

Effect of Formulation Variables on Cure Kinetics, Mechanical, and Electrical Properties of Filled Peroxide Cured, Ethylene-propylene-diene Monomer Compounds

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ABSTRACT: Peroxide crosslinkable ethylene-propylene-diene monomer (EPDM) compounds are formulated systems in which the base polymer generally comprises only a small fraction of the total composition. Knowledge of the intercomponent dependency is therefore crucial for successful product development. In this study, we have investigated the effect of formulation components on key material properties of cured, filled, and oil extended EPDM. In studying the impact of individual components, the clay filler was found to have a significant and negative effect on cure performance and to a lesser extent on the dielectric strength as well. On the other hand, the oil plasticizer was found to have a positive effect on recovery of the cure efficiency in filled compounds. It was also found

that the interaction of the filler, the plasticizer oil, and the peroxide impacted both the mechanical properties as well as the dielectric strength. Given the complexity of the system, a statistical experimental design method was adopted to study the interactions of the components and their impact of final properties. For selected compositions, the cure behavior and the evolution of properties with extent of cure were studied. The cure was also modeled and compared to previously proposed models available in the literature. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2191–2200, 2011

Key words: activation energy; crosslinking; curing of polymers; dielectric properties; elastomers

INTRODUCTION

Cured ethylene-propylene-diene monomer (EPDM) compounds are used in many high temperature applications such as molded hoses, belts, gaskets, electrical accessories and automotive parts. These vulcanized materials are tailored to meet end-use properties. Depending on applications, key compound properties include mechanical properties such as tensile strength, elongation at break, compound flexibility (tensile modulus, Dynamic Mechanical Analyzer (DMA) shear modulus, Shore A), and chemical and heat resistance. The latter is primarily driven by the extent of crosslinking. In wire and cable applications, electrical properties are also important, including electrical breakdown strength and dissipation factor for an insulation compound and volume resistivity for a semiconductive compound. These property requirements lend to complex formulations and the impact and interdependence of each component on final properties need to be kept in mind for successful compound development.

Owing to their enhanced vulcanizate properties, peroxide cured EPDM compounds are widely practiced in the applications mentioned above. Extensive work has been done on EPDM vulcanizates and the main factors influencing their cure efficiency. These include peroxides, coagents, fillers, oils, and antioxidants.^{1–3} Work has also been published on vulcanized blends of EPDM with Polypropylene,⁴ Ethylene-vinyl acetate⁵ and natural rubber.⁶

An example of a typical EPDM formulation can be found in the work by Pal and De,⁷ where peroxide vulcanization of silica filled EPDM was studied. It was found that tensile strength and elongation at break increased with increasing filler content. Shore A hardness and set properties were also found to improve with increased filler. However in that study, the amount of oil extender was kept constant for all compositions. A qualitative review on the use of ethylene-propylene polymers as insulation compounds for electrical applications such as power cables, flexible cords, appliance cables, mining cables, and molded electrical accessories and the effect of different formulation components was conducted by Brown.⁸ However, very little attention has been given to the evolution of material properties with the extent of cure in these systems or the interplay between key formulation variables. This work addresses the gap via a detailed statistical

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TABLE I
List of Formulation Per Design of Experiments (in wt %, Balance Being EPDM)

Run	DOE Pattern	[Pox] (wt %)	Sunpar oil (wt %)	Translink-37 (wt %)
1	++-	3	2	35
2	+++	1	10	35
3	---+	1	10	15
4	a00	1	6	25
5	00a	2	2	25
6	0a0	2	6	15
7	0	2	6	25
8	0	2	6	25
9	+++	3	10	15
10	0A0	2	6	35
11	00A	2	10	25
12	+-	3	2	15
13	---	1	2	15
14	+++	3	10	35
15	+-	1	2	35
16	A00	3	6	25

analysis of the effect of each formulation component on the key material properties.

