Optimization of Propellant Binders – Part I: Statistical Methodology

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Abstract

The development of new propellant binder systems requires the thermodynamic calculation of physico-chemical data as well as the adaption of the mechanical properties in order to achieve a reliable innerballistic profile of the resulting propellant. However, in most cases the mechanical data may not be easily predicted due to the complex interactions between the components of the binder like the resin, the curing agent or possibly plasticizers and curing catalysts. Therefore, this study focusses on the capability of the multivariate analysis on the prediction of the E-modulus of a system comprising nitrocellulose as well as GAP, Desmodur N100 and an energetic plasticiser. Using this method, an equation has been derived which, within the regression intervall, may be used for the prediction of the E-modulus as a function of the components mentioned above.

Keywords: Propellant binder, Multivariate analysis, E-modulus, Nitrocellulose, GAP, Desmodur N100

1 Introduction

In literature several studies focus on the properties of propellants comprising mixtures of glycidyl azide polymer (GAP) and nitrocellulose (NC) as energetic binders. For example GAP was incorporated as an energetic plasticizer in propellant formulations comprising cyclotetramethylene trinitramine (RDX) and triaminoguanidine nitrate (TAGN) as oxidiser and NC as binder [1]. Since in this study GAP was used as an energetic plasticizer substitute for dioctyl adipate (DOA), the force of the resultant gun propellant increased. Whereas in this study the GAP concentration within the binder varied in a range from zero to maximum 17 percent, in another study [2] a GAP concentration in the range from 33 to 60 percent was utilized resulting in solid rocket propellants with attractive burning characteristics. The authors attribute the good burning rate and pressure rate exponent of these systems to the NC whereas they conclude that the GAP within the binder may improve the low temperature mechanical properties of the propellants. Also studies focus on the properties of gun propellants having GAP concentrations in the binder variing in the range from 55 to 65 percent [3, 4]. In these studies it is reported that propellant formulations consisting of the GAP/NC binder and an energetic plasticizer (DNDA) as well as RDX as oxidizer may be created, which have a force in the range of 1290 J/g. Furthermore, these propellants may burn at comparatively low temperatures in the range of 3325 K and hence be utilized as high energy, low erosion gun propellants. Also it is found that the impact sensivity and the friction sensitivity of these formulations are much lower than with conventional NC based gun propellants. However, all these studies do not thouroughly investigate the mechanical properties as a function of the composition.

Yet, for the development of propellants it is important to correlate both the thermodynamic as well as the mechanical properties as a function of their composition. In contrast to codes, which usually calculate thermodynamic values in a quite good agreement with the experimentally determined values, there are no suitable codes on a theoretical basis available that could calculate the mechanical properties of such materials.

However, in the complex mixtures used for the formulation of propellants there is no degree of freedom available. Hence, by changing the concentration of one component, the overall mixture must change and therefore the experimental data of a test series imply also information about the binary or even ternary interrelations of the components and their influence on the parameter in focus. An appropriate method of choice to determine such correlations may be the use of statistical methods like for instance the multiple regression analysis. In many cases with this method mathematical expressions are found that enable the calculation of the interesting parameter as a function of the composition in good agreement with the experimental result provided that the calculation is performed within the regression limit.

2 Experimental

2.1 Experimental Design

In this study the data of a former experimental design were used and completed. Hence a five level orthogonal experimental design regarding the concentration of GAP, N100, NC and the plasticiser DNDA as well as the concentration of the catalyst (cat) was used instead of a conventional simplex lattice or simplex centroid mixture design. Consequently, 23 different mixtures were formulated. Since for every mixture the mechanical data were

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determined five times, in the first approach a cross table having the data of 115 experiments resulted. Using this data a first statistical analysis was performed and five additional mixtures having the desired mechanical properties (a high deformation energy) were calculated. Afterwards these mixtures were processed, mechanically characterised and the resultant data used to improve the model. Hence, alltogether 28 different mixtures were created resulting in a total of 140 measurements.

2.2 Preparation of the Samples

The GAP prepolymer (GAP ICT 3-98, Karlsruhe Germany), having an equivalent weight of 1.224 g/mmol and the NC (SWSH 6266,N: 13,2%, WNC, Aschau Germany), having an equivalent weight of 0.812 g/mmol were dried at 55 °C under vacuum for 12 hours. With trifunctional hexamethylene-isocyanate (Desmodur N100, Bayer, Leverkusen, Germany) as curing agent, the polyurethane network was made. If not mentioned otherwise, the polyurethane was cured with a well balanced ratio of the isocyanate- and the hydroxygroups (R = 1). The binders were kneaded in a horizontal mixer at 45 °C and additionally plasticised with acetone where neccessary.

