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Optimization of the Filler Content of Filled Polyester Resin

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Synopsis

A method for the constrained optimization of the filler content in polyester resin was demonstrated. The fillers investigated included marble, clay, pecan shell flour, and hollow microspheres in various concentrations. The method of optimization included an experimental design to generate data and a polynomial regression analysis to determine the mechanical property constraint functions. The constraints were well approximated by linear functions, and linear programming was used to find optimum compositions for several possible applications.

INTRODUCTION

Fillers may be used in a resin as an extender or to provide improvements in certain properties. In any case, one goal will always be important, i.e., to minimize the cost of the filled resin to be used for any particular application. As shown in Table I, most fillers are less expensive than the resin displaced. Thus, the cost of the filled resin decreases continuously with increasing filler content, and the goal of minimizing cost becomes synonomous with the goal of maximizing filler content. However, fillers affect the prop-

TABLE I
Density and Costs of Resins and Fillers

Material	Density, g/ml	Cost, $/lb	Cost, $/liter
Polyester resin	1.21	0.25	0.666
I.G. 101 Microballoons	0.34	0.69	0.517
Nut shell flour	1.30	0.04	0.114
Marble			
Gamma-Sperse 255	2.71	0.012	0.072
RO-40	2.71	0.005	0.030
P4-40	2.71	0.005	0.030
Clay			
Hydrite 10	2.58	0.026	0.148
Hydrite Flat D	2.58	0.014	0.080
Hydrite MP	2.58	0.015	0.085

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erties of the resin system, and the necessity of maintaining these properties within certain bounds limits the maximum amount of filler that can be added. This complicates the problem considerably. Furthermore, the complexity of the problem increases rapidly as the number of variables, i.e., types of filler, resin composition, cure conditions, etc., and the number of constraining properties increase.

In general, such a problem can be solved most efficiently if treated as a constrained optimization. As an example of the utility of this approach, the problem of formulating a mixed filler system for a polyester resin to yield a composite at minimum cost with mechanical properties held within certain bounds was investigated.

STATEMENT OF THE PROBLEM

The problem can be stated in general terms as follows:

$$\text{minimize } C = b_0 + \sum_{i=1}^{n} b_i x_i \qquad (1)$$

subject to

$$x_i \geq 0 \qquad (2)$$

and

$$a_0 + \sum_{i=1}^{n} a_{ij} x_i + \sum_{i=1}^{n} d_{ij} x_i^2 + \sum_{i=1}^{n} f_{ij} x_i x_k \quad (\geq, \leq b_j) \text{ for}$$

$$j = 1, \ldots, m \text{ and } i \neq k \qquad (3)$$

where C = objective function, cost per volume of composite; x_i = volume fraction of filler i; b_0 = resin cost, cost per volume; b_i = cost reduction factor for filler i, cost per volume; a_0, a_{ij}, d_{ij}, f_{ij} = coefficients of regression equation for component i and property j; and b_j = constraint for property j.

Solution of this general problem requires application of nonlinear optimization techniques. The mathematical solution of the problem can be simplified if the second order and interaction terms in the constraint equations are all negligible, because linear programming can then be used. This does not simplify the experimental problem, however, since it must be shown that these terms can be ignored. In either case, the approach to the problem and the end result are the same.

SELECTION OF VARIABLES AND CONSTRAINTS

The constraints to be imposed depend upon the end use of the composite, but any type and number of properties could be specified as constraints. Since the mechanical properties and density of a filled polyester must often be considered, the constraints selected for this problem were tensile strength, secant modulus, flexural strength, and density.

The choice of resin and fillers depends upon cost, availability, properties desired, and the individual effects of the fillers on the properties of interest. For maximum utility, a semiflexible polyester resin consisting of 10 wt-% Cyanamid EPX-187-3 and 90 wt-% Cyanamid EPX-279-1, with 25 pph styrene added, was used. From qualitative considerations of an earlier study,[1] four types of fillers were chosen for this work. These were clay, marble, pecan shell flour, and Emerson and Cumings I.G. 101 microballoons. The microballoons were chosen primarily for density reduction and the others, primarily to reduce cost. Of course, marble, clay, and shell flour yield composites of different appearances. The average particle sizes for each filler were chosen arbitrarily to yield a mixed filler of very wide particle size distribution with high loadings of each type.