Cure chemistry of peroxide crosslinked EPDM is fairly well understood. The ter-polymerization of ethylene, propylene and a diene monomer produces elastomeric products commonly known as EPDM rubbers. Incorporation of diene monomer results in pendant double bonds to enhance crosslinking efficiency of the polymer. Recent model compound studies, by Peters et al.,⁹ of peroxide initiated crosslinking of low molecular weight EPDM model compounds revealed that both addition and combination reactions exist as pathways for peroxide mediated cure. Identification of all the structures involved in the actual polymer itself remains elusive. However, recent investigations by Zachary et al.¹⁰ on EPDM curing have shown that the crosslinking process yielded the existence of persistent allyl radicals. For ENB (Ethylidienenorbornene) EPDM systems the more stable secondary radical was found to be the dominant species. Orza et al.¹¹ have recently studied the extent of conversion of dienes and the utilization of initiators during EPDM crosslinking via solid state proton NMR. In a typical experiment EPDM having 4.5% ENB was crosslinked using 2.5 phr Perkadox 14-40 (BPB) peroxide at 173°C. The peroxide crosslinking efficiency, defined as the number of crosslinks formed per peroxide functionality was found to be 173%. The diene conversion was found to be 19%. An important finding was that the peroxide efficiency falls to 50% if no ENB is present. Increasing the ENB content increased the peroxide crosslinking efficiency, but decreased the percentage conversion of ENB. The number of addition cycles per EPDM macroradical was found to be low, about 0.8, indicating that termination of the free

radical sequence by combination was relatively faster than the addition reaction. All this fundamental information on mechanism and structural effects has a role to play while choosing the right grade of EPDM and the appropriate processing conditions for manufacturing end-use products.

An example of typical formulation has been published by DuPont Dow Elastomers.¹² In this publication, the guideline formulation comprises 54% EPDM, 2.7% LDPE, 2.7% Zinc Oxide, 32.4% treated calcinated clay, 2.7% Paraffin wax, 2.7% Red Lead (90% dispersion in ethylene propylene rubber- EPR), 0.8% Polymerized 1,2 dihydro 2,2,4-trimethylquinoline, 0.54% Vinyl silane and 1.35% dicumyl peroxide (DCP). This formulation provided a starting point for this work, focusing on the major ingredients (EPDM, oil, clay, and peroxide).

This investigation focuses on studying the effect of formulation additives on material properties of cured, filled, extended EPDM. In addition to detailed formulation effects on ultimate properties, this work also investigates the evolution of key compound properties with the progression of cure. Given the complexity of a typical EPDM compound formulations, and to assess the significance and influences of the different components, a statistically designed set of experiments, Design of Experiment (DOE), method was used in conducting the present work adopted. In the design, the impact of plasticizer oil, clay filler, and peroxide on mechanical and electrical insulation properties were investigated using a response surface design. Finally, cure data for selected compositions were modeled and the results are compared to previously proposed models for such systems available in the literature.

EXPERIMENTAL

In a first series of experiments effect of individual formulation components were explored which was then followed by a detailed DOE approach to understand, in a systematic fashion the interactive effects of the various formulation components (factors) on resulting key properties (responses). Design of experiments and data analysis was performed using JMP statistical software package from SAS Corp. Features such as Analysis of variance (ANOVA) was used to estimate the relative contribution of each factor to the overall measured responses. Response Surface Methodology (RSM) was used to find the optimal response within specified ranges of the factors. To obtain the effects of each of the formulation components, a 3-factor Central Composite Design (CCD) with 2 center points was used as shown in Table I. This DOE as a response surface design permitted the analysis of the main effects, interaction effects and curvature effects associated with the modeling.

TABLE II
Selected Formulations for Studying the Evolution of Properties During Cure

Run	[Pox] (wt %)	Sunpar oil (wt %)	Translink-37 (wt %)
17	1.5	8	35
18	1.5	15	35

MATERIALS

Nordel IP 4640 (EPDM, 40 Mooney viscosity, 4.9% Ethylidienenorbornene - ENB) from Dow Chemical Company, Sunpar oil 2280 (paraffin oil) from Sunoco Corp., DICUP-R (dicumyl peroxide) from SigmaAldrich and Translink 37 (Calcined Surface Modified Aluminum Silicate) from BASF Corp. were used as received.

Compounds preparation

A 250 cc Brabender batch mixer was used for compound preparation. First, the resin was charged in the mixer which was set at 120°C and was fluxed for 5 min at 15 rpm. The solid filler and plasticizer oil were subsequently added and the material was mixed for 10 min at 120°C. Finally, peroxide was added last and the full formulation was mixed further for an additional 5 min at 120°C.

For studying the evolution of properties as a function of the extent of cure, thick plaques (1.9 mm) were compression molded at 175°C and cured in the press for 3, 5, 10, and 15 min, respectively; after which they were quenched in a ice/water mixture. For ultimate properties of cured compounds, additional plaques were cured at 175°C for 15 min as shown in Table II. These were 1.01 mm thick for electrical testing and 1.9 mm thick for mechanical property testing.

