Flexural Strength, Toughness, and Fracture Properties of Polyester Composites

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SYNOPSIS

Flexural behavior of particle-filled fiber-reinforced polyester composite was investigated by varying the polymer and fiber contents. The polymer content was varied between 10% and 18% of the total weight of the polyester composite (PC) and the glass fiber content was varied up to 6% (by weight of PC). The chopped glass fibers were 13 mm long. The fine aggregates were well graded, with particle size varying from 0.1 to 5 mm, and were mainly composed of quartz. The fine aggregates and glass fibers were also pretreated with a coupling agent (γ-methacryloxypropyltrimethoxysilane, γ-MPS) to improve the mechanical and fracture properties of the polyester composites. In general, the addition of fibers increased the flexural strength, toughness, fracture properties, and failure strain (strain at peak stress), but the flexural modulus of polyester composites remained almost unchanged. The addition of 6% fiber content and silane treatment increased flexural strength of 18% PC by 95% to 41.6 MPa (6,040 psi). Crack resistance curves, based on the stress intensity factor (K_R-curve), have been developed for the fiber-reinforced PC systems. A two-parameter relationship was used to predict the complete flexural stress–strain data. There is good agreement between the predicted and measured stress–strain relationships.

INTRODUCTION

Particle-filled polymer composite is produced using dry aggregates as filler and polymerizing monomers as binder. The composition of polymer composite is determined by its applications, of which loading stress levels and chemical environment are especially important. The high-strength, rapid-setting, and corrosive resistance enable the polymer composite to be a material potentially used for structural repairs and for new constructions, which are regularly exposed to strong alkaline environments.[1-4] Polyester polymer is one of the most popular polymer binders used in PC.[5] Polymer composites are being used in many applications, as summarized in Table I. Polyester composite (PC) exhibits brittle failure[6,7] and, therefore, the improvement of its postpeak, stress–strain behavior is important. Hence, developing better PC systems and also characterizing the flexural strength, toughness, and fracture properties, in terms of constituents, are essential in aiding the efficient utilization of PC. In order to improve the postpeak behavior and toughness, glass fibers can be added to the PC matrix. Substantial experience and broader knowledge of the optimal compositions, properties, and stress–strain relationships of the fiber-reinforced PC are necessary with respect to design, production, and quality control. The postpeak behavior and the strain-softening stress–strain relationship are essential in evaluation of the performance of the material for impact, earthquake, and fatigue loading.

In this study, the flexural properties of the glass-fiber-reinforced, particle-filled polyester composites are investigated at room temperature. For the PC systems, a well graded blasting sand was used as the filler and the polymer content was varied between 10% and 18% by weight of the composite. The glass fibers added up to 6% by weight of the composite. The effect of the silane coupling agent on the behavior of the polyester composite was also studied.

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Table I Some Applications of Polymer Composites[18]

Applications	Advantages
Overlays	
Bridge decks	Fast setting, ease of placement, resistance to corrosion
Floors	
Repairs	
Repair of bridge decks	Rapid setting, good adhesion to most surfaces, impervious to water and deicing salts
Concrete floors	
Structural repairs	
Precast products	Short curing time, higher strength to weight ratio, long durability, high toughness
Machine tool applications	Casting (in place), higher damping than cast iron, low cost, dynamic and thermal stability, noise control
Special applications	
Grouting	Rapid setting, chemical resistance, high strength, low permeability, good bonding
Waste encapsulation	
New materials	

A simple expression is used to predict the flexural stress–strain relationships of PC.

EXPERIMENTAL

Table II summarizes the constituents of the polyester composites used in this study. The room temperature viscosity of the unsaturated polyester monomer varied between 40 and 50 poise. Polymerization of unsaturated polyester, dissolved in styrene (a mix of 65% unsaturated polyester, 35% styrene), is by free radical copolymerization. Cobalt napthenate (0.3% by weight of resin) was used as the promoter and methyl ethyl ketone peroxide (1.5%) was used as the initiator. The blasting sand, with subangular particles, had a coefficient of uniformity of 5.8 and was obtained by mixing commercially available blasting sand, numbers 1, 2, 3, 4, and 5, in equal weight proportions. The sand particles were composed mainly of quartz and had a specific gravity of 2.65. The grain size ranged from 0.1 to 5 mm and was compared to fine aggregate, as recommended by ASTM C33-85 in Figure 1. The chopped glass fibers

Table II Composition of the Polyester Composites

Composite	Content	Remarks
Aggregates (blasting sand)	82%–90% (by weight of PC)	Addition of the well graded aggregates as fillers (0.1 to 5 mm) increases the stiffness of the polyester composites and decreases its cost.[6]
Polyester (Dion Iso-6315)	10%–18% (by weight of PC)	One of the most popular binders used. The polyester composites can attain a high strength in a few hours.[6]
Glass fibers (13 mm long)	0%–6% (by weight of PC)	Glass fibers (13 mm long and 0.013 mm in diameter) increase the toughness of the polyester composites.[15]
Silane (γ-MPS)	2% (solution)	Improves the aggregate–polyester and glass fiber–polyester bonds. The resultant composites have better properties.[8]
Voids (air)	1%–22% (by volume of PC)	Voids affect the mechanical properties of the composite. The voids are minimized by appropriately proportioning the constituents forming the composite and by compacting or vibrating the specimen.

