

Statistical Analysis Applied to Film Development: Grafted PVA-Based Water-Soluble Film

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Synopsis

A statistically designed experiment was used to optimize the physical properties of a cold water-soluble film by establishing reliable estimates of the effects of the independent variables of the system. The system consisted of polyvinyl alcohol (low molecular weight, 88% hydrolyzed) to which is grafted ethyl acrylate by a ceric ion technique. To the grafted PVA is added a higher molecular weight PVA to strengthen film.

Introduction

All scientific disciplines are making increased use of statistically designed experiments in order to obtain maximum information from a minimum amount of data. This paper deals with a practical application of statistical methods to develop a polymeric chemical system wherein physical properties are optimized. Although a specific application is discussed, the approach, outlined in six steps below, is applicable generally in chemical systems.

(A) Define the problem. The problem must be defined in terms of numerically measurable quantities. Then the dependent variables must be determined, i.e. the responses to be measured. This requires a degree of familiarity with the system under study.

(B) Determine the independent variables to be examined and their levels. Some exploratory experiments may be necessary to develop the required insight into the variables which are of first-order importance.

(C) Choose an appropriate design. Obviously, the aid of a statistician or some knowledge of statistics is required.

(D) Experimentally measure the dependent variables (desired responses).

(E) Using least squares, estimate the parameters in the assumed mathematical relationships and predict responses as continuous functions of the independent variables.

(F) Experimentally test predicted values. The experiments should lie between design points, i.e., between the levels at which the original experiments were carried out. Optimizing the desired properties can be achieved by investigating those regions of the factor space which seem promising within the range of the independent variables.

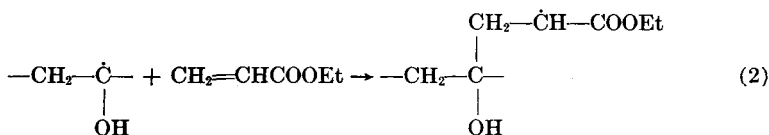
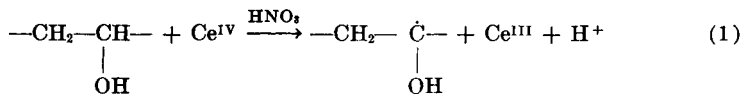
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This paper deals with the application of the above outlined approach to the problem of developing a water-soluble packaging film.

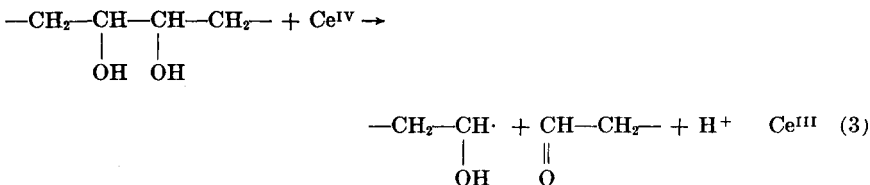
Discussion

A water-soluble packaging film should be: readily water-soluble, non-tacky at high relative humidity, yet permanently plasticized at low relative humidity; heat- and/or water-sealable; tough and stretchable for resistance to high speed machining and wear; transparent and colorless; printable.

A system which gave a film with reasonably good properties was chosen for development. This system consisted of an 88% hydrolyzed, low molecular weight polyvinyl alcohol (PVA-L) to which was grafted ethyl acrylate by the ceric ion technique of Mino and Kaizerman.¹



The reaction is straightforward, except that ceric ion preferentially attacks 1,2-glycol sites, cleaving the backbone, thus reducing the molecular weight and the related physical properties.



Since about 1% of 1,2-glycol links exist in the PVA, a large ceric ion concentration can have adverse effects.

The PVA concentration, the amount of nitric acid (for grafting), temperature, and time were empirically fixed. The two remaining independent variables of importance are the ceric ion concentration and the level of ethyl acrylate.

Since grafted PVA-L films exhibited poor tensile strength, a high molecular weight, 88% hydrolyzed PVA (PVA-H) was blended with the graft prior to casting in order to increase the tensile strength. This introduced a third independent variable.