Property evaluation

The mechanical properties of the samples were measured on dogbones at 23°C and 35% R.H. The properties were determined at a crosshead speed of 508 mm/min according to ASTM D412.

Dynamical Mechanical Analysis (DMA) was performed on a AR1000N Rheometer fitted with DMA fixtures to measure the equilibrium modulus at elevated temperatures. Measurement temperature ranged from 30 to 200°C at a ramp rate of 5°C/min. The angular frequency was held constant at 6.283 rad/s. The storage and loss moduli were reported as a function of temperature.

Durometer Shore A hardness was measured at 23°C and 35% R.H on two 1.9 mm samples stacked one on top of the other. A hardened steel rod (1.1–1.4 mm diameter) with a truncated 35° cone (0.79 mm

diameter) was used as the indentation foot. The final value is reported as the mean of five independent readings.

For the electrical insulation properties, AC breakdown voltage measurements were performed on compression molded ~ 1.01 mm plaques which were degassed for 16 h in a 65°C vacuum oven and then for two days at 25°C before testing. Dielectric strength was measured using a Hipotronics D149 Series AC Dielectric Breakdown Tester. The breakdown strength of samples held between opposing cylindrical electrodes was measured in transformer oil (Univolt 61N) while the voltage was ramped at 0.5 kV/s until failure. The result from each test was reported as the mean of four different measurements.

Crosslinking kinetics were evaluated using a Moving Die Rheometer (MDR), which was set at 100 cycles per minute, and at an arc of 0.5°. The torque data correlated to the degree of crosslinking, and was obtained as a function of cure time. For this study, the MDR chamber was set at temperatures ranging from 140 to 175°C.

Gel content was determined by decahydronaphthalene (decalin) solution extraction in a round bottom flask fitted with a reflux condenser according to test method ASTM D 2765. The gel content was measured with accounting for the amount of the solid filler in the compositions.

RESULTS AND DISCUSSION

Effect of individual components on compound properties

Cure behavior

Figure 1 shows the cure profiles as measured by MDR for 60 min at 175°C. Peroxide at 1.5 wt % was added to each of the formulations, which contained various amounts of plasticizer oil and filler. The base formulation (0, 0) comprising only the peroxide in EPDM, plateaus at about 12M-m/0.113 in Figure 1. The fully formulated compound (8, 35) comprising the peroxide, 8 wt % paraffin oil and 35 wt % filler in EPDM, plateaus just about in the same region.

Interestingly, introducing only 8 wt % oil (8, 0) in the base formulation (0, 0) resulted in significant suppression of the cure of the system. As pointed out in the prior section and noted in the figure below, the cure rate is not impacted much. One explanation for this behavior is that the alkoxy radicals from the peroxide may have been partially consumed by reaction with the oil which may result in its molecular weight increase in the oil at the expense of EPDM crosslinking. The most surprising result, however, is the effect of the filler on the cure of the base formulation. On adding of

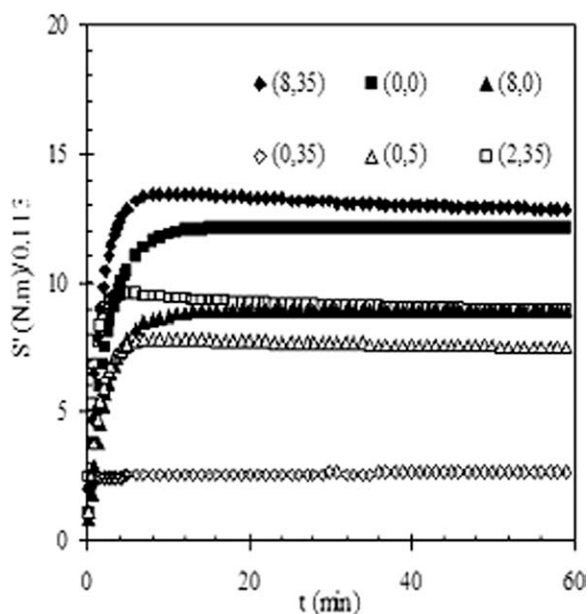


Figure 1 MDR Cure profiles showing effect of individual components. (0, 0) No oil, no filler, (0, 5) No oil, 5% filler, (0, 35) No oil, 35% filler, (8, 0) 8% oil, no filler and (8, 35) 8% oil, 35% filler. All formulations contain 1.5% peroxide.

