA/GPR Composites

Sample no.	Name of the toughening particle	Weight %		Notations ^a
		Toughening particle	GPR	
1	PMMA core			
	TP 2	2	98	TP 2/GPR
	TP 5	5	95	TP 5/GPR
2	TP 10	10	90	TP 10/GPR
	FA Core			
	FATP 2	2	98	FATP 2/GPR
3	FATP 5	5	95	FATP 5/GPR
	FATP 10	10	90	FATP 10/GPR
	FA/AMP core			
4	FA/AMP 2	2	98	FA.AMP 2/GPR
	FA/AMP 5	5	95	FA.AMP 5/GPR
	FA/AMP 10	10	90	FA.AMP 10/GPR
4	FA/VES core			
	FA/VES 2	2	98	FA.VES 2/GPR
	FA/VES 5	5	95	FA.VES 5/GPR
	FA/VES 10	10	90	FA.VES 10/GPR

^a Resin: accelerator: catalyst = 100: 1 ml of 1% solution: 1 ml of 1% solution.

molecular weight silicone oil was spread over each of the Teflon-coated surfaces as releasing agent. A square aluminum frame of dimensions of $0.3 \times 28 \times 28$ cm with one side open was placed on the Teflon-coated surface of one of the iron plates; the second iron plate was placed above the frame in such a way that the Teflon-coated surface was facing the frame. Then, the two iron sheets were held tightly together by bolts and nuts. The appropriately formulated GPR resin (Table IV) was stirred for 20 min and degassed for 10 min by applying vacuum to remove the air bubbles formed during stirring and then poured into the mold. The mold was then allowed to stand for 12 h for complete curing of the resin. After that, the sheet was taken out and cut to the required specimen size according to ASTM specifications for tensile, flexural, 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 cooled in a desiccator, whereas calcium carbonate was used as provided. However, in either case, the filler was mixed with the resin-accelerator mixture and stirred at room temperature for 20 min with a mechanical stirrer at 250 rpm 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 the properties studied and to avoid possible errors obtained because of nonuniform distribution of the fillers.

Techniques employed

Thermogravimetric analysis (TGA)

The weight-loss measurements as a function of temperature for all composite compositions were carried

out by using a Mettler TA 3000 system, at a heating rate of 20°C/min in air. Weight of the material taken was 6–9 mg and TGA was run up to 800°C.

Scanning electron microscopy (SEM)

For nonconducting samples prior to taking the SEM picture, it is inevitable to give the surface to be photographed a conducting coating known as sputter coating with gold. In the present investigation, sputter coating was done with a sputter coater (Hitachi Ltd., S-415A model, Tokyo, Japan) used to examine the tensile fracture surface of various filled and modified polymeric systems at 25 K and the magnification was done up to $\times 500$.

Transmission electron microscopy (TEM)

The toughened multilayered core shell particles were embedded in polyester resin and ultramicrotomed into 100-nm-thick sections. Staining was conducted for 48 h in a 2% osmium tetroxide solution. The electron micrographs were taken with a JEOL Jem 200cx instrument by using an accelerating voltage of 60 kV.

Environmental stress crack resistance

The test specimens for tensile, flexural, impact, and hardness properties were prepared as per ASTM specifications for all the composites with different formulations (FA/GPR, PMMA-based TP/GPR, FATP/GPR, FA.AMP core/GPR, FA.VES core/GPR). The prepared specimens were exposed to various adverse environmental conditions for 30 days and then tested

to study the effect of the environmental conditions on the properties.

Water resistance

The test samples were kept immersed in pure water for 30 days, taken out, wiped with filter paper to remove moisture, and tested for tensile, flexural, impact, and hardness properties.

Resistance to boiling water

The test specimens were placed in a boiling water bath for 8 h per day for 30 days and then tested.

Acid resistance

A 5% (by volume) solution of hydrochloric acid was prepared in distilled water. The test specimens were immersed in it for 30 days and tested for the above-mentioned mechanical properties.

Alkali resistance

The test specimens were prepared according to specifications, kept immersed in 5% (by weight) solution of sodium hydroxide for 30 days, and then tested.

Salt water resistance

The specimens prepared as per standard specifications were kept submerged in 5% (by weight) solution of sodium chloride for 30 days and then tested.

Solvent resistance

The test samples were immersed in distilled toluene for 30 days, cleaned well, and then tested for tensile, flexural, impact, and hardness properties.

Weathering resistance

For tensile, flexural, impact, and hardness tests, samples were cut according to standard specifications left exposed to the atmosphere (28–35°C and relative humidity 27–30%) day and night for 30 days and tested.

Freeze–thaw resistance

The specimens were kept at ~0–5°C during the night in the freezing compartment of a refrigerator for 12 h and at room temperature for 12 h during the day. This is one freeze–thaw cycle. The specimens were subjected to 30 such cycles before being tested.

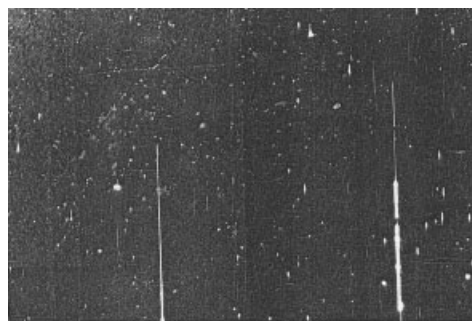


Figure 2 TEM picture of TP/GPR.

RESULTS AND DISCUSSION

Multilayered core-shell particles with PMMA, FA, FA.AMP, and FA.VES as core were synthesized by sequential emulsion polymerization and used as filler for the GPR resin in the present study. The formation of multilayers on the core-shell particles were confirmed by using TEM studies.

Transmission electron microscopic analysis

The preparation of well-defined particles with concentric layers is expected to be greatly assisted by crosslinking of the copolymers forming these layers, because this presents a kinetic barrier to thermodynamically driven rearrangements of different layers within the particles for preparation of PMMA-PS core shell particles. Lee and Rudin^{14,15} reported that well-defined core-shell morphology is obtained when the two polymers are sufficiently crosslinked and have shown that allylmethacrylate (ALMA-crosslinking agent) is particularly efficient in restricting rearrangements of phases. The crosslinking and graftlinking of the copolymers forming the phases in the toughening particles, therefore, provide conditions which are commensurate with good control of particle morphology.

This is confirmed by Figure 2, which shows a TEM of thin film cast from dispersion of the PMMA core toughening particles in GPR matrix. In Figure 2, the PMMA core is seen as transparent particles which can be seen to be dispersed uniformly. In Figures 3–5 the black-colored FA particles surrounded by the TP layer cores are seen distributed in the GPR matrix. The rubbery phases appear darker than the glassy phases, thereby clearly revealing the morphology of the particles and, in each case, showing that it is consistent with the designed particle structure, thereby revealing that the rubbery and glassy copolymers are layered uniformly surrounding the PMMA core. Such uniform distribution of particles may enhance the thermal stability and the mechanical properties of the formed composite. Figure 3 (TEM picture of FA TP/GPR film)

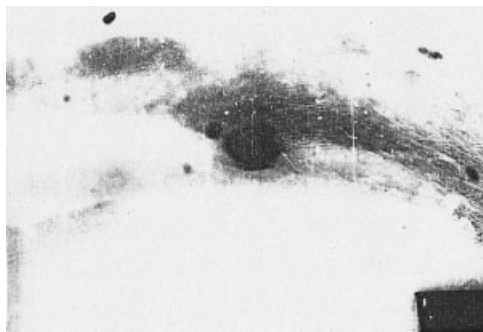


Figure 3 TEM picture of FATP/GPR.

reveals the presence of black-colored FA particle (surrounded by the TP layers) cores distributed in the GPR matrix and the formation of rubbery and glassy layers surrounding the FA particle in the FA TP/GPR composite. From the observations, it may be concluded that the rubbery and glassy layers are formed around FA and the interfacial bonding is improved considerably compared to that of FA/GPR, as revealed by the improvement in all mechanical properties. The micrographs also show that the particle size distributions are relatively narrow. The contrast between the phases almost certainly is due to degradation and evaporation of the glassy (layer) copolymer,¹⁶ leading to higher electron density in the rubbery phases. The outer glassy layers of the particles are not visible because they are of almost identical composition to the glassy matrix of GPR crosslinked with Styr with which they mix.