A three-factor central composite design was chosen to determine the experimental program. This design is shown schematically in Figure 1.

The design consists of levels corresponding to the coordinates of the vertices of a cube and the six axial points. The center point completes the

TABLE I
Coded Levels of Variables in the Design

Variable	Levels				
Coded level	-1.68	-1	0	1	1.68
Ceric ion, meq./g. PVA	0.029	0.112	0.233	0.255	0.437
Ethyl acrylate, wt.-% in graft	5	15.1	30	44.9	55
PVA-H, wt.-% in blend	34	40.5	50	59.5	66

design and is run in replicate to provide an estimate of experimental error at an intermediate level of the three variables. In Table I are shown the coded levels of each variable.

Since grafting is carried out prior to blending, the points on the lower plane in Figure 1 (i.e., the projection of the cube to 0% PVA-H) permit optimizing the unblended graft film, indicating whether blending is indeed necessary.

All nine grafts (the projected points) were prepared, and from these were prepared the 14 blend points plus the center in quadruplicate giving a total of 27 films to be tested. The responses measured for all films were the tensile strength, tab tear strength, Elmendorf tear strength, per cent elongation at break, modulus, rupture time in water, and solution time in water.

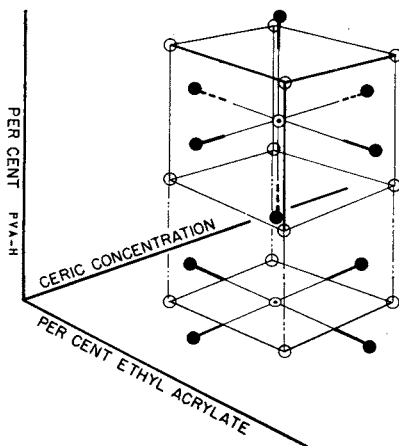


Fig. 1. Central composite design.

Experimental

The preparation of a film corresponding to the central design point is given below as a typical synthesis.

PVA-L (60 g.) was dissolved in 350 ml. of water by heating to 90°C. and allowing to cool to room temperature. Ceric solution (31.0 ml. of 0.45*N* ceric ammonium nitrate in 0.5*N* HNO₃) was added rapidly, and

the mixture was stirred 20 min. During this period the orange color of the ceric ion disappears.

Distilled ethyl acrylate (27.6 ml.) was then added at 25–30°C. The mixture was allowed to stir for $\frac{1}{2}$ hr., the temperature being maintained below 30°C. during the brief exotherm period. The per cent solids was determined as 18.6% by weight loss, corresponding to 34% graft (99% conversion). The mixture was partially neutralized to pH 3.1 with 13.35 ml. of 1.99*N* sodium hydroxide.

A 50% (by weight) blend of PVA-H with the graft solution was prepared by combining 100 g. of graft solution (18.6% solids) with 192.5 g. of PVA-H solution (9.76% solids). The solution was filtered through a coarse fritted funnel. Solids in the blend were found to be 12.8%.

The resin was evaluated by examining a hand cast film. The film was prepared by drawing down the solution with a doctor blade on Mylar polyester film supported on a glass plate to obtain, on drying, an average film thickness of 1.4 mils.

Physical measurements were made according to ASTM Standards, Pt. 9, Designation D882-61T, 1961 (tensile strength, elongation, and initial modulus), Designation D1922-61T, 1961 (Elmendorf tear) and Designation D1938-62T, 1962 (tab tear).

The four replicates of the above run gave the results shown in Table II.

Results

Table II shows the results obtained for the four films prepared according to the method described in the Experimental Section.

These are typical of the results for the 27 films. The experimentally determined responses were submitted to statistical analysis. A digital computer was used to fit approximating functions (second-degree polynomials) to the designed portion of the data by the method of least squares. When the quadratic components could not be estimated reliably, linear approximations were used.

Since the contours obtained through least-squares estimation are based on functions which can only approximate the true surface, and since the prediction error due to the random error in the estimated parameters increases with the distance from the center of the experimental region, the reliability of the contours becomes low toward extremes of the design region.

