Experimental and Statistical Study of the Effects of Material Properties, Curing Agents, and Process Variables on the Production of Thermoplastic Vulcanizates

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ABSTRACT: A comprehensive experimental study together with statistical analysis was performed to identify the optimal process conditions, materials selection, and curing system for the production of thermoplastic vulcanizates (TPVs) based on EPDM rubber and polypropylene. Two types of curing systems were studied together with five different types of EPDM rubber. The TPV products were assessed according to elastic modulus and degree of swelling (indicators of crosslink density), ultimate tensile strength, ultimate elongation, tear strength, and compression set. A design of experiments method was applied to minimize the number of experiments and to obtain response surface and regression models for this complex and highly interactive system. From the modeling results, optimum values for the influential factors were obtained to achieve the target end product properties. It was found that a phenolic resin-based curing system gave the best product properties and that the most influential factors were the rubber characteristics (ethylene content, ethylidene norbornene content, and molecular weight) and the polypropylene content in the formulation. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 764–777, 2010

Key words: twin screw extruder; thermoplastic vulcanizate; response surface; regression modeling; optimization; design of experiments

INTRODUCTION

Thermoplastic vulcanizates (TPV) are a class of thermoplastic elastomer based on rubber and plastic compositions where the rubber phase is dynamically vulcanized. The microstructure of TPVs consists of a thermoplastic matrix (continuous phase) that contains a dispersed cured rubber phase.[1,2] Many commercial TPVs have been developed for various applications in automotive parts, cable insulation, footwear, packaging, and medical industries because of their excellent weatherability, low density, and relatively low cost.[3,4]

Dynamic vulcanization is the process of mixing a thermoplastic and a rubber, which is later, crosslinked under dynamic conditions. The process is performed at high shear rates above the melting temperature of the thermoplastic and also at sufficiently high temperature to activate and complete the vulcanization process. The end product consists of crosslinked rubber particles dispersed in a thermoplastic matrix, which results in the elasticity of a thermoset rubber combined with the melt processability of a thermoplastic. TPVs can be produced via several different processes; however, on an industrial scale, they are typically made by extrusion processes, which allow for a large degree of process flexibility.[5]

A blend of EPDM (ethylene–propylene–diene monomer) rubber and PP (polypropylene) is the basis for most of the commercial TPVs on the market today. The saturated main chain in EPDM rubber accounts for the excellent stability against heat, oxygen, and ozone degradation. The high crystallinity and melting point of PP imparts rigidity and some heat and oil resistance.[5]

To improve the melt processablity and reduce the hardness of the TPVs, extender oil is added during TPV processing. Crosslinking of the rubber phase is the essential step in the TPV process to achieve the desired tensile strength and elasticity. All mechanical properties, e.g., modulus, hardness, tear and tensile strength, compression set, creep, and relaxation strongly depend on the amount of crosslinking as measured by crosslink density.[6]

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Generally, dynamically vulcanized polyolefin elastomer TPVs are vulcanized using phenolic cure systems or by using sulfur and an appropriate sulfur accelerator.[2] Problems with odor and bloom are associated with the use of sulfur curatives. Free radical vulcanization initiators such as organic peroxides have had limited use for crosslinking polyolefin-based TPV due to the tendency for the peroxide to degrade polypropylene.[6] New studies show that peroxide crosslinked EPDM/PP-based TPVs can be improved by the use of methacrylate coagents to help minimize the degradation of PP.[7] Recently, the phenolic cure system has received more attention due to elimination of drawbacks associated with sulfur and peroxide curing, and also by showing surprising improvements in oil resistance and elastomeric recovery.[8] These promising results conceivably could be attributed to the formation of a small amount of *in situ* graft copolymer between EPDM and the *in situ* modification of PP with phenol during the dynamic vulcanization with phenolic curatives.[9]

There are various influential parameters which have either direct or indirect effects on the TPV production process and the end product properties. Raw material properties, formulation, and processing conditions are the main factors to consider. Although a considerable amount of work has been conducted in the field of extrusion process design for TPV applications, very few published studies are available which use a thorough statistical approach to optimize the process and achieve specific targets. Besides simply monitoring the process for evidence of stability and capability, it is desirable to understand the relationships between the various factors and responses. Design of experiments (DOE) is an efficient method of information gathering where multiple variations are present in a studied system, whether under the full control of the experimenter or not. DOE provides a method to first conduct a study in a systematic way with a small number of experiments and second to statistically analyze and investigate the results with respect to correlations or causality relationships between factors and responses.

This article presents a comprehensive investigation using DOE methodologies to identify the influential effects of various parameters on the end product quality of extruded TPVs. The studied TPV formulation factors were the amount and type of rubber, plastic, oil, and curing agent used. The main operational factors were extruder screw configuration, sequence of feeding points, number of mixing steps, extruder temperature, and screw speed (RPM). The TPV physical and chemical properties studied (responses) were hardness, ultimate tensile strength, ultimate elongation, compression set, tear strength, elastic modulus, and degree of swelling (the last two being indicators of crosslink density). Surface response and regression analysis techniques were applied for statistical analysis and modeling. The main objective of the study was to obtain highly crosslinked TPV products (fully cured) with desirable physical properties. The following studies were performed to meet this objective:

Screening: The primary purpose of the experiment was to screen out and optimize the process factors for different EPDM rubbers.

Comparative: Evaluating and comparing all the influential factors on the final TPV properties to find the appropriate rubber formulation and cure system.

Response surface and regression modeling: The experiment was designed and performed to allow estimation of interaction effects, and consequently provide an idea of the (local) shape of the investigated response surface. Regression models provided a mathematical function for several influential factors and were used for further optimization.

MATERIALS AND PROCEDURES

Materials

Five grades of EPDM rubber were supplied by Lanxess Corp. (Orange, TX) as listed in Table I. Polypropylene homopolymer (ProFax 6823) was supplied by Basell Polyolefins (Bayport, TX).

Two crosslinking systems were used as follows:

1. Peroxide crosslinking using Varox® DBPH (2,5-dimethyl-2,5-di(tertbutyl peroxy)hexane) together with coagent (Synpro PLC-4185, 75% TAIC (Triallyl isocyanate) on a 25% silicate binder).
2. Phenolic resin crosslinking using SP-1045 resin (SI Group, Schenectady, NY) together with Tin(II) Chloride and Zinc Oxide activators.

TABLE I
Characteristics of EPDM Rubber Grades Used in the Study

Rubber no.	Mooney (ML(1+4)@125°C)	ENB content (wt %)	Ethylene content (wt %)	Oil content (wt %)	M_w (×1000)
1	45	4.5	66	50	700
2	54	4	59	50	900
3	43	9.8	62	50	700
4	53	4	64	25	400
5	94	6.5	53	0	500

TABLE II
Material List in TPV Formulations for Two Curing Systems

Phenolic resin curing	Peroxide curing
EPDM rubber	EPDM rubber
Polypropylene	Polypropylene
Parafinnic oil	Parafinnic oil
SP-1045 resin	Varox® DBPH
ZnO	Coagent PLC
Stearic acid	Naugard 445
Naugard 445	Talc
$SnCl_2$	
Talc	

Talc was used as a dispersant filler. The full list of materials used in the formulations is provided in Table II.

Experimental procedure

The TPV samples were produced using a 27 mm-diameter corotating twin-screw extruder (Model ZSE27MX-48D, Leistritz, Nuremberg, Germany) with an L/D of 48 : 1 and 12 zones with individual temperature control. The twin screws were assembled using individual screw elements including conveying, kneading, and high shear mixing elements in such a way that the screw configuration provided variable shearing conditions. Gravimetric feeders (Brabender Technologie, Mississauga, ON, Canada) and liquid injection pumps were utilized for feeding the solid and liquid ingredients.

