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Statistical DOE and Modeling for Repeated Measures in Rubber Research

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Introduction

- Ethylene Propylene Diene rubber (EPDM) is a synthetic rubber widely used in applications such as transportation, infrastructure, industry and consumer applications.
- Dow, as a leading manufacturer of EPDM, continuously innovates in the development of EPDM products to achieve superior end use properties including color stability in automotive weatherstrip.
- This poster demonstrates the power of statistical DOE and modeling to support the development of new EPDM rubbers with superior color stability. Monte Carlo Simulation based DOE is a new development for repeated measures modeling in rubber research.

Methods & Objectives

- Color stability property is measured repeatedly over time on the same experimental unit (i.e., a cured sample from a specific polymer grade) in a weathering chamber, as repeated measures. The color stability test process is described in Fig 1.
- Given a list of synthesized polymer grades, D-Optimal DOE plan is developed to draw cause and effect conclusions on polymer microstructure factors and color stability metric (Delta E).
- Number of repeated measures is evaluated to attain 80% statistical power detecting main and interaction effects using Monte Carlo Simulation.
- Time dependence between repeated measures is estimated through Random Coefficients Modeling (RCM) due to unequal time intervals in the real data collection.
- The objective is to develop fundamental understanding of EPDM Weatherstrip discoloration mechanism and validate hypotheses on EPDM polymer microstructure factors for color stability property.