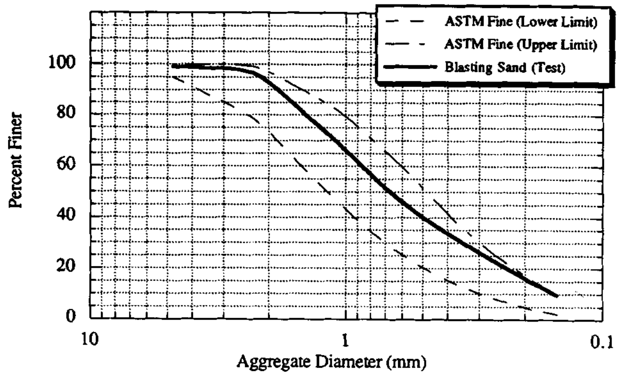


Figure 1 Particle size distribution of blasting sand, compared to ASTM C33-85 for fine aggregates.

used in this study were 13 mm long and had a diameter of 0.013 mm, a tensile strength of 2,500 MPa (363 ksi), and a modulus of 70 GPa (10,160 ksi). The glass fiber elements had up to about 800 glass strands bonded together. The silane coupling agent (γ-methacryloxypropyltrimethoxysilane, γ-MPS) was introduced into the PC by pretreatment of glass fibers and aggregates.[8] The aggregates and glass fibers were treated by wetting them with 2% aqueous solution of silane coupling agent. The trimethoxy group underwent hydrolysis in an aqueous solution and hydroxyl groups were then available to form oxane bonds to the sand and glass fiber surface (Fig. 2). The treated aggregates and fibers were allowed to dry at 100°C for 24 h, prior to mixing with the resin. PC specimens were compacted in three layers in a teflon-lined aluminum mold, with dimensions 230 mm × 50 mm × 50 mm. All the flexure and fracture studies were performed on 33 mm thick PC specimens. The PC specimens were first cured at room temperature for a day and at 75°C for an additional day prior to testing.[9] A total of 92 beam specimens were tested. The experimental program was divided in four series. The first series included 24 unreinforced beams that were tested for statistical evaluation of the flexural strength, the second series included 36 beams with and without glass fibers, the third series included 24 beams with silane-treated aggregates and fibers, and the fourth series included 8 silane-treated fiber reinforced notched beams. A diamond saw (2 mm thick) was used to notch the specimens to a maximum depth of 38 mm. During the test, the crosshead speed of the closed loop servo hydraulic testing machine was maintained constant at 0.05 mm/min. The specimens were tested in four-point bending (in some instances, mentioned on the corresponding plots, three-point bending was used). For the notched beam specimens, the crack mouth opening displacement (CMOD) was measured, using knife edges glued to the specimen.[10] The deflection of the beams was measured using a Linear Variable Differential Transducer (LVDT) with an accuracy of 2.5×10^{-3} mm (10^{-4} in.). For each test, both the load vs. load-point deflection (for all specimens), and the load vs. crack mouth opening displacement (for notched specimens), were monitored continuously using X–Y recorders (Fig. 3).

RESULTS AND DISCUSSION

The average density for the unreinforced systems ranged between 1.96 and 2.15 Mg/m^3. Figure 4 shows the variation in porosity with the fiber and polymer content. The porosity was affected significantly by the workability of the mix and varied considerably within the range of the variables. The subjective measure of the workability was estimated, based on a scale of four, with four being the best and zero the worst (Fig. 5). Subjective workability assessment was based on the mix flowability, compactability, fiber balling, and handling ease or difficulty. Of the unreinforced systems, the 14% PC had good workability and low porosity (Fig. 5). For this reason, 24 beams were tested for statistical evaluation of the flexural strength, modulus, and failure strain.

