

PROPERTIES CONSTRAINED COST OPTIMIZATION
OF POLYESTER-FILLER SYSTEMS WITH NON-LINEAR
PROPERTY-COMPOSITION RELATIONSHIPS

by

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I. INTRODUCTION

The 1970 volume of reinforced thermosets was estimated at more than one billion pounds, which is higher than all the reinforced plastics/composites of 1969⁽²⁶⁾. The performance that can be built into a reinforced plastic (RP) part is largely the product of the particular resin and reinforcement. Polyester resins are the most widely used and their production is expected to grow at the healthy rate of 10-15% per year at least, through the year 1975. One recent development which promises to account for considerable polyester consumption in the future is water-extended polyesters (WEP) for making low cost decorative objectives d'art and simulated wood carvings of high quality⁽²⁰⁾.

Various fillers are used to achieve almost any property desired in an end product. The furniture industry, which used 37 million pounds of filled polyester in 1967, is expected to consume 225 million pounds by 1975⁽⁴³⁾. Cultured marble sales have grown from \$3 million in 1964 to \$77 million in 1969 and are expected to reach \$500 million by 1975. Ninety-five percent of this production is filled polyesters⁽⁴²⁾.

Future developments in this fast-growing field will depend on further intensive research in finding the appropriate filler(s) for the resin(s) selected, the effect of these fillers on the mechanical properties, polymer-filler matrix and their properties, etc. Due to the large number of fillers available on the market, an approach towards the optimization of the filler content will be very useful in minimizing the cost of the end product.

The purpose of this investigation was to study the effect of selected fillers on the mechanical properties of polyester resin and to formulate a procedure for optimization of the filler content, using the property-composition relationships developed from an appropriate, statistically designed experiment.

II. LITERATURE REVIEW

Reinforced plastics are composites in which a resin is combined with a reinforcing agent to improve one or more properties of the plastic matrix. Reinforced plastics provide designer, fabricator, equipment manufacturer and consumer flexibility of engineering properties to meet different environments and requirements.

Although both thermoplastic and thermosetting resins are used, the latter definitely predominate. The reinforcing agent can be fibrous, powdered, spherical, crystalline or whisker and made of organic, inorganic, metallic or ceramic material⁽⁴⁶⁾.

This investigation deals with the particulate reinforcement of polyester resins. Accordingly, a review of the literature concerning the resin system is presented, followed by a review of the particulate fillers. The polymer-filler matrix and the effect of fillers on the mechanical properties of the resin are discussed next. Finally, the development of the response surface equations by regression analysis and optimization techniques are considered.

The Resin Matrix

The polyester family of thermosetting resins forms a vital base for the entire reinforced plastics industry. Products designed around polyester resins can compete very well with more conventional materials in a great number of fields because of the tremendous versatility of these resins compared to phenolics, aminoplastics, epoxies, silicones, poly-

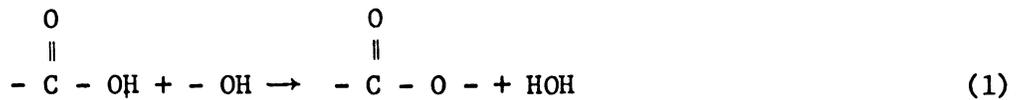
urethanes, etc. Polyesters have been very popular owing to its following advantages⁽²⁹⁾:

1. Ease of handling (polymerizing 100% at room temperature, if needed).
2. Good general chemical, electrical, mechanical and physical properties.
3. Solidification without evolution of gaseous or liquid by-products.
4. Good dimensional stability; can also be made flame resistant, corrosion resistant, heat resistant and stable against effects of heat and light.
5. Excellent wetting properties, high filler and pigment loading possible.
6. Molded with compression or match-metal dies, laminated, pultruded, filament wound, transfer molded, bag molded, drape molded, sprayed up, hand layed-up and cast. Mold release is good and short production cycle times are possible.
7. Easily available in various forms at low price.

The Chemistry of Polyesters. Polyesters are broadly classified into saturated and unsaturated polymers. Essentially, a polyester is the result of a reaction of a dicarboxylic acid with a dihydric alcohol, but variations of this reaction (esterification) encompass many basic materials, resulting in resins with widely different properties.

Esterification consists of the reaction of a carboxylic acid group with a hydroxyl group to form an ester group and a liberated water

molecule as shown in equation (1)



For a linear polymer to be formed, all reactants must be bi-functional, i.e., a dibasic acid and a dihydric alcohol (glycol). Further, to make a thermosetting resin, the linear polymer must react to form a three dimensional matrix. This is done by using a dibasic acid or glycol (or both) containing double bonded carbon atoms. Thus, an unsaturated polyester resin is formed with reactive sites along the polymer chain. The chemistry and structure of polyesters is discussed in great detail in the literature^(7,45).

Curing of Polyester Resin. The catalyzed resin begins to gel and adequate curing is needed, before it can attain its full properties. The final curing reaction is an "addition" polymerization because no by-products result.

The mechanism of physical changes by which polyester resins gel and cure is reduced to three separate steps, each depending on the resin reactivity, inhibitor, catalyst used and curing temperature. Gelation is defined by the point at which the resin, after being catalyzed, ceases to be a viscous liquid and becomes a soft, elastic, rubbery solid. Secondly, the gel thickens and becomes slightly harder, with a slight increase in temperature. Thirdly, a strong exotherm occurs, brought on by the full result of the chemical action of the polymerization. This accounts for the curing in some types of molding, although ultimate properties are not always immediately developed and in many cases a post

cure is desirable⁽³⁰⁾.

The stresses developed during curing can be relieved only if the molded piece is post cured at a temperature higher than the maximum temperature attained during the cure. This peak exotherm temperature is lowered by fillers and reinforcements, which, being inert, absorb the heat from the resin, but lengthen the gel time only if a room temperature cure is used or if inhibitory effect is contributed.

Monomers, Catalysts, Promoters and Inhibitors. Monomers added to the unsaturated resin serve two purposes: they act as a solvent for the unsaturated polyester, which is either high in viscosity or a solid; they copolymerize with the unsaturated polyester chain, thus yielding a cured thermoset product. These have made it possible to make polyesters practical to apply, to permit a commercially acceptable fiber wet-out, to improve the physical, chemical and thermal properties of polyester resins and their cured products, to cure at greatly increased rates and to greatly increased degrees of completion and to vary the properties of the resulting polyesters by choice of the monomers employed⁽⁷⁾.

The vinyl monomer most commonly used is styrene due to its low cost, good polymerization ratio and high solubility. Monomer content ranges from 20 to 60 percent depending on the final viscosity desired⁽²⁰⁾. Oleesky discusses the relative merits and effects of various monomers⁽³¹⁾.

Polyester resins are readily polymerized by free radical catalysts. Organic peroxides such as benzoyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide are most commonly used because of low cost, ready availability and ease of handling. The peroxide splits to give two free

radicals which add to a double bond in the polyester, generating a new free radical which in turn adds to a styrene molecule generating another new free radical, which in turn adds to a polyester double bond, etc., until the entire mass has set to a rigid solid.

To prevent premature gelation during production, storage and shipment, an inhibitor such as hydroquinone or p-tert-butyl catechol which acts as a free radical trap is added to the resin during manufacture.

The reaction steps are described as follows⁽³²⁾:

1. Less than one percent of the unsaturated double bonds are reacted in the pre catalyzed base polyester-monomer combination.
2. After catalyzing and initiation, when 40-60 percent of the unsaturation has been taken up, gelation occurs. The gel hardens and initial volume shrinkage of the resin occurs, as the propagation proceeds and 40-60 percent of the total unsaturation is converted.
3. An incomplete cure exists without the development of full properties when 80 percent of the unsaturation has been utilized
4. An optimum cure and full properties are realized after 92 to 95 percent of the total unsaturation has been converted.

The above process is accelerated at room temperature by adding a promoter like cobalt naphthenate, which at 0.5 percent of the resin weight concentration, reduces the time from 15 hours to 39 minutes for a resin catalyzed with one percent MEK peroxide. Accessory promoters, or accelerators, such as dimethyl aniline, further reduce the gel time to 9 minutes at 0.1 percent concentration⁽²⁰⁾. Different concentrations of catalyst and promoters produce different effects on the gel characteristics of the resin.

Polyester Formulation

Polyesters are composed of the following three basic components: unsaturated dibasic acids (e.g., fumaric acid and maleic anhydride), saturated dibasic acids (e.g., adipic, phthalic and isophthalic acids) and glycols (e.g., ethylene, propylene, diethylene and dipropylene glycols)⁽²¹⁾. These and other components are suitably blended to obtain resins to meet widely different requirements.

Boenig⁽⁷⁾ has discussed the effects of formulation on the cured resin properties. The more important conclusions are as follows: structural elements of unsaturated polyesters that affect the properties of the cured products include structure and ratio of acid and glycol components, molecular weight and their distribution, type of end groups, distribution of various repeating units and type of unsaturation. An adipic-fumaric acid combination yields a "flexible" resin while a "rigid" resin is obtained if a high density of unsaturation and short chain compounds like maleic acid, phthalic acid and propylene glycol are present. A resilient resin has intermediate composition and properties. Selected mechanical properties of these three resins are compared in Table 1, page 9.

Particulate Fillers

Fillers may be classified in a number of different ways according to their chemical composition (e.g., calcium carbonate, silica), source (e.g., mineral, organic, inorganic, agricultural, synthetic), function (e.g., reinforcement, bulk, cost reduction), physical form (e.g., fiber,

Table 1

Typical Mechanical Properties of Representative
Unfilled Polyester Castings (29)

<u>Type of Resin</u>	<u>Density gm/ml</u>	<u>Tensile Strength psi</u>	<u>Ultimate Elongation %</u>	<u>Flexural Strength psi</u>	<u>Flexural Modulus of Elasticity psi x 10⁶</u>	<u>Compressive Strength psi</u>
Rigid	1.22	10,500	1.8	16,700	0.69	22,500
Resilient	1.22	7,000	8	16,000	0.40	30,700
Flexible	1.11	1,360	65	*	*	*

* Too flexible to test.

platelet, particulate, whisker) etc. (22,33,44). Fillers, which may be described as inert materials added to a polymer composition to modify its properties or reduce cost, are finding increasing use in very specific applications due to the properties they contribute. Still, one of the most important requirements is that they reduce the cost of the finished product. Hence, the following classification is given, based on cost per pound:

1. Lowest cost - 1/2 to 1 c - mostly inorganic fillers such as slate flour, silica, dry ground clays and calcium carbonate. Soapstones, tales, etc., 200-325 mesh category.

2. Low cost - 2 to 5 c - have better color and size control and are available in finer particle sizes, e.g., silica, wet ground calcium carbonate, water levigated clays, etc.

3. Medium cost - 6 to 15 c - pumice, diatomaceous earth, micro-silicates, coated calcium carbonates, etc., with color, micron size, oil absorption and bulk properties controlled.

4. High cost - 20 to 50 c - mostly synthetic like synthetic forsterite, talc, mullite, neonovacite silica, etc., and other more closely graded materials.

5. Extra high cost - above 50 c - synthetic and specially prepared materials like silica gel, microballoons and microspheres are available.

The volumetric cost of fillers is more important for it is the amount of resin being displaced by the filler that is significant. A table of the fillers used in this investigation is given in table 3, page 30, along with their cost on a weight and volume basis.

Fillers offer a variety of benefits such as increased strength and stiffness; reduced cost, shrinkage, exothermic heat and thermal expansion coefficient; improved heat resistance and surface appearance; reduced porosity and crazing; improved wet strength, fabrication mobility, abrasion resistance and impact strength; increased viscosity, etc. Fillers also have some disadvantages for they may limit the method of fabrication, inhibit cure of certain resins and shorten the pot life of the resin⁽⁴⁷⁾.

Effect of Fillers on the Mechanical Properties of the Composite

Composites are considered to be combinations of materials differing in composition or form on a macroscopic scale. All of the constituents in the composite retain their identities and do not dissolve or otherwise completely merge with each other. Composites can be classified into three broad categories--fibrous, laminar and particulate⁽³⁹⁾. Only the particulate composites and the theory of their reinforcement is considered in this review.

A number of sources in the literature present tables, listing the effect of fillers on the properties of plastics^(14,36).

Alford and Veatch⁽¹⁾ studied the effect of three fillers: glass microballoons, wood flour and mineral filler on polyester resin properties and report that the density of the final resin depends directly on the density of fillers used. Tensile strength, compressive strength and flexural strength were all reduced as the volumetric percentage of

fillers increased, there being little difference among them when they were compared on a true volume basis. The polyester resin containing 33 percent by weight of glass microballoon particles was relatively 3 times as flexurally rigid as the unfilled resin and was 6 times as flexurally rigid as the resin containing a similar amount of mineral filler.

A non-fibrous filler like silica in polystyrene reduces tensile strength, ultimate elongation and impact resistance, but increases the density⁽¹⁵⁾.

In a study⁽²⁵⁾ which compared the effects of silica, phenolic and thermoplastic spheres on glass reinforced polyester, it was found that the flexural modulus and strength properties show a moderate decrease with increasing filler content. The compressive properties also showed a similar trend. All three fillers decreased the density, the effect of the thermoplastic spheres being the most notable.

Schwarzl et al.⁽³⁵⁾ have found that the ratio of shear modulus of composite material to shear modulus of unfilled material rapidly increases as the filler concentration increases. A simple linear equation was found to be adequate to calculate the density as a function of filler loading by volume.

Solid glass spheres have been found to produce more uniform and predictable stress patterns in reinforced plastics with resultant gains in flexural and compressive strength and modulus of elasticity⁽¹²⁾.

The fibrous fillers improve the tensile strength while particulate fillers like silica, calcium carbonate and kaolin do not^(14,36).

Bostwick and Carey⁽⁸⁾ report that silica, clay and calcium carbonate decreased the tensile strength and ultimate elongation of low density polyethylene. High density polyethylene behaved similarly when filled with asbestos dust, silica-alumina and wood flour⁽¹³⁾.

It may generally be stated that "Particulate, inorganic fillers may be used to raise the modulus but they are detrimental to the strength of plastics"⁽²³⁾.

It has also been found that fillers like calcium carbonate, china clay, silica, carbon black and magnesium silicate increase the tensile yield strength from 3220 psi to 3330, 3700, 4470, 3930 and 3390 respectively, for high density polyethylene⁽¹⁵⁾. Similar behavior has been noticed in medium density polyethylene, especially at higher filler loadings of over 33 percent by weight. The tensile strength and yield strength were increased in most cases by clay, silica and calcium carbonate. The secant modulus (at one percent strain) always increased with increasing filler content.