The TPV samples were produced by either one or two-pass extruder mixing. In one-pass mixing, EPDM rubber and polypropylene were preblended in the first three zones of the extruder and then curing agents and oil were introduced into the process (Fig. 1). In two-pass mixing experiments, one complete extrusion pass was used to create the preblended product of EPDM rubber and polypropylene. The preblended sample was then re-extruded in the second pass to react with the curing agents. The effect of the number of mixing steps on the final product properties was considered as one of the experimental factors.

The extrusion experiments were conducted at a screw speed of 250 rpm and at different barrel temperatures. The residence time of the blends in the extruder was kept constant at $\sim$ 120 s by adjusting the extrusion rate. For all experiments, the molten extrudate was quenched in a water bath, pelletized, and then dried at room temperature. The dried samples were then used for further characterization.

During the experimental studies, sensors located on the extruder continuously measured the melt temperature, melt pressure, barrel temperatures, and motor load. All extruder variables were monitored, recorded, and adjusted at the operator control panel via an Allen-Bradley PLC interface (Compact Logix L32E).

Test specimens were prepared by compression molding using a Pasedena press heated to 190°C. Tensile and tear testing were performed according to ASTM D-412 and D-624, respectively, using an Instron tensile testing machine (Norwood, MA). Shore A hardness was measured according to ASTM D-2240. Room temperature compression set was determined according to ASTM D-395, after oven ageing the samples for 24 h at 70°C.

Rectangular test pieces with dimension of $40 \times 20 \times 2\ \text{mm}^3$ were used for swelling tests. The test specimens were weighed (m_1) and then immersed in toluene at 23°C for 48 h. The swollen samples were removed from the solvent and blotted with filter paper to remove excess solvent from the surface of the samples before being weighed (m_2) to an accuracy of 0.1 mg at room temperature. Degree of swelling was calculated as follows:

$$\mathrm{DOS}(\%) = \frac{(m_2 - m_1)}{m_1} \times 100 \tag{1}$$

A Rheologic Dynamic Analyzer (Rheometrics Inc, NJ) employed in a frequency sweep mode was used

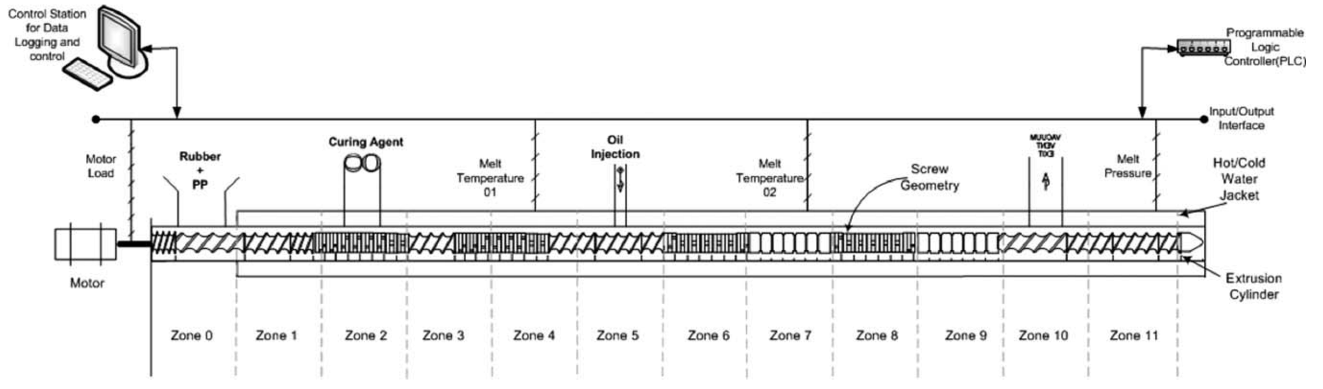
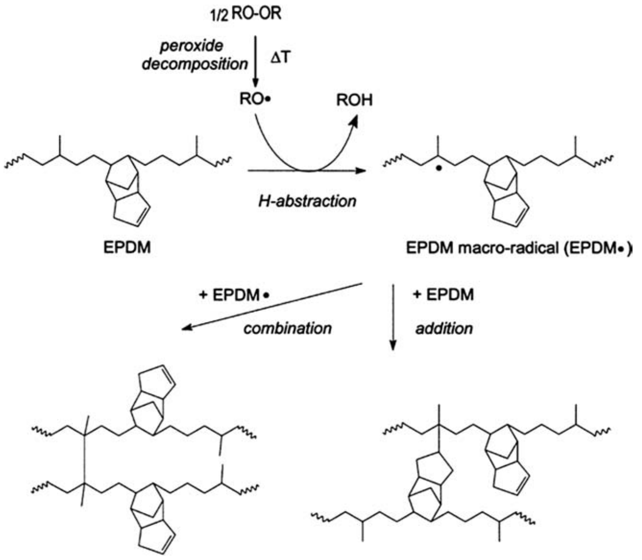


Figure 1 Extruder screw configuration and material feeding locations.



Scheme 1 Simplified peroxide curing of EPDM.[11]

to determine the elastic modulus (G') and related stress–strain properties. Sample discs with a diameter of 25 mm and thickness of 2 mm were used. The samples were preheated for 10 min at 230°C and then the measurement was carried out at constant temperature in the frequency range of 0.1 to 100 rad/s. As the output result from the RDA is the vector of elastic modulus in the specified frequency range, the accumulated elastic modulus was estimated according to the following equation.

$$\overline{G'} = \int_{\omega_1}^{\omega_2} G'(\omega)d\omega \tag{2}$$

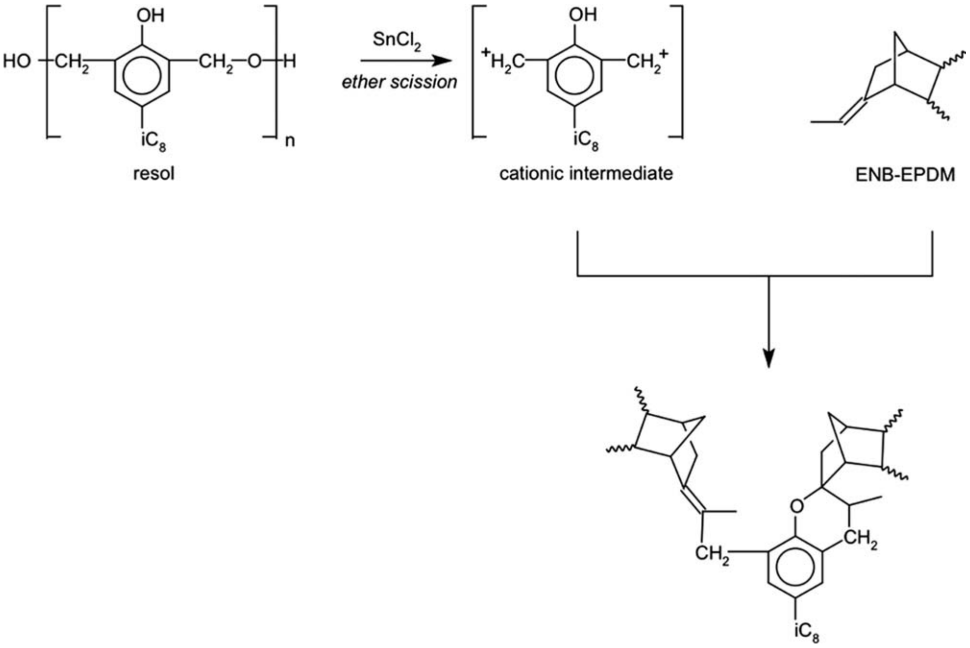
Chemistry of EPDM crosslinking

Most EPDM applications require crosslinking, which can be achieved through accelerated resin curing or coagent-assisted peroxide curing. The simplified and generally accepted mechanism of peroxide curing of EPDM is shown in Scheme 1.[10]

Crosslinking is initiated by the thermal decomposition of peroxide, which is the overall rate-determining step. Theoretically, the crosslink density should equal the peroxide dosage, but in practice, it is smaller as a result of side reactions. Peroxide decomposition produces free radicals, which then react with the EPDM polymer to form macroradicals.