OBJECTIVE FUNCTION

Since it was shown in our earlier study[1] that the volumes of resin and the selected fillers are additive, the coefficients for the objective function (the cost per unit volume of the filled resin) can be calculated from the cost of resin and fillers. For this case, the objective function is

$$C = 0.666 - 0.636X_1 - 0.586X_2 - 0.552X_3 - 0.149X_4 \qquad (4)$$

where C = cost per volume of the composite, \$/liter; and X_1, X_2, X_3, X_4 = volume fractions of marble, clay, pecan shell flour, and I.G. 101 microballoons, respectively.

CONSTRAINT FUNCTIONS

It is also necessary to formulate functions to describe the relation between the selected constraints and the independent variables of the problem. Since volumes are additive, a density function can be calculated easily from the densities given in Table I. For this problem, the density constraint function is

$$D = 1.21 + 1.50X_1 + 1.37X_2 + 0.09X_3 - 0.87X_4 \qquad (5)$$

where D = composite density, g/cm^3.

The functions for the remaining constraints—tensile strength, secant modulus, and flexural strength—must be generated from experimental data taken to describe the response of the mechanical properties with respect to the levels of the independent variables. The most efficient method for collecting the required data is by following a statistical experimental design. Also, the data must be taken for at least three levels of each variable to determine curvature for a second-order model.

Experimental Design and Data

The levels of the filler contents (the independent variables) are specified for each experimental formulation by an experimental design. If a complete factorial design for four variables at three levels were used, 3^4, or 81 formulations would have to be prepared and tested for each property. The number of formulations could be reduced by compounding responses or by using an incomplete design. However, the loss of information resulting from the use of confounded or incomplete factorial design could introduce uncertainty into the optimization.

If precision of measurement of dependent variables is high, which it is in this study, experimental designs can be used that are more efficient than the complete factorial design without loss of information. One of these, the rotatable central composite design of Box and Wilson,[2] was selected for this study. The Box-Wilson design is basically a two-level factorial design augmented by additional axial points and a replicated center point. For four variables, this design yields a five-level experiment requiring only 27 formulations, including three replicates of the center point. The only loss of information is that experimental error can be estimated for the center point only, but this is not critical for our purposes.

TABLE II
Coded Values for a Four-Variable Box-Wilson Design

Experiment no.	Variable X_1	X_2	X_3	X_4	
1	2	0	0	0	
2	−2	0	0	0	
3	0	2	0	0	
4	0	−2	0	0	axial
5	0	0	2	0	points
6	0	0	−2	0	
7	0	0	0	2	
8	0	0	0	−2	
9	1	1	1	1	
10	1	1	1	−1	
11	1	1	−1	1	
12	1	1	−1	−1	
13	1	−1	1	−1	
14	1	−1	1	−1	
15	1	−1	−1	1	
16	1	−1	−1	−1	factorial
17	−1	1	1	1	points
18	−1	1	1	−1	
19	−1	1	−1	1	
20	−1	1	−1	−1	
21	−1	−1	1	1	
22	−1	−1	1	−1	
23	−1	−1	−1	1	
24	−1	−1	−1	−1	
25	0	0	0	0	
26	0	0	0	0	center
27	0	0	0	0	points

The design for four variables in terms of coded variables is shown in Table II. The range of each variable was set arbitrarily with the limitation that the maximum total volume fraction of fillers could not exceed 0.5. At higher loadings, it is difficult to blend resin and fillers uniformly or to mold uniform samples. On this basis, actual values for the concentrations of individual fillers in each formulation were calculated to conform to the design. The formulations used in the designed experiment are given in Table III.