A very recent study⁽²⁾ concludes that rigid particulate fillers like marble, clay and nut shell flour increase the tensile strength of a ductile resin matrix and that hollow and solid glass spheres decreased tensile strength at higher loadings. However, all the fillers improved the secant modulus and decreased the ultimate elongation.

Effect of Filler Particle Size

Alter⁽²⁾ has reported correlations between filler particle size and the mechanical properties of the composites, as functions of the recip-

rocal of the filler particle size. The tensile strength, yielded strength and secant modulus increased with decreasing particle size, while the ultimate elongation decreased. The flexural strength has also been shown to increase similarly for a silica filled polyester resin⁽³⁹⁾.

Polymer-Filler Interaction

The nature of the interactions which give rise to the polymer-filler bond has been studied for many fillers and it is now generally agreed that van der Waals forces are sufficient to cause reinforcing effects, but there is also ample evidence for chemical "grafting" of polymer molecules to filler surfaces. The high degree of adhesion produced by chemical interactions probably contributes to the superior reinforcing properties in these cases⁽⁴⁸⁾.

Nielson has developed approximate stress-strain equations for the two cases of perfect adhesion and no adhesion. He has shown that⁽²⁸⁾ irrespective of polymer-filler adhesion, a rigid filler should lead to loss in ultimate elongation and impact strength. Tensile strength may be increased if a good adhesive bond is realized. These predictions, which are in general agreement with observations, are based on the assumption that the polymer fails when the actual average strain in the polymer matrix reaches the ultimate strain of the unfilled polymer and that the polymer obeys Hooke's law. Using Bueche's expression for the actual strain in a filled polymer, for the case of an adhering filler

$$US = (US_0) (1 - f^{1/3})$$

$$TS = (E) (US)$$

$$W = \frac{(E) (US)^2}{2}$$

where US is the ultimate strain, TS the tensile strength, W the area under the stress-strain curve, E the Young's Modulus and f the volume fraction of the filler. E and f are related by the following equation

$$E = E_0 (1 + 2.5 f + 14.1 f^2)$$

The subscript 0 denotes the unfilled polymer. Nielson's modified Eilers and Van Dijck relation predicts an increase in TS with filler loading for f greater than 0.4.

For the case of no adhesion, the filler particles do not carry any of the load but only occupy space and thus act as diluent. Hence, assuming no stress distortion is present, the maximum TS is given by

$$TS = TS_0 (1 - f^{2/3})$$

Kenyon et al.⁽¹⁸⁾ have examined the effect of adhesion and found that the tensile strength for the case of good adhesion showed an increase over that of the base resin while the tensile strength for the case of no adhesion showed a significant decrease.

Nature of the Matrix

The nature of the matrix exerts an important influence on the effect of fillers on the mechanical property. The matrix material is the primary load bearing element of a particular composite. It can respond to

an applied tensile stress in two ways: (1) as a ductile material experiencing large plastic deformation or (2) as a brittle material experiencing little or no plastic deformation. Likewise, the inclusion of particles can impart reinforcement in two ways: (1) if the matrix material is ductile, the particles can block dislocation motion, or slip, and thereby limit plastic deformation; (2) if the matrix is brittle and fractures by crack propagation from existing cracks, the particles can limit the size of the initial cracks and thereby control strength. In order to give reinforcement to the ductile material, the included particles must have a greater shear strength than the matrix; otherwise, the dislocations can cut through the particles. "When brittle-matrix composites are considered, the particle-matrix bond exerts a greater influence on strength than for the ductile-matrix composite"⁽¹⁰⁾. For without particle-matrix bonding, the particles act like voids which are known to markedly reduce the strength of brittle materials.

Regression Analysis

The analysis of the data involves the following operations:

(1) fitting the postulated model to the data by least squares techniques and (2) testing the significance of regression. It has been shown⁽¹⁷⁾ that the BMD computer program⁽⁴¹⁾ "Multiple regression with case combinations" can be satisfactorily applied to the quadratic regression analysis of the type normal in this kind of investigation. The program makes use of the matrix method of computation.

Optimization

The composite materials development problem has as its objective the maximization or minimization of some primary response of the product. The values that x_i , $i = 1, \dots, n$ may assume are limited in two ways: (1) the x_i values are restricted to definite ranges imposed by process capability, and (2) there are specifications on secondary properties of the composite materials.

A constrained optimization problem consists of obtaining solutions which are generally superior to the experimental observations, but simultaneously satisfying the constraints imposed. This problem can be solved through mathematical programmings, which are classified according to the form of the objective function and constraints. If both are linear, the problem is one of linear programming. Jones⁽¹⁷⁾ has applied linear programming to a composition problem whose response was adequately represented by linear models.

The case where the objective function and/or constraints are non-linear is termed non-linear programming. For example, the objective function and/or the secondary property constraints are normally quadratic response surface models. The region enclosed within the secondary property constraints is frequently not convex.

Zoutendijk⁽⁴⁰⁾ has reviewed several categories of general non-linear programming methods with special emphasis on their computational aspects. However, none of the four methods, viz. dual methods, small step gradient methods, large step gradient methods (also called method of feasible directions) and interior point methods is entirely suitable for a

composite material development application.

The application of direct search methods to the general non-linear programming problem has been discussed by Wilde and Beightler⁽³⁸⁾. These methods generally require fewer computations per iteration and they are easily programmed. Among the methods discussed are gradient search, pattern search, gradient partan (parallel tangents) and sequential simplex. Biles⁽⁶⁾ has examined the first two methods in detail and has recommended the pattern search method for handling constrained problems of the composite material development type due mainly to its simplicity, faster convergence, flexibility and ability to be used on small computers.

III. EXPERIMENTAL DESIGN

If we accept the premise that new knowledge is gained most often by careful analysis and interpretation of data, then it is paramount that considerable thought and effort be given in planning their collection in order that maximum information be obtained for the least expenditure of resources⁽³⁷⁾.

The main considerations connected with the exploration of a response surface are: (1) the choice of a proper model that could approximate the response in the region of interest, (2) the testing of the adequacy of the model in representing the response surface in that region, and (3) a suitable design for collecting observations, for fitting the model and testing the adequacy of fit⁽²⁷⁾.

In experiments dealing with mixtures, the response surface of a given independent variable y is studied as a function of q factors. The q factors (components) are all represented by a proportion, X_i of the total mixture.

Thus,
$$\sum_{i=1}^q X_i = 1 \quad (1)-(1)$$

and $0 \leq a_i \leq X_i \leq b_i \leq 1$, where $i = 1, 2, \dots, q$ and a_i and b_i are constraints on the X_i imposed by the physical situation.

A response equation may be linear, quadratic, cubic, special cubic, etc., and is intended to describe responses over the mixture space. A lower order polynomial is preferable, in view of its simpler method of estimation.

Two basic designs can be used in estimating linear response surface models⁽⁶⁾. The 2^n factorial design requires 2^n points for the complete model, compared to the $n + 1$ points necessary for estimating a linear model. Since 9 components are present in the mixtures employed in this investigation, the factorial design requires 2^8 or 256 points compared to the 9 points necessary for estimating a linear model. It is to be noted that n is the number of independent variables and is equal to 8 due to the relationship given by the equation (1)-(1).

Even if partial factorials like $\frac{1}{2} \cdot 2^n$ or $\frac{1}{4} \cdot 2^n$ were used, the number of experiments required is inconveniently high. In addition, the chances of losing some of the important interaction terms increases.

The Simplex design requires exactly $(n + 1)$ design points, which achieves the objective of minimum experimentation.

Quadratic models require experimentation at more than two levels. The 3^n factorial design, although applicable, yields 6561 points for n equal to 8. Fractionating does not help very much either. The Central composite design devised by Box and Wilson⁽⁹⁾ requires a 2^n factorial structure with an augmenting system consisting of a center point and 2^n axial points. The total number of points is $[2^n + 2n + 1]$. For n equal to 8, it is 273, which is still too high and far exceeds the number needed.

Scheffe⁽³⁴⁾ introduced the topic of mixture experiments for the case $a_i = 0$ and $b_i = 1$ for $i = 1, 2, \dots, q$, as given in equation (1)-(1). The $\{q, m\}$ Simplex Lattice design is defined as a design which uniformly covers the factor space with each factor having $(m + 1)$ equally spaced values from 0 to 1 such that

$$\sum_{i=1}^q X_i = 1$$

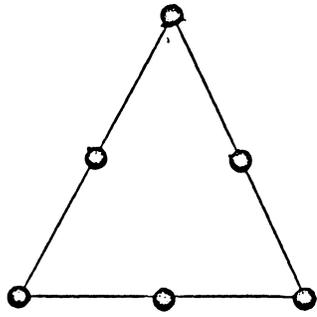
q is the number of components and hence the number of vertices (one for each component in the mixture) and $(m - 1)$ points along each edge. For example, a complete $\{3,2\}$ lattice would consist of observations taken at the following points $(1, 0, 0)$, $(0, 1, 0)$, $(0, 0, 1)$, $(0.5, 0.5, 0)$, $(0.5, 0, 0.5)$ and $(0, 0.5, 0.5)$ which are seen to lie on the plane $X_1 + X_2 + X_3 = 1$ in the first octant. Figure 1 illustrates this and also includes a redrawn two-dimensional simplex. A $\{4,3\}$ lattice is also presented as a three dimensional simplex (tetrahedron). In general, the q dimensional factor space will reduce to a $(q - 1)$ dimensional polyhedron.

If the vertices at each end of the edge are included, there are $(m + 1)$ design points associated with each edge of the simplex. These $(m + 1)$ points are located at

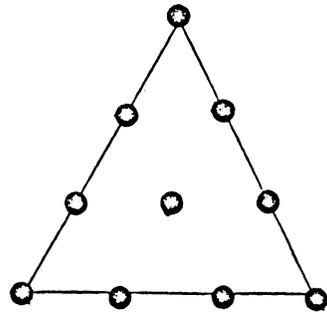
$$X_i = 0, 1/m, 2/m, \dots, 1$$

The total number of points in a simplex lattice design is $[(q + m - 1)!/m!(q - 1)!]$. If $m = 2$, the number of design points is $[q + 1)!/2!(q - 1)!]$, which is exactly the number of coefficients in the quadratic model in $(q - 1)$ independent variables. For the case of q equal to 9 and m equal to 2, the number of design points is 45, which is convenient to handle.

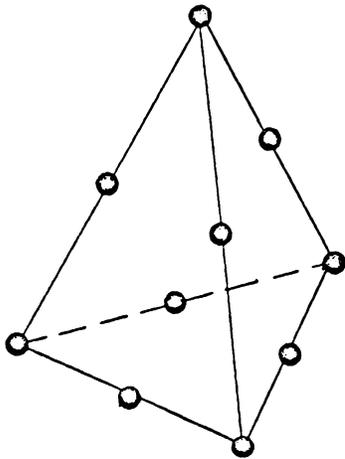
This simplex lattice design needs to be modified for this particular investigation since not all components in the mixture have the same constraints. That is, some components have different lower and upper bounds. In this case, a_i and b_i are different for each i , in equation (1)-(1).



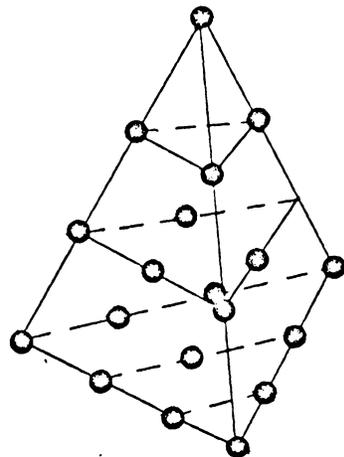
{3,2} Simplex Lattice



{3,3} Simplex Lattice



{4,2} Simplex Lattice



{4,3} Simplex Lattice

Figure 1. $\{q,m\}$ Simplex Lattice Designs for Three and Four Component Systems.

The extreme vertices design, developed by McLean and Anderson⁽²⁴⁾, is most appropriate for this situation.

These constraints placed on the individual factors describe an irregular hyper-polyhedron of $(q - 1)$, i.e., 8 dimensions. The vertices and centroids of this figure describe a unique set of points (the design of the experiment) which may be used to estimate the response surface.

The quadratic model

$$y = B_0 + \sum_{i=1}^q B_i X_i + \sum_{i=1}^q B_{ii} X_i^2 + \sum_{i=1}^{q-1} \sum_{j=i+1}^q B_{ij} X_i X_j$$

contains $[(q + 2)(q + 1)/2]$ terms and the experimental design must have at least these many points.

The design points are computed as follows. For q components there are q vertices. One component is at its maximum allowable fraction, while all the others are present at their minimum allowable fraction. These maximum and minimum levels will be the upper and lower constraints of each component, thus permitting the investigation of the entire factor space that is intended to be covered. Once the constraints for each factor are given, all the points of the basic design are uniquely determined. The vertices of the design must fall on the upper or lower constraints of $(q - 1)$ factors.

$$\text{Let } X_j \geq a_j, j = 1, 2, \dots, q$$

where j is the number of the component and a_j is the lower constraint on the j^{th} component. The coordinates of the i^{th} vertex will be

$$\begin{aligned}
X_1(i) &= a_1 \\
X_2(i) &= a_2 \\
&\vdots \\
X_i(i) &= 1 - a_1 - a_2 - \dots - a_{i-1} - a_{i+1} - \dots - a_q \\
&\vdots \\
X_q(i) &= a_q
\end{aligned}$$

Thus, the i^{th} component in the i^{th} vertex is calculated from the summation property of the constituents of the mixture.

The hyperpolyhedron so constructed contains a variety of centroids. There is one located in each boundary 2-dimensional face, 3-dimensional face, ..., r -dimensional face ($r \leq q - 2$) and the centroid of the hyperpolyhedron. The centroids of the 2-dimensional faces, in other words, the mid-points of the edges, are calculated as a linear combination of the vertices at the ends of the edge. The coordinates of the midpoint will be

$$X_{jk}(i) = [X_j(i) + X_k(i)]/2 \quad j \neq k$$

where

$$j = j^{\text{th}} \text{ vertex}$$

$$k = k^{\text{th}} \text{ vertex}$$

$$i = i^{\text{th}} \text{ component, } 1, 2, \dots, q$$

$X_{jk}(i) = i^{\text{th}}$ coordinate (of the i^{th} component) at the midpoint of the edge joining the j^{th} and k^{th} vertices.

This generates $\Sigma (q - 1)$ points.