As demonstrated in the scheme, the crosslinking can occur in two ways: by combination of two active sites of EPDM macroradicals or by addition of a new EPDM molecule to the active site of an EPDM macroradical. Coagents, which are not shown in the scheme for the purpose of simplicity, are used to enhance the peroxide crosslinking efficiency. Coagents are built into the elastic EPDM network,[10,12] and upon peroxide decomposition, their domains are rapidly crosslinked via free radical addition. The objective of any TPV study is to maximize the above reaction pathways that lead to the production of crosslink products and minimize any side reactions, which would ultimately decrease the final crosslink density and affect the final product quality.

As shown in Scheme 2,[13] It has been demonstrated that the resin, a phenol/formaldehyde oligomer, is degraded into monophenolic units, which eventually connect two EPDM chains via chroman and/or



Scheme 2 Simplified phenolic resin crosslinking chemistry.[13]

methylene-bridged structures. Tin (II) chloride activates the scission of the dimethylol ether linkage of the resin, yielding benzyl cations that add to the EPDM unsaturation.[5,13]

Design of experiments

Design of Experiment (DOE) is a structured, organized method that is used to determine the relationship between the different factors affecting a process and the output of that process (response) through observance of forced changes made methodically as directed by systematic tables. There are four interrelated steps in building a DOE:

Defining an objective of the study, e.g., better understanding of the system, sorting out important variables, or finding an optimum response.

Defining variables that will be manipulated during the experiments (factors) and their levels or ranges of variation.

Defining variables that will be measured to describe the outcome of the experimental runs (responses).

Choosing one standard design that is compatible with the objective, number of factors, and precision of measurements and has a reasonable cost.

DOE objective

An essential characteristic for comparison of TPVs is the crosslink density of the rubber phase. Fully cured samples are desired to achieve good elastic properties and two responses were assigned to measure crosslink density: degree of swelling and elastic modulus (G'). After achieving the desired cure state, further optimizations were carried out to attain the best physical properties. The main objective of the design of experiments was, therefore, to obtain TPV materials with a good level of crosslink density and with optimum physical properties.

DOE factors

Although there are numerous experimental factors that contribute to the final properties of the TPVs, the factors selected in this experimental study were believed to be the most critical ones. The influential factors in the extrusion process for TPVs can be grouped into two categories: operational and formulation. Operational factors are related to the characteristics of the extrusion process. The studied operational factors were barrel temperature (Factor *J*), screw speed (Factor *K*), screw configuration (Factor *L*), and feeding or injection sequence (Factor *M*). We also investigated the effect of one versus two-pass extruder mixing (Factor *E*). In the first case, the rubber and plastic phases were intimately blended, and then dynamically cured in one pass. In the second case, blending and curing operations were performed independently. The effect on morphology and product quality was investigated.

Various materials are used in TPV recipes and most have significant effects on the end product properties. The amount and type of EPDM rubber (Factor *A*), polypropylene (Factor *B*), oil (Factor *C*), and curing agent (Factor *D*) were the major

TABLE III
Factors and Responses Information

					Range	
	Parameter	Name	Units	Type	Low	High
Factors	A	EPDM Rubber	%	Numeric	55	75
	B	Polypropylene	%	Numeric	5	20
	C	Oil	%	Numeric	0	35
	D	Curing agent	%	Numeric	0.2	2.4
	E	Number of Passes	–	Categorical	N/A	
	F	EPDM Rubber Type	–	Categorical	N/A	
	G	Ethylene Content	%	Numeric	53	66
	H	Molecular Weight (Mw)		Numeric	400	900
	I	ENB	%	Numeric	4	9.8
	J	Barrel Temperature	°C	Numeric	180	220
	K	Screw Speed	Rpm	Numeric	200	350
	L	Screw Configuration	–	Categorical	N/A	
	M	Feeding Sequence	–	Categorical	N/A	
Responses	Y1	Hardness	Shore A	Numeric	N/A	
	Y2	Elastic Modulus	kPa	Numeric		
	Y3	Compression Set	%	Numeric		
	Y4	Tear Strength	kN/m	Numeric		
	Y5	Tensile Strength	MPa	Numeric		
	Y6	Elongation	%	Numeric		
	Y7	Degree of Swelling	%	Numeric		

influential factors studied here, and these were categorized under formulation type.

The combination of both operational and formulation factors for each rubber will result in a very large experimental matrix. A factor reduction approach was used to reduce the number of experiments and simplify the analysis of the responses. The factors with less effect were screened out in the first stage of the DOE study and the resulting optimal values for each variable were applied in the second stage. These variables were determined to be barrel temperature, screw speed, screw configuration, and feeding sequence. Table III gives the range of experiments for all the variables studied. It was found that a high shear screw configuration (Fig. 1), moderate barrel temperatures for peroxide curing, and moderate screw speed (250 rpm) resulted in the highest degree of curing. In the second phase of the DOE, formulation factors and number of mixing steps were investigated.

DOE methodology for the aforementioned factors was applied using various rubbers. Therefore, according to the DOE approach, rubber type is another effect involved in the design and analysis of the experiment. This factor can be incorporated in the design in two ways: categorical and numeric. Categorical is used when there is no value assigned to the parameter and it is labeled, e.g., rubber 1 and 2 (Factor *F*). However, categorical factors can sometimes be expressed by defining characteristics. In this study, three rubber characteristics were used as an indicator of each rubber: ethylene content (Factor *G*), molecular weight (Factor *H*), and Ethylidene Norbornene (ENB) content (Factor *I*). The more significant effect and wider value range for these characteristics was the reason for using them in the analysis. To remove the effect of factor magnitudes on the analysis, the factors are normalized to the range of −1 to 1. The analysis and model estimation are performed for both actual and coded forms.

DOE responses

In the DOE approach, some of the outputs of the experiments were selected as the responses to be measured and optimized. The responses in this study were categorized into two types: properties that influence crosslink density (primary responses) and properties that influence physical properties (secondary responses). The crosslink density was measured by degree of swelling (Response Y_7) and elastic modulus (Response Y_2). Physical properties measured were hardness (Response Y_1), compression set (Response Y_3), tear strength (Response Y_4), ultimate elongation (Response Y_6), and tensile strength (Response Y_5). These two response types are intercorrelated since the physical properties are essentially dependent on the crosslink density.

