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OPTIMIZATION STUDIES ON THE DEVELOPMENT OF NYLON-6 FILMS WITH HIGH TENSILE STRENGTH

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Key Words: Nylon-6 Films, Response Surface Methodology, Degradation, Antioxidant, Aging Time, Optimization

ABSTRACT

Several factors influence the tensile strength during the degradation of nylon-6 films viz. antioxidant concentration, aging time and aging temperature. A 3×5 experimental design has been adopted to study the effect of these factors using Response Surface Methodology. A linear second-order model has been developed to optimize and to study the interaction effects on tensile strength of the nylon-6 films.

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INTRODUCTION

Thermal degradation of nylon-6 most often impairs its physical properties [1-3]. The presence of polar amide group in its backbone results in better thermal stability than other polymers [4-7]. Structural changes during the thermal oxidation of nylon-6 films stabilized with several antioxidants were studied by various workers [8-16]. They found that the various parameters such as aging time, aging temperature and antioxidant concentration affects the strength of the nylon-6 films.

Response surface methodology (RSM) is an effective tool to optimize the process and process variables [17]. An experimental design such as the central composite rotable design (CCRD) to fit a model by least square technique has been selected during the studies. If the proposed model is adequate, as revealed by the diagnostic checking provided by an analysis of variance (ANOVA), the 3-D plots can be usefully employed to study the response surface and locate the optimum.

The objectives of this study were:

1. To establish the relationships between the factors affecting the quality of nylon-6 films such as concentration of antioxidant, aging temperature, and aging time and the response that is relevant to the quality (tensile strength) and

2. To establish a set of optimum conditions for obtaining the nylon-6 films with maximum tensile strength.

EXPERIMENTAL

Materials

Film grade nylon-6 chips (molecular weight-8000) were obtained from LML Fibers Ltd., Kanpur, India. Formic acid (Purity 85%) (AR-Grade) and methylene chloride (Purity 98%) (AR-Grade) were used as solvents for dissolving nylon-6 chips and antioxidant.

Irganox-1098 [N, N'hexamethylene bis(3,5-ditert-butyl-4-hydroxy-hydrocinnamide)] was used as an antioxidant for stabilizing the nylon-6 films against thermal degradation and was supplied by CIBA-GEIGY Ltd., Basel, Switzerland.

Preliminary Analysis of Materials

The nylon-6 granules were dried in an oven to remove the entrapped moisture. The used solvents were checked for their purity. The antioxidant was purified by recrystallization.

Experimental Design

Tensile strength was the only response (Y) measured in the study. The experimental region extended from –2 to +2 in terms of the coded independent variables X_i. The coding facilitated the computations for regression analysis and optimum search. The levels of independent variables like antioxidant concentration, aging time and aging temperature are listed in Table 1. The range of experimental design (actual values) was decided based on the preliminary studies. The coded independent variables (X_i) were related to x_i by the following equations:

$$X_1 = (x_1 - 75)/25; \; X_2 = (x_2 - 130)/15; \; X_3 = (x_3 - 0.30)/0.15$$

TABLE 1. Variables and their Levels for the Central Composite Design

		Symbols		Levels				
Variables	**Unit**	**Coded**	**Uncoded**	**-2**	**-1**	**0**	**+1**	**+2**
Aging Time	Hours	X_1	x_1	25	50	75	100	125
Aging Temperature	°C	X_2	x_2	100	115	130	145	160
Antioxidant Concentration	wt %	X_3	x_3	0	0.15	0.30	0.45	0.60

TABLE 2. Central Composite Design Arrangement and Response

Experiment No.	Variable levels[a]			Response (Tensile strength) (Kg/cm^2)
	X_1	X_2	X_3	Y
1	-1	-1	-1	404.91
2	-1	-1	+1	414.53
3	-1	+1	-1	371.13
4	-1	+1	+1	382.45
5	+1	-1	-1	407.09
6	+1	-1	+1	418.42
7	+1	+1	-1	344.03
8	+1	+1	+1	355.35
9	-2	0	0	426.41
10	+2	0	0	372.21
11	0	-2	0	424.59
12	0	+2	0	328.48
13	0	0	-2	375.92
14	0	0	+2	398.57
15	0	0	0	437.00
16	0	0	0	437.00
17	0	0	0	437.00
18	0	0	0	437.00
19	0	0	0	437.00
20	0	0	0	437.00

[a] Coded Values

A central composite rotatable design (CCRD) was adopted as in Table 2 [18]. This design was specifically suited for analyses with second order polynomials. The CCRD combined the vertices of a hypercube whose coordinates are given by the 2^{n-1} factorial design (runs 1-8) with the 'star' points (runs 9-14). The star points were added to the factorial design to provide for estimation of curvatures of the model [19]. Six replicate experiments (runs 15-20), at the center of the design, were performed. In earlier studies, co-author randomized the experiments in order to minimize the effects of unexplained variability in the observed responses due to extraneous factors [20]. The similar approach was implemented in the present study.