In Figure 1 the cube inscribes a sphere of radius 1—or in other words, the cube has the dimensions of two coded units on a side (see Table I for coding). The reliability on the surface of the inscribed sphere is quite good but falls off as the corners of the cube are approached. Figure 2 illustrates the relative width of the 95% confidence interval as a function of the distance from the center of the design for both linear and quadratic surfaces.

Figures 3–6 illustrate the contour surfaces obtained in a cube of four units on a side (distance 2.5 from center to corners). By using a proper multiplier for the relative confidence interval, the confidence interval for a

TABLE II
Film Test Results of Replicated Center Point^a

Film	Tensile strength, psi	Tear strength, g. ^b		Solubility		Elongation, %	Modulus × 10 ⁻⁸ , psi
		Tab	Elmendorf	Rupture time, sec.	Solution time, min.		
1	4920	21	3.5, 3.0	20	3	219	0.12
	<i>5690</i>	<i>33</i>	4.0, 3.0				
	4920	24	3.0, 3.0				
	4920	25	3.0, 3.5				
	4770	23	3.5, 4.5				
2	5500	38	3.0, 2.5	15	2	234	0.12
	4920	47	2.5, 2.5				
	7230	49	3.0, 3.0				
	6620	55	3.0, 3.0				
	5830	56	3.5, 3.5				
3	6920	18	2.5, 4.0	20	2	243.5	0.15
	6620	19	3.0, 3.5				
	6770	19	3.0, 3.0				
	<i>10170</i>	18	3.0, 3.0				
	6670	18	3.5, 3.0				
4	5690	24	3.5, 4.0	20	3.5	253	0.09
	5330	24	4.5, 3.0				
	<i>7540</i>	20	3.5, 4.0				
	5080	25	3.5, 3.0				
	5080	23	3.0, 3.5				

^a *Italic values in the table were disregarded as a result of statistical tests.*

^b The value in grams/mil is obtained by dividing the table value by the film thickness and multiplying by 16.

given response is obtained as a function of distance from the design center. The multipliers are shown in Table III.

Thus, from Figure 2 at a distance, say, of 1.5, it would give a relative confidence interval of 0.650 for a linear fit and 0.395 for a quadratic fit. Using the multipliers, the 95% confidence limits would be ±6.5 g./mil in tear strength, ±1206.5 psi for tensile strength, ±36.3% elongation, and ±0.083 × 10⁸ psi for modulus.

The large error in the measurements of tab tear strength, rupture time, and solution time relative to the changes in those responses over the ex-

TABLE III
Multipliers for Response Surfaces Shown (Relative Confidence Interval × Multiplier = Confidence Interval for Given Distance)

Tear strength ^a	Tensile strength ^a	Elongation ^b	Modulus ^b
10.0	184.1	76.2	0.129

^a Linear fit.

^b Quadratic fit.

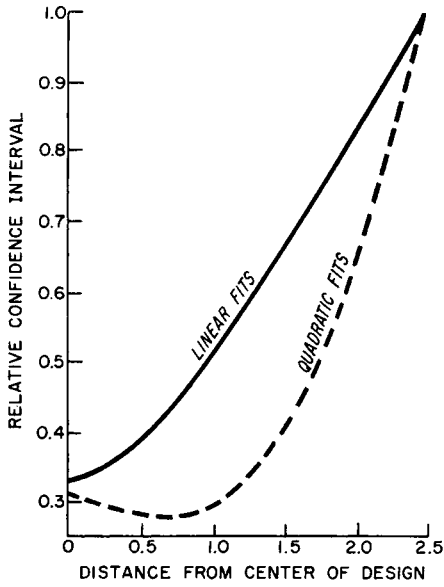


Fig. 2. Relative size of confidence limit (95%) as a function of distance from the center of design.