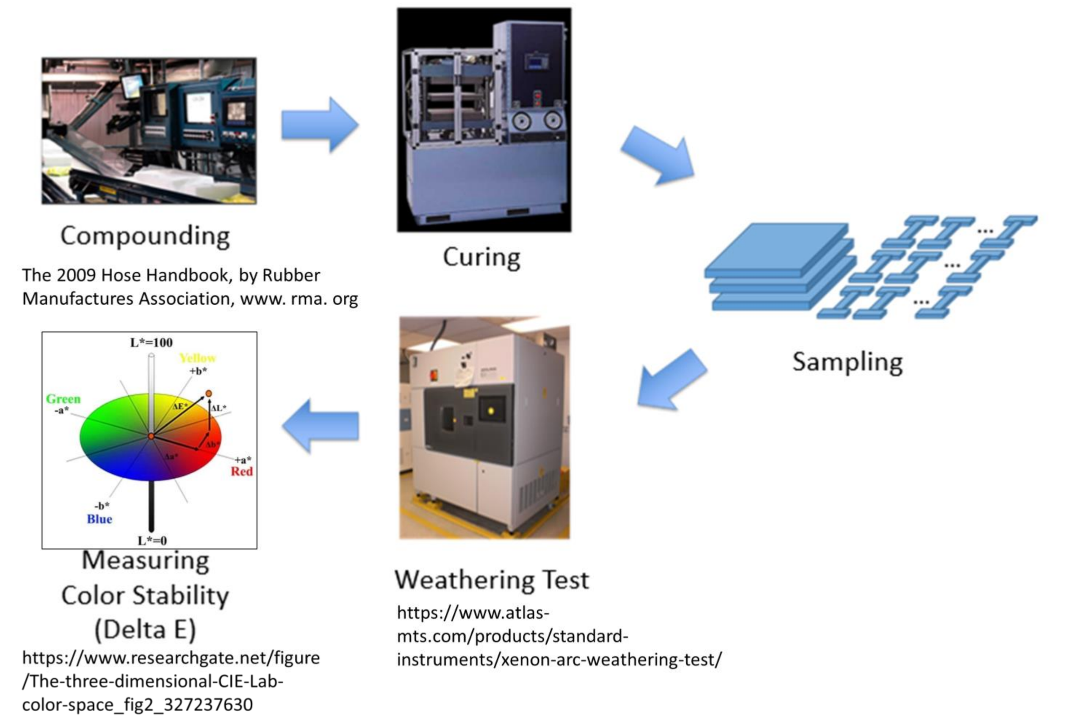

Fig 1. Process Diagram for Color Stability Test

Results

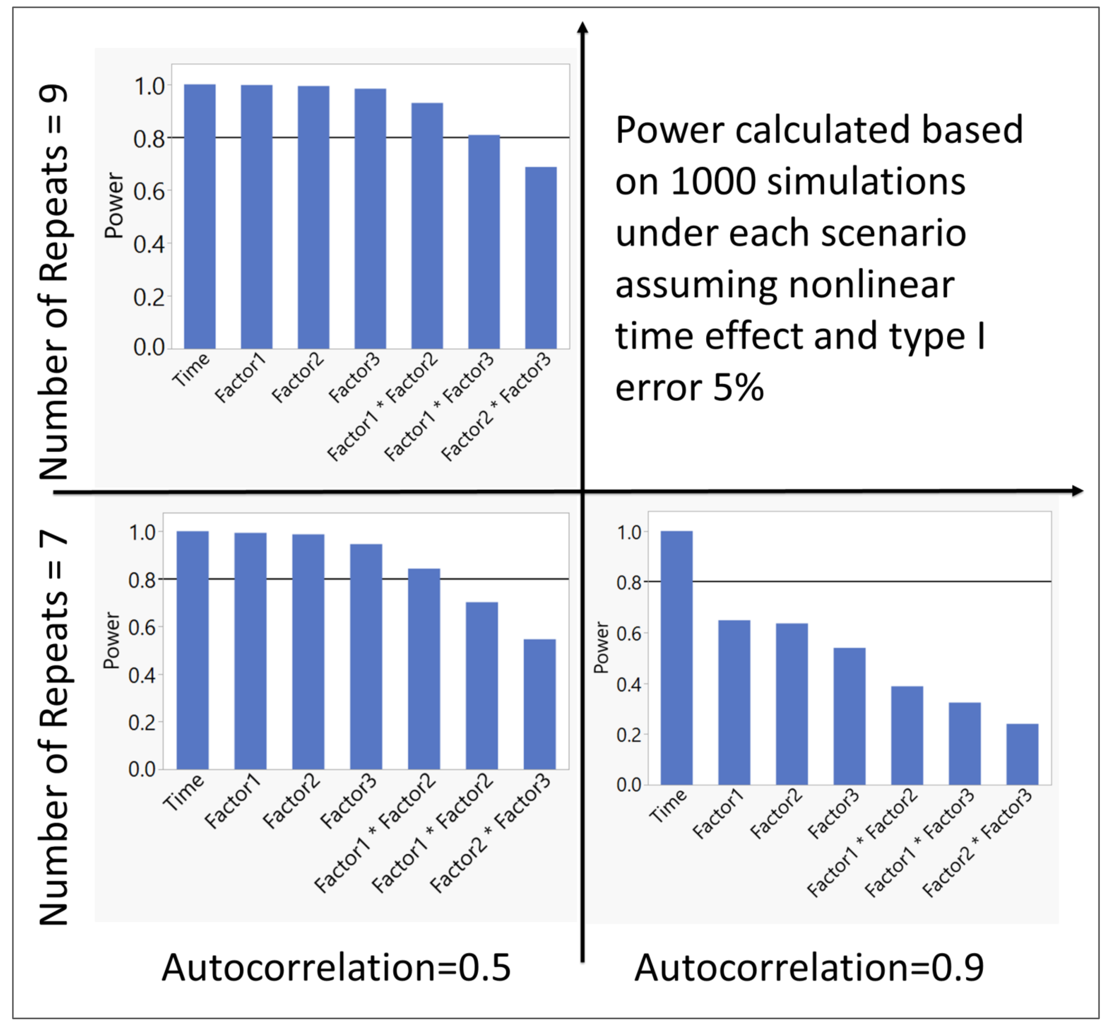

Fig 2. Monte Carlo Simulation Based Power Analysis at Different Levels of Autocorrelation

$$y_{ijk} = \mu + trt_i + time_j + trt \times time_{ij} + \alpha_i + \beta_i X_{time_j} + e_{ijk}$$

EPDM sample specific intercept and slope effects

$$\begin{bmatrix}\alpha_i \\ \beta_i\end{bmatrix} \sim NIID\left(\begin{bmatrix}0 \\ 0\end{bmatrix}, \begin{bmatrix}\sigma_\alpha^2 & \sigma_{\alpha\beta} \\ \sigma_{\alpha\beta} & \sigma_\beta^2\end{bmatrix}\right)$$