For analysis of the experimental design by RSM, it is assumed that 'n' mathematical functions, b_k (k=1,2,3, ...,n), exist for each of the response variables Y_k, in terms of 'm' independent processing factors, x_i (I=1,2,3, ...,m), such as [21]:

$$Y_k = f_k (x_1, x_2, ...,x_m) \qquad (1)$$

In our case, n=1 and m=3

Y= Tensile Strength (Kg/cm^2)
x^1= Aging Time (hr)
x^2= Aging Temperature (°C)
x^3= Concentration of Antioxidant (wt%)

The unknown functions, f_k, was assumed to be approximately by a second degree polynomial equation:

$$Y_k = b_{k0} + \sum_{i=1}^{3} b_{ki} X_i + \sum_{i=1}^{3} b_{kii} X_i^2 + \sum_{i\neq j=1}^{3} b_{kij} X_i X_j \ldots\ldots \qquad (2)$$

where b_{ko} is the value of the fitted response at the center point of the design i.e. (0,0,0), b_{ki} , b_{kii} , and b_{kij} are the linear, quadratic, and cross-product regression terms, respectively.

EXPERIMENTAL

The film of nylon-6 with and without antioxidant was cast on a clean glass plate from a solution made from formic acid and methylene chloride and it was heated to 45-50°C for about 30 minutes for drying the sample. After evaporation of the solvent, the dried film was cooled and then carefully removed from the glass plate. The films of uniform thickness were cut for further analysis.

Analysis of Films

Aging of the films was done in an air circulatory oven having digital controls at five different temperatures of 100°, 115°, 130°, 145°, and 160°C for time periods up to 125 hours. The aged samples were taken out from the oven and sealed in polyethylene bags purged with N_2 and are kept in a dark chamber.

Formation of oxygenated and unsaturated groups were studied by infrared spectra of the samples which were recorded with Perkin-Elmer (model 599-B) infra-red spectrophotometer in the wavelength range of 4000-200 cm^{-1} [10]. Change in tensile strength was measured in an automatic tensile tester.

Each set of experimental design was replicated five times and average value of response was taken for further analysis of the experimental design.

Analysis of Data

The regression analysis was conducted using the "Stepwise Variable Selection Backward Elimination" procedure for fitting the model represented by Equation 2 to the experimental data [22]. Maximization of the polynomial thus fitted was performed by numerical techniques using the mathematical Optimizer procedure of the Quattro Pro Software package (Quattro Pro for Windows Ver. 5.0) that deals with constraints. The mapping of the fitted response surfaces was achieved using surfer program (Surfer Access System, Version 3.0, 1987 Golden Software Inc., Golden, Co., USA). The response surfaces and the corresponding contour plots for this model were plotted as a function of two variables while keeping the other variable at an optimum value.

RESULTS AND DISCUSSION

Diagnostic Checking of the Fitted Model

The coefficient of determination (R^2) is the proportion of variability in the data explained or accounted for by the model and large values of R^2 indicate a better fit of the model to the data. Regression analysis indicated that the fitted quadratic model accounted for 98.68% of the variation in the experimental data (Table 3), which was highly significant.

The model for Y was:

$$Y = 425.64 - 11.65X_1 - 28.59X_2 - 11.34X_1^2 - 19.41X_2^2 - 15.62X_3^2$$

TABLE 3. Estimated Coefficients of the Fitted Quadratic Equation for Tensile Strength

Coefficients	Estimated Coefficients	Standard Error
b_{k0}	425.64***	10.75
b_{k1}	-11.65*	3.20
b_{k2}	-28.59***	3.20
b_{k11}	-11.34**	4.58
b_{k22}	-19.41*	4.58
b_{k33}	-15.62**	4.58

*P<0.01; **P<0.05; ***P<0.001
d.f. = 7; R^2 = 0.9

In Table 3, the significance of the coefficients of the quadratic model (Equation 2) at P<0.05, 0.01, and 0.001 demonstrated that for tensile strength, only two linear and three quadratic terms of the model were significant.