It is desirable to augment the above extreme vertices simplex lattice design with the centroid of the hyperpolyhedron, which is the linear com-

bination of all admissible vertices. This augmented design permits the investigation of the interior of the simplex. The centroid of the simplex is calculated from the relation

$$X_i (c) = [X_i (1) + X_i (2) + \dots + X_i (q)]/q$$

where

$X_i (1)$ is the coordinate of the i^{th} component in vertex 1

$X_i (2)$ is the coordinate of the i^{th} component in vertex 2 and so on

$X_i (c)$ is the coordinate of the i^{th} component at the centroid

The above equation can also be written as

$$X_i (c) = [(q - 1) a_i + X_i (i)]/q$$

since the component i is at its lower constraint value of a_i at all $(q - 1)$ vertices except at the i^{th} vertex, where it is at its upper constraint, equal to $X_i (i)$.

This centroid point, being the most strategically situated one, is replicated $r - 1$ times [$(r - 1)$ equal to 2] to give rise to a sum of squares with $r - 1$ degrees of freedom and the total of these sums of squares from the r points belongs to the component of error in the analysis of variance.

Since each experimental point utilizes n samples and there are r centroid points, i.e., 1 centroid point repeated $r - 1$ times, an analysis of variance is done. A F -test between the among replications mean square and within replications mean square gives an estimate of the composition variance and testing variance.

The augmented extreme vertices simplex lattice design for mixture problems is uniquely determined, once the constraints for the chosen factors to be used in the experiment are decided on. In addition, the

design allows the investigation of the extreme points in the factor space as well as internal points. This design can also be applied sequentially to locate the optimum treatment combination.

Selection of Components and Their Volumetric Loading

In order to have a broader range of applicability of results, the materials chosen for this investigation were widely different from each other in their cost, property improvement and characteristic nature. The selection of the resins is discussed under the selection "Determination of Experimental Conditions," page 31.

The six fillers used, their density, mean particle size and cost are presented in table 3, page 30. A range of particle sizes was desirable to obtain higher filler loadings. Marble was the cheapest filler that improved physical properties and also permitted high loadings. Clay and wollastonite gave tensile and flexural strength improvements. The pecan shell flour improved mechanical properties and absorption at low cost. Glass microballoons and foamed thermoplastic microspheres were higher in cost and decreased the mechanical properties, but were necessary to decrease the density.

The total loading or viscosity increase determined the following individual filler loadings. The five fillers: clay, marble, IG101 glass, microballoons, Saran microspheres and wollastonite had a volumetric lower and upper bounds of 0.01 and 0.25 respectively. To assure sufficient absorption properties of the castings, the filler pecan shell

flour had a lower limit of 0.05. Its upper limit was 0.29.

The flexible polyester resin, rigid polyester resin and styrene monomer were varied from 0.56, 0.05, 0.05 fractions on the lower bound to 0.80, 0.29 and 0.29 on the upper bound. In every case these fractions always summed to unity according to the experimental design.

The composition of each experimental point, computed according to the augmented, extreme vertices, simplex lattice design is presented in coded values in Table 2, page 28.

Table 2

Coded Values for an Eight Variable, Augmented,
Extreme Vertices, Simplex Lattice Experimental Design

No. ^a	X1	X2	X3	X4	X5	X6	X7	X8	X9
1	0	-3	-3	-3	-3	-2	1	-2	-2
2	-1	-1	-3	-3	-3	-2	1	-2	-2
3	-1	-3	-1	-3	-3	-2	1	-2	-2
4	-1	-3	-3	-1	-3	-2	1	-2	-2
5	-1	-3	-3	-3	-1	-2	1	-2	-2
6	-1	-3	-3	-3	-3	- .5	1	-2	-2
7	-1	-3	-3	-3	-3	-2	2	-2	-2
8	-1	-3	-3	-3	-3	-2	1	- .5	-2
9	-1	-3	-3	-3	-3	-2	1	-2	- .5
10	-3	0	-3	-3	-3	-2	1	-2	-2
11	-3	-1	-1	-3	-3	-2	1	-2	-2
12	-3	-1	-3	-1	-3	-2	1	-2	-2
13	-3	-1	-3	-3	-1	-2	1	-2	-2
14	-3	-1	-3	-3	-3	- .5	1	-2	-2
15	-3	-1	-3	-3	-3	-2	2	-2	-2
16	-3	-1	-3	-3	-3	-2	1	- .5	-2
17	-3	-1	-3	-3	-3	-2	1	-2	- .5
18	-3	-3	0	-3	-3	-2	1	-2	-2
19	-3	-3	-1	-1	-3	-2	1	-2	-2
20	-3	-3	-1	-3	-1	-2	1	-2	-2
21	-3	-3	-1	-3	-3	- .5	1	-2	-2
22	-3	-3	-1	-3	-3	-2	2	-2	-2
23	-3	-3	-1	-3	-3	-2	1	- .5	-2
24	-3	-3	-1	-3	-3	-2	1	-2	- .5
25	-3	-3	-3	0	-3	-2	1	-2	-2
26	-3	-3	-3	-1	-1	-2	1	-2	-2
27	-3	-3	-3	-1	-3	- .5	1	-2	-2
28	-3	-3	-3	-1	-3	-2	2	-2	-2
29	-3	-3	-3	-1	-3	-2	1	- .5	-2
30	-3	-3	-3	-1	-3	-2	1	-2	- .5
31	-3	-3	-3	-3	0	-2	1	-2	-2
32	-3	-3	-3	-3	-1	- .5	1	-2	-2
33	-3	-3	-3	-3	-1	-2	2	-2	-2
34	-3	-3	-3	-3	-1	-2	1	- .5	-2
35	-3	-3	-3	-3	-1	-2	1	-2	- .5
36	-3	-3	-3	-3	-3	.5	1	-2	-2

Table 2 - continued.

No. ^a	X1	X2	X3	X4	X5	X6	X7	X8	X9
37	-3	-3	-3	-3	-3	- .5	2	-2	-2
38	-3	-3	-3	-3	-3	- .5	1	- .5	-2
39	-3	-3	-3	-3	-3	- .5	1	-2	- .5
40	-3	-3	-3	-3	-3	-2	2.5	-2	-2
41	-3	-3	-3	-3	-3	-2	2	- .5	-2
42	-3	-3	-3	-3	-3	-2	2	-2	- .5
43	-3	-3	-3	-3	-3	-2	1	.5	-2
44	-3	-3	-3	-3	-3	-2	1	- .5	- .5
45	-3	-3	-3	-3	-3	-2	1	-2	.5
46	-2.5	-2.5	-2.5	-2.5	-2.5	-1.5	1.5	-1.5	-1.5
47	-2.5	-2.5	-2.5	-2.5	-2.5	-1.5	1.5	-1.5	-1.5
48	-2.5	-2.5	-2.5	-2.5	-2.5	-1.5	1.5	-1.5	-1.5

^a The same numbering system is used in Table 4.

-3	0.01
-2.5	0.0367
-2	0.05
-1.5	0.0767
-1	0.13
- .5	0.17
0	0.25
.5	0.29
1	0.56
1.5	0.5867
2	0.68
2.5	0.80

Table 3Properties of the Components Used

No.	Name of Component	Density g/ml	Mean Particle Size Microns	Cost c/lb	Cost c/liter
1	Clay	2.580	4.5	1.97	11.20
2	Marble	2.710	40.0	0.50	3.00
3	Glass Microballoons	0.340	62.0	69.00	52.00
4	Saran Microspheres	0.032	30.0	350.00	26.30
5	Wollastonite	2.890	30.0	1.85	11.80
6	Pecan Shell Flour	1.300	125.0	2.50	7.16
7	Polyester Resin-Flexible	1.148	-	26.80	67.80
8	Polyester Resin-Rigid	1.335	-	18.00	56.50
9	Styrene	0.900	-	11.50	22.81

IV. EXPERIMENTAL

This section describes the plan of experimentation, the method of procedure, the data and results.

Plan of Experimentation

The plan of experimentation consists of four sections. The first section is concerned with the statistical design of the experiment and computation of suitable experimental points; the second section includes the preparation of mold pieces for testing, their testing for mechanical properties and the collection of data. Regression analysis of the data to obtain the proper response surface equations is described under section three. Optimization of the filler content, subject to chosen constraints, is described in section four.

The experimental design is discussed under "Experimental Design," page 19.

Method of Procedure

In this section, the experimental techniques involved in sample preparation, the testing of the samples and the applicability of the standard test methods are presented.

Determination of Experimental Conditions. The determination of experimental conditions includes the selection of fillers, choice of resins, determination of catalyst level, curing conditions and proper testing

speeds. The selection of fillers is described under "Experimental Design," page 26.

The choice of the resins was based on the measurability of the resin mechanical properties. The resin should preferably have a high ultimate elongation so that the resin-filler system would not be too brittle when highly filled. However, it should not be so flexible that the flexural strength is unmeasurable even when filled or that the ultimate elongation exceeds the maximum of 50 percent that is measurable. It has been reported⁽¹⁹⁾ that a mixture of 70 percent flexible resin and 30 percent rigid resin has these properties. It has also been recently found⁽¹⁷⁾ that a 90/10 mixture is suitable. It was therefore decided to vary the ratio of flexible to rigid resin from about 52/48 to 94/6 so that all possible combinations could be studied for better results.

The flexible resin chosen was the American Cynamid, EPX-279-1 and the rigid resin was the American Cyanamid EPX-187-3.

The determination of the catalyst level was carried out by slightly altering the amount of the promoter, cobalt naphthenate, and the accelerator, dimethyl aniline, so as to have a gel time of approximately 300 to 400 seconds. This allowed sufficient time for mixing the catalyst and resin well and pouring the resin into the mold, but increased the viscosity of the mixture rapidly enough to minimize the settling of heavier filler particles.

The speed of testing affects the creep effects inversely till the creep effects level off to a minimum at a particular speed. Higher speeds do not increase the tensile or flexural strengths and it is desirable to test the specimens just above this particular speed. The

speeds selected were the recommended speeds⁽¹⁷⁾ of one inch per minute for the tensile tests, two inches per minute for the flexural tests, and 0.05 inches per minute for the compression tests⁽⁴⁾.

Sample Preparation. The true densities of all the fillers were taken from the manufacturer's literature. The densities of the flexible and rigid resin and styrene were determined individually in their uncatalyzed state. These densities are given in table 3, page 30. The experimental design points, all of which represented the different compositions on a volumetric basis, were recomputed on a weight basis using the density data.

According to this calculation, the six fillers were accurately weighed and well mixed. The two resins and styrene were separately weighed and mixed. Then the fillers and the resins were blended in a plastic container with an air driven stirrer.

The catalyst system level was computed on the basis of the total weight of the resin present, excluding the styrene monomer added as a variable component but including the about 25 weight percent styrene in the resin as supplied. The promoter, 6 percent cobalt naphthenate, was set at 0.14 weight percent and the accelerator, dimethyl aniline, was set at 0.07 percent by weight. The promoter and accelerator were added by a syringe to the well blended filler-resin mixture and mixed. One percent by weight of the catalyst, methyl ethyl ketone peroxide, was added to the mixture from a syringe and well mixed for 40 to 50 seconds, taking care not to introduce any air bubbles. The catalyzed resin was poured into a RTV-Silastic Rubber mold. Gelation occurred in about 300

to 400 seconds and the samples were demolded after another 400 seconds. The samples were then post cured in an oven at 70°C for 19 to 21 hours.

After all the samples were prepared, the surface of each sample was sanded to a flat surface on a wide belt sander at Polytron Corporation of Virginia, Christiansburg, Virginia.

Sample Testing. Standard testing procedures were employed to determine the mechanical properties of the molded samples. The tensile properties were determined according to the ASTM D 638 "Standard Method of Test for Tensile Properties of Plastics."⁽³⁾

Five tensile specimens were made for each sample. The specimens were of standard shape and the cross-sectional area of the flat section as cast was 0.5 x 0.5 inches. After sanding, the depth ranged from 0.4 to 0.5 inches.

The specimens were measured with a micrometer to the nearest one thousandth of an inch and tested on an Instron Universal Testing Machine equipped with wedge action grips. After fastening the specimen in the grips, a previously calibrated Instron strain gauge extensometer with a one-inch gage length was attached to the specimen. The crosshead moved at a speed of one inch per minute until rupture occurred. Strain was recorded directly on a chart movement of four inches for ten percent strain. The chart moved at ten times the speed of the crosshead. A typical load versus strain curve is presented in Appendix A, page 79. The data from the charts was punched on cards and the yield tensile strength, ultimate percentage elongation, secant modulus at one percent strain, the mean and the standard deviation of the observed values were calculated by

the computer.

The flexural properties were determined in accordance with ASTM D 790, "Standard Method of Test for Flexural Properties of Plastics"⁽⁵⁾. Due to the flexibility of the high-resin, low-filler samples, the prescribed dimensions were not used. The cast specimens were 5.0 inches long, 0.7 inches deep and 0.5 inches wide. The width ranged from 0.4 to 0.5 inches after sanding. A 2.0 inch span length was used to prevent the slippage of the specimen in the grips. These dimensions are not in agreement with the ASTM requirements that "the depth shall not exceed the width" and "the span shall be 16 times the depth"⁽⁵⁾. Thus, this procedure gives only comparative results, rather than absolute results.

The specimens were tested on an Instron Universal Testing Machine with an Instron Flexure Jig. The specimens were placed in the jig and the crosshead moved at a speed of two inches per minute until rupture occurred. The chart speed was 20 inches per minute. A typical load versus deflection curve is presented in Appendix B, page 80. The flexural strength and the modulus of elasticity in flexure were calculated using the computer.

The compression strength was determined according to ASTM D 695 "Standard Method of Test for Compressive Properties of Rigid Plastics"⁽⁴⁾. This test was carried out on the Instron Universal Testing Machine equipped with compression cell. The crosshead moved at 0.05 inch per minute while the chart moved at 0.5 inch per minute. A typical load versus deformation curve is presented in Appendix A, page 79. The mean compressive strength and its standard deviation were calculated by the

computer.

The density of the samples was calculated by measuring the volume of different pieces and their weight in air. The mean value was recorded as the density.

Data and Results

The data and results of this investigation are presented in this section.

The Effect of Fillers on Mechanical Properties. Tensile strength, secant modulus (tensile) at one percent strain, ultimate percentage elongation, flexural strength, flexural modulus, compressive strength and density were the properties measured for each experimental sample. Using the same system of numbering as is used in the table giving the experimental design (page 28) the above mean property values are reported in table 4, on page 38 for each experimental sample. The cost of each sample composition is also included for comparison purposes. The cost and the particle size of the fillers used are given in table 3, page 30.

Regression Analysis

The data for all the samples were utilized in obtaining a good regression equation. A full second order polynomial was fitted using a BMD computer program⁽⁴¹⁾.

Optimization of Filler Content

The cost of the formulation was expressed as a function of the various components in the mixture and this relationship was used as the objective function whose value had to be minimized, subject to the constraints set. A pattern search method was selected for use in the optimization and was employed for the calculations on the computer. The best of several solutions was selected as the suitable solution. Regression analysis and optimization are discussed in detail in the discussion section, page 49.