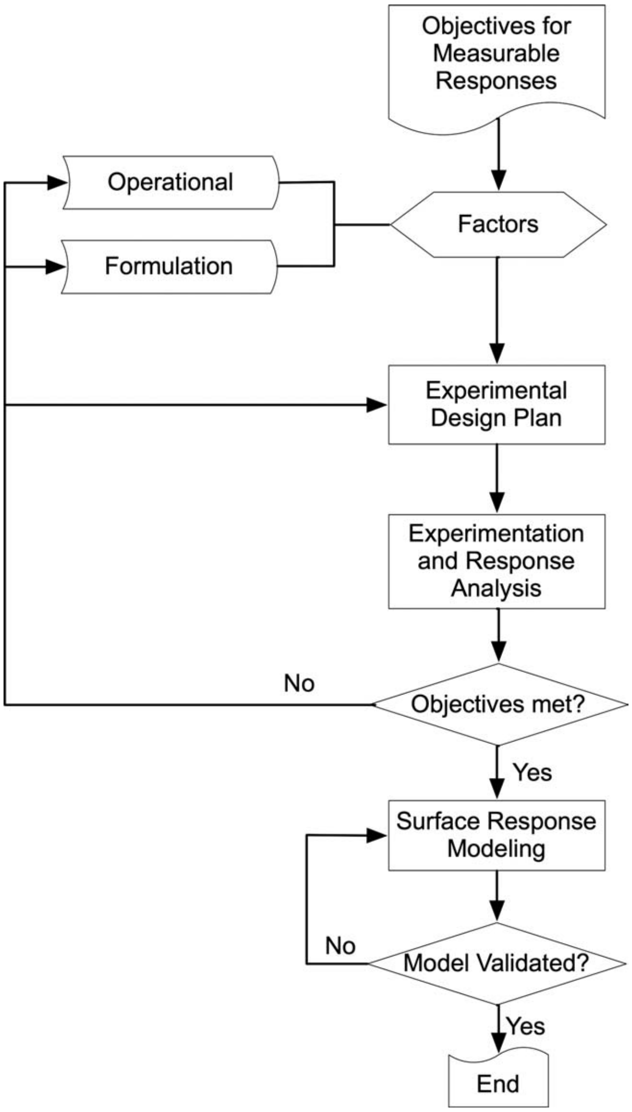


Figure 2 DOE Flow Chart.

DOE methods

The choice of DOE method depends on the objectives of the experiment and the number of factors to be investigated. Choosing the factor ranges (levels) is the essential step for obtaining the appropriate DOE method. The most popular experimental designs are two-level designs since they are simple and economical; they also give most of the information required to go to a multilevel response surface experiment if one is needed. Two-level designs have simply a "high" and a "low" setting for each factor. One of the popular two level methods is factorial design that was used to attain the optimal operational factors (Factors *J*–*M*).

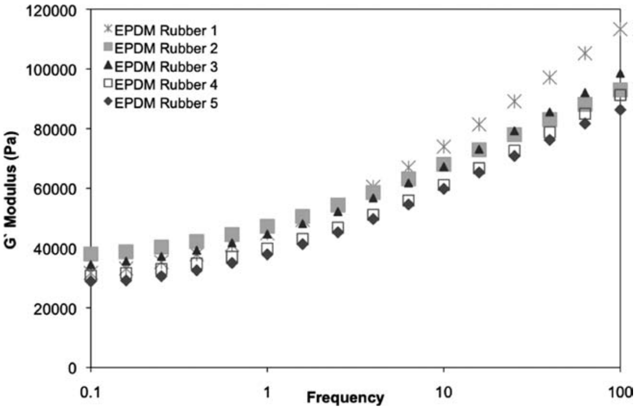


Figure 3 G' Elastic modulus results for resin cured TPVs.

To estimate interaction and accordingly to obtain an idea of the shape of the response surface, the response surface method (RSM) was used for the second phase of the DOE. The central composite design (CCD), which is one of the response surface methods, was applied for the formulation factors (Factors A–D) and number of mixing steps (Factor E). In CCD, in addition to the "high" and "low" levels, center point and intermediate levels were also considered.

Figure 2 summarizes the DOE approach used in this study. Defining the objectives, factors to be manipulated and desired responses are the steps necessary before experimental work can begin. The end product testing and response analysis provides information for the objective assessment. If both crosslink density and physical property conditions are not satisfied, depending on the DOE phase (primary or secondary), first either operational or formulation factors are altered and then the DOE plan is modified until the objectives are met.

DOE responses were carried forward to the next step: surface response analysis and modeling. The initial point of modeling is the computation of the effects. This effect list will suggest the appropriate model type with or without interaction. The models were estimated from regression analysis. The regression model is valuable when one wants to make predictions for the dependent variables based on the factors. For an n-run experimental design, the model for the experimental data can be described as follows:

$$y^k = b_0^k + \sum_i b_i^k X_i + \sum_i \sum_j b_{ij}^k X_i X_j + e^k \tag{3}$$

where, y is an $n \times 1$ vector or response data for one of the outputs for an experiment, k is the output number, b_0, b_i, and b_{ij} are the model intercept, the matrix of the regression coefficients for individual factors, and for two factor interaction, respectively. X_i and X_j are the matrix of individual factor values for n runs and e is a vector of independent error from the experiment. The least squares regression technique was used to obtain the model coefficients. Note that in model regression, each response (k) is analyzed separately and consequently the identification is established. Because the factors were analyzed in two formats, actual and coded, the regression model was also estimated in these two forms.

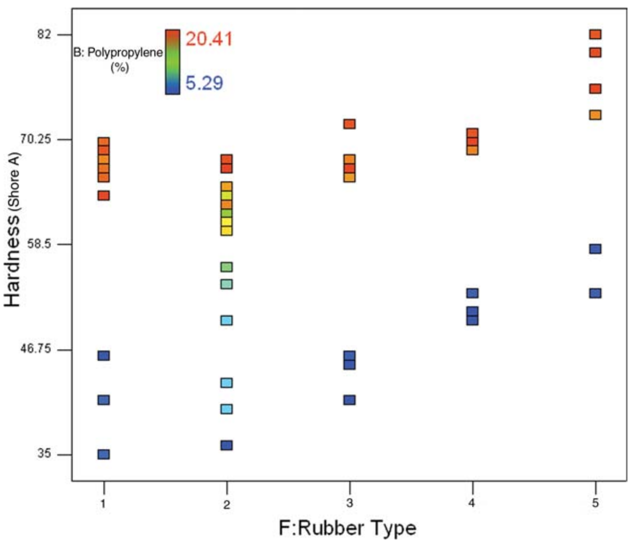


Figure 4 Hardness results for different EPDM rubbers - resin cured. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

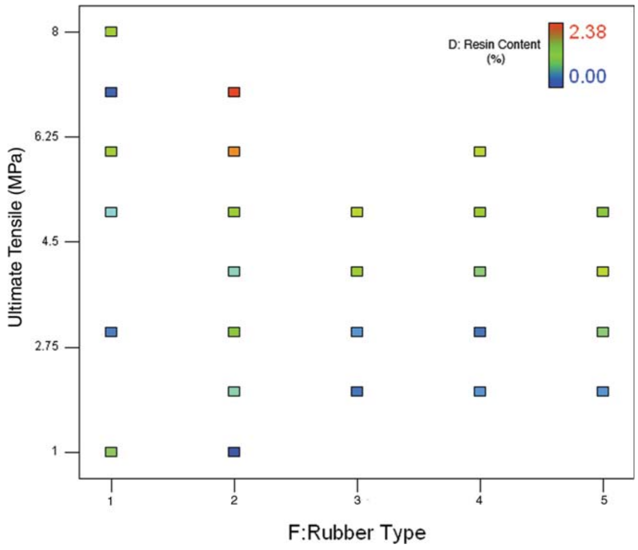


Figure 5 Ultimate tensile results for different EPDM rubbers—resin cured. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

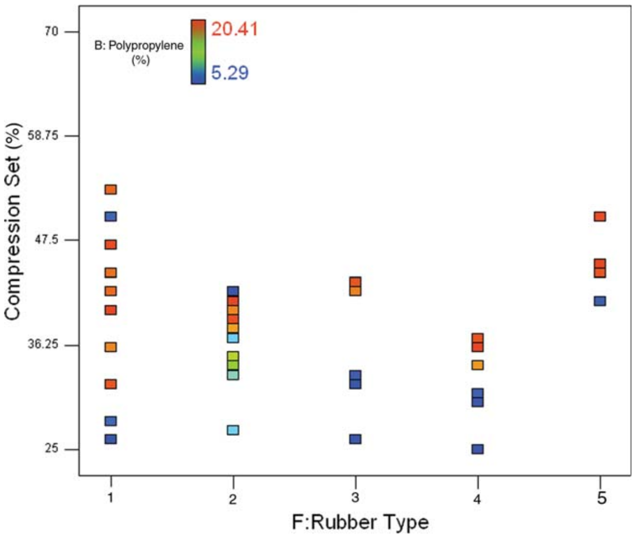


Figure 6 Compression Set results for different EPDM rubbers—resin cured. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Analysis of variance models (ANOVA) was used to check the selected model and examine the *F* tests on the regression coefficient. The *F* test provides information about eliminating the insignificant coefficients. Residual analysis, related diagnostics plots, and calculation of model characteristics were used to verify the correctness of the model and ANOVA assumptions. Some of the main model characteristic terms used in this study were as follows: standard deviation, coefficient variation, PRESS, R^2, Adequate Precision, and Predicted and adjusted R^2.[14] The resulting regression model was validated against a separate set of experiment data.