The optimum conditions to yield maximum tensile strength are presented in Table 4. The model provides the information about the influence of each variable on the tensile strength of nylon-6 films. However, these are the opti-

TABLE 4. Optimum Conditons for Maximum Tensile Strength of Nylon-6 Films

Variables	**Coded Values**	**Uncoded Values**
Aging Time (hrs)	-0.5135	62.2
Aging Temperature (°C)	-0.7363	119
Antioxidant Concentration (Wt%)	0	0.3
Maximum Tensile Strength (Kg/cm^2)	439.15	

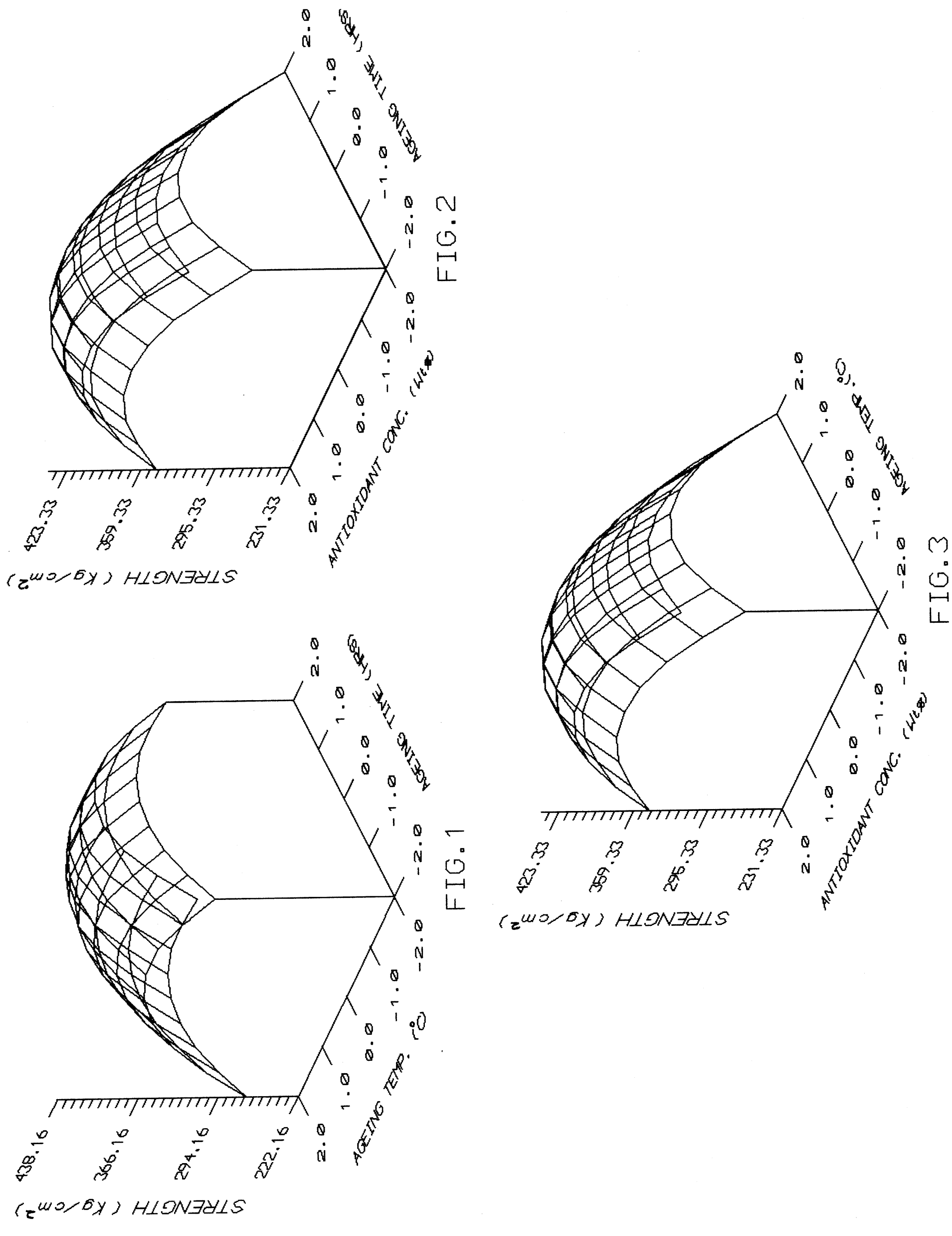

Plate 1. Response surface representation of various process parameters on the strength of Nylon-6 films.