The TEM pictures of FA.AMP core/GPR and FA.VES core/GPR films are presented in Figures 4 and 5, respectively. From these figures, it can be observed that FA particles are perfectly bond with rubbery (BA/Sty) and glassy (MMA/EA) copolymer compared to that in FATP/GPR. This observation is in agreement with the fact that these surface-treated systems have better mechanical and thermal properties. This may be due to the perfect compatibility of particles by crosslinking with (EGDMA) as well as coupling agents (AMP or VES). In the case of crosslinking

agent, they played a role in crosslinking and graftlinking with rubbery and glassy layers. However, the coupling agent plays an important role in enhancing the filler–resin interaction, by bonding with deposited layered filler surface. Because of such reasons, the highly crosslinked network of coupling agent treated, FA core-shell-based multilayered particle toughened GPRs are the best system with superior properties. Figures 2–5 also reveal that the dispersions of the toughening particles are good. The micrographs also confirm that the morphology and size of the toughening particles are unaffected by blending process.

Mechanical properties

The content of core-shell particles in the composites was limited to only 10%. When added beyond 10%, the viscosity of the GPR increased drastically because of immediate swelling of the slightly crosslinked thermoplastic layers on the core-shell particles in Styr present in the GPR. Because of this swelling, the mixture became a gel very shortly after addition into GPR and even before being poured into the mold. The results of the mechanical properties such as tensile strength, tensile modulus, tensile elongation, flexural strength, flexural modulus, impact strength, and hardness of GPR composites with various core-shell particles (PMMA.core, FA.core, FA.AMP.core, and FA.VES.core) are given in Figures 6–9.

Tensile properties

The tensile properties of the various multilayered core-shell particle toughened polyester particulate composites are given in Figures 6–7. It is seen that the inclusion of toughened particles in the polyester matrix has increased the area under stress–strain curve, which is a measure of toughness. It can be inferred that the addition of particles up to 10% by weight of matrix GPR has toughened the system without much affecting (deteriorating little) the tensile strength and tensile modulus. Figure 6 shows >100% increase in the tensile strength for FA.AMP 10 and FA.VES 10.



Figure 4 TEM picture of FA AMP core/GPR.



Figure 5 TEM picture of FA.VES core/GPR.

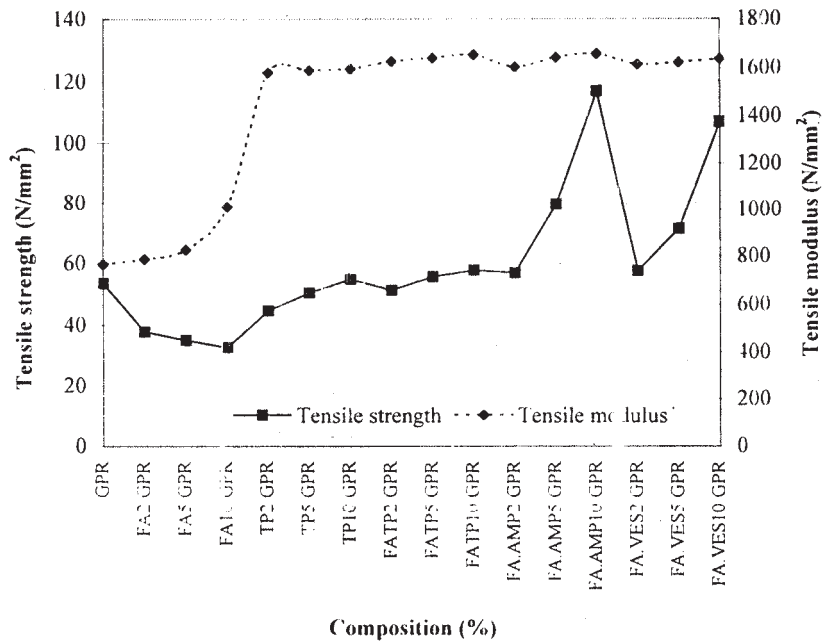


Figure 6 Tensile properties of multilayered core-shell particle-toughened FA/GPR.

This dramatic increase may be attributed to the efficient bonding of the FA particle to the surrounding thermoplastic core and the GPR matrix through the coupling agent. Addition of FA up to 40% as a filler into GPR matrix has decreased the tensile strength by 65% (18.6 MPa) and increased the tensile modulus (1373 MPa) drastically. This is in accordance with the observation that the addition of inorganic particles decreases the strength because of poor interfacial

bonding between the particle and matrix due to incompatibility between the two systems. The system FATP/GPR had better strength and slightly higher modulus compared to untreated FA/GPR. The reason for the above observation may be that the deposited polymeric layers have improved the bonding between the FA and GPR matrix at the interface. FA.AMP core/GPR and FA.VES core/GPR had still better strength and modulus because the coupling agents

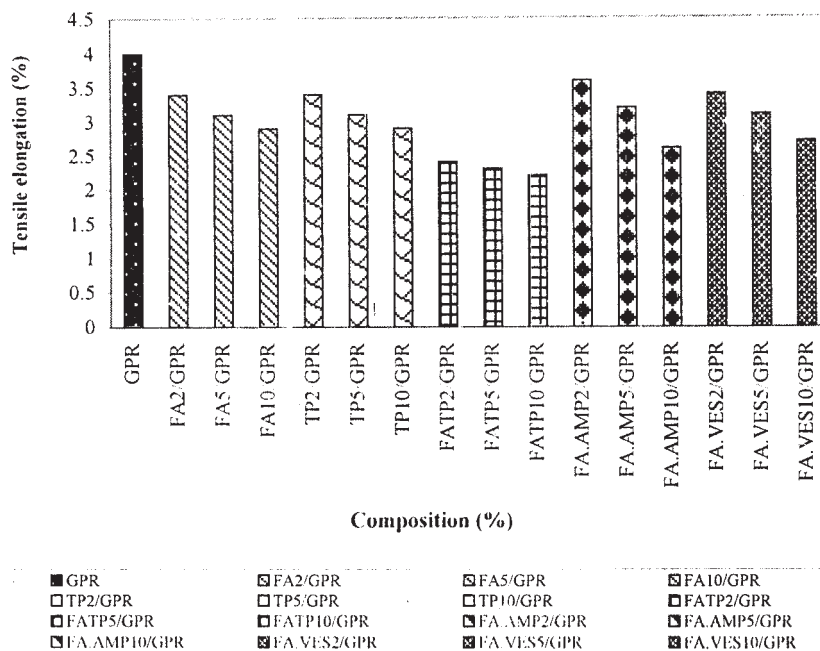


Figure 7 Tensile elongation of multilayered core-shell particle-toughened FA/GPR.

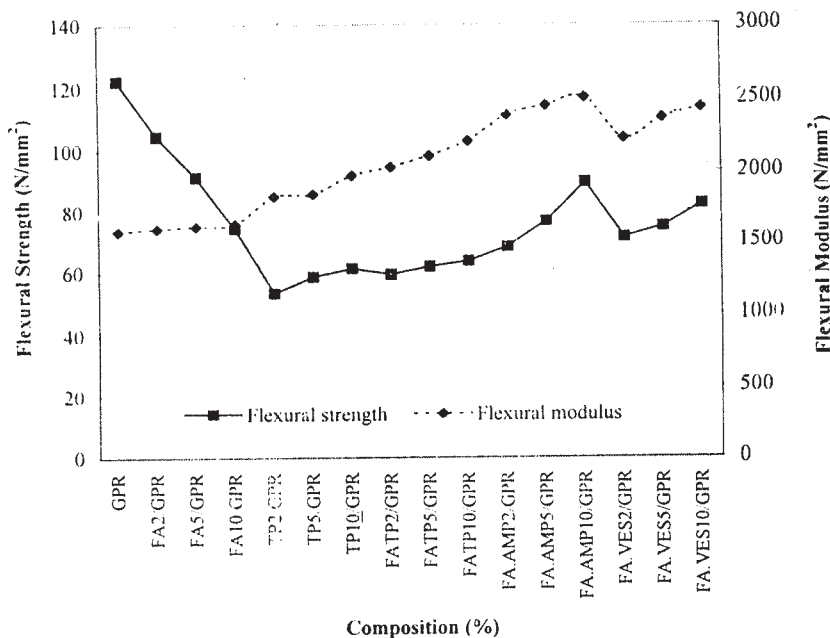


Figure 8 Flexural elongation of multilayered core-shell particle-toughened FA/GPR.