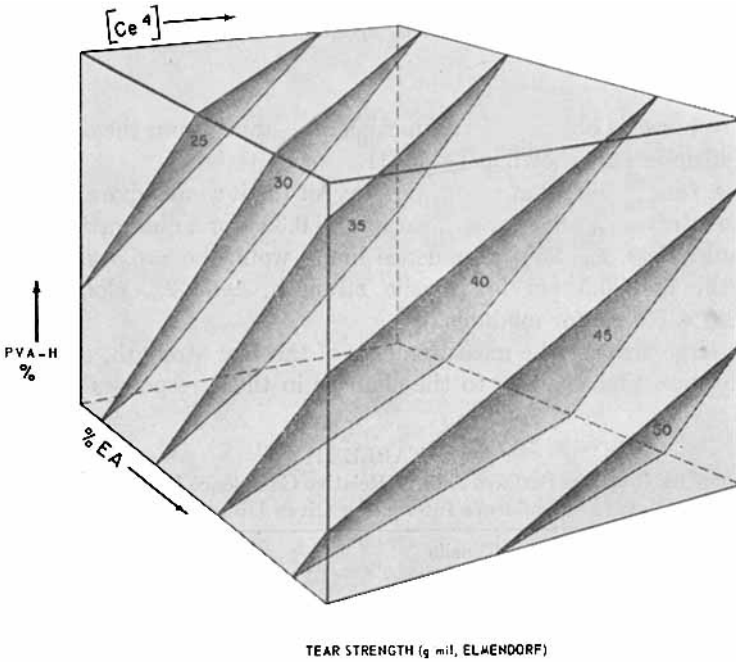


Fig. 3. Tear strength (Elmendorf).

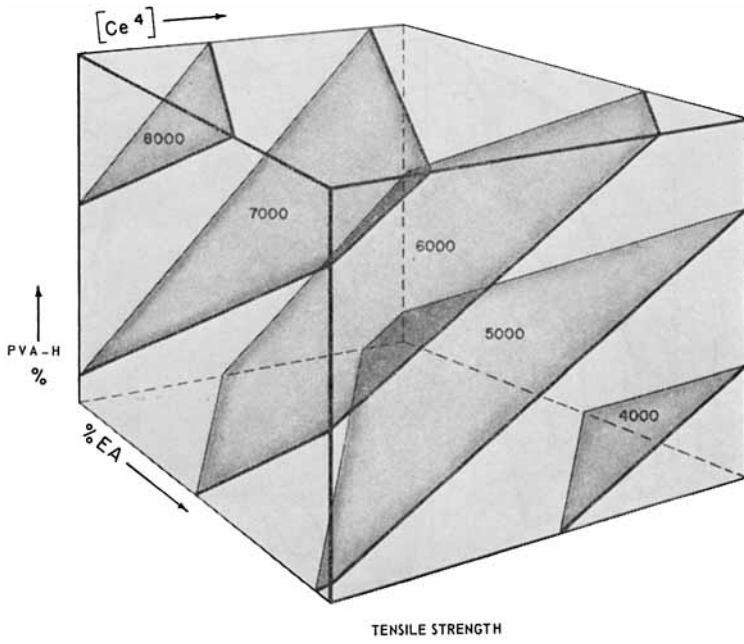


Fig. 4. Tensile strength.

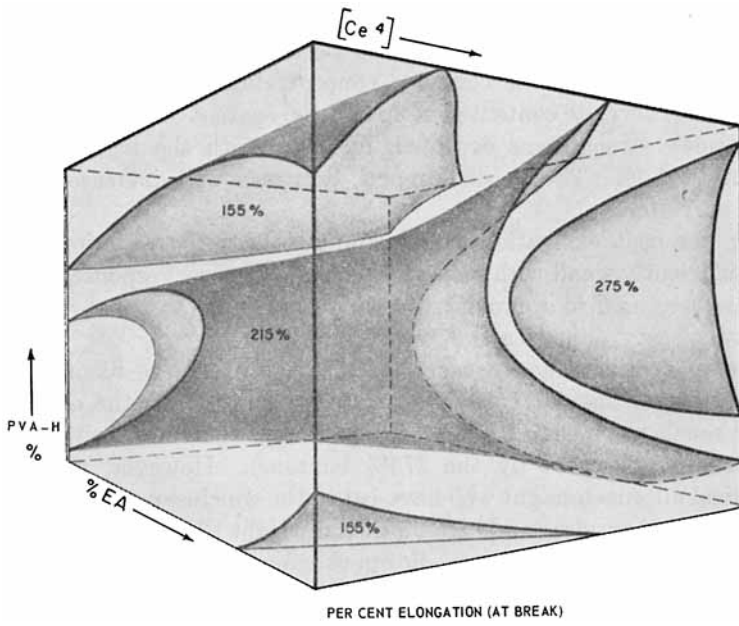


Fig. 5. Elongation at break.

