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Modeling of setting stresses in particle reinforced polymer composites using finite element analysis

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Rice University, 1990
RICE UNIVERSITY

MODELING OF SETTING STRESSES IN
PARTICLE REINFORCED POLYMER COMPOSITES
USING FINITE ELEMENT ANALYSIS

by

ALADIN MOHAMMED BORIEK

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ABSTRACT

This work uses three-dimensional Finite Element Analysis (FEA) to investigate the effect of geometric arrangement of particulate reinforcement in highly filled polymer composites (such as polymer concrete) on the setting stresses that develop in these materials during cure due to resin shrinkage during polymerization. These composites were initially modeled by systems reinforced with spherical particles packed in simple cubic (SC) and face-centered cubic (FCC) arrangements within the polymer matrix. A pronounced decrease in setting stresses was observed in the FCC system, which has a greater aggregate to resin ratio and more of resin domains per unit cell. A hexagonal-close-packed arrangement of hexagonal, prism-shaped aggregate was also analyzed and found to develop higher stresses, indicating that aggregate shape has an effect on setting stresses.

A second set of models investigated the effect of size gradation and geometric arrangement of spherical reinforcing particles on setting stresses. The maximum stresses occur at the particle-resin interface, underlining the importance of resin/aggregate adhesion. Reduction of setting stresses by a factor of two was observed in systems with efficient packing, achieved with proper size gradation and close-packed geometry.
model gives a realistic representation of actual particle reinforced polymer composites.

FEA results were used to develop an empirical equation for maximum setting stresses for Particle reinforced polymer composites.

A probabilistic model for the distribution of voids in polymer composites was developed by solving a non-linear constrained optimization problem. The probability distributions of voids was used with a specially developed algorithm to generate the voids distributions in specific composites. The effect of voids on setting stresses in FRA models was discussed. In polymer composites voids tend to act as stress relief. This effect is more pronounced in poorly packed systems.

This study provides an understanding of setting stress distribution in polymer composites. This work provides guidelines for optimizing the amount, shape and particle size distribution of the reinforcing aggregate in polymer composites so as to minimize setting stresses, thus leading to composites with significantly enhanced strength.
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CHAPTER 1

INTRODUCTION

1.1 POLYMER COMPOSITES

A composite is a material with two or more distinct components which interact so as to produce a system with enhanced properties. The term "composite" has evolved over a period of years. Some use it to characterize a system or process of combining two or more reinforcing materials in a binding matrix. Others use it to designate a new multiphase material having characteristics derived from its processing and from its microstructure. The individual phases are usually firmly bonded together at their interface. In this thesis we deal with composites, which consist of reinforcing elements (particles or fibers) surrounded by a continuous polymeric matrix, and more specifically, polymer concrete. Polymer concrete (PC) is a composite consisting of mineral aggregate (sand and gravel) and an organic resin binder that hardens by polymerization. Various types of PC's are finding increasing use in load-bearing structures. Most of the work discussed in this thesis used as models unsaturated polyester/styrene PC systems in which the
binder is an unsaturated polyester resin*, which cure via addition polymerization mechanisms with styrene, to generate cross-linked networks. However the conclusions are applicable to all PC systems that develop setting stresses during their cure.

1.2 PREPARATION AND PROCESSING OF POLYMER CONCRETE

A preparation of resin-bound concrete was described by Michaels (Michaels, 1956). This system may contain as little as four percent resin by weight and develops a tensile strength of up to 1100 lb/in². This was achieved with the use of surface active agents to improve the wetting of the aggregate by the resin. With efficient mixing of the resin and the aggregate particles, the resin forms a uniform coating over each particle. The strength of polymer concrete depends primarily on the properties of the resin (inherent shrinkage, strength, Poisson’s ratio, modulus of elasticity), and the relative amounts of resin and aggregate. If there are voids present in the composite the strength depends also on the volume fraction of the voids (usually due to air bubbles trapped in the PC system).

Processing technology assists in the design and preparation of polymer composites with desirable performance properties. The strength of the PC system depends primarily on the ability of the cured resin to transfer stresses. The two most important properties that control the ability of the resin to transfer stresses

* Unsaturated polyesters are thermosetting matrix resins which, in the presence of peroxide catalysts, cure to a solid insoluble, infusible, cross-linked polymer (Margolis, 1986). Polyesters are the most widely used resin systems in PC, since they offer an attractive combination of reasonable cost, viscosities that are not too high, and volatility problems (due to styrene) which are readily controlled.
are its elastic modulus and strength and its adhesion to the aggregate. During the processing of the reinforcing aggregate, it is imperative that the aggregate be given the proper surface treatment directed toward compatibility with the resin. These chemical surface treatments help ensure a strong adhesion between the aggregate and the resin. The suitability of particle reinforced polymer composites for different applications is also dependent on the ratio of compressive to tensile strength, Young’s modulus, inherent shrinkage of the resin, creep, permeability to water, and chemical resistance.

1.3 COMPARISON BETWEEN CONVENTIONAL CONCRETE AND POLYMER CONCRETE

Table 1 shows a comparison of various physical properties between conventional, portland cement concretes and polymer concrete systems. Most Polymer concretes are remarkably superior to ordinary concrete in tensile and flexural strength, as a consequence of the macromolecular nature of their binder. It is possible to formulate PC systems that harden in 8 hours or less at ambient temperature (18-20 °C). At higher temperatures it is possible to obtain hardening times that are as short as a few minutes.

1.4 APPLICATION OF POLYMER CONCRETE

Numerous applications of polymer concrete composites have been reported in a review by Kirlikovali (Kirlikovali, 1981). These include: repair of concrete road pavings, precast wall panels, tunnel support and lining, pipes, dome structures, offshore structures, heavy-duty industrial floors, sport arenas, and structure joint
TABLE 1

Physical Properties Of Polymer Concrete (PC) Compared With Ordinary Portland Cement Concrete

<table>
<thead>
<tr>
<th>Property</th>
<th>Polymer Concrete</th>
<th>Portland Cement Concrete</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength (MN/m²)</td>
<td>50-80</td>
<td>20-40</td>
</tr>
<tr>
<td>Tensile strength (MN/m²)</td>
<td>4-6</td>
<td>1-2</td>
</tr>
<tr>
<td>Flexural strength (MN/m²)</td>
<td>15-25</td>
<td>4-5</td>
</tr>
<tr>
<td>Water Permeability (10⁻⁴ ft/yr)</td>
<td>0</td>
<td>5-6</td>
</tr>
<tr>
<td>Hardness (impact hammer)</td>
<td>50-60</td>
<td>30-35</td>
</tr>
<tr>
<td>Acid resistance (% wgt loss after 3 mos in )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) 15% HCl</td>
<td>2-3</td>
<td>25-30</td>
</tr>
<tr>
<td>(b) 15% H₂SO₄</td>
<td>1.0-1.3</td>
<td>40-45</td>
</tr>
<tr>
<td>Corrosion by distilled water</td>
<td>None</td>
<td>Severe</td>
</tr>
<tr>
<td>Setting time (days)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) To 60% of strength</td>
<td>0.1-0.2</td>
<td>2-3</td>
</tr>
<tr>
<td>(b) To 85% of strength</td>
<td>0.2-0.5</td>
<td>7-15</td>
</tr>
</tbody>
</table>
repairs. Polymer concrete would be eminently suitable for structures on the lunar surface, since it can utilize local aggregate which constitutes 80%-90% of the system, requires no water, and can be erected and hardened much faster than ordinary portland cement concrete and develop four-to-five fold greater strength, especially in flexure. It is noteworthy that to-date the use of polymer concrete for large-scale load-bearing structures is considerably more prevalent in West Germany, Japan and the Soviet Union, than in the U.S. The reasons for this may lie in the low cost of conventional concrete in the U.S. and the conservatism of the American building industry.

1.5 SHRINKAGE STRESS FIELDS: PRIOR WORK

An important consideration in the design of composites is the development of shrinkage stress fields around inclusions during the cure of the composite. This means that the cured composite is in fact considerably pre-stressed, even in the absence of external loads. If the magnitude of these shrinkage stresses exceeds the composite strength they may readily lead to cracking even under no external load (Theocaris, 1974).

Shrinkage stress fields were first determined experimentally. Early attempts include the use of a hollow glass sphere with small bonded resistance strain gauges and thermocouples embedded into the setting resin (Lee and Neville, 1967). In this manner both compressive shrinkage stresses and temperature rise due to the exothermic cure reaction were continuously recorded. The amount of shrinkage stresses developing during each stage of the polymerization process could be accurately determined. The nature of cure-shrinkage and thermal contrac-
tion stresses is the same: they are both tensile throughout the resin domains.

An interesting paper by Daniel and Durelli (Daniel and Durelli, 1962) presents methods of studying shrinkage stress in matrices cast around rigid inclusions. They introduced a method for the study of the relative or dimensionless stress distribution using rubber models with inserted inclusions. Elasticity solution for shrinkage-fit stresses can be used to model the residual stresses in polyester-resin/glass fiber composites that arise when the material is cooled from the post-curing temperature. Photoelastic investigation of shrinkage stresses has been attempted in several studies (Koufopoulos, 1968 and Theocaris, 1970). An interesting study on the thermal stresses and shrinkage stresses of concrete/polymer composite cylinders was presented by Ishizaki (Ishizaki, 1986). A mathematical solution for estimating thermal stress and shrinkage stress of concrete/polymer composite cylinders were derived. The analysis was based on the assumption that every concentric cylindrical of the composite consisted of homogeneous and isotropic material and adhesion between all layers was perfect.

Paipetis (Paipetis, 1977) discussed special composite structures in which the reinforcing phase has an optimum arrangement to support a given load. These structures at macroscopic level appear to have the microscopic characteristics of a composite.

None of this prior work deals effectively with setting stresses in highly-filled PC systems. In these composites, the aggregate particles occupy up to 75% of the total volume. Consequently the resin phase is not continuous but rather is confined in the small discrete domains between the aggregate particles. Since these domains cannot change in volume to accommodate the polymerization shrinkage of
the resin during cure, these composites develop setting stresses, which can seriously impair the strength of these composites.

1.6 RETRACTIVE FORCES IN THE RESIN: FUNCTIONAL DEPENDENCE

The retractive force is dependent on number of variables. The general expression may be written in reduced form as follows:

\[
F_{\text{retractive}} = f \left[ \frac{df}{dv}, \frac{dv}{dm}, D.P., dV_p, \frac{m}{V} \right]
\]  \hspace{1cm} (1.1)

where

\[
\frac{df}{dv} = \text{retractive force generated by the volume change in a single polymerization step (units: Newtons-cm}^3)\]

\[
\frac{dv}{dm} = \text{volume change in a single polymerization step (units: cm}^3)\]

\[
D.P. = \text{degree of polymerization in a single polymerization step (dimensionless).}
\]

\[
dV_p = \text{molar volume of polymer (units: cm}^3)\]

\[
m = \text{number of moles.}
\]

\[
V = \text{actual volume of resin domain (cm}^3)\]

The retractive forces are resisted by the adhesive forces at the interface and the cohesive forces in the resin interior. The shrinkage forces can be computed by integrating the retractive force over the volume of the resin domains as follows:
\[ F_{\text{shrinkage}} = \int_V F_{\text{retractive}} \, dV \] (2)

1.7 PACKING OF REINFORCING PARTICLES: PRIOR WORK

The science of particle packing can be defined as the selection of proper sizes and proportions of particulate material so that the spaces between the larger particles are filled with smaller particles, the new smaller spaces filled with still smaller particles, and so on. McGeeary, 1961 has introduced an idealized experimental study of particle packing. This was an attempt to extend the study of idealized packing of spheres of different sizes initiated by Furnas (Furnas, 1931).

Simulations of complete random packing models involving disks or spheres exist in the literature, but are time consuming to conduct. Lotwick (Lotwick, 1982) simulated a complete random packing of disks in \( \mathbb{R}^2 \), and compares his results with those of Tanemura (Tanemura, 1979). The goal of Lotwick’s work was to develop a simulation of packing models having given packing density.

1.8 ADHESION, WETTING AND INTERFACES: PRIOR WORK

Adhesion between the resin and reinforcing particles is a vital factor which affects the mechanical properties of polymer composites. As concluded by Plueddemann (Plueddemann, 1974), a strong interface bond results in a composite with a higher stiffness and higher static strength. However, it leads to more brittle and more notch-sensitive composites. A suitable compromise of the two is required in actual designs.
The nature of the interface between the aggregate particles and matrix is very critical in determining the mechanical properties of particle reinforced polymer composites. If the interface is strongly bonded, matrix cracks can cross the interface and the composite fails in a brittle manner. However, if the interface is weakly bonded, then debonding and aggregate pullout can lead to nonbrittle response of the composite. Normal tensile stresses are the most effective stresses at the interface. These stresses arise from the inhibition of the shrinkage of the matrix.

The surface energy theory of adhesion as described by Zisman (Zisman, 1963) suggests that good adhesion may be obtained between a polymer and any surface of a higher critical surface tension. The polymer in its liquid state should have a contact angle with the surface as small as possible in order to obtain good spreading (Piatti, 1978).

Wetting may be thought of as the process of achieving molecular contact. The extent of wetting may be defined as the number of molecular contacts between the two phases comprising the system relative to that exhibited when wetting is complete. In order to provide complete wetting, the coupling agent must have a surface tension lower than the critical surface tension \( \gamma_c \) of the mineral surface. The agent also needs a surface tension higher than that of the liquid resin. While at first this seems straightforward (all solid minerals have high \( \gamma_c \)), many hydrophilic minerals exposed to air have a layer of absorbed water which lowers the effective \( \gamma_c \) to 29–47 dynes/cm, the same range as that of the resins. Thus polar adhesives which could either absorb or displace the water may be necessary for successful bonding.
Silane coupling agents (SCA) are monomeric silicon chemicals used in a wide range of applications because of their ability to chemically bond organic polymers to inorganic materials (e.g. mineral fillers and glass). The disparity in surface free energy between the hydrophilic mineral aggregate (mostly silicon oxides) and the organic resins requires the use of SCA. These are silanes with the general structure \( R' - Si(OR_3) \) in which the organofunctional group \( R' \) attaches to the resin, while the alkoxy groups attach (either directly or following hydrolysis) to the aggregate surface.

As stated by Piatti (Piatti, 1978) the most successful coupling agents for thermosetting resins are reactive with the resin since chemical reaction does seem necessary for stability. Silane coupling agents improve adhesion between organic and inorganic phases of the composite by adhering to the individual components with different portions of the same molecule, thus bridging the interface. In practice, the silane can be applied to the filler in a separate primary treatment step, or it can be added directly to the resin and will migrate to the resin/aggregate interface during processing. As reported by Haque (Haque, 1986) the silane was added directly to the resin. It was found that the addition of SCA increases the level of flexural strength in unpromoted PC system cured at 100 C ° from \( 2.13 \times 10^7 \pm 0.002 \times 10^7 \) to \( 2.39 \times 10^7 \pm 0.02 \times 10^7 \).

The performance of SCA in glass-reinforced polyesters has been well described in the literature (Plueddemann, 1963, Sterman and Bradley, 1961). They showed that the silane technology developed for the glass-polyester composites was applicable to many common mineral-filled polyesters. Kumins and Roteman (Kumins, 1963) suggested that the boundary region, of which the
coupling agent is a part, between a high modulus reinforcement and a lower modulus resin can transfer stresses most uniformly if it has modulus intermediate between that of the resin and the reinforcement. The restrained layer theory suggests that SCA function by "tightening up" the polymer structure at the interface while simultaneously providing silanol groups for bonding to the mineral surface. Since poor wetting would severely decrease the strength of the cured composite all current formulations include coupling agents that promote resin-aggregate adhesion via different chemisorption processes.

1.9 SCOPE OF THIS RESEARCH

The work discussed in this thesis investigates the location and distribution of setting stresses in various types of highly filled polymer composites consisting of reinforcing particles in a cured resin matrix.

The finite element method was chosen as the numerical technique to solve the problem of determining setting stress distribution. Three-dimensional models with different contents of reinforcing particles (packing factors)* and different geometric arrangement of these particles will be introduced. This enabled us to analyze both the effect of packing factor as well as the geometric arrangement of the reinforcing particles on local setting stress distribution. The origin of setting stresses in PC systems and finite element modeling of setting stresses will be introduced in some detail in Chapter 3.

* We define packing factor as the occupied volume by the reinforcing particles divided by the total volume of the composite.
In our first (and simplest) models we have treated the randomly packed particles as an ordered arrangement of separate clusters extended repeatedly in three-dimensions. This is supported by the fact that manufacturing processes aim at complete mixing, insuring regular spatial arrangement of the reinforcing particles without groupings or conglomerates. We have analyzed first PC systems containing spherical particles of a single size, packed either in simple cubic or face-centered cubic arrangements (Chapter 4). We also considered a hexagonal close packed arrangement of hexagonal prism-shaped particles. We then proceeded to analyze systems with different sized particles (Chapter 5). This analysis includes arrangements in which the largest particles were packed in either simple cubic or face centered cubic configurations. Smaller particles were placed in the interstices between the largest particles, resulting in various models with different values of the packing factor. In subsequent models we consider fairly random arrangements (FRA) of quasi-spherical aggregate particles that are much closer to the actual physical PC systems; we analyze the location and distribution of setting stresses in these systems. Based on the results of three-dimensional finite element analysis of different models, we developed an empirical equation which can be used for the prediction of maximum setting stresses in optimal systems, where the PC is assumed to have the reinforcing particles in a perfect spherical shape arranged in an orderly fashion. This equation was found to work also for the FRA models (Chapter 6). We then apply a non-linear constrained optimization technique to determine the probability distribution of voids in composites based on fairly random arrangement of quasi spherical and quasi-ellipsoidal void/aggregate domains. These probability distributions are used with especially an developed algorithm to generate the voids distributions in specific composites. These voids exist in the
matrix domain as air bubbles. The effect of volume fraction, size distribution and location of voids on the magnitude and distribution of setting stresses in these composites is analyzed (Chapter 7). We also analyze the effect of volume ratio of aggregate to resin on the magnitude of setting stresses in composites that contain reinforcing particles, resin and void domains.

The results of this work provide guidelines for optimizing the aggregate content, shape and particle size distribution of the reinforcing aggregate in polymer composites so as to minimize the magnitude of setting stresses. The minimization of setting stresses should lead to composites with significantly higher strength.
References


CHAPTER 2

THEORETICAL ANALYSIS

2.1 TECHNIQUE FOR MODELING COMPOSITE MATERIALS

Modeling techniques of composite materials are usually based on microstructural models possessing regular geometry and topology: the composite is developed from a basic cell extended repeatedly in two or three-dimensions. The concentration of one phase in the other, the geometric arrangement of the aggregate particles and the size distribution of the aggregate are very important factors in modeling the composites. Geometric modeling of the phases consisting of a single inclusion surrounded by a proper amount of a matrix has developed by Hashin (Hashin, 1970 and Dow, 1965). Solutions of pairs of inclusions surrounded by an infinitely extended matrix were given for cylindrical, rigid (Goree, 1967) or elastic inclusions (Shioya, 1973) by means of proper numerical techniques.

2.2 STATISTICALLY ISOTROPIC COMPOSITES

If the effective stress/strain relation is independent of the choice of coordinate system, the composite is said to be a statistically isotropic. The simplest case is
dilute concentration of of spherical particles surrounded by an infinite medium (the resin). The definition of "dilute" is that the state of strain in any one particle in the composite body under homogeneous boundary conditions is not affected by the other particles. Thus the strain is that of a single particle in an infinite matrix. Assume that this composite was cooled down by $\Delta T$. The average shrinkage stresses can be expressed in the following equations:

$$\bar{\sigma} = \frac{(\alpha_{\text{resin}} - \alpha_{\text{agg}}) \Delta T}{(1 + \mu_{\text{resin}}) + \frac{1 - 2\mu_{\text{agg}}}{2 E_{\text{resin}}}}.$$

(2.1)

The stresses in the resin domain is defined by the radial and the tangential components. These are defined in the following equations:

$$\sigma_{rr} = \frac{\bar{\sigma} R^3}{r^3},$$

(2.2)

$$\sigma_{\theta\theta} = \frac{\bar{\sigma} R^3}{2 r^3},$$

(2.3)

where $R$ is the radius of the spherical particle and $r$ is the distance from the center. If we set $r$ equal $R$ (i.e. at the interface) both the radial and the tangential of the shrinkage stress component of the resin will approach its maximum. On the other hand if $r \gg R$, the shrinkage stresses will approach its minimum value.

2.3 SHRINKAGE STRESSES IN A SINGLE–PARTICLE COMPOSITE
Consider a single-particle composite consisting of a sphere surrounded by a shell of resin subjected to thermal shrinkage. The shrinkage of the resin shell depends on the volume fraction of the resin domains *. Assume that there are uniformly distributed normal forces of magnitude \( \sigma \) per unit volume due to the shrinkage of the polymer. Then \( \sigma \) is the uniform normal surface traction, or the normal surface stress. The bulk modulus for this type of composite was investigated by Hill (Hill, 1963). Assuming that the relation between the stress components and strain components is given by:

\[
\sigma_{ij} = \left[ B - 0.667 \, G \right] \frac{\Delta V}{V} \delta_{ij} + 2 \, G \, e_{ij},
\]

where \( \delta_{ij} = 0 \) if \( i \neq j \), and \( = 1 \) if \( i = j \), then the result of the application of these forces is to cause ideally an infinitesimal volume change without change in shape. If the fractional decrease in volume is denoted by \( \frac{\Delta V}{V} \), this is given by:

\[
\sigma_{\text{shrinkage}} = B_{\text{composite}} \left[ \frac{\Delta V}{V} \right].
\]

Thus \( B_{\text{composite}} \) is the bulk modulus of the composite and \( \sigma_{\text{shrinkage}} \) is an all around tensile stress in an isotropic material. The only forces acting on this composite element are normal forces. The magnitude of the corresponding stress components is equal to \( \sigma \). Under these conditions the composite body is said to be in a

* Resin volume fraction is the volume of the resin domains divided by the total volume of the composite. For voids free composites, it is equal to 1 minus the packing factor.
state of uniform hydrostatic stress. Assume that we apply a hydrostatic pressure $P$ to the resin shell. This pressure is assumed to be distributed uniformly over the outer surface of the resin shell which models the cure shrinkage of resin due to the chemical reaction. The resin contracts laterally onto the aggregate particle surface during the chemical reaction and the stresses are defined by equation (2.2) and (2.3). The energy density is defined as follows:

$$U = \frac{1}{2} B_{\text{composite}} \left( \frac{\Delta V}{V} \right)^2.$$  (2.6)

The uniform pressure $P$ which is applied to the external surface of the resin shell of radius $R$ produces an infinitesimal inward displacement $U$. The fractional decrease in total volume is $3U/R$, while the average strain is a compressive one of the amount $U/R$. Applying the divergence theorem (Gauss's theorem) * one can obtain an expression for the average strain:

$$\int_V e_{ij} \, dV = \frac{1}{2} \int_S \left( n_i u_j + n_j u_i \right) \, dS,$$  (2.7)

where, $V$ is the region, $S$ its surface, $u_i$ the displacement, and $n_i$ the unit outward normal. By equating the work done by the pressure to the total strain energy expressed in terms of average strain as in equation (2.8) the apparent bulk modulus of the composite element is computed as follows:

* This theorem is useful in many applications. In particular, it serves the purpose of avoiding the direct evaluation of a surface integral of a vector over a closed surface $S$, by replacing that integral by a volume integral over the interior $R$, if the divergence of a vector is of a convenient form in $R$.  

\[ B = \frac{PR}{3U}. \] (2.8)

Using elementary, spherically-symmetric and the assumption of an elastic fields the solution could be easily obtained (Hill, 1963). The final result shows that the displacement which is radially inward has magnitude \( u \) at distance \( r \) where:

\[ B (u/U) = (B_{\text{resin}} + 1.333 \ G_{\text{resin}}) r/R \quad \ldots \ldots \text{(aggregate).} \] (2.9)

\[ B (u/U) = (B_{\text{agg}} + 1.333 \ G_{\text{agg}}) r/R - (B_{\text{agg}} - B_{\text{resin}}) V_{\text{agg}} R^2/r^2 \quad \ldots \ldots \text{(resin).} \] (2.10)

\[ B_{\text{composite}} = V_{\text{agg}} B_{\text{resin}} + V_{\text{resin}} B_{\text{agg}} + 1.333 \ G_{\text{resin}}. \] (2.11)

Since the aggregate is simply compressed uniformly, the shear modulus does not enter. The resin shell is under uniform compression with a non uniform strain involving no change in volume. The compressive radial \( (\sigma_{\text{rad}}) \) and hoop stresses \( (\sigma_{\text{hoop}}) \) are given by the following equations:

\[ \sigma_{\text{rad}} = \frac{3 \ G_{\text{comp}}}{B_{\text{comp}} R} \left[ B_{\text{agg}} (B_{\text{resin}} + 1.333 \ G_{\text{resin}}) \right] \ldots \ldots \text{(aggregate).} \] (2.12)

\[ \sigma_{\text{rad}} (\text{resin}) = \frac{3 \ G_{\text{comp}}}{B_{\text{comp}} R} \left[ \begin{array}{c} B_{\text{resin}} (B_{\text{agg}} + G_{\text{resin}}) \\ + 1.333 \ G_{\text{resin}} (B_{\text{agg}} - B_{\text{resin}}) \frac{V_{\text{agg}} R^3}{r^3} \end{array} \right]. \] (2.13)
\[ \sigma_{\text{hoop (agg)}} = \frac{3 \, G_{\text{comp}}}{B_{\text{comp}} \, R} \left[ B_{\text{agg}} (B_{\text{resin}} + 1.333 \, G_{\text{resin}}) \right]. \] (2.14)

\[ \sigma_{\text{hoop (resin)}} = \frac{3 \, G_{\text{comp}}}{B_{\text{comp}} \, R} \left[ B_{\text{resin}} \, B_{\text{agg}} - \frac{2}{3} \, G_{\text{resin}} \right. \\
\left. + 1.333 \, G_{\text{resin}} \left( B_{\text{agg}} - B_{\text{resin}} \right) \frac{V_{\text{agg}} \, R^3}{r^3} \right]. \] (2.15)

The relationship between the hydrostatic pressure which was applied to the outer surface of the resin shell and the inward displacement is expressed in the following equation:

\[ P_{\text{hydro}} = \frac{3 \, U}{R} \left[ \frac{1.333 \, G_{\text{resin}} \left( V_{\text{agg}} B_{\text{agg}} + V_{\text{resin}} B_{\text{resin}} \right) + B_{\text{agg}} \, B_{\text{resin}}}{V_{\text{agg}} B_{\text{resin}} + V_{\text{resin}} B_{\text{agg}} + 1.333 \, G_{\text{resin}}} \right]. \] (2.16)

Substituting equation (2.15) in equation (2.11) one can obtain a general expression for the bulk modulus for the spherical composite element.

\[ B_{\text{comp}} = \frac{1.333 \, G_{\text{resin}} \left( V_{\text{agg}} \, B_{\text{agg}} + V_{\text{resin}} \, B_{\text{resin}} \right) + B_{\text{agg}} \, B_{\text{resin}}}{V_{\text{agg}} \, B_{\text{resin}} + V_{\text{resin}} \, B_{\text{agg}} + 1.333 \, G_{\text{resin}}}. \] (2.17)

The modulus of rigidity for the spherical aggregate does not appear here since the induced shrinkage stress in the aggregate is purely hydrostatic and uniform. Substituting the above expression in equation (2.8) the average shrinkage stress
expression for a spherical composite element is as follows:

\[
\sigma_{\text{shrinkage}} = \frac{\Delta V}{V} \left[ \frac{1.333 G_{\text{resin}} (V_{\text{agg}} B_{\text{agg}} + V_{\text{resin}} B_{\text{resin}}) + B_{\text{agg}} B_{\text{resin}}}{V_{\text{agg}} B_{\text{resin}} + V_{\text{resin}} B_{\text{agg}} + 1.333 G_{\text{resin}}} \right]. \tag{2.18}
\]

Equation (2.18) can be used to calculate the shrinkage stress in a single particle composite, where a resin shell is cemented to a spherical particle.