Depending on the consistency of the resultant polymers, different methods for the preparation of the test specimen having a $100 \times 10 \times 4$ mm geometry must be used. Low viscous mixtures were mould casted and then cured at 50 °C for several hours. Medium low viscous mixtures were pressed between two plates, cured like mentioned before and then cut into samples with the desired geometry. Highly viscous binder systems were extruded by using a ram press. In this case strands having a geometry of $100 \times 4 \times 2000$ mm were formed which after curing were cut. Since shortly after curing all polymers still might change their mechanical properties, the test specimen were stored for about one month in order to achieve stable mechanical properties of the specimen.

2.3 Stress-strain Measurements

The mechanical properties such as, E-modulus, maximum tensile strength and toughness were determined by using an apparatus of Zwick (Zwick, model No. 147670) at a temperature of 23 °C with a test speed of 50 mm/s. More detailed information about the test method can be found elsewhere [5].

3 Results

Based on the experimental results, the following equation for the calculation of the E-modulus has been derived,

$$\begin{aligned}\text{Elastic Modulus} = & -2745.09 + 0.0059768 \cdot \text{Conc}^3_{NC} \\ & + 1.60914 \cdot \text{Conc}_{GAP} + 2614.55 \cdot R \\ & + 80567.5 \cdot \text{Conc}_{CAT} - 80468.6 \cdot R \cdot \\ & \text{Conc}_{CAT} \end{aligned} \qquad (1)$$

where the Elastic modulus is given in MPa and R is the ratio of the concentration of the isocyanate groups of the curing agent to the concentration of the hydroxy groups of the GAP polyole and the NC.

Several statistical tests were performed to validate the equation above. For example the T-statistics shown in Table 1 for the regression parameters are used to test the null hypothesis that a coefficient in the model is equal to zero. The T-statistics are calculated by dividing the estimates by their respective standard errors. Another important parameter in statistics is the P-value, which is a propability value used to judge the significance of each T-statistic. Small P-values lead to a rejection of the hypothesis that the corresponding parameter equals zero, given that all other terms currently in the model will be retained. An important note should be made about this two tests: they test the statistical significance of a given coefficient having accounted for the effect of all the other variables. They test wether or not a variable adds significantly to the fit given that all other variables will be retained. However, once a single variable is removed, the results of all other tests may change considerably [6].

In the Table 1 the P-values of all listed coefficients are zero leading to the conclusion that all the variables considered in the model contribute in a statistical significant way to the E-modulus and hence may not be removed from the model. In fact, by using this methodology all statistical insignificant variables have been removed so as to derive a model as simple as possible.

Table 2 represents an analysis of variance (ANOVA) table. The ANOVA table splits the variability of the

Table 1. Multiple regression analysis regarding the E-modulus of the specimen

Parameter	Estimate	Standard-Error	T-Statistic	P-Value
CONSTANT	– 2745.09	76.5686	– 35.8514	0.0000
NC^3	0.0059768	0.0000734234	81.4019	0.0000
GAP	1.60914	0.377041	4.26782	0.0000
R	2614.55	110.851	23.5861	0.0000
Kat	80567.5	2035.32	39.5846	0.0000
R*Kat	– 80468.6	3648.46	– 22.0555	0.0000

Table 2. Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	6.51852E7	5	1.3037E7	3997.26	0.0000
Residual	420733.0	129	3261.5		
Total (Corr.)	6.5606E7	134			

R-squared = 99.3587 percent
R-squared (adjusted for d.f.) = 99.3338 percent
Standard Error of Est. = 57.1095
Mean absolute error = 43.2444
Durbin-Watson statistic = 0.934721 (P = 0.0000)
Lag 1 residual autocorrelation = 0.532576

response variable E-modulus into two components: a model or regression component SSR which represents the amount of variability of the response variable explained by the regression model and a residual component SSE representing deviations around the fitted model. Since the sum of squares of the model is about 150 times higher than the value for the residual it may be concluded that the choosen model quite well represents the experimental data. The F-ratio and associated P-value test the statistical significance of the fitted model as a whole. A small value such as that shown in table 2 indicates that the collection of independent variables taken together represents a significant improvement over a model with only one constant term.