Table 4

Properties of Experimental Samples

No.	Density g/ml	Tensile Strength $\times 10^{-3}$,psi	Flexural Strength $\times 10^{-3}$,psi	Compression Strength $\times 10^{-3}$,psi	Secant Modulus $\times 10^{-3}$,psi	Flexural Modulus $\times 10^{-3}$,psi	Ultimate Elongation %	Cost Cents/liter
1	1.524	1.790	5.066	6.992	96.772	75.821	6.25	46.03
2	1.540	2.174	5.746	6.995	144.436	98.033	3.50	45.05
3	1.255	1.992	5.158	6.744	150.662	200.548	3.75	50.93
4	1.218	1.810	4.812	7.759	104.285	73.772	4.75	47.84
5	1.561	2.547	6.320	6.841	192.286	238.093	2.75	46.10
6	1.370	2.619	6.527	8.425	176.678	255.389	2.83	45.56
7	1.353	1.742	5.350	9.087	76.219	119.019	13.00	52.82
8	1.375	2.740	6.457	10.320	170.477	203.992	3.16	51.47
9	1.323	2.647	7.008	11.265	158.520	196.839	4.50	47.44
10	1.556	1.756	4.930	5.053	120.088	178.962	4.75	44.06
11	1.271	1.495	4.193	5.049	105.821	144.552	5.50	49.94
12	1.234	1.326	3.922	5.826	68.542	92.949	8.83	46.86
13	1.571	2.012	5.710	5.072	149.286	106.484	3.50	45.12
14	1.360	2.093	5.640	6.273	123.925	90.966	4.25	44.58
15	1.369	1.354	4.322	7.250	57.920	84.523	13.30	51.84
16	1.391	2.676	6.291	8.583	172.846	212.616	3.50	50.48
17	1.339	2.391	5.931	9.483	155.229	84.923	4.00	46.45
18	0.986	1.055	3.020	6.851	68.198	87.952	10.00	55.82
19	0.950	0.979	3.111	7.875	49.265	39.920	12.70	52.74
20	1.293	1.529	4.401	4.697	117.360	89.910	4.25	51.00
21	1.102	1.579	4.645	6.073	101.706	76.399	5.50	50.46
22	1.085	1.178	3.822	9.195	49.636	93.970	20.25	57.72
23	1.107	2.134	5.855	8.791	140.909	171.469	5.00	56.36
24	1.055	1.951	5.627	10.742	113.217	149.987	8.16	52.33

Table 4 - continued

No.	Density g/ml	Tensile Strength $\times 10^{-3}$,psi	Flexural Strength $\times 10^{-3}$,psi	Compression Strength $\times 10^{-3}$,psi	Secant Modulus $\times 10^{-3}$,psi	Flexural Modulus $\times 10^{-3}$,psi	Ultimate Elongation %	Cost Cents/liter
25	0.913	0.831	2.405	7.880	28.853	39.518	16.70	49.66
26	1.255	1.551	4.641	4.123	88.557	145.391	7.10	47.92
27	1.065	1.362	3.995	6.659	60.385	47.749	9.25	47.37
28	1.047	1.170	3.550	9.325	36.676	22.903	20.00	54.64
29	1.070	2.074	5.458	9.936	98.425	117.795	6.10	53.28
30	1.018	2.096	5.961	14.849	101.368	121.118	11.70	49.25
31	1.599	1.701	6.842	5.523	113.891	92.042	4.75	46.18
32	1.408	2.061	5.786	6.140	151.090	233.562	2.75	45.63
33	1.390	1.488	4.923	7.655	69.508	127.688	11.75	52.90
34	1.413	2.648	6.893	8.795	188.910	238.930	2.75	51.54
35	1.361	2.683	6.832	8.820	177.011	228.251	3.83	47.51
36	1.218	2.230	4.952	7.444	125.650	167.862	4.75	45.09
37	1.200	1.742	5.723	8.605	65.118	118.473	15.67	52.35
38	1.221	2.967	7.502	11.180	168.391	209.106	3.25	51.00
39	1.170	2.837	7.476	12.713	147.005	187.590	6.58	46.96
40	1.181	1.376	4.225	13.302	35.650	47.539	28.10	59.62
41	1.204	2.465	6.813	16.235	106.444	121.308	9.83	58.26
42	1.152	2.156	7.116	10.277	93.620	127.054	24.30	54.23
43	1.266	3.671	8.489	20.086	183.699	233.242	3.00	56.90
44	1.174	3.725	8.810	17.021	184.266	188.491	5.17	52.87
45	1.122	3.467	8.203	17.576	163.933	205.205	7.50	48.84
46	1.259	2.222	5.554	8.330	138.991	81.023	4.50	50.25
47	1.259	2.101	5.449	9.419	130.262	78.496	5.50	50.25
48	1.259	2.089	5.560	9.391	133.316	78.339	5.25	50.25

V. DISCUSSION

This section contains discussion of the literature, experimental procedure, results obtained from tests, experimental design, multiple regression analysis and optimization with examples. The limitations imposed upon the results as well as recommendations for future study are also presented.

Discussion of Literature

There is considerable information in the literature on particulate filled elastomers and thermoplastics and fiber reinforced thermosets. Particulate filled thermosets have not yet received the adequate attention they deserve. The effects of different fillers on the mechanical properties of various plastics have been studied. Positive as well as negative effects have been reported. There have been a few attempts to predict the mechanical properties quantitatively. However, since these depend on a variety of factors, correlations based on single characteristics such as particle size, volumetric filler content, adhesion, effect of temperature, etc., are not applicable in a general case. The polymer-filler interactions and the reinforcement effects demand serious attention since the existing information is inadequate and very approximate. The only practical method at present appears to be to develop individual empirical equations through experiments for the particular set of fillers and resins one is concerned with.

A pertinent study⁽¹⁾ of particulate filled polyesters has reported a general reduction of strength to an equal extent by three types of fillers. However, a closer examination reveals that, at 20 percent volume, marble filler gives a tensile strength of 4400 pounds per square inch while glass microballoons give only 2300. Microballoons and wood flour differed by over 1000 pounds per square inch. The same phenomenon was exhibited for compression strength and flexural strength values, but to a varying degree. Thus the effect of different fillers can not be well represented by a single graph, if their individual effects are important.

Discussion of Experimental Design

The augmented, extreme vertices, simplex lattice design employed in this investigation has made it possible to explore a very wide experimental space, both on the surface and inside of the total experimental region. In addition, it allowed every component to be varied between any reasonable limits of composition.

By setting the lower limit of every component at some positive value (not equal to zero), each component is present in every experiment and hence all the interaction terms and their coefficients are preserved in the multiple quadratic regression equation. In other words, even if the interaction effect in a particular case is small, it can never be zero. This gives an idea of the relative interaction effects between the various components.

The lower and upper limits set on each component can be varied with in any reasonable limits as long as the composition is physically possible to obtain.

It is, however, inconvenient to plot the results obtained from an experiment designed by this method, since all the components vary from one experiment to another and there is no single definite value held constant, which can serve as a reference. This difficulty can be partly remedied by a similar $\{q,m\}$ design, in which m is set greater than 2. The higher the value of m , more the midpoints $(m-1)$. This would enable the variation caused by the $(m-1)$ different ratios between the two components, while all the others are held constant, to be very easily recognized.

Thus, the design is a very flexible and versatile one and can be suitably modified for experiments of similar nature.

Discussion of Procedures

The procedures for sample preparation and testing are discussed in this section.

Sample Preparation Procedure

The most important aspect of the sample preparation is the good mixing of all the components, without introducing too many air bubbles. It was noticed that in cases where some bubbles are present in the uncatalyzed mixture, if the mixture were allowed to stand for a few minutes, most of the bubbles came to the surface and slow mixing at this

point will almost eliminate them. The mixture could be catalyzed at this time and poured. The catalyst system level used was very effective in not only minimizing the settling of heavier fillers, but also in controlling the low density fillers from accumulating at the surface. This was mainly accomplished by good mixing and the reasonably quick gel time.

Testing Procedure

The testing procedures were based on ASTM standards. The tensile and compression tests are exactly in accordance with the standards, while the flexural tests were not. This was due to the very flexible nature of the low filler-high resin specimens. The modifications of the standard flexural procedure consisted of (1) the depth exceeding the width of the specimen, (2) the span to depth ratio being less than 16 to 1. This prevented the specimen from slipping in the flex jig during testing.

Thus, while the tensile strength, secant modulus (tensile) and compression strength can be termed as "absolute" values and are comparable to the literature values, the flexural strength and flexural modulus can be utilized for qualitative comparison only.

Reproducibility of Results

A measure of the reproducibility of the results is obtained by calculating the standard deviation of the different mechanical properties for each experimental point and expressing it as a percentage of the mean value. The ranges of standard deviations generally observed

in each case are given below.

<u>Property Tested</u>	<u>Ranges of Standard Deviation</u>
Tensile Strength	1 - 4%
Compression Strength	1 - 4%
Flexural Strength	1 - 5%
Secant Modulus	1 - 7%
Flexural Modulus	2 - 12%

The experimental error is thus under five percent for all tests. The secant modulus and flexural modulus calculations necessitated the measurement of the slope of the load-elongation and load-deflection curves, respectively. This introduces some additional error. Further, in the case of flexural modulus, the initial maximum slope had to be measured. However, it was noticed that this slope varied considerably and very often it was not well defined either, as can be seen from the sample flexural test curves shown in Appendix B , page 80. An error of 5.0 percent in recording and reading the deflection can cause as much as 15,000 psi difference in the calculated flexural modulus. Hence, it is perhaps not surprising that the flexural strength data shows as much variation as it does.

Error Introduction

Sample Preparation versus Sample Testing

The experimental design purposely included two replications of the centroid point so that the variance introduced by sample preparation (composition error) and by sample testing (testing error) can be

established. Considering the three values of flexural strength (5553.9 psi, 5648.9 psi, 5560.4 psi) for the same composition (one original and two replicated centroid experiments) each is a mean of the five samples tested. A F-test between the among replications (tests) mean square and the within replications (samples) mean square shows that the differences among the three tests are not significant, when tested against the differences among the samples. In fact, both of them contributed almost identical amounts of variance.

A similar F-test with tensile strength values gives the same result, except that the composition mean square was higher than the testing mean square, though not significantly. However, the compression strength values showed that the mean square due to composition was highly significant, when tested against the mean square due to testing.

Since the same composition was used for all the three different tests and the variance due to testing was not significant in all the three tests, it can be concluded that the testing of the samples does not introduce any significant errors. Further, since only the compression strength was significantly affected by the small changes in essentially the same composition, it can be concluded that only compression test values were affected by the distribution of the minute air bubbles and the larger than average size particles which vary from one to the other composition.

Discussion of the Effects of Fillers, Resins and
Monomer on Mechanical Properties of Polyester Resin

This section includes a discussion of the effect of fillers, resins and monomer on each of the mechanical properties studied as well as some other qualitative effects noticed during the investigation. The results are compared with the reports in the literature. The properties of all the compositions prepared are listed in Table 4, page 38, using the same numbering system as is used in the table giving the experimental design, Table 2, page 28. There are 9 vertices or design points, each containing a maximum fraction of one of the 9 components. Hence each vertex point will show the effect of one component predominately. Mostly these points (experiment numbers 1, 10, 18, 25, 31, 36, 40, 43, 45) are used to discuss the effect of each component.

Effect on Density. The fillers affect the density of the composite in the same order as their individual densities. The low density fillers, glass microballoons and saran microspheres decrease the density, the effect of the latter being greater, since it is about ten times lighter than the former. Pecan shell flour is only slightly denser than the composite where all components are at their minimum values. This is easily computed to be 1.1913 grams/ml. Thus, shell flour increases the density only very slightly. The high density fillers, clay, marble and wollastonite, increase the density rapidly in the same order. The resins show small decreasing effect while the styrene, being only three-fourths as heavy as the mixture, reduces the density more sharply.

The fact that a linear correlation can predict the density very well shows that density is a linearly additive property and that there are negligible filler-resin interactions, such as absorption or dissolution, and that the indicated filler content approaches a true volume percent very closely.

Effect on Tensile Strength. The rigid fillers--clay, marble and wollastonite--improved the tensile strength very moderately and almost to the same extent while the pecan flour gave a very definite increase due to its slightly fibrous nature. The glass microballoons and saran microspheres caused sharp decreases, the latter having a larger negative effect. These results are in accordance with the conclusions of Alter⁽²⁾ for a ductile resin matrix. Clay appears to give the best results among clay, marble and wollastonite.

The rigid resin gives almost three times the tensile strength of the flexible resin. This agrees with the reported conclusions of Boenig⁽⁷⁾ based on the compositions of the flexible and rigid polyester resins. Styrene shows a remarkable increase in tensile strength, justifying Boenig's statement "Generally the tensile strength is high at high styrene levels"⁽⁷⁾.

Effect on Ultimate Elongation. All the six fillers produced significant reductions in ultimate elongation, though the effects of glass microballoon and saran microspheres were less. The rigid resin permits very little elongation compared to the flexible resin. Styrene allows an intermediate elongation. These effects are consistent with the reported information in the literature^(8,15,29).

Effect on Flexural Strength and Flexural Modulus. The flexural strength was improved by marble, shell flour, clay and wollastonite in that order, though the first three had very similar effects. The low density fillers reduced the flexural strength, the saran microspheres showing a higher reduction. The improvement noticed is in contrast to that reported by Alford and Veatch⁽¹⁾. The rigid resin showed a dramatic improvement and is in agreement with the data of Boenig⁽⁷⁾. It has been attributed to the different glycols and acids used in the two resins. Styrene also causes a large improvement in flexural strength and it is attributed by Boenig⁽⁷⁾, to the low degree of unsaturation in the resins used.

The flexural modulus is also affected in a similar fashion, except that the glass microballoons show an increase in modulus and marble causes a significant improvement.

Effect on Compression Strength. All the fillers significantly reduced the compression strength. The saran microsphere and glass microballoons gave higher compression strengths due to the more uniform and predictable stress pattern they produce. Shell flour gave the highest compression strength among the other fillers and was followed by clay, wollastonite and marble, in that order. The rigid resin showed the largest increase followed by styrene. These agree with the results reported by Oleesky⁽²⁹⁾ and Boenig⁽⁷⁾.

Effect on Secant Modulus. Pecan shell flour, marble wollastonite, clay and glass microballoons showed improvements in secant modulus and only the saran microspheres showed a small decreasing effect. The rigid resin gave the highest improvement, followed by styrene.