2.4 COMPOSITE SPHERES ASSEMBLAGE

The composite spheres assemblage was first introduced by Hashin (Hashin, 1962). This assemblage is composed of a gradation of sizes of spherical particles embedded in a continuous matrix. The size distribution of the particles has a specific characteristic. The size gradation of the particles is such that each composite sphere has \(a/b\) is constant, while still having a volume filling configuration. In each composite sphere the volume ratio of inner spherical core to matrix shell is equal to the constant \(a/b\), the concentration of the suspension. The composite spheres assemblage is shown in Figure 1. A composite sphere is defined by an isotropic spherical particle 2 enclosed in concentric shell 1. Assume that at the external boundary \(r = b\) is subjected to purely radial displacement \(u_r(b) = \varepsilon^0 b\).

If the body is filled out with composite spheres, which diminish to infinitesimal size, then the limit as the remaining volume goes to zero the effective bulk modulus of this composite material converges to the bulk modulus of a homogeneous sphere of radius \(b\). The value of the composite sphere assemblage
Figure 1

Composite spheres assemblage; composite cylinders assemblage.

a = radius of particle
b = radius of outer resin shell
a/b = constant
is that it is a real physical material, in the sense that we can actually construct it, for which we can calculate some effective property measures exactly. The simplicity of the composite assemblage concept and the fact that it allows for the exact calculation of some effective properties make it tempting to model real materials as an assemblage.

2.5 HYDROSTATIC PRESSURE MODEL

Figure 2 shows a representative cross-section of a volume element for a two-phase PC system at the beginning of curing of the resin. This element has a characteristic dimension which is much larger than that of the characteristic dimension of the inhomogeneities. Assume that we have a particle reinforced polymer composite in which there are two phases are present. Let $V$ denote the total volume of the composite element and assume that the individual volumes of the individual phases are $V_{\text{resin}}$ and $V_{\text{agg}}$. We denote here their interface by $S_{\text{resin/agg}}$. We assume that the composite is under hydrostatic pressure. This hydrostatic pressure models a uniform shrinkage by the resin domains due to chemical reaction during the curing of the resin material. This hydrostatic pressure is just enough to bring the aggregate-particles to touch each other, so that we have a uniform shrinkage by the resin material. The conditions for a macroscopically homogeneous deformation field on the representative volume can then be applied. The representative volume is shown in Fig. 2.

The average stress caused by the hydrostatic pressure is defined by

$$
\bar{\sigma}_{ij} = \frac{1}{V} \int_{V} \sigma_{ij}(x) \, dv,
$$

(2.19)
Fig 2. A representative composite element under hydrostatic pressure

1. aggregate domain
2. resin domain
and the average strain by

\[ \bar{\varepsilon}_{ij} = \frac{1}{V} \int_V \varepsilon_{ij}(x) \, dv \]
\[ = \frac{1}{2V} \int_S (u_i n_j + u_j n_i) \, ds, \]  \hspace{1cm} (2.20)

where \( n_i \) denotes the outward normal to the surface \( S \). The average strain in the composite can be written as function of the average strains of the individual phases and their volume fractions.

\[ \bar{\varepsilon}_{ij} = v_{\text{resin}} \varepsilon_{ij}^{\text{resin}} + v_{\text{agg}} \varepsilon_{ij}^{\text{agg}} \]

\[ - \frac{1}{2V} \int_{S_{\text{resin/agg}}} ( [u_i] n_j + [u_j] n_i) \, dS_{\text{resin/agg}}, \]  \hspace{1cm} (2.21)

where \( v_{\text{resin}} \) and \( v_{\text{agg}} \) are the volume fractions of the resin and aggregate respectively. The average strain in the resin domain, \( \varepsilon_{ij}^{\text{resin}} \) is given by:

\[ \bar{\varepsilon}_{ij}^{\text{resin}} = \frac{1}{V_{\text{resin}}} \int_{V_{\text{resin}}} \varepsilon_{ij}^{\text{resin}} \, dV_{\text{resin}}, \]  \hspace{1cm} (2.22)

and the average strain in the aggregate domain, \( \varepsilon_{ij}^{\text{agg}} \) is given by:

\[ \bar{\varepsilon}_{ij}^{\text{agg}} = \frac{1}{V_{\text{agg}}} \int_{V_{\text{agg}}} \varepsilon_{ij}^{\text{agg}} \, dV_{\text{agg}}, \]  \hspace{1cm} (2.23)

and the jump of the displacement across \( S_{\text{agg/resin}} \) is \([u_i] \) with
\[
[u_i] = \left. u_i^{agg} \right|_{S_{resin/agg}} - \left. u_i^{resin} \right|_{S_{resin/agg}},
\]

(2.24)

Assuming equilibrium in the stress field in \(V_{resin}\) and \(V_{agg}\) and continuity of the traction vector at \(S_{resin/agg}\), it immediately follows that

\[
\bar{\sigma}_{ij} = v_{resin} \bar{\sigma}_{ij}^{resin} + v_{agg} \bar{\sigma}_{ij}^{agg},
\]

(2.25)

where

\[
\bar{\sigma}_{ij}^{resin} = \frac{1}{V_{resin}} \int_{V_{resin}} \sigma_{ij}^{resin} \, dv_{resin},
\]

(2.26)

and

\[
\bar{\sigma}_{ij}^{agg} = \frac{1}{V_{agg}} \int_{V_{agg}} \sigma_{ij}^{agg} \, dv_{agg},
\]

(2.27)

The definition of average strain and average stress in terms of surface integrals as presented above is essential in formulating a general theory for particle reinforced polymer composites in which internal defects and discontinuities in the displacement field are allowed. We will follow here the steps of Russel and Acrivos (Russel, Acrivos, 1972) to derive an equation of the average shrinkage stress in the representative composite element in Figure 2. The effective, linear stiffness as stated by Christensen (Christensen, 79) is as follows:

\[
\bar{\sigma}_{ij} = C_{ijkl} \varepsilon_{kl},
\]

(2.28)

Assume that the materials for aggregate-particles and the resin are isotropic.
The stress strain relations for the aggregate-particles and the resin can then be given by the following two equations:

\[ \sigma_{ij}^{agg} = \lambda_{agg} \delta_{ij} \varepsilon_{kk}^{agg} + 2 \mu_{agg} \varepsilon_{ij}^{agg}. \]  \hspace{1cm} (2.29)

\[ \sigma_{ij}^{resin} = \lambda_{resin} \delta_{ij} \varepsilon_{kk}^{resin} + 2 \mu_{resin} \varepsilon_{ij}^{resin}, \]  \hspace{1cm} (2.30)

where \( \lambda \) and \( \mu \) are the Lamé constants, the average stress formula (2.28) can be written in the following form:

\[ \bar{\sigma}_{ij} = \frac{1}{V} \int_{V - \sum_{n=1}^{N} V_n} \sigma_{ij}^{resin} \, dv + \frac{1}{V} \sum_{n=1}^{N} \int_{V_n} \sigma_{ij}^{agg} \, dv, \]  \hspace{1cm} (2.31)

where \( N \) is the number of aggregate-particles in the representative volume element with volumes designated by \( V_n \), and \( V - \sum_{n=1}^{N} V_n \) designates the volume of the resin domains. Equation (2.31) can then be written in the following form:

\[ \bar{\sigma}_{ij} = \frac{1}{V} \int_{V - \sum_{n=1}^{N} V_n} (\lambda_{resin} \delta_{ij} \varepsilon_{kk} + 2 \mu_{resin} \varepsilon_{ij}) \, dv \]

\[ + \frac{1}{V} \sum_{n=1}^{N} \int_{V_n} \sigma_{ij}^{agg} \, dv. \]  \hspace{1cm} (2.32)

The first integral can be decomposed into two different integrals as follows:

\[ \bar{\sigma}_{ij} = \frac{1}{V} \int_{V} (\lambda_{resin} \delta_{ij} \varepsilon_{kk} + 2 \mu_{resin} \varepsilon_{ij}) \, dv \]
\[-\frac{1}{V} \sum_{n=1}^{N} \int \left( \lambda_{\text{resin}} \delta_{ij} \varepsilon_{kk} + 2 \mu_{\text{resin}} \varepsilon_{ij} \right) dv \]
\[+ \frac{1}{V} \sum_{n=1}^{N} \int \sigma_{ij}^{ggg} dv. \quad (2.33)\]

The average stress can be written as a function of the average strains as follows:

\[\bar{\sigma}_{ij} = \lambda_{\text{resin}} \delta_{ij} \varepsilon_{kk} + 2 \mu_{\text{resin}} \varepsilon_{ij} \]
\[+ \frac{1}{V} \sum_{n=1}^{N} \int \left( \sigma_{ij}^{ggg} - \lambda_{\text{resin}} \delta_{ij} \varepsilon_{kk} + 2 \mu_{\text{resin}} \varepsilon_{ij} \right) dv. \quad (2.34)\]

The above equation is for the average shrinkage stress based on an applied hydrostatic pressure to the representative volume.

2.6 COMPUTER-GENERATED AND MECHANICAL PACKINGS

Dense random packings of spherical particle, similar in many ways to those obtained with ball bearings, have been generated with a number of different computer algorithms by the sequential addition of spheres onto triangular sites on the surface of a cluster (Johnson, 1983). This procedure was first introduced by Bennett (Bennet, 1972) and Adams (Adams, 1972) begins with a triangular seed and additional spheres are added at triangular surfaces sites, chosen to be as close as possible to the center of the original seed. Molecular dynamics (Rahman, 1967) and Monte Carlo (Abraham, 1980) methods haroman have also been used to generate dense random packed structures, but generally with smaller numbers of particles than the other methods.
McGeary, 1961 has introduced an idealized experimental study of particle packing. This was an attempt to extend the study of idealized packing of spheres of different sizes initiated by Furnas (Furnas, 1931). Boriek (Boriek, 1989) introduced different models for packing spherical particles of different sizes. A comparison between McGeary’s and Boriek’s methods is introduced in Table 2.

2.7 IDEAL PACKING OF MULTIPLE SIZED PARTICLES

Harr (Harr, 1977) examined a collections of uniform spheres which may include a mixtures of particles of different sizes. Here, we are using his approach substituting the voids by polymer material. Assume that the volume fraction of the polymer and specific gravities of spherical aggregate particles are \( V_{1\text{,resin}} \), \( V_{2\text{,resin}} \), \( V_{3\text{,resin}} \), \ldots, \( V_{i\text{,resin}} \), and \( S_{1\text{,agg}} \), \( S_{2\text{,agg}} \), \( S_{3\text{,agg}} \), \ldots, \( S_{i\text{,agg}} \) in order of decreasing size of particles \( (R_1 > R_2 > \cdots > R_i) \). The weight per unit volume \( W_1 \) of aggregate for the model with the largest particles will then be:

\[
W_1 = (1 - V_{1\text{,resin}}) S_{1\text{,agg}} \gamma_w. 
\]  
\[ (2.35) \]

Similarly, the weight per unit volume of the next smaller particles is as follows:

\[
W_2 = (1 - V_{2\text{,resin}}) S_{2\text{,agg}} \gamma_w. 
\]  
\[ (2.36) \]

Assume now a mixed packing between the \( R_1 \) particles and \( R_2 \) particles, without altering the packing of the larger particles. The largest possible volume fraction of the resin when the composite is reinforced only with the largest particles. Consequently, for a binary PC system, the ratio of the weights for the most
### TABLE 2
Comparison Between Boriek/Akin/Armeniades Paper and Mechanical Packing Paper

<table>
<thead>
<tr>
<th>Subject</th>
<th>Boriek/Akin/Armeniades</th>
<th>Mechanical Packing</th>
</tr>
</thead>
<tbody>
<tr>
<td>diameter ratio of spheres</td>
<td>SC 1: 2.36 : 3.33 : 5.69</td>
<td>1 : 7 : 38 : 316</td>
</tr>
<tr>
<td></td>
<td>FCC 1 : 3.27</td>
<td></td>
</tr>
<tr>
<td>Distribution</td>
<td>narrow size range (4)</td>
<td>same</td>
</tr>
<tr>
<td>Packing factor</td>
<td>SC GROUP 75.1%</td>
<td>95.1%</td>
</tr>
<tr>
<td></td>
<td>FCC GROUP 79.2%</td>
<td></td>
</tr>
<tr>
<td>Packing method</td>
<td>Numerical</td>
<td>Experimental</td>
</tr>
<tr>
<td>Method of Packing</td>
<td>largest particles are in SC</td>
<td>particles are packed</td>
</tr>
<tr>
<td></td>
<td>or FCC arrangements</td>
<td>by vibration technique</td>
</tr>
<tr>
<td>Procedure of binary, ternary and</td>
<td>largest particles acted as</td>
<td>same</td>
</tr>
<tr>
<td>quarternary packings</td>
<td>a fixed porous filter bed</td>
<td></td>
</tr>
<tr>
<td>Ratio of number of spheres * for</td>
<td>3:1:1</td>
<td>69000:490:1</td>
</tr>
<tr>
<td>ternary Packing</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- This is the major significant difference between the two approaches.
efficient packing is as follows:

$$
\xi = \frac{W_1}{W_1 + W_2}
$$

$$
= \frac{(1 - V_{1\text{resin}}) S_{1\text{agg}}}{(1 - V_{1\text{resin}}) S_{1\text{agg}} + V_{1\text{resin}} (1 - V_{2\text{resin}}) S_{2\text{agg}}}.
$$

(2.38)

Continuing the process of replacing part of the resin domains with smaller particles without changing the total volume occupied by the larger particles, the contribution of the successively smaller particles will form the terms of the geometric sequence:

$$
\xi, 1 - \xi, \frac{(1 - \xi)^2}{\xi}, \frac{(1 - \xi)^3}{(\xi)^2}, \ldots..
$$

(2.39)

In terms of the volume fraction of the resin this can be written as:

$$
\frac{1}{(1 + V_{1\text{resin}})}, \frac{V_{1\text{resin}}}{(1 + V_{1\text{resin}})}, \frac{V_{1\text{resin}}^2}{(1 + V_{1\text{resin}})}, \ldots..
$$

(2.40)

Each term in the above equation represents the volumes of the respective particle sizes, the proportions, by volume, of each size required to obtain a packing of minimum volume fraction of the resin is found by dividing each of the relevant quantities in the above equation by the sum of their terms. Equation (2.40) can be rewritten in the following form:
\[
\frac{1}{1 + V_{\text{resin}}} \left( 1, V_{\text{resin}}, V_{\text{resin}}^2, \ldots \right). \tag{2.41}
\]

The proportions, by volume, of each size to obtain the most efficient packing (or minimum resin volume fraction) is found by dividing each of the relevant quantities by (2.39) and (2.40) by the sum of their terms.

2.8 NUMERICAL METHOD OF SOLUTION

2.8.1 FINITE ELEMENT METHOD

To use mathematical models on a computer one needs numerical methods. Exact analytical solutions exist only for simple problems. The finite element method (FEM) is a general technique for numerical solution of differential and integral equations in engineering. Finite element methods can treat complicated geometry, general boundary conditions and variable or non-linear material properties. The Finite element method was used here to investigate the setting stress field generated in polymer composite systems upon the shrinkage of the resin material.

2.8.2 STRAIN ENERGY CONCEPT

The strain energy expression in three-dimensions may be expressed as

\[
U = \frac{1}{2} \int_V [\varepsilon]^T [\sigma] \, dV, \tag{2.42}
\]
where \([\sigma]\) is the stress vector and \([\varepsilon]\) is the corresponding strain vector. By means of Hook’s law the strain energy can be expressed in terms of the stress components:

\[
U = \int_V \left[ \frac{1}{2E} \left( \sigma_x^2 + \sigma_y^2 + \sigma_z^2 \right) \right.
\]
\[
- \frac{v}{E} \left( \sigma_x \sigma_y + \sigma_y \sigma_z + \sigma_z \sigma_x \right)
\]
\[
+ \frac{1}{2G} \left( \tau_{xy}^2 + \tau_{yz}^2 + \tau_{zx}^2 \right) \right] \, dV.
\] (2.43)

where \(E, G\) and \(v\) are Young’s modulus, shear modulus and Possion’s ratio\(^\ddagger\) of the material. For the case of plane stress, \(\sigma_z = \tau_{xz} = \tau_{yz} = 0\), the above equation can be reduced to

\[
U = \int_V \left[ \frac{1}{2E} (\sigma_x^2 + \sigma_y^2) - \frac{v}{E} \sigma_x \sigma_y + \frac{1}{2G} \tau_{xy}^2 \right] \, dV.
\] (2.44)

For a plane-strain condition,

\[
\sigma_z = v (\sigma_x + \sigma_y),
\] (2.45)

and thus

\[
U = \frac{dU}{dV}
\]

\(^\ddagger\) S. D. Poisson discovered that when a bar of material is extended in tension, a lateral change in dimension also occurs, usually a contraction, the ratio of the lateral contraction to the longitudinal extension now being known as Poisson’s ratio \((v)\). For an isotropic material, \(v\) is a constant, and \(E\) and \(v\) together define fully the elastic properties of the material.
\[ \frac{1}{2E} \left[ (\sigma_x^2 + \sigma_y^2) - 2\nu(\sigma_x \sigma_y) + 2(1 + \nu)\sigma_{xy}^2 \right]. \quad (2.46) \]

Since we are assuming that the PC is an isotropic elastic composite, the form of the elastic energy function is independent of the choice of the coordinates in the deformed material. This implies that the strain energy function remains unchanged in its form by all orthogonal transformations of the coordinates. The stress can simply be expressed as the derivative of the strain energy \( U \) with respect to strain as:

\[ \sigma_{ij} = \frac{\partial U}{\partial \varepsilon_{ij}}. \quad (2.47) \]

The finite element method is based on an integral formulation. It requires the minimization of the total potential energy (\( \Pi \)). Akin (Akin, 1985) stated the theorem of minimum total energy very clearly. It states: "The displacement field that satisfies the geometric boundary conditions and corresponds to the state of equilibrium is the one that minimizes the Total Potential Energy". in the case of stress-strain analysis the potential energy is given by the internal potential (elastic) energy (strain energy) minus the work of external forces on the body. This can be stated symbolically as

\[ \Pi = U - W, \quad (2.48) \]

which can be applied equally well to an entire body or an element in the body. The strain energy, given by half the product of the stress and strain integrated over
the volume of the body, can be related to displacements in the body. The displace-
ments in the body are related to the nodal displacements through the interpolation
functions. Then the strain energy is expressed at the element level by the integral:

\[ U_e = \frac{1}{2} \int_{\text{vol}} \{ T \}^T [H]^T [D] [H] \{ T \} \, dV. \]  \hspace{1cm} (2.49)

where the \( H \) matrix relates the strains to the displacements, the \( D \) matrix
embodies the constitutive relations between stress and strain, and the \( T \) vector
contains the nodal displacements. It is noteworthy that the outside two terms give
the strain, one of which can be multiplied by the \( D \) matrix to give stress, thus giv-
ing the desired strain energy. The quantity within the strain energy expression,

\[ \int_{\text{vol}} \{ H \}^T [D] [H] \, dV, \]  \hspace{1cm} (2.50)

is recognized as the element stiffness matrix. The total potential energy depends
only on the unknown displacement, \( \{ T \} \), so it can be minimized by setting its
variation with respect to \( \{ T \} \) equal to zero, giving the familiar expression

\[ [S] \{ T \} - \{ F \} = 0, \]  \hspace{1cm} (2.51)

where \( F \) includes all types of forces generalized to the nodes.

As stated by Akin (Akin, 1986), the solution that yields a stationary value of
the integral functional and satisfies the boundary conditions is equivalent to the
solution of an associated differential equation, known as the Euler equation †.

† The Euler Equation: \( \frac{d}{dx} \left[ \frac{\partial F}{\partial u} - \frac{\partial F}{\partial u'} \right] = 0 \), is a necessary condition for optimizing the integral: \( \int_a^b F(x, u, u') \, dx \), subject to: \( u(a) = A, \, u(b) = B \), where: \( a, b, A, \, \text{and} \, B \) are given constants.
References


CHAPTER 3

MODELING OF SETTING STRESSES

3.1 ORIGIN OF SETTING STRESSES

PC systems suffer from a major drawback, due to the polymeric nature of their binder: setting stresses which arise from constraints in polymerization shrinkage. These setting stresses can cause considerable impairment of both the short-term strength of the composite, as well as its long-term load bearing properties. A comparison between the overall level of setting stresses in polyester, epoxy and acrylic PC systems is shown in Table 3, as well as their cure shrinkage, at different temperatures and resulting compressive, tensile and flexural strengths.

Setting stresses are generated during the curing process due to shrinkage of the polymerizing resin (cure shrinkage). Polymerization shrinkage arises from the fact that in the starting material the monomer molecules are located at a Van der Waals' distance (3-5 A) from one another, while in the corresponding polymer, these units are linked by covalent bonds with distances of ca. 1.5 A (Bailey, 1973).
<table>
<thead>
<tr>
<th>Material</th>
<th>Polyester PC* (unpromoted)</th>
<th>Polyester PC* (promoted)</th>
<th>Epoxy PC**</th>
<th>Acrylic PC***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cure Temperature</td>
<td>100</td>
<td>60</td>
<td>60</td>
<td>85</td>
</tr>
<tr>
<td>Volume Change With Cure (%)</td>
<td>-0.6</td>
<td>-0.5</td>
<td>-0.4</td>
<td>-2.5</td>
</tr>
<tr>
<td>Overall level of setting stress †</td>
<td>26.1</td>
<td>32</td>
<td>15.6</td>
<td>41</td>
</tr>
<tr>
<td>Compressive strength (MN/m²)</td>
<td>54 ± 9.1</td>
<td>63 ± 9.2</td>
<td>76 ± 9.8</td>
<td>50.06 ± 3.08</td>
</tr>
<tr>
<td>Tensile strength (MN/m²)</td>
<td>6.4 ± 1.5</td>
<td>6.4 ± 1.0</td>
<td>no data</td>
<td>4.6 ± 0.35</td>
</tr>
<tr>
<td>Flexural strength (MN/m²)</td>
<td>23 ± 5.6</td>
<td>25 ± 5.1</td>
<td>32 ± 1.2</td>
<td>27.55 ± 0.94</td>
</tr>
</tbody>
</table>

* Conventional polyester PC with 12.5 wt% resin (Dion Iso-6315) and aggregate ranging from #4 to #200 mesh. Cured with Benzoyl Peroxide; dimethylaniline added in promoted systems.

** Conventional epoxy PC with 12.8 wt% resin (Epon 828, Versamid 140 at a weight ratio of 1.8 ) and aggregate ranging from #4 to #200 mesh.

*** Ordinary acrylic PC system with 17 wt% acrylic cement and aggregate ranging from #8 to #100 mesh size.

† as a (%) of flexural strength.
Polymerization shrinkage entails a reduction in the volume of the resin binder (cure shrinkage), which, in systems where the resin is the continuous phase, is accommodated by a reduction in the overall volume. PC systems, however, contain so much aggregate (up to 80% by volume) that the solid particles are nearly close-packed and the resin is largely confined to the small spaces between particles. This severely restricts the ability of the composite to contract in response to the cure-shrinkage forces. Soon after the onset of polymerization a small amount of resin shrinkage brings the aggregate particles hard against each other, thus preventing further reduction in volume; consequently the resin in the interparticle spaces is forced to complete its polymerization at constant volume. This inhibition of cure shrinkage gives rise to setting stresses, which increase as polymerization proceeds to completion. These stresses can be relieved either by an adhesive failure in which the matrix pulls away from the reinforcing aggregate particles, forming microcracks or voids; or by cohesive failure of the material within a resin domain. The generation of setting stresses is shown schematically in Figure 3.

The degree to which cure shrinkage has been inhibited in a given PC system can be readily assessed by comparing its actual cure shrinkage with the expected free shrinkage, based on the volume fraction of resin and its inherent polymerization shrinkage. Thus, a PC system based on an unsaturated poleyster/styrene and containing 25% by volume resin which has an inherent polymerization shrinkage of 8% in volumetric strain ($\varepsilon_v = 0.08$), should show a cure shrinkage of 2% (8% x 0.25) in order to be free of setting stresses. PC systems based on methyl methacrylate (which has a 21% polymerization shrinkage) would require cure shrinkage of 5.3% (at 25% resin content) in order to be free of setting stresses.
Fig. 3a: Schematic diagram of a typical PC system at the start of cure, showing the resin domains between nearly close-packed aggregate particles.

Fig. 3b: Cure-shrinkage has progressed to the point of bringing the aggregate particles hard against each other, so that the resin is forced to cure at constant volume, generating setting stresses.

Fig. 3c: Qualitative plots of volume change and stress as a function of polymerization, showing the onset of setting stresses when cure-shrinkage is inhibited.
However most commercial PC systems show much lower cure shrinkages, indicating the presence of substantial setting stresses (Haque and Armeniades, 1986).

3.2 HINDERED SHRINKAGE

The role of setting stresses in reducing PC strength was assessed by comparing the strength of "ordinary" polyester/styrene PC. with the corresponding strength of special experimental "stress-free" systems, in which setting stresses were eliminated by the addition of carefully measured amounts of a chemical agent, which expands during resin cure, thus counteracting polymerization shrinkage. The compressive and splitting tensile strength measurements were performed according to the ASTM C-116 standards using 7.62 cm. dia. by 10.16 cm. long specimens. Flexural tests were performed on bar-shaped specimens $21.6 \times 3.8 \times 1.3 \text{ cm}$, according to the ASTM D-790 Standard, using a 3-point loading mode (Haque, 1986).