Statistical Analysis

Factors, such as material variability (polymer, aggregates, promoter, initiator), degree of compaction,

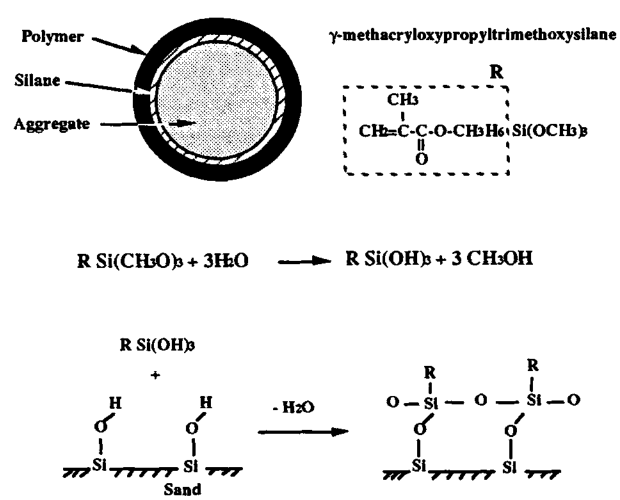
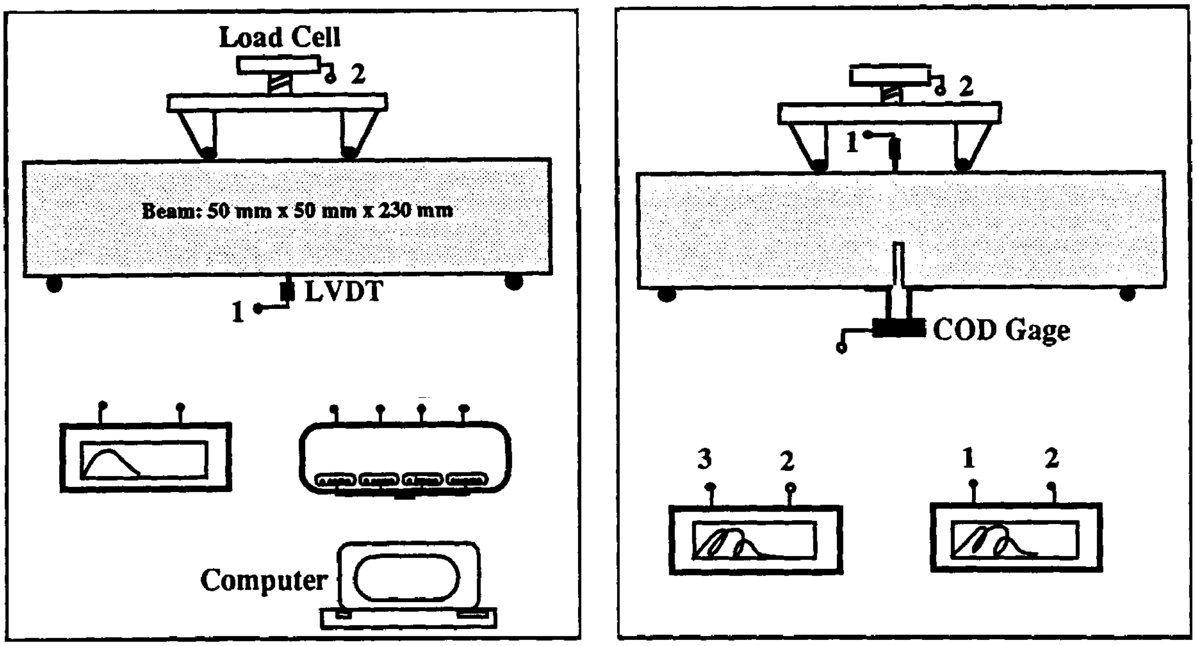
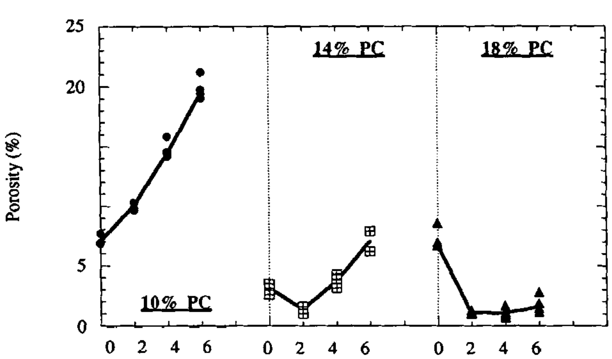
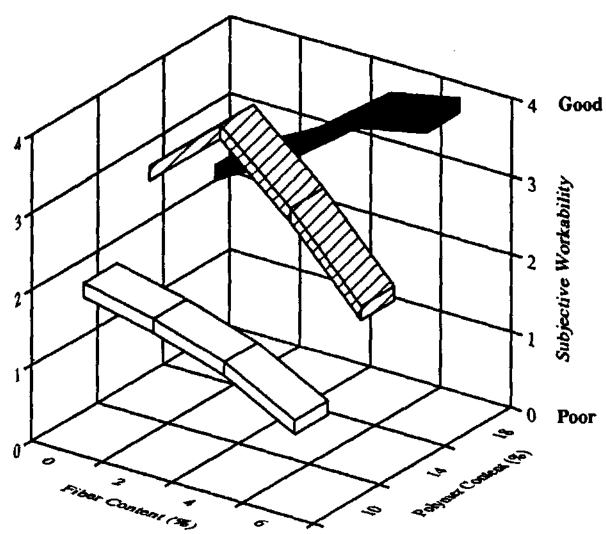