35 wt % filler (0, 35) to the base resin, the cure process is completely blocked, resulting in virtually total loss of cross-linking. Decreasing the amount of filler to 5 wt % (0, 5) is shown to assist in recovering some of the cure, but nowhere close to that of the base system (0, 0) or the fully formulated compound (8, 35). When 2 wt% of oil is added (2, 35) to the above filler formulation (0, 35) the cure is recovered somewhat. These effects of filler and oil on crosslinking are believed to be related to acid-catalyzed decomposition of peroxide on the clay surface. It is known that in general many fillers, including some clays, interfere with peroxide crosslinking due to acidity-induced ionic peroxide decomposition, with complete suppression of crosslinking in some cases.¹³ It is also known that additives that preferentially adsorb on the surface of the filler can prevent undesirable interference reactions between filler and peroxide.¹³ These effects have been discussed specifically in the case of EPDM.¹⁴ To reconcile all of the data presented in Figure 1, we hypothesize that the vinyl silane-treated clay (Translink 37) used in this study must contain some acidic sites that are readily accessible by the peroxide, despite the presence of the silane coating, in the absence of oil. Consistent with the above references,^{13,14} it is proposed that inclusion of the oil during compounding effectively blocks the clay surface, thus significantly reducing or preventing the unproductive acid catalyzed decomposition of peroxide. Passivation of clay with oil has been observed in related systems.¹⁵

Mechanical properties

Figure 2 shows a plot of the elongation at break versus peak stress of each of the samples discussed previously. The results are in line with the cure behavior discussed previously. The base, unfilled compound, as expected, exhibits poor mechanical properties, thus the requirement for a filled system. The addition of the plasticizer oil increases elongation, with no significant impact on tensile strength. The filled system with no plasticizer oil resulted in the worst mechanical properties, reminiscent of a "green" (noncrosslinked) compound. Clearly, the best properties were obtained with a filled and plasticized composition. Further optimization data of this system will be discussed in light of the results obtained from the DOE formulations.

Dielectric breakdown strength

The dielectric strength from these simple formulations exhibited an interesting behavior as shown in Figure 3. The crosslinked base resin (no filler, no oil) exhibited a dielectric strength typical of such polymer systems. The addition of plasticizer oil appears to have a marginal effect on the dielectric strength, or at least no negative impact. One key result is the significant negative impact of the filler when used alone, which resulted in a drastic loss of this property. The full formulation (oil and plasticizer) showed a recovery in the property, but not as good as the plasticized system with no filler. This result points to the importance of the choice of filler to not only retain excellent dielectric performance, but also formulation optimization for cost purposes.

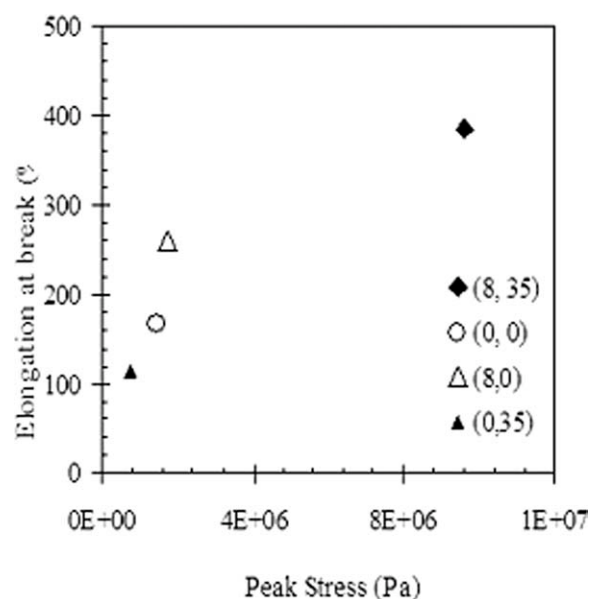


Figure 2 Stress-Strain data, effect of individual components: (0, 0) No oil, no filler, (0, 35) No oil, 35% filler, (8, 0) 8% oil, no filler and (8, 35) 8% oil, 35% filler. All formulations contain 1.5% peroxide