The regression model predicts the response values in a predefined range of factors. However, it is desirable to predict the model responses within real limitations and constraints for the factors and certain goals for the responses. In DOE analysis, this step is called optimization and it works based on the best-obtained regression model. In this study, it was attempted to achieve specific target values for cross-link density and physical properties (responses) with respect to the most practical operation variables (factors). This numerical optimization helps to find the best (optimal) factor levels to simultaneously satisfy all operational constraints.

RESULTS AND DISCUSSION

The experiments were divided into two stages to simplify the DOE table and obtain more reliable models. The first stage dealt with finding the best operational factors (*J*, *K*, *L*, and *M*) for maximum curing efficiency. Figure 1 shows the extruder set-up used in the experiments. As seen from Figure 1, curing agents were introduced early in the process (Zone 2 of the extruder) to achieve maximum time for blending of the PP, EPDM, and curing agents. A high shear screw configuration was found to be optimal and it reinforced the importance of good mixing in TPV production. The barrel temperatures were found to be optimal at 200°C for resin curing and 180°C for peroxide curing experiments. Screw speed was found to be optimal at 250 rpm.

The second experimental stage results, which dealt with finding the best TPV formulations, are reported according to the curing system used. The same factors were applied in both cases, which allowed

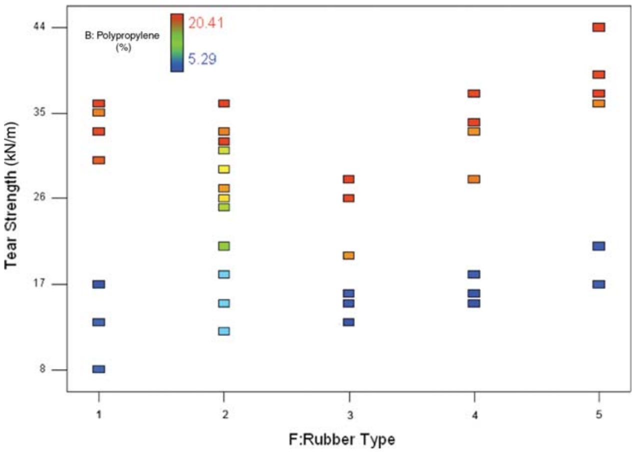


Figure 7 Tear Strength results for different EPDM rubbers—resin cured. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

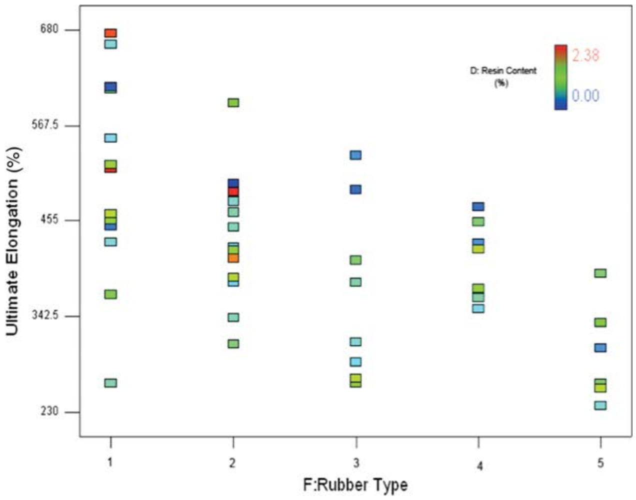


Figure 8 Ultimate Elongation results for different EPDM rubbers—resin cured. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
ANOVA Table for Hardness of One Mixing Step Resin Cured

					P VALUE
Source	Sum of squares	Degree of freedom	Mean square	*F* value	Prob > *F*
Model	6058.65	9	673.18	114.4	<0.0001
A-Rubber	106.54	1	106.54	18.11	0.0001
B-Polypropylene	632.3	1	632.3	107.45	<0.0001
C-Oil	106.12	1	106.12	18.03	0.0001
D-Resin curative	157.09	1	157.09	26.7	<0.0001
E-Number of passes	21.6	1	21.6	3.67	0.0624
F-rubber type	592.66	4	148.17	25.18	<0.0001

comparison of the curing efficiency using the two types of curing systems. Two types of regression modeling, linear and 2FI (two factor interaction), were performed for all results, and their accuracy was compared. For each curing system, experimental results were compared based on the type of rubber.

The "ideal" rubber for TPV applications should provide for efficient vulcanization, contribute to a uniform dispersion of small, highly crosslinked particles, and also give maximum elastic properties. All of these properties are directly related to the rubber characteristics listed in Table I, which have an influential effect on the final TPV properties. For example, it is known that increasing ethylene content in the rubber formulation improves processability of the rubber as well as tensile strength, but it has a negative effect on elastic properties such as compression set. Processing conditions also have a significant effect on the final product quality. To understand this complex process, a thorough statistical analysis was performed, taking into account the contributions of each parameter on the final product quality, as well as interaction effects.

Resin curing experiments

Resin-cured TPV experiments were performed based on a predefined DOE table, and the effects of various numerical and categorical inputs as well as their significance on the resulting models were investigated.

The elastic modulus results are an indication of the curing efficiency. Figure 3 depicts typical elastic modulus curves obtained for each rubber over the given range of frequencies. As mentioned previously, the area under each curve was integrated [eq. (2)] to obtain a quantitative comparison of results and the integral values were used as a response in the statistical modeling section.

Figure 4 shows the hardness results obtained with all five types of rubbers. The polypropylene content in the TPV recipe logically has the most influence on hardness, regardless of the rubber type. Interestingly, for EPDM Rubber 5, the overall hardness results (for the same polypropylene content) are the highest in comparison to the other four rubbers. It can also be seen that for the first three rubbers, the