AMP and VES form chemical bonds with FA as well as GPR matrix and deposited layers. This leads to better adhesion between the FA and deposited layers and the polymeric GPR system. Similar to our report, other authors¹⁷ also observed that thermoplastic-toughened particles with surface epoxy groups, when added to epoxy resin, enhanced the toughness of the latter without much affecting the strength. This is expected to be due to the bond formation between the core-shell par-

ticles through the glycidyl groups on their surface and the matrix. The tensile elongation data and modulus are shown in Figures 6 and 7. The PMMA-based TP/GPR and FATP/GPR, FA.AMP core/GPR, and FA.VES core/GPR systems have much improved tensile strength and modulus, but also lead to a greater decrease in the elongation at failure, compared to the nontoughened resin. This behavior is contrary to the expectation that increasing the amount of elastomeric

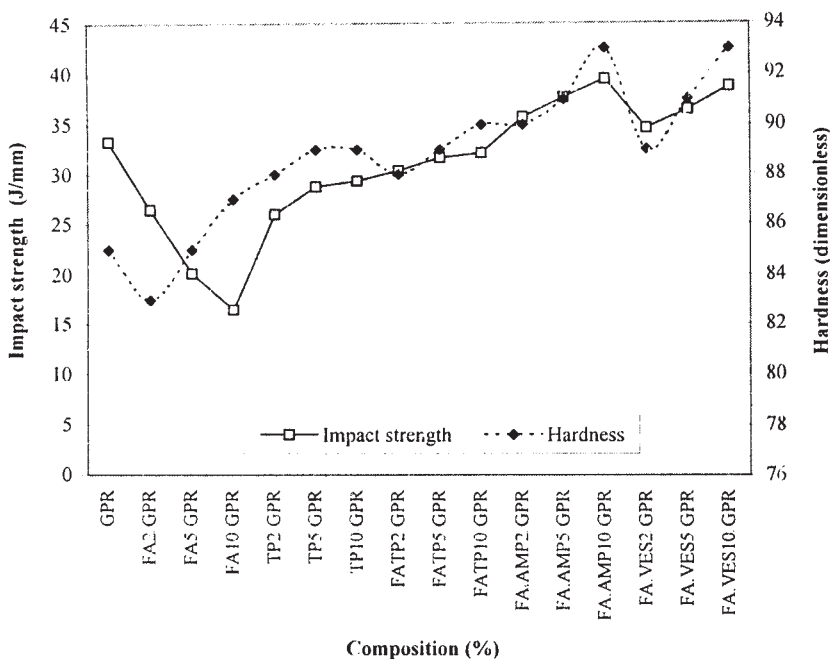


Figure 9 Impact and hardness properties of multilayered core-shell particle-toughened FA/GPR.

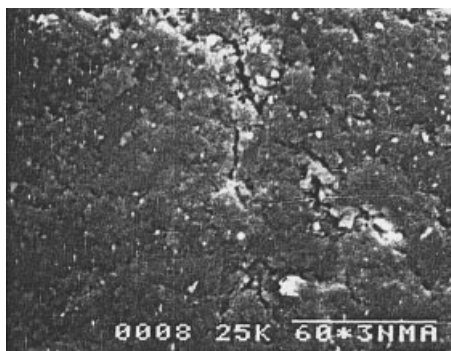


Figure 10 SEM picture of TP10/GPR.

toughening agent should lead to a reduction in the stiffness and increase in elongation at break. This may be due to the role played by the coupling agents (AMP or VES) in enhancing the interfacial bonding between the filler and the matrix.

Flexural properties

The flexural properties of the particulate composites are presented in Figure 8. While adding FA to $\approx 40\%$, the flexural strength was decreased drastically ($\approx 66\%$ reduction, 58.9 MPa) and the modulus increased tremendously (2506 MPa). When FA was coated with rubbery and glassy layers of polymer and used as filler, the strength reduction was only 35–40% and modulus increased to about (4.4–35%) up to 10% addition. This shows that coating of FA particles with rubbery and glassy layers has improved the interfacial strength because of improved compatibility between particle surface and the matrix.

When the FA was treated with silane-coupling agents, namely AMP and VES, before being coated with polymer layers, the flexural strength and modulus were improved appreciably. This may be explained based on the fact that generally fillers are inert during the reaction; once the polymerization takes place on the surface of the filler, reactive sites may be created on the filler surface, thereby improving the interfacial properties between the filler and the matrix through chemical bonding. Thus, the presence of coupling agent improves the bonding/material contact between the filler and the matrix thereby decreasing the void content. The decrease in void content is known to increase the modulus. However, once the filler is surface modified with silane-coupling agent, thereby creating active sites on the filler, the filler itself has active sites on its surface for further reactions with the deposited polymer layers. If this activated filler is coated with rubbery and glassy polymers, the interfacial bonding is still more improved, thereby enhancing the mechanical properties. The PMMA-based TP/GPR toughened composite has a decreased flexural

strength and an increased modulus, but the effect was found to be less pronounced compared to that of FA/GPR composites, as shown in Figure 8.

Impact strength

The impact strength of the particulate composites is given in Figure 9. The FA/GPR composites have the least impact strength. FATP/GPR composites have slightly better values. The impact strength of the composites are in the order FA.AMP core/GPR > FA.VES core/GPR > PMMA-based TP/GPR > FATP/GPR > FA/GPR. This is in accordance with the well-known fact that the toughness of the GPR can be considerably increased by the incorporation of rubbery phase.

Several authors have reported a decrease of toughness when the rubber content is above a certain value, which varies from 10 to 20 wt % depending on the size of the rubber particle.¹⁸ In our study, the impact strength increases with the increasing amount of toughened particles up to 10%. Stamhuis¹⁹ pointed out similar findings in talc-filled polypropylene (PP) systems by using styrene-butadiene-styrene (SBS) as an impact modifier. Impact modifiers have affinity for the filler particles and partially encapsulated or coated talc particles rather than simply existing as separate domains in the bulk matrix. This encapsulation reduces stress concentration at the particle–polymer interface. The interface was further improved by silane-coupling agent leading to better impact performance.²⁰ Similar to these results, in our study also, the composite systems containing FA.AMP core/GPR (surface treated by AMP) had the best impact properties. These data are consistent with the conclusion from the tensile data that FA.AMP core/GPR has higher crosslink density and also explains the greater toughness compared to other toughened composites.

Hardness

The shore D hardness values of the various composites are given in Figure 9. It can be seen that the hardness values were improved only moderately.

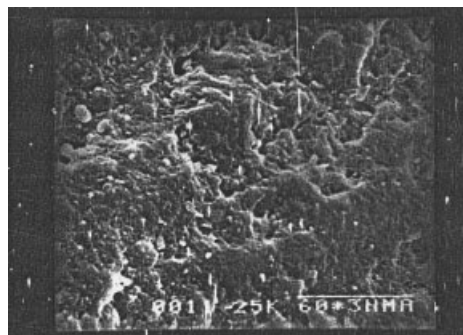


Figure 11 SEM picture of FATP10/GPR.

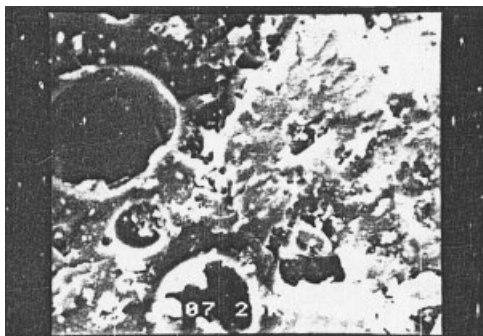


Figure 12 SEM picture of FAAMP core10/GPR.



Figure 13 SEM picture of FAVES core10/GPR.

Analysis of results of the mechanical studies reveals that the incorporation of FA decreased the tensile strength, flexural strength, and impact strength tremendously and increased the flexural modulus. This is due to the poor interfacial bond between the inorganic FA and organic GPR. The deposition of rubbery and glassy polymer layers on the FA to improve its compatibility to GPR matrix was found to increase the strengths significantly. This is because after deposition of polymeric layers on FA particles, the adhesion with the GPR matrix should have been improved because of the permeation of Styrene monomer in the GPR into the slightly crosslinked top polymer layer of the particle and subsequent crosslinking with the least amount of voids. The surface treatment of FA with silane-coupling agents AMP and VES further improves the bonding between FA and deposited polymeric layers with still lesser amount of voids, leading to improved strength, modulus, and toughness.

The thermoplastic (PMMA) core-shell multiple layered particles also increase the toughness and strength of the GPR for similar reasons.