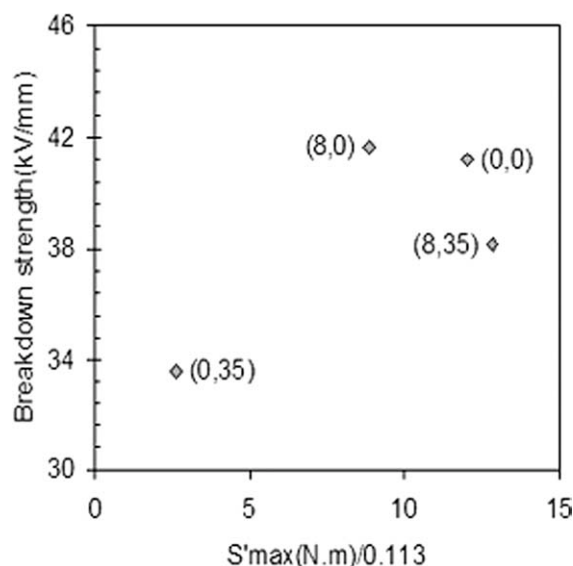


Figure 3 Dielectric breakdown strength, effect of individual components: (0, 0) No oil, no filler, (0, 35) No oil, 35% filler, (8, 0) 8% oil, no filler and (8, 35) 8% oil, 35% filler. All formulations contain 1.5% peroxide.

Component interactions

Crosslinking kinetics

Figure 4 shows MDR torque profiles for runs 17 and 18. The half-lives of the peroxide used at 140°C and 160°C are 43.1 min and 5.5 min, respectively. Since a plateau torque can be indicative of full cure the most optimum curing conditions appears to be around 30 min at 160°C. Under more practical vulcanization conditions this would translate to about 10–12 min at temperatures in the range of 170–180°C. One must note however, that under manufacturing conditions, additional time will be

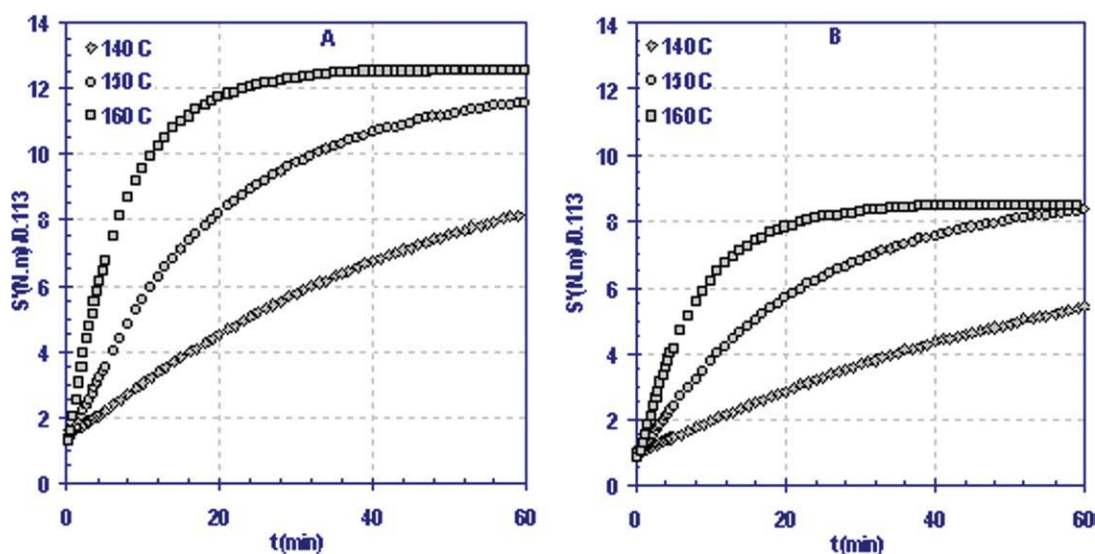


Figure 4 MDR torque profiles at different temperatures, (A) for Run 17 and (B) Run 18. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

needed to bring the material to cure temperature. This will depend on the thickness of the article being cured, for example the wall thickness of cable insulation. It is worth noting from these MDR data in Figure 4 that increasing the amount of plasticizer oil in the formulation does not affect the kinetics but suppresses the level of ultimate cure.

Various mechanistic and phenomenological models exist to describe the cure behavior of formulated rubber compounds. Arillaga et al.¹⁶ demonstrated that the Isayev model is appropriate for use with data collected via MDR. Isayev et al.¹⁷ proposed the following model for cure

$$\alpha = \frac{Kt^n}{1 + Kt^n} \quad (1)$$

α is the degree of cure at time t defined by the ratio of the torque at time t to the equilibrium torque. Equation (1) can be rearranged to

$$\ln\left(\frac{\alpha}{1 - \alpha}\right) = n \ln t + \ln K \quad (2)$$

The slope of the plot of $\ln\left(\frac{\alpha}{1 - \alpha}\right)$ versus $\ln t$ gives n which is the order of the cure reaction. The intercept gives the information about the overall rate constant for the process.

$$K = K_0 e^{-\frac{E_a}{RT}} \quad (3)$$

An Arrhenius plot of the rate constant, K and temperature T , yields the activation energy E_a and the pre-exponential factor.