TABLE III
Composition of Samples for Box-Wilson Experimental Design

Marble (RO-40), vol-%	Clay (Hydrite flat D), vol-%	Nut shell flour (100 P), vol-%	Microballoons (I.G. 101), vol-%	Total filler, vol-%
14	6	9	10	39
0	6	9	10	25
7	12	9	10	38
7	0	0	10	26
7	6	13	10	36
7	6	5	10	28
7	6	9	20	42
7	6	9	0	22
10.5	9	11	15	45.5
10.5	9	11	5	35.5
10.5	9	7	15	41.5
10.5	9	7	5	31.5
10.5	3	11	15	39.5
10.5	3	11	5	29.5
10.5	3	7	15	35.5
10.5	3	7	5	25.5
3.5	9	11	15	38.5
3.5	9	11	5	28.5
3.5	9	7	15	34.5
3.5	9	7	5	24.5
3.5	3	11	15	32.5
3.5	3	11	5	22.5
3.5	3	7	15	28.5
3.5	3	7	5	18.5
7	6	9	10	32
7	6	9	10	32
7	6	9	10	32

Test formulations were prepared and cured according to the procedure described earlier.[1] Samples of each formulation were then tested to determine tensile and flexural properties by methods described in our previous article.[1] The tensile strength, flexural strength and secant modulus for each formulation are given in Table IV.

TABLE IV
Properties of Experimental Samples for Optimization

Sample no.[a]	Cost, \$/liter	Density, g/ml	Tensile strength, lb/in.^{2}	Flexural strength, lb/in.^{2}	Secant modulus,[b] (lb/in.^{2}) $\times 10^3$
1	0.478	1.42	2680	5870	236
2	0.567	1.21	2710	7050	174
3	0.487	1.40	2770	5920	244
4	0.511	1.24	2510	6970	168
5	0.500	1.32	2820	6330	227
6	0.544	1.31	2650	6780	200
7	0.507	1.23	2470	5700	222
8	0.537	1.40	3180	8520	201
9	0.464	1.37	2580	5250	258
10	0.479	1.46	3240	7130	254
11	0.486	1.37	2720	6170	257
12	0.501	1.45	3140	7140	243
13	0.499	1.29	2480	5770	220
14	0.514	1.38	3180	7790	233
15	0.521	1.28	2440	5990	205
16	0.536	1.37	2880	7690	192
17	0.508	1.27	2500	5480	216
18	0.523	1.35	2940	7600	205
19	0.531	1.26	2440	5980	189
20	0.545	1.37	2960	7880	203
21	0.544	1.18	2350	5920	169
22	0.599	1.27	2860	7680	137
23	0.566	1.18	2340	6250	173
24	0.581	1.27	2810	8300	175
25	0.521	1.32	2740	6410	210
26	0.521	1.32	2730	6890	215
27	0.521	1.32	2700	6820	218
Unfilled resin	0.666	1.21	2520	8240	97

[a] The same sample numbering system is used in Tables II, III, and IV.
[b] Ratio of stress to strain at 1% strain.

Regression Analysis

Constraint functions were generated by applying polynomial regression analysis to the data. A Biomedical Computer Program[4] and an IBM 360 computer were used for the analysis. Four mathematical models were fitted to each set of data. These models were the following:

I.
$$y = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} b_i x_i^2 + \sum_{\substack{i=1 \\ i \neq k}}^{n} c_i x_i x_k \tag{6}$$

II.
$$y = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} b_i x_i^2 \tag{7}$$

III.
$$y = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{\substack{i=1 \\ i \neq k}}^{n} c_i x_i x_k \tag{8}$$

IV. $$y = a_0 + \sum_{i=1}^{n} a_i x_i \tag{9}$$

By applying standard F-statistics, all of the above models were shown to fit the data with a 99% confidence interval. An indication of the relative quality of fit of the models to the data is given by the range of residuals (the sum of the absolute values of the largest positive and negative differences between observed and calculated values) for the four models. The ranges of residuals for the models are given in Table V.

