Flexible Development

Statistical Design of Experiments accelerates the optimization of plastic products

Polyamides are used in a large variety of applications: for example as fuel and cooling system parts in the automotive industry, as material for cables and conduits in electronics, for pneumatic tubes, as protective films and for packaging in the food and chemical sector. The demand for new materials which fulfill various requirements is high. In addition these new products should be developed in shorter time and in close contact to the customer – "Simultaneous Engineering" is the keyword. Still, nobody is willing to accept higher prices.

Design and development of new materials are generally based upon already existing chemicals and processes. For balancing different demands, Statistical Design of Experiments ("DoE") is a powerful tool. It allows reducing the number of trials and thus the cost, without affecting the accuracy of the results. With the help of modern software – for instance the DoE expert system STAVEX – this technology can be used also without extensive statistical knowledge.

Polyamide in offshore tubes

One practical example of use is the development for an offshore tube. Polyamides are used as an inner layer for big size tubes with different metallic components which are used for pipelining crude oil. The polyamide layer thus is exposed – at temperatures from -40 to 80°C – to chemicals, water, hydrogen sulfide, ammonia and carbon dioxide and in addition to mechanical pressure and stress. Due to the high investment the installed oil pipeline should have a maximum lifetime. From these requirements the key properties for such materials can be derived: Low swelling in crude oil, dimensional stability, high impact strength at low temperatures, and good flexibility.

The world of experimental design is divided into two categories: On the one hand the factors, on the other hand the target or response variables. If the first have an influence on the latter, they may be called "influence factors" or "important factors". This means that the response variables follow their law – or "model". The aim is to identify these influence factors, to estimate the model parameters and to find the best factor setting.

These three operations are executed automatically by STAVEX. Moreover, the software differentiates between three stages: Screening, modeling and optimization. This accounts for the fact that the model can be estimated with a higher exactness if fewer factors have to be incorporated. In the present example, the process is sufficiently well-known and the influence factors can be restricted to a few. This means that the software directly suggests an optimization stage. Three response variables were considered: Swelling in an oil/brine water mixture, impact strength at -40°C and lifetime in an oil/brine water mixture at 120°C.

Polyamides can be produced on the base of amino acids, lactams, diamines and dicarboxylic acids; their structure can be partially crystalline or amorphous. The spectrum of properties is mainly governed by the ratio of amide to methylene groups. This ratio influences the degree of hydrogen bonding, the water uptake, and thus the melting point, density and chemical stability. In the large set of possible monomer combinations, Polyamide 11 and 12 exhibit a good balance of these properties. Therefore Polyamide 12 was chosen as the base polymer. The other influence factors are viscosity, stabilization and content of plasticizer and impact modifier. Due to the extrusion process viscosity variation is limited; thus we can omit to investigate its influence.

Figure 1: Oil platform – no paradise island for polyamides

The first Statistical Design model is based on a plasticizer variation from 0 to 20%, an impact modifier variation from 0 to 30% and an organic or inorganic stabilization system. The STAVEX proposal is a pentagon plan with 12 trials. From these 12 different materials test bars were made by injection molding and stored in an autoclave with oil/brine water mixture at 120°C. At the beginning and after each removal of test bars the autoclave was inertized with nitrogen.

This first experimental run yielded the following results: Lifetime, swelling and impact strength do not depend on the chemical stabilization system. The optimum for lifetime lies at around 3000 hours with medium plasticizer and high impact modifier content. The optimum for cold impact strength is at 24 kJ/m² for 30% impact modifier and no plasticizer (Fig. 2). On the contrary, the lowest degree of swelling with 1.7 is given by 10% plasticizer and no impact modifier.

Based on these findings, a second design was generated with the same variation ranges of plasticizer and impact modifier content. The central composite plan comprised 9 experiments; as response variables we now considered cold impact, elongation after 3000 hours storage, swelling (desired target value: 0%), length change and tensile modulus. The test conditions were the same as in the first Statistical Experimental Design. Here again, the optimal factor settings differ for the different response variables. A higher content of impact modifier has a positive effect on cold impact strength, lifetime and elongation. A high content of plasticizer leads to a low degree of swelling. However it has a negative impact on the other response variables. To summarize these contradictory results: the best product for an offshore pipeline must be a compromise between impact modifier and plasticizer content, keeping in mind which properties are most important.