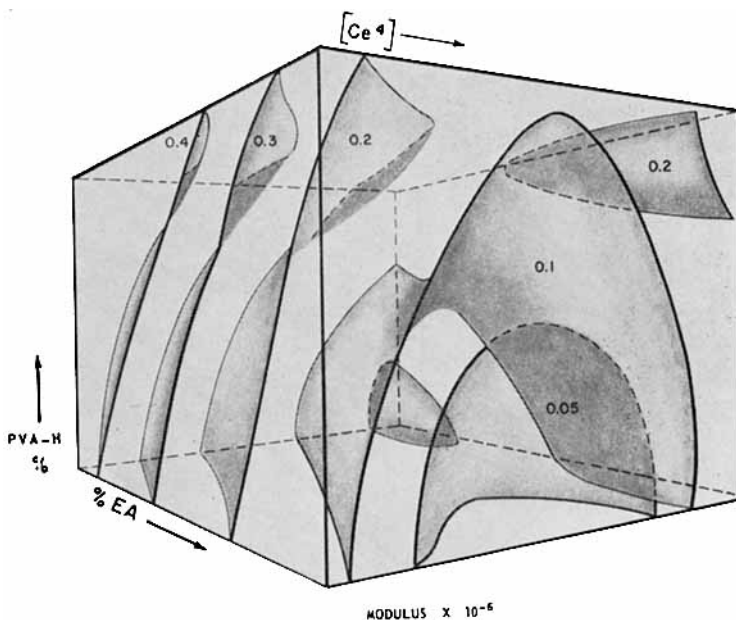


Fig. 6. Modulus.

perimental region did not permit estimation of a meaningful mathematical model which would relate these to composition variables.

A linear approximation was used to relate Elmendorf tear strength (Fig. 3) and tensile strength (Fig. 4) to composition variables, since no reliable quadratic relationships could be found. The tear strength can be seen to rise with the ceric ion concentration. It rises most steeply as the ethyl acrylate content goes up and the content of PVA-H goes down. The tensile strength, as expected, increases with the higher molecular weight PVA-H. The tensile strength decreases with increased ceric and ethyl acrylate.

For per cent elongation and modulus, where the experimental error was sufficiently small with respect to changes in these responses, quadratic models were used to approximate their relationships to the three composition variables. (Figs. 5 and 6, respectively.)

The quadratic surface for elongation in Figure 5 can be likened to a tree trunk lying on its side. At lower ceric concentrations, the elongation is never much more than 215%. Elongation does increase with ceric concentration (evidenced by the 275% contour). However, the standard empirical approach might well have led to the conclusion that, for medium levels of ethyl acrylate and high molecular weight PVA, ceric concentration has little effect on elongation. For packaging purposes, a high elongation is desirable, so regions of interest lie within the "tree trunk."

Figure 6 shows the saddle-shaped contours for modulus. At low ceric concentration, the contours are closer together; at high ceric concentration,

TABLE IV
Designed Films: Predicted Properties and Properties of Hand (H) and Drum (D) Cast Film Properties

Film	Coded Levels		Thickness mils		Tensile strength, psi		% Elongation,		$\times 10^{-4}$, psi Modulus		Tear (Elmendorf) g./mil					
	Ethyl	Ceric acrylate	PVA-H	H	D	H	D	Pred.	H	D	Pred.	H	D			
1	1	0	-0.75	1.4	1.7	4600	4070	6640	260	169	294	0.07	0.07	42.5	74	575
2	-1	1	None	1.8	1.6	3100	3200	3040	281	278	305	0.05	0.01	511	402	532
3	-1	0	0	1.1	2.3	6600	5910	6800 ^a	220	153	200 ^a	0.25	0.33	34	51	35 ^a
4	1.5	1	-1.	1.1	1.6	3800	4480	5500	305	243	325	0.13	0.03	48	(608)	129
5 ^b	1	1	-1	1.1	1.6	4200	4765 ^c	5800	260	233 ^c	308	0.08	0.06	46	93	7
6	-1	1	-1	1.0	2.1	5700	5110	5800	190	148	190	0.15	0.23	40	48	57

^a Average of a large number of runs.