Random Effects Covariance Parameter Estimates

Covariance Parameter	Subject	Estimate	Std Error	95% Lower	95% Upper	Wald p-Value
Var(Intercept)	Sample ID	1.66	0.74	0.21	3.12	0.0253*
Cov(Intercept,Time(80,1894))	Sample ID	0.35	0.40	-0.44	1.13	0.3834
Var(Time(80,1894))	Sample ID	0.59	0.26	0.08	1.10	0.0227*
Residual		0.60	0.08	0.47	0.78	

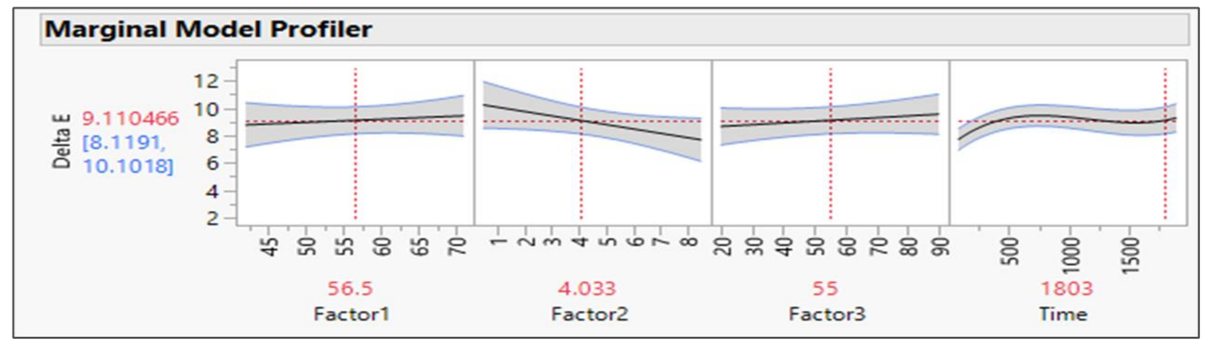

Fig 3. Random Coefficient Model Specification, Variance – Covariance Parameter Estimates and Marginal Model Profiler