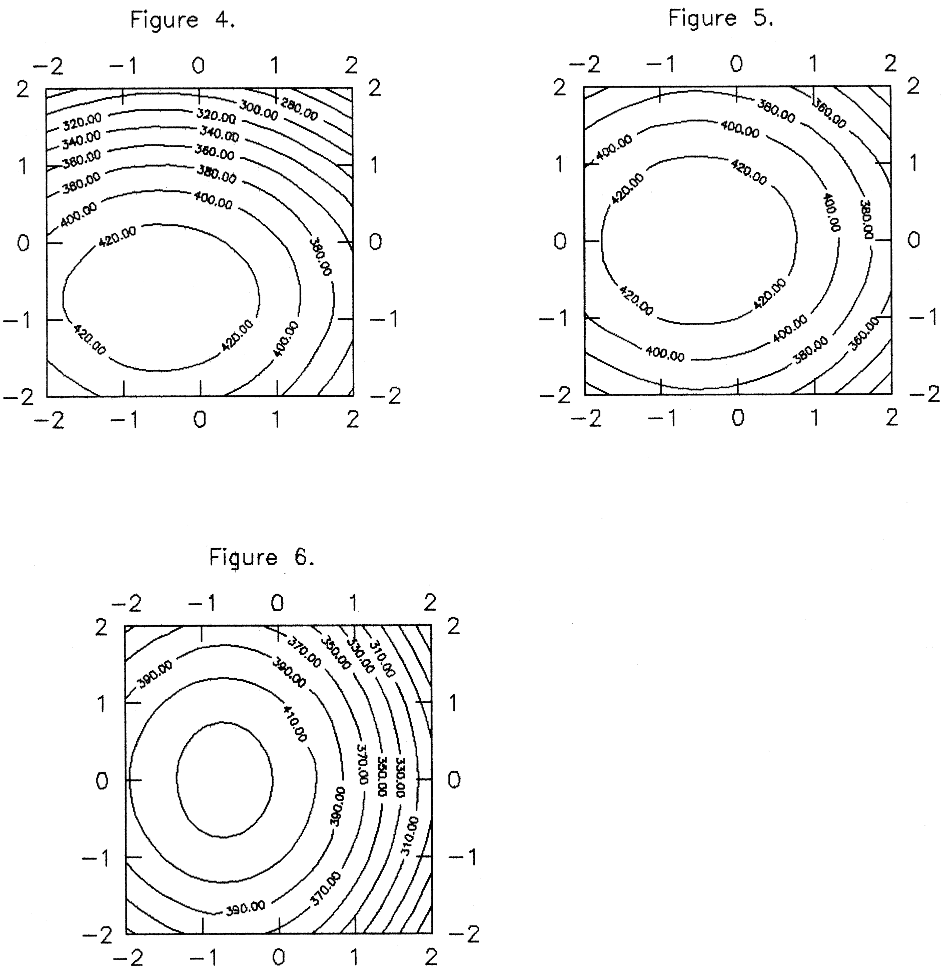

Plate 2. Corresponding contour plots of the Response Surfaces in Plate 1.

mized conditions that provide the information to produce high strength nylon-6 films.

The response surfaces in Plate 1 (Figures 1-3) and the corresponding contour plots in Plate 2 (Figures 4-6) are based on the above model (Y) with one variable kept constant at the optimum level and varying the other two within the experimental range.

The surface plot of tensile strength as a function of aging temperature and time demonstrated the maximum strength at an optimum aging temperature

119°C for optimum time 62.2 hour (Figure 1). Increasing or decreasing the time at the optimum temperature resulted in decreased strength. However, it is observed that for low aging time strength of the material increases with the decreasing temperature upto a certain level whereas for higher aging time the pattern follows a parabolic path showing that increasing or decreasing temperature beyond the optimum level resulted in reduced strength.

It is clear from Figure 2 that at a lower level of temperature and center level of concentration response approaches to maximum whereas at higher temperature strength reduces. The similar effects were observed in the case of response (tensile strength) as a function of concentration and time, however, the response approaches towards maximum near the centre value of time i.e., 75 hours and showing the greater effect of aging time in interaction with concentration on response (Figure 3).

CONCLUSION

It may be concluded that the system of tensile strength of nylon-6 films can effectively be optimized using response surface methodology and with a minimum number of experiments. Computerized computations, model building and generation of three-dimensional graphs will go a long way to unraveling the complexity of the preparation of nylon-6 films with the different variables used. The optimum conditions for obtaining a better quality of nylon-6 films i.e., resistant to degradation were the aging time 62.2 hours, aging temperature 119°C, and antioxidant concentration 0.3 wt%.

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