TABLE V
Regression Model Characteristics of Seven Responses for Resin-Cured TPVs

		Model characteristics									
Response variables	Model type	Significant terms	*F* value	Std. Dev.	Mean	C.V. %	PRESS	R^2	Adj. R^2	Pred. R^2	Adeq. precision
Hardness	Linear	A, B, C, D, F	114.4	2.43	60.37	4.02	386.85	0.96	0.95	0.94	37.64
	2FI	A, B, C, D, E, F, AB, BC, BD	93.27	1.5	60.37	2.48	N/A	0.99	0.98	N/A	36.44
Degree of Swelling	Linear	E, F	58.93	18.2	102.38	17.78	20558.54	0.94	0.9205	0.8904	29.79
	2FI	F	113.32	7.41	102.38	7.24	N/A	0.99	0.98	N/A	48.60
Elastic Modulus	Linear	A, B, C, F	13.66	2.44	8.34	29.35	3.8 × 105	0.75	0.70	0.61	15.77
	2FI	A, B, C, F	6.7	2.11	8.34	25.28	N/A	0.91	0.77	N/A	11.02
Compression set	Linear	A, B, C, D, F	7.51	5.81	38.63	15.05	3104.3	0.62	0.54	0.15	13.31
	2FI	A, B, C, D, F	2.57	6.15	38.63	15.92	N/A	0.79	0.48	N/A	8.84
Tear strength	Linear	B, F	46.58	2.93	25.51	11.48	562.27	0.91	0.89	0.85	21.60
	2FI	B, F, AB	26.43	2.20	25.51	8.64	N/A	0.97	0.94	N/A	18.28
Ultimate tensile	Linear	B, D, F	21.64	0.86	4.55	18.92	47.73	0.83	0.79	0.73	15.71
	2FI	B, F	9.20	0.77	4.55	16.90	N/A	0.93	0.83	N/A	11.45
Ultimate elongation	Linear	B, E, F	4.53	82.81	429.6	19.5	4.77 × 105	0.50	0.39	0.15	8.02
	2FI	A, F, AD, BD, EF	3.41	64.09	424.60	15.09	N/A	0.90	0.63	N/A	7.80

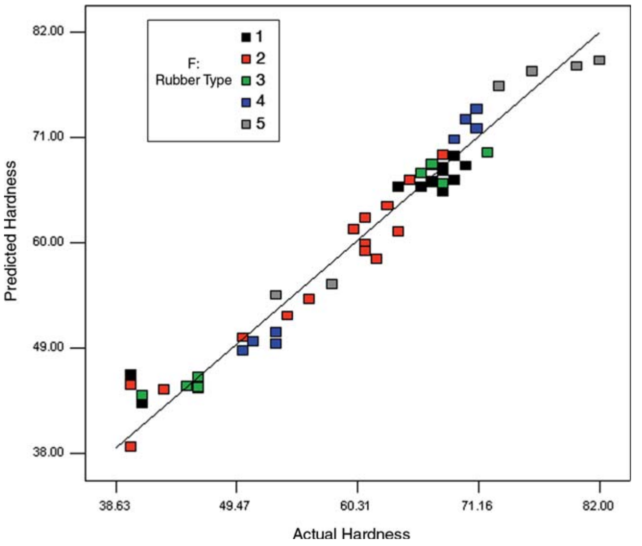


Figure 9 Comparison of predicted versus actual hardness for resin cured TPVs (Predicted values are from the 2FI model). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TPV hardness is approximately the same and that there is an increasing trend for Rubbers 4 and 5. The oil content in the rubber itself is important to account in making a TPV recipe. The first three rubbers contain 50 wt % of a parafinnic extender oil, whereas Rubber 4 contains 25 wt % and Rubber 5 is not oil extended (Table I). The increasing hardness trend between the highest to the lowest oil content in rubber was observed despite the fact that the total oil amount in the TPV formulation was kept constant.

Ultimate tensile strength is another important property for TPVs, since it can be related to the durability of the product. The higher the tensile strength, the more stress the material can withstand when subjected to tension, compression, or shearing. Figure 5 shows the tensile strength results as a function of resin curative level in the recipe for each EPDM rubber. In general, there is an increase in tensile strength with increasing curative level, which is as expected considering that the crosslink density should increase. However, results vary slightly between the different EPDM rubbers. In this case, it can be seen that the highest tensile strength results were obtained for Rubber 1 and the lowest for Rubber 5. Comparison of the rubber characteristics indicates that one of the significant factors is the ethylene content of the rubber. The higher the ethylene content in the EPDM rubber, the higher the crystallinity which contributes to higher tensile strength.

The tear strength and compression set are shown in Figures 6 and 7. Similar to the hardness results, compression set and tear strength are directly correlated to the polypropylene content in the TPV recipe. The difference in results for various rubber types can be attributed to the combination of all formulation factors. Statistical models are needed to determine the significance of each of these factors.

The ultimate elongation results are shown in Figure 8. The decreasing trend can be attributed to the combination of the oil content and ethylene content in the rubber formulation. In this case, there is no dependency on resin curative content, which indicates that there is a strong effect of the other factors present.

It is obvious from the above results that more than one factor is influencing the output result, and therefore, a statistical analysis was performed. The statistical analysis consisted of finding significant factors for each output response and the model significance according to the ANOVA. A typical ANOVA table for hardness results is shown in Table IV. It shows that all of the factors other than the number of passes are significant. Linear and 2FI modeling was performed to determine the influence of each factor and the results are presented in Table V. Under the significant terms, we have contributions from both numerical (*A, B, C,* and *D*) and categorical (*E* and *F*) factors. The type of rubber used (*F*) is the most important factor because it is significant for all output responses, and it proves the importance of the rubber characteristics for TPV applications. Polypropylene content (*B*) is also a significant factor for almost all output responses. The number of passes (*E*) is the least significant factor as it plays a role in only three responses (Y_1, Y_2, and Y_7; see Table III). This confirms that sufficient curing can be performed in one

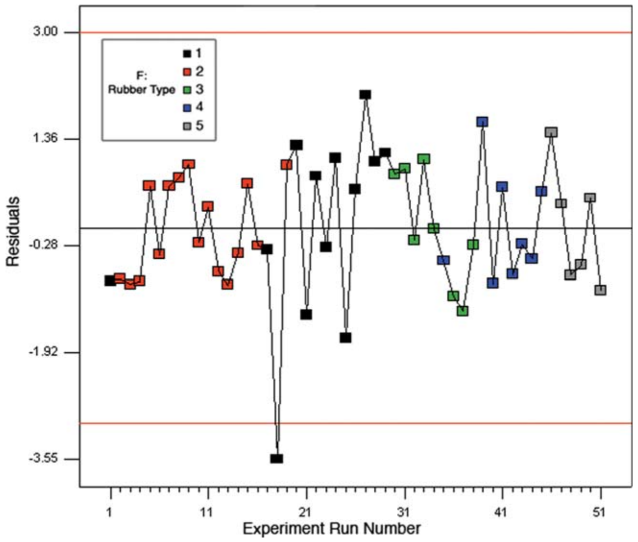


Figure 10 Residuals of ultimate tensile of resin cured samples for one set of experimental data (Regression model is 2FI model). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

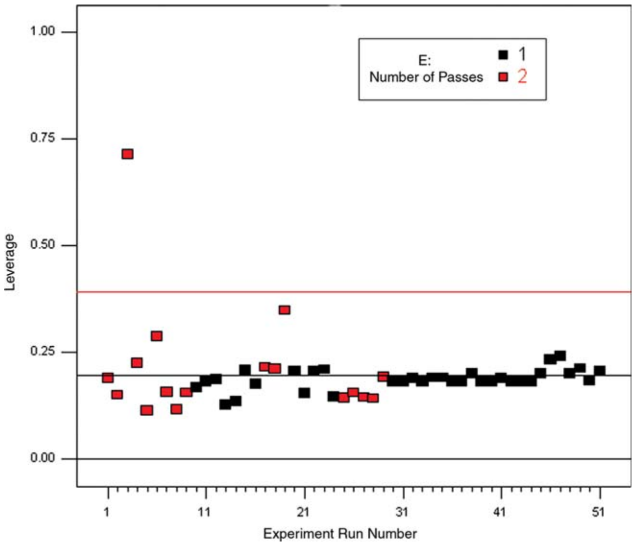


Figure 11 Leverage for ultimate elongation for resin cured TPVs based on 2FI model. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pass without hindering the product quality. The main difference between the two statistical models is the fact that the 2FI (two factor interaction) model considers the interactions between the factors, whereas the linear model does not. Consequently, 2FI modeling resulted in better accuracy in predicting the experimental results according to the standard deviation, C.V.%, and R^2 values. However, it can be seen from Table V that interaction between the factors is evident only for hardness and ultimate elongation and that the predictions obtained by linear models are also in an acceptable range. The accuracy of the linear hardness model for all types of rubbers can be seen in Figure 9. The ultimate tensile strength model residuals are shown in Figure 10. As seen from this figure, residuals are randomly scattered and show no trend which indicates that the model is significant, i.e., residuals do not contain structure that was not accounted for in the model. The leverage results for the ultimate elongation model for one- and two-step mixing are shown in Figure 11. It can be noted that there are no significant outliers from the main body of data. Thus, the possibility of one particular outlier dominating the regression model is eliminated.

