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Nonlinear Constrained Optimization of Filled Polyesters

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Synopsis

An efficient method for optimization of a formulation problem subject to nonlinear constraints was demonstrated. Specifically, a nine-variable polyester–filler system was investigated experimentally. The investigation included selection of an efficient experimental design, regression analysis, and study of optimization methods. Recommended procedures are reported, along with examples and discussion of several typical applications.

INTRODUCTION

Fillers are often used in a resin to modify properties and to reduce the cost. The fillers to be used for an application are selected frequently on the basis of prior practice, and a particular formulation is developed by successive experimentation. This is an expensive and inherently slow approach that often hampers the development of a new product. Moreover, the selection of trial formulations depends entirely upon the judgment of the experimenter, which introduces additional delays. Finally, the data collected in the course of developing a formulation for one application is often not very useful in developing a formulation for another application.

The exploratory development could be accelerated and made in a more general way if the problem were considered to be a constrained optimization problem. That is, the development could be accelerated if experiments were conducted to determine composition–property relations which could then be used as constraint equations in a formal search for the optimum formulation for each application of interest. A program typical of this approach consists of five steps. (1) experimental design, (2) data collection, (3) regression analyses of the data, (4) specification of constraints, and (5) constrained optimization.

In this work, the problem of formulating minimum-cost filler–polyester resin–styrene systems, subject to specified constraints on mechanical properties, was used as an example of the constrained optimization approach to an exploratory formulation study. A general procedure was selected and used to determine the effects of various fillers on resin properties efficiently and to optimize the composition subject to property constraints. Other types of variables, such as cure conditions or process variables, could have been included. The results of example optimizations are also discussed.

EXPERIMENTAL DESIGN AND DATA COLLECTION

Choice of the experimental design is a crucial step that involves selection of variables, selection of the statistical method to be used, and specification of the experimental region to be studied. Usually, variables are selected on the basis of qualitative or semiquantitative expectations. For example, if a range of resin properties is desired, a mixture of two compatible resins may be used, and resin composition is chosen as a variable. Once the variables have been selected, an experiment can be designed. To be most useful for exploratory work, the experiment must include as much of the region of interest as possible and must define the important effects adequately without becoming too costly. This can be very difficult and normally requires some preliminary information if the experiment is to be designed well.

The components selected for study in this work and the composition ranges used are listed in Table I. The six fillers selected vary widely in cost, particle size, and effect on mechanical properties, but all have been used as fillers in composites. The components of the resin (flexible polyester, rigid polyester, and added styrene monomer) were also varied so that the matrix properties could be varied. Since the volumetric fractions of the nine components must sum to unity, there are eight independent variables. The particular components chosen are currently used commercially; therefore, compositions developed from the program to meet particular performance criteria can be compared to those in use.

The flexible resin used in this study was American Cyanamid EPX-279-1 and the rigid resin used was EPX-187-3. All tests were made from one lot

TABLE I
Properties of the Components Used

Component	Density, g/ml	Mean particle size, μ	Cost, ¢/lb	Cost, ¢/liter	Ranges used, vol-%
1. Clay	2.580	4.5	1.97	11.20	1-25
2. Marble	2.710	40.0	0.50	3.00	1-25
3. Glass microballoons	0.340	62.0	69.00	52.00	1-25
4. Saran microspheres	0.032	30.0	350.00	26.30	1.25
5. Wollastonite	2.890	30.0	1.85	11.80	1-25
6. Pecan shell flour	1.300	125.0	2.50	7.16	5-29
7. Polyester resin–flexible	1.148	—	26.80	67.80	58-80
8. Polyester Resin–rigid	1.335	—	18.00	56.50	5-29
9. Styrene	0.900	—	11.50	22.81	5-29

of each resin. Additional styrene was added to this mixture as required by the designed experiment. A 6 wt-% cobalt naphthanate–dimethyl aniline–MEK peroxide catalyst system was used. The levels of the catalyst system components were set to give a gel time of 300 to 400 sec. The levels used for all tests were 0.14 wt-% cobalt naphthanate solution, 0.07 wt-% dimethyl aniline, and 1.0 wt-% MEK peroxide, based on the total resin, as received. The promoters were added to the resin–filler mixture and mixed. The catalyst was added and mixed for 40 sec, taking care to minimize air entrainment. The reacting mass was hand poured into cold RTV-Silastic rubber molds, and the gelled pieces were removed from the molds after 800 sec. The pieces were postcured in an oven at 70°C for 20 hr. Before testing, the sample surfaces were sanded flat and parallel. The reproducibility of the mixing and cure procedures was checked by replicating several points. The final properties of the replicates were identical, within the limits of experimental errors involved in the property tests.