Since the production of zero-shrinkage systems requires special cure conditions, most field-erected PC structures develop setting stresses, which must be taken into account in structural design. In an ordinary PC system, containing 75% by volume mineral aggregate in polyester/styrene matrix, the measured strength was $6.1 \times 10^7 \text{ N/m}^2$, $6.2 \times 10^6 \text{ N/m}^2$ and $2.4 \times 10^7 \text{ N/m}^2$ in compression, tension, and flexure respectively, compared to $7.3 \times 10^7 \text{ N/m}^2$, $7.13 \times 10^6 \text{ N/m}^2$ and
$3.0 \times 10^7 \text{ N/m}^2$ for the corresponding specially formulated zero-shrinkage system that was free of setting stresses *. Flexural modulus for both systems is $7.1 \times 10^9 \text{ N/m}^2$. These measurements indicate that the setting stresses reduce the flexure strength of the composite by 20%. Using these values we calculate the actual cure shrinkage of the composite (based on 25% resin by volume) and obtain the hindered shrinkage of the resin which generates the setting stresses:

$$\sigma_{setting} = (3.0 - 2.4) \times 10^7 = 6 \times 10^6 \text{ N/m}^2.$$  \hspace{1cm} (3.1)

This corresponds to a linear hindered shrinkage for the composite:

$$\left[\frac{\Delta L}{L}\right]_{\text{composite (hindered)}} = \frac{6 \times 10^6}{7.1 \times 10^9} = 8.4507 \times 10^{-4}.$$  \hspace{1cm} (3.2)

Assuming that we have an isotropic and homogeneous composite, this linear hindered shrinkage represents one third of the total volumetric shrinkage:

$$\left[\frac{\Delta V}{V}\right]_{\text{composite (hindered)}} = 3 \times 8.4507 \times 10^{-4} = 2.5352 \times 10^{-3}.$$  \hspace{1cm} (3.3)

* In both ordinary and zero-shrinkage formulated with appropriate resin/mineral coupling agents PC systems failure occurs by the propagation of cracks through the resin and aggregate particles rather than at the resin/particle interface.
When this is subtracted from the free shrinkage of 0.02 (8% resin shrinkage × 0.25 resin volume fraction) it gives the actual cure-shrinkage of the composite:

$$\left[ \frac{\Delta V}{V} \right]_{\text{composite(actual)}} = 0.02 - (2.5352 \times 10^{-3}) = 1.74 \times 10^{-2}. \quad (3.4)$$

This shrinkage is concentrated in the resin phase, which occupies 25% of the total volume. Hence, the actual shrinkage of the resin at the onset of impingement of the aggregate particles is:

$$\left[ \frac{\Delta V}{V} \right]_{\text{resin(actual)}} = \frac{(1.74 \times 10^{-2})}{(0.25)} = 6.992 \times 10^{-2}. \quad (3.5)$$

The difference between this (actual) shrinkage of the resin and its free shrinkage of 8% gives the amount of hindered shrinkage which generates the setting stresses:

$$\left[ \frac{\Delta V}{V} \right]_{\text{resin(hindered)}} = 0.08 - 0.06992 = 1.01 \times 10^{-2}. \quad (3.6)$$
3.3 FUNCTIONAL DEPENDENCE OF SETTING STRESSES

The setting stresses generated in the polymer composite systems may depend on a large number of variables. The general expression may be written in reduced form as follows:

\[ \sigma_{\text{setting, rel}} = f \left( V_{\text{resin/agg}}, g, \alpha_{\text{agg}}, \beta, v_{\text{resin}}, S, A_d, \zeta, \phi, V_{f\text{voids}}, \alpha_{\text{voids}} \right). \quad (3.7) \]

where:

\[ \sigma_{\text{setting, rel}} = \text{setting stresses as a fraction of the strength of the composite.} \]

\[ V_{\text{resin/agg}} = \text{volume ratio of resin aggregate.} \]

\[ g = \text{factor depending on the geometric arrangement of aggregate particles.} \]

\[ \beta = \text{ratio of elastic moduli between resin and aggregate.} \]

\[ v_{\text{resin}} = \text{Poisson's ratio of the resin.} \]

\[ S = \text{factor depending on aggregate shape.} \]

\[ A_d = \text{factor depending on resin aggregate adhesion.} \]

\[ \zeta = \text{factor depending on the percentage of inherent shrinkage of the resin.} \]
\[ \Phi = \text{degree of polymerization of the cured polymer.} \]

\[ V_{f\text{voids}} = \text{volume fraction of the voids.} \]

\[ \alpha_{\text{agg}} = \text{factor depending on the size distribution of aggregate particles.} \]

\[ \alpha_{\text{voids}} = \text{factor depending on size distribution of aggregate particles.} \]

The following assumptions are considered in our model:

1. The composite is statistically isotropic, i.e., the stress-strain relationships are independent of the choice of coordinate system.
2. Both the polymer matrix and the aggregate respond elastically to imposed stresses.
3. Perfect and uniform adhesion * exists between the aggregate and the resin.

* The average degree of polymerization is given by the number of monomer molecules polymerized per polymer molecule formed. The number of polymer molecules formed is equal to the number of chain centers, or initiators (Allcock, 1981). It can be presented in the following formula:

\[ \overline{DP} = \frac{[M]_0 - [M]}{[GA]_0}, \]  \hspace{1cm} (3.8)

where:

\[ DP = \text{the average degree of polymerization.} \]

\[ [M]_0 = \text{initial concentration of the monomer.} \]

\[ [M] = \text{concentration of the monomer after time } t. \]

\[ [GA]_0 = \text{number of chain centers (number of polymer molecules formed).} \]
(A_d = 1).

4. Cure-shrinkage forces within the resin are isotropic and develop uniformly throughout.

5. Setting stresses arise during curing process of the resin when the aggregate start to touch each other.

6. The setting stresses and their distribution is identical in all resin and aggregate domains except those next to surface of the composite.

7. The resin has cured completely to a 3-dimensional polymer network.

8. Thermal stresses due to temperature changes during cure are neglected.

3.4 FICTITIOUS COOLING STRAINS

The setting stresses and strains in the cured composite can be simulated by a thermal shrinkage model, in which the resin (with an assumed bulk thermal expansion coefficient, (\( \alpha = 2.58 \times 10^{-4} \, ^\circ C^{-1} \)) shrinks against a thermally invariant aggregate particles (\( \alpha = 0.0 \)). A fictitious temperature difference (\( \Delta T \)) was assumed, based on the hindered shrinkage of the resin and its thermal expansion coefficient and was applied everywhere in the composite. When the aggregate particles become close packed the resin can contract no longer and a stress field is generated in the composite. The composite models that were developed in this

* The interface between the aggregate domains and the resin is a plane or geometric surface in space, infinitely thin and identical with the boundary of the aggregate particles and resin domains. A structural continuity is assumed to exist at the interface.
research was analyzed using PAFEC* as the finite element analysis code. The model is very powerful since it can treat both free shrinkage and hindered shrinkage processes in composites with arbitrary shape and different geometric arrangements of aggregate particles and resin domains. This model is also independent of the material properties of the different phases of the composite, which makes it a general model for treating setting stresses in PC systems. As expected, during free shrinkage of the resin, the composite remains free of setting stresses. Assuming that setting stresses arise when the aggregate particles start to touch each other, the fictitious temperature difference is calculated from the amount of hindered shrinkage in the resin:

\[ \Delta T_{\text{fictitious}} = \left( \frac{\Delta V}{V} \right)_{\text{resin (hindered)}} (\alpha)^{-1}_{\text{bulk}} \]  

(3.9)

Using equation (3.6) we obtained a value of the hindered shrinkage of the resin \((1.01 \times 10^{-2})\) for a PC system with a volume fraction of the resin of 25%. This corresponds closely to the resin volume fraction of our model with FCC particle geometry \((V_{f\text{resin}} = 26\%)\) and is used to calculate \(\Delta T_{(FCC)}\). For the SC and HCPP arrangements the hindered shrinkage of the resin is modified in accordance with the different resin contents resulting in different values for the fictitious temperatures.

* PAFEC is a computer program capable of carrying out an enormous range of engineering calculations using the finite element method. This scheme is fully described in the PAFEC 75 manual (PAFEC, 1975).
\[ \Delta T_{(MODEL)} = \Delta T_{(FCC)} \times \frac{V_f(MODEL)}{V_f(FCC)}. \] (3.10)

3.5 MODELING OF THE SETTING STRESS FIELD

The setting stress field is generated by observing the response (strain, stress) of the composite to a stimulus (temperature difference). We assume that we have uniform shrinkage which can be translated into a uniform decrease in the temperature of the composite by \( \delta T \). This is a scalar (non directional) stimulus but the response, the shrinkage strain, is a second order tensor \( \varepsilon_{ij} \) because it relates the displacement vector \( (u_i) \) with the position vector \( (x_j) \). Hence the thermal expansion, is also a second order tensor \( \alpha_{ij} \) thus:

\[ \varepsilon_{ij} = \alpha_{ij} \delta T. \] (3.11)

Being symmetric, this strain tensor can be referred to its principal coefficients of linear thermal expansion \( \alpha_1, \alpha_2, \alpha_3 \). The principal coefficients describe the volume change so that for axes at right angles:

\[ \alpha_{volumetric} = \alpha_1 + \alpha_2 + \alpha_3, \] (3.12)

where \( \alpha_{volumetric} \) represents the coefficient of cubical expansion or the volumetric thermal expansion. Since we are assuming isotropic material, only one value is required to describe the thermal expansion which is:
\[ \alpha_{\text{volumetric}} = 3\alpha. \quad (3.13) \]

Likewise the strain tensor is symmetric. The volumetric shrinkage strain is expressed in terms of the principal linear strains as follows:

\[ \varepsilon_{\text{volumetric}} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3. \quad (3.14) \]

The above volumetric shrinkage strain was used to calculate the fictitious temperature difference as follows:

\[ \varepsilon_{\text{volumetric}} = \alpha_{\text{volumetric}} \delta T. \quad (3.15) \]

### 3.6 THERMAL EXPANSION COEFFICIENT OF PC SYSTEMS

Assuming that the PC system is a macroscopically isotropic composite, the following expression has been obtained for the thermal expansion coefficient (Berlin, 1986).

\[ \alpha_{\text{comp}} = \hat{\alpha} + \frac{\alpha_{\text{agg}} - \alpha_{\text{resin}}}{\frac{1}{K_{\text{agg}}} - \frac{1}{K_{\text{resin}}}} \left[ \frac{1}{K_{\text{comp}}} - \left( \frac{1}{K} \right) \right]. \quad (3.16) \]

where:

\[ \hat{\alpha} = V_{\text{agg}} \alpha_{\text{agg}} + V_{\text{resin}} \alpha_{\text{resin}}. \quad (3.17) \]

\[ \left( \frac{1}{K} \right) = \frac{V_{\text{agg}}}{K_{\text{agg}}} + \frac{V_{\text{resin}}}{K_{\text{resin}}}, \quad (3.18) \]
where $K_{agg}$, $K_{resin}$ and $K_{comp}$ are the bulk moduli of the aggregate particles, resin and composite, respectively. The value for $K_{comp}$ can be determined experimentally or calculated as follows:

$$\frac{K_{comp}}{K_{resin}} = \frac{2 \times \Omega (1 + V_{agg}) \frac{(1 - 2 \mu_{resin})}{1 + \mu_{resin}}}{\Omega \times \psi [1 - V_{agg}]}, \quad (3.19)$$

where:

$$\Omega = \frac{K_{agg} - K_{resin}}{K_{agg} + \frac{2 (1 - 2 \mu_{resin})}{1 + \mu_{resin}} K_{resin}} \quad (3.20)$$

and $\psi$ can be written in the following form:

$$\psi = 1 + \frac{V_{resin}}{V_{agg}} [V_{agg} \bar{V}_{agg} + V_{resin} (1 - \bar{V}_{agg})], \quad (3.21)$$

where $V_{agg}$ is the true volume fraction of the aggregate particles, $\bar{V}_{agg}$ is the maximum volume fraction for a given geometry, e.g. $\bar{V}_{agg} = 0.74$ for face-centered cubic packing of spherical aggregate-particles.

### 3.7 FINITE ELEMENT MODELING

Finite element analysis was used to obtain the local distribution of setting stresses in different models of PC systems as a function of inherent resin shrinkage, and the shape, geometric arrangement and packing factor of the reinforcing aggregate particles. In the finite element method, the boundary and interior of the
solution domain is subdivided by imaginary lines (or surfaces) into a finite number of discrete sized subregions (finite elements) after which a standardized stiffness analysis is performed.

The finite elements of the assemblage of the actual continuum are interconnected at nodes or nodal points. Most of the nodes usually lie on the element boundaries where adjacent elements are considered to be connected. The actual variation of the field variable (displacement and stress) inside the continuum is unknown. It is assumed that the variation of the field variable inside a finite element can be approximated by a simple interpolating functions which are defined in terms of the values of the field variable at the nodal points. When field equations like the equilibrium equations for the continuum are written, the new unknowns will be the nodal values of the field variables. By solving the field equations, which are generally in the form of matrix equations, the nodal values of the field variable will be known. Now the assemblage functions define the field variable throughout the assemblage of elements.

The three-dimensional finite element analysis proved to have great potential for aiding in understanding the behavior and response of the complicated models for the polymer composites. The elements that were used throughout this thesis are isoparametric. Isoparametric elements are among the most common type of element being used to obtain finite element solutions. In these elements the displacement functions are also used to describe the element geometry. The interpolation function for the isoparametric element is applied to the global coordinates so that all the global coordinates can be defined for any given point in the element in terms of the local coordinate system of that element. The three dimensional
Isoparametric elements that were used throughout this investigations were 10 node points (tetrahedral) and 15 node points (wedge). The 10 node points in the elements corresponds to four corners of a tetrahedral element and six mid-side node points. The 15 node points in the elements correspond to six corners of a wedge element and 9 mid-side nodes. Each node point has three displacement ($u$, $v$ and $w$) and six stress degrees of freedom ($\sigma_x$, $\sigma_y$, $\sigma_z$, $\tau_{xy}$, $\tau_{yz}$, and $\tau_{zx}$). Thus each of the 10 point node element possesses 90 degrees of freedom. For the 15 node points element, a 135 degrees of freedom is possessed by that element. Each model can be divided into any desired number of elements. Of course as the number of elements increases the total number of independent degrees of freedom also increases but not at the same rate.

3.7.1 BOUNDARY CONDITIONS

In order to prevent the finite element model from moving freely through space (rigid-body), each of the possible degrees of freedom must be constrained somewhere on the model. For the three-dimesional models, this is done by imposing boundary conditions in the form of enforced zero displacements at appropriate nodal point (the origin of the largest aggregate particle). In all the three-dimensional analyzed models throughout this thesis, there are five different symmetry planes for each model. All the nodal points at the symmetry planes were restrained from movement in the perpendicular direction of that particular plane.
3.7.2 MATERIAL PROPERTIES AND LOADING CONDITIONS

We have assumed linear, elastic, and isotropic materials. Because of the assumption of isotropy, the properties of the materials that were used throughout this analysis do not vary with direction. A more detailed discussion about isotropy is introduced in Appendix D. The material properties of interest are the Young’s modulus of elasticity, Poisson’s ratio and thermal expansion coefficient of the resin material.

The real properties of the materials are provided to the computer program except for the thermal expansion of the aggregate particles where a fictitious value (zero) has been applied to agree with the fact that the aggregate particles do not shrink upon the polymerization process of the resin. The fictitious temperature difference has been applied to all the nodal points in the analyzed models. This fictitious temperature difference is computed for each analyzed model based on the ratio of the resin volume fraction of the analyzed model and the face-centered cubic (FCC) model (equation 13). The results of the FEA give a complete picture of the setting stress distribution in terms of the nodal stress values. These stresses are given in global axes as well as in the principal axes *

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* The primary objective of the undertaken FEA is to determine the principal setting stresses of the analyzed models. These principal setting stresses are perpendicular to each other and they act on mutually orthogonal planes which are passing through each nodal point in the continuum under load on which there are no shearing stresses. The planes in question are called principal planes.
References


CHAPTER 4

POLYMER COMPOSITES REINFORCED

WITH SINGLE-SIZED PARTICLES

4.1 INTRODUCTION: AGGREGATE PARTICLE GEOMETRY

In the previous chapter we introduced a modeling technique for setting stresses which are generated in polymer composites reinforced with solid particles. In this chapter we will compute setting stresses for composites reinforced with perfect spherical particles as well as hexagonal prism-shaped particles \(\dagger\). As a first approach we are considering polymer composites reinforced with single-sized particles which have an orderly packing. We analyzed three different aggregate particle geometries: simple cubic (SC), face-centered cubic (FCC) and a hexagonal close-packed system of hexagonal prisms (HCPP). The computer program PAFEC was used as the finite element analysis code (PAFEC, 1986). Figure 4 shows complete unit cells for the three geometries. We also consider the shape of aggregate particles: spheres and hexagonal prisms. The symmetric boundary con-

\(\dagger\) This work was published as part of a technical paper (Boriek, 1988).
Fig. 4 Graphical representation of the complete unit cells of SC, FCC and HCP arrangements of spherical aggregate particles.
ditions that were applied to these models force the resin to shrink in a constant-volume domain, so the required field of setting stress is generated in the entire composite. This analysis is used to predict the locations for any possible micro-cracks that may originate for each aggregate particle shape and geometric arrangement of the reinforcing particles.

For the simple cubic arrangement of spherical particles each sphere touches four nearest neighbors in a given layer and every layer is the same; the highest points of the spheres in the lower layer contact the lowest points of corresponding spheres in the upper layer. In the FCC arrangement the spherical particles are placed so that each sphere in a given layer contacts four other spheres in the same layer and rests in the depression between four adjacent spheres of the lower layer. In the HCPP arrangement, each prism touches six of its nearest neighbors in the same layer and rests in the space between three adjacent prisms in the layer below.

4.2 RESULTS: THREE-DIMENSIONAL FEA ANALYSIS

4.2.1 SC ARRANGEMENT OF SPHERICAL PARTICLES

The SC arrangement has the lowest packing factor (0.52) among the aggregate particle geometries. Figure 5 ‡ gives a graphical representation of a single symmetry element of this model. The location of certain nodes, selected as

‡ The nodal numbers on the diagrams in this chapter and chapter 5 are carefully numbered so it would be easy for the reader to determine the location of a specific nodal point from one diagram or the other. For example, In all models with SC arrangements of the largest particles the nodal point 8 is a contact point between the largest particles.
Fig. 5 Graphical representation of the analyzed element of simple cubic arrangement of spherical aggregate particles
representative of the range of setting stresses was computed for this model. The magnitude of setting stresses relative to the splitting tensile strength of the composite is shown in Table 4. Due to the nature of the hindered shrinkage forces that generate setting stresses, the tensile components of these stresses is high throughout the composite. The highest tensile stresses occur at the polymer-particle interface * (nodes 9 and 10). This suggests that any microcracks that may occur in a composite with this type of aggregate geometry would be likely to originate on these locations. A compressive radial stress and the highest shear stress occur at the point of contact between the aggregate (node 8). The magnitude of shear stresses are considerably low throughout the composite except for contact points between the spherical aggregate. Nodes 13 through 25 have high maximum principal tensile stresses and very low shear stresses. The three components of principal stresses are positive in the resin domain, indicating that setting stresses are tensile in nature. Figures 5(a), 5(b), 6(a) and 6(b) show maximum stress contours for the individual phases of the SC model (resin and aggregate respectively). The postprocessing were constructed using PATRAN software ** (PATRAN II, 1985).

4.2.2 FCC ARRANGEMENT OF SPHERICAL PARTICLES

* The stresses at all interfacial nodes have two values (on the resin and aggregate phases). We report here the higher of the two values.

** PATRAN is an extremely powerful graphic system that contain different modules such as conceptual solid modeling, advanced geometry modeling, finite element modeling and solid composites design and analysis.
Maximum Stress Contours in the Aggregate Domain of the SC Model

Figure 6(a)
(View B)

Maximum Stress Contours in the Aggregate Domain of the SC Model

Figure 6(b)
(View A)

Maximum Stress Contours in the Resin Domain of the SC Model

Figure 6(c)
Maximum Stress Contours in the Resin Domain of the SC Model

Figure 6(d)
TABLE 4

SC Model: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 5 (relative to splitting tensile strength of the composite)

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<tr>
<th>node</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
<th>$\sigma_3$</th>
<th>$\sigma_{\text{mean}}$</th>
<th>$\sigma_{\text{max}}$</th>
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<td>.109</td>
<td>.361</td>
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<td>.513</td>
<td>.507</td>
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<td>.011</td>
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</table>

** maximum mean tensile stress

*** maximum shear stress
Figure 7 shows a graphical representation of the analyzed element of this model with the location of selected nodes. The relative magnitude of setting stresses at these points is given in Table 5. This model has a higher packing factor than the simple cubic (0.74 vs. 0.52) and shows in general lower tensile setting stresses (25% lower than in the simple cubic model). A hydrostatic state of stress occurs at node 12, which has the highest magnitude of tensile stresses. This suggests that any microcracks that might form in a composite with FCC arrangement of spherical aggregate particles would be likely to originate at the center of the resin domain. The shear stresses induced in the aggregate are relatively higher than in the simple cubic arrangement, due to the compressive radial stresses that occur at the points of contact between the aggregate particles.

4.2.3 HCP ARRANGEMENT OF HEXAGONAL, PRISM-SHAPED PARTICLES

In order to examine the effect of particle shape on the magnitude and distribution of local setting stresses we analyzed an HCP arrangement of hexagonal, prism-shaped aggregate. Figure 8 gives a graphical representation of this model, which has a packing factor of 0.82. The relative magnitude of the setting stresses at the selected nodal points is shown in table 6. A thin layer of resin is assumed to surround the particles, separating even their flat surfaces. A quasi-hydrostatic state of stress exists at node 1 which is located at the center of the resin domain. Node 1 also shows the highest value of mean tensile stress throughout the composite. This suggests that the center of the resin domain is the most probable location for the origination of microcracks in such composites. A high compressive stress occurs at node 5 which is a point of contact between the aggregate. Node 5
Fig. 7  Graphical representation of the analyzed element of face-centered cubic of spherical aggregate particles
### TABLE 5

FCC Model: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 7 (relative to splitting tensile strength of the composite)

<table>
<thead>
<tr>
<th>node</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
<th>$\sigma_3$</th>
<th>$\sigma_{\text{max}}$</th>
<th>$\tau_{\text{max}}$</th>
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<tr>
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<td>-0.012</td>
<td>0.115</td>
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<td>-0.013</td>
<td>-0.04</td>
<td>-0.002</td>
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Fig. 8  Graphical representation of the analyzed element of HCP arrangement of hexagonal, prism-shaped aggregate particles
### TABLE 6

**HCPP MODEL**: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 8 (relative to splitting tensile strength of the composite)

<table>
<thead>
<tr>
<th>node</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
<th>$\sigma_3$</th>
<th>$\sigma_{\text{mean}}$</th>
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also has the highest shear stress component for the same reason. The non-spherical shape of the aggregate is responsible for the higher tensile stresses throughout the composite.

4.3 DISCUSSION

The 3-dimensional FEA undertaken here offers a complete picture of the stress distribution for these models of polymer composites. The results show that in systems with spherical aggregate the higher the packing factor the lower the magnitude of the tensile setting stresses due to the hindered shrinkage of the resin. For the FCC arrangement the magnitude of tensile mean stresses are lower than for the simple cubic arrangement.

In a simple cubic arrangement of spherical aggregate, the tensile setting stresses are highest at the resin-to-particle interface. Stress-induced microcracks are therefore likely to start at the interface and propagate throughout the resin domain. The highest shear stress components exist at the points of contact between the aggregate. It is believed that the main factor responsible for the high tensile setting stresses is the high resin content for this specific aggregate geometry (48%).

In the FCC arrangement of spherical particles compressive setting stresses arise at the points of contact between particles (node 4 and 2). The magnitude of the shear setting stresses in the FCC arrangement are relatively higher than for the SC arrangement. The highest tensile stresses exist at the center of the resin domain
which suggest that origin of possible microcracks for such a system with this aggregate geometry may start at the center of the resin domain. Analysis of results for both SC and FCC arrangements of aggregate particles suggests that the setting stresses induced in the aggregate by the inhibition of shrinkage of the resin are relatively high at the center of the aggregate.

In the HCPP arrangement the FEA analysis shows that the non-spherical shape of the aggregate causes the setting stresses to be slightly higher in magnitude compared to the FCC arrangement of spherical particles, even though the packing factor of the latter is lower (82% vs. 74%). This suggests that the aggregate shape has a very significant effect on the magnitude and distribution of setting stresses in these composites. The shape of the resin domain in the interstices is dependent on both the geometry and shape of the aggregate particles. Figure 9 shows different shapes of the resin domain for different arrangement of aggregate particles. The results suggest that the larger the resin domain in the interstices, the higher the magnitude of tensile setting stresses.

Other factors that may affect setting stresses in polymer/aggregate systems are the ratio of elastic moduli of the two components and the inherent cure shrinkage of the resin. Figure 10 shows the effect of the aggregate-to-resin modulus ratio on the setting stresses for the different analyzed geometries. It can be seen that this effect is pronounced only when the moduli of the two components approximately differ by a factor of 25 or less. For the polymer/mineral aggregate composites with moduli ratios of ca. $10^2$ that were analyzed here, changes from one mineral aggregate to another are expected to have negligible effects on setting stresses. The effect of inherent resin shrinkage on setting stresses is illustrated in
Fig. 9  Comparison of the 3-d resin domains
(a) SC arrangement of spherical particles
(b) FCC arrangement of spherical particles
(c) HCP of hexagonal, prism-shaped prisms
Fig. 10  Effect of Young's modulus ratio of aggregate to resin on setting stresses for different aggregate arrangements
Fig. 11. As the percentage of inherent shrinkage increases, the setting stresses tend to increase linearly for both SC and FCC arrangements of spherical aggregates. The nonlinear increase for the HCPP arrangement is due to the non-spherical shape of the aggregate. From the above analysis it is quite clear that the higher the packing factor of spherical aggregates the lower the average magnitude of the setting stresses in polymer composites. Both the geometric arrangement of the aggregate as well as the aggregate shape have a profound effect on the magnitude and distribution of the setting stresses. From the analysis of the HCCP model the results show that the hexagonal, prism-shaped aggregate particles introduce significantly higher tensile stresses than the spherical particles. The effect of size and shape shape of individual resin domains on the tensile setting stresses is also pronounced. Comparing the relative sizes and shapes of the resin domains in the FCC and SC arrangements, one also concludes that setting stresses are higher in the larger resin domains.
Fig. 11 Effect of inherent resin shrinkage on setting stresses for different aggregate arrangements
References


CHAPTER 5

POLYMER COMPOSITES REINFORCED

WITH MULTIPLE-SIZED PARTICLES

5.1 INTRODUCTION

In the previous chapter, we analyzed the magnitude and distribution of setting stresses in polymer composites (PC) filled with solid spherical or hexagonal prism, shaped particles of the same size, placed in orderly arrangements and found that the setting stresses depend primarily on resin content and the shape of the aggregate particles. This work was published separately as a technical paper (Boriek, 1988). This chapter examines the effects of size gradation and geometric arrangement of multiple-size spherical aggregate particles on the setting stress field of the cured composite.

As a first approach we considered the aggregate particles to be spherical and to have an orderly packing in simple cubic (SC) and face-centered cubic (FCC) arrangements of the largest particles. Due to the symmetry, inherent in these packing systems, one needs to analyze only one-sixteenth of a cube which has its
vertices passing through the center of the largest spherical particles. The boundary conditions applied in the analyzed models specify the displacement field for all the nodal points that lie on the symmetry planes. These nodal points are constrained in the perpendicular direction to the symmetry planes, Setting stresses and strains in the cured composite were simulated using the same thermal cure-shrinkage model as before in (Boriek, 1988). Three-dimensional finite element analysis was used to investigate the setting stress field using the PAFEC finite element program (PAFEC 1975, PAFEC 1986).

5.2 AGGREGATE PARTICLE GEOMETRY

As a first approximation to modeling well-packed PC systems with multiple-size aggregate we assumed that the aggregate particles are spherical and have an orderly packing, which can be analyzed in terms of a cubic lattice. Due to the symmetry inherent in these arrangements one needs to analyze only one-sixteenth of the unit cell, formed by the centers of the largest spherical particles.