Other effects. There were also a number of secondary or side effects observed during the investigation. The resin viscosity was increased rapidly by the addition of fillers. Too high an increase is undesirable, as good mixing is made difficult and an excessive number of air bubbles are formed in the molded piece. The limiting viscosities for each filler were generally higher than 30 percent by volume, except clay and wollastonite for which the limiting value was around 25 percent. Clay filler particles, due to their very small size (5 microns mean), had a high surface area per unit weight to be wetted. Wollastonite, even though it is larger, (30 microns mean), due to its acicular shape, presents a large area to the resin. These factors cause the limiting viscosity to be lower for these fillers.

The effects of clay and rigid resin on gel time were significant. Clay and the rigid resin, at 25 and 29 volume percent respectively, increased the gel time from about 300 seconds to 1700 and 1000 seconds respectively. The rigid resin contains maleic or phthalic acids, which have a lower reactivity than the adipic or fumaric acid present in the flexible resin. Their effect, as has been reported by Boenig⁽⁷⁾, is to increase the gel time.

The styrene monomer increased the exotherm temperature significantly and also caused higher volumetric shrinkage. Both effects agree with the reported data of Boenig⁽⁷⁾.

Discussion of Multiple Regression Analysis

Fitting response surface equations to experimental data is accomplished by multiple regression techniques. The response Y is related to a set

of independent variables X_i , $i = 1, \dots, n$ according to the general linear model

$$Y = B_0 + \sum_{i=1}^p B_i z_i$$

where B_i is the coefficient of the i^{th} term in a fitted equation in $(p+1)$ terms. The model is linear in its coefficients, not necessarily in the z_i . The z_i represent expressions in terms of the x 's, such as x_i , $x_i x_j$ and x_i^2 . Thus, the linear response surface equation and the quadratic equation are both forms of the same general linear model.

In order to use multiple regression techniques with a non-linear fitted equation (in this case, a full quadratic equation of 45 terms), it is necessary to create new variables from the original set x_i , $i=1, \dots, n$. These new variables are products of selected original variables. For example,

$$z_{n+1} = x_1^2$$

and

$$z_{2n+1} = x_1 x_2$$

for a quadratic model in n independent variables. n equals 8 in this investigation since the total number of components is 9.

The fitted quadratic equation contains one intercept, eight linear terms, eight pure quadratic terms and twenty-eight mixed quadratic terms. The eight original variables (the volumetric fractions of the first eight components) and the mean value of the dependent variable (the mechanical properties) were punched on cards and a simple computer program was used to obtain the new variables such as x_1^2 , x_2^2 , ..., $x_1 x_2$, $x_1 x_3$... etc., on cards. Styrene, being the 9th variable was

not used in these calculations. However, it equals the sum of the first eight variables subtracted from unity.

This card deck contains the 44 independent variables (8 original and 36 newly created) and the one independent variable such as tensile strength, flexural strength, compression strength, secant modulus, flexural modulus, ultimate elongation or density. The BMD "Multiple Regression with case combinations" computer program⁽⁴¹⁾ was employed, with the above deck being the data.

Table 5 on page 52 presents regression coefficients obtained for each of the seven properties.

It can be seen from the large numerical values of the mixed quadratic terms that the interaction effects were significantly important for all the correlations except for density which was extremely well-represented by a linear relation. However, no uniform trend is indicated by the regression coefficients of the interaction terms. Any such tendency is made more difficult to be observed by the changing sign of the intercept.

An indication of the closeness of fit of the equations to the data is given by the F-test, the range of residuals (the absolute sum of the largest positive and negative differences between the actual value of the dependent variable and the value estimated by the regression equation) and the standard error of the estimate. These values are given for each correlation in Table 6, page 54.

Good correlations were obtained in every case except for flexural modulus and ultimate elongation. This is not surprising since the

Table 5

Multiple Regression Coefficients of the Mechanical Properties

No.	Regression Coefficient/ of the term	Density g/ml	Tensile Strength x10 ⁻³ ,psi	Flexural Strength x10 ⁻³ ,psi	Compression Strength x10 ⁻³ ,psi	Secant Modulus x10 ⁻³ ,psi	Flexural Modulus x10 ⁻³ ,psi	Ultimate % Elongation
1	X1	1.37649	- 8.30127	- 2.34888	- 39.64063	1002.01953	169.62500	- 16.67578
2	X2	1.57042	- 7.09424	-27.54419	- 59.70703	1629.29297	-5728.50000	- 62.40625
3	X3	-1.02582	-21.63770	-12.17529	- 62.36328	- 352.51563	-1199.25000	- 95.16797
4	X4	-1.10082	- 9.71753	27.37280	189.74609	- 81.35156	249.31250	95.49219
5	X5	1.58401	2.44946	- 4.52295	-122.58594	2420.97656	1757.56250	3.07031
6	X6	0.27504	2.90845	14.45068	73.64063	772.81641	- 616.18750	7.92749
7	X7	0.08755	- 6.43823	40.03906	35.10156	- 343.25000	- 263.43750	281.85938
8	X8	0.34322	20.61328	30.09766	- 44.92969	1074.62500	-1331.75000	159.19141
9	(X1)(X1)		- 7.71655	-16.92944	44.83057	-2155.00391	-2975.50000	274.98700
10	(X2)(X2)		9.08789	53.30981	101.76807	-1105.36328	8393.23438	255.80249
11	(X3)(X3)		15.42944	8.18237	76.96167	13.96094	718.08203	147.88989
12	(X4)(X4)		- 2.22876	-36.45020	-172.27441	- 519.60156	1055.59766	133.17725
13	(X5)(X5)		- 8.48608	57.11914	164.73364	-2817.23438	-4557.83938	262.67041
14	(X6)(X6)		- 5.30078	-51.98022	- 39.24219	- 339.00781	892.10547	81.66504
15	(X7)(X7)		- 0.30304	-38.89282	- 31.96094	11.95313	- 282.28516	-122.84961
16	(X8)(X8)		-16.96362	-21.78906	100.91406	- 913.50000	3096.87500	118.20703
17	(X1)(X2)		29.33862	84.08960	232.82031	- 728.76172	1921.69141	376.96777
18	(X1)(X3)		47.36865	64.44873	128.16406	2623.29688	4527.61719	104.22510
19	(X1)(X4)		24.84985	17.16772	- 86.23828	234.59766	-2257.87891	- 73.63379
20	(X1)(X5)		39.57031	61.38916	268.80859	1095.66016	1716.82422	332.00366
21	(X1)(X6)		29.41357	32.34082	108.14063	2082.10938	5741.64453	156.30957
22	(X1)(X7)		3.99146	-13.40576	- 41.67188	-1422.62500	- 599.68750	-176.10406
23	(X1)(X8)		-23.88110	-65.21484	- 59.08594	- 938.62500	2106.81250	276.51953

Table 5 - continued.

No.	Regression Coefficient/ of the term	Density g/ml	Tensile Strength $\times 10^{-3}$, psi	Flexural Strength $\times 10^{-3}$, psi	Compression Strength $\times 10^{-3}$, psi	Secant Modulus $\times 10^{-3}$, psi	Flexural Modulus $\times 10^{-3}$, psi	Ultimate % Elongation
24	(X2) (X3)		30.83545	72.40283	134.72266	- 250.17188	8423.48047	258.69629
25	(X2) (X4)		9.19482	30.31128	- 96.21094	-2007.03516	6859.47266	242.61792
26	(X2) (X5)		20.39624	93.95874	270.19141	-1650.10547	361.38672	417.03931
27	(X2) (X6)		10.86279	45.68140	82.95313	-1340.91406	2110.63281	287.88379
28	(X2) (X7)		- 4.85352	- 9.80786	- 44.73047	-2446.31250	4790.12500	-123.57422
29	(X2) (X8)		-10.35767	- 1.75781	- 55.46484	- 533.87500	10493.00000	333.15234
30	(X3) (X4)		15.76978	- 4.81396	- 41.16016	- 424.95703	-1336.08594	221.25879
31	(X3) (X5)		17.52173	24.20850	156.94141	- 947.02344	-5302.31641	178.97192
32	(X3) (X6)		5.84326	- 2.23145	- 18.14844	36.89453	-3415.91406	84.68555
33	(X3) (X7)		13.64160	-23.22705	3.35547	- 99.75000	940.50000	68.37500
34	(X3) (X8)		-17.32886	-10.82813	-128.26563	169.06250	3120.87500	147.24609
35	(X4) (X5)		9.15894	17.69849	- 19.21875	-2115.65234	568.75391	129.55566
36	(X4) (X6)		-19.10693	-70.59912	-262.41016	-2000.56250	-3387.25000	97.59766
37	(X4) (X7)		3.33643	-65.34473	-272.25781	- 161.93750	-1968.06250	-197.08203
38	(X4) (X8)		-31.37109	-61.69531	-333.67578	-1949.37500	1411.93750	- 23.81641
39	(X5) (X6)		- 7.03296	- 6.73853	120.37500	- 952.28516	2079.11719	190.75439
40	(X5) (X7)		-10.91260	-30.48633	30.62500	-3131.12500	-2125.06250	-226.73438
41	(X5) (X8)		-27.97339	-22.51172	5.89844	- 916.75000	2386.12500	288.11328
42	(X5) (X7)		- 8.58203	-17.31396	-173.57422	-1370.00000	36.43750	-128.65625
43	(X6) (X8)		-21.02295	-23.69141	- 99.07813	- 272.87500	3128.68750	142.53125
44	(X7) (X8)		-20.08594	-34.40625	57.77344	-1093.25000	168.43750	-437.58984
45	Intercept	1.13249	7.20898	- 1.36665	12.42926	327.78809	544.71973	- 99.53694

X1=Clay X3=Glass

X2=Marble X4=Saran Microspheres

X5=Wollastonite

X6=Pecan Shell Flour

X7=Flexible Resin

X8=Rigid Resin

$$1 - \sum_{i=1}^8 X_i = \text{Styrene}$$

Table 6Comparison of the Multiple Regression Analyses

<u>Property Correlated</u>	<u>Confidence Limit</u>	<u>Range of Residuals</u>	<u>Standard Error of Estimate</u>
Density, gms/ml	>99%	0.093	0.022
Secant Modulus, psi	>99%	9437	5956
Flexural Strength, psi	>95%	385	315
Tensile Strength, psi	>90%	319	195
Compression Strength, psi	>90%	1309	1057
Ultimate Elongation, %	<80%	5.441	2.960
Flexural Modulus, psi	<80%	60712	62271

flexural modulus data were somewhat dispersed and showed a higher variance. The ultimate elongation data were not well defined, especially in the case of more flexible samples. These factors made the data difficult to correlate well in the above cases. Due to their poor correlation, these two properties were not made use of in optimization, thus avoiding any misleading "optimums" from being obtained, especially when one of the above two properties forms a "tight" constraint.

Discussion of Optimization

The optimization procedure, a description of the method of optimization, example optimization results for various constraints and conclusions drawn from the optimization results are discussed in this section.

Optimization Procedure

Selected applications for the polyester filler composite were chosen and the minimum physical properties required for satisfactory application and performance were determined. These were set as the constraints to be satisfied and many possible solutions were obtained. That solution which gave the required properties at minimum cost was accepted as the final optimum composition.

Constrained Pattern Search Method

A very useful multivariable search method is the pattern search method of Hooke and Jeeves⁽¹⁶⁾. This procedure can be used as either a sequential experiment procedure or a computational procedure for locating the optimum of a mathematical equation. It is applied in the latter sense to this research.

Pattern search progresses from an initial base point \underline{x}^0 by evaluating small displacements and moving in the direction which effects an improvement. After all the n dimensions have been so evaluated, a pattern move is made by accelerating through the current base point to a distance twice that from the initial base point to the current base point. If the acceleration move yields an improved solution, it serves as the next base point. If not, the acceleration step is shortened until improvement is achieved. This operation is repeated until an optimum is found.

The pattern search procedure can be easily modified to accommodate constrained problems as well. From some point within the feasible region, (it is necessary that this initial point satisfy all the constraints or else this point is rejected as a starting point) a perturbation is made in the direction of increasing x_1 . A check is made to determine if this perturbation yields an improvement in the objective function. If an improvement is realized, a check is then made to determine if the perturbation causes any constraint to be violated; that is, whether the move steps across a constraint. If a constraint is violated, the move is not made. This operation is repeated for all x_i . An

acceleration step is made just as in the unconstrained case described above, except that the step is shortened if the acceleration moves beyond a constraint. This procedure is repeated until no move can be made without violating any constraint. Such a point is an indicated optimum and is different from the true optimum. This procedure is not guaranteed to locate a true optimum, especially in the case where the feasible region is not convex. Hence, this procedure was applied from several feasible starting points and the best indicated solution was selected as a final solution.

Pattern search is computationally efficient and has excellent ridge-following properties. The computation time for pattern search increases linearly with the number of independent variables, compared to the cube of dimensionality for procedures which require the evaluation of derivatives.

Optimization Examples

The cost of the final composite, which was to be minimized, served as the objective function. Since the cost is volumetrically additive, the cost function is

$$\begin{aligned}
 c = & 0.667 - 0.555X_1 - 0.637X_2 - 0.147X_3 \\
 & - 0.404X_4 - 0.549X_5 - 0.5944X_6 + 0.110X_7 \\
 & - 0.102X_8 - 0.4379 \left(1 - \sum_{i=1}^8 X_i\right).
 \end{aligned}$$

c is the cost in dollars per liter. 0.667 is the cost per liter of a 90/10 flexible-rigid mixture, which was used as the reference cost of resin alone. The individual coefficient for each x_i is the reduction

in cost, expressed in dollars per liter, for unit volume (liter) of the particular x_i component. This is obtained by subtracting the volumetric cost of each component from the reference cost of the resin. The last component x_9 is a dependent variable since the sum of all x_i s must equal unity. Hence it is expressed in terms of the other independent variables.

The response surface equations developed were used to describe the behavior of the composite over the range of compositions examined.

The first case studied in detail was a possible composition for general furniture application. The constraints placed on the properties were:

1. Density \leq 1.5 grams/ml
2. Tensile strength \geq 2500 psi.
3. Flexural strength \geq 6500 psi.

The additional constraints placed were that (1) the sum of all the components must not exceed unity, (2) the sum of all the six fillers must not exceed 55 percent, (3) all components must be present in the composite, even if their fraction be very small.

A total of nine different initial compositions were examined and the indicated optimum cost, optimum composition and the value of density, tensile and flexural strengths were calculated for that composition. These results, along with the starting point for each solution, are given in Table 7, page 59.