The next problem is to choose an appropriate experimental design. For this system of eight independent variables, $2^8 = 256$ or $(2^8 + 2 \times 8 + 1) = 273$ experiments would be required for a two-level factorial or rotatable central composite design, respectively. Aside from the fact that a two-level factorial does not develop second-order effects and that a rotatable design cannot be adapted easily to include most of the sample space in this type of problem, the experimental effort required is prohibitive for an exploratory study. The design chosen for this problem is the simplex lattice design developed by Scheffe[1] and discussed by Biles[2] in detail.

The simplex lattice design is basically a polyhedral design with the variables forming the vertices. The design includes three types of experiments: (1) a vertex where one component is set at its maximum allowable level and all other variables are set at their minimum levels, (2) at least one point spaced between each pair of vertices, and (3) the centroid of the polyhedron. In general, the experiments required are given by the following equation:

$$\text{experiments} = (q + m + 1)!/(m + 1)!(q)! \qquad (1)$$

where q = number of independent variables and m = number of points between two vertices. If only the midpoints brtween vertices are used ($m = 1$), the number of experiments required by the design is 45 experiments plus the centroid, for a total of 46. This is one more experiment than the number of coefficients required for a complete quadratic expression of a response variable in eight independent variables. Therefore, this is the minimum number of experiments required to uniquely determine a function with one degree of freedom, a statistical minimum number of experiments. Thus, the required response functions can be developed from the simplex lattice design experiment with the least expenditure of time. Of course, the experimental responses must be measured accurately if an equation for the response is to be determined from a minimum number of experiments. Hopefully, some interaction (x_ix_j) terms and some pure quadratic (x_i^2)

terms will have zero coefficients, i.e., the terms will be unimportant. Each zero coefficient adds another degree of freedom. This will be discussed in more detail later.

The 45 experimental compositions and the three replicated centroid compositions used in this designed experiment are given in coded form in Table II. Test formulations were prepared according to the experimental design, cured, and tested as described in an earlier study[3] for density, tensile strength, flexural strength, compressive strength, secant modulus, flexural modulus, and ultimate tensile elongation. Multiple tests were performed on each experimental formulation and the results averaged to determine

TABLE II
Coded Values for an Eight-Variable, Augmented, Extreme Vertices, Simplex Lattice Experimental Design[a]

Expt. no.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9
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	−0.5	1	−2	−2
7	−1	−3	−3	−3	−3	−2	2	−2	−2
8	−1	−3	−3	−3	−3	−2	1	−0.5	−2
9	−1	−3	−3	−3	−3	−2	1	−2	−0.5
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	−0.5	1	−2	−2
15	−3	−1	−3	−3	−3	−2	2	−2	−2
16	−3	−1	−3	−3	−3	−2	1	−0.5	−2
17	−3	−1	−3	−3	−3	−2	1	−2	−0.5
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	−0.5	1	−2	−2
22	−3	−3	−1	−3	−3	−2	2	−2	−2
23	−3	−3	−1	−3	−3	−2	1	−0.5	−2
24	−3	−3	−1	−3	−3	−2	1	−2	−0.5
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	−0.5	1	−2	−2
28	−3	−3	−3	−1	−3	−2	2	−2	−2
29	−3	−3	−3	−1	−3	−2	1	−0.5	−2
30	−3	−3	−3	−1	−3	−2	1	−2	−0.5

(continued)

TABLE II (*continued*)