Figure 2 Interface modification due to the addition of silane coupling agent.



and curing conditions will affect the properties of PC. Hence, it is appropriate to quantify the variation in strength of the material in terms of mean, standard deviation, and distribution. The distribution of the 14% PC flexural strength is represented by a histogram in Figure 6. A total of 24 specimens were tested. The data points are also plotted on a normal probability scale in Figure 7 (coefficient of correlation $R = 0.98$). Linear variation of the data on the probability plot shows that the data may adequately be represented by a normal distribution. The mean flexural strength is 16.45 MPa (2,390 psi) and the coefficient of variation (COV) is 5%. Figure 8 shows the normal distribution of the flexural modulus ($R = 0.97$). In this case, the mean is 11 GPa (1,600 ksi) and the coefficient of variation is 8.5%. The flexural failure strain distribution is shown in Figure 9 ($R = 0.94$). The mean failure strain is 0.15% and the coefficient of variation is 10%.





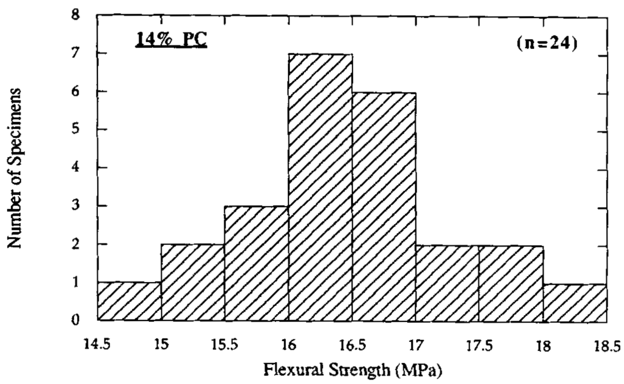


Figure 6 Histogram for flexural strength of the 14% PC system.

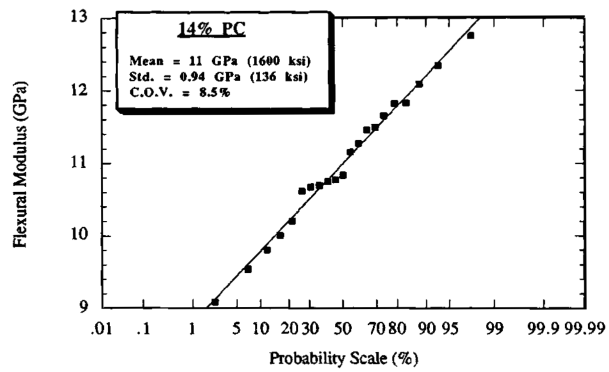


Figure 8 Normal probability plot for flexural modulus of the 14% PC system.

18% and the fiber content varied from 0% to 6% (by weight of PC). The enhancement of the unreinforced PC properties may be achieved by the addition of glass fibers, the treatment with a silane coupling agent, or both. The general directions of the improved stress–strain curve of the resulting material are shown in Figure 10. The improvement may be achieved by increasing the (1) strength, (2) failure strain, (3) modulus, or (4) by improving the post-peak curve.

The first series of specimens were tested in four-point bending to determine the effect of glass fibers on the flexural properties of PC. The results, which consist of a total of 36 specimens, are presented in Figure 11. Within the range of variables investigated, the addition of glass fibers improved the flexural strength of the 14% and 18% PC system, but decreased the strength of the 10% system. In the 10% PC system, there is an inadequate amount of polymer to bind the aggregates and fibers, resulting in reduced workability, increased porosity, and reduced strength. The flexural strength varied from about 13 MPa (1,890 psi) for the 10% PC and 6% fiber content, to about 33 MPa (4,800 psi) for the 18% PC with 6% fiber content. With the addition of 6% glass fiber, the flexural strength of the 18% PC was increased by 80%. Typical flexural stress–strain relationship for the 18% PC system, reinforced with glass fibers up to 6%, are shown in Figure 12. The following may be concluded from the test results:

1. More than a 250% increase in failure strain is observed and the strain of 0.17% for the unreinforced PC was increased to 0.6% for the 6% glass fiber-reinforced PC (Fig. 13). Adding fibers to the PC produced a bridging effect at the crack tip and hence slows the crack propagation, which results in an increase of the failure strain.
2. The flexural modulus was 11 GPa (1,600 ksi) and remained almost unchanged with the increase in fiber content (Fig. 14). The standard deviation was about 0.94 GPa (136 ksi). The modulus did not increase, due to the ad-

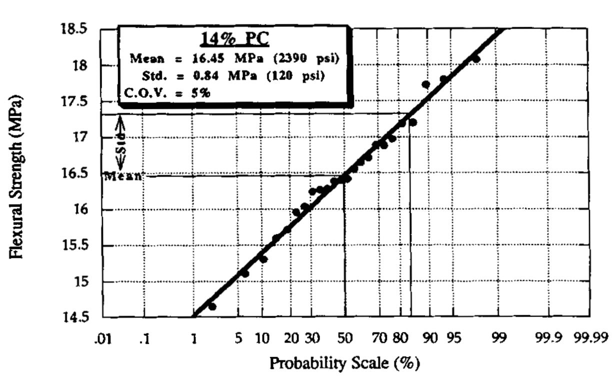


Figure 7 Normal probability plot for flexural strength of the 14% PC system.