A close examination of the results reveals several interesting features. Most important of all, perhaps, is the fact every starting point leads to a different optimum composition. There is no unique

Table 7

Best Indicated Optimum Solutions for General Furniture Applications

No.	Clay X1	Marble X2	Micro balloon X3	Micro sphere X4	Wollas- sphere X5	Shell Flour X6	Flex. Resin X7	Rigid Resin X8	Sty- rene X9	T.S. ^a psi	F.S. ^b psi	Density g/ml	Cost c/liter
1	0.007 (0.010)	0.006 (0.010)	0.000 (0.010)	0.008 (0.010)	0.150 (0.010)	0.170 (0.170)	0.180 (0.560)	0.140 (0.170)	0.339	6530	6511	1.4989	31.60
2	0.105 (0.010)	0.080 (0.010)	0.001 (0.010)	0.010 (0.010)	0.020 (0.010)	0.150 (0.050)	0.300 (0.560)	0.040 (0.290)	0.294	4751	6500	1.4997	32.53
3	0.043 (0.130)	0.047 (0.010)	0.008 (0.010)	0.010 (0.010)	0.090 (0.010)	0.172 (0.170)	0.238 (0.560)	0.126 (0.050)	0.266	5871	6502	1.5000	33.00
4	0.014 (0.010)	0.123 (0.120)	0.003 (0.010)	0.003 (0.010)	0.016 (0.010)	0.183 (0.050)	0.226 (0.460)	0.190 (0.190)	0.242	6375	6508	1.4997	33.86
5	0.110 (0.037)	0.090 (0.037)	0.030 (0.037)	0.030 (0.037)	0.030 (0.037)	0.120 (0.077)	0.330 (0.489)	0.040 (0.177)	0.220	3995	6501	1.5000	34.75
6	0.084 (0.090)	0.091 (0.090)	0.000 (0.010)	0.003 (0.010)	0.010 (0.010)	0.139 (0.110)	0.258 (0.280)	0.108 (0.120)	0.307	5674	6503	1.5000	33.06
7	0.010 (0.010)	0.014 (0.010)	0.007 (0.010)	0.140 (0.010)	0.290 (0.130)	0.060 (0.050)	0.000 (0.560)	0.001 (0.050)	0.478	6036	6571	1.4998	18.95
8	0.015 (0.010)	0.002 (0.010)	0.000 (0.060)	0.050 (0.060)	0.210 (0.160)	0.134 (0.060)	0.186 (0.300)	0.040 (0.100)	0.363	5384	6510	1.4999	28.17
9	0.104 (0.010)	0.020 (0.010)	0.053 (0.060)	0.077 (0.060)	0.160 (0.160)	0.140 (0.060)	0.200 (0.300)	0.065 (0.100)	0.181	5000	6501	1.4999	30.34

Note: Constraints Applied: Density \leq 1.5000; Tensile Strength \geq 2500; Flexural Strength \geq 6500.

The values enclosed in parentheses were the starting points for that optimization.

^a T.S. = Tensile Strength

^b F.S. = Flexural Strength

optimum solution but several solutions are possible. The indicated optimum cost does not vary very much in the first six examples, even though the costs are based on different compositions. Thus, even a single indicated optimum will suffice to have a fairly accurate estimate of the cost, while the composition may not necessarily be the best or representative.

In every case, at least one of the property constraints served as a "tight" constraint. Very often a second constraint was also binding. These were the flexural strength and density constraints. This indicates that the pattern search did not terminate prematurely upon being bound by a single constraint but invariably tried to move in other directions to locate a better optimum and very often this was done successfully.

The synthetic fillers, glass microballoons and saran microspheres, were specified at negligible fractions only, in all the indicated optimum compositions. This is to be expected since the tensile and flexural strength requirements were fairly high and the above two fillers would have only decreased these properties, if present in larger fractions. Further, the high density limit of 1.5 grams/ml made it unnecessary for these low density, high cost fillers to be included.

The pecan shell flour filler was specified at significant levels of between 12 to 18 percent by volume in all the indicated optimum compositions. As it is a widely used filler in actual practice for furniture application and wood-like properties, the optimums can be taken as reasonably close to real values.

A careful analysis of the trends exhibited by the high density fillers--clay, marble and wollastonite--in the tensile and flexural strength values shows that, while they are comparable in the mechanical properties, their order of preference would be clay, wollastonite, marble. However, on a cost basis, the order would be marble, clay, wollastonite. Thus, on an overall basis, they are interchangeable to a certain extent. The six indicated optimum compositions prove that they are indeed interchangeable. Thus, clay is present in three of the six compositions and ranges from 8.0 to 11.0 percent. Marble and wollastonite are in four and two compositions, respectively, and their values range from 8.0 to 12.3 percent and 9.0 to 15.0 percent, respectively. These figures show that the order of preference based on cost has exerted a greater influence in the selection of these fillers.

The flexible resin fraction specified was always appreciably less than the fraction in the starting point, no doubt due to the fact that it was the costliest component and was in fact costlier than the reference cost of the 90/10 flexible-rigid resin mixture. A similar trend is exhibited by the second costliest material, the rigid resin.

The styrene level was fairly high and was as much as the combined resin fraction and varied from 10.8 to 33.0 percent. The total filler content was about 35 percent, only example number 5 selecting a 41 percent content. Although a higher level would have reduced the cost, the high density fillers would have then increased the total density beyond the 1.5 grams/ml constraint.

The total resin fraction ranged from 34.0 to 40.0 percent and it is desirable to have at least this amount of resin for good binding of fillers.

Example number 7 gave an unusually low cost of 18.95 cents/liter, but it had eliminated all resins and contained only saran microspheres, wollastonite and styrene. Styrene was specified at 47.8 percent. This suggested the desirability of constraining the level of the low cost styrene to an acceptable maximum level or else excessive rigidity will result. A decrease in the mechanical properties would occur, if the styrene content increases over about 50.0 weight percent.

Examples 8 and 9 illustrate the effect of the step size chosen on the indicated optimum. The step size is the increment specified for each x_i variable and it is reduced to one-tenth and one-hundredth of the original step size before the solution is accepted as the indicated optimum. While examples 8 and 9 had the same starting points, the former had step sizes of 0.16, 0.15, 0.14, 0.13, 0.12, 0.11, 0.17 and 0.18 for the eight independent variables and the latter had a uniform step size of 0.06 for all x_i s. The final cost as well as composition were different in the two cases. Hence, in all the optimization attempts at least two different step sizes were tried.

The second case examined was the simulation of the properties of the binder used in the polyester Terrazzo-type floor tile. Doyle⁽¹¹⁾ has discussed at length the manufacture and properties of the floor tiles. His data were used to set the following constraints in this optimization:

1. Density \leq 1.75 grams/ml
2. Tensile Strength \geq 3,100 psi
3. Flexural Strength \geq 3,300 psi
4. Compression Strength \geq 14,000 psi
5. Secant Modulus \geq 310,000 psi

The density and compression were revised values of those reported by Doyle as his properties apply to the actual tile, which contains 70 percent by weight of marble chips. The chips would not appreciably affect the other properties and hence they are taken as reported. The additional constraints placed were that (1) all fillers be present in positive fractions, (2) the sum of all fillers not exceed 55 percent, (3) the sum of all components not exceed unity and (4) the styrene fraction be not greater than 33 percent of the total resin volume.

The optimization was attempted for several initial points and three step sizes were tried. The best indicated optimum called for 1.8, 2.1 and 2.0 volume percent of clay, marble and wollastonite respectively. Glass microballoons and saran microspheres were at negligible levels and the flexible resin, rigid resin and styrene were specified at 28, 29, and 19 volume percent. The only filler significantly present was pecan shell flour, which was at 18 percent. For this composition, the properties, as calculated, will be

1. Density = 1.3974 grams/ml
2. Tensile Strength = 6,550 psi
3. Flexural Strength = 8,519 psi
4. Compression Strength = 14,000 psi
5. Secant Modulus = 467,502 psi

The cost of this composition will be 41.46 cents/liter compared to the 50.09 cents/liter for the binder reported by Doyle⁽¹¹⁾. The 50.09 figure was obtained by subtracting the cost of the marble chips (5.25 cents/liter) occupying 45 volume percent from the total material tile cost of 29.7 cents/liter. If the optimum composition reported above were employed, the tile would cost only 25.0 cents/liter and would yet have all the required properties, thus achieving a 19 percent reduction in cost.

The binder, as reported by Doyle⁽¹¹⁾, contains a total of 32 volume percent resin, 20 percent styrene and 23 and 22 percent of limestone and china clay respectively. It is interesting to note that in spite of the marble and clay fillers (which are similar to the above fillers) considered, the optimization yielded only about 2.0 percent of each, while the new filler pecan shell flour was selected at 18 percent. This indicates that a thorough search for better fillers in floor tile production is most desirable.

Effect of Property Constraints on Cost

Different property constraints will have different effects on the final cost of the composite. To examine these effects as well as to find the optimum cost and composition for various furniture applications and wood simulation, a total of twelve different sets of constraints were utilized and eight different starting points and two step sizes were tried for each set. The best solution, on the basis of cost, is reported in Table 8, page 65 for each set. An additional

Table 8
Effect of Property Constraints on Cost
Best Indicated Optimum Solutions for Various Constraints

No.	Clay X1	Marble X2	Micro balloon X3	Micro sphere X4	Wollas- sphere X5	Shell Flour X6	Flex. Resin X7	Rigid Resin X8	Sty- rene X9	T.S. ^a psi	F.S. ^b psi	Density g/ml	Cost c/liter
1	0.021	0.058	0.002	0.003	0.120	0.346	0.286	0.060	0.104	4512 (1500)	3592 (2500)	1.5789 (1.8000)	29.68
2	0.029	0.048	0.017	0.016	0.089	0.342	0.268	0.087	0.104	4600 (1500)	3298 (2500)	1.5000 (1.5000)	30.76
3	0.060	0.031	0.002	0.210	0.100	0.193	0.120	0.260	0.024	4172 (1500)	2655 (2500)	1.2000 (1.2000)	33.35
4	0.030	0.019	0.072	0.230	0.010	0.175	0.248	0.109	0.107	1995 (1500)	2651 (2500)	1.0000 (1.0000)	37.01
5	0.007	0.009	0.210	0.155	0.018	0.147	0.225	0.125	0.104	1727 (1500)	2522 (2500)	0.8998 (0.9000)	41.08
6	0.043	0.191	0.007	0.009	0.053	0.248	0.344	0.002	0.103	4009 (2500)	5933 (3500)	1.6569 (1.8000)	29.91
7	0.000	0.098	0.023	0.025	0.094	0.305	0.349	0.004	0.102	3215 (2500)	3629 (3500)	1.5000 (1.5000)	31.66
8	0.114	0.011	0.019	0.204	0.120	0.169	0.206	0.158	0.107	3468 (2500)	3687 (3500)	1.2000 (1.2000)	34.37
9	0.033	0.162	0.008	0.008	0.105	0.234	0.347	0.000	0.103	3945 (2500)	6154 (5000)	1.6747 (1.8000)	30.31
10	0.065	0.130	0.000	0.191	0.133	0.031	0.218	0.128	0.104	4236 (2500)	7189 (5000)	1.4993 (1.5000)	32.33
11	0.059	0.012	0.003	0.256	0.110	0.099	0.276	0.079	0.106	2773 (2500)	5001 (5000)	1.2000 (1.2000)	35.25
12	0.016	0.008	0.002	0.157	0.210	0.097	0.255	0.091	0.104	3614 (2500)	7472 (6500)	1.4992 (1.5000)	32.63

Note: The values enclosed in parenthesis denote the constraints applied to that property in that optimization.

^a T.S. = Tensile Strength; ^b F.S. = Flexural Strength.

constraint applied in all cases was that the styrene fraction be equal to or less than 30 percent of the total fraction of the flexible and rigid resins. The constraints on the x_i s were the same as before.

The first set of constraints examined were as follows:

1. Density ≤ 1.8 grams/ml.
2. Tensile Strength ≥ 1500 psi
3. Flexural Strength ≥ 2500 psi.

After the best solution for this set of constraints was determined, the density constraint was changed from 1.8 to 1.5, 1.2, 1.0 and 0.9, the others remaining the same in all these four sets of constraints.

Next, the tensile and flexural strength constraints were increased to 2500 and 3500 psi respectively and again the density was varied from 1.8 to 1.5 and 1.2. The above procedure was repeated for yet another set of tensile and flexural constraints, 2500 and 5000 psi respectively. A final set had a 1.5 density constraint while the tensile and flexural constraints were 2500 and 6500.

The best optimum cost indicated for each set was plotted against the density constraint for that set. A curve was drawn, connecting all those points which had similar tensile and flexural constraints. This cost versus density graph, presented on page 67, clearly illustrates the dependence of final cost on the density limit. An increase of 1000 psi and 5000 psi in the tensile and flexural strength constraints increased the cost by less than 1.0 and 2.0 cents only. However, a change of only 0.3 in the density affects the cost by over 2.5 cents. This effect increases as the allowable density decreases. For example, the reduction

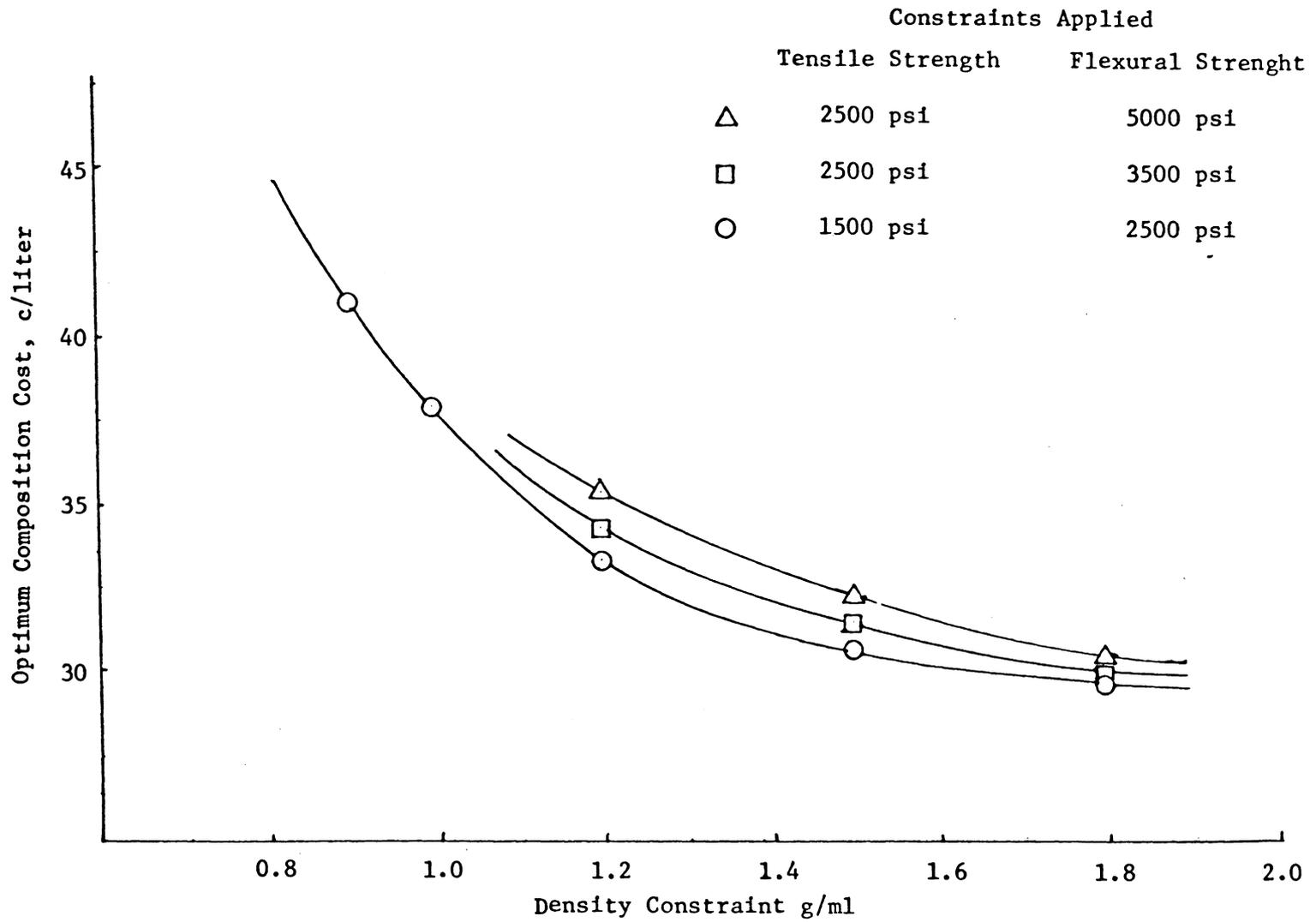


Figure 2. Effect of constraints on Optimum cost.