^b This run is the same as one of the design points in the original design.

^c These results are the average for two independent runs.

there is only a slight change with high molecular weight PVA. As the ethyl acrylate increases, the direction of change reverses (due to the saddle shape). In order to minimize the modulus at high ceric concentrations, a decrease in high molecular weight PVA and ethyl acrylate is necessary; at low ceric concentration, the high molecular weight PVA would again have to be decreased but the ethyl acrylate would have to increase. This finding emphasizes the merit of the statistical approach as well as the pitfalls of the standard empirical approach based on holding all but one of the variables constant.

With a knowledge of the variable interactions, films can be designed "on paper" and their properties predicted. Although the axial points of the design extend from -1.68 to $+1.68$, the contours of the response surfaces were reported from -1.5 to $+1.5$ increments of 0.5 . Thus the results lie within the factor space where the reliability is greatest.

Using the reported results, a number of films were designed by varying the ceric level from -1 to $+1.5$, the ethyl acrylate from -1 to 1.5 , and the PVA-H from -1.5 to 0 .

Of the designed films, six were chosen for over all good properties. Film 2, for example, was chosen to have maximum tear strength; film 3 for maximum modulus and tensile strength; film 4 for maximum elongation.

All six compositions were prepared. In addition to hand casting, as had been done in the initial study, all samples were also cast on a heated, Mylar polyester film-coated drum to obtain correlation between hand drawing and quasi-commercial casting.

The results are shown in Table IV. Generally, very good agreement was found between predicted and observed values, and between hand and drum cast samples.

Film 3 gave a satisfactory performance with respect to subsequent requirements imposed by commercial casting, slitting, rewinding, and high speed packaging as well as product compatibility and storage stability.

Conclusions

Statistical analysis permitted, with a minimum number of experiments, the establishment of reliable estimates of the interactions of the variables in preparing a water-soluble packaging film. The nonlinear relationships (particularly modulus and elongation) would have precluded an economical determination by standard empirical methods.

With the interactions known, a satisfactory film could be designed which met all specifications.

The authors are indebted to a number of people for the execution of this work and wish to express their appreciation particularly to: Dr. D. W. Behnken, who set up the design and participated in many useful discussions; Mr. R. M. King, who carried out the statistical analysis of the results; Mr. J. T. Geoghegan and Mrs. Schemear, who prepared the polymers; Dr. B. L. Williams and Mr. E. L. McCarthy, who evaluated the films.

Reference

1. Mino, G., and S. Kaizerman, U. S. Pat. 2,922,768 (June 26, 1960).

Résumé

Une expérience élaborée statistiquement a été employée pour déterminer les propriétés physiques optimales d'un film soluble dans l'eau, en établissant des estimations valables des effets des variables indépendentes du système. Le système est le suivant: de l'alcool polyvinylique (de bas poids moléculaire, hydrolysé à 88%) sur lequel on a greffé de l'acrylate d'éthyle par une technique à l'ion cérique. On ajoute au PVA greffé un PVA de plus haut poids moléculaire afin de rendre le films plus résistant.

Zusammenfassung

Eine statistisch ausgelegte Verwuchsreihe wurde zur Erreichung optimaler physikalischer Eigenschaften eines kaltwasserlöslichen Films durch verlässliche Ermittlung des Einflusses der unabhängigen Variablen des Systems verwendet. Das System bestand aus Polyvinylalkohol (niedriges Molekulargewicht, 88% hydrolysiert), auf welchen Äthylacrylat in einem Cerionenverfahren aufgepfropft wird. Dem gepfropften PVA wird zur Erzielung einer hohen Festigkeit des Films höhermolekulares PVA zugesetzt.

Received May 4, 1964