Two groups of models were considered, based on the packing of the largest particles with radius \( R_a \): simple cubic (SC) and face-centered cubic (FCC). Within each model group the placement of successively smaller particles (with radii \( R_b, R_c, R_d \)) produces specific models with different packing factors and different shapes of the resin domains. Thus in the SC group, when the spaces at the body center of the unit cells are filled with the second-size (\( R_b \)) particles, the two sets of particles form a body-centered cubic pattern, in which the unit cell contains one \( R_a \) particle (eight particles in each of the corners, shared by eight adjacent
cells) and one \( R_b \) particle at the body center of the cell. This model is denoted as BC11 and has a packing factor of 62.9\%. In the next models of the SC group we place the smaller, \( R_c \) particles at the centers of the six faces of the unit cell so that the two sets of particles form a face-centered cubic pattern, in which the unit cell contains one \( (R_a) \) and 3 \( (R_c) \) particles (one \( R_c \) particle on each of the six faces shared by two adjacent cells). This is the FC13 model, which has a packing factor of 63.5\%. Suboptimal particle distributions, which contain insufficient number of \( R_c \) particles to fill all spaces on the faces of the \( (R_a) \) are modeled by systematic removal of \( R_c \) particles from either the bases or from the lateral faces of the unit cell (models FC12 and FC11). Particle distributions containing three different sizes are accommodated in the SC model group by combining the BC11 pattern with FC13, FC12, or FC11. The resulting models (BC/FC13, BC/FC12 and BC/FC11) have unit cells that contain \( R_a \) particles at the corners, \( R_b \) particles at the body center, and \( R_c \) particles on the cube faces. A fourth set of even smaller spherical particles \( R_d \) can be incorporated in the SC group by filling the interstices formed between the \( R_a \), \( R_b \), and \( R_c \) particles with smaller \( R_d \) particles. These form a simple cubic pattern of their own, which is superimposed on the patterns of the larger particles. This model is denoted as BC/FC13/SC and has a packing factor of 75.2\%.

The second group of models is based on FCC packing of the largest \( (R_a) \) particles, with the smaller \( (R_b) \) particles placed in the octahedral interstices of the \( R_a \) spheres, which gives them also an FCC arrangement. This is the FCC4 model with each unit cell containing 4 \( R_a \) and 4 \( R_b \) particles. It has a packing factor of 79\% and is characterized by high resistance to shear, due to locking of the close-
packed $R_a$ particles.

Figure 12 shows the geometric arrangement of the different spherical particles in these models. Table 7 lists the number of spheres of each size per unit cell, the corresponding packing factors (PF), calculated by dividing the total volume of the particles by the volume of the unit cell, the diameter ratios of the individual spheres, and the weight ratios of the different spheres for each model.

5.3 SHAPE OF THE RESIN DOMAIN

Each different size gradation and geometric arrangement of the aggregate particles produces resin domains with characteristic sizes and complex shapes. The intricate differences between models were used to study the effect of two major parameters on setting stresses: the relative amounts of resin and aggregate (measured simply by the packing factor) and the shape differences between the resin domains in each model. A parameter is used to characterize the shape of resin domain ($\xi_1$): this is expressed in terms of a dimensionless volume-to-surface ratio. Figure 13 shows the effect of polymer volume fraction and polymer shape factor on maximum setting stresses for the analyzed models.

The general formula for the $\xi_1$ factor is:

$$\xi_1 = \frac{\text{(volume of the polymer domain)}}{\text{(surface area of the aggregate particles)}} \times \frac{\text{(length of unit cell)}}{} (5.1)$$

Calculations of $\xi_1$ for the different analyzed models are stated in Appendix A.
Fig. 12 Schematic representation of the geometric arrangement of aggregate particles for the different analyzed models showing sections through the center of the unit cell, i.e. the cube, formed by the largest particles
TABLE 7

Characteristics of the different particle distribution models

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<th>Diameter Ratio</th>
<th>Weight Ratio</th>
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<td>1</td>
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<tr>
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<tr>
<td>BC/FC13</td>
<td>1 Rₐ at corners, 1 Rₐ at center, 3 Rₐ at faces</td>
<td>74.1%</td>
<td>1:0.586:0.414</td>
</tr>
<tr>
<td>BC/FC12</td>
<td>1 Rₐ at corners, 1 Rₐ at body center, 2 Rₐ at faces</td>
<td>70.33%</td>
<td>1:0.586:0.414</td>
</tr>
<tr>
<td>BC/FC11</td>
<td>1 Rₐ at corners, 1 Rₐ at body center, 1 Rₐ at faces</td>
<td>66.6%</td>
<td>1:0.586:0.414</td>
</tr>
<tr>
<td>BC/FC13/SC</td>
<td>1 Rₐ at corners, 1 Rₐ at body center, 3 Rₐ at faces, 4 Rₐ</td>
<td>75.2%</td>
<td>1:0.586:0.414:0.176</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B. FCC Packing of Largest (Rₐ) Particles</th>
<th>Packing Factor</th>
<th>Diameter Ratio</th>
<th>Weight Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC*</td>
<td>4 Rₐ in FCC packing</td>
<td>74%</td>
<td>1</td>
</tr>
<tr>
<td>FCC4</td>
<td>4 Rₐ in FCC packing, 4 Rₐ in octahedral sites Rₐ particles (also FCC)</td>
<td>79.3%</td>
<td>1:0.414</td>
</tr>
</tbody>
</table>

* Analyzed in chapter 4.
Figure 13  Effect of Polymer Volume Fraction and Polymer Shape Factor on Maximum Tensile Stresses

\[ y = 0.26274 + 2.4817x \quad R^2 = 0.684 \]

\[ y = 6.3297e-2 + 1.1555x \quad R^2 = 0.748 \]
5.4 RESULTS AND DISCUSSION

5.4.1 BC11 MODEL

Table 8 lists the principal setting stress values at selected nodes of this model as a fraction of the splitting tensile strength † with their locations shown in Figure 14. It shows a significant decrease in the setting stresses throughout the composite when compared to a system containing only the $R_a$ particles in a SC arrangement (table 4). The maximum principal tensile setting stress at the center of the $R_a$ particle is reduced by more than 57% of its value for the SC model * . This reduction is mainly due to the lower volume fraction of the resin (0.36 vs 0.48 in the SC model). The tensile stresses at the interface of the $R_a$ particles (nodes 7, 10, 11, 12) ‡ have also decreased significantly. Node 9, however, has a higher shear stress than the SC model. Nodes 16, 17, 18 and 19 have relatively high tensile stresses since they are located at the interface between the resin and the $R_b$ particle.

† Since the setting stresses in the resin are tensile in nature they were normalized throughout this paper on the basis of the tensile strength of the composite, which is easily determined by splitting tensile measurements. We used a PC system based on unsaturated polyester/styrene as our model for both resin cure shrinkage and tensile strength of the composite.

* Since PC in general deform and break macroscopically in a brittle mode. Since the setting stresses are tensile in nature, we chose to evaluate the maximum tensile stresses to determine which locations in these composites are likely to originate cracks.

‡ The stresses at all interfacial nodes have two values (on the resin and the aggregate phases). We report here the higher stresses.
### TABLE 8

BC11 Model: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 14 (relative to splitting tensile strength of the composite)

<table>
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<th>$\sigma_3$</th>
<th>$\sigma_{\text{mean}}$</th>
<th>$\tau_{\text{max}}$</th>
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<tbody>
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<td>.272</td>
<td>.089</td>
<td>.253</td>
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<td>.411</td>
<td>.394</td>
<td>.364</td>
<td>.390</td>
<td>.024</td>
</tr>
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</table>

** largest value of mean nodal tensile stress
*** maximum nodal shear stress
Fig. 14  Graphical representation of the composite elements of the BC11 models
The BC11 model differs from the previously analyzed system with single-size particles in SC arrangement (Boriek, 1988) by the inclusion of the $R_b$ particle into the unit cell. In order to illustrate the effect of two particle sizes on the setting stresses we compare the nodal normalized maximum setting stresses in the BC11 model with the corresponding nodal points with a composite reinforced with single size particles (SC) that was analyzed in the previous chapter. The BC11 model shows significantly lower stresses than the SC arrangement. A major factor is undoubtedly its lower resin content (36 vs. 48% for single-particle SC) since the setting stresses are generated in the resin domains. However, the presence of the smaller, $R_b$ particles alters the shape of the resin domain, lowering the tensile stresses in the corresponding nodal points of the SC model. The tensile stresses at the interface of the $R_a$ particles (nodes 7, 10, 11, 12) have also decreased significantly. Node 8, however, has a higher shear stress than in the SC model. Nodes 16, 17, 18 and 19 have relatively high tensile stresses since they are located at the interface between the resin and the $R_b$ particle.

5.4.2 FC13, FC12 AND FC11 MODELS

Table 9 lists the normalized principal setting stresses of the FC13 model at selected nodes, with their locations shown in Figure 15. The packing factor for FC13 is 62% (resin volume fraction 0.38). It is interesting to compare the setting stresses we considered the maximum principal stress as the failure criterion throughout this analysis. We used a polyester PC system as our model for both the resin cure shrinkage (8%) and splitting tensile strength (8.59 \times 10^6 \text{ N/m}^2).
TABLE 9
FC13 Model: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 15 (relative to splitting tensile strength of the composite)

<table>
<thead>
<tr>
<th>node</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
<th>$\sigma_3$</th>
<th>$\sigma_{\text{mean}}$</th>
<th>$\tau_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.270</td>
<td>0.204</td>
<td>0.025</td>
<td>0.166</td>
<td>0.123</td>
</tr>
<tr>
<td>2</td>
<td>0.269</td>
<td>0.016</td>
<td>-0.123</td>
<td>0.054</td>
<td>0.196</td>
</tr>
<tr>
<td>3</td>
<td>0.433</td>
<td>0.417</td>
<td>0.396</td>
<td>0.415*</td>
<td>0.041</td>
</tr>
<tr>
<td>4</td>
<td>0.278</td>
<td>0.159</td>
<td>0.109</td>
<td>0.182</td>
<td>0.085</td>
</tr>
<tr>
<td>5</td>
<td>0.373</td>
<td>0.001</td>
<td>-0.104</td>
<td>0.030</td>
<td>0.239</td>
</tr>
<tr>
<td>6</td>
<td>0.155</td>
<td>0.035</td>
<td>-0.329</td>
<td>-0.060</td>
<td>0.222</td>
</tr>
<tr>
<td>7</td>
<td>0.320</td>
<td>0.240</td>
<td>0.130</td>
<td>0.230</td>
<td>0.095</td>
</tr>
<tr>
<td>8</td>
<td>0.311</td>
<td>0.145</td>
<td>-0.267</td>
<td>0.053</td>
<td>0.289**</td>
</tr>
<tr>
<td>9</td>
<td>0.217</td>
<td>0.076</td>
<td>-0.205</td>
<td>0.029</td>
<td>0.211</td>
</tr>
<tr>
<td>10</td>
<td>0.434</td>
<td>0.271</td>
<td>0.132</td>
<td>0.279</td>
<td>0.151</td>
</tr>
<tr>
<td>11</td>
<td>0.336</td>
<td>0.259</td>
<td>0.132</td>
<td>0.242</td>
<td>0.102</td>
</tr>
<tr>
<td>12</td>
<td>0.378</td>
<td>0.215</td>
<td>0.125</td>
<td>0.239</td>
<td>0.127</td>
</tr>
<tr>
<td>13</td>
<td>0.423</td>
<td>0.312</td>
<td>0.214</td>
<td>0.316</td>
<td>0.105</td>
</tr>
<tr>
<td>14</td>
<td>0.311</td>
<td>0.174</td>
<td>0.021</td>
<td>0.169</td>
<td>0.145</td>
</tr>
<tr>
<td>15</td>
<td>0.336</td>
<td>0.241</td>
<td>0.045</td>
<td>0.207</td>
<td>0.146</td>
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<tr>
<td>16</td>
<td>0.421</td>
<td>0.403</td>
<td>0.386</td>
<td>0.403</td>
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<tr>
<td>17</td>
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<td>0.416</td>
<td>0.395</td>
<td>0.379</td>
<td>0.397</td>
<td>0.019</td>
</tr>
<tr>
<td>19</td>
<td>0.415</td>
<td>0.390</td>
<td>0.378</td>
<td>0.394</td>
<td>0.019</td>
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<td>0.398</td>
<td>0.376</td>
<td>0.395</td>
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<td>0.146</td>
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<td>0.194</td>
<td>0.045</td>
<td>0.199</td>
<td>0.105</td>
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<tr>
<td>24</td>
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<td>0.401</td>
<td>0.385</td>
<td>0.399</td>
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</tr>
<tr>
<td>25</td>
<td>0.424</td>
<td>0.413</td>
<td>0.386</td>
<td>0.408</td>
<td>0.019</td>
</tr>
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<td>26</td>
<td>0.451</td>
<td>0.316</td>
<td>0.169</td>
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<td>0.141</td>
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<tr>
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<td>0.432</td>
<td>0.421</td>
<td>0.391</td>
<td>0.414</td>
<td>0.021</td>
</tr>
</tbody>
</table>

* highest value of mean tensile stress
** maximum shear stress
Graphical representation of the composite elements of the FC13 model
stresses of this model with the BC11 since the resin contents in the two models are similar (0.38 and 0.36 respectively) but their resin domains have substantially different shapes. Even though the resin volume fraction in the FC13 model is slightly lower, the tensile setting stresses at Node 3 are higher and the shear stresses lower. Note that Node 3 lies at the center of the resin domain in the FC13 model but is the center of the \( R_b \) particle in BC11. The maximum principal setting stresses at the interface between resin and \( R_c \) particles (Nodes 4, 13, 17, 21 and 22) are significantly lower than the corresponding stresses at the interface between resin and the \( R_d \) particles (Nodes 10, 11 and 12).

Tables 10 and 11 list the normalized principal setting stresses in the FC12 and FC11 models, with node locations shown in Figures 16 and 17 respectively. Since these two models are derived from FC13 by selective removal of certain \( R_c \) particles, we can compare the stress values at corresponding nodes, which are located at the particle/polymer interface in FC13, but within the resin domain in the other two models. In general the overall stress level in a particular model increases significantly with the resin volume fraction. In addition, the magnitude of local setting stresses depend on the location of the individual nodal points. These are higher when a node lies at a particle/resin interface than when it is at the resin interior. For example Node 13 which is at the interface in FC13 has normalized maximum principal stress of 0.423. This value decreases slightly in FC12 where Node 13 lies in the resin interior (despite the slight increase in resin volume fraction) and increases greatly in FC11, where the resin content is higher and Node 13 lies at a particle/resin interface.
TABLE 10

FC12 Model: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 16 (relative to splitting tensile strength of the composite)

<table>
<thead>
<tr>
<th>node</th>
<th>$\sigma_1$</th>
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<th>$\sigma_3$</th>
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* highest value of mean tensile stress
** maximum shear stress
**TABLE 11**

FC11 Model: Magnitude of tensile and shear components of the setting stresses acting on
the nodal points of Figure 17 (relative to splitting tensile strength of the composite)

<table>
<thead>
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<th>Node</th>
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* highest value of mean tensile stress
** maximum shear stress
Graphical representation of the composite elements of the FC12 model
Fig. 17 Graphical representation of the analyzed composite element of the FC11 model
5.4.3 BC/FC13, BC/FC12 AND BC/FC11 MODELS

These models contain particles of three different sizes in each unit cell. Their analyzed elements are shown respectively in Fig. 18, 19 and 20 with normalized setting stresses listed in tables 12, 13, and 14. Model BC/FC13 has the lowest resin content (25.9%). The other two models are constructed by selective removal of $R_c$ particles and contain more resin (30.6 and 33.4%).

In general, the setting stresses in these multizize particle models are lower than the corresponding stresses in models with similar resin contents but fewer particle gradations. Compare for example model BC/FC13 (three-size particles), with the previously analyzed (Boriek, 1988) FCC model having single-size particles, shown in Figure 7 and Table 5. Both models contain 26% resin but the setting stresses in BC/FC13 are significantly lower. Similar (but less pronounced) trends can be observed by comparing BC/FC11 (33.4% resin, three-size particles) with BC11 (36% resin, two-size particles). These results indicate that the subdivision of the resin domains effected by particle gradation serves to lower setting stresses. Comparison of the stresses at specific nodal points in models with the same geometry but with different particle gradations demonstrates that the stress at a given node has a high tensile value when the node lies at the resin/particle interface. The tensile setting stresses are lower when the node occurs in the resin interior, become minimal when the node is at the particle center, and change to compressive at the points of contact between particles. The maximum principal compressive stresses are not critical in PC systems. This is because their compressive strength is almost an order of magnitude higher than their tensile strength.
Fig. 18 Graphical representation of the analyzed composite element of the BC/FC13 model
Fig. 19. Graphical representation of the analyzed composite element of the BC/FC12 model.
Fig. 20 Graphical representation of the analyzed composite element of the BC/FC11 model
TABLE 12

BC/FC13 Model: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 18 (relative to splitting tensile strength of the composite)

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* highest value of mean tensile stress
** highest value of mean compressive stress
*** maximum shear stress
TABLE 13

BC/FC12 Model: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 19 (relative to splitting tensile strength of the composite)

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* highest value of mean tensile stress
** maximum shear stress
TABLE 14

BC/FC11 Model: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 20 (relative to splitting tensile strength of the composite)

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* highest value of mean tensile stresses
** highest value of mean compressive stresses
*** maximum shear stress
5.4.4 BC/FC13/SC AND FCC4 MODELS

These two models contain the largest number of particles per unit cell (9 and 8 respectively) and have the lowest resin contents among the analyzed models (25 and 21%). They also show the lowest setting stresses (Figs. 21 and 22, Tables 15 and 16). In BC/FC13/SC the low resin content is achieved by the use of four different size particles to fill much of the space created by the relatively inefficient SC packing of the largest \( R_d \) spheres. In FCC4 the close packing of both sets of particles yields the lowest resin content with only two different size particles.

5.5 DISCUSSION

Figure 23 shows a plot of the maximum setting stresses in each of the analyzed models plotted against the volume ratios of aggregate to resin. There is a general trend for models with multiple particle size gradation and efficient packing arrangement to give composites with lower setting stresses. This is not surprising since the cure shrinkage forces that produce setting stresses are generated in the resin domains. However, several models depart considerably from this trend. Systems with a single particle size (such as FCC) or with deliberately introduced packing defects (such as BC/FC12) show relatively high setting stresses despite their low resin contents. Conversely, systems that are very efficiently packed (such as FCC4) or that use multiple size gradations to reduce resin content (such as BC/FC13 and BC/FC13/SC) show relatively low setting stresses (Compare, for instance, the setting stresses of FCC and BC/FC13, both with about the same
Fig. 21 Graphical representation of the analyzed composite element of the BC/FC13/SC model
Fig. 22. Graphical representation of the composite elements of the FCC4 model.
TABLE 15

BC/FC13/SC Model: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 21 (relative to splitting tensile strength of the composite)

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* highest value of mean tensile stresses
** highest value of mean compressive stresses
*** maximum shear stress
TABLE 16

FCC4 Model: Magnitude of tensile and shear components of the setting stresses acting on
the nodal points of Figure 22 (relative to splitting tensile strength of the composite)

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** highest value of mean tensile stresses
\(\dagger\) highest value of mean compressive stresses
\(\ddagger\) maximum shear stress
Fig. 23. Effect of Volume Ratio of Aggregate to Resin on Maximum Setting Stresses
volume ratio of aggregate to resin (2.85)). The common characteristic of the systems with low setting stresses is the subdivision of the resin content of each unit cell into a large number of small domains. In an effort to assess the additional contribution of this characteristic (along with resin content) to the lowering of setting stresses, we have plotted in Figure 24 the maximum setting stress in each system against the number of resin domains per unit cell divided by resin volume fraction (volume occupied by resin divided by the total volume of the composite). The fit of the individual points onto the regression line shows a remarkable improvement over Figure 23. It is noteworthy that the particle size gradation of well-packed systems with low setting stresses (such as BC/FC13 and BC/FC13/SC) falls within the ASTM C33 grading specification for fine aggregates for use in concretes. This is not the case for the FCC4 model in which the high packing factor is due primarily to the close packing of the largest \( R_a \) spherical particles. However, this type of close packing cannot be achieved with commercial mineral aggregate, where individual particles depart progressively from spherical shape and uniform size as they become larger.

In general these models show that the use of properly graded and closely packed spherical particles in a PC system can at best reduce the setting stresses by a factor of 2. In commercial systems, where the shape as well as gradation of the aggregate particles depart from ideality, the expected improvement in strength with multigraded fillers is not as high. Nevertheless, in previous experimental work, the flexural strengths of two PC systems, one filled with multigraded sand (packing factor is 0.73), the other filled with Ottawa sand of uniform particle size (packing factor is 0.54) were found to be \( 2.460 \times 10^7 \, N/m^2 \) (Burleson, 1978) and
Fig. 24  Effect of Volume Fraction and Number of Resin Domains on Maximum Setting Stresses
2.17×10^7 \text{ N/m}^2 (Burleson, 1974) respectively. Assuming the flexural strength of the stress-free material to be ca. 3×10^7 \text{ N/m}^2, the use of multigraded aggregate causes a 45% reduction in peak setting stresses, in good agreement with the prediction of this work.

The foregoing analysis of different models of graded aggregate particles in PC systems has also shown that the maximum tensile setting stresses invariably occur at the resin/particle interface. This is not surprising in view of the large mismatch in both the elastic modulus and Poisson's ratio between the resin and aggregate particles. Consequently, it is important to formulate the different PC systems so as to insure good adhesion between resin and mineral aggregate. * Within the constraints of these models (i.e. regularly packed spherical particles) the most effective means for lowering setting stresses is efficient packing and proper gradation of the reinforcing particles.

* This is usually achieved in practice by chemical additives, which act as coupling agents between the inorganic filler and organic resin (e.g. silane coupling agents).
References


D., Burleson J., 1974. unpublished data


CHAPTER 6

A REALISTIC MODEL FOR PARTICLE REINFORCED

POLYMER COMPOSITES

6.1 INTRODUCTION

The PC models analyzed in the previous chapters, which consider orderly arrangements of perfectly spherical aggregate particles in the composite, give an idealized representation of the PC systems. Actual composites (such as polymer concrete) usually employ mineral aggregate, consisting of solid particles that deviate considerable from ideal spheres. In this chapter we introduce a more complex model based on a fairly random arrangement (FRA) of quasi-spherical particles. This model gives a more realistic representation of the actual PC systems.

6.2 THE FAIRLY RANDOM ARRANGEMENT (FRA) MODEL

PC systems are usually reinforced with aggregate particles (sand, gravel, mineral fillers, etc.) which are generally irregular in shape, but may be approxi-
mated as spheroids. The size distribution of these particles is usually within the ASTM C33 grading specification and covers a broad range. We introduce here a realistic model of the actual composites: it contains quasi-spherical and quasi-ellipsoidal particles ranging within the ASTM C33 size gradation; they are packed in arrangements that are almost random but retain some rudimentary spatial order in that smaller particles usually occupy the spaces between the larger particles. We call this model the fairly random arrangement (FRA). The criteria used in constructing the FRA model are: a) the particles are quasi-spherical or quasi-ellipsoidal in shape. b) they occupy more than 50% of the space with the largest particles touching each other. c) for systems with relatively high packing factors, the particles sizes range over an order of magnitude. The characteristics of the FRA models are shown in Table 17. Figure 25 shows a unit cell ‡ which is a representative cross-section of a volume element for a two-phase PC system at the end of the curing process. The composite is structured from this unit cell by extending it repeatedly in two-dimensions to form a lattice. Figure 26 shows the finite element network of 1656 isoparametric elements and 4015 nodes for the FRA example which is shown in Figure 25. Thus the FRA model represents a random cross section through the thickness of an actual composite.

6.3. RESULTS: FRA VS SPHERICAL AGGREGATE MODELS

‡ The requirement of symmetric cell model is essential because it provides a logically sound microstructural model which reduces the information necessary to predict realistically setting stresses distribution in PC systems.
## TABLE 17

**CHARACTERISTICS OF THE FRA MODELS**

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<th>Weight ratio of aggregate particles †</th>
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<td>(FRA-78)</td>
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</table>

† normalized on the smallest particle weight.
Figure 26  The Finite Element Network of the FRA Model
(1656 elements and 4015 nodes)
The previously analyzed PC models, which contained spherical aggregate particles packed in ordered geometric patterns may be considered to be "ideal" PC systems. In these systems the setting stresses were kept to a minimum by maximizing the aggregate-to-resin ratio and minimizing the size of individual resin domains by optimum size gradation of the aggregate: each particle of smaller size would fit exactly into the interstices formed by the geometric arrangement of the larger particles. The FRA model by its very nature is expected to fall short of these optimal conditions. In this section we examine the setting stresses developed in FRA models with different volume ratios of aggregate to resin and compare the results with the setting stresses, calculated for "ideal" models with corresponding aggregate-to-resin ratios.

6.3.1. THE FRA-65 THROUGH FRA-86 MODELS

In order to investigate both volume ratio of aggregate to resin and size distribution of the aggregate particles on the magnitude and distribution of setting stresses, we constructed six different FRA models. This was accomplished by replacing particular aggregate domains in the FRA-86 model by resin domains. These models are shown in Figures 28 through 33. Tables 18, 19 and 20 show the magnitude of setting stresses acting on the nodal points of a sample volume in these models (Figure 27). In general the higher the volume ratio of aggregate to resin the lower the setting stresses. However, the maximum setting stress in the FRA-71 model is higher than the FRA-69 model. This is because the FRA-69 model has a broader distribution of the aggregate sizes.
Figure 27  Schematic representation of sample representative elements of FRA models
Figure 28  Schematic representation of the FRA-86 model
Figure 29  Schematic representation of the FRA-82 model
Schematic representation of the FRA-78 model
Figure 31  Schematic representation of the FRA-71 model
Figure 32  Schematic representation of the FRA-69 model
Schematic representation of the FRA-65 model
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**TABLE 18**

FRA-65 and FRA-86 Models: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 27 (relative to splitting tensile strength of the composite)
TABLE 19

FRA-69 and FRA-82 Models: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 27
(relative to splitting tensile strength of the composite)

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<td>.3550</td>
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<tr>
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<tr>
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<td>.4058</td>
<td>.4571</td>
<td>.4255</td>
<td>.3543</td>
<td>.4295</td>
<td></td>
</tr>
</tbody>
</table>
In all these models setting stresses are higher at the interface between the resin and the aggregate particles and lower at contact points between the reinforcing particles. Models that represent a composite with an efficiently packed particles (such as FRA-86 model) do have the lowest setting stresses among the analyzed models. On the other hand, models that represent composites with a poorly packed reinforcing particles (such as FRA-65 model) do have the highest setting stresses among the analyzed models. Any significant increase in the volume ratio of aggregate to resin may result in a significant decrease in tensile setting stresses at the interior of the resin domains or at the interface between the resin and the aggregate particles. However, this may result in an insignificant change in setting stresses at the contact points between particles. It is noteworthy that high value of volume ratio of aggregate to resin may not be enough to obtain low setting stresses. The composite has to be reinforced with a broad size distribution of the efficiently packed particles. For example, in models FRA-71 and FRA-69, setting stresses are higher in FRA-71 model despite the higher volume ratio of aggregate to resin.

The size gradation of the reinforcing particles may also affect the setting stresses in these composites. We have analyzed models with different size gradations and note that the broader the size distribution of the particles the lower the setting stresses. For example Models FRA-82 and FRA-86 have the lowest setting stresses among the FRA analyzed models.
6.3.2 CORRESPONDING SPHERICAL AGGREGATE MODELS

The symmetry inherent in the previously examined "ideal" models of geometrically arranged spherical particles has facilitated the three dimensional analysis of the setting stresses in these models. The introduction of randomness in the more realistic FRA models does away with three-dimensional symmetry. Consequently the FRA model is two-dimensional, representing a given cross-section of the actual composite. Figure 34 shows the finite elements of the representative symmetric module of the spherical aggregate. This network contains 528 isoparametric elements‡ and 1991 nodes.