TABLE V
Regression Range of Residuals

Model	Tensile strength, lb/in.^{2}	Secant modulus, lb/in.^{2}	Flexural strength, lb/in.^{2}
I. Second-order polynomial	263	41,877	651
II. Linear and mixed quadratic terms	371	41,880	1,041
III. Linear and pure quadratic terms	337	52,753	868
IV. Linear model	371	52,752	1,024

As should be expected, the full second-order model (model I) gave the lowest range of residuals; however, the improvement over the linear model (model IV) was not great, and both models yielded satisfactory confidence limits for the regressions. Since optimization is much more difficult if second-order terms are retained, the linear model was selected for further analysis. The constraint functions obtained by linear regression of the data are

$$\sigma_T = 2{,}802 + 1{,}667X_1 + 2{,}361X_2 + 1{,}542X_3 - 4{,}650X_4 \tag{10}$$

$$\sigma_F = 9{,}889 - 6{,}324X_1 - 5{,}650X_2 - 9{,}317X_3 - 15{,}839X_4 \tag{11}$$

$$E = 98{,}696 + 617{,}878X_1 + 656{,}910X_2 + 227{,}000X_3 + 72{,}488X_4 \tag{12}$$

where σ_T = tensile strength, psi; σ_F = flexural strength, psi; E = secant modulus, psi; and X_1, X_2, X_3, X_4 = volume fractions of marble, clay, pecan shell flour, and I.G. 101 microballoons, respectively.

OPTIMIZATION

Since the mechanical property constraints can be expressed as linear functions of the fractions of individual fillers, the optimum (minimum cost) for any set of constraints can be located by linear programming. Restated, our optimization problem is now

$$\text{minimize } C = b_0 + \sum_{i=1}^{n} b_i x_i \tag{13}$$

subject to

$$x_i \geq 0 \tag{14}$$

and

$$a_0 + \sum_{i=1}^{n} a_{ij}x_i \qquad (\geq, \leq b_j). \tag{15}$$

This problem can be solved for unique optimum values easily, and an IBM program was used to locate example optimum solutions with an IBM 360 computer.

Examples

To demonstrate the power of using an optimization approach for formulation, optimum formulations were determined for several sets of constraint limits that might correspond to quite different applications. The applications considered were a general molding application, a wood simulation application, a marble simulation application with density restrictions, and a marble simulation application without density restrictions.

For a general moding formulation, the constraints imposed were $D \leq$ 1.35 g/cc, $\sigma_T \leq$ 1512 psi (60% of σ_T of resin), $\sigma_F \geq$ 6588 psi (80% of σ_F of resin), and $E \leq 242.5 \times 10^3$ psi (250% of E of resin). The optimum formulation determined was X_1 (marble) = 0. X_2 (clay) = 0,082, X_3 (shell flour) = 0.304, X_4 (microballoons) = 0, which gave a cost per unit volume of 45¢/liter (a reduction of 21.6¢/liter from the resin cost of 66.64¢/liter). The active constraints for the optimum were density and flexural strength. Therefore, if a cheaper formulation is needed, the density or flexural strength or both constraints must be relaxed.

For a wood simulation application, the constraints imposed were $D \leq$ 1.10 g/cc, $\sigma_T \geq$ 1,512 psi (60% of σ_T of resin), $\sigma_F \geq$ 4,940 psi (60% of σ_F of resin), and $E \leq 242.5 \times 10^3$ psi (250% of E of resin). For this case, the optimum formulation determined was $X_1 = 0$, $X_2 = 0$, $X_3 = 0.156$, and $X_4 = 0.143$. The formulation cost was 55.9¢/liter (a reduction of 10.7¢/liter). The active constraints were again density and flexural strength.

If a cheaper formulation is desired, one of these constraints must be relaxed. Since low density is desirable, the flexural limit should be relaxed. If this is done, then more shell flour and microballoons can be added. As an illustration, suppose that the flexural strength constraint is relaxed to 3290 psi. In this case, the optimum formulation for wood simulation is $X_1 = 0$, $X_2 = 0$, $X_3 = 0.359$, $X_4 = 0.164$, and the formulation cost becomes 44.4¢/liter (a reduction of 22.2¢/liter).

Thirdly, consider optimization for a simulated stone application in which density must be restricted. For this case, the following constraints are imposed: $D \leq$ 1.50 g/cc, $\sigma_T \geq$ 1,512 psi, $\sigma_F \geq$ 4,940 psi, and $E \leq 242.5 \times 10^3$ psi. The optimum formulation is $X_1 = 0.115$, $X_2 = 0$, $X_3 = 0.320$, $X_4 = 0$. The cost of the formulation is 41.6¢/liter, and the active constraints are flexural strength and secant modulus.