Expt. no.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9
31	−3	−3	−3	−3	0	−2	1	−2	−2
32	−3	−3	−3	−3	−1	−0.5	1	−2	−2
33	−3	−3	−3	−3	−1	−2	2	−2	−2
34	−3	−3	−3	−3	−1	−2	1	−0.5	−2
35	−3	−3	−3	−3	−1	−2	1	−2	−0.5
36	−3	−3	−3	−3	−3	0.5	1	−2	−2
37	−3	−3	−3	−3	−3	−0.5	2	−2	−2
38	−3	−3	−3	−3	−3	−0.5	1	−0.5	−2
39	−3	−3	−3	−3	−3	−0.5	1	−2	−0.5
40	−3	−3	−3	−3	−3	−2	2.5	−2	−2
41	−3	−3	−3	−3	−3	−2	2	−0.5	−2
42	−3	−3	−3	−3	−3	−2	2	−2	−0.5
43	−3	−3	−3	−3	−3	−2	1	0.5	−2
44	−3	−3	−3	−3	−3	−2	1	−0.5	−0.5
45	−3	−3	−3	−3	−3	−2	1	−2	0.5
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] Key to coded values:

Coded value	Volumetric fraction
−3	0.01
−2.5	0.0367
−2	0.05
−1.5	0.0767
−1	0.13
−0.5	0.17
0	0.25
0.5	0.29
1	0.56
1.5	0.5867
2	0.68
2.5	0.80

the response. The results of these property measurements and the calculated cost for each experimental composition are presented in Table III.

REGRESSION ANALYSIS

A complete second order polynomial,

$$Y = B_0 + \sum_{i=1}^{8} B_i X_i + \sum_{i=1}^{8} B_{ii} X_i^2 + \sum_{i=1}^{7} \sum_{j=1+1}^{8} B_{ij} X_i X_j \qquad (2)$$

where Y = property, X_i = volume fraction of component i, and B_0, B_i, B_{ii}, B_{ij} = empirical constants, was fitted to each property, except density,

TABLE III. Properties of Experimental Samples

Expt. no.	Density g/ml	Tensile strength ×10⁻³ psi	Flexural strength ×10⁻³, psi	Compression strength ×10⁻³, psi	Secant modulus ×10⁻³, psi	Flexural modulus ×10⁻³, psi	Ult. elong., %	Cost, ¢/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
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	30.25

by using a "Biomedical Computer Program."[4] Since density versus composition follows a linear relation, it was fitted to

$$\text{Density} = B_0 + \sum_{i=1}^{8} B_i X_i \tag{3}$$

where x_i = volume fraction of component i and B_0, B_i = empirical constants. The equations represented the responses quite well, but they are cumbersome. Therefore, the effect of eliminating interaction and quadratic terms was developed by reevaluating the response equations with various quadratic terms or combinations of quadratic terms eliminated and examining the errors between calculated and experimental responses statistically for each case. Since the regressions can be performed very rapidly by a modern computer and since many interaction terms can be eliminated on the basis of experience (for example, little interaction between clay and marble filler is to be expected), reducing the regression equations to simpler forms that still adequately represent the response is not difficult nor time consuming.

Since the regression analysis could only be performed with a linear equation with the available "Biomedical Computer Program," the second-order polynomial, eq. (2), was linearized before regression analysis was done. This linearized equation was in the form

$$Y = A_0 + \sum_{i=1}^{8} A_i Z_i + \sum_{j=9}^{16} A_j Z_j + \sum_{k=17}^{45} A_k Z_k \tag{4}$$

where these terms corresponded to the terms of the second-order polynomial as follows:

$$A_0 = B_0 \tag{5}$$

$$\sum_{i=1}^{8} A_i Z_i = \sum_{i=1}^{8} B_i X_i \tag{6}$$

$$\sum_{d=9}^{16} A_d Z_d = \sum_{i=1}^{8} B_{ii} X_i^2 \tag{7}$$

$$\sum_{k=17}^{45} A_k Z_k = \sum_{i=1}^{7} \sum_{j=i+1}^{8} B_{ij} X_i X_j. \tag{8}$$

Regression for each property was performed by deleting square terms (Z_9 through Z_{16}) and interaction terms (Z_{17} through Z_{45}) one at a time. When one term at a time is deleted, the F-test for F-distribution, which is expressed as

$$F_{n,n-1} = \frac{SS_{\text{base}} - SS_{\text{base}-1}}{S^2} \tag{9}$$

where n = degrees of freedom in numerator for F-distribution, $n - 1$ = degrees of freedom in denominator for F-distribution, SS_{base} = sum of