of the density limit from 1.0 to 0.9 increases the cost by 4.0 cents. A similar trend is exhibited by the tensile and flexural strength constraints, their effects increasing as the density decreases. Slope of the cost versus density curve varies from 3.5 through 0.8 to 0.25 cents/0.1 gram per ml at the low, medium and high density regions respectively.

The various sets of constraints examined and the optimum compositions reported cover a wide range of possible applications such as decorative components, frames, moldings, rosettes, panels, drawer fronts, overlays, cast table tops and bases, flooring tiles, wall products, consumer goods, vacuum dies, building accessories, specialty construction materials, simulated marble, etc. A knowledge of the required mechanical properties in each case will be needed so that proper constraints can be specified during optimization.

It may be noted in passing that the optimum compositions indicate that sometimes it is cheaper to add an appreciable amount of the high cost, low density fillers (glass microballoons and saran microspheres, especially the latter) to reduce the density to a lower than needed value thereby making it possible to add more of the low cost, high density fillers, thus increasing the density to the maximum limit but lowering the final cost more than is possible otherwise.

Recommendations

Based on the information gained from the present investigation, the following recommendations are made for future research.

1. The investigation of other particulate fillers and different polyester resins may be the next step. The same approach may be applied to other systems like epoxies, phenolics, elastomers, etc. Fibrous reinforcement material can be studied in a similar way, since the theoretical prediction of their reinforcement has not been entirely successful.

2. A number of important properties like hardness, impact strength, heat distortion temperature, creep effects, exotherm temperature may be studied and correlations may be obtained for their variation with composition.

3. The effect of process variables such as cure temperature, duration of cure may be studied using a modified simplex lattice design.

4. The effect of each component on the final property may be studied in detail by designing the experiments in a similar fashion, but with two or three midpoints between any two vertices.

5. The possibility and the effects of employing a higher fraction of styrene may be investigated, since the optimum styrene fractions have been consistently higher than those generally used in practice.

6. Stepwise multiple regression may also be applied to the data, thus eliminating the insignificant regression coefficients from the final correlation.

Limitations

The possibility of using more fillers to reduce to cost as well as to study a larger experimental space is somewhat limited by the

rapidly increasing viscosity of the filler-resin system. The very small clay filler particles and the acicular structured wollastonite had upper limits of about 25 volume percent each, while the other fillers had higher limits. The lower limit of fillers was set at one percent to avoid zero interaction effects.

VI. CONCLUSION

The following conclusions have been reached from this study on the effect of fillers on the mechanical properties of polyester resins and the constrained optimization of the composition of the composite:

1. The method of experimentation, regression analysis and optimization employed in this investigation is an efficient and viable method for similar applications, new product development and component comparison.
2. Optimization by non-linear methods does give feasible and acceptable solutions.
3. The simplex lattice design is very economical for this type of experiments and is also flexible enough to enable one to investigate any specific experimental space. The vertices lead to a qualitative ranking of the components, on any desired basis.
4. Multiple regression relations, where new variables are created from old variables for a quadratic equation, can represent the variation of mechanical properties with composition satisfactorily.
5. The flexural modulus and ultimate elongation data are more difficult to correlate due to the nature of the scattered data.
6. The initial points as well as the step sizes affect the values of the indicated optimum.
7. Density is a linear function of composition. Other properties require higher order relationships.
8. The limiting density of the final product exerts a deciding influence on the final cost of the product, the cost decreasing as the

permissible density is raised. Other mechanical property requirements do not change the final cost to any appreciable extent.

9. This procedure can be applied to more than nine components as well, as long as the time and budget elements can be satisfied.

10. For this set of components, the equations developed can be used to examine any reasonable constraints and a possible optimum composition.

The above conclusions are to be qualified, by stating that they are subjected to the materials used, conditions employed and methods applied in this investigation.

VII. SUMMARY

This investigation was carried out to formulate a general procedure for the constrained optimization of components of a polyester resin-filler composite and to develop quantitative relationships between the mechanical properties and composition.

The components examined included the six fillers, clay, marble, glass microballoons, saran microspheres, wollastonite and pecan shell flour. The effects of various ratios of flexible and rigid polyester resins and styrene monomer were also studied. The augmented extreme vertices simplex lattice design was employed to calculate the composition of 48 experimental points so a quadratic model may be fitted to the data.

Samples were made according to the calculated composition and were tested, according to standard methods, to obtain the density, tensile strength, flexural strength, compression strength, secant modulus, flexural modulus and ultimate elongation. Multiple regression analysis was performed to develop the regression coefficients for each property. Linear regression was adequate for density only, quadratic regression being necessary for all the other properties. Qualitative conclusions about the effect of each component were drawn.

A pattern search computer program was employed to optimize the composition and minimize the total cost, while satisfying all the constraints. Examples studied included various furniture applications and polyester terrazzo-type floor tiles. The effects of different constraints were examined. It was observed that the final cost varied

inversely with the density constraint and was also highly dependent on density. Other mechanical property constraints affected the final cost directly but not appreciably. Non-linear constrained optimization was shown to lead to realistic, feasible solutions and applicability for similar studies of other systems was established.

VIII. BIBLIOGRAPHY

1. Alford, H. E., and F. Veatch, "Glass Microballoon Particles, A Low Density Filler," *Modern Plastics*, Vol. 39, No. 3, 1961, pp. 141-146.
2. Alter, H., "Filler Particle Size and Mechanical Properties of Polymers," *J. Appl. Polymer Sci.*, Vol. 9, 1965, pp. 1525-1531.
3. ASTM Standards, Part 27, ASTM D 638, American Society for Testing and Materials, 1970, pp. 190-203.
4. ASTM Standards, Part 27, ASTM D 695, American Society for Testing and Materials, 1970, pp. 224-230.
5. ASTM Standards, Part 27, ASTM D 790, American Society for Testing and Materials, 1970, pp. 302-309.
6. Biles, W. E., "A Constrained Optimization Methodology for Composite Materials Process Development," Ph.D. Dissertation, Virginia Polytechnic Institute and State University, 1971.
7. Boenig, H. V., "Unsaturated Polyesters," Elsevier Publishing Co., Amsterdam, 1964, pp. 55-145.
8. Bostwick, B. and R. H. Carey, "Filled Polyethylene Compounds," *Ind. Eng. Chem.*, Vol. 42, 1950, p. 849.
9. Box, G. E. P. and K. B. Wilson, "On the Experimental Attainment of Optimum Conditions," *J. Royal Statistical Society, Series B*, Vol. 13, 1951, pp. 1-45.
10. Corten, H. T., "Micromechanics and Fracture Behavior of Composites," *Modern Composite Materials*, (L. J. Broutman and R. H. Krock, Editors), Addison-Wesley Publishing Co., Reading, Mass., 1967, pp. 62-77.
11. Doyle, E. N., "The Development and Use of Polyester Products," McGraw-Hill Book Company, 1969.
12. Etlinger, J. H., "Glass," *Modern Plastic Encyclopedia*, 1970, p. 340.
13. Furter, W. F., "Filled Linear Polyethylene Compositions," *Can. J. Chem. Eng.*, Vol. 42, 1964, pp. 77-81.
14. Holiday, L., "Composite Materials," Elsevier Publishing Co., Amsterdam, 1966, p. 248.

15. Ibid., pp. 254-255.
16. Hooke, R., and T. A. Jeeves, "Direct Search Solution of Numerical and Statistical Problems," J. Association of Computing Machines, Vol. 8, April 1961, pp. 212-229.
17. Jones, W. C., "The Effect of Fillers on Mechanical Properties of Polyester Resins and a Constrained Optimization of Filler Content," M.S. Thesis, Virginia Polytechnic Institute and State University, 1970., Contents published by Jones, W. C., and A. L. Fricke, "Optimization of the Filler Content of Filled Polyester Resin," J. Appl. Polymer Sci., Vol. 15, 1971, pp. 1109-1118.
18. Kenyon, A. S., and H. T. Duffey, "Properties of a Particulate-Filled Polymer," Polymer Eng. Sci., Vol. 7, No. 6, 1967, pp. 189-193.
19. Kovaly, K. A., "Handbook of Plastic Furniture Manufacturing," Technomic Publishing Co., 1970, pp. 24-30.
20. Leitheiser, R. H., "Polyesters," Modern Plastic Encyclopedia, 1969, pp. 172-176.
21. Ibid., 1965, p. 234.
22. Ibid., 1965, pp. 372-376.
23. Livingston, D. I., "Particulate Inorganic Filler Reinforced Polymeric Materials," Modern Composite Materials (L. J. Broutman and Krock, Editors), Addison-Wesley Publishing Co., Reading, Massachusetts, 1967, p. 499.
24. Mclean, R. A., and V. L. Anderson, "Extreme Vertices Design of Mixture Experiments," Technometrics, Vol. 8, No. 3, August, 1966, pp. 447-454.
25. Morehouse, D. S., and H. A. Walters, "Foamed Thermoplastic Microspheres in Reinforced Polyesters," J. Society of Plastic Engineers, Vol. 25, May 1969, p. 45.
26. Morrison, R. S., "Reinforced Thermosets," Modern Plastic Encyclopedia, 1970, pp. 267-272.
27. Murty, J. S., and M. N. Das, "Design and Analysis of Experiments with Mixtures," Annals of Mathematical Statistics, Vol. 39, No. 5, 1968, pp. 1517-1539.
28. Nielson, L. E., Simple Theory of Stress-Strain Properties of Filled Polymers," J. Appl. Polymer. Sci., Vol. 10, 1966, pp. 97-103.

29. Oleesky, S. S., and J. G. Mohr, "Handbook of Reinforced Plastics," Reinhold Publishing Co., New York, 1964, pp. 5-23.
30. Ibid., p. 21.
31. Ibid., pp. 29-30.
32. Ibid., p. 36.
33. Ibid., pp. 196-266.
34. Scheffe, H., "Experiments with Mixtures," J. Royal Statistical Society, Series B., Vol. 20, 1958, pp. 344-360.
35. Schwarzl, F. R., H. W. Bree and C. J. Nederveen, "Mechanical Properties of Highly Filled Elastomers," Proceedings 4th International Congress on Rheology, Providence, Rhode Island, 1963, pp. 241-264.
36. Seymour, R. B., "Fillers for Molding Compounds," Modern Plastic Encyclopedia, 1966, p. 596.
37. Steel, R. G. D., and J. H. Torrie, "Principles and Procedures of Statistics," McGraw-Hill, 1960, p. 88.
38. Wilde, D. J., and C. S. Beightler, "Foundations of Optimization," Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1967.
39. Witt, R. K., and E. P. Cizek, "Effect of Filler Particle Size on Resins," Ind. Eng. Chem., Vol. 46, No. 8, 1954, pp. 1635-1639.
40. Zoutendijk, G., "Non-linear Programming: A Numerical Survey," J. SIAM Control, Vol. 4, No. 1, 1966, pp. 194-210.
41. "Multiple Regression with Case Combinations," Biomedical Computer Programs, W. J. Dixon, Editor, University of California Press, Berkeley and Los Angeles, California, 1968, pp. 258-275.
42. "Plastics Marble: A Little Known Market Takes Off," Modern Plastics, Vol. 47, January, 1970, p. 76.
43. "Plastics Transform Tradition-bound Industry," Modern Plastics, Vol. 46, December, 1969, pp. 62-68.
44. "Fillers," Encyclopedia of Polymer Science and Technology, Interscience Publishers, New York, Vol. 6, 1969, pp. 740-762.
45. "Polyesters," Encyclopedia of Polymer Science and Technology, Interscience Publishers, New York, Vol. 11, 1969, pp. 129-167.

46. "Reinforced Plastics," Encyclopedia of Polymer Science and Technology, Interscience Publishers, New York, Vol. 12, 1969, p. 1.
47. Ibid., p. 8.
48. Ibid., p. 50.