In order to achieve a proper comparison between the setting stresses calculated in selected FRA models and the corresponding perfect sphere models with the same aggregate -to-resin ratio, we conducted a plane strain analysis of three perfect sphere models: BC/SC, FC13/SC, and BC/FC13/SC. In the BC/SC model, the largest particles are arranged in a simple cubic pattern. The spaces at the body center of the unit cell are filled with the second size \(R_b\) particles. A third set of even smaller particles \(R_d\) fill the interstices formed between \(R_a\), \(R_b\) particles. The \(R_d\) particles form a simple cubic pattern on their own. This model is denoted BC/SC and has a packing factor of 69%. In the FC13/SC model, The

‡ The isoparametric elements have proven to be remarkably efficient in two-dimensional elastic analysis. The elements are called isoparametric since the same (iso) local coordinate parametric equations (interpolation functions) used to define any quantity of interest within the elements are also utilized to define the global coordinates of any point within the element in terms of the global special coordinates of the nodal points (Akin, 1982).
Figure 3.4 The Finite Element Network of the Spherical Aggregate Model (528 elements and 1991 nodes)
largest particles in this model (the $R_a$ particles) and a smaller set of particles ($R_c$) are arranged in a face-centered cubic pattern, in which the unit cell contains one ($R_a$) and 3 ($R_c$) particles. A third set of even smaller particles ($R_d$) fills the interstices between ($R_a, R_c$) particles. The ($R_d$) particles for a simple cubic pattern on their own. We denote this model as FC13/SC model. The arrangement of the reinforcing particles in the BC/FC13/SC model is discussed in chapter 5. Figure 33 shows the a network of 528 isoparametric elements and 1991 nodal points of the representative symmetric module of the spherical aggregate models.

Tables 21 through 23 list the normalized principal stresses of these models at selected nodes, with their locations shown in Figure 35 through 37 respectively. In BC/SC model, the stresses at the interfacial nodal points (Nodes 1, 2, 5, 11, 13, 16, and 20) are significantly higher than the stresses at the interior of the resin domain. The stresses in this model are significantly higher than the FRA-71 model.

For the FC13/SC model, the maximum setting stresses at the interface between the resin and the aggregate particles (Nodes 1, 2, 5, 11, 13, 16, 17, 18, and 19) are significantly higher than the stresses at the interior of the resin domains. The maximum stresses in this model is significantly lower than FRA-78 model. Both of these models have identical packing factor. In the FRA-78 model the reinforcing particles are arranged in a fairly random arrangement. The size distribution of the reinforcing particles in the FRA-78 model is different from the one in the FC13/SC model.
<table>
<thead>
<tr>
<th>Node</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
<th>$\sigma_3$</th>
</tr>
</thead>
<tbody>
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<td>.1241</td>
<td>.2403</td>
</tr>
<tr>
<td>2</td>
<td>.2143</td>
<td>.1036</td>
<td>.2237</td>
</tr>
<tr>
<td>3</td>
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<td>.0281</td>
<td>.0299</td>
</tr>
<tr>
<td>4</td>
<td>.0429</td>
<td>.0273</td>
<td>.0260</td>
</tr>
<tr>
<td>5</td>
<td>.2041</td>
<td>.0508</td>
<td>.2006</td>
</tr>
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<td>6</td>
<td>.0437</td>
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<td>.1966</td>
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<td>8</td>
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</tr>
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<td>9</td>
<td>.1942</td>
<td>.0402</td>
<td>.1927</td>
</tr>
<tr>
<td>10</td>
<td>.0496</td>
<td>.0277</td>
<td>.0286</td>
</tr>
<tr>
<td>11</td>
<td>.2270</td>
<td>.1324</td>
<td>.2392</td>
</tr>
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<td>12</td>
<td>.1962</td>
<td>.0469</td>
<td>.1958</td>
</tr>
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<td>13</td>
<td>.2226</td>
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<tr>
<td>20</td>
<td>.2143</td>
<td>.0764</td>
<td>.2135</td>
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</table>

**TABLE 21**

BC/FC13/SC Model: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Fig. 35 (relative to splitting tensile strength of the composite)
### TABLE 22

BC/SC Model: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 36 (relative to splitting tensile strength of the composite)

<table>
<thead>
<tr>
<th>Node</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
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</tr>
</thead>
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<td>0.2432</td>
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<td>2</td>
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<td>0.2328</td>
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<td>3</td>
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<td>0.0403</td>
<td>0.0388</td>
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<tr>
<td>4</td>
<td>0.0644</td>
<td>0.0410</td>
<td>0.0390</td>
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<tr>
<td>5</td>
<td>0.2102</td>
<td>0.0804</td>
<td>0.2271</td>
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<tr>
<td>6</td>
<td>0.0523</td>
<td>0.0461</td>
<td>0.0364</td>
</tr>
<tr>
<td>7</td>
<td>0.2258</td>
<td>0.0551</td>
<td>0.2236</td>
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<tr>
<td>8</td>
<td>0.0506</td>
<td>0.0392</td>
<td>0.0332</td>
</tr>
<tr>
<td>9</td>
<td>0.2209</td>
<td>0.0484</td>
<td>0.2195</td>
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<tr>
<td>10</td>
<td>0.0551</td>
<td>0.0337</td>
<td>0.0329</td>
</tr>
<tr>
<td>11</td>
<td>0.2564</td>
<td>0.1493</td>
<td>0.2698</td>
</tr>
<tr>
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<td>0.2213</td>
<td>0.0524</td>
<td>0.2209</td>
</tr>
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<td>0.1950</td>
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<td>0.2124</td>
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<td>0.0528</td>
<td>0.2209</td>
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<td>0.0452</td>
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<td>0.0461</td>
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<td>0.0432</td>
<td>0.0432</td>
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<tr>
<td>25</td>
<td>0.0756</td>
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</table>
TABLE 23

FC13/SC Model: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 37 (relative to splitting tensile strength of the composite)

<table>
<thead>
<tr>
<th>Node</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
<th>$\sigma_3$</th>
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<td>0.3049</td>
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<td>0.2979</td>
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<td>0.0577</td>
</tr>
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<td>4</td>
<td>0.0759</td>
<td>0.0528</td>
<td>0.0475</td>
</tr>
<tr>
<td>5</td>
<td>0.2688</td>
<td>0.0753</td>
<td>0.2623</td>
</tr>
<tr>
<td>6</td>
<td>0.0932</td>
<td>0.0613</td>
<td>0.0572</td>
</tr>
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<td>7</td>
<td>0.2779</td>
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<td>0.2758</td>
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<td>0.3331</td>
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<td>0.2768</td>
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<td>0.2492</td>
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<td>0.2647</td>
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<td>0.3220</td>
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<td>0.0823</td>
<td>0.0632</td>
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<td>0.0864</td>
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<td>0.0637</td>
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<tr>
<td>26</td>
<td>0.1969</td>
<td>0.1919</td>
<td>0.2794</td>
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</table>
Figure 35  A Two-Dimensional Representation of the BC/FC1/SC Model
Figure 36  A Two-Dimensional Representation of the BC/SC Model
Figure 37 A Two-Dimensional Representation of the FC13/SC Model elements of FRA models
For BC/FC13/SC model, setting stresses at interfacial points (Nodes 1, 2, 5, 7, 9, 11, 12, 13, 15, ... and 20) are significantly higher than stresses at the interior of the resin domain (Nodes 3, 4, 6, 8, 10 and 14). The level of maximum setting stresses in this model is significantly lower than FRA86 model where the aggregate particles are quasi spherical and quasi-ellipsoidal in shape and arranged in a fairly ordered fashion. It is noteworthy that the size distribution of the BC/FC13/SC model is very different from the FRA-86 model.

6.4 EMPIRICAL EQUATION FOR MAXIMUM SETTING STRESSES

In Chapter 3, we introduced a general expression for the parameters affecting in PC systems (equation 3.6). These parameters are: (a) the relative amounts of resin and aggregate in the composite, (b) geometric arrangement of aggregate particles (c) the elastic modulus of the polymer and aggregate respectively, (d) Poisson's ratio of the resin, (e) aggregate shape and size distribution of aggregate particles, (f) adhesion between the aggregate and resin, (g) the inherent cure shrinkage of the resin, (i) the degree of polymerization of the resin, and (j) the (possible) presence of voids (air bubbles) and their distribution in the composite.

A general empirical equation for the maximum setting stresses in polymer composites reinforced with different sizes of aggregate particles is developed here based on the results obtained from three-dimensional finite element analysis for different models in previous work (Boriek, 1988 and Boriek, 1989). Use of this equation allows us to predict the maximum setting stresses in polymer composite systems reinforced with multiple sizes of spherical particles arranged in an orderly fashion. This equation can also be used to predict maximum setting stresses in PC
systems reinforced with quasi-spherical or quasi-ellipsoidal particles arranged in a fairly random manner.

The prediction of maximum setting stresses depends on the availability of material parameters such as the elastic moduli and Poisson’s ratios for both resin and aggregate, and the inherent cure shrinkage of the resin. The composite is assumed to be isotropic. Also both the resin and aggregate are expected to respond elastically to the generated setting stresses. Perfect adhesion between resin and aggregate is also assumed as well as isotropic cure-shrinkage forces within the resin, which develop uniformly throughout the composite. We have ignored any thermal stresses generated by temperature changes during the cure of the resin. The distribution of the setting stresses is assumed to be uniform through the bulk of the cured composite. The resin was assumed to complete its curing process to a three-dimensional polymer network. This equation is applicable only to void-free systems.

$$\sigma_{max, rel} = \zeta e^{(V_{resin})} V_{resin/agg} (g(\alpha), S_w) \sum_{k=0}^{3} \psi_k (g(\alpha), S_w) \beta^k, \quad (6.1)$$

where:

$$\sigma_{max, rel} = \text{maximum principal tensile setting stress in the PC as a fraction of the tensile strength of the composite.}$$

$$\psi_k (g(\alpha), S_w) = \text{functions depending on size distribution (\alpha), geometric arrangement (g) and shape of the aggregate particles;}$$
\( S_w \) (where \( S_w \) is the weighted average of \( S_r \), the ratio of the minor to major axes of aggregate particles).

\[ v_{\text{resin}} = \text{Poisson's ratio of the cured resin.} \]

\[ \zeta = \text{inherent shrinkage of the resin (in volume \%)} \]

\[ V_{\text{resin/agg}}(g(\alpha), S_w) = \text{resin to aggregate volume ratio in the composite. This ratio is uniquely defined for each geometric arrangement and size distribution of a given shape of aggregate particles.} \]

\[ \beta = \text{logarithmic value of the ratio of respective tensile moduli of aggregate and resin.} \]

The least-square technique was used to compute the \( \psi_k(g(\alpha), S_w) \) for the different analyzed models.

### 6.4.1 PRACTICAL USE OF THE EMPIRICAL EQUATION

Table 24 shows the computed values for \( \psi_k(g(\alpha), S_w) \) for different PC systems reinforced with an ordered arrangement (SC and FCC models) as well as a fairly random arrangement of aggregate particles (FRA-86 model). These values can be used to predict the magnitude of the maximum setting stresses in these systems under the previously stated assumptions. The equation can be applied to any PC system reinforced with aggregate particles. The volume fraction, size distribution and geometric arrangement of the reinforcing particles determines unique values for \( \psi_k(g(\alpha), S_w) \) for a particular PC system.
TABLE 24

Computed Values of $\psi(g(\alpha), S_w)$ for Different Models

<table>
<thead>
<tr>
<th>Model</th>
<th>$V_{f,\text{resin}}^\dagger$</th>
<th>$\psi_1(g(\alpha), S_w)$</th>
<th>$\psi_2(g(\alpha), S_w)$</th>
<th>$\psi_3(g(\alpha), S_w)$</th>
<th>$\psi_4(g(\alpha), S_w)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>0.48</td>
<td>2.45279</td>
<td>5.45786</td>
<td>-3.34282</td>
<td>0.78352</td>
</tr>
<tr>
<td>FCC</td>
<td>0.260</td>
<td>3.76812</td>
<td>8.75806</td>
<td>-4.66523</td>
<td>0.87585</td>
</tr>
<tr>
<td>BC/FC13/SC</td>
<td>0.248</td>
<td>3.0972</td>
<td>-2.9354</td>
<td>7.5653</td>
<td>-2.1774</td>
</tr>
<tr>
<td>FRA–86</td>
<td>0.140</td>
<td>5.1305</td>
<td>13.1551</td>
<td>-6.5167</td>
<td>2.1365</td>
</tr>
</tbody>
</table>

$^\dagger V_{f,\text{resin}}$ is the volume fraction of the resin in the composite.
Assuming that the volume ratio of resin to aggregate, the size distribution of the aggregate particles and the shape of the particles, materials properties (Poisson's ratio, modulus of elasticity and inherent shrinkage of the resin) are known, one can determine which system is the closest to the actual composite so the proper choice of the values of $\psi_k(g(\alpha), S_w)$ can be done. These values are dependent only on geometric arrangement, size distribution and shape of the reinforcing particles. For example, a composite system based on unsaturated polyester/styrene and reinforced with Ottawa sand which is quasi-spherical and the volume fraction of the resin is 14% and the size distribution of the particles falls within the ASTM C33 standard system. The maximum setting stresses for a system with the previous characteristics are estimated according to the developed equation to be 33.86% of the splitting tensile strength of the composite. This can be used to estimate the maximum load that can be applied to the composite system before fracture.

6.5 LEAST SQUARES FORMULATION

In order to reduce the influence of errors in the data one can use a greater number of data points than the number of unknowns. The resulting problem is to solve an overdetermined linear system i.e. to find a vector $x \in \mathbb{R}^n$ such that $Ax$ is the best approximation to the known vector $b \in \mathbb{R}^m$, where $A \in \mathbb{R}^{m \times n}$ and $m > n$. This is formulated as the least squares problem.

The least-square technique can be used to solve for $\psi_k(g(\alpha), S_w)$. In this case, this technique is usually used to minimize the $l_2$ norm of the error vector $(A \psi - y)$, which means that we obtain the closest vector of the space spanned by
the columns of \( A \) to the vector \( y \). We assume that \( r = b - Ax \), where \( r \) is the vector of the residuals of \( x \). The residual of a least squares solution is orthogonal to the subspace and is represented as follows:

\[
R(A) = \{ Ax | x \in \mathbb{R}^n \},
\]

(6.2)

thus, the right hand side \( b \) is decomposed into two orthogonal components

\[
b = Ax + r,
\]

(6.3)

where \( r \) is perpendicular to \( Ax \). The range space of \( A \), \( R(A) \), is a space of dimension \( \geq \) minimum \( (k, n) \). The decomposition of \( b \) is always unique, even when the least squares solution \( x \) is not unique (Lawson, 1974 and Bjorck, 1987). The problem can be formulated as follows:

\[
\begin{aligned}
\text{minimize} & \quad || A \psi(g(\alpha), S_w) - y ||_2, \quad A \in \mathbb{R}^{k \times n}, \quad y \in \mathbb{R}^n, \\
\end{aligned}
\]

(6.4)

and,

\[
|| r ||_2 = || A \psi(g(\alpha), S_w) - y ||_2,
\]

(6.5)

where \( || r ||_2 \) is the Euclidian vector norm defined by \( || r ||_2 = \sqrt{\sum r^2_i} \). If \( A \) has linearly independent columns, that is, if \( x \neq 0 \) implies \( Ax \neq 0 \), then the matrix
$A^T A$ is nonsingular $\dagger$. Equation (6.4) represents a linear least squares problem and $\psi(g(\alpha), S_w)$ is the linear least squares solution of the system $\| A \psi(g(\alpha), S_w) - y \|_2$. In this technique, the sum of the squares of the residual is minimized. The entries of matrix $A$, the vector $\psi(g(\alpha), S_w)$, and the vector $y$ are defined as follows:

$$
A = \begin{bmatrix}
\beta_1 V_{\text{resin/agg}} & \beta_1 V_{\text{resin/agg}} & \cdots & \beta_1 V_{\text{resin/agg}} \\
\beta_2 V_{\text{resin/agg}} & \beta_2 V_{\text{resin/agg}} & \cdots & \beta_2 V_{\text{resin/agg}} \\
\vdots & \vdots & \ddots & \vdots \\
\beta_n V_{\text{resin/agg}} & \beta_n V_{\text{resin/agg}} & \cdots & \beta_n V_{\text{resin/agg}} \\
\end{bmatrix}
$$

$$
\psi(g(\alpha), S_w) = \begin{bmatrix}
\psi_1(g(\alpha), S_w) \\
\vdots \\
\psi_k(g(\alpha), S_w)
\end{bmatrix}, \text{ and}
$$

$$
y = \begin{bmatrix}
\sigma_{\text{max, rel}_1} \\
\sigma_{\text{max, rel}_2} \\
\vdots \\
\sigma_{\text{max, rel}_n}
\end{bmatrix}
$$

$\dagger$ The square matrix $A$ is nonsingular if it has an inverse $A^{-1}$ satisfying the relation: $A^{-1} A = A A^{-1} = I_n$. Otherwise, $A$ is said to be singular.
6.5.1 LEAST SQUARES SOLUTION: QR DECOMPOSITION

The QR decomposition is used to solve the above least square problem. The method was originally introduced by Francis (Francis, 1962/1962). If we assume that $A \in \mathbb{R}^{m \times n}$, $b \in \mathbb{R}^m$ and if we let $Q \in \mathbb{R}^{m \times m}$ be an orthogonal matrix. The following equation is true since the orthogonal transformation preserve the Euclidean length. It follows that the $l_2$ of the residuals can be expressed by the following equation:

$$||Ax - b||_2 = ||Q^T(A\psi(g(\alpha), S_w) - y)||_2,$$  \hspace{1cm} (6.6)

and hence the following is the equivalent least squares problem

$$\text{minimize}_{\psi(g(\alpha), S_w) \in \mathbb{R}^n} ||Q^TA\psi(g(\alpha), S_w) - Q^Ty||_2,$$  \hspace{1cm} (6.7)

which is equivalent to equation (6.4).

6.5.2 ERROR ANALYSIS: FRA AND BC/FC13/SC MODELS

Figure 38 shows the residuals plotted against the maximum setting stresses for the FRA-86 model. We note that the residuals are closest to zero for the smallest values of the stresses. This indicates that the empirical equation is best for low values of setting stresses in this specific model. The dispersion of the res-
iduals is greater for the values of normalized setting stresses in excess of 0.30. The residuals for a given range of normalized stresses do not appear to be significantly imbalanced by sign.

Fig 39 shows the residuals are plotted against the normalized setting stresses for the BC/FC13/SC model. The residuals can be contained in an horizontal band except for point A which is considered an outlier. This indicates that the equation works pretty well for composites reinforced with multiple-sized spherical particles.

6.6 DISCUSSION

In this chapter we have analyzed two types of composites are analyzed: (1) systems based on fairly random arrangement of reinforcing quasi-spherical or quasi-ellipsoidal particles. (2) systems based on ordered arrangements of spherical particles. Figure 40 shows a plot of the maximum setting stresses in both types of the composites plotted against the volume ratios of the aggregate to resin. Setting stresses in the FRA models are significantly higher than the corresponding stresses in models reinforced with spherical particles arranged in ordered fashion. Compare for example, FRA-69 and FC13/SC models, which have the same aggregate to resin ratio and slight differences in the size distribution of their reinforcing particles. Models with orderly arrangement of perfect spherical particles have

‡ An outlier is an extreme observation. Residuals that are considerably larger in absolute values than others, say three or four standard deviations from the mean, are potential outliers (Montgomery, 1982).
The Distribution of the Residuals in the FRA Model

Figure 39
significantly lower stresses than composites reinforced with quasi spherical and quasi-ellipsoidal particles arranged in a fairly random arrangement pattern.

In general, both types of composites have the same trend, the setting stresses are lower for models with multiple size gradation and efficient packing of the reinforcing particles of the composite. Model FRA-69, however, has a slightly lower maximum setting stresses than FRA-71 model. The reinforcing particles have a broader size distribution in the FRA-69 model. The maximum setting stresses occur at the interface between the resin and the aggregate particles, indicating the importance of resin/aggregate adhesion. The minimization of setting stresses can be achieved by using systems reinforced with proper size gradation of spherical particles packed in an efficient manner to reduce the volume ratio of resin to aggregate, which reduce setting stresses in these composites.
References


CHAPTER 7

VOIDS DISTRIBUTION IN POLYMER COMPOSITES

7.1 INTRODUCTION

The PC systems examined in the previous chapters consist of two phases, the polymerized resin, and the reinforcing aggregate particles. We are considering here systems which contain three phases: polymer, aggregate, and voids. In PC systems, voids are generated by two main factors: (1) poor wetting of the aggregate particles by the resin, and (2) air entrainment in the raw polymer composite. Since poor wetting of the aggregate particles by the resin would severely decrease the strength of the cured composite, current formulations include coupling agents that promote resin-aggregate adhesion and virtually eliminate surface voids. However, air entrainment is a constant problem in composite manufacturing processes, occurring usually originally when the resin is still in the liquid phase. Consequently the resulting voids are quasi-spherical in shape and are located within the resin domains.

Most composite manufacturing processes include degassing steps by vibration or vacuum. These procedures usually eliminate the larger voids. However,
small voids (ca. 1 mm or smaller in size) have sufficiently low buoyancy for the surface tension forces to keep them trapped inside the resin. In the cured composite these voids are zero-strength domains, often initiating the formation of cracks and aiding the propagation of cracks. Hence, their presence is highly undesirable. In this study we analyze the effect of small spherical voids on the magnitude of setting stresses in PC systems with a fairly random arrangement. Three main factors are considered: void content and location within the resin domain as well as the overall resin content of the composite.

We assume maximum void contents of ca 0.02, based on experimental measurements on specially formulated PC systems.*

The FRA model is used in void containing systems. A probabilistic approach is used to determine the distribution of voids in PC systems. Fig. 41 shows the FRA model that was used here as an example for the investigation of voids distribution and their effect on setting stresses in PC systems. Particular domains which are denoted as A, B, ..., V are representative of the voids or aggregate domains depending on results obtained from a specially developed algorithm.

Vipulanadan (Vipulanadan, 1987) introduced the following formula for the volume fraction of voids in PC systems:

\[ V_{voids} = 1 - \gamma_{PC} \left[ \frac{W_{resin}}{\gamma_{resin}} + \frac{(1 - W_{resin})}{\gamma_{agg.}} \right] \]

where:

\( V_{voids} \) = the volume fraction of voids
\( W_{resin} \) = the ratio of resin weight to the total weight of polymer concrete.
\( \gamma_{PC}, \gamma_{resin}, \) and \( \gamma_{agg.} \) = densities of polymer concrete, resin and aggregate particles respectively.
This algorithm uses the probability distributions obtained from an optimization technique.

7.2 OPTIMIZATION TECHNIQUE

7.2.1 ASSUMPTIONS

The following assumptions are considered in our optimization procedure:

1. There are $m$ representative composite symmetric cells.$^\dagger$

2. Each cell consists of a resin matrix containing $n$ individual domains; each of these domains may be either an aggregate particle or a void.

3. The void/aggregate domains can be distributed in any random fashion (Figure 41 shows an example of a representative cell, where these domains are distributed in a fairly random manner.

4. The size distribution of void/aggregate domains ($v_i$, $i = 1, ..., n$) is known.

5. Voids are likely to be spherical in shape and relatively small in size.

6. In the cured composite, it is unlikely for two voids to be found in contact with each other, since they would be likely to coalesce into a single void before the resin hardened.

$^\dagger$ The requirement of symmetric cell model is essential because it provides a logically sound microstructural model which reduces the information required to introduce a fairly realistic prediction to the distribution of voids in PC systems.
Figure 41

FRA MODEL

Fairly Random Arrangement of Void/Aggregate Domains
7. The total volume fraction of voids\(^\dagger\), \(V_{\text{voids}} \in \mathbb{R}\) is known.

The probability distribution \(P \in \mathbb{R}^n\) of void/aggregate domains is computed so that:

\[
V^T P = V_{\text{voids}} \tag{7.1}
\]

where \(P\) is an \(n\)-dimensional vector whose entries are \(p_i\)'s (where \(p_i\) is the probability of domain \(i\) being a void). \(V \in \mathbb{R}^n\) is an \(n\)-dimensional vector whose entries are \(v_i\), \(i = 1, \ldots, n\) (where \(v_i\) are the volume ratios of void/aggregate domains normalized on the smallest domain volume) and the superscript \(T\) denotes the transpose of a vector. The probabilities \((p_i)\) can be computed using a constrained least squares technique, which can be stated in the following form:

\[
\text{minimize}_{P \in \mathbb{R}^n} \quad \left| \left( V_{\text{voids}} \right) - V^T P \right| \tag{7.2.a}
\]

subject to

\[
\epsilon^T P = 1 \tag{7.2.b}
\]

\(\dagger\) The volume fraction of voids \(V_{\text{voids}}\) is the total volume of void domains divided by the total volume of the composite. It is equal to \(\{ 1 - (\text{sum of resin volume fraction + aggregate volume fraction}) \}\). In our mathematical formulation, we assume that \(0 < V_{\text{voids}} < 1\), \(V_{\text{voids}} = 0\) indicates a composite free of voids and \(V_{\text{voids}} = 1\) indicates that the composite contains two phases: resin and voids.
0 \leq P \leq e, \hspace{1cm} (7.2.c)

where e and 0 are n-dimensional vectors whose entries are equal to unities and zeros respectively. Since it is more likely that void domains are spherical in shape and relatively smaller in size than the aggregate domains, an a priori assumption for our optimization problem is that the probability \( p_i \) is directly proportional to shape factor of the void/aggregate domains \( \zeta_i \) which can be considered as a measure for the effect of the shape of these domains on the \( p_i \). The probabilities \( p_i \)'s are inversely proportional to volume ratios of the void/aggregate domains ( \( v_i \) ) i.e.

\[
p_i \propto \frac{\zeta_i}{v_i} \hspace{1cm} i = 1, 2, ..., n. \hspace{1cm} (7.3)
\]

The shape factor \( \zeta_i \) for the domain \( i \), is directly proportional to the ratio between its minor and major axes ( \( a_i \) and \( b_i \) respectively ) i.e.

\[
\zeta_i \propto \frac{a_i}{b_i} \hspace{1cm} i = 1, 2, ..., n. \hspace{1cm} (7.4)
\]

Relations (2) and (3) can be written in the following form:

\[
p_i = \frac{a_i \theta_i}{b_i v_i} \hspace{1cm} i = 1, 2, ..., n, \hspace{1cm} (7.5)
\]
where $\theta_i$'s are specific weights to be determined. Equation (4) can be written in the following form:

$$ p_i = \frac{s_i \theta_i}{v_i}, \quad i = 1, 2, \ldots, n, \quad (7.6) $$

where $s_i$ is the ratio between the major and minor axis of domain $i$ which can be computed using information given about the geometric arrangement of these domains. Let $\theta$ be a vector of dimension $n$ whose entries are $\theta_i$, then the optimization problem can be formulated in terms of the the vector $\theta$ as follows:

$$ \text{minimize}_{\theta \in \mathbb{R}^n} \quad \left| (V_{f, \text{voids}}) - S^T \theta \right| \quad (7.7.a) $$

subject to

$$ \hat{V}^T \theta = 1 \quad (7.7.b) $$

$$ 0 \leq \theta \leq \overline{V}, \quad (7.7.c) $$

where $S$, $\hat{V}$, and $\overline{V}$ are n-dimensional vectors ‡, and their entries are $s_i$, $s_i/v_i$, and
\( v_i / s_i \) respectively. Problem (7.7) has a non-differentiable objective function. This is a disadvantage since special methods are needed to deal with the nondifferentiability. Consequently, we loose the advantage of widely used well-developed algorithms that require differentiability. For this reason, we introduce an equivalent formulation to problem (7.7), namely the linear programming formulation (LPF).