The initial part of the cure profiles after the induction period due to heat up is more relevant

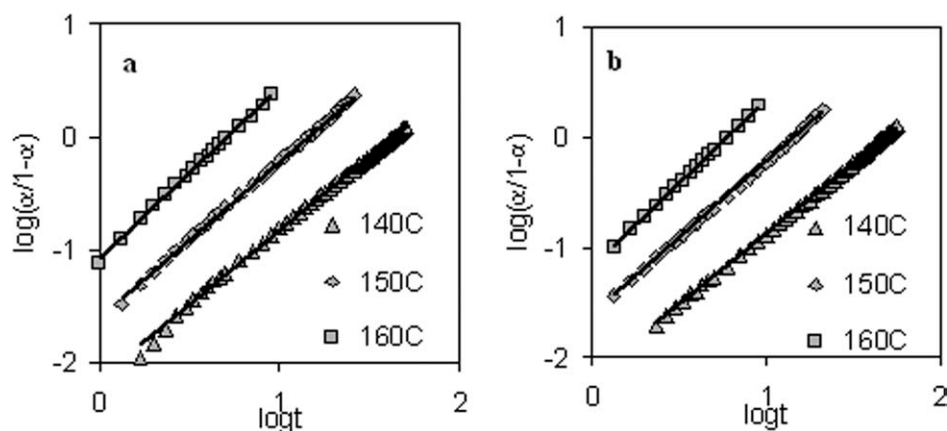


Figure 5 Isayev's model fit to data from MDR torque profiles of run 17(a) and run 18(b).

for this analysis. Figure 5 shows the data fit to Isayev's model at 140, 150, and 160°C and Figure 6 show an Arrhenius plot of the rate constant, K and temperature T . The average order n , of the reaction as calculated from the model at these temperatures is 1.4. This agrees very well with the published order of filled EPDM vulcanizates.¹⁶ The kinetic parameters as calculated from the model are listed in Table III. The parameters are in close agreement with those published in the literature.¹⁶ It is also interesting to note the impact of the filler to oil ratio. A higher oil or extender level seemed to give a lower activation energy and higher pre-exponential factor. This may be a result of increased interaction of oil with the peroxide as a result of its increased concentration. Further work is necessary to exactly understand the nature of such interactions. Overall, in the unfilled systems the oil seemed to just reduce the ultimate level of cure without significantly impacting the cure rate.

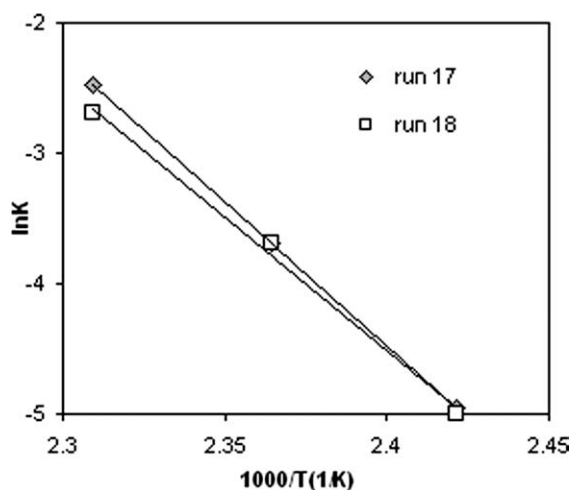


Figure 6 Arrhenius plot run 17 and run 18.

Evolution of compound properties with cure

As discussed earlier, the crosslinking chemistry of EPDM has been studied and structural characterization has been undertaken. One of the aspects of the focus areas of this study is the evolution of properties during the curing process. Since most of the end products are based on vulcanized materials to deliver the required mechanical properties, it is useful to track the evolution of those properties during the vulcanization step. Looking at the MDR data, one can observe that the S'_t/S'_{max} ratio plateaus somewhere between 10 and 15 min (Fig. 7) at 175°C for both formulations 17 (A) and 18 (B). This is indicative of completion of cure during this time interval. To obtain information about property evolution with cure, several plaques were cured at 3, 5, 10, and 15 min by compression molding and were immediately frozen to stop the progression of cure. These plaques were analyzed for mechanical properties, Shore A and gel content (Figs. 7 and 8). Peak stress appears to increase with the growth of crosslinking network and equilibrates somewhere between 10 and 15 min cure time. No trend was found in the Young's moduli of the samples. Ultimate elongation is shown to decrease with increasing network formation as expected. It is interesting to see the trends in gel and shore A. A very flat gel profile for sample 17 (A) in Figure 8 would suggest that the same amount of gel is present throughout the cure period. This may be misleading however, as decalin gel extraction is performed at 160°C for 6 h, thus additional peroxide