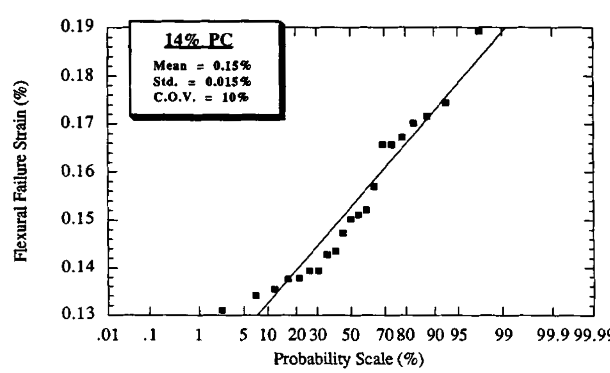


Figure 9 Normal probability plot for flexural failure strain of the 14% PC system.

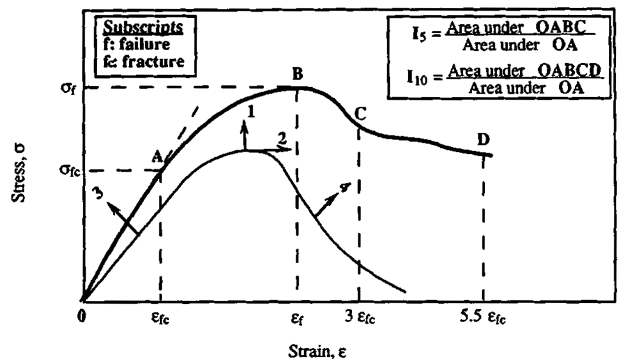


Figure 10 Characterization of changes in stress–strain relationship and definitions for toughness indices.

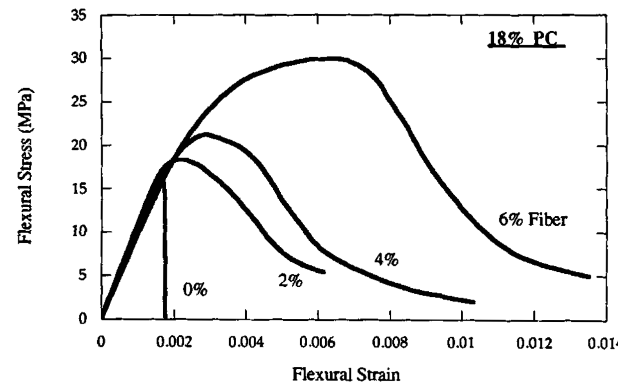


Figure 12 Effect of glass fibers on the flexural stress–strain relationships of 18% PC.

dition of glass fibers, because of the following factors: (a) the addition of fibers generally resulted in an increase in void ratio, due to reduced workability, and (b) only up to 6% of fibers were used and fibers partly replaced the aggregates with similar modulus.

Postpeak Properties and Toughness

The postpeak properties and toughness may be quantified by three methods, as follows:

Method 1. Measuring the toughness (or energy absorbed) of the reinforced PC, as defined by the area under the stress–strain curve, up to a defined endpoint (see Fig. 10) is Method 1. This area is then compared to the unreinforced PC to quantify the relative improvement due to the addition of fibers. As summarized in Table III, for a strain endpoint of 1.3%, there was an increase of about 1440% when 6% of fibers were added to the 18% PC system.

Method 2. Determining the toughness indices, as recommended by the ASTM C1018 is Method 2.[11,12] These indices provide a fundamentally significant indication of material behavior, relative to a reference level, such as elastic–plastic behavior (elastic up to first crack and perfectly plastic thereafter). Toughness indices I_5 and I_{10} represent the ratio between the area under the stress–strain curve, limited by endpoint strain equal to 3 ϵ_{fc} and 5.5 ϵ_{fc}, respectively, and the area up to first crack strain (ϵ_{fc}) (Fig. 10). The I_{10}/I_5 ratio of 2 corresponds to elastic–perfectly plastic behavior and plastic deformation between deflection limits for the corresponding indices in each ratio. If the ratio of I_{10}/I_5 is approaching 2, the material behavior is considered to be approaching elastic–perfectly plastic behavior. The variation of I_5, I_{10}, and I_{10}/I_5 with fiber content for the 18% PC system is shown in Figure 15. The indices I_5 and I_{10} for the unreinforced PC are equal to 1 (brittle material). With the addition of 6% glass fibers, I_5 increased to about 7 and I_{10} to about 15 (I_{10}/I_5 = 2.1).