### 7.2.2. LINEAR PROGRAMMING FORMULATION

The linear programming technique was used to obtain the probability distributions of void/aggregate domains in the FRA model. The LPF can be stated as follows:

\[
\begin{align*}
\text{minimize} & \quad \lambda_1 + \lambda_2 \\
\text{subject to} & \quad \lambda_1, \lambda_2 \in \mathbb{R}
\end{align*}
\]  

(7.8)

Subject to

\[
\lambda_1 + \lambda_2 + S^T \theta = (V_{fvoids})
\]  

(7.8.a)

\( \dagger \) The entries of the vector \( \overline{V} \) can be viewed as scaled volume ratios of void/aggregate domains. When the domain is nearly spherical in shape, the factor \( s_i \) will be close to unity. This would not affect the value of the probability. However, when the shape of the domain is far from sphericity, \( s_i \) will be smaller than unity which would increase the scaled volume ratio of this particular domain and hence decrease its probability of being a void.
\[ \lambda_1 \geq 0 \]  
\[ \lambda_2 \geq 0 \]  
\[ \hat{V}^T \theta = 1 \]  
\[ 0 \leq \theta \leq \bar{V}, \]

Appendix B presents the LPF for the QPSOL. For our problem, the linear programming technique gives unsatisfactory results. For this reason we introduce an equivalent formulation, namely the quadratic programming formulation (QPF).

### 7.2.3 THE QUADRATIC PROGRAMMING FORMULATION (QPF)

The QPF of our problem can be stated in the following form:

\[
\text{minimize} \quad -2 \left( V_{\text{voids}} \right)^T \theta + \frac{1}{2} \theta^T \left( 2SS^T \right) \theta 
\]

subject to

\[ \hat{V}^T \theta = 1 \]

The QPSOL is a set of subroutines which are designed to locate a minimizer of a quadratic function subject to linear constraints and simple upper and lower bounds on the variables (Gill, 1984). A subroutine was written to call the QPSOL. This subroutine is listed in APPENDIX E.
where \((2SS^T)\) is the Hessian matrix \((H)^*\) of the objective function in \((7.9.a)\). \(H\) is symmetric and its entries are \(H_{i,j} = a_i a_j / b_i b_j\), \(i, j = 1, ..., n\). In the above problem the Hessian matrix is singular. In fact, this is a rank-one matrix that has only one positive eigenvalue which is equal to \((2S^T S)\), and the other \(n-1\) eigenvalues are zero. The QPF consists of a convex quadratic objective function in \((7.9.a)\), which is minimized over a compact constraint set \(\{ \theta \in \mathbb{R}^n : \nabla^T \theta = 1, 0 \leq \theta \leq \bar{V} \}\). Since the objective function is convex, each local solution is a global one and since it is minimized over a compact set, the solution exists (Apostol, 1974). However, the solution is not unique. A modification of the QPF is needed to enforce the uniqueness of the solution on our problem. The Hessian matrix has to be perturbed to force the positive definiteness property\(^\dagger\). This can be accomplished by adding a small value \(\varepsilon^2\) to the diagonal entries of the Hessian. The smallest possible \(\varepsilon\) is slightly larger than the magnitude of the most negative eigenvalue of \(\nabla^2 f(x)\).

\(^*\) A continuously differentiable \(f : \mathbb{R}^n \rightarrow \mathbb{R}\) is said to be twice continuously differentiable at \(x \in \mathbb{R}^n\), if \(\partial^2 f / \partial x_i \partial x_j\) exists and is continuous, \(1 \leq i, j \leq n\); the Hessian of \(f\) at \(x\) is then defined as the \(n \times n\) matrix whose \(i, j\) element is:

\[
\nabla^2 f(x)_{ij} = \frac{\partial^2 f(x)}{\partial x_i \partial x_j}, \quad 1 \leq i, j \leq n.
\]

The Hessian is always symmetric as long as \(f\) is twice continuously differentiable. If the Hessian matrix of \(F\) is constant, \(F\) is said to be a quadratic function. In this case, \(F\) can be expressed as:

\[
F(x) = \frac{1}{2} x^T G x + c^T x + \alpha
\]

where \(G\) is a constant matrix, \(c\) is a vector and \(\alpha\) is a scalar.

\(^\dagger\) The positive definiteness of the Hessian of the objective function guarantees the existence of a unique solution over the compact feasible region \(\{ \theta \in \mathbb{R}^n : \nabla^T \theta = 1, 0 \leq \theta \leq \bar{V} \}\).
A simpler algorithm was introduced by Dennis (Dennis, 1983) that may result in a larger $\varepsilon$. Dennis calculated an upper bound $b_1$ on $\varepsilon$ using the Gerschgorin circle theorem * and since

$$b_2 = \max_{1 \leq i \leq n} \{ d_{ii} \}$$

is also an upper bound on $\varepsilon$, Dennis chose $\varepsilon$ so it satisfies the criteria: $\varepsilon = \min \{ b_1, b_2 \}$. This approach leads to the following modified quadratic formulation (MQPF).

### 7.2.4 The Modified Quadratic Programming Formulation

The MQPF can be stated as follows:

$$\begin{align*}
\text{minimize} & \quad -2 \langle V_{f \text{voids}} \rangle S^T \theta + \frac{1}{2} \theta^T (2 S S^T + \varepsilon I) \theta \\
\text{subject to} & \quad \hat{V}^T \theta = 1
\end{align*} \tag{7.10}$$

---

* Let $A \in \mathbb{R}^{n \times n}$ be symmetric with eigenvalues $\lambda_1$, ..., $\lambda_n$. Then

$$\begin{align*}
\min_{1 \leq i \leq n} \lambda_i & \geq \min_{1 \leq i \leq n} \{ a_{ii} - \sum_{j=1, j \neq i}^{n} |a_{ij}| \}, \\
\max_{1 \leq k \leq n} \lambda_k & \geq \max_{1 \leq k \leq n} \{ a_{kk} + \sum_{j=1, j \neq k}^{n} |a_{kj}| \}.
\end{align*}$$

It follows from this theorem that if $A$ is a strictly diagonally dominant, then $A$ is a positive definite.
\[ 0 \leq \theta \leq \overline{V}. \]  
\tag{7.10.c}

In (7.10.a), if \( \varepsilon \) is chosen properly the MQPF would consist of a strictly convex quadratic objective function. This function is minimized over a linear constraint and simple upper and lower bounds. A unique solution can be found using the QPSOL. In order to study the behavior of \( \varepsilon \) in the MQPF, one has to introduce an equivalent formulation using the model trust-region strategy. This strategy is one of the most successful globalization techniques in constrained optimization. The main idea of this strategy is to add a ball constraint which restricts the size of the step taken by the algorithm (El-Alem, 1988). This approach leads to the so-called trust-region quadratic programming formulation (TRQPF).

7.2.5 TRUST-REGION QUADRATIC PROGRAMMING FORMULATION

The TRQPF for our problem can be stated as follows:

\[
\text{minimize}_{\theta \in \mathbb{R}^n} - 2 \langle V_{\text{voids}} \rangle S^T \theta + \frac{1}{2} \theta^T (2 S S^T) \theta
\tag{7.11.a}
\]

subject to

\[ \hat{V}^T \theta = 1 \]  
\tag{7.11.b}

\[ 0 \leq \theta \leq \overline{V} \]  
\tag{7.11.c}

\[ ||\theta||_2 \leq \delta, \]  
\tag{7.11.d}
where $|| \cdot ||_2$ designate the $l_2$ norm and $\delta$ is a positive constant represents the radius of the trust region, which depends on $\varepsilon^\dagger$. In the formulation of problem (7.10), the choice of $\varepsilon$ affects the behavior of the solution. Very large values of $\varepsilon$ cause either numerical ill-conditioning in the problem, which would decrease the accuracy of the numerical solution, or inconsistency of the hyperplane (7.11.b) and the trust region ball (7.11.d). Consequently, the feasible region will be empty (Appendix-C). The value of $\varepsilon$ has to be chosen sufficiently large that the Hessian matrix is safely positive definite (Dennis, 1983).

### 7.3 REALIZATION OF VOIDS DISTRIBUTION ALGORITHM

The solution of the MQPF provides a set of probabilities for each distinct value of the volume fraction of voids ($V_{f_voids}$) in the representative composite cell of the FRA model of a PC system. An algorithm is developed to determine the distribution of void domains in PC system based on the probability distributions of voids (PDV’s). This algorithm is implemented in a computer program which is written in C language (See Appendix E). Different experimental values for the total volume fraction of the voids have been employed in the algorithm. For each particular range of values for the volume fraction of the voids, there is a corresponding specific voids distribution. For a certain volume fraction of the voids, the computed probabilities for domains $v_1$, $v_2$, ..., $v_n$ which satisfy the objective function of the nonlinear optimization problem, are sorted in descending order.

$\dagger$ Large values of $\varepsilon$ is an indication that the size of the trust region ($\delta$) is small and vis-versa.
The corresponding volumes for each domain are arranged in the same order. The sum of the volumes of \( k \) domains which have the highest probabilities is used to decide whether or not the domain \( i \) is a void. The volume fraction of these domains should be less or equal to the value for the given volume fraction of voids. Since voids tend to lower their surface energies, it is unlikely that two voids are in contact. A data file was written in a form of a square matrix with entries of 0 or 1. These data provide information about the contact between each domain and other domains. It also provides information about which of the domains lies on the symmetry plane. An entry of 1 is an indication that domain \( i \) is in contact with domain \( j \). If any of the diagonal entries of the matrix has the value 1, then domain \( i \) lies on a symmetry plane. Two tests are performed. The first examines whether domain \( i \) is in contact with any of the \( v_1, \ldots, v_{i-1} \). If there is a contact between \( v_i \) and any of the previous domains, the algorithm will consider the domain with the smaller probability to be an aggregate particle. The other test verifies that none of the voids lie on the symmetry plane of the model, since this mean that the voids are in contact. The domains which satisfy the above conditions will be considered voids. So the algorithm ensures that these possible void domains do not touch the boundary of the representative unit cell of the composite and do not touch each other. A selective models with different distributions of voids and different voids volume fraction will be examined later for their effect on the magnitude and distribution of setting stresses. These models based on a fairly random arrangement of aggregate particles.

For each range of the assumed values of the volume fraction of the voids there is a specific voids distribution associated with it. For each distribution of the
voids the state of stress was analyzed so one can realize the effect of the distribution of these voids on the setting stress distribution in PC systems.

The computer program results show four distinct size distributions of voids in these composites, depending on the computed PDV's. The volume fractions of voids in these models \( V_{f,\text{voids}} \) are in the range between 0.003 and 0.023%. Figures 42 and 43 show a two-dimensional and three-dimensional representation of the PDV's obtained for this range of voids volume fractions. Table 25 shows void locations for the different analyzed FRA models. Figures 44 (a, b, c, and d) show representative elements of voids containing models for different voids distributions as well as different volume ratios of aggregate to resin.

7.4 FEA OF VOIDS CONTAINING SYSTEMS

We have used the same finite element network developed in the previous chapter for the FRA example. A plane strain analysis is considered *. The modeling of void domains could be done by removing the finite elements of the void domain. Alternatively we can assign a fictitious, very low modulus of elasticity to the elements of the void. The second approach is adopted in this analysis. The computer program PAFEC (PAFEC, 1986, Henshell, 1975) is used as the FEA code to solve for the setting stress field. This field is simulated by means of the thermal shrinkage model introduced previously in chapter 3.
TABLE 25

LOCATIONS OF THE VOID DOMAINS IN THE (FRA−V_{resin})_{N_v} MODELS

<table>
<thead>
<tr>
<th>MODEL</th>
<th>Volume fraction of voids</th>
<th>Relative size of voids*</th>
<th>Domain content</th>
</tr>
</thead>
<tbody>
<tr>
<td>(FRA−.133)_0</td>
<td>0.0</td>
<td>0.0</td>
<td>A through T are aggregate</td>
</tr>
<tr>
<td>(FRA−.133)_1</td>
<td>0.0031</td>
<td>0.0128</td>
<td>J is a void</td>
</tr>
<tr>
<td>(FRA−.133)_2</td>
<td>0.0063</td>
<td>0.0128, 0.0135</td>
<td>M and J are voids</td>
</tr>
<tr>
<td>(FRA−.133)_4</td>
<td>0.0141</td>
<td>0.0128, 0.0135, 0.0145, 0.0175</td>
<td>M, J, V and L are voids</td>
</tr>
<tr>
<td>(FRA−.133)_5</td>
<td>0.0186</td>
<td>0.0128, 0.0135, 0.0145, 0.0175, 0.0189</td>
<td>M, J, V, L and G are voids</td>
</tr>
<tr>
<td>(FRA−.347)_0</td>
<td>0.0</td>
<td>0.0</td>
<td>A, B, D, E, G, H, J, M, L, K, V, O, P, Q, R, S, T, U are resin domains</td>
</tr>
<tr>
<td>(FRA−.347)_1</td>
<td>0.0031</td>
<td>0.0128</td>
<td>A, B, D, E, G, H, M, L, K, V, O, P, Q, R, S, T, U are resin domains J is a void domain</td>
</tr>
<tr>
<td>(FRA−.347)_2</td>
<td>0.0063</td>
<td>0.0128, 0.0135</td>
<td>A, B, D, E, G, H, L, K, V, O, P, Q, R, S, T, U are resin domains M and J are void domains</td>
</tr>
<tr>
<td>(FRA−.347)_4</td>
<td>0.0141</td>
<td>0.0128, 0.0135, 0.0145, 0.0175</td>
<td>A, B, D, E, G, H, K, O, are resin domains M, J, V and L are void domains</td>
</tr>
<tr>
<td>(FRA−.347)_5</td>
<td>0.0186</td>
<td>0.0128, 0.0135, 0.0145, 0.0175, 0.0189</td>
<td>A, B, D, E, H, K, O, P, Q, R, S, T, U are resin domains M, J, V, L and G are voids</td>
</tr>
</tbody>
</table>

* as a fraction of the largest size of the reinforcing aggregate particles.
Probability Distributions of Possible Void Domains for Different Voids Volume Fractions

Figure 42
Probability Distribution of Voids

Figure 43
Different size distributions of voids in specific FRA models are examined for their effect on both the magnitude and distribution of setting stresses. These models are characterized by their resin content (expressed as the volume fraction of resin in the composite, occupied by resin \( V_{\text{resin}} \)) and by the number of voids per unit cell, \( N_{\text{voids}} \). Individual models are designated by the actual values of these parameters. Thus \( (\text{FRA}-0.133)_{4} \) designate a composite with a 0.133 resin volume fraction and 4 voids per unit cell. The characteristics of several FRA models of a well-packed composite are shown in Table 26. It is noteworthy that these models represent well packed systems with the same resin volume fraction (0.133) but different volume ratios of resin to aggregate.

7.5 RESULTS

7.5.1 EFFECT OF OVERALL RESIN CONTENT \( V_{\text{resin}} \)

In chapter 6 we have established a baseline of void-free composites. We have computed the setting stresses of two void-free FRA models with low and high resin volume fraction respectively: FRA-65 and FRA-86. The results show that the magnitude of setting stresses increases with increasing resin content.

To assess the effect of \( V_{\text{resin}} \) on setting stresses in the presence of voids, two

* As is well-known, when the axis perpendicular to the \( x-y \) plane is denoted by \( z \), the plane strain condition can be expressed as \( \varepsilon_{z} = \frac{\partial w}{\partial z} = 0 \) and \( \sigma_{z} = \nu (\sigma_{x} + \sigma_{y}) \), where \( w \) is the displacement component in the \( z \) direction, \( \varepsilon_{z} \) denotes the strain in the same directions and \( \sigma_{x}, \sigma_{y}, \sigma_{z} \) are the stress components.
### TABLE 26

**CHARACTERISTICS OF THE \((FRA-V_{\text{resin}})_{N}\) MODELS**

<table>
<thead>
<tr>
<th>MODEL ((FRA-.133)_N)</th>
<th>Volume ratio of aggregate to resin</th>
<th>Packing factor</th>
<th>Weight ratio of aggregate particles ‡</th>
</tr>
</thead>
</table>

**volume of reinforcing aggregate particles to the total volume of the composite.**

‡ normalized on the smallest particle weight.
systems with different values of packing factors and two identical distribution of voids are analyzed. Comparing stresses of the \((FRA-.347)\) and \((FRA-.347)_1\), one would find that at nodal points 1, 9, 11, 13, 15 the setting stresses are lower in the model with a single void. Now compare the setting stresses in both \((FRA-.133)\) and \((FRA-.133)_1\) models. The maximum setting stresses in the voids-free model is slightly higher at Nodes 2, 4, 6, 8, 10 and 14 which gives an indication that introducing a single void in close-packed systems is likely to cause insignificant relief of setting stresses. However, a single void per unit cell in poor packed systems may significantly relieve setting stresses in the surrounding resin domains.

Now, consider systems with different values of \(V_{\text{resin}}\) and same high \(V_{f_{\text{voids}}}\). For example \((FRA-.347)_5\) and \((FRA-.133)_5\) models. The setting stresses are higher in the first one (e.g. Nodes 2, 3, 4, 5, 7, 8, 10, ..., and 15 have significantly higher stresses). This is due to the high value of resin volume fraction. We can also observe that both of these systems demonstrate lower tensile setting stresses than the corresponding voids-free systems. This difference in stresses is more pronounced for poorly packed systems.

7.5.2 VOIDS DISTRIBUTION EFFECT

In Table 27, the two models \((FRA-.133)_1\) and \((FRA-.133)_5\) are analyzed to study the effect of a low value of \(V_{f_{\text{voids}}}\) in well-packed PC systems. In comparing the maximum setting stress trends around a particular void domain along a
### Table 27

(FRA-.133)_1 and (FRA-.133)_5 Models: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 44 (a) and (b) respectively (relative to splitting tensile strength of the composite).

<table>
<thead>
<tr>
<th>Node</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
<th>$\sigma_3$</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
<th>$\sigma_3$</th>
</tr>
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<td>1</td>
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<td>.1722</td>
<td>.1856</td>
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<td>.3003</td>
<td>.3400</td>
<td>.2774</td>
<td>.3345</td>
</tr>
<tr>
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<td>.1143</td>
<td>.2380</td>
<td>.2458</td>
<td>.1245</td>
<td>.2431</td>
</tr>
<tr>
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<td>.3226</td>
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<td>.3574</td>
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<tr>
<td>5</td>
<td>.1765</td>
<td>.1123</td>
<td>.1729</td>
<td>.1395</td>
<td>.1075</td>
<td>.1340</td>
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<tr>
<td>7</td>
<td>.3231</td>
<td>.2072</td>
<td>.3022</td>
<td>.2987</td>
<td>.1686</td>
<td>.2789</td>
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<td>.2033</td>
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<td>.2729</td>
<td>.2258</td>
<td>.2628</td>
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<tr>
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<td>.2163</td>
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<td>.2025</td>
</tr>
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<td>.1375</td>
<td>.2545</td>
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<tr>
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<td>.1422</td>
<td>.2628</td>
<td>.2797</td>
<td>.1595</td>
<td>.2687</td>
</tr>
</tbody>
</table>
particular void domain along a particular path for the (FRA−.133)₁ model, one finds that the distribution of the average maximum setting stresses follow the same trend as (FRA−.133)₅ model despite the large difference in both the distribution and the volume fraction of the voids in these models. This is not surprising since the magnitude of stresses depends primarily on the resin volume fraction in these systems. In poorly packed systems the existence of voids relief setting stresses. The maximum stresses at the resin/aggregate interface are slightly lower than the corresponding void-free model. This difference becomes insignificant at locations away from the void. In Table 28, the two analyzed systems are (FRA−.347)₁ and (FRA−.347)₅ . The results show that the setting stresses at most of the nodal points are higher in the one with a lower voids volume fractions (e.g Nodes 1, 4, ..., 12, 14, and 15).

Figures 45 through 47 show the distribution of maximum normalized setting stresses along paths A, B, and C of Figures 27, 44(c) and 44(d) respectively. These stresses have common trend, the maximum stresses increase in the direction towards interfacial points between the different phases and they decrease away from these points. The highest stresses lie at the contact points between the three phases; resin, aggregate particles and void. The stresses in (FRA−.347)₅ are slightly lower than (FRA−.347)₁, indicating that the local stresses around the interface between a specific void domain and the resin domain may be lower when the voids volume fraction is significantly higher. Along path B, the maximum tensile setting stresses are lowest at the contact points between the aggregate particles. There are compressive stresses at the contact points between aggregate particles.
### TABLE 28

**(FRA-.347)₁ and (FRA-.347)₅ Models**: Magnitude of tensile and shear components of the setting stresses acting on the nodal points of Figure 44 (c) and (d) respectively (relative to splitting tensile strength of the composite)

<table>
<thead>
<tr>
<th>node</th>
<th>$\sigma₁$</th>
<th>$\sigma₂$</th>
<th>$\sigma₃$</th>
<th>$\sigma₁$</th>
<th>$\sigma₂$</th>
<th>$\sigma₃$</th>
</tr>
</thead>
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<tr>
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<td>.0896</td>
<td>.1001</td>
<td>.1103</td>
<td>.0976</td>
<td>.1004</td>
</tr>
<tr>
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</tr>
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<td>.4452</td>
<td>.3684</td>
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<tr>
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<td>.2979</td>
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<tr>
<td>15</td>
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<td>.3924</td>
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</tbody>
</table>
Figure 44  Schematic representation of sample representative elements of FRA models (c) (FRA-0.133)\textsubscript{1} (d) (FRA-0.133)\textsubscript{5}.

- **Aggregate**
- **Void**
- **Resin**
Figure 44  Schematic representation of sample representative elements of FRA models (c) (FRA-0.347)\(^1\) (d) (FRA-0.347)\(^5\).

Legend:

- Aggregate
- Void
- Resin
Maximum Setting Stress Distribution in a in FRA with 65% Factor Model as an Example of a Void-Free System

Figure 45
Maximum Setting Stress Distribution in FRA Model with ca. 65% Packing Factor and a Single Void Domain per Unit Cell

[Graph showing stress distribution across different paths labeled PATH A, PATH B, and PATH C.]

Figure 46
Maximum Setting Stress Distribution in FRA Model with a 65% Packing Factor and Five Void Domains per Unit Cell

Figure 47
7.6 DISCUSSION

The overall level of setting stresses is low in the resin domains surrounding the voids. The effect of voids on setting stresses depends on the volume fraction of voids and the packing factor. In poorly-packed systems, high volume fraction of voids would have more pronounced effect on setting stresses as compared to lower volume fraction of voids. In these systems setting stresses are significantly lower than void-free systems. However, for well-packed systems this effect is less pronounced, actually the stresses are affected only at nodal points that lie in the resin surrounding the voids. For nodal stresses which lie away from the void, the magnitude of maximum setting stresses are slightly lower than void-free system. The overall level of setting stresses for a composite with a high volume fraction of voids (e.g. ca. 0.023) is significantly lower than void-free systems. This is more pronounced in poorly-packed systems. For systems with a small volume fraction of voids (e.g. ca. 0.005) the overall level of setting stresses is slightly lower than void-free system. Generally, the setting stresses are at the highest level along the interface between the resin and the aggregate in both void-free and void-containing systems. The effect of voids as a setting stress relieving factor is more pronounced when these voids are located in the center of the resin domain. This effect diminishes when voids are touching the interface between the resin and the aggregate.

The volume fraction of resin has a significant effect on the magnitude and distribution of setting stresses in polymer composites. The magnitude of setting stresses increases with resin volume fraction both in the absence and presence of
voids. As a stress relieving factor the effect of voids is more pronounced in systems with high resin volume fraction.

Numerical techniques (For example, nonlinear constrained optimization) can be used for the prediction of voids distribution in polymer composite systems.
REFERENCES


Henshell, R. D., PAFEC 75 Theory, Results, PAFEC Ltd., Nottingham, (1975).


CHAPTER 8

CONCLUSIONS AND SIGNIFICANCE OF THIS RESEARCH

8.1 CONCLUSIONS

1. The higher the packing factor of spherical aggregates the lower the average magnitude of the setting stresses in the polymer composite systems.

2. The geometric arrangement of the aggregate affects significantly the magnitude and distribution of the setting stresses in polymer composites.

3. The aggregate shape has a profound effect on the magnitude and distribution of the setting stresses. Hexagonal, prism-shaped particles introduce significantly higher tensile stresses than spherical aggregate.

4. The effect of shape of the resin domain in the interstices has a pronounced effect on the tensile setting stresses. Comparing the relative sizes and shapes of the resin domains in the FCC and SC arrangements, one concludes that setting stresses are higher in the larger resin domains.
5. There is a general trend for models with multiple particle size gradation and efficient packing arrangement to develop lower setting stresses. This is not surprising since the cure shrinkage forces that produce setting stresses are generated in the resin domains. However, several models depart considerably from this trend. Systems with a single particle size (such as FCC) or with deliberately introduced packing defects (such as BC/FC12) show relatively high setting stresses despite their low resin contents. Conversely, systems that are very efficiently packed (such as FCC4) or that use multiple size gradations to reduce resin content (such as BC/FC13 and BC/FC13/SC) show relatively low setting stresses.

6. The common characteristic of systems with low setting stresses is the subdivision of the resin content of each unit cell into a large number of small domains.

7. In general these models show that the use of properly graded and closely packed spherical particles in a PC system can at best reduce the setting stresses by a factor of 2. In commercial systems, where the shape as well as gradation of the aggregate particles depart from ideality, the expected improvement in strength with multigraded fillers is not as high. Nevertheless, in previous experimental work, the flexural strengths of two PC systems, one filled with multigraded sand (packing factor 0.73), the other filled with Ottawa sand of uniform particle size (packing factor 0.54) were found to be $2.46 \times 10^7 N/m^2$ and $2.17 \times 10^7 N/m^2$ respectively. Assuming the flexural strength of the stress-free material to be ca. $3 \times 10^7 N/m^2$, the use of multigraded aggregate causes a 45% reduction in peak setting stresses, in good agreement with the prediction of this work.
8. The foregoing analysis of different models of graded aggregate particles in PC systems has also shown that the maximum tensile setting stresses invariably occur at the resin/particle interface. Consequently, it is important to formulate the different PC systems so as to insure good adhesion between resin and mineral aggregate.

9. In polymer composites voids act as stress relief. This effect is more pronounced in poorly packed systems.

10. The stress distribution around a void is independent of the value of the voids volume fraction i.e. no infractive effects.

11. The existence of a a given void volume fraction affects primarily the setting stresses in the surrounding resin domain.

12. If the volume fraction of voids is significantly high for well packed systems, the level of setting stresses will decrease slightly at locations away from the void domain. However, for poor packed systems these stresses seem to decrease not only in locations away from the void domains but in other locations near the void domain as well.

