Tipps&Tricks with G^raf^Compounder

No. XI

Fillers Dominant Influence on Dynamic Hardening

Introduction:
It is assumed that the filler content of a mixture alone determines the hardening factor.

To confirm or refute this hypothesis, a study on the dynamic behavior of a mixture was conducted following the guidelines of a statistical experimental design (Box Behnken Design) (Fig. 1). The aim was to assess the influence of the filler and plasticizer content. A mixture based on NBR was predefined, and the fillers—carbon black, silica, as well as the plasticizer—were varied. The target hardness of the vulcanizate was approximately 70°ShA ± 5°, as specified by the requirements.

Procedure:
The mixtures were blended in a 1 L laboratory internal mixer according to the experimental design guidelines. Sheets were vulcanized in a laboratory press, and their properties were tested. The fillers and the plasticizer were varied within the following ranges:
- Carbon Black N550: 27 phr – 67 phr
- Silica (Coupsil 6109): 20 phr – 60 phr
- Plasticizer (Mesamoll): 5 phr – 19 phr

Hardness, the static and dynamic modulus (Cstat and Cdyn), along with other physical properties, were tested.

Results:
As expected, the influence of fillers on hardness was significant, while the plasticizer had a smaller effect. Fig. 2 shows the dependency of hardness on the amount of fillers. The influence of the plasticizer can be estimated from the position of

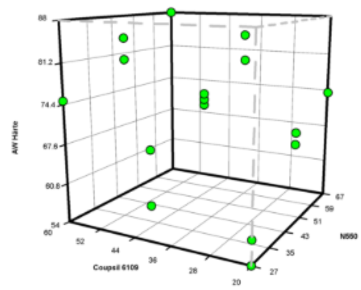

Fig. 1: 3 Parameter DoE with NBR compound and Cb 550, SiliPlastizicer Variation (Box Behnken Design)

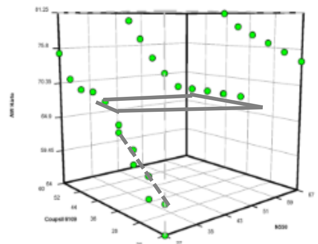

*Fig. 2: Hardness 70°ShA over CB and Silica content. Area indicate equal Hardness.
Dotted line: Calculation with point correction*

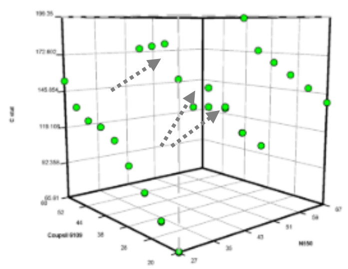

Fig. 3: Cstat over CB 550 and Silica for compounds with equal Hardness. Dotted Arrow points to an outlier according statistical analysis.

the points for the same carbon black amounts but varying silica content.

- Based on the values and their analysis, the sole influence of fillers cannot yet be concluded. Therefore, a simulation was conducted to clarify the extent of the plasticizer's influence at different filler levels. For this purpose, mixtures with similar hardness and their Cstat (Fig. 3), Cdyn, and hardening factor (Fig. 4) were calculated to minimize the variation of the plasticizer as much as possible.
- Additionally, it was necessary to investigate how erroneous data affects the simulation results.

Impact of Data Errors:
- In the initial simulation, the data was directly taken from the DoE. Two or three carbon black amounts were chosen, and the silica content was increased in five phr steps. It was found that for a carbon black content of 27 phr, no mixtures of similar hardness could be maintained with increasing silica content and simultaneous oil increase. At higher carbon black levels, the hardness could only be kept relatively constant within narrow limits despite increasing silica and plasticizer content (Fig. 2). Statistical analysis (ANOVA) indicated that the corner point (Carbon Black 27 phr; Coupsil 6109 20 phr) was an outlier. This value was corrected using the Point Prediction Tool (Design Expert®). The results of the simulation with the corrected value are also shown in Figs. 2, 3, and 4. In all figures, both calculations—with and without correction—are displayed. The points highlighted with arrows were caused by measurement errors in the corresponding Cstat property, resulting in deviations in the hardening factor.

Conclusion:
- The values of Cstat and Cdyn increase steadily with filler content. The plasticizer has a minor effect on this increase.
  - At CB 550 47 phr, deviations from the steady

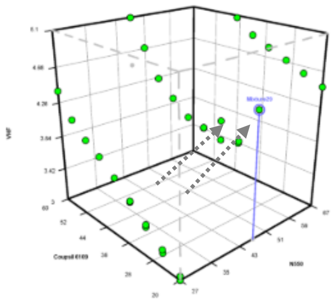

Fig. 4: Dynamic Hardeing Factor over CB 550 and Silica for eaual hardness compounds. Dotted arrows show measurement errors for Cdyn or Cstat. according statistic analysis.

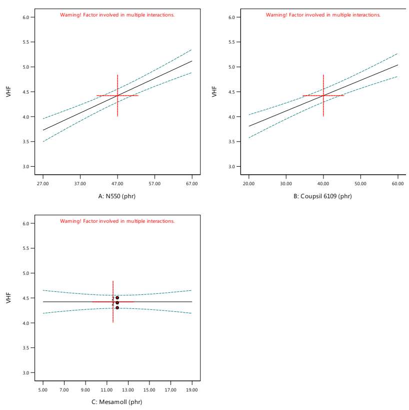

Fig. 5.: Influence of CB 550, Silica and Plasticizer on the Dynamic Hardending Factor

increase with rising silica content in the range of 25 phr to 45 phr are observed. These inconsistencies do not align with all other values, and statistics show larger deviations compared to hardness (Fig. 2 – CB 550 – 47 phr).
- The hardening factor increases with the amount of carbon black and silica since both Cstat (Fig. 3) and Cdyn (no figure) change in the same way (Fig. 4). The influence of measurement errors is noticeable.
- The plasticizer's impact on the properties shown here is significantly lower, as demonstrated by the summary graph (Fig. 5).

Summary:
The simulation was primarily conducted to visualize the dependency of the hardening factor on the filler content. The result is a strategy for identifying and correcting errors in unsystematically constructed data files. This possibility is demonstrated on a file of designed experiments as a first step. The GraphCompounder allows identifying the data used for the calculations in any data set, which can then be repeated and corrected through experiments if necessay like in this example.

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