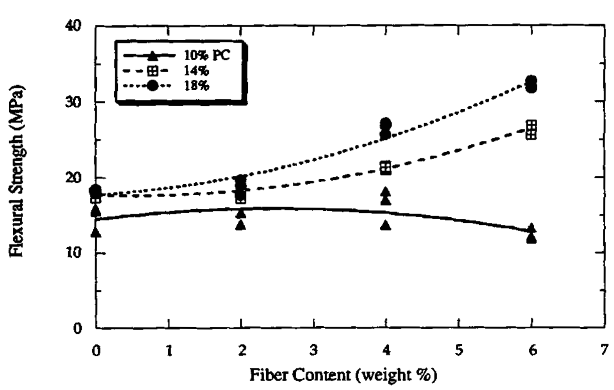


Figure 11 Effect of glass fibers on the flexural strength of the PC systems.

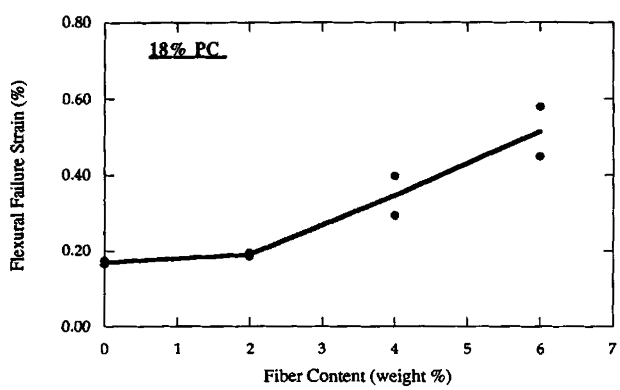


Figure 13 Effect of glass fibers on the flexural failure strain of 18% PC.

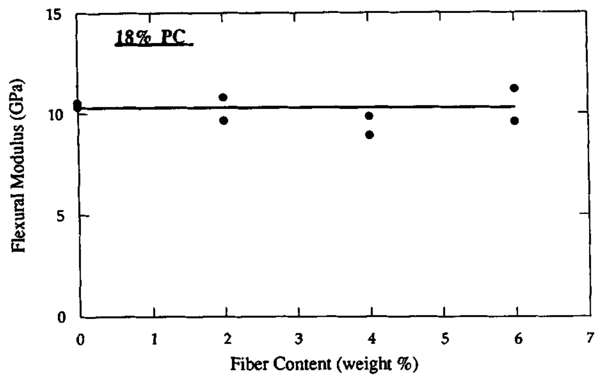


Figure 14 Effect of glass fibers on the flexural modulus of 18% PC.

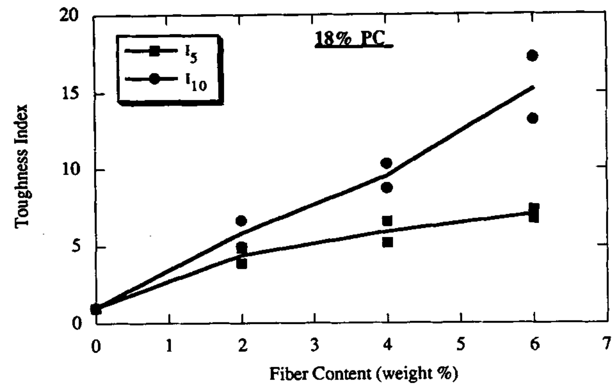


Figure 15 Variation of toughness indices with fiber content for 18% PC.

Method 3. Choosing relationships to represent the stress–strain response and using its parameters to describe the shape of the stress–strain curve is Method 3. A two-parameter relation [eq. (1)] has been used in predicting the stress–strain relationship of PC.[13] This relationship may be written as

$$Y = \frac{X}{q + (1 - q - p)X + pX^{(q+p)/p}} \quad (1)$$

where Y and X are defined as follows:

$$Y = \frac{\sigma}{\sigma_f} \quad \text{and} \quad X = \frac{\epsilon}{\epsilon_f} \quad (2)$$

where σ and ϵ are the stress and strain, σ_f and ϵ_f are the strength and the failure strain, and p and q (p and q vary from 0 to 1) are the material parameters to be determined from the experimental data. The parameter q is the ratio of secant modulus at peak stress to initial modulus and the lower the value of parameter q, the greater the nonlinear prepeak behavior of the PC system. This is also reflected by the decreasing value of parameter q with an increase in fiber content, as summarized in Table III, for the 18% PC system. The parameter p controls the postpeak curve and is determined by the least square fit of the experimental data points. The steeper the descending stress–strain curve, the smaller the p value ($p = 0$ for brittle material). Figure 16 shows the normalized stress–strain relationships; the predictions agree well with the experimental results. As shown in Fig. 16, the postpeak curve of the 6% fiber reinforcement descends rapidly than the 4% fiber system and only the parameter p (method 3) quantitatively describes this important observation. The results summarizing the three methods are included in Table III.