Also important information about the derived fit is given by the summary statistics given above. For example the R-squared represents the percentage of variability of the E-modulus which has been explained by the fitted regression model. However, more detailed information about the fit is given by using the adjusted R-squared, which bases on the number of observations used to fit the data. It is more appropriate than the ordinary R-squared because it takes into account a newly added variable: Usually by adding a new variable to the fit, the R-squared rises even though the new variable may not improve the fit. In contrast to this, the adjusted R-squared may get smaller. In this study both R-squared values indicate that more than 99 percent of the variability are explained by the fitted regression model.

Other informative statistics are the Durbin-Watson statistic and the Lag 1 residual autocorrelation for which this study indicates significant autocorrelation of the data. Indeed, a plot of the studentized residuals versus the row number (Figure 1) indicates that the data are autocorrelated due to the fact, that the experiments were not randomized. However, not all autocorrelation may be assigned to serial autocorrelation as Figure 2 indicates.

Otherwise, if all studentized residuals were randomized they would follow a normal distribution and in Figure 2 fall on a straight line. In this diagram three points can be seen that deviate far from values that would put them on the straight regression line illustrated in Figure 2. Yet, this points are not troublesome because in the normal distribution up to 5 percent of the values may deviate substantially from the straight line. The other data points form three straight lines rather than one single straight line. It has been pointed out earlier in this report that the samples must be prepared by using three different methods: It is well known in literature that the preparation method significantly influences the mechanical properties of polymeric materials [7]. These systematic errors in the determination of the mechanical properties of the propellant binder have to be coped with and can not be changed.

However, in Figure 3 the calculated E-modulus corresponds very well with the experimental values. Yet, since the mean absolute error of the fit has a value of 43 MPa, for very soft mixtures or rather mixtures having a low E-modulus the calculated data should be taken with care. As can be seen in Figure 4, for the calculation of the E-modulus there should be taken into account that for some mixtures like for

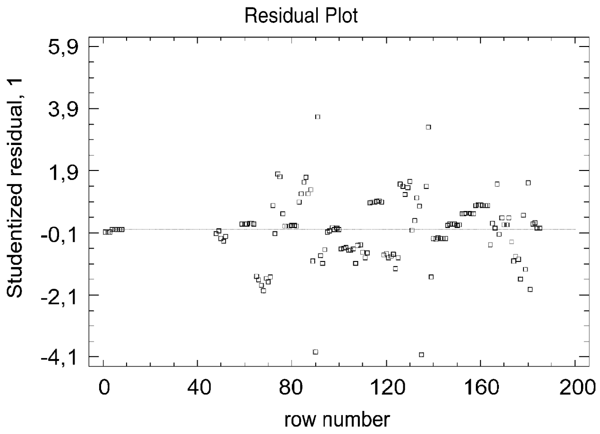

Figure 1. Residual plot of the E-modulus versus row number of the experiments

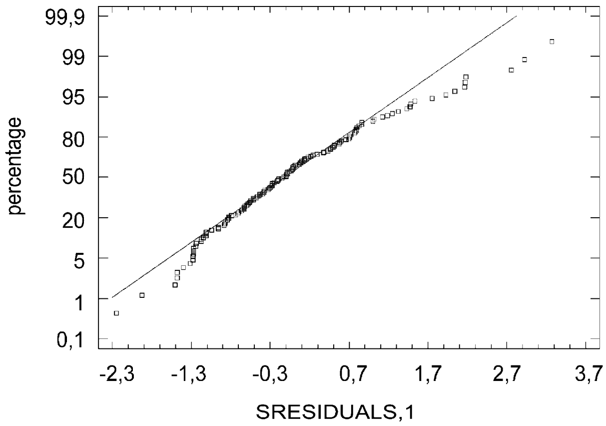

Figure 2. Normal propability plot of the studentized residuals

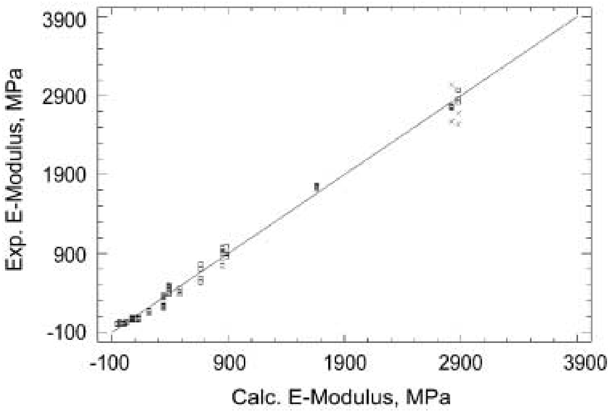

Figure 3. Observed versus predicted E-modulus

Table 3. Composition of the additionally tested binder compositions

specimen	NC. %	GAP. %	N100. %	DNDA. %	Akardit. %	Kat. %
TGAPNC27	53.9	9.9	18.9	15.3	2.0	0.03
TGAPNC28	39.2	20.5	17.8	20.6	2.0	0.03
TGAPNC29	44.1	12.1	17.5	24.3	2.0	0.03
TGAPNC30	49.0	5.2	17.7	26.1	2.0	0.03
TGAPNC31	26.6	56.1	15.3	0.0	2.0	0.03