Interfacial morphology

It is well known that the mechanical properties of filled polymer materials depend critically upon the filler-matrix interfacial adhesion.

Examination of the tensile fractured surfaces of the composites by SEM analysis. This gives information about how impact modifiers and coupling agents affect the morphology of the composite. The SEM picture of the tensile fractured surface of TP/GPR (Fig. 10) shows that there is perfect compatibility between PMMA-based multilayered core-shell particles and GPR matrix. Actually, the particles could not be seen in the matrix. The toughened particles were well dispersed on the GPR matrix. In the case of FATP/GPR (Fig. 11) also the particles are well dispersed in the matrix and there is good interfacial bonding due to the chemical interaction between the deposited layers and the GPR matrix. The toughened particles are not bro-

ken because of the multiple layers one over the other (i.e., rubbery layer followed by glassy layer).

Figures 12 and 13 show microstructures of the composites with FA.AMP core/GPR and FA.VES core/GPR. Particle pull out can be seen in these composites. This may be due to the fact that in the presence of the coupling agent the glassy and rubbery layers of polymers are bonded strongly to the FA surface through chemical (covalent) bonds. Hence, on applying tensile stress, the toughening particle, being very strong, does not break, leading to a crack propagation through the interface. Cavities could be seen in the picture. Even though particle pull out happens in this case, it is at a higher tensile strength because of better bonding in these composites compared to that in FA/GPR composites (Fig. 14).

Thermal stability

TGA technique was employed to get information on thermal stability of the core-shell particle-filled composites. All the FA/GPR, PMMA-based TP/GPR, FATP/GPR, FA.AMP core/GPR, and FA.VES core/GPR were subjected to TGA at a heating rate of 20°C/min in an air atmosphere. Figure 15 gives the TGA data obtained for the present system. The figure shows clearly that there are two stages of thermal decomposition (while FA does not show any appreciable weight loss during scan and practically there is no 100% thermal decomposition in FA). The formation of

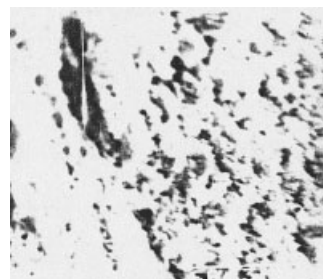


Figure 14 SEM picture of FA/GPR.

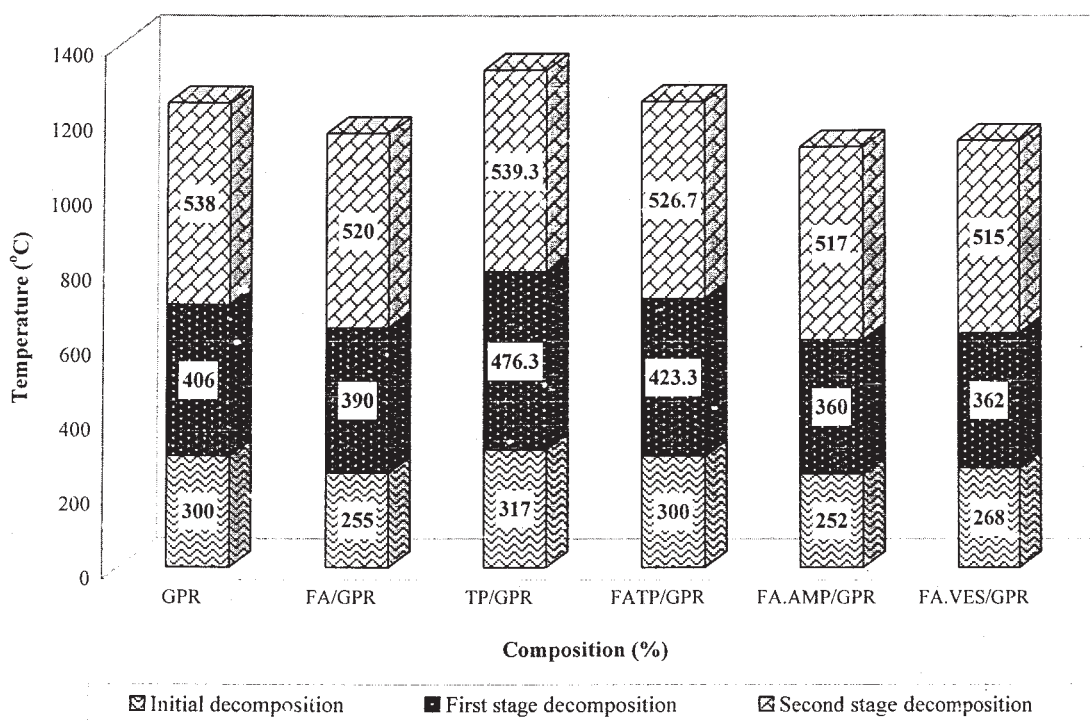


Figure 15 Thermal stability of GPR, FA/GPR, and multilayered core-shell particle-toughened GPR composites.

two distinct DTG peaks substantiates the presence of two-stage decomposition mechanism in particle-toughened GPR matrix and the degradation mechanism of particle-toughened GPR is beyond the scope of this study.

The results from thermal analysis of fully cured resin, TP/GPR, and FATP/GPR exemplify the thermal behavior of the materials and are described here. The rate of weight loss for the fully cured nontoughened and FA-filled untreated GPR is low, <255°C, but at temperatures >390°C, rapid loss of the entire sample mass occurs. FATP/GPR shows initial weight loss of moisture taken up during storage; the sample weight then remains constant until \approx 300°C, at which point it begins to slowly reduce. Finally, the thermogravimetric curve of the fully cured resin sample containing 10% FATP displays the same behavior as the sample of fully cured unmodified resin. Hence, the results from thermogravimetry show that the preformed toughening particles are thermally stable under the full curing condition and at the normal use temperature envisaged for these materials. In the case of surface-modified FATP/GPR with two different silane coupling agents, the improved thermal stability at their higher concentration may be due to the perfect compatibility between the filler-matrix interface.

From Figure 15, it is evident that PMMA-based TP/GPR is the best system (476.3°C) when compared to GPR (406°C), FA/GPR (390°C), FATP/GPR (423°C), FA.AMP core/GPR (360°C), and FA.VES core/GPR (362°C) in improving the thermal stability. This may

be explained by the fact that highly crosslinked network in PMMA-based TP/GPR decomposes at a high temperature. So the thermal stability increases.

Considering the two silane-treated core-shell toughened systems, FA.AMP core/GPR and FA.VES core/GPR, the AMP-based one is the best system. This is due to the presence of the highly reactive $-\text{NH}_2$ group present in AMP, which predominantly undergoes a Michael-type of addition with the GPR matrix, thus enhancing the properties of the entire system. The vinyl-based silanes also show better crosslinking due to the presence of double bond ($-\text{C}=\text{C}-$), but such a strengthening effect is only less pronounced compared to AMP-based samples. Hence, the various systems may be arranged in the order of decreasing thermal stability as follows: FA.AMP core/GPR > FA.VES core/GPR > FATP/GPR > PMMA-based TP/GPR > FA/GPR.

Environmental stress-crack resistance

Scrutiny of literature and our earlier work^{5,6} reveals that 2% level of coupling agent loaded on fiber showed maximum increase over the untreated composite compared to the lower (1%) or higher (8%) levels of coupling agents.²¹ Hence, FA was treated with up to 2% silane coupling agent (AMP or VES) and FA.AMP core/GPR and FA.VES core/GPR composites were fabricated. The tensile, flexural, impact, and hardness properties of FA/GPR, FA.AMP core/