Table III Toughness and Post-Peak Properties of 18% PC System

Fiber Content (%)	Method 1		Method 2		Method 3	
	TT[a]	Increase	I_5	I_{10}	q	p
0	2.3	—	1	1	1	0
4	15.6	600%	5.9	9.5	0.76	0.26
6	35.5	1440%	7.1	15.1	0.32	0.03

[a] TT: Total Toughness in MPa.

Effect of Silane Coupling Agent

Using the silane-treated constituents in PC improved the workability for the 10% PC system. This improvement is probably due to the modification of the filler surface, which became smoother and, therefore, increased the flowability of the polymer,

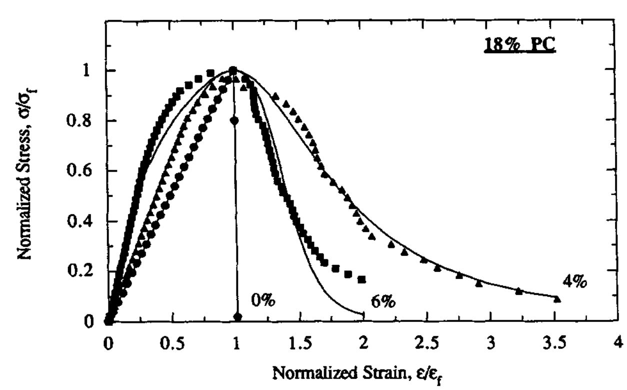


Figure 16 Two-parameter model prediction (solid curve) and measured stress–strain relationships.

leading to a better dispersion of the constituents. It has been observed that silane-treated fillers provide lower viscosities in filler resins than do untreated fillers.[14] The PC specimens with treated aggregates (third series with 24 beams) were tested to determine the enhancement in flexural strength due to the silane treatment. The results (average of 2 specimens tested in three-point bending) are shown in Figure 17. The increase in flexural strength is compared to that of the untreated PC. The maximum increase was 70%. It is noted that the treated, unreinforced PC, with the lowest polymer content (10%), has a higher strength than the untreated PC with the highest polymer content (18%). As shown in Figure 17, the increase in flexural strength due to silane treatment is dependent on the polymer content. The highest strength for the silane-treated, fiber-reinforced system (18% polymer and 6% fiber) was 41.6 MPa (6040 psi). Silane treatment had the highest effect on the 10% PC system, showing up to 70% increase in flexural strength, and the lowest effect was on the 18% polymer and 6% glass fibers (less than 10% increase). The effect of silane on the increase in flexural modulus of glass fiber-reinforced PC is shown in Figure 18.

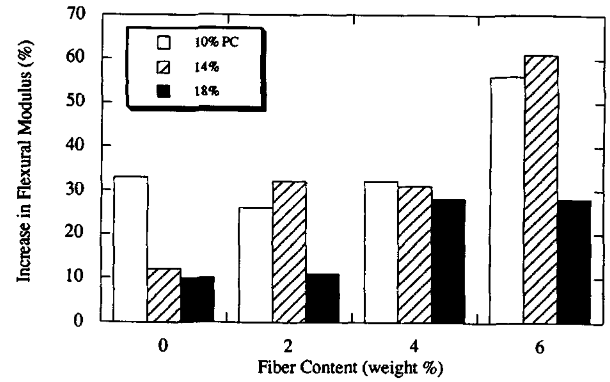


Figure 18 Effect of silane coupling agents on the flexural modulus of glass fiber-reinforced PC systems (three-point bending test).

Fracture Properties

The performance of PC materials is affected by cracks[15] and their growth during loading. Hence, eight silane-treated glass fiber-reinforced PC beam specimens were tested in four-point bending to quantify the resistance of the material during crack growth. The notch-to-depth ratio varied from 0.26 to 0.80. The data points needed to plot the fracture resistance curves are shown in Figure 19. Using the concept of linear elastic fracture mechanics (LEFM), the relationship between elastic crack mouth opening displacement ($CMOD^e$) and the corresponding crack length in four-point bending can be represented as[16]

$$CMOD^e = 4\sigma a V(\alpha)/E' \tag{3}$$

where σ is the net stress ($6\,M/bd^2$); M is the applied pure bending moment; α is equal to $(a + H_0)/(d + H_0)$ with H_0 being the clip gage holder thickness; a is the crack length; E' is equal to E (modulus) for plane stress and $E/(1 - \nu^2)^{0.5}$ for plane strain where ν is the Poisson's ratio. An empirical formula, with 1% accuracy for any α, is used to calculate $V(\alpha)$ and is expressed as

$$V(\alpha) = 0.8 - 1.7\alpha + 2.4\alpha^2 + 0.66/(1 - \alpha)^2 \tag{4}$$

Hence, if during slow growth, $CMOD^e$ could be determined at various loading levels by unloading the