TABLE IV
Coefficients of Regression Equations

Terms	Density	Elongation	Compression strength	Tensile strength	Flexural strength	Flexural modulus	Secant modulus
X_1	1.37649	95.98950	−0.02732	0.00078	−0.00283	0.14554	1.79251
X_2	1.57042	167.01782	−0.05128	−0.00615	−0.01668	−5.75500	0.70308
X_3	−1.02582	−14.61224	−0.04799	−0.00967	−0.02015	−1.22441	−0.29696
X_4	−1.10084	109.44629	−0.03456	−0.00979	−0.02067	0.22113	−1.35077
X_5	1.58401	160.08569	−0.06056	−0.00244	−0.01579	1.72925	1.58983
X_6	0.27504	82.41577	−0.03130	−0.00383	0.00103	−0.63911	0.50197
X_7	0.08755	290.07031	−0.12926	−0.01465	−0.00056	−0.33234	−0.64604
X_8	0.34422	256.43359	−0.22232	−0.00569	−0.02062	−1.35132	0.43842
X_1^2	0.0	182.80933	−0.05150	−0.02704	−0.04074	−2.97189	−3.16558
X_2^2	0.0	39.53931	0.00961	−0.00091	0.01035	8.39853	−0.30142
X_3^2	0.0	84.78394	0.02581	0.00139	−0.00693	0.72176	−0.41278
X_4^2	0.0	137.30420	−0.00937	−0.00172	−0.01476	1.06233	0.57664
X_5^2	0.0	119.84521	0.05115	−0.01412	0.03872	−4.55200	−2.13765
X_6^2	0.0	25.01221	−0.02219	−0.00174	−0.04392	0.89334	−0.21522
X_7^2	0.0	−113.98730	0.07174	0.00431	−0.01337	−0.23637	0.16125
X_8^2	0.0	37.80859	0.21372	0.00680	0.01492	3.09570	−0.41095
X_1X_2	0.0	0.0	0.0	0.0	0.0	1.93091	0.0
X_1X_3	0.0	0.0	0.0	0.0	0.0	4.53545	0.0
X_1X_4	0.0	0.0	0.0	0.0	0.0	−2.24657	0.0
X_1X_5	0.0	0.0	0.0	0.0	0.0	1.72719	0.0
X_1X_6	0.0	0.0	0.0	0.0	0.0	5.74762	0.0
X_1X_7	0.0	−270.89063	0.0	0.0	0.0	−0.56160	−2.24062

X_1X_8	0.0	0.0	0.0	0.0	0.0	2.11084	0.0
X_2X_3	0.0	0.0	0.0	0.0	0.0	8.43297	0.0
X_2X_4	0.0	0.0	0.0	0.0	0.0	6.87164	0.0
X_2X_5	0.0	0.0	0.0	0.0	0.0	0.37309	0.0
X_2X_6	0.0	0.0	0.0	0.0	0.0	2.11751	0.0
X_2X_7	0.0	−342.40527	0.0	0.0	0.0	4.83197	−1.45135
X_2X_8	0.0	0.0	0.0	0.0	0.0	10.49878	0.0
X_3X_4	0.0	0.0	0.0	0.0	0.0	−1.32475	0.0
X_3X_5	0.0	0.0	0.0	0.0	0.0	−5.29202	0.0
X_3X_6	0.0	0.0	0.0	0.0	0.0	−3.41042	0.0
X_3X_7	0.0	0.0	0.0	0.0	0.0	0.98099	0.0
X_3X_8	0.0	0.0	0.0	0.0	0.0	3.12524	0.0
X_4X_5	0.0	0.0	0.0	0.0	0.0	0.58264	0.0
X_4X_6	0.0	0.0	0.0	0.0	0.0	−3.37820	0.0
X_4X_7	0.0	−196.06665	0.0	0.0	0.0	−1.92389	1.13045
X_4X_8	0.0	0.0	0.0	0.0	0.0	1.41870	0.0
X_5X_6	0.0	0.0	0.0	0.0	0.0	2.08801	0.0
X_5X_7	0.0	−372.80078	0.0	0.0	0.0	2.08035	−2.25305
X_5X_8	0.0	61.21167	0.00910	−0.01003	−0.00587	2.39307	0.27681
X_6X_7	0.0	−188.13574	0.0	0.0	0.0	0.07410	−1.06024
X_6X_8	0.0	0.0	0.0	0.0	0.0	3.12915	0.0
X_7X_8	0.0	−520.73828	0.29166	2.00905	0.02934	0.20239	−0.40131
Intercept	1.13249	−114.19733	0.07269	0.01064	0.01384	0.56932	0.47450