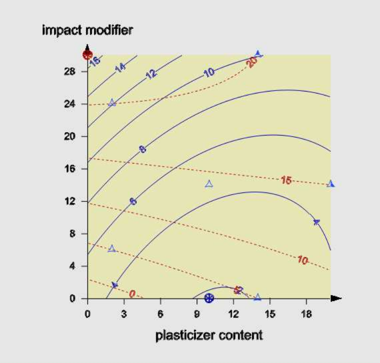

Figure 2: Cold impact strength (dotted line) and swelling. The optimal factor settings are each marked by a star.

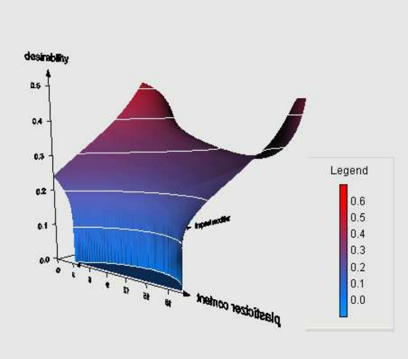

Figure 3: Surface plot of the desirability function. The highest values correspond to the best compromise between the responses.

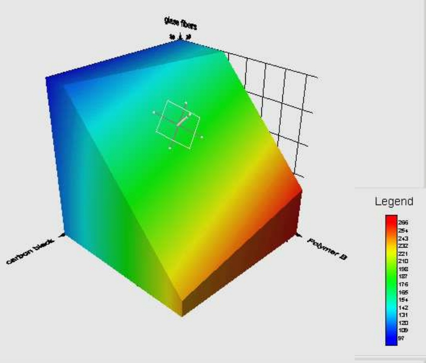

Figure 4: Flow length as a function of three factors (carbon black, glass fibres and Polymer B).

One could have described this compromise in the software very well with a desirability function. This can be calculated as the geometrical mean of selected response variables. In our example, we have weighted swelling and cold impact strength strongest; the other factors were considered as less important. The nearer the response variables are to their desired target values, the nearer the desirability function is to the value of one. Then the decision for the best compromise is easy: It is sufficient to select the factor settings corresponding to the highest desirability value (Fig. 3).

A Polyamide 12 suitable for fuel system applications

Fuel system applications require heavy duty materials, which withstand fuel ageing at temperatures between 60 and 100°C, mechanical stress and impact at -40°C. Especially for the American market, these products have to be antistatic. The polyamides in question should furthermore be characterized by good processability in order to allow for all possible design geometries of connectors and fuel filters.

For the optimization of these features, the following influence parameters were identified: Polyamide type, amount of glass fibers and carbon black and addition of a second polymer. Response variables are resistivity before and after fuel ageing, impact strength and flow length of the polymer melt. The Experimental Design chosen was a Box-Behnken plan with 13 trials, covering an amount of glass fibers from 20 to 30%, an amount of carbon black from 17 to 20% and additional polymer from 0 to 15%. The polyamide which was chosen as the polymer matrix is already known to have a very good stability against many chemicals in the automotive area.

The best values for resistivity lie at a proportion of 25 to 30% glass fibers, 18 to 19% carbon black and 10 to 15% additional polymer. Here the fit quality was only moderate/good. The variables cold impact and flow length also show an optimum for these glass fiber and carbon black contents (Fig. 4). However, there remains a conflict of interest: on the one hand, high cold impact values forbid the addition of a second polymer but, on the other hand, for high flow length 15% additional polymer is needed. The mathematical fit for these two variables is very good.

Conclusion

The second application leads to similar conclusions as the one described before: Finding a simultaneous optimum for all variables is not possible; using the desirability function could give an even clearer representation of the compromise. But in each case the Statistical Design of Experiments yields a Polyamide recipe which allows a safe long-term service in a challenging environment.

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