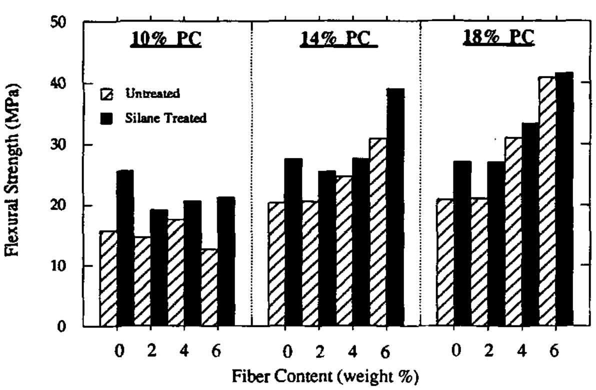


Figure 17 Effect of silane coupling agents on the flexural strength of glass fiber-reinforced PC systems (three-point bending test).

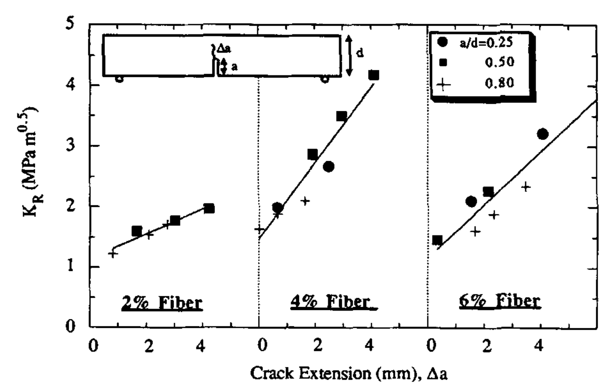


Figure 19 Typical K_R-Δa relationships for 18% PC with silane-treated blasting sand and glass fibers.

specimens, and hence using eq. (3), it would possible to determine the corresponding crack length. A numerical iterating procedure was used to determine the corresponding crack length a. Crack extension Δa is equal to $(a - a_i)$, where a_i is the initial crack length. Assuming a beam of cross section $b \times d$, with effective crack length a, the stress intensity factor was calculated using the equation for the four-point bending developed by Brown and Srawley.[17] The relationship is as follows:

$$K_I = 6Ma^{1/2}Y(a/d)/bd^2 \quad (5a)$$

where

$$Y(a/d) = 1.99 - 2.47(a/d) + 12.97(a/d)^2 - 23.17(a/d)^3 + 24.80(a/d)^4 \quad (5b)$$

Glass fiber-reinforced polyester PC shows substantial amount of nonlinearity up to peak stress and, hence, resistance curves (R-curves, ASTM E 561–81) are used to characterize the resistance to fracture during slow stable crack extension in such materials.

To construct the K_R curve, effective crack length, based on the CMOD method, was used. Once the load P and the corresponding effective crack length is known from the test records, the value of K_I was obtained from eq. (5). As shown in Figure 19, the $K_R - \Delta a$ relationship (solid lines) can be best expressed in the following linear form

$$K_R = K_0 + \rho(\Delta a) \quad (6)$$

where K_0, and ρ are parameters that are obtained from least square fit of the data. The parameter K_0, for 18% PC (treated blasting sand) with 2, 4, and 6% fibers, are 1.13, 1.16, and 1.15 MPa $m^{0.5}$ and the values for ρ are 0.20, 0.56, and 0.43 MPa $m^{0.5}$/mm respectively.

CONCLUSIONS

The influence of glass fibers and the silane coupling agent on particle-filled polyester composite (PC) was investigated at room temperature. Based on the experimental study, the following can be concluded:

1. Addition of glass fibers increased the flexural strength and the strain at peak stress, but did not change the flexural modulus of the PC systems. The 18% PC with 6% glass fiber had a flexural strength of 33 MPa (4,800 psi), which is about an 80% increase over the unreinforced PC system.
2. Use of silane treated aggregates and fibers further improved the strength of the PC systems. Silane treatment had the greatest effect on the 10% PC system. Silane treatment increased the flexural strength (three-point bending) of 18% PC with 6% glass fiber to 41.6 MPa (6,040 psi), a 95% increase over the unreinforced PC.
3. The toughness increased by more than 1440% when 6% glass fibers were added to the polymer composite. The toughness index ratio, I_{10}/I_5, varied between 1 and 2.1 for the glass fiber PC systems investigated.
4. The two-parameter relationship effectively predicted the flexural stress–strain relationships for the reinforced and unreinforced PC.
5. Crack resistance curves, based on the stress intensity factor ($K_R - \Delta a$ relationship) have been found to be best approximated by linear relationships.

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