squares for no deletion, $SS_{\text{base}-1}$ = sum of squares for one deletion, and S^2 = standard deviation, would approximate

$$F_{n,n-1} = \frac{SS_{\text{base}} - SS_{\text{base}-1}}{S^2} \simeq t^2$$

which is a t-distribution. Therefore, when terms were deleted one at a time, the effect of deleting a term was tested according to a t-distribution with 3 degrees of freedom and 95% confidence limits. Results of deletion of one term at a time showed that many interaction terms can be deleted, which was expected. When all these terms that satisfied the t-test were deleted together, the F-test was applied, which is

$$F_{n,n-x} = \frac{(SS_{\text{base}} - SS_{\text{base}-M})/M}{S^2} \tag{11}$$

where M is the number of terms deleted. This test also was satisfied with confidence limits of 95%.

Further regression analyses were performed by using this new equation (after deletions) as a basis and deleting one or more terms each time. A successful regression was used as a new base, and the procedure was repeated. This procedure was very successful for most properties. It was found that only seven interaction terms were important for elongation; two, for compression strength; two, for tensile strength; two, for flexural strength; and seven, for secant modulus. However, in the case of flexural modulus, no interaction terms could be deleted.

It should be noted that these regression equations are statistical approximations. Therefore, after individual deletions have been performed, a final recheck of the equation should be made to see if the effect of deletion of these terms is still negligible. The successful elimination of terms one at a time is not always indicative of the absence of interaction. Elimination of combinations of these terms is necessary for better approximation of the regression equation. The equation for flexural modulus is a good example of the necessity to recheck the final equation. In this particular case, several interaction terms were successfully deleted one at a time with confidence limits higher than 94%. However, deletion of combinations of these terms were not successful. The confidence limits for most bases tried were less than 75%. Therefore, no terms were deleted for this property equation since the effects of combinations of these terms, when deleted, were significant. The coefficients of the terms for each property are listed in Table IV.

SELECTION OF CONSTRAINTS AND OPTIMIZATION

Property specifications are defined for a given application and are used as constraints. Using these values and the response equations determined by regression analysis, one can determine the composition for optimum cost. Formally, this is stated as

$$\text{min. cost} = A_0 + \sum_{i=1}^{8} A_i X_i \tag{12}$$

subject to

$$B_{0j} + \sum_{i=1}^{8} B_{ij}X_i + \sum_{i=1}^{8} C_{ij}X_i^2 + \sum_{i=1}^{7} \sum_{k=i+1}^{8} D_{ikj}X_iX_k(\geq,\leq)\ Y_j \quad (13)$$

$$X_i \geq 0$$

$$\sum_{i=1}^{6} X_i \leq N$$

where cost = cost of formulation, X_i = volume fraction of component i, Y_j = constraint of property j, A_0, A_i, B_0, B_{ij}, C_{ij}, D_{ijk} = empirical constants, and N = maximum permissible volume fraction of filler. Of course, it may be desirable to maximize or minimize a property while holding the cost within a certain limit, i.e., treat cost as a constraint. This can be done by merely interchanging the appropriate equations between objective function and constraints in the formal problem statement. However, since one is usually interested in minimum cost, the problem statement given is most common.

The optimization can now be performed. Several optimization schemes were tested, and the pattern search technique, which has also been shown to be an efficient method by Biles,[2] was found to work best. The pattern search method was used to obtain optima for various combinations of constraints in this work. In pattern search, the calculation proceeds from an initial feasible composition (a composition that satisfies all constraints) to other more favorable compositions, according to specified step increments of the independent variables, until an optimum or a constraint is reached. If a constraint is reached, the calculation proceeds along the constraint until a constrained optimum (maximum along the constraint) or an intersection with a second constraint is reached. Thus, a local optimum will likely be one of three types: (1) an unconstrained optimum with no active constraints (no properties equal to the specified values), (2) a constrained optimum with one active constraint (one property equal to the specified value), or (3) a constrained optimum with two active constraints (two properties equal to the specified values). All three types of local optima have been determined in this study. In some cases an optimum was determined in which three constraints were active. This was not the usual case since this requires that the optimum coincide with the point of intersection of three surfaces.