APPENDIX A

Sample Instron Test Curves

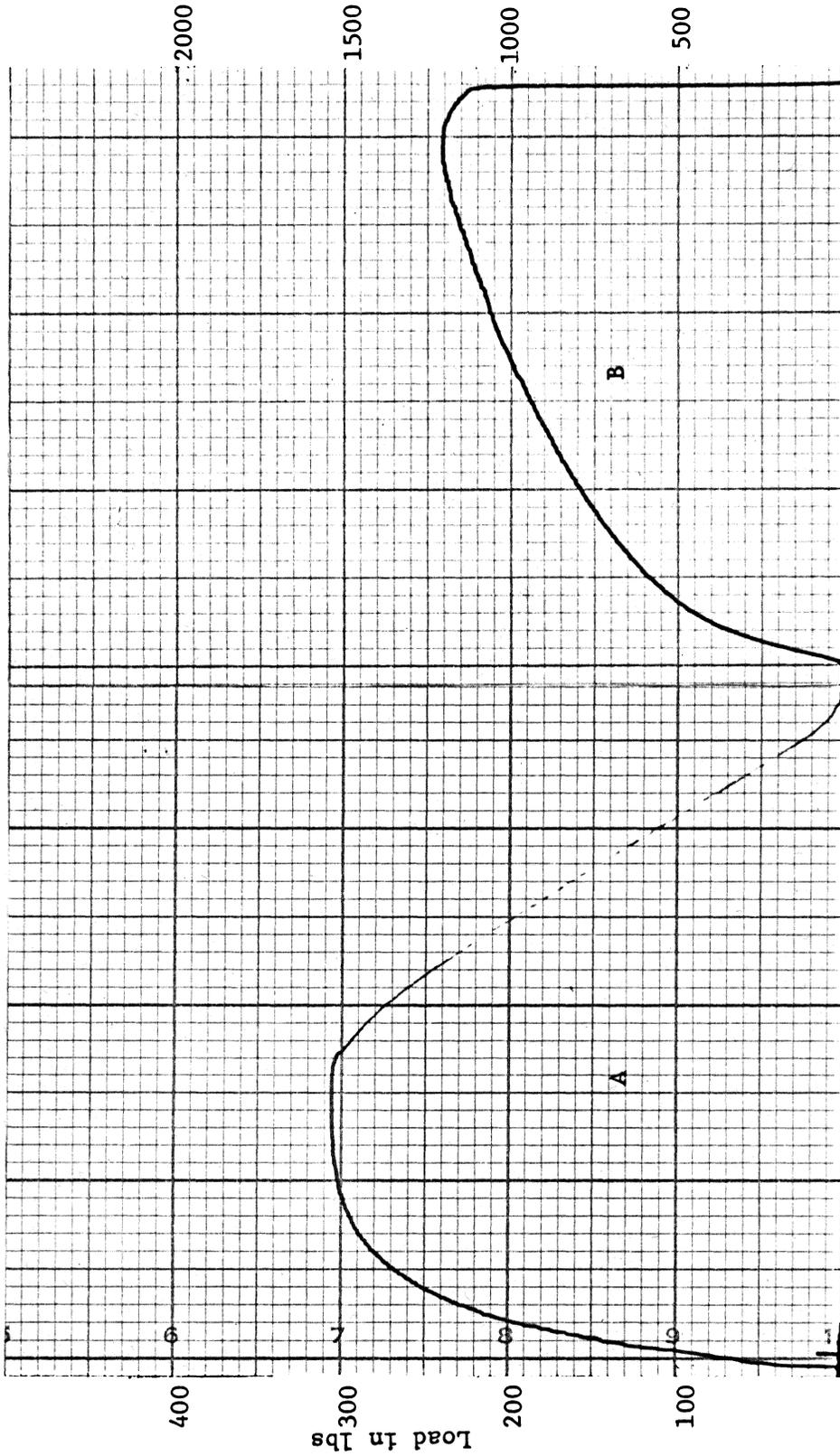


FIGURE 3. A: Tensile Curve - 4" = 10% Strain
B: Compression Curve

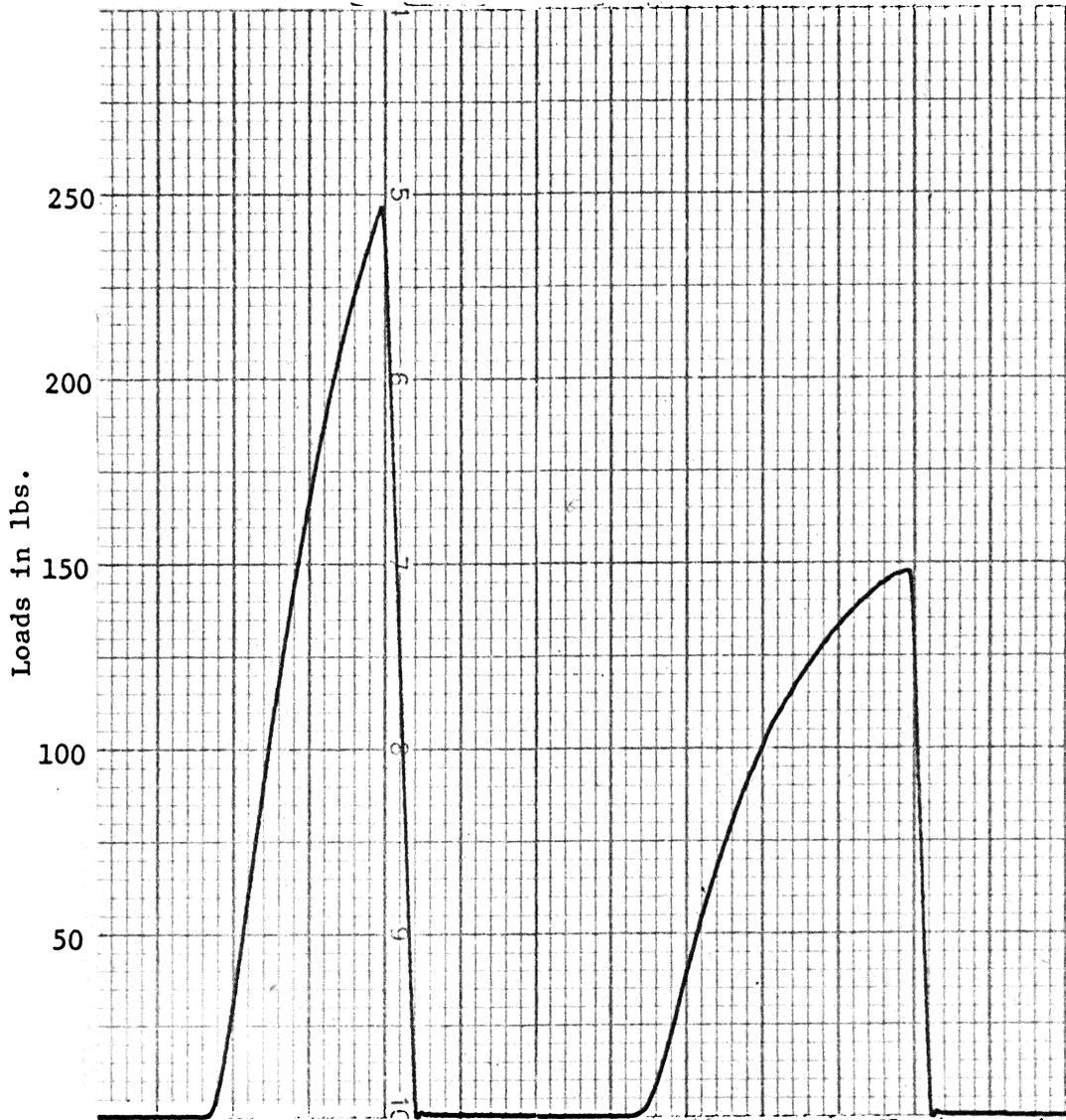


FIGURE 4. Flexural Curves. 10" = 1" deflection.

APPENDIX B

Apparatus

This appendix contains descriptions of the equipment and apparatus used in this investigation.

Air Stirrer. Three inches diameter three blade stirrer, air powered. Manufacturer unknown, obtained from Chemical Engineering Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia. Used to blend resins, styrene, fillers and catalyst.

Balance. Triple Beam Ohaus, 610 gram capacity, sensitivity 0.1 gram. Distributed by Phipps & Bird, Inc., Richmond, Virginia. Used to weigh resins, styrene and fillers.

Balance. Electric, capacity 160 grams. Sensitivity 0.0001 gram, Type H15, No. 263600. Manufactured by Mettler Instrument Corporation, Hightstown, New Jersey. Used to weigh density specimens.

Instron Universal Testing Instrument. Model TT-D-L, Serial No. 1566, 20,000 pound capacity, crosshead speed 0.002 to 2.0 inches per minute. The instrument and the accessories were manufactured by Instron Corporation, Canton, Massachusetts and are located in a climate controlled room in Norris Hall, Virginia Polytechnic Institute and State University, Blacksburg, Virginia. Used to test tensile, flexural and compression specimens.

Instron Strain Gauge Extensometer. Model No. G51-12, Serial No. 1305, gage length 1.0 inch, range 0-50 percent strain, flat specimen 0.5 x 0.5 inch maximum. Used to measure the strain of tensile specimens.

Instron Tension Cell. Catalog No. G-01-7, Serial No. 296-D, full scale range 0-1000 lbs. Used to measure the load for tensile and flexural specimens.

Instron Tension-Compression Cell. Catalog No. G-02-1, Serial No. 238-FR, full scale range 0-10,000 lbs. Used to measure the load for compression test specimens.

Instron Wedge-Action Grips. Catalog No. G-61-10F, Load capacity 20,000 pounds, grip faces 0.250-0.500 inch. Used to grip the tensile pieces.

Instron Flexure Jig. Catalog No. G-63-7, gage length 2, 4, 6, 8 inches. Used to hold the flexural specimens.

Micrometer. Range 0-1.0 inch. Sensitivity 0.0001 inches. Manufactured by Mitutoyo Manufacturing Company, Ltd., Japan. Used to measure dimensions of test specimens.

Mold. RTV silicone rubber obtained from Magnolia Plastics, Atlanta, Georgia. The mold contained five cavities for compression, flexural and tensile specimens according to ASTM dimensions.

Compression specimen -

Width - 0.50 in. Depth - 0.50 in. Length 1.0 in.

Flexural specimen -

Width - 0.70 in. Depth - 0.50 in. Length 5.0 in.

Tensile specimen -

Width overall - 0.75 in. Width of flat section - 0.50 in.

Length of flat section - 2.25 in. Overall length - 8.50 in.

Radius of fillet - 3.00 in. Depth - 0.50 in.

Oven. Precision Scientific Company, Catalog No. 1250, 110 volts, 5.5 amps at 60 cycles, 600 watts. Serial No. 100-2761. Temperature range 35-180°C. Used to post cure specimens.

Sander. Wide-belt. Ramco, Model No. 42, Serial No. 398. Manufactured by Robert A. Martin Company, Chicago, Illinois. Located at the Polytron Corporation of Virginia, Christiansburg, Virginia. Used to sand the top surface of the test specimens.

Sieves. U. S. Standard Sieve Nos. 50, 60, 70, 80, 100, 120, 140, 170, 200, 230 and 325. Manufactured by Fisher Scientific Company, Inc., Pittsburgh, Pennsylvania. Used to screen fillers for determination of particle size distribution.

Sieve Shaker. Combs Giratory Riddle, Manufactured by Great Western Manufacturing Company, Leavenworth, Kansas.

Time Clock. Time-it, Catalog No. 69230. Accurate to 0.1 seconds. Manufactured by Precision Scientific Company, Chicago, Illinois. Used to measure gel times.

APPENDIX C

Materials

This section contains the source and a description of all materials used in this investigation.

Acetone. Technical grade. Obtained from Axton Cross Corporation, Salem, Virginia. Used to clean resin from the mold, stirrer and beakers.

Cobalt Naphthenate. Six percent cobalt metal obtained from Polytron Corporation of Virginia, Christiansburg, Virginia. Used as room-temperature cure promoter with MEK peroxide.

Dimethyl Aniline. N, N-Dimethyl Aniline, reagent grade. Obtained from the manufacturers, Fisher Scientific Company, Fair Lawn, New Jersey. Used as an accessory room-temperature-cure promoter with cobalt naphthenate.

Filler. IG101 Microballoons, Industrial grade hollow microspheres. Obtained from the manufacturers, Emerson & Cuming, Inc., Canton, Massachusetts.

Filler. Saran Microspheres XD-7051.04, foamed thermoplastic spheres. Obtained from the manufacturers, The Dow Chemical Company, Midland, Michigan.

Kaolinite. Hydrated Aluminum Silicate (clay), Hydrite Flat D. Obtained from the manufacturers, Georgia Kaolin Company, Elizabeth, New Jersey. Used as a filler for the polyester resin.

Marble. Course ground marble (92% minimum Calcium Carbonate), grade Industrial Filler. Obtained from the manufacturers, Georgia

Marble Company, Tate, Georgia. Used as a filler for the polyester resin.

Methyl Ethyl Ketone Peroxide. Obtained from the Polytron Corporation of Virginia, Christiansburg, Virginia. Used as the catalyst for the polyester resin.

Pecan Shell Flour. Pecan shell flour, grade 100P. Manufactured by Southeastern Reduction Company, Valdosta, Georgia. Obtained from Polytron Corporation of Virginia, Christiansburg, Virginia. Used as a filler for the polyester resin.

Polyester Resin. Flexible, grade EXP-279-1, Batch 4MO-064-A. Obtained from the manufacturers, American Cyanamid Company, Wallingford, Connecticut. Used in formulation of resin system.

Polyester Resin. Rigid, grade EPX-187-3, Batch 4FO-076-D. Obtained from the manufacturers, American Cyanamid Company, Wallingford, Connecticut. Used in formulation of resin system.

Styrene. Monomer, stabilized, ungraded. Obtained from Polytron Corporation of Virginia, Christiansburg, Virginia. Used in formulation of resin system.

Wollastonite. Wolcron CF 97-50 Wollastonite. Obtained from the manufacturers, Pfizer, Minerals, Pigments & Metals Division, Clifton, New Jersey. Used as a filler for the polyester resin.

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PROPERTIES CONSTRAINED COST OPTIMIZATION
OF POLYESTER-FILLER SYSTEMS WITH NON-LINEAR
PROPERTY-COMPOSITION RELATIONSHIPS

by

V. K. Natarajan

(ABSTRACT)

A general procedure for the constrained optimization of components of a polyester resin-filler composite is formulated and quantitative relationships between the mechanical properties and composition are developed.

The fillers examined were clay, marble, glass microballoons, saran microspheres, wollastonite and pecan shell flour. The effects of various ratios of flexible and rigid polyester resins and styrene monomer were also studied. The augmented, extreme vertices, simplex lattice design was employed to calculate the composition of 48 experimental points.

Samples made according to the design were tested by standard methods to obtain the density, tensile, flexural and compression strengths, secant and flexural moduli and ultimate elongation. Multiple regression analysis yielded satisfactory regression coefficients for all properties except the flexural modulus and ultimate elongation. Linear regression was adequate for density only, quadratic regression being necessary for all other properties. Qualitative conclusions about the effect of each component were drawn.

A pattern search computer program was employed to optimize the composition at the minimum total cost, while satisfying all the constraints. Examples studied included various furniture applications and polyester terrazzo-type floor tiles. The effects of different constraints were evaluated.

The final cost varied inversely with the density constraint and was highly dependent on density. Other mechanical property constraints affected final cost directly but not appreciably. Non-linear constrained optimization was shown to lead to realistic, feasible solutions and applicability of this method for similar studies of other systems was established.