13. Probabilistic techniques are very useful in the modeling of voids distribution in polymer composites. The nonlinear constrained optimization technique that was used in the analysis of voids distribution is a method of dealing with computing the distribution of voids in polymer composites. This technique can be used for both particle and fiber reinforced polymer composites.
8.2 SIGNIFICANCE OF THIS WORK

This work contributes to the understanding of the distribution of setting stresses in particle reinforced polymer composites. It should aid the design and formulation of PC systems with lower setting stresses by means of efficient aggregate packing (lower polymer content) and proper gradation and shape of the reinforcing particles. It also recommends that proper coupling agents be used to achieve good adhesion between the resin and the mineral aggregate, since the analysis of most of the models has shown that the maximum setting stresses occur at the resin/particle interface.

This work presents the first attempt to build up three-dimensional models for particle reinforced polymer composites containing single-sized aggregate as well as multiple size particles the aggregate particles with various packing arrangements.

This work has also generated for the first time models that can be considered realistic representations of the actual composites: the FRA model. This enabled us to treat both spherical and nonspherically shaped reinforcing particles, as well as orderly and nonorderly arrangements of these particles.

Analysis of the various three-dimensional finite element models of these composites led to the formulation of a single empirical equation that will enable the prediction of maximum setting stresses for PC systems reinforced with single or different sizes of spherical or quasi spherical particles. This equation is extremely helpful in the design and formulation of PC systems. Knowledge a priori
of the magnitude of maximum setting stresses would aid the prediction of the maximum loads that can be safely applied.

A new approach in determining the size distribution of voids resulting from air bubbles was also introduced in this work. A nonlinear optimization technique was used to determine the probability distribution of void/aggregate domains in FRA models. The probability distributions of these domains was used with a specially developed algorithm to determine the voids distribution in such composite. This new technique can be used to determine voids distribution in both particle or fiber reinforced systems, which makes it a general method of determining voids distribution in polymer composites. Various models which include some of the computed distributions of the voids were examined for their effect on the magnitude and distribution of setting stresses in polymer composite. This work contributes to the understanding of the voids effect on both the magnitude and distribution of setting stresses.

The results of this work are expected to provide guidelines for optimizing the aggregate content, shape and particle size distribution of the reinforcing aggregate in polymer composites so as to minimize the magnitude of setting stresses. The minimization of setting stresses would lead to a composite with a significantly high strength.
APPENDIX A

CALCULATIONS OF THE SHAPE FACTOR ($\xi_1$)

A parameter is used to characterize the shape of resin domain ($\xi_1$): this is expressed in terms of a dimensionless volume-to-surface.

The general formula for the $\xi_1$ factor is:

$$\xi_1 = \frac{\text{volume of the polymer domain}}{\text{(surface area of the aggregate particles)} \times \text{(length of unit cell)}}$$  \hspace{1cm} (A.1)

In the SC model the packing factor is 52%. The reinforcing particles in this model have the same size. The radius of the particle is assumed to be 10 units. The resin shape factor $\xi_1$ is evaluated as follows:

The surface area of spherical particles in a unit cell ($A_s$) is:

$$A_s = 4 \pi R^2 = 4 \pi (10)^2 = 1256.63 \text{ units}^2$$  \hspace{1cm} (A.2)

The general formula for the resin volume for each packing is as follows:
volume of the resin = (volume fraction of the resin) \times (volume of the cubic cell) \tag{A.3}

\[ V_{resin} = 0.48 \times (20)^3 = 3840 \text{ units}^3 \tag{A.4} \]

\[ \xi_{1,SC} = \frac{3840}{(1256.63) \times (20)} = 0.15279 \tag{A.5} \]

Equation (1) is applied to evaluate $\xi_1$ for the SC group. The surface area for the resin domain in the FC11 model is calculated using the surface area of spherical particles in a unit cell ($A_s$).

\[ A_{s,FC11} = 4 \pi \times [R_a^2 + R_c^2] \tag{A.6} \]
\[ = 4 \pi [ (10)^2 + (4.14214)^2 ] \]
\[ = 1472.4 \text{ units}^2 \]

\[ V_{resin,FC11} = 0.44 \times (20)^3 \tag{A.7} \]
\[ = 3520 \text{ units}^3 \]

\[ \xi_{1,FC11} = \frac{3520}{(1472.4) \times (20)} = 0.1195 \tag{A.8} \]

For the FC12 model, the packing factor is 60%. The surface area of the aggregate particles $A_s$ is computed as follows:

\[ A_{s,FC12} = 4 \pi \times [R_a^2 + 2(R_c)^2] \tag{A.9} \]
\[ = 4 \pi [ (10)^2 + (4.14214)^2 ] \]
\[ = 1522.67 \]
\[ V_{\text{resin FC12}} = 0.40 \times (20)^3 = 3200 \text{ units}^3 \]  \hspace{2cm} (A.10)

\[ \xi_{1 \text{ FC12}} = \frac{3200}{(1522.67) \times (20)} = 0.1051 \]  \hspace{2cm} (A.11)

For the BC11 model the volume fraction of the resin is 36%. The surface area of the aggregate particles \( A_s \) is:

\[ A_{s \text{ BC11}} = 4 \pi \times (R_a^2 + R_b^2) \]
\[ = 4\pi [(10)^2 + (5.8578)^2] \]
\[ = 1687.84 \text{ units}^2 \]  \hspace{2cm} (A.12)

Volume of the resin domain \( V_{\text{resin}} \) is computed as follows:

\[ V_{\text{resin}} = 0.36 \times (20)^3 = 2880 \text{ units}^3 \]  \hspace{2cm} (A.13)

\[ \xi_{1 \text{ BC11}} = \frac{2880}{(1687.84) \times (20)} = 0.0853 \]  \hspace{2cm} (A.14)

For the FC13 model the volume fraction of the resin is 0.38 and the two spherical particles which are located in the interstices have the same size. \( \xi_1 \) for this model is:

\[ \xi_{1 \text{ FC13}} = \frac{[V_{\text{resin FC13}} \times (a)^3]}{4 \times (a) \times \pi \times (R_a^2 + 3R_c^2)} \]
\[ = \frac{[0.38 \times (20)^3]}{4 \times (20) \times \pi \times [(10)^2 + 3 \times (4.14214)^2]} \]
\[ = 0.07985 \]  \hspace{2cm} (A.15)
For the BC11/FC11 model the volume fraction of the resin is 66.667%. The \( \xi_1 \) for this model is calculated as follows:

\[
\xi_{1 \text{BC11/FC11}} = \frac{[V_{\text{resin}} \times (a)^3]}{4 (a) \pi (R_a^2 + R_b^2 + R_c^2)}
\]

\[
= \frac{[0.333 \times (20)^3]}{4 \pi((10)^2 + (5.8578)^2 + (4.14214)^2)}
\]

\[
= 0.07005
\]

\[
\xi_{1 \text{BC11/FC12}} = \frac{[V_{\text{resin}} \times (a)^3]}{4 (a) \pi (R_a^2 + R_b^2 + 2R_c^2)}
\]

\[
= \frac{[0.2967 \times (20)^3]}{4 \times (20) \pi((10)^2 + (5.8578)^2 + 2(4.14214)^2)}
\]

\[
= 0.05601
\]

\( \xi_1 \) for the BC11/FC13 model is calculated as follows:

\[
\xi_{1 \text{BC11/FC13}} = \frac{[V_{\text{resin BC11/FC13}} \times (a)^3]}{4 \times (a) \pi \times [R_a^2 + R_b^2 + 3R_c^2]}
\]

\[
= \frac{0.259 \times (20)^3}{4 \times (20) \pi((10)^2 + (5.8578)^2 + 3(4.14214)^2)}
\]

\[
= 0.0443
\]
for the BC11/FC13/SC model is calculated as follows:

\[
\xi_{1, BC11/FC13/SC} = \frac{[V_{resin} \times (a)^3]}{4 \pi (a^2 + R_a^2 + R_b^2 + 3R_c^2 + 4R_d^2)} \quad (A.21)
\]

\[
\xi_{1, BC11/FC13/SC} = \frac{[0.248 \times (20)^3]}{80 \pi [(10)^2 + (5.8578)^2 + 3(4.14214)^2 + 4(1.758)^2]} = 0.0398 \quad (A.22)
\]

\[
\xi_{FCC} = \frac{[0.26 \times (28.28428)^3]}{4 \times 4(28.28428) \pi (10)^2} = 0.04138 \quad (A.23)
\]

\[
\xi_{FCC4} = \frac{[0.207 \times (28.28428)^3]}{4 \times 4(28.28428) \pi [(10)^2 + (4.14214)^2]} = 0.0281 \quad (A.24)
\]
APPENDIX B

The QPSOL is used to solve the quadratic programming problem for the probabilities of the void/aggregate domains. It is a set of subroutines which are designed to locate a minimizer of a quadratic function subject to linear constraints and simple upper and lower bounds on the variables. If the quadratic function is strictly convex, a global minimizer is found; otherwise, a local minimizer is found. The following is the linear programming formulation for the QPSOL.

\[
\begin{align*}
\text{minimize} \quad & c^T \theta \\
\text{subject to} \quad & 1 \leq \begin{bmatrix} \theta \\ A \theta \end{bmatrix} \leq u,
\end{align*}
\]

Where \( c \) is a constant \( n \)-vector and \( A \) is \( m \times n \) matrix. Our problem may be formulated in the following form:

\[
\begin{align*}
\text{minimize} \quad & \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \theta_1 \\ \vdots \\ \theta_n \end{bmatrix} \\
\text{subject to} \quad & \begin{bmatrix} 1, 1, 0, \ldots, 0 \\ \theta \end{bmatrix} \leq \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \theta_1 \\ \vdots \\ \theta_n \end{bmatrix} \leq u,
\end{align*}
\]
such that

\[
\begin{bmatrix}
0 \\
\vdots \\
\vdots \\
0 \\
V_{f voids}
\end{bmatrix} \leq 
\begin{bmatrix}
\lambda_1 \\
\lambda_2 \\
\vdots \\
\theta_1 \\
\vdots \\
\theta_n
\end{bmatrix} \leq 
\begin{bmatrix}
\infty \\
\infty \\
\vdots \\
v_1 \\
v_2 \\
v_3 \\
\vdots \\
v_n \\
V_{f voids} \\
1
\end{bmatrix}
\begin{bmatrix}
1 \\
1/\nu_1 \\
\vdots \\
1/\nu_n
\end{bmatrix}
\begin{bmatrix}
1 \\
1/\nu_1 \\
\vdots \\
1/\nu_n
\end{bmatrix}
\begin{bmatrix}
\lambda_1 \\
\lambda_2 \\
\vdots \\
\theta_1 \\
\vdots \\
\theta_n
\end{bmatrix}
\begin{bmatrix}
\theta \\
A \theta
\end{bmatrix} \leq u,
\]

The following is a general form of the QPF

\[
\text{minimize } \quad c^T \theta + \frac{1}{2} \theta^T H \theta
\]

subject to

\[
\begin{bmatrix}
\theta \\
A \theta
\end{bmatrix} \leq u,
\]

where \( c \) is a constant \( n \)-dimensional vector and \( H \) is a constant \( n \times n \) symmetric matrix. \( A \) is an \( m \times n \) matrix. \( l \) and \( u \) are constant \( n \)-dimensional vectors. The QPF of our problem can be stated as follows:
\[
\text{minimize } \begin{bmatrix} -2V_{f_{\text{voids}}} & -2V_{f_{\text{voids}}} & \ldots & -2V_{f_{\text{voids}}} \end{bmatrix} \begin{bmatrix} \theta_1 \\ \theta_2 \\ \vdots \\ \theta_n \end{bmatrix} \\
+ \frac{1}{2} \begin{bmatrix} \theta_1, \theta_2, \ldots, \theta_n \end{bmatrix} \begin{bmatrix} a_1^2 & a_1a_2 & \ldots & a_1a_n \\ b_1^2 & b_1b_2 & \ldots & b_1b_n \\ a_2^2 & a_2^2 & \ldots & \cdot \\ b_2b_1 & b_2b_1 & \ldots & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ a_n^2 & a_na_2 & \ldots & a_n^2 \\ b_nb_1 & b_nb_1 & \ldots & b_nb_n \end{bmatrix} \begin{bmatrix} \theta_1 \\ \theta_2 \\ \vdots \\ \theta_n \end{bmatrix}
\]
subject to
\[
\begin{bmatrix} 0 & 0 & \cdots & 0 & 1 \\ 0 & 0 & \cdots & \cdot & 1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & \cdot & 1 \\ \end{bmatrix} \leq \begin{bmatrix} \theta_1 \\ \theta_2 \\ \cdot \\ \cdot \\ \cdot \\ \theta_n \end{bmatrix} \leq \begin{bmatrix} \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \theta_n \end{bmatrix}
\leq \begin{bmatrix} v_1 \\ v_2 \\ \cdot \\ v_n \\ 1 \end{bmatrix}.
\]
The MQPF can be stated in the following form:

$$\text{minimize} \quad c^T \theta + \frac{1}{2} \theta^T (H + \varepsilon I) \theta$$

subject to

$$1 \leq \begin{bmatrix} \theta \\ A\theta \end{bmatrix} \leq u,$$

where $\varepsilon$ is the perturbation value for the Hessian matrix ($H$), and $I$ denotes the identity matrix. The above equation can be written in the following form:

$$\text{minimize} \quad c^T \theta + \frac{1}{2} \theta^T (\overline{H}) \theta$$

subject to

$$1 \leq \begin{bmatrix} \theta \\ A\theta \end{bmatrix} \leq u,$$

where $\overline{H}$ is the modified Hessian matrix. It is the following $n \times n$ matrix:

$$\begin{bmatrix}
\frac{a_1^2}{b_1^2} + \varepsilon & \frac{a_1a_2}{b_1b_2} & \ldots & \frac{a_1a_n}{b_1b_n} \\
\frac{a_2a_1}{b_2b_1} & \frac{a_2^2}{b_1^2} + \varepsilon & \ldots & \cdot \\
\cdot & \cdot & \ddots & \cdot \\
\cdot & \cdot & \cdot & \frac{a_n^2}{b_n^2} + \varepsilon
\end{bmatrix}$$
A subroutine for the formulation of the quadratic programming problem is developed. Different simulations are considered for each value of the voids volume fraction (\( V_{f_\text{voids}} \)). For each simulation, \( \varepsilon \) is increased until a unique * global minimizer is obtained. The results are summerized in Fig. 2 where the volume fractions of the void/aggregate domains are plotted against the probabilities that these domains are voids.

* A unique solution is obtained if the output indicator of the QPSOL informs us of finding a unique global minimizer.
APPENDIX C

We consider here the behavior of the parameter $\varepsilon$ in problem (7.10) (equivalently, the radius of the trust region $\delta$ in (7.11)). Problem (7.11) can be written in the following form:

$$\text{minimize } f(\theta) \quad \text{subject to}$$

$$\hat{V}^T \theta = 1 \quad \text{(C1-a)}$$

$$\theta \leq \theta \leq \bar{V} \quad \text{(C1-b)}$$

$$\frac{1}{2} (\theta^T \theta - \delta^2) \leq 0, \quad \text{(C1-c)}$$

where $f(\theta)$ is defined as follows:

$$f(\theta) = -2 (V_{f_{voids}}) S^T \theta + \frac{1}{2} \theta^T (2S S^T) \theta. \quad \text{(C1-d)}$$

Problem (7.10) can be written as follows:

$$\text{minimize } f(\theta) + \frac{\varepsilon}{2} \theta^T \theta \quad \text{subject to}$$

$$\hat{V}^T \theta = 1 \quad \text{(C2-a)}$$
\[ 0 \leq \theta \leq \overline{V}. \]  

(C2-c)

It is convenient to introduce the Lagrangian function \( L : \mathbb{R}^n \times \mathbb{R} \times \mathbb{R}^{2n} \to \mathbb{R} \) associated with problems (C2). It can be expressed in the following form:

\[
L(\theta, \lambda, \mu) = f(\theta) + \frac{\varepsilon}{2} \theta^T \theta + \lambda (\hat{\nabla}^T \theta - 1) + \mu^T (\theta - \overline{V}) - \hat{\mu}^T \theta,
\]

where \( \lambda \in \mathbb{R} \) and \( \mu = (\overline{\mu}, \check{\mu})^T \in \mathbb{R}^{2n} \) are the Lagrange multiplier vectors. It is noteworthy that the feasible region (C2-b and C2-c) form a non empty compact set (e.g. \( \theta_i = v_i / n \, s_i, i = 1, ..., n \) is an interior point), thus the existence of at least one solution is guaranteed.

The first order necessary conditions (Fiacco, 1968) for a point \( (\theta^*, \lambda^*, \mu^*) \) to be a solution of problem C2 are as follows:

\[
\nabla f(\theta^*) + \varepsilon \theta^* + \lambda^* \hat{\nabla} + \mu^* - \hat{\mu}^* = 0
\]

(C3-a)

\[
\hat{\nabla}^T \theta^* = 1
\]

(C3-b)

\[ 0 \leq \theta^* \leq \overline{V} \]

(C3-c)

\[ \overline{\mu}^* \theta^* = 0 \]

(C3-d)

\[ \hat{\mu}^* \theta^* = 0 \]

(C3-e)
\[ \hat{\mu}^* \geq 0 \] (C3-f)

\[ \mu^* \geq 0. \] (C3-g)

Now, consider problem (C1). Its Lagrangian function is given by the following formula:

\[
L_2(\theta, \mu, \lambda) = f(\theta) + \frac{\mu_0}{2} (\theta^T \theta - \delta^2) \\
+ \lambda (\hat{\nu}^T \theta - 1) + \mu^T (\theta - \overline{\nu}) - \hat{\mu}^T \theta,
\]

where \( \mu_0 \in \mathbb{R} \) is a positive parameter depends on \( \delta \).

The first order necessary conditions for \((\theta^*, \lambda^*, \mu^*)\) to solve (C1) are:

\[ \nabla f(\theta^*) + \mu_0 \theta^* + \lambda^* \hat{\nu} + \mu^* - \hat{\mu}^* = 0 \] (C4-a)

\[ \dot{\theta}^* = 1 \] (C4-b)

\[ 0 \leq \theta^* \leq \overline{\nu} \] (C4-c)

\[ \frac{1}{2} (\theta^*^T \theta^* - \delta^2) \leq 0 \] (C4-d)

\[ \mu_0 (\theta^*^T \theta^* - \delta^2) = 0 \] (C4-e)

\[ \mu^* T (\theta^* - \overline{\nu}) = 0 \] (C4-f)

\[ \hat{\mu}^* T \theta^* = 0 \] (C4-g)
\[ \mu_o^* \geq 0 \quad \text{(C4-h)} \]

\[ \bar{\mu}^* \geq 0 \quad \text{(C4-i)} \]

\[ \hat{\mu}^* \geq 0. \quad \text{(C4-j)} \]

Since the Hessian matrix is positive definite, the trust region in problem (9), (equivalently, B1) must be active (i.e. \(|\|\theta\||_2 = \delta\)) and hence \(\mu_o > 0\). Now, consider (C1-e), we have:

\[ \nabla f(\theta) = -2 (V_{f \text{voids}}) S + 2 S S^T \theta. \]

Substituting the above equation in (C3-a), we can obtain the following equation:

\[ \theta^* = -(2S S^T + \varepsilon I)^{-1} (-2 V_{f \text{voids}} S + \lambda^* \hat{V} + \bar{\mu}^* - \hat{\mu}^*). \]

Let \(\eta(\varepsilon) = ||\theta||_2\)

\[ \eta(\varepsilon) = ||(2SS^T + \varepsilon I)^{-1} \psi||_2, \]

where \(\psi = -2V_{f \text{voids}} S + \lambda \hat{V} + \bar{\mu} - \hat{\mu}. \)

then,

\[ \eta'(\varepsilon) = - \frac{\psi (2SS^T + \varepsilon I)^{-3} \psi}{||\theta||_2}, \]

and so \(\eta'(\varepsilon) < 0\) as long as \(\psi \neq 0\). Thus \(\eta\) is a monotonically decreasing func-
tion in $\varepsilon$ which implies that $\| \theta \|_2 \propto 1/\varepsilon$. Similarly, from (C4-a), $\| \theta \| \propto 1/\mu_o$. Now as $\varepsilon \to \infty$ then, $\| \theta \|_2 \to 0$, and hence $\mu_o \to \infty$. A contradiction would arise since $\hat{\nabla}^T \theta = 1$. This indicates that for large values of $\varepsilon$ (equivalently, $\mu_o$ is large) the hyperplane (7.11.b) will not intersect with the sphere (7.11.d) which would lead to inconsistent constraints. We conclude that for a large value of $\varepsilon$ we should expect either inconsistency of the constraints or numerical ill-conditioning in the problem.
APPENDIX D

ISOTROPY

D.1 ELASTIC CONSTANTS OF AN ISOTROPIC MATERIALS

The stresses acting at a point in a solid can be represented by the stresses acting on an elemental cube at that point. There are nine stress components acting on the front faces of the elemental cube. The component \( \sigma_{ij} \) represents the force per unit area in the \( i \) direction on a face whose normal is the \( j \) direction. Rotational equilibrium requires that \( \sigma_{ij} = \sigma_{ji} \). Thus, there are only six stress components; \( i = j \) are the normal stresses while \( i \neq j \) are the shear stresses. The most generalized form, Hooke’s law can be written:

\[
\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \quad i, j = 1, 2, 3
\]

Where \( C_{ijkl} \) are the elastic constants or stiffnesses. The above equation can be written in the expanded form as follows:

\[
\begin{bmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{12} \\
\sigma_{13} \\
\sigma_{23}
\end{bmatrix} =
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{33} & C_{34} & C_{35} & C_{36} \\
C_{44} & C_{45} & C_{46} \\
C_{55} & C_{56} \\
C_{66}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
\varepsilon_{23} \\
\varepsilon_{13} \\
\varepsilon_{12}
\end{bmatrix}
\]
The $\sigma_{23}$, $\sigma_{13}$, and $\sigma_{12}$ represents the shear stresses while $\varepsilon_{23}$, $\varepsilon_{13}$, and $\varepsilon_{12}$ represent the engineering shear strains. For the case of symmetry with respect to a plane, $C_{ij}$ has 13 independent components as:

$$C_{ij} = \begin{bmatrix}
    C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\
    C_{22} & C_{23} & 0 & 0 & C_{26} \\
    C_{33} & 0 & 0 & C_{36} \\
    C_{44} & C_{45} & 0 \\
    C_{55} & 0 \\
    C_{66}
\end{bmatrix} \begin{bmatrix}
    \varepsilon_{11} \\
    \varepsilon_{22} \\
    \varepsilon_{33} \\
    \varepsilon_{23} \\
    \varepsilon_{13} \\
    \varepsilon_{12}
\end{bmatrix}$$

Where coordinate $x_3$ is a normal to the plane of symmetry. For isotropic materials where elastic properties are independent of direction, only two constants are independent for isotropic materials, reduces to:

$$\begin{bmatrix}
    \sigma_{11} \\
    \sigma_{22} \\
    \sigma_{33} \\
    \sigma_{23} \\
    \sigma_{13} \\
    \sigma_{12}
\end{bmatrix} = \begin{bmatrix}
    C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\
    C_{22} & C_{12} & 0 & 0 & 0 \\
    C_{33} & 0 & 0 & 0 \\
    C_{11} & 0 & \frac{(C_{11}-C_{12})}{2} & 0 \\
    \sigma_{13} & 0 & \frac{(C_{11}-C_{12})}{2} \\
    \sigma_{12}
\end{bmatrix} \begin{bmatrix}
    \varepsilon_{11} \\
    \varepsilon_{22} \\
    \varepsilon_{33} \\
    \varepsilon_{23} \\
    \varepsilon_{13} \\
    \frac{(C_{11}-C_{12})}{2} \varepsilon_{12}
\end{bmatrix}$$

In terms of the compliance matrix, the following relationship is valid for isotropic materials:

$$\begin{bmatrix}
    \varepsilon_{11} \\
    \varepsilon_{22} \\
    \varepsilon_{33} \\
    \varepsilon_{23} \\
    \varepsilon_{13} \\
    \varepsilon_{12}
\end{bmatrix} = \begin{bmatrix}
    S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\
    S_{11} & S_{12} & 0 & 0 & 0 \\
    S_{11} & 0 & 0 & 0 \\
    2(S_{11}-S_{12}) & 0 & 2(S_{11}-S_{12}) \\
    2(S_{11}-S_{12}) & 0 \\
    2(S_{11}-S_{12})
\end{bmatrix} \begin{bmatrix}
    \sigma_{11} \\
    \sigma_{22} \\
    \sigma_{33} \\
    \sigma_{23} \\
    \sigma_{13} \\
    \sigma_{12}
\end{bmatrix}$$
Where \( C_{11} \) and \( C_{12} \) or \( S_{11} \) and \( S_{12} \) are the independent constants.

The elastic constants which were used in this study are Young's modulus \( E \), Poisson's ratio \( \nu \), shear modulus \( G \), and bulk modulus \( K \). Only two of these are independent because \( E \), \( G \), \( \nu \), and \( K \) are interrelated:

\[
E = 2G(1 + \nu) \quad \text{and} \quad K = \frac{E}{3(1 - 2\nu)}.
\]

The relationships between these elastic constants and compliance are as follows:

\[
E = \frac{1}{S_{11}} \quad \nu = -\frac{S_{12}}{S_{11}} \quad G = \frac{1}{2} (S_{11} - S_{12}).
\]

The compliance are related to the stiffnesses as follows:

\[
S_{11} = \frac{C_{11} + C_{12}}{(C_{11} - C_{12})(C_{11} + 2C_{12})},
\]

\[
S_{12} = \frac{C_{12}}{(C_{11} - C_{12})(C_{11} + 2C_{12})}.
\]
APPENDIX E

SUPPORTING COMPUTER PROGRAMS
This Program is designed to compute the coefficients for the
Empirical Equation (6.1) which is used for the prediction of
maximum setting stresses in particle reinforced polymer composites.

NRA : # of rows of A (input)
NCA : # of columns of A (input)
A  : NRA by NCA matrix containing the coefficient matrix
of the least square system to be solved (input).
LDA : Leading dimension of A exactly as specified in the
dimension statement. (input)
B  : Vector of length NRA containing RHS of the least square system.
TOL : Scalar containing the non-negative tolerance used to determine
the subset of columns of A to be included in the solution (input)
X  : Vector of length NCA, containing the solution vector with
components corresponding to the columns not used set to zero (output)
RES : Vector of length NRA, containing the residual vector B.
KBASIS : Scalar containing the # of columns used in the solution.

QR : work vector of length nra*nca, representing an nra by nca
matrix which contains information from the QR factorization
of A. If A is not needed, QR can share the same storage locations as A
QRAUX : work vector of length nca containing information about
the orthogonal factor of the QR factorization of A.
IPUT : integer work vector of length nca containing the
pivoting information for the QR factorization of A
WORK : work vector of length 2*nca - 1

LSQRR solves the linear least squares problem.
It calculates QR decomposition with pivoting of a matrix A and
tests the diagonal elements against the supplied tolerance TOL.
The routine LSQRR is first used to compute QR decomposition of A
pivoting with all rows free, is used. The truncated least square
problem is then solved using IMSL routine LQRLS (which compute the
coordinate transformation, projection and solution for the least
square problem.