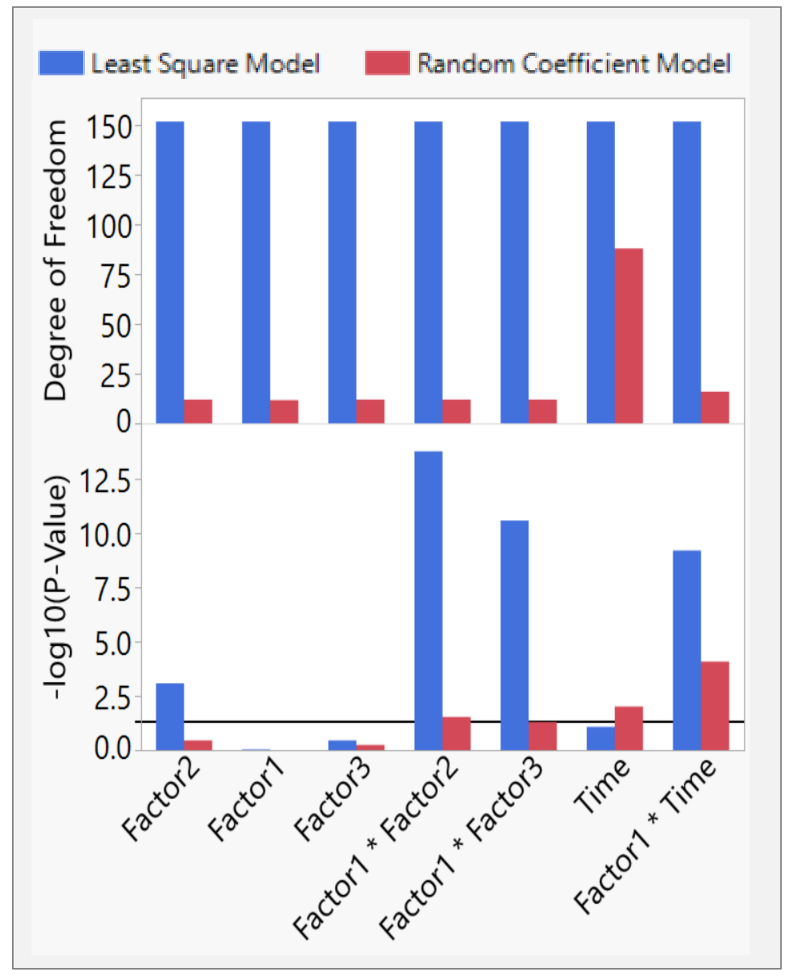

Fig 4. Degree of Freedom and –log10(P-Value) for Model Terms in Least Square Model vs. Random Coefficient Model. Cut-off P-Value = 0.05 (reference line)

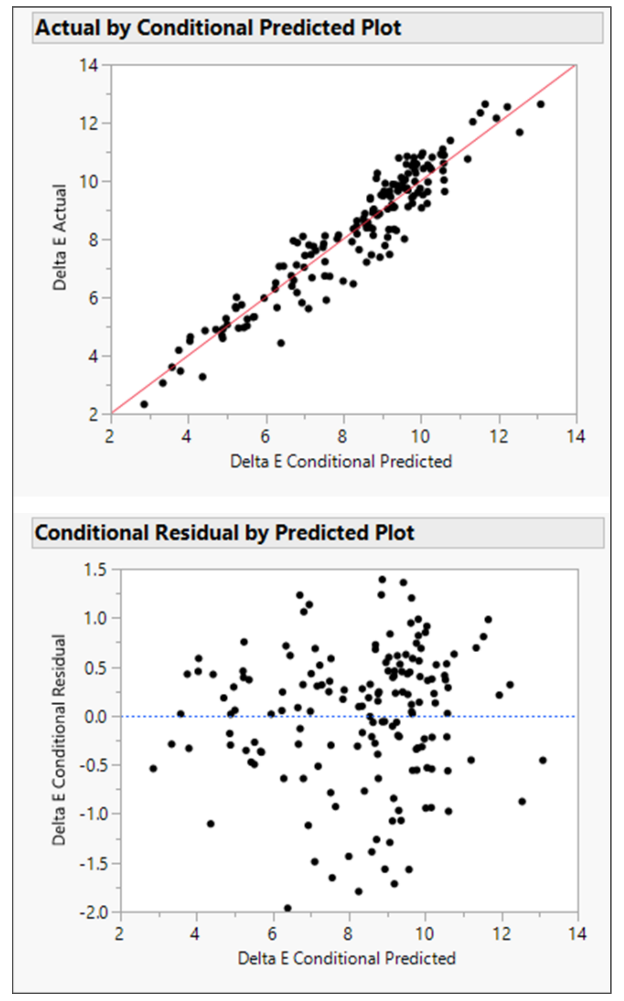

Fig 5. Model Prediction Plot and Residual Plot for Random Coefficient Model

- Results (Fig 2) shows that number of repeated measures should be at least 9 per cured sample for the repeated measure DOE.
- Random effects covariance parameter estimates in RCM (Fig 3) demonstrated there are significant differences in starting Delta E (Var(Intercept)=1.66) and changing rates of Delta E (Var(Time)=0.59) among cured samples.
- Fig 4 shows that treating data as independent in a Least Square Model could severely inflate degree of freedom and be overconfident about the significance results of factors compared to treating time dependent color metric properly in RCM.
- Significant Interaction between Factor1 and time identified from RCM indicates color stability depends on the level of Factor1.
- Model prediction plot and residual plot in Fig 5 indicates that RCM has good model fit and meets RCM model assumption.

Conclusions

We developed fundamental understanding of EPDM Weatherstrip discoloration mechanism and validated hypotheses on EPDM polymer microstructure factors for color stability property:

1. Identified the dominant microstructure factor for EPDM discoloration
2. Identified significant interaction between two microstructure factors suggesting alternative polymer design

References

Gelman, A., & Hill, J. (2006). Data Analysis Using Regression and Multilevel/Hierarchical Models (Analytical Methods for Social Research). Cambridge: Cambridge University Press. doi:10.1017/CBO9780511790942