TABLE III
Kinetic Parameters Calculated Using Isayev's Model

Run	E_a (kJ/mol)	K_0 (1/s)	n
17	183.82	1.26E + 21	1.4
18	171.13	3.10E + 19	1.39

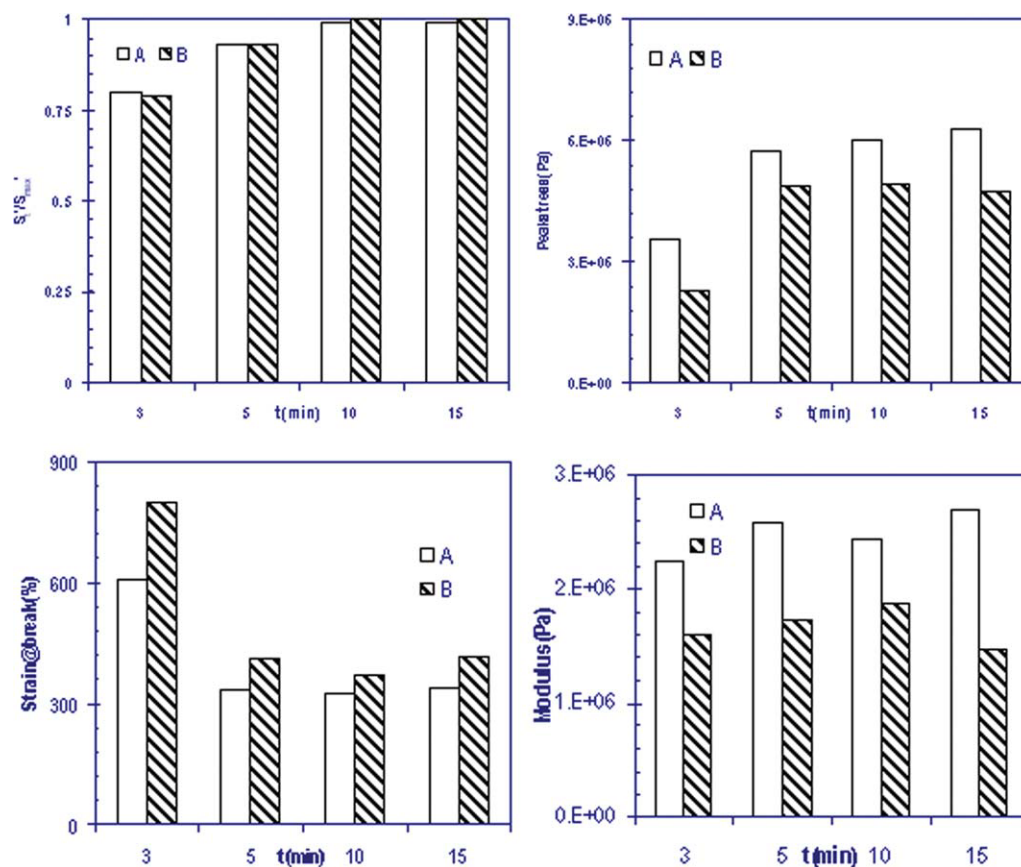


Figure 7 Evolution of properties during cure for 17 (A) and 18 (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decomposition may have taken place during the analysis step itself rendering these results questionable. Overall, it appears that the samples essentially kept on curing during the extraction process at elevated temperatures and so the same amount of gels were extracted each time for both samples. Based on this observation, it is suggested that future work should consider removing the

unreacted peroxide via an appropriate degassing or extraction step before conducting the gel analysis. In this manner, it may be possible to capture the state of the polymer at the end of the cure step and eliminate subsequent reactions.