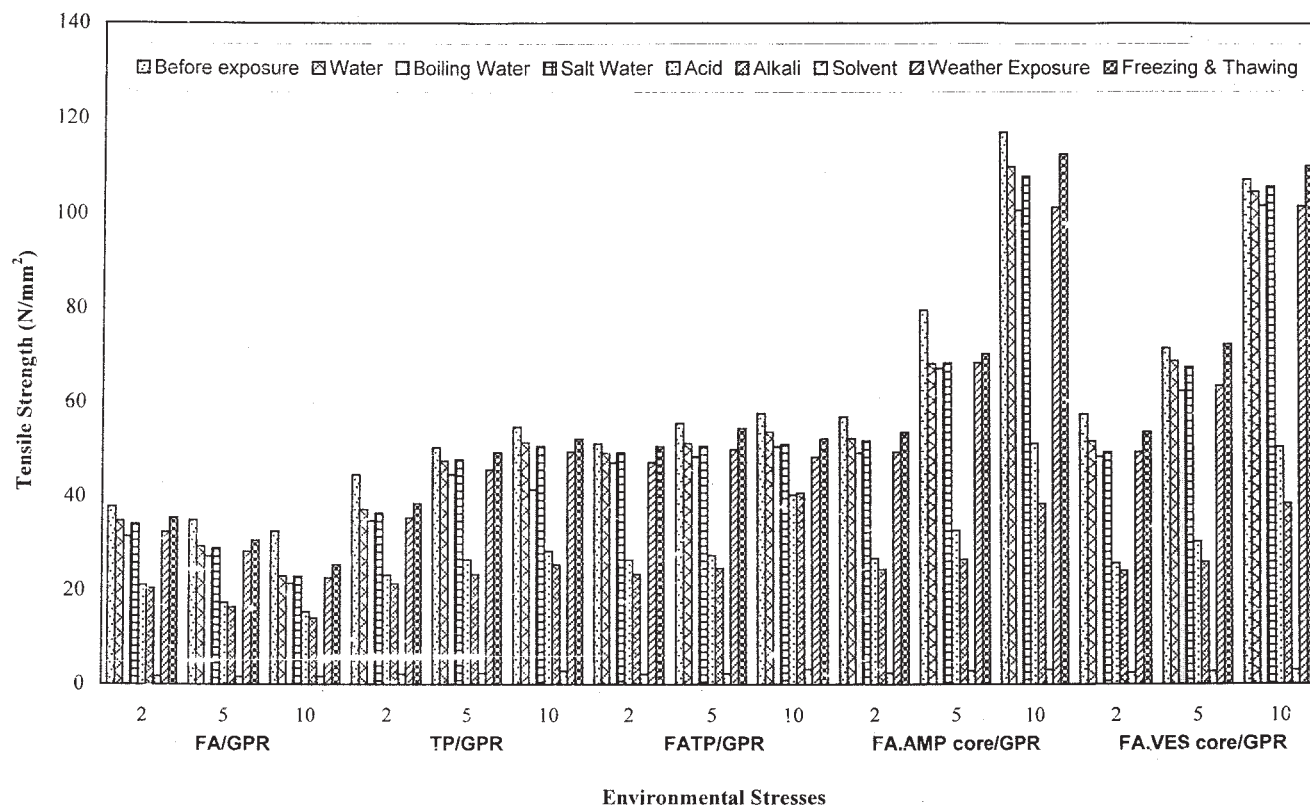


Figure 16 Effect of environmental stresses on tensile strength of multilayered core-shell particle-toughened FA/GPR composites.

GPR, and FA.VEScore/GPR were investigated before and after exposure to the different environmental conditions.

Water resistance

Water alters the properties of the polymeric matrix²² and a growing body of evidence indicates that water has a distinct influence upon the matrix–filler interface.^{23,24} The tensile strength of FA/GPR was found to be less than that of FA.AMP core/GPR and FA.VES core/GPR at all compositions after 30 days of immersion in water at room temperature and in boiling water (Fig. 16). This shows that the coupling agent treated particles have definitely enhanced the water resistance of FA/GPR. This may be due to the enhanced filler dispersion and interfacial adhesion between FA and polyester matrix by adding coupling agent. The tensile strength of FA/GPR, FA.AMP core/GPR, and FA.VES core/GPR as decreased after exposure to cold and boiling waters (more on the latter). For a composite material exposed to an environment in which the temperature and moisture levels vary with time in a prescribed manner, the parameters such as the temperature, total mass of moisture, and moisture- and temperature-induced stresses inside the material are important. The moisture and heat diffuse into the untreated composites by a Fickian mecha-

nism.²⁵ The nature of the diffusion process in the coupling agent treated composites was not studied. However, it is known that moisture absorption in many polymers lowers the glass transition temperature. Moreover, the absorbed water may hydrolyze the interfacial bond. The absorbed water which has diffused into the matrix may also act as the plasticizer²⁶ and may concentrate near hydrophilic sites in the polymer; in microvoids or cracks or debond the FA–matrix interface, which would decrease the strength.²⁷ It is seen from Figures 17 and 18 that the modulus or stiffness was decreased and elongation was increased on immersion in water, more so in boiling water due to the weakening of the interfacial bond due to the water diffusing into the matrix and plasticizing or opening the voids.

The incorporation of fillers in the polyester matrix resulted in a drastic reduction in the elongation at break.⁵ In the presence of CA, this elongation decreased further. This may be contributed by the decreased deformability of a rigid interface between the filler and the matrix component due to the decreased void content. The silane-coupling agent created additional interfacial crosslinking in the treated composite leading to efficient load transfer between the matrix and the filler and thus high moduli. As the elongation is reciprocal to the stiffness of the material,^{28,29} the results show that surface-treated FA imparts a greater

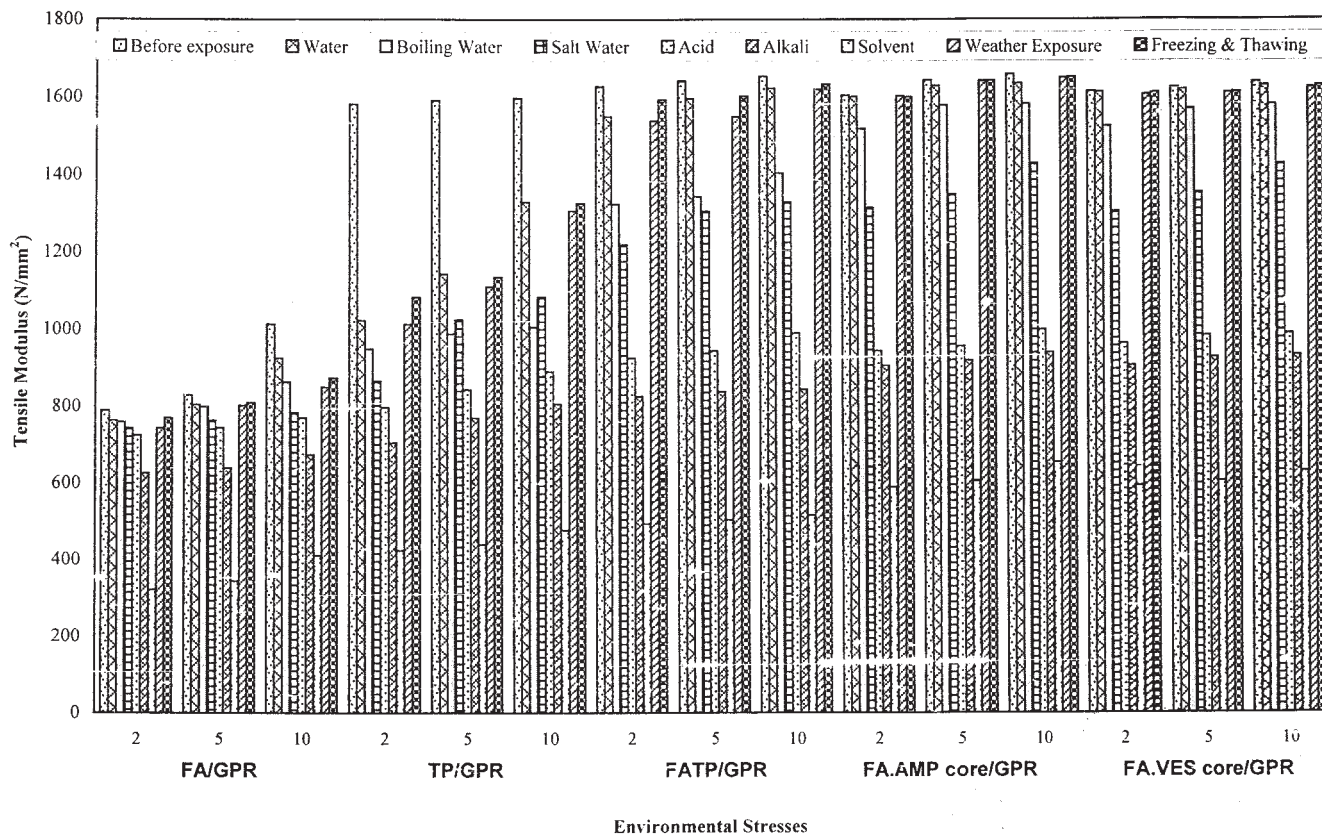


Figure 17 Effect of environmental stresses on tensile modulus of multilayered core-shell particle-toughened FA/GPR composites.

stiffening effect than that of the untreated FA. When exposed to water, the interfacial bonds by CA-treated multilayered core-shell particles may be broken by hydrolysis (more effectively, boiling water), leading to decrease stiffness and increased elongation.