As mentioned previously, each factor can have either a positive or negative influence on the output results. Also, the type of rubber is the significant factor for all model outputs, which indicated the importance of rubber in the formulation (Table V). To further investigate which one the characteristics in the rubber content is the most important, a linear regression model, which takes into account the molecular weight, ethylene content, and ENB content of the rubber was obtained. The justification for using these three factors related to the rubber content in further modeling lies in the fact that they had a wide range of values and more related to the polymer characteristics.

The model was obtained in the coded format to give the same significance to each factor during the regression calculation (Table VI). As the number of passes was found not to be a significant factor in the previous model, it was not considered in this case. It is obvious that both ethylene content and molecular weight of the rubber have significant effects on almost all outputs. The ENB content was found to be influential for the degree of swelling response, which is expected considering that crosslink density is highly dependant on ENB content. The advantage of this type of modeling is that it provides insight into which characteristics of the rubber are the most significant for TPV applications.

Figure 12 shows the contour plots of ultimate tensile strength response as a function of ethylene content and molecular weight of the rubber in the formulation. Figure 12(a) represents the model output with lower polypropylene content in the formulation, and Figure 12(b) with higher polypropylene content. As seen from the figures, tensile strength shows the same trend for the lower and higher

TABLE VI
Linear Regression Model Parameters and Characteristics for Resin-Cured TPVs Considering Ethylene Content, Molecular Weight, and ENB Content as Factors (Factor G, H, and I)

	Model parameters										
Response variables	Intercept	A	B	C	D	G	H	I	Std. Dev.	R^2	Significant terms
Hardness	61.76	13.30	22.97	21.74	7.16	−3.77	−4.53	−0.28	3.00	0.94	A, B, C, D, E, F
Degree of swelling	−1049.13	−2089.2	−1772.3	−2231.1	−655.1	−45.6	−48.8	−2.36	28.39	0.83	G, H, I
Elastic modulus ($\times 10^7$)	1.24	1.1	1.0	1.98	2.64	−3.14	−3.51	−6.90	2.54	0.72	A, B, C, D, F
compression set	24.11	−42.31	−20.53	−68.27	−17.11	−3.20	−0.13	0.93	7.98	0.38	A, B, C, D
Tear strength	24.07	3.79	13.01	1.98	3.72	−2.19	−2.20	−4.17	3.32	0.88	All
Ultimate tensile	4.39	2.55	3.46	3.88	1.76	0.82	0.37	−0.51	0.93	0.78	B, D, G
Ultimate elongation	324.21	−167.47	−108.7	−248.6	−74.73	62.58	36.49	−32.77	109.8	0.25	G

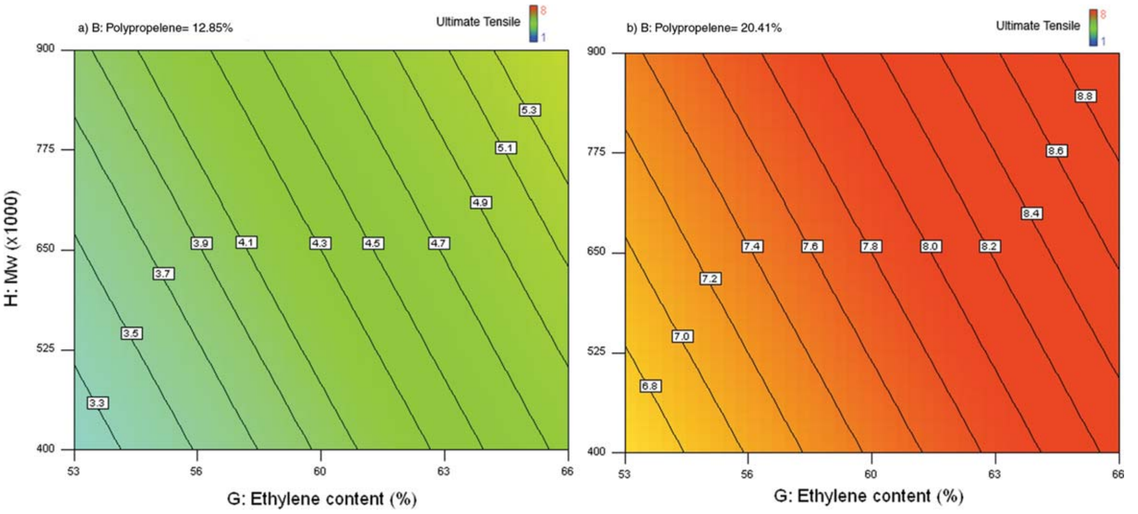


Figure 12 Contour plot of ultimate Tensile results for resin cured TPVs based on 2FI model: (a) Polypropylene Content = 12.85% and (b) Polypropylene Content = 20.41%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polypropylene content formulations. At both levels, the ethylene content and molecular weight of the rubber have an increasing effect on the ultimate tensile result. Figure 13 is a contour plot showing the dependency of tear strength on polypropylene and EPDM rubber content. It can be seen that increasing the plastic content in the recipe has a positive effect on tear strength while increasing the rubber content has a negative effect. Figure 14 shows the ultimate tensile and hardness surface responses as a function of rubber and plastic content used in the TPV recipe. As expected, hardness shows a strong dependence on plastic content, whereas ultimate tensile results are positively influenced by both factors.

Peroxide curing experiments

TPV Experiments using a peroxide curing system were performed and a statistical analysis was done in the same way as with the resin curing experiments. Table VII gives a summary of the linear and 2FI regression models for all the output properties. The superiority of the 2FI model in comparison to the linear model is shown in this case as well, which was expected due to the presence of interaction factors in the model. It can be seen from the table that the modeling accuracy based on standard deviation, C.V.%, R^2, and Adequate Precision is lower in comparison to models obtained from the resin-cured experiments. This is due to difficulties in controlling the dosing of the peroxide curing agents, which resulted in larger variability in the product properties. In general, the TPV properties were inferior in comparison to the products obtained using the resin curing system.

Optimization

Thus far, the effect of various factors on several different responses was investigated. The results confirmed that one factor could influence some output properties in a positive way, whereas others could have an effect in a negative way. Although the output models provided some insights into the significance of the studied factors, as well as into the interactions between them, the optimal TPV formulation was still not obvious. Hence, an optimization of statistical results was needed. A graphical optimization method was used to obtain the optimal formulation.