Table 4. E-moduli of the specimen

specimen	E-modulus exp. MPa	E-modulus old fit. MPa	E-modulus new fit. MPa	error old fit. %	error new fit. %
TGAPNC27	904.93	698.72	884.06	22.79	2.31
TGAPNC28	364.03	255.27	345.78	29.88	5.01
TGAPNC29	430.57	353.58	484.78	17.88	– 12.59
TGAPNC30	643.45	496.96	664.11	22.77	– 3.21
TGAPNC31	81.44	90.79	75.22	– 11.48	7.64

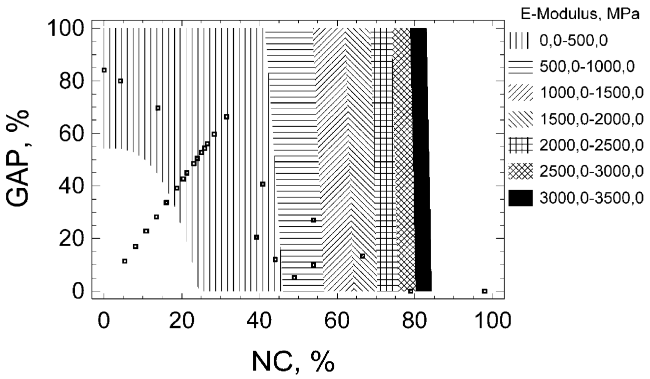

Figure 4. E-modulus versus concentration of GAP and NC (cat: 0.03%, R: 1.2)

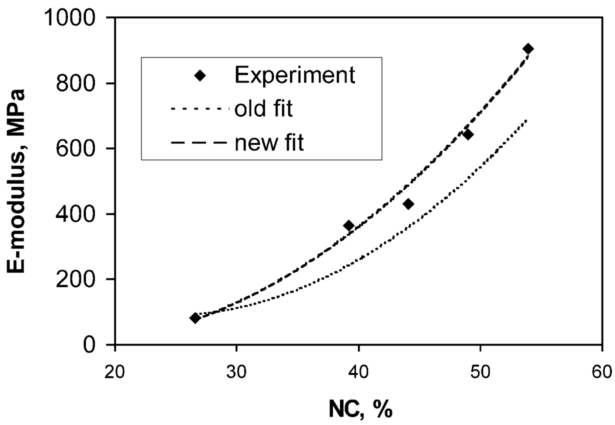

Figure 5. E-modulus of five additional samples with the same deformation energy calculated by the first regression fit.

example mixtures having less than 18 percent NC and less than 26 percent GAP the regression fit is not covered by experimental values and therefore the calculated values are likely to be pure mathematical abstraction, but the compositions of interest are covered by the experimental data and the regression fit may be used for predictions.

Figure 5 illustrates the experimental and the calulated E-modulus of the five additionally tested binder compositions used for the improvement of the Fit-function. The composition of these specimen as well as their E-moduli are represented in the tables below and it is clear that these samples differ considerably in their composition. Yet, the E-modulus may be calculated in good agreement with the experimental data thus indicating the great usefulness of the multiple regression analysis.

4 Conclusions

In this study the capability of the multivariate analysis on the prediction of the E-modulus of a system comprising nitrocellulose as well as GAP, Desmodur N100 and an energetic plasticizer was investigated. Therefore, a five level orthogonal experimental design matrix regarding the concentration of the ingredients was used. A first statistical analysis resulted in the formulation of five additional mixtures having the desired mechanical properties, which were then processed and mechanically characterised in order to improve the model. With this additional data a multiple regression fit resulted that can be used to calculate the E-modulus of the binder system as a function of the composition in good agreement with the experimental results. Hence, the great usefulness of the multiple regression analysis for the prediction of the mechanical properties of a binder has been shown. With this, new propellant binders having improved mechanical and thermodynamical properties may be created.

5 References

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