To explore the effect of the observed improvement on the adhesive bonding between FA and the polyester resin, the flexural properties were recorded after subjecting to environmental stress. The flexural strength was decreased drastically in boiling water ($\approx 56\%$ for FA/GPR and 14–35% for FA.AMP core/GPR and FA.VEScore/GPR). Even in cold water, more deterioration of flexural strength (42%) for FA/GPR was observed than for FA.AMP core/GPR and FA.VEScore/GPR (1.8–28%). Similar observations were made by other authors for mica/epoxy surface-treated and untreated samples³⁰ and were attributed to the hydrophobicity imparted by the coupling agents to the resin-filler interface leading to the formation of fewer microcracks at the interface or in the matrix on loading.³¹

In cold as well as hot water, the flexural strength was found to be deteriorated more than the tensile strength (Figs. 19 and 16) for both FA/GPR, FA.AMP core/GPR, and FA.VEScore/GPR. This is in agreement with the fact that the effect of temperature and

moisture on the flexural properties of composites is perhaps greater than for any other mechanical properties³² because the bottom and top sample surfaces are attacked first and that is where the maximum tensile and compressive stresses are located. This is because the bending test is much more sensitive to moisture attack than tensile tests.³³ For instance, in the sheet application of composites, bending failure seems to be more critical than other modes.

The flexural modulus was decreased drastically (68%) in boiling water and moderately (28%) in cold water for FA/GPR. In the presence of coupling agent, the deterioration was found to be $\approx 40\%$ less in boiling water and up to 25% in cold water (Fig. 20). The impact and hardness properties were also decreased following exposure to water (Figs. 21 and 22). For instance, 16 and 23% decrease in impact strength for FA/GPR was observed in cold and boiling water. The hardness was decreased by 20% for FA/GPR and 15% for FA.AMP core/GPR and FA.VEScore/GPR in cold and boiling water. Both properties were found to be superior for the FA.AMP core/GPR and FA.VEScore/GPR over FA/GPR after immersion in cold/boiling water. This can be attributed to an increase in adhesion between the matrix and filler together with the role played by the coupling agent to improve the

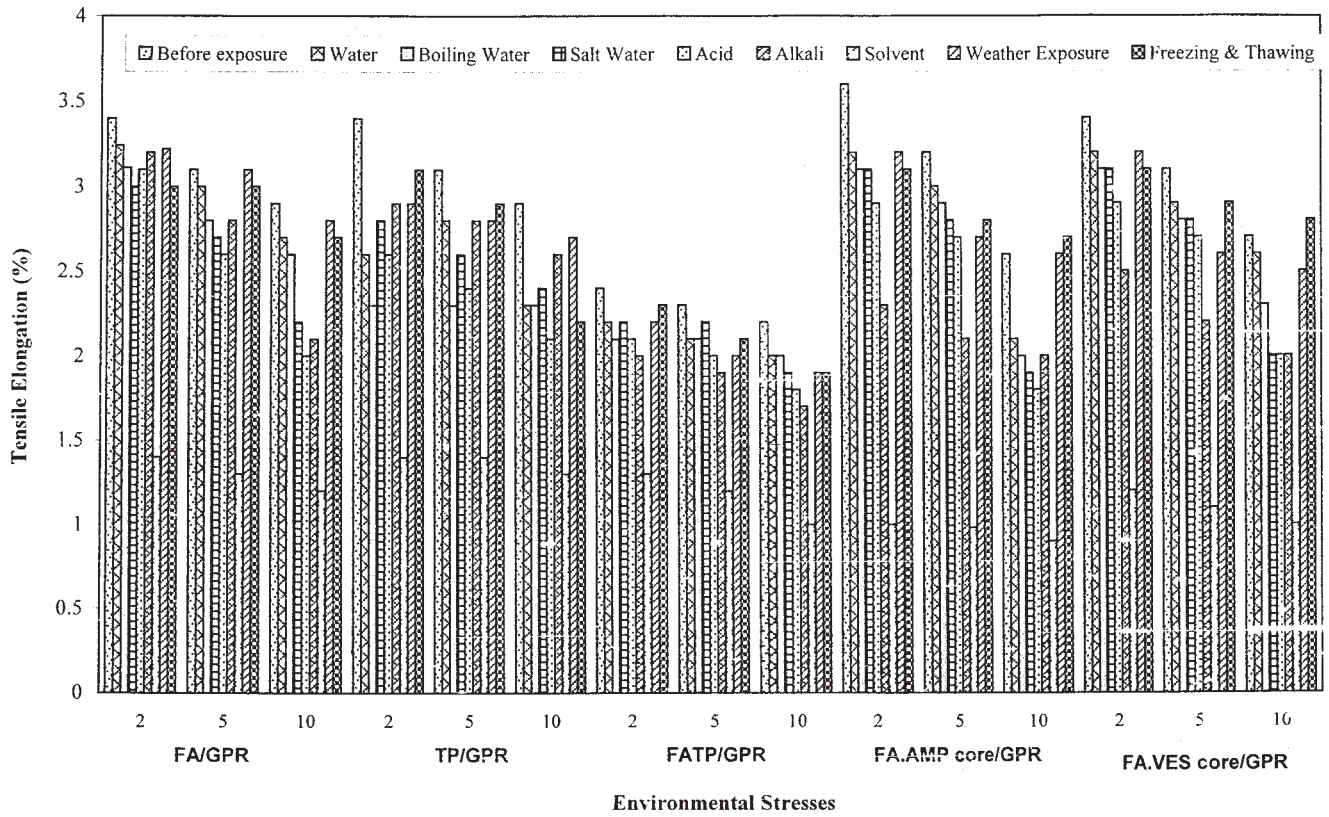


Figure 18 Effect of environmental stresses on tensile elongation of multilayered core-shell particle-toughened FA/GPR composites.