EXAMPLES AND DISCUSSION

As examples, several sets of constraints that are suitable for different applications were specified, and optimum compositions were determined for each set. In some cases, it was necessary to imposed additional constraints, such as the maximum permissible amount of one component, but this can be done very easily without any additional experimental work.

One set of constraints that was imposed was for a general molding composition, case I. The constraints imposed were: density, $D \leq 1.2$ g/cm^3;

tensile strength, $\sigma_T \geq 3000$ psi; flexural strength, $\sigma_F \geq 2500$ psi; compressive strength, $\sigma_u \geq 5000$ psi; secant modulus, $SM \geq 4\times10^5$ psi; flexural modulus, $FM \geq 4\times10^5$, elongation, $E \geq 15\%$. Additional constraints imposed were on total filler, $\sum_{i=1}^{6} X_i \leq 0.55$; and on total styrene, $1 - \sum_{i=1}^{8} X_i \leq {}^1/_3(X_7 + X_8)$. The results for the best optimum found are given in Tables V and VI.

It can be seen from Tables V and VI that density, flexural strength, and elongation are active constraints, i.e., equal to the limiting permissible value, while the added styrene constent is 32.5% of the resin content $(X_7 + X_8)$, which is very close to the constraint of 33.3%. The total filler content is about 52.5%, which is also close to the constraint of 55%. The cost of this formulation is 32.0 ¢/liter.

Several local optima were found in the search for the optimum. The optimum given is the best located for this example, but it cannot be stated unequivocally that it is the global optimum. However, it is possibly significant that, although all optima calculated were constrained, the best optimum exhibited the largest number of active constraints. These different optima were calculated using different starting points, indicating that the direction of approach to the boundaries of the constrained region can affect the optimum calculated. Therefore, it is necessary to perform optimization from various starting points within the constrained or feasible region to be reasonably certain that the best, or global, optimum has been determined. The added time and expense is relatively insignificant since the optimization can be performed very rapidly on a modern computer.

The formulation corresponding to the best optimum specifies shell flour and Saran beads primarily as fillers with some clay and marble. Hollow glass beads and wollastonite are virtually eliminated. Marble is cheaper than other fillers, but this cost advantage is apparently offset by its high density versus flour and by its adverse effect on properties versus clay and flour. The high elongation constraint requires a high ratio of flexible to rigid resin to offset the loss in elongation resulting from the high filler loading. It is interesting to note that the procedure automatically selected a formulation that is not drastically different from several that have evolved in practice for applications where good mold duplication is a necessity.

For wood-simulated parts, the density of 1.2 g/cm^3 used for the constraint for general molding, case I, is too high. Also, the ultimate elongation limit of 15% for general molding is probably higher than necessary since wood is a rigid material. Therefore, an optimum formulation for wood-simulated parts, case II, was calculated to fit the following constraints: $D \leq 1.05$ g/cm^3, $\sigma_T > 3000$ psi, $\sigma_F \geq 2500$ psi, $\sigma_i \geq 3000$ psi, $SM \geq 3\times10^5$ psi, $FM > 4\times10^5$, and $E \geq 5\%$. The results are given in Tables V and VI and show that only the lightest of the cheaper fillers (flour) was specified to any great degree; the remainder of the filler specified is primarily high-cost, density-reducing fillers (hollow glass beads and Saran beads). The ratio of styrene to resin is very close to 1:3 as before, but the total filler content was lowered