Increasing the oil level from 7% in sample 17 to 15% in sample 18 resulted in a substantial reduction of the gel level of the fully cured material, but once

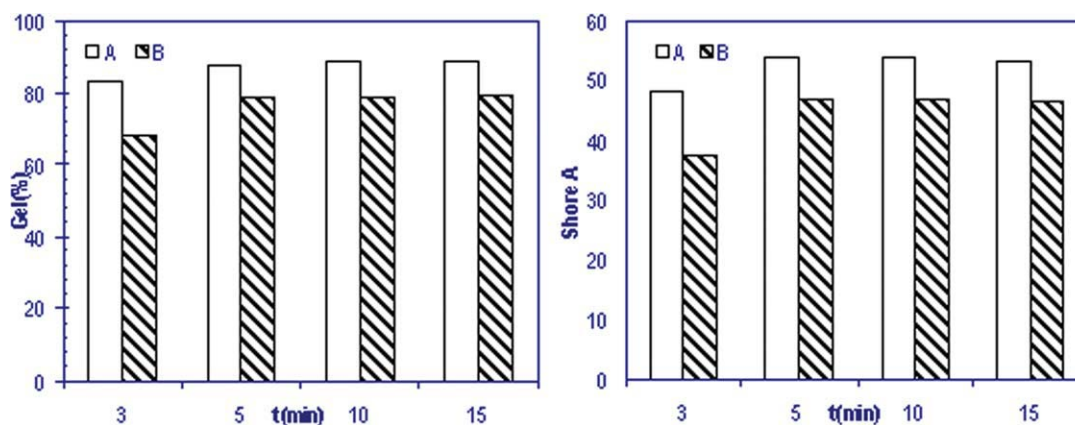


Figure 8 Evolution of Gel Level and Shore A with cure, formulations 17(A) and 18 (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

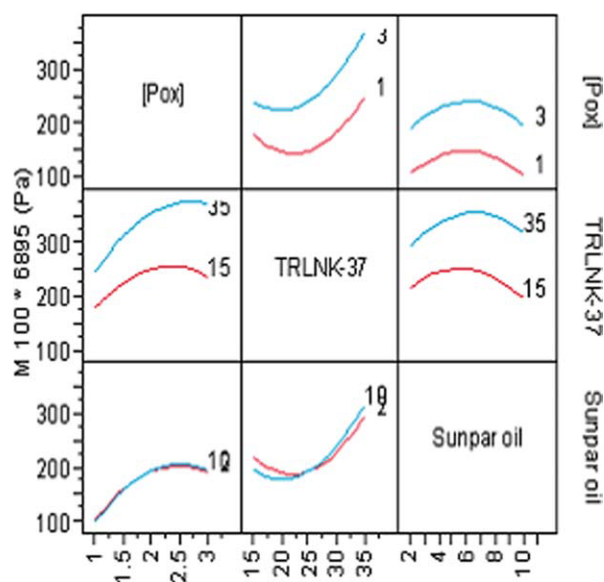


Figure 9 Interaction profile for three composition factors on tensile modulus at 100% elongation (M_{100}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

again the data fails to capture the evolution of gel level with cure for reasons discussed earlier.

Finally, the Shore A data as function of cure time (Fig. 8) do not show a significant change as function of cure, but rather, by and large this property is a function of the composition as a whole rather than the extent of cure. It is also noted however, that the amount of plasticizer had a significant impact on the compound Shore A as seen from the results of in 18 (B) versus 17 (A). For an oil-free formulation it is reported that increasing network density results in increase of Shore A value.⁷ It is also well established that for these types of formulations there may be significant network heterogeneity and so correlation of extent of crosslinking with measured properties may not be straightforward.

Mechanical properties of cured compounds

One of the measures often looked at to gauge the flexibility of rubbery materials is the tensile modulus at 100% elongation (M_{100}). From the present experiments, the data show a very good agreement between JMP prediction and the actual data ($R^2 = 0.96$). From sorted parameter estimates, the filler and peroxide stood out as the most important factors affecting M_{100} . Using All pairs Tukey-Kramer analysis on M_{100} by peroxide level, it is observed that the difference between the 1 and 3% loadings were statistically significant in affecting this quantity while data at 2% were not statistically different enough from either of the two. Using All pairs Tukey-

Kramer analysis on M_{100} by the amount of filler used, it is observed that the difference between the 15 and 35% loadings were significant while data at 25% were not statistically different from data at 15 and 35%. The interaction profile for three factors on M_{100} is shown in Figure 9. As suggested, the filler and peroxide emerge as the most important factors. Curvature in all the profiles implies that the square terms are significant in the model.

Another important property is the tensile strength of the compound. A reasonable agreement between the JMP model fit and the actual data was seen ($R^2 = 0.88$