Since the third case calls for only a 43.5 vol-% filler loading, a cheaper formulation could be obtained if the active constraints were relaxed. Examining the constraint equations, we see that marble has a smaller negative effect on flexural strength than shell flour and a larger positive effect on secant modulus. Further, we note that density may become an active constraint if we attempt to replace shell flour with marble. Since neither of these properties is too important for stone simulation, a much cheaper formulation would be obtained if these constraints were eliminated. Therefore, consider the constraints $\sigma_T \geq 1512$ psi and $\sigma_F \geq 4940$ psi. For this case, the optimum formulation is $X_1 = 0.708$, $X_2 = 0.10$, $X_3 = 0$, and $X_4 = 0$, at a cost of 15.8¢/liter.

This serves to show the effect of relaxing a possibly unnecessary constraint, but it also illustrates what can happen if an important physical effect is ignored. The optimization has led to an unrealistic solution—an impossible filler loading of 81 vol-%—because a constraint for maximum loading was not replaced on the solution. From the experimental tests, it is known that the maximum filler loading possible is about 55 vol-%. Suppose the optimum is recalculated for the constraints $\sigma_T \geq 1512$ psi, $\sigma_F \geq 4940$ psi, and loading $= \Sigma x_i \leq 0.55$. For this case, the optimum is $X_1 = 0.55$, $X_2 = 0$, $X_3 = 0$, $X_4 = 0$, giving a formulation cost of 31.6¢/liter (a reduction of 35¢/liter), and the only active constraint is the total filler loading.

DISCUSSION

The examples serve to show the power of the optimization approach for filler formulation. It should be emphasized that this approach could be expected to work just as well if the constraint equations were nonlinear; the optimization would just be more complicated. Therefore, the approach does not depend upon the applicability of linear programming. Further, the study was not meant to be exhaustive. Thus, constraints such as impact strength, hardness, viscosity, and gloss and variables such as filler particle size and resin composition were not considered.

To include additional constraints is not difficult; this only requires measuring more dependent variables for the formulations specified by the experimental design. For example, hardness and gloss could be included by measuring these properties for pieces made for other tests. In fact, total loading was added as a constraint in one example. Introduction of new variables is much more difficult. This requires modification of the experimental design and investigation of additional points, followed by reevaluation of the constraint equations. The power of the method is undeniable. In this example study, low-cost formulations have been determined for a range of applications that includes wood and stone simulation, and the properties can be estimated approximately for each optimum formulation from the empirical relations.

It is interesting to note that no more than two fillers are specified for any one application, even though four were used in the experimental work, and that the optimization automatically specified the best fillers as well as the filler concentrations. Equally important is the direction provided for future efforts. The active constraints are enumerated by the optimization, and attention is focused on these. Work can then be directed toward better definition of the active constraint for a particular application, or toward substitution of a more appropriate filler for the one that has the most detrimental effect on the constraint of interest. Consider the formulation for wood simulation. The active constraints are density and flexural strength, and the density constraint cannot be relaxed. Therefore, a low-density filler must be included, but it has a very detrimental effect on flexural strength. Thus, we are led directly to a reconsideration of the flexural strength constraint and a search for a low-density filler that has less effect on the flexural strength. Finally, the low-density filler is quite expensive, and certainly a cheaper equivalent would be sought. The optimization aids in this, also, since the effect of a change in filler cost on formulation cost can be calculated.

In all of the example cases, the optimum occurred outside the region of the experimental design. Since this requires extrapolation of the constraint equations, the optima are only approximations to the true values. If a more accurate optimum is required, further experimental work in the region of approximate optimum must be done. However, this requires less effort than that required for an exhaustive investigation of the entire experimental space.

In summary, application of optimization techniques yields approximate optimum values for various applications, and the constraint equations permit some extrapolation outside the experimental region if their form is reasonable. Efforts to define property requirements for an application are simplified by analysis of the active constraints, since the active constraints automatically enumerate the limiting properties. Even if the limiting property can not be changed, the active constraint function indicates which filler should be excluded. Further, some direction is provided for screening of possibly substitutes for the excluded filler. Thus, the optimization method can be used to locate an accurate optimum within the experimental region, to approximate an optimum outside the experimental region, or to provide direction for sequential experimental development.

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