TABLE V
Optimum Formulations and Costs for Example Cases

Case no.	Volume Fraction of Component											Cost, ¢/liter
	Clay X_1	Marble X_2	Glass beads X_3	Saran beads X_4	Wollastonite X_5	Shell flour X_6	Total filler $\sum_{i=1}^{6} X_i$	Flexible resin X_7	Rigid resin X_8	Total resin $(X_7 + X_8)$	Styrene X_9	
I	0.050	0.025	0.000	0.200	0.013	0.235	0.523	0.115	0.245	0.360	0.117	32.0
II	0.021	0.010	0.112	0.161	0.010	0.168	0.482	0.119	0.271	0.390	0.128	38.0
III	0.014	0.010	0.086	0.190	0.010	0.178	0.488	0.069	0.316	0.385	0.127	36.5
IV	0.001	0.005	0.153	0.175	0.005	0.105	0.444	0.088	0.330	0.418	0.138	41.2
V	0.021	0.005	0.169	0.179	0.005	0.106	0.485	0.074	0.313	0.387	0.128	40.2
VI	0.005	0.005	0.162	0.165	0.005	0.130	0.472	0.136	0.277	0.413	0.115	41.4

TABLE VI
Constraints and Properties of Calculated Optimum Cases[a]

Case no.	σ_T, psi	σ_F, psi	σ_C, psi	D, g/cm³	SM, 10³ psi	FM, 10³ psi	E, %	Total filler, vol-%	Styrene-to-resin ratio
I	(≥3000)	(≥2500)	(≥5000	(≤1.2)	(≥400)	(≥400)	(≥15)	(≤55)	(≤33)
	5022	2500	6035	1.200	512	430	15.0	52.3	32.5
II	(≥3000)	(≥2500)	(≥3000)	(≤1.05)	(≥300)	(≥400)	(≥5)	(≤55)	(≤33)
	4721	2500	4764	1.050	363	402	5.8	48.2	32.8
III	(≥3000)	(≥1500)	(≥3000)	(≤1.05)	(≥300)	(≥400)	(≥5)	(≤55)	(≤33)
	5134	1528	3000	1.050	383	518	18.5	48.8	33.0
IV	(≥3000)	(≥1500)	(≥3000)	(≤0.95)	(≥300)	(≥400)	(≥5)	(≤55)	(≤33)
	4813	1501	3080	0.950	302	473	12.8	44.4	33.0
V	(≥3000)	(≥1000)	(≥3000)	(≤0.95)	(≥300)	(≥400)	(≤55)	(≤55)	(≤33)
	4789	1003	3061	0.950	330	476	10.6	48.5	33.1
VI	(≥3000)	(≥2000)	(≥3000)	(≤0.95)	(- - - -)	(- - - -)	(≥4)	(≤55)	(≤33)
	4233	2004	4064	0.950	283	345	4.00	47.2	27.8

[a] Constraints are given in parentheses.

from 52.5% to about 48.2%. For this optimum, density and flexural strength are the active constraints. The calculated cost of the formulation is 38.0 ¢/liter, which is 6 ¢/liter higher than the cost for the optimum higher-density formulation. Thus, lowering the density from 1.2 to 1.05 g/cm^3 costs 6 ¢/liter plus a loss in elongation.

Since there were two active property constraints (D and σ_F) for the case II optimum, the effect of relaxing the flexural strength constraint on the cost is of interest. Therefore, the optimization was repeated for the constraints of case II, except that the flexural strength constraint was lowered from $\sigma_F \geq 2.5 \times 10^3$ psi to $\sigma_F \geq 1.5 \times 10^3$ psi. The results are given in Tables V and VI. The cost is 36.5 ¢/liter, which is 1.5 ¢/liter less than the cost for the optimum in case II. Density and compression strength are active constraints, and flexural strength is very close to the constraint. The styrene:resin ratio is 1:3, the filler content is 44.8%, and the ratio of flexible to rigid resin is 0.22:1.0. It is interesting to note that the cost was reduced by decreasing the total filler and decreasing the flexible resin content. Note also that the elongation for case III is 18.5%, much higher than the value for case II, even though the flexible to rigid resin ratio for case III is less than half of the ratio for case II. Elongation is increased by reduction in total filler and by substitution of a deformable filler (Saran beads) for other, more rigid fillers. Again, this demonstrates the ease with which the effects of changes in properties on formulation can be evaluated to aid one in developing an understanding of the responses of a complicated system.

A series of cases, cases IV, V, and VI, were run to determine the effect of further lowering the density to 0.95 g/cm^3. Feasible solutions could not be found for the same constraints used in case II (except for $D \leq 0.95$ g/cm^3), nor could feasible solutions be found when the flexural strength was also reduced to 2000 psi.