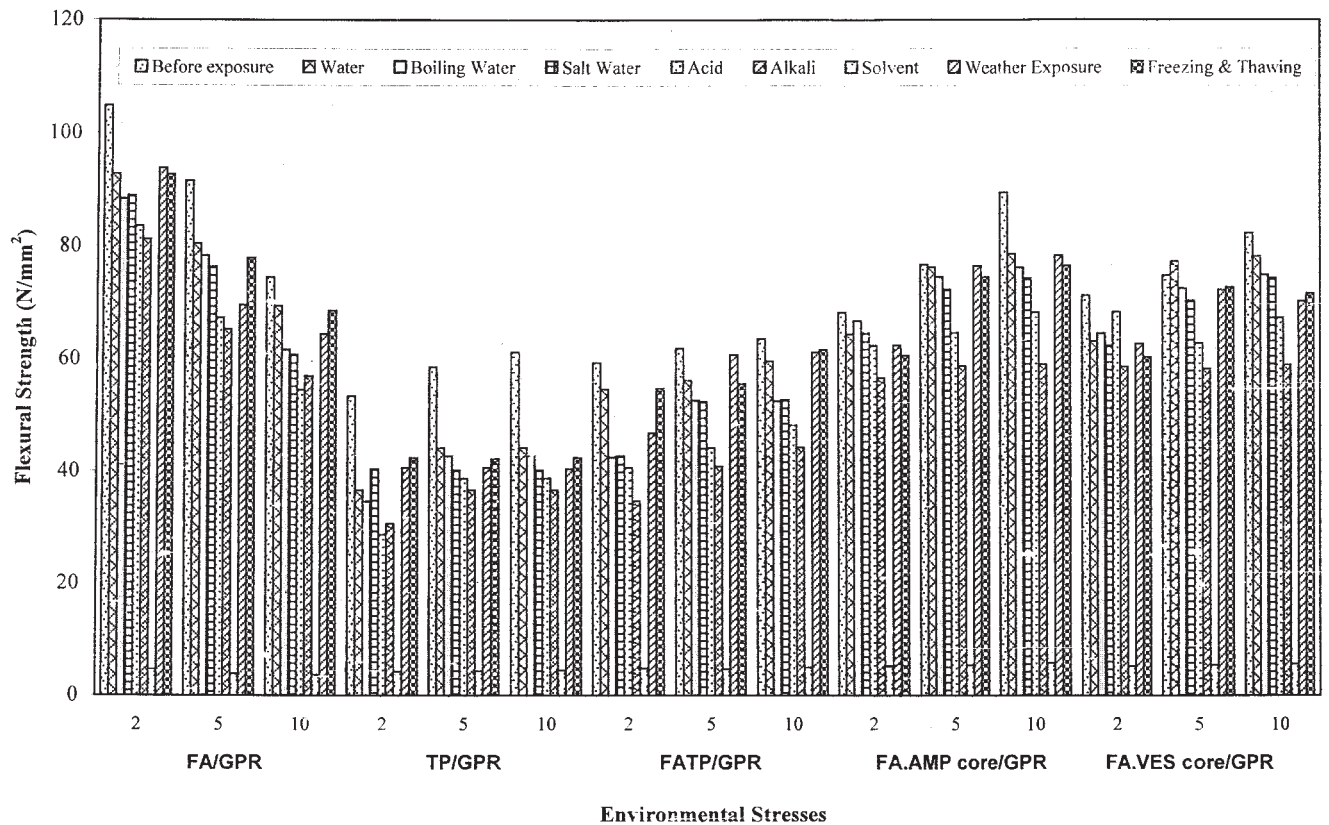


Figure 19 Effect of environmental stresses on flexural strength of multilayered core-shell particle toughened FA/GPR composites.

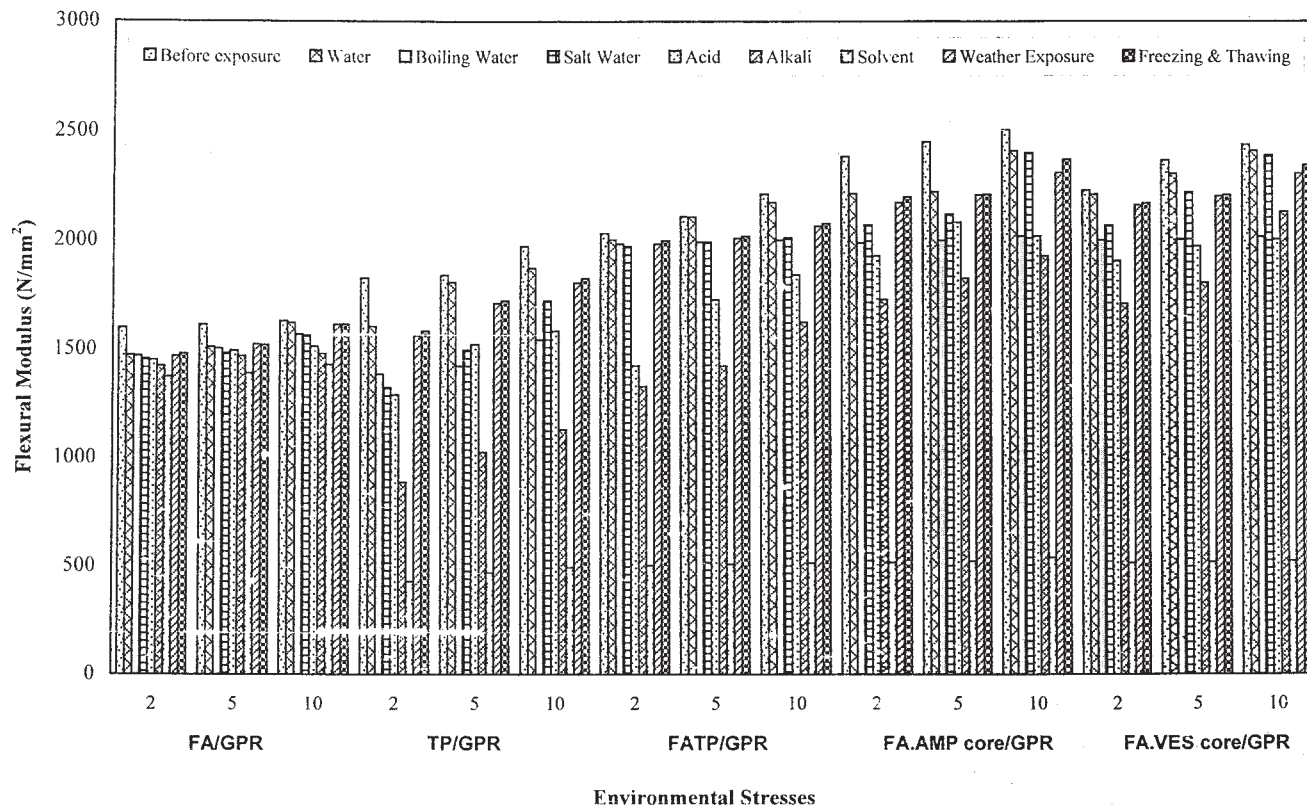


Figure 20 Effect of environmental stresses on flexural modulus of multilayered core-shell particle-toughened FA/GPR composites.

dispersion of the filler in the matrix and reduction in the tendency of fillers to agglomerate.

Salt water resistance

The tensile strength and modulus and impact strength (Figs. 16, 17, and 21) of FA/GPR and FA.AMP core/GPR and FA.VEScore/GPR immersed in salt water were found to be higher than those immersed in pure water. Lesser deterioration of tensile strength may be attributed to a decreased rate of diffusion of water into the matrix in the presence of salt and the higher modulus may be attributed to the salt water inducing a different swelling behavior in the resin. A reverse trend was observed in the flexural strength, flexural modulus, and hardness. Both were found to be deteriorated more than that in pure water (Figs. 19, 20, and 22), because in a flexural test, this swelling causes the surface to be under tension and leads to a lower flexural strength.

Acid resistance

The tensile strength was decreased by 14 and 56% for FA/GPR and FA.AMP core/GPR and FA.VEScore/GPR. Drastic reduction in tensile modulus and increase in elongation were observed for FA/GPR. This

may be due to the interaction of the acid with the inorganic FA particles leading to dissolution and removal from the matrix. Surface treatment of FA with CA and toughening particles has moderated the reduction of modulus by making the FA particles less susceptible to attack by the acid. Flexural strength, compressive strength, flexural modulus, impact strength, and hardness of FA/GPR and FA/CA/GPR were also decreased considerably in acid (Figs. 16–22).

Alkali resistance

On immersion in alkali for 30 days, all mechanical properties (tensile strength, tensile modulus, flexural strength, flexural modulus, compressive strength, impact strength, and hardness) deteriorated drastically (Figs. 16–22). This may be attributed to the hydrolysis of the ester linkages in the polyester matrix leading to degradation in the polymer chains and decreased molecular weight as well as the hydrolysis of the interfacial bonds in the presence of the coupling and toughening agents.

Solvent resistance

The test specimens were immersed in toluene for 30 days before being tested. The test results are given in