---------------------------------------------------------------------------------

implicit double precision(a-h, o-z)
dimension a(20, 4), sigovers(20), dnu(20), beta(20), zeta(20)
dimension res(20), theta(20), resagg(20)
read (*, *) nra, nca
lda = nra
tol = 10.0d-18
Do 10 i=1, nra
   Read (*, *) resagg(i), beta(i), dnu(i), zeta(i), sigovers(i)
10  continue
   do 20 i = 1, nra
      bxepnu = exp(dnu(i))*beta(i)*resagg(i)
      a(i, 1) = bxepnu
      a(i, 2) = bxepnu*zeta(i)
      a(i, 3) = bxepnu*zeta(i)**2
      a(i, 4) = bxepnu*zeta(i)**3
20  continue
Call DLSQRR (nra, nca, a, lda, sigovers, tol, theta, res, kbasis)

write(*, 22) kbasis
   format (3x, 'The number of linear independent columns = ', i2)
21  write(*, 21)
22  format (/)
   do 30 ii=1, 4
      write(*, 25) ii, theta(ii)
30  continue
   format (5x, 'theta(', i2, ', ') = ', d20.10)
31  write (*, 21)
32  sum=0.0d0
   do 40 ji=1, nra
50   write(*, 35) ji, res(ji)
35  format (5x, 'The Residual(', i2, ', ') = ', d20.10)
   computing the residuals
   res(ji) = res(ji)*res(ji)
   sum    = sum + res(ji)
   resnorm = dsqrt(sum)
40  continue
   stop
end
program intrp
C---------------------------------------------------------
c      Reads two portions of a PAFEC output file, the one describing
  the nodal locations, the other describing the nodal stresses on
  an element-by-element basis. Description of the input file format
  is in intrp.doc, which contains user instructions. A node may occur
  in more than one element, and the stresses at the node may not be
  the same in different elements. This program averages the stresses
  at each node and outputs this mean stress. The user is asked for
  the coordinates of the point at which stresses are needed, and for
  the number of nodes to be used in the interpolation of stress at
  this point. The closest nodes to the point are selected, then the
  mean stresses at these nodes are used to interpolate the stress
  at the point. The interpolation is a weighted average of the mean
  stresses at the nodes, where the weights are inversely proportional
  to the distance between the point and the node, and are normalized
  to sum to 1. The max shear at the point is calculated from the
  interpolated principal stresses at the point sptau = (sp1 - sp3)/2.
c      implicit logical (q)
c      character*30 znfile, zefile
      parameter (noddim=1000, neledi=3000)
c      integer inin(10), nn(neledi), nnum(noddim)
c      dimension d(noddim), x(noddim), y(noddim), z(noddim),
c             w(noddim), s1(neledi), s2(neledi), s3(neledi),
c             svn(neledi), sln(noddim), s2n(noddim), s3n(noddim),
c             svmn(noddim), staun(noddim)
c-----------------------------------------------------------
c      open output file

c      open(unit=3, status='unknown', file='intrp.out')
c      rewind 3
qbug = .false.
c      ask user how many nodes to use

c      print *, ' use how many nodes to interpolate stress?'
c      read *, npts
      write(3,*) ' The ', npts,
      ' closest nodes will be used'
c      write(3,*) ' to interpolate stresses at specified point.'
c      write(3,*)

c      read nodal locations

c      print *, ' node file name ?'
c      read(*, '(a30)'), znfile

c      open (unit=1, status='old', file=znfile)

c      if (qbug) write(3,*), nodal input'
nnodes = 0
5 continue
   read(1,*,end=10) i, x(i), y(i), z(i),
   k, x(k), y(k), z(k)
   if (qbug) write(3,*) i, x(i), y(i), z(i),
   k, x(k), y(k), z(k)
nodes = nnodes + 2
   if (nnodes.gt.nnodes) then
      write(*,*) ' increase noddim array size in intrp',
      write(3,*) ' increase noddim array size in intrp'
      stop
eendif
nnnum(nnodes-1) = i
nnnum(nnodes) = k
  goto 5
10 continue
   if (i.gt.k) nnodes = nnodes - 1
   if (qbug) write(3,*)' nnodes ',nnodes,' nnum ',
      (nnnum(kk),kk=1,nnodes)
close(unit=1, status='keep')
   read element-oriented stress file
   print *,' element file name?'
   read(*,'(a30)') zefile
   open(unit=2, status='old',file=zefile)
   if (qbug) write(3,*)' element input'
i = 1
7 continue
   read(2,*,end=9) ne, nn(i), sx, sy, sz,
   s1(i), s2(i), s3(i), svm(i)
   if (qbug) write(3,*) ne, nn(i), sx, sy, sz,
      s1(i), s2(i), s3(i), svm(i)
i = i + 1
   if (i.gt.neledi) then
      write(*,*) ' increase neledi array dimension in intrp',
      write(*,*) ' increase neledi array dimension in intrp'
      stop
eendif
  goto 7
9 continue
   nedat = i - 1
   if (qbug) write(3,*)' nedat ',nedat
close(unit=2, status='keep')
   scan element information to
   get avg stress at nodes
   if (qbug) write(3,*)' finding mean stress at nodes'
do 14 i = 1, nnodes
   num = nnnum(i)
   fnval = 0.0
s1n(num) = 0.0
s1n(num) = 0.0
s1n(num) = 0.0
svmn(num) = 0.0
do 15 ne = 1, neda
  if (nn(ne).eq.num) then
    fnval = fnval + 1.0
    s1n(num) = (1/fnval)*s1(ne) + s1n(num)*(fnval-1)/fnval
    s2n(num) = (1/fnval)*s2(ne) + s2n(num)*(fnval-1)/fnval
    s3n(num) = (1/fnval)*s3(ne) + s3n(num)*(fnval-1)/fnval
    svmn(num) = (1/fnval)*svmn(ne) + svmn(num)*(fnval-1)/fnval
    staun(num) = (s1n(num) - s3n(num))/2.0
    if (qbug) write(3,*), num - node number, num
    if (qbug) write(3,*), ne - line of element file, ne
    if (qbug) write(3,*), fnval, fnval, s1, s1(ne),
       s2, s2(ne), s3, s3(ne), svmn, svmn(ne), s1n, svmn, s2n, s2n(num),
       s3n, s3n(num),
       staun, staun(num)
  endif
15 continue
mean stresses at nodes output
  write(3,*), ' mean stresses at nodes'
  write(3,*), ' node s1n  s2n  s3n  svmn  staun'
300 format(1x, i4, 5(1x, g12.6))
do 65 i = 1, nnodes
   num = nn(num(i))
   write(3, 300) num, s1n(num), s2n(num), s3n(num),
            svmn(num), staun(num)
65 continue
ask user where he wants to know stress
print *, ' coordinates of point at which stress needed?'
write(3,*),
write(3,*), ' coordinates of point at which stress found'
read(*,*) xp, yp, zp
write(3,*), ' xp ', xp, ', yp ', yp, ', zp ', zp

calculate distances
if (qbug) write(3,*), ' calculating distances'
if (qbug) write(3,*), num x y z d
do 20 i = 1, nnodes
   num = nn(num(i))
   d(num) = sqrt((x(num) - xp)**2 + (y(num) - yp)**2 +
          (z(num) - zp)**2)
   if (qbug) write(3,*), num, x(num), y(num), z(num), d(num)
continue

find npts closest nodes

if (qbug) write(3,*)' finding ',npts,' closest nodes'
do 40 j = 1, npts
dmin = 1.0e3
if (qbug) write(3,*)' j ',j

loop over nodes
do 30 i = 1, nnodes
num = nnum(i)
if (qbug) write(3,*)' i ',i,' num ',num

is i a previously found closest pt?
qskip = .false.
do 50 jj = 1, j-1
if (num.eq.imin(jj)) qskip = .true.
continue
if (qbug) write(3,*)' qskip ',qskip

if i not previously found, check it against all other pts.
if (.not.qskip) then
if node num closer than all previously checked nodes on this time thru, designate it the closest node
if (d(num).lt.dmin) then
dmin = d(num)
imin(j) = num
if (qbug) write(3,*)' IMIN REDEFINED'
endif
endif
if (qbug) write(3,*)' d(num) ',d(num)', dmin ',dmin,
imin(j) ',imin(j)

continue
continue
write(3,*)' ',write(3,*) npts,' closest nodes'
write(3,*) (imin(kk),kk=1,npts)

calculate weights at 3 closest nodes
if (qbug) write(3,*)' ',if (qbug) write(3,*)' calculating raw weights'
if (qbug) write(3,*)' i num d(num) w(num)'
wtsum = 0.0
do 60 i = 1, npts
num = imin(i)
if (d(num).lt.1.0e-5) then
w(num) = 1.0e5
else
w(num) = 1/d(num)
endif
  if (qbug) write(3,*), i, num, d(num), w(num)
  wtsum = wtsum + w(num)
end
continue
if (qbug) write(3,*), wtsum
continue
if (qbug) write(3,*), calculating normalized weights
  if (qbug) write(3,*), num, w
    do 70 i = 1, npts
      num = imin(i)
      w(num) = w(num)/wtsum
    end
    if (qbug) write(3,*), num, w(num)
    continue
    calculate interpolated stress at point
    if (qbug) write(3,*), stresses and weights at closest nodes
      if (qbug)
        .write(3,*), i, num, s1n, s2n, s3n, svmn, w
      do 75 i = 1, npts
        num = imin(i)
        if (qbug) write(3,*),
          i, num, s1n(num), s2n(num), s3n(num), svmn(num), w(num)
        continue
        if (qbug) write(3,*), interpolating stress at specified point
          if (qbug) write(3,*), intermediate results
            if (qbug) write(3,*), j, num, sp1, sp2, sp3, spvm
              sp1 = 0.0
              sp2 = 0.0
              sp3 = 0.0
              spvm = 0.0
            do 80 j = 1, npts
              num = imin(j)
              if (qbug) write(3,*), j, num, s1n, s2n, s3n, svmn, w
                if (qbug) write(3,*), j, num, s1n(num), s2n(num), s3n(num),
                  svmn(num), w(num)
                  sp1 = sp1 + w(num)*s1n(num)
                  sp2 = sp2 + w(num)*s2n(num)
                  sp3 = sp3 + w(num)*s3n(num)
                  spvm = spvm + w(num)*svmn(num)
                if (qbug) write(3,*), sp1, sp2, sp3, spvm
                  if (qbug) write(3,*), sp1, sp2, sp3, spvm
                continue
                sptau = (sp1 - sp3)/2.0
              write(3,*),'
              write(3,*), interpolated stresses at specified point
              write(3,*), spvm, spvm
              write(3,*), sp1, sp1
              write(3,*), sp2, sp2
              write(3,*), sp3, sp3
              write(3,*), sptau, sptau
c    close output file
   close(unit=3, status='keep')
c
   stop
   end
# This program generates the realizations of voids distributions
# in realistic models for polymer composites. It uses the probability distributions
# which are generated from the modified quadratic programming formulations.
#include <stdio.h>
#include <iostream.h>
#include "dfs.h"

#define EVSIZE 10  /* number of EV values to try on problem */
#define SIZE 21    /* Size of the problem == # of entries */
#define TRUE   1
#define FALSE  0
#define LT     1
#define EQ     0
#define GT    -1

float evs[EVSIZE]; /* a number of evs to try on problem */
int evsize;        /* actual number of evs to use */

struct vp_pair pvs[SIZE];   /* Static array of problem entries.
                             Contains the initial values. */

int touching[SIZE][SIZE];   /* adjacency matrix from data file */

struct vp_pair aggregates[SIZE]; /* The aggregates end up in this array */
struct vp_pair voids[SIZE];    /* The voids end up in this array */
int aggregate_size = 0;      /* Number of aggregates found */
int void_size = 0;           /* Number of voids found */

/* Compares two vp_pairs passed to it during sorting. Return a negative,
   positive or zero value depending on whether the first’s probability is
   greater than, lesser than, or equal to the second’s in order to sort in
   DESCENDING ORDER. */
int vp_compare(pv1, pv2)
struct vp_pair *pv1;
struct vp_pair *pv2;
{
    if (pv1->prob < pv2->prob)
        return 1;
    else if (pv1->prob > (*pv2).prob)
        return -1;
    else return 0;
}

/* Main function. Inputs the data into the pvs array, and the graph
into the "touching" array. It also outputs both of these values,
so that we can compare to the originals for debugging. It then
calls the main workhorse routine which puts the input into the void
and aggregate arrays. These values are output into their respective output files

*/
main()
{
int i;
char filename[256];
extern void input_evs(), input_vps(), output_vps(), output_debug();
extern void input_touch(), output_touch();
extern void tricky_thing();

input_evs(evs,&evsize, "evs.inp");
input_vps(pvs, SIZE, "data.inp"); /* input data */
input_touch(touching, SIZE, "graph.inp"); /* input graph */

/* sort the input according to probability in descending order */
qsort(pvs, SIZE, sizeof(struct vp_pair), vp_compare);

/* Apply algorithm */
for (i = 0 ; i < evsize; i++) {
    aggregate_size = 0;    /* Number of aggregates found */
    void_size = 0;          /* Number of voids found */
    tricky_thing(pvs, touching, SIZE, evs[i]);
    /* Output voids */
    sprintf(filename, "%s%d", "voids.out", i);
    output_vps( voids, void_size, filename);

    /* Output aggregates */
    sprintf(filename, "%s%d", "aggs.out", i);
    output_vps( aggregates, aggregate_size, filename);
}

/* Output pvs for debugging purposes */
output_debug(pvs, SIZE, evs, evsize, "pvs.out");

/* Input the number of evs and the evs... */
void input_evs(evs, sizeptr, file_name)
float *evs;
int *sizeptr;
char file_name[];
{
    FILE *fp = fopen(file_name, "r");
    int i;

    if (fp == NULL) {
        printf("Could not open evs file %s, file_name");
        exit(0);    /* So much for that idea .... */
    }
}
*sizeptr = 0;
    fscanf(fp, "\%d", sizeptr);
    if (*sizeptr > SIZE) {
        printf("Too many evs : \%d is the limit, EVSIZE \);
        exit(0); /* So much for that idea .... */
    }

    for (i = 0; i < *sizeptr; i++) {
        /* scanning the evs to use... */
        fscanf(fp, "\%lf", &evs[i]);
    }

    fclose(fp);
}

/* Input the probabilities and volumes array */
void input_vps(pvs, size, file_name)
    struct vp_pair *pvs;
    int size;
    char file_name[];
{
    FILE *fp = fopen(file_name, "r");
    int i;

    if (fp == NULL) {
        printf("Could not open data file \%s, file_name\);
        exit(0); /* So much for that idea .... */
    }

    for (i = 0; i < size; i++) {
        /* scanning the probability and volume one element pair at a time */
        fscanf(fp, "\%lf\%lf", &pvs[i].prob, &pvs[i].vol);

        pvs[i].index = i;
    }

    fclose(fp);
}

/* Output the probabilities and volumes array */
void output_vps(pvs, size, file_name)
struct vp_pair *pvs;
int size;
char file_name[];
{
    FILE *fp = fopen(file_name, "w");
    int i;

    if (fp == NULL) {

printf("Could not open %s, file_name); 
return;
}

for (i = 0; i < size; i ++) {
    /* print the probability and volume one element pair at a time */
    fprintf(fp, "%lf %lf (%d)0, pvs[i].prob, pvs[i].vol, pvs[i].index);
}

fclose(fp);

/* Output the probabilities and volumes array and evs for debugging */
void output_debug(pvs, size, evs, evsize, file_name)
struct vp_pair *pvs;
int size;
float *evs;
int evsize;
char file_name[];
{
    FILE *fp = fopen(file_name, "w");
    int i;

    if (fp == NULL) {
        printf("Could not open %s, file_name); 
        return;
    }

    for (i = 0; i < size; i ++) {
        /* print the probability and volume one element pair at a time */
        fprintf(fp, "%lf %lf (%d)0, pvs[i].prob, pvs[i].vol, pvs[i].index);
    }

    fprintf(fp, "evs are:0);
    for (i = 0; i < size; i ++) {
        /* print the evs... */
        fprintf(fp, "%lf (%d)0, evs[i], i ");
    }

    fclose(fp);
}

/* Input the "touching" graph */
void input_touch(graph, size, file_name)
int graph[SIZE][SIZE];
int size;
char file_name[];
{
    FILE *fp = fopen(file_name, "r");
int i, j;
if (fp == NULL) {
    printf("Could not open %s0, file_name); return;
}

for (i = 0; i < size; i++)
    for (j = 0; j < size; j++)
        fscanf(fp, "%d", &graph[i][j]);

close(fp);

/* Output the "touching" graph */
void output_touch(graph, size, file_name)
    int graph[SIZE][SIZE];
    int size;
    char file_name[];
{
    FILE *fp = fopen(file_name, "w");
    int i, j;

    if (fp == NULL) {
        printf("Could not open %s0, file_name); return;
    }

    for (i = 0; i < size; i++) {
        for (j = 0; j < size; j++)
            fprintf(fp, "%d ", graph[i][j]);

        fprintf(fp,"0);
    }

    fclose(fp);
}

/* Add to the aggregates from pvs */
void add_to_aggregate(i)
    int i;
{
    printf("adding %lf to aggregates0, pvs[i].vol); aggregates[aggregate_size++] = pvs[i];
}

/* Add to the voids from pvs */
void add_to_void(i)
    int i;
{
    printf("adding %lf to voids0, pvs[i].vol;
    voids[void_size++] = pvs[i];
}

/* Move all the rest of the pvs array as aggregates */
void rest_are_aggregates(i)
int i;
{
    for (; i < SIZE; i++) {
        add_to_aggregate(i);
    }
}

int test_for_symmetry_plane(i)
int i;
{
    return touching[i][i];
}

double sum_of_all_previous_voids()
{
    double rv = 0.0;
    int i = void_size;
    for (i = 0; i < void_size; i++) {
        rv += voids[i].vol;
    }
    return rv;
}

int touches_any_of_the_previous_voids(i)
int i;
{
    int j;
    for (j = 0; j < i; j++) {
        if (touching[pvs[i].index][voids[j].index] != 0) {
            return 1;
        }
    }
    return 0;
}

void tricky_thing(pvs, graph, size, ev)
int graph[SIZE][SIZE];
struct vp_pair *pvs;
int size;
float ev;
{
    int j = 0, i = 1, last_void_index = 0;
    double sum = 0.0;

    printf("i = 1: ");

    if (ev < pvs[0].vol) {
        printf("The model has no voids0;
        exit(0);
    }
    else if ((ev == pvs[0].vol) && graph[pvs[0].index][pvs[0].index]) {
        printf("The %d is the only void in the model0, pvs[0].index);
        exit(0);
    }
    else if (graph[pvs[0].index][pvs[0].index]) {
        add_to_aggregate(0);
    }
    else add_to_void(0);

    repeat:

    if (i >= size)
        return;

    printf("i = %d: ", i + 1);

    if (graph[pvs[i].index][pvs[i].index] == 1) {
        printf(" tested ok for symmetry plane ");
        add_to_aggregate(i);
        i ++;
        goto repeat;
    }
    else {
        sum = sum_of_all_previous_voids() + pvs[i].vol;

        printf("sum = %lf, ev = %lf ", sum, ev);

        if (sum > ev) {
            rest_are_aggregates(i);
        }
        else if (sum < ev) {
            if (touches_any_of_the_previous_voids(i))
                add_to_aggregate(i);
            else add_to_void(i);

            i ++;
            goto repeat;
        }
        else {
            if (touches_any_of_the_previous_voids(i))


add_to_aggregate(i);
else add_to_void(i);

rest_are_aggregates(i);
}
This subroutine calls QPSOL, which is a set of Fortran subroutines designed to locate the minimum value of an arbitrary quadratic function subject to linear constraints and simple and upper bounds. If the quadratic function is convex, a global minimum is found; otherwise, a local minimum is found. The following are description of the input and output arguments of the subroutine.

*************** INPUT PARAMETERS ***************

ITMAX is an upper bound on the number of iterations to be taken during the LP phase or the QP phase.

MSG_LVL indicates the amount of intermediate output desired.

NCLIN is the number of general linear constraints in the problem.

N is the number of variables (i.e., the dimension of X).

NCTOTL must be set to N + NCLIN.

NROWA is the declared row dimension of A.

NROW is the declared row dimension of array ESS.

NCOL is the declared column dimension of the array ESS.

BIGBND is a positive real variable whose magnitude denotes an "infinite" component of l and u. Any upper bound greater than or equal to BIGBND will be regarded as plus infinity.

A is a real array of declared dimension (NROWA,N). The ith row of A contains the coefficients of the ith general constraint, i=1 to NCLIN.

BL is a real array of dimension NCTOTL that contains the lower bounds for all the constraints, in the following order: the first N elements of BL contain the lower bounds on the variables, the next NCLIN elements of BL contain the lower bounds for the general linear constraints.

BU is a real array of dimension NCTOTL that contains the upper bounds for all the constraints, in the same order described above under BL. To specify a non-existant upper bound (i.e., Uj = infinity), the value used must satisfy BU (j) is greater than or equal to BIGBND.

CVEC is an array of dimension N containing the coefficients of the linear term of the objective function.
FEATOL is a real array of dimension NCTOTL containing positive
tolerances that define the maximum permissible violation
in each constraint in order for a point to be considered
feasible, i.e. constraint j is considered satisfied if its
violation does not exceed FEATOL(j).

COLD is logical variable that indicates whether the user
whics to specify the initial working set. In general, COLD
should be set to .TRUE. for the first call of QPSOL, and
the initial working set will then be selected by QPSOL.

*************** INPUT/OUTPUT PARAMETERS **********************

ISTATE is an integer array of dimension NCTOTL that indicates the
status of every constraint with respect to the working set.

X is areal array of dimension N that contains the current
estimate of the solution.

INFORM is an integer that indicates the result of QPSOL.

ITER is an integer that gives the number of iterations performed
in either the LP phase or the QP phase, whichever was last entered.

OBJ is the value of the quadratic objective function at X if X is
feasible (INFORM is less than or equal to 5), or the sum of
infeasibilities at X otherwise.

CLAMDA is a real array of dimension NCTOTL that contains the lagrange
multiplier for every constraint with respect to the current
working set. The first N components contain the multipliers
for the bound constraints on the variables, the remaining
components contain the multipliers for the bound constraints
on the variables.

IW is an integer array of dimension LINEW, which provides
integer workspace for the QPSOL

LINEW is the dimension of IW, and must be at least N+2+min(N,NCLIN).

W is a real array of dimension LENV, which provides real workspace
for the QPSOL.

LENW is the dimension of W. If LP = .TRUE. and NCLIN < N, LENV
must be at least 2NCON**2 + NROWA + 2NCON.

double precision vi(n)

integer itmax, msglvl, n, nclin, nctotl, nrowA
integer nrowH, ncolH, inform, iter, leniw, lenw
parameter ( n = 21 )
parameter ( nrowA = 2 )
parameter ( nclin = 2 )
parameter ( nrowH = 21 )
parameter ( ncolH = 21 )
parameter ( nctol = 23 )
parameter ( leniw = 100 )
parameter ( lenw = 1000 )

logical cold, lp, orthog
external qphess

integer inform, ii, jj
integer istate(nctol), iw(leniw), i, msglvl
double precision bigbnd, obj, featol(nctol)
double precision A(nrowA, n), bl(nctol), bu(nctol), cvec(n)
double precision feaol(nctol), hess(n, n), x(n)
double precision clamda(nctol), w(lenw), p(n)
double precision emach, emach1, expv, drteps, drtepl

msglvl = 0
open input file
ccc open (unit=3, status = 'unknown', file = 'volfrac.dat')
c ask user about the expected value of the volume fraction of voids
c print*, 'enter the expected value of the volume fraction of voids'
read*, expv

c ask the user how many possible void domains
ccc print*, 'enter number of possible void domains'
c OBc set the problem dimensions.
c N = the number of variables
c NCLIN = the number of general linear constraints.
c NCTOL = the total number of variables and general constraints
c Define number of iterations allowed to find a feasible point
c and the same number to minimize the quadratic function.
itmax = 40
c Bounds greater than BIGIND will be treated as plus infinity
    bigbnd = 10.d+9

c computing the machine epsilon EMACH

EMACH=1.0
3 EMACH=EMACH*.5
    EMACH1=EMACH+1.0
    IF (EMACH1 .GT. 1.0) GO TO 3

Any bound or linear constraint may be violated by as much as FEATOL.
c DRTEPS = DSQRT (EMACH)
DO 26 JJ = 1, NCTOTL
    FEATOL(JJ) = 10.0d-6
26 CONTINUE

C a COLD start is needed for the first call to QPSOL
C We want to solve a linear programming.
C Use an orthogonal factorization of the matrix of constraints
C in the working set.
    COLD = .TRUE.
    LP = .FALSE.
    ORTHOG = .TRUE.
    C
    print*, 'N = ', n
    print*, 'NCOLH = ', ncolH
    print*, 'NCOLH = ', ncolH

C Read the volume fraction of the possible voids domains
    Do 10 i=1, n
        read(*, *) vi(i)
10 continue
C Read the linear part of the objective function CVEC
C Read the general constraint matrix A
    do 20 i = 1, n
        cvec(i) = -2.0d0*expv
    a(1,i) = 1.0d0
    a(2,i) = 1.0d0 / vi(i)
20 continue
C Read the lower bound on X and A*X.
    do 21 i = 1, n
        bl(i) = 0.0d0
21 continue
    bl(22) = 0.0d0
    bl(23) = 1.0d0
C Read the upper bound on X and A*X
    do 22 i = 1, n
        bu(i) = vi(i)
22 continue
    bu(22) = expv
    bu(23) = 1.0d0
C mn = -1
33 continue
mn = mn + 2
drtep1 = drteps * 10.0d0 ** mn

do 23 i = 1, nrowH
   do 24 j = 1, ncolH
      HESS (i, j) = 2.0d0
   continue
   HESS (i, i) = 2.0d0 + drtep1
continue

Solve the problem
   print*, cvec = ',', cvec
   print*, 'lp =', LP
   print*, 'A =', a
   print*, 'bl =', bl
   print*, '
   print*, 'bu =', bu
   print*, '
   print*, 'Hess = ', Hess

   Call QPSOL(ITMAX, MSGVLVL, N, NCLIN, NCTOTL, NROWA, NrowH,
   NCOLH, BIGBND, A, BL, BU, CVEC, FEATOL, HESS,
   QPHESS, COLD, LP, ORTHOG, ISTATE, X, INFORM,
   ITER, OBJ, CLAMDA, IW, LENIW, W, LENW )

Test for an error condition.
   print*, 'Inform = ', inform

   print*,
   if (INFORM .GE. 1) GO TO 33

   do 30 ii = 1, n
      p(ii) = x(ii) / vi(ii)
      write(6, 1035) ii, p(ii)
   continue
   sum = 0.0d0
   do 36 ij = 1, n
      sum = sum + p(ij)
   continue
   print*, 'sum = ', sum
write (6, 3000) INFORM
if ( DRTEP1 .LE. 20) GO TO 33

1035 format (5x, 'p('i2,') = ', d20.10)
3000 format (/32H QPSOL TERMINATED WITH INFORM =, I3)

999 stop
end

C*******************************************************************************

Subroutine QPHess(n, NrowH, NcolH, jthcol, Hess, x, Hx)

This subroutine will compute the Hessian matrix.

integer n, NrowH, NcolH, jthcol
double precision Hess(NrowH, NcolH), x(n), Hx(n)
double precision xi
call zerovc (NrowH, Hx, NcolH, 1)

Do 200 i = 1, NrowH
c xi = x(i)
c
  do 100 j = 1, NcolH
      Hx(j) = Hx(j) + Hess (j, i) * xi
  100 continue
200 continue
return
end