A feasible solution, case IV, was obtained when the flexural strength was reduced to 1500 psi. The calculated cost of the best optimum is 41.2 ¢/lb. Density and flexural strength are active constraints, while compressive strength and secant modulus are close to the constraints. The formulation contains primarily glass and Saran beads as fillers, with some flour. That is, the density has been reduced by substituting glass beads for solid fillers. The total filler is 44.4%, the styrene: resin ratio is slightly less than 1:3, and the flexible resin:rigid resin ratio is 0.27:1. It is interesting to note that this same solution was obtained for several calculations in which the non-active constraints were lowered.

In case V, the flexural strength constraint was relaxed to $\sigma_F \geq 1000$ psi (all other constraints being the same as for case IV) and the optimum determined. The results are given in Tables V and VI. The calculated optimum cost is 40.2 ¢/liter, and density and flexural strength are active constraints. This was obtained primarily by increasing the amount of glass filler used. The total filler content is 48.5%. Thus, relaxing the flexural strength constraint to 1000 psi produces a saving a 1.0 ¢/liter.

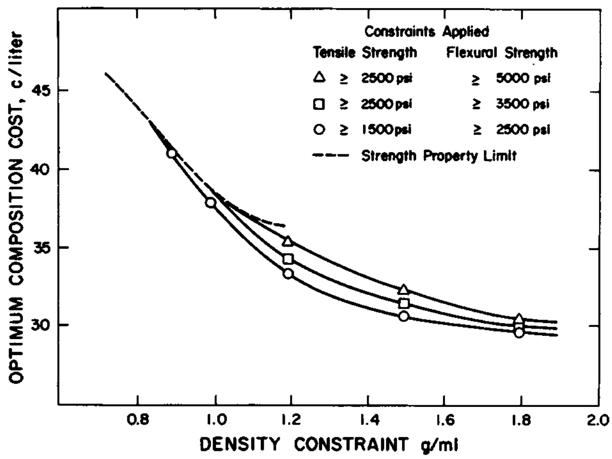

Fig. 1. Effect of density of filled polyester on optimum cost.

In searching for the highest obtainable flexural strength at a density of 0.95 g/cm³, we obtained a solution which is labeled case VI. This is given in Tables V and VI. It can be seen that a flexural strength of 2000 psi is attainable if one is willing to accept a flexural modulus of 3.45×10^5 psi and a secant modulus of 2.83×10^5 psi for the material. The calculated cost is 41.4 ¢/liter, which is almost the same as the cost for case IV.

From the discussion of the example calculation results, it should be obvious that this method of investigation is rapid, flexible, and realistic. Most importantly, the experimental work can be directed toward solution of a range of problems rather than toward a single problem. The initial development of a formulation can be done mathematically rather than experimentally, which is much less expensive and much more rapid. Calculated solutions for a particular problem should be checked experimentally and further work done in a confined sample space, if necessary. Additional constraint equations for properties, e.g., pour viscosity or hardness, that must be specified for a particular application can be added, if necessary. If an additional component is desired, its effect on the property equations could be evaluated by performing $(n + 2)$ additional experiments, which n is the original number of independent components. Optimization for particular solutions could then proceed as before. It is worth noting that one can gain an understanding of the response of the system to changes in formulation rapidly by optimizing the system repeatedly as one or more of the property constraints is changed, as is shown by Figure 1 for the effect of change in density. The ability to develop such an understanding may be the most valuable reward for doing this type of investigation. Finally, the penalty cost for setting a constraint is determined. For example, the cost of lowering the density from 1.2 to 1.05 g/cm³ is 6 ¢/liter, unless the flexural strength constraint can also be lowered. If the flexural strength constraint is also lowered from 2500 psi to 1500 psi, the penalty cost is only 4 ¢/liter. Thus, if the density constraint of 1.05 g/cm^3 must be met, the investigator's attention is directed toward determining if the 1000 psi difference in flexural strength is worth 2 ¢/liter more to the user.

CONCLUSIONS

A general method for nonlinear constrained optimization of complex formulation problems has been demonstrated and found to be feasible. The method permits formulations to be determined for specific applications from a minimum of general experimental data. It was demonstrated that parametric studies of the effect of property specifications on formulation can be conducted mathematically rather than experimentally using this method.

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