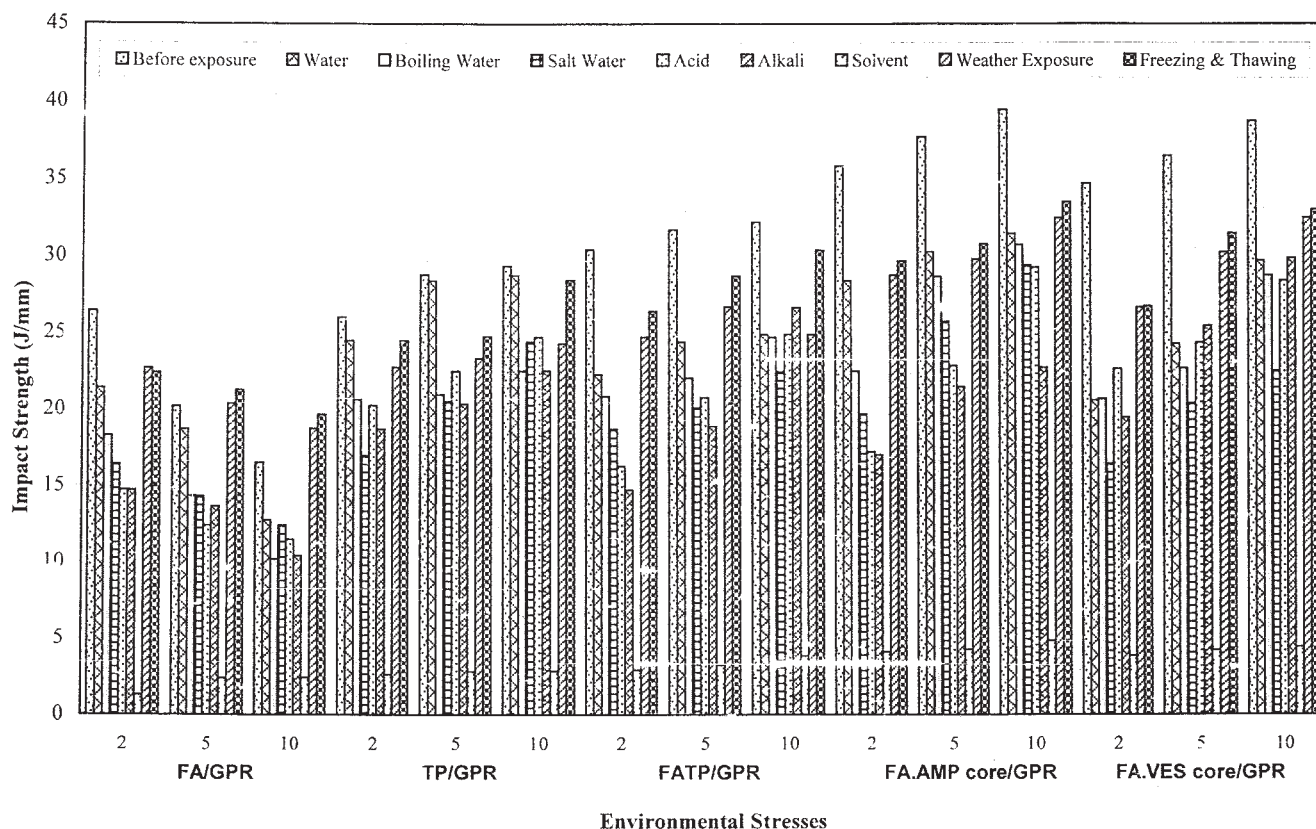


Figure 21 Effect of environmental stresses on impact strength of multilayered core-shell particle-toughened FA/GPR composites.

Figures 16–22. After immersion in toluene, a loss of 50–70% in tensile strength and >50% in tensile modulus were observed. More drastic deteriorations were found in flexural strength (95%), impact strength (90%), hardness (40–50%), and flexural modulus ($\approx 80\%$). All the mechanical properties deteriorated greatly because the Sty part of the unsaturated polyester resin would be swollen in toluene (toluene being a good solvent for polystyrene). The specimens became soft and flexible on contact with toluene as seen by visual examination. Even the addition of coupling agents in small quantities does not seem to influence the solvent resistance. At higher concentrations of coupling agents, the mechanical properties were slightly improved.

Freeze–thaw resistance

The tensile strength was not much affected for FA/GPR and FA.AMP core/GPR and FA.VEScore/GPR. The tensile modulus was decreased and tensile elongation increased for FA/GPR. Flexural strength and flexural modulus were decreased appreciably for both FA/GPR, FA.AMP core/GPR, and FA.VEScore/GPR. Surface treatment with CA and toughening particles have improved the modulus and decreased the elon-

gation and in general enhanced the freeze–thaw resistance. The impact strength and hardness were decreased only moderately (Figs. 16–22).

Weather resistance

The mechanical properties of FA/GPR, FA.AMP core/GPR, and FA.VEScore/GPR were affected only slightly, when tested after exposure to weather for 30 days (Figs. 16–22). Thus, although the exact mechanism of the crosslinking and coupling agents ability to improve resistance to moisture and other chemicals is unknown, this study has shown that the crosslinking and coupling agents do affect the interface between the fiber and the resin and also provide enhanced chemical resistance to the filler–matrix interface and other chemicals is unknown.

Considering the multilayered core shell particle toughened systems, FA.AMP core/GPR is the best system in enhancing all mechanical properties (Figs. 6–9). This is due to the presence of highly reactive $-\text{NH}_2$ group in AMP, which predominately undergoes the Michael-type of addition with polymer matrix, thus enhancing the environmental stress crack resistance of the FA/GPR system compared to other particle-toughened systems.

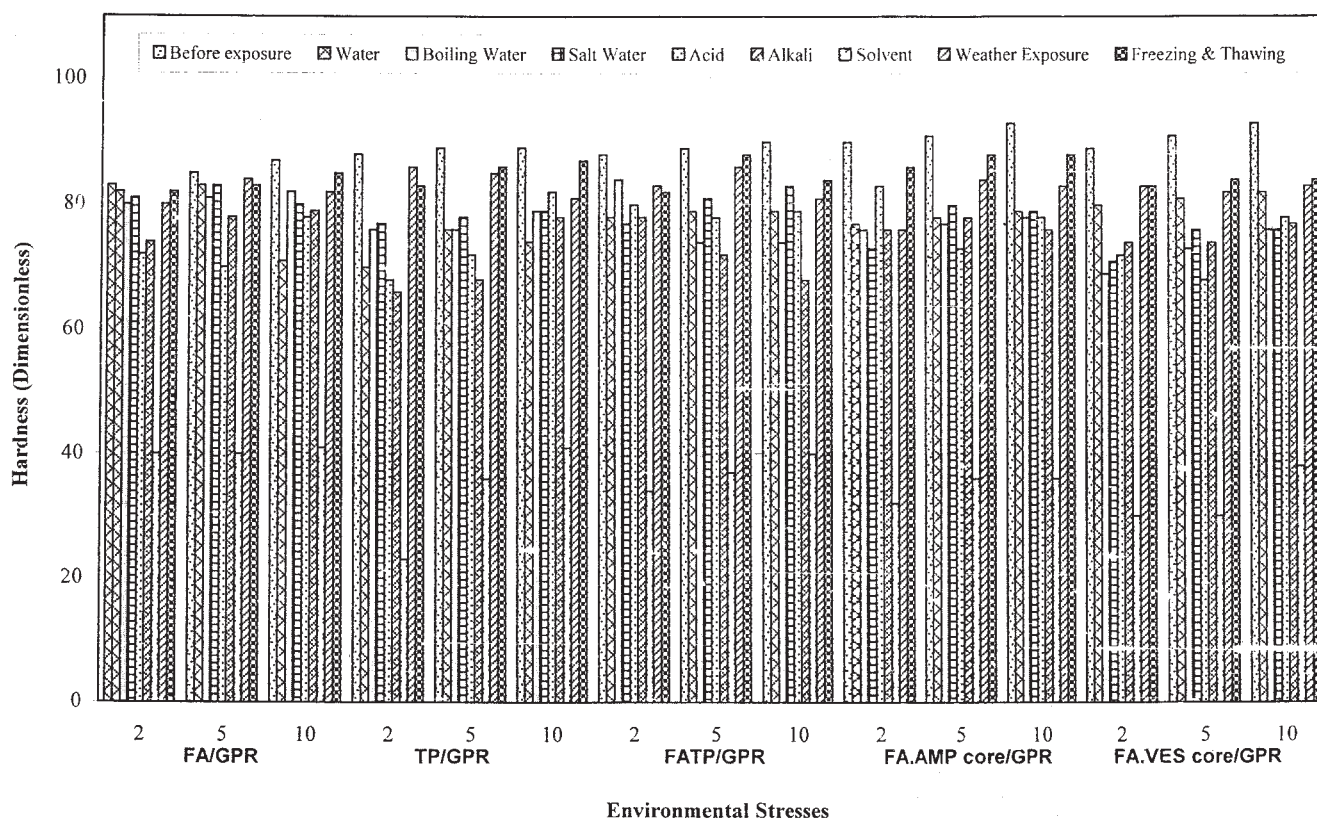


Figure 22 Effect of environmental stresses on hardness of multilayered core-shell particle-toughened FA/GPR composites.

CONCLUSIONS

The following conclusions can be made. Tensile strength and modulus increased slightly while incorporating 2.5, and 10% by weight of multilayered core shell particles in GPR matrix. Flexural strength was decreased appreciably and the modulus increased enormously on adding the multilayered core-shell particles. Better improvements in the impact strength and hardness were observed for multilayered core-shell particle-toughened FA/GPR compared to FA/GPR systems. Hence, toughened particles can be added up to 10% by weight to GPR system without much affecting the ease of processing and mechanical properties with better toughness. AMP-based surface-treated FATP/GPR was found to be the best system with improved toughness while comparing with all other particle toughened systems. The thermal stability was found to be almost unaffected on inclusion of toughened particles. FA.AMPcore/GPR has higher environmental stress crack resistance than FA.VEScore/GPR and FA/GPR.

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