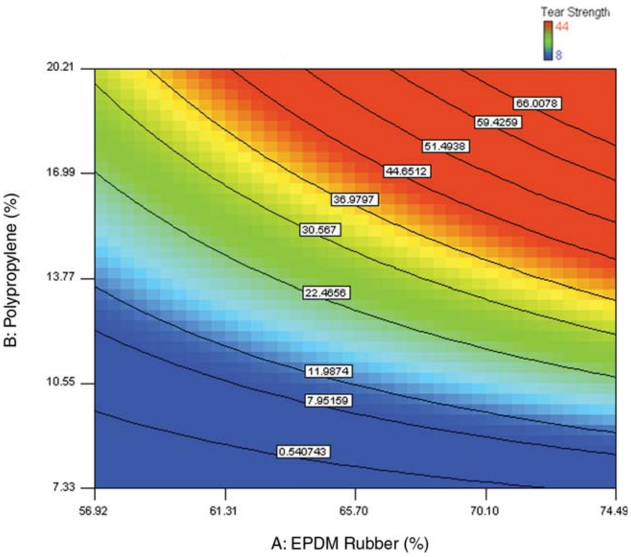


Figure 13 Contour plot of tear strength results for resin cured TPVs based on linear model. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

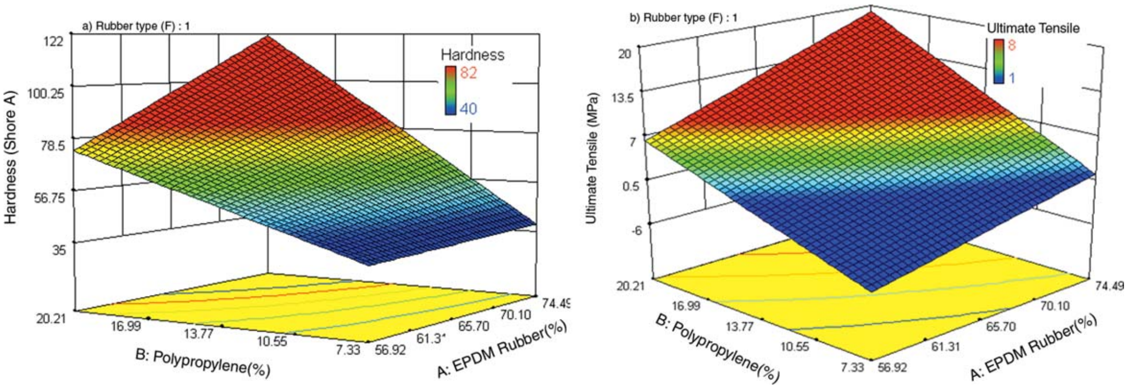


Figure 14 (a) Hardness and (b) Ultimate Tensile response surfaces with respect to rubber and polypropylene content for EPDM rubber no. 1 and resin curing system. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

This method involved overlaying all model responses in the form of contour plots with specified constrains on inputs and desired goals. The resulting graph consisted of optimal areas and shaded areas. Shaded parts of the graph represent the experimental areas that did not meet the specification. The target ranges based on typical requirements were set for each output, and the optimization was performed. To show the concept of optimization, the following optimization problem was chosen:

$$\text{target}\, Y_1 = 60 - 70\ (\text{Shore A}),\ Y_3 < 50\%,$$
$$Y_5 = 6 - 8\,\text{MPa},\ Y_6 > 300\%$$
$$\text{subject to}\ A,\ B,\ C, D\ (\text{within the specified range}) \quad (4)$$

Figure 15 depicts the overlay plot for the specified hardness range between 60 and 70 Shore A, ultimate tensile strength between 6 and 8 MPa, and ultimate elongation greater than 300%. The compression set upper limit was set to 50%. The plot shows a very narrow area in which the desired outputs can be obtained. The corresponding formulation factors showed that Rubber 1 is the best candidate for TPV production and a resin-based curing system is desirable. The results were validated by performing three experiments using the formulation obtained from the statistical optimization and the final product properties were in the desired ranges. The standard deviation of results was within 3% or less for all four studied outputs.

TABLE VII
Regression Model Characteristics of Seven Responses for Peroxide-Cured TPVs

		Model characteristics									
Response variables	Model type	Significant terms	F value	Std. Dev.	Mean	C.V. %	PRESS	R^2	Adj. R^2	Pred. R^2	Adeq. precision
Hardness	Linear	B,E	45.34	4.59	48.68	9.43	894.61	0.9097	0.8896	0.8579	20.190
	2FI	E, AE, BE, CE, DE	39.17	2.81	46.68	5.78	N/A	0.9837	0.9586	N/A	21.472
Degree of swelling	Linear	A, C, F	9.96	58.93	158.31	37.23	1.708E+05	0.7836	0.7049	0.5163	10.661
	2FI	A,F	3.27	70.62	158.31	44.61	6.54e+05	0.8305	0.5763	N/A	6.958
Elastic modulus	Linear	A,F	9.59	12.9	5.035	25.77	7.76E+05	0.7777	0.6960	0.5330	13.028
	2FI	A,F	10.90	7.95	5.03	15.08	N/A	0.9861	0.8956	N/A	14.656
Compression set	Linear	A,B,C,D	4.69	16.80	44.50	37.75	12019.63	0.5102	0.4014	0.2275	7.821
	2FI	E, AB, AC, AE, BE, CE, DE	12.80	7.61	44.50	17.09	N/A	0.9517	0.88773	N/A	14.477
Tear strength	Linear	E,F	45.66	2.15	17.35	12.37	211.86	0.9103	0.8903	0.8473	22.407
	2FI	ALL	20.93	1.79	17.35	10.33	N/A	0.9695	0.9236	N/A	16.25
Ultimate tensile	Linear	E,F	15.09	0.65	3.06	21.30	18.86	0.7702	0.7192	0.6219	13.64
	2FI	AB, AD, CD	5.96	0.61	3.06	20.08	N/A	0.9017	0.7504	N/A	8.713
Ultimate elongation	Linear	A,B,C,D,E,F	5.55	123.34	502.58	24.54	654000	0.5521	0.4526	0.2868	8.468
	2FI	ALL	5.66	85.27	502.68	16.96	N/A	0.8969	0.7384	N/A	10.013

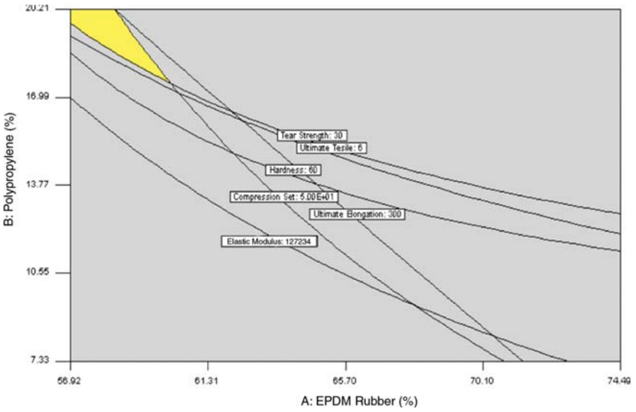


Figure 15 Optimal formulation area to achieve eq. (4) scenario objective by graphical optimization method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

With the purpose of improving the overall quality of a multicomponent TPV system, a comprehensive experimental and statistical analysis was performed. The design of experiments was divided into two stages: a preliminary stage to determine the optimum operational variables, and a final stage, to determine the optimum TPV formulation and rubber characteristics. This two stage approach was used to avoid models with an abundant number of factors, which could lead to false results.

Regression modeling provided insights into the significance of each factor in obtaining the desired TPV properties. 2FI modeling was found to be superior to linear modeling since it took into account interactions between the factors in the model. Finally, analysis of the statistical results was performed, which identified the optimum rubber characteristics and TPV formulation to obtain the desired TPV final properties. The model results were validated by experiments.

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NOMENCLATURE

b_0	Model intercept
b_i	Model regression coefficients for individual factors
b_{ij}	Model regression coefficients for interaction
DOS	Degree of swelling (%)
e	Vector of independent error from the experiment
G'	Elastic modulus (Pa)
k	Response number
m_1	Weight of specimen for swelling test (g)
m_2	Swollen sample weight (g)
X	Matrix of individual factor values
y	Response
ω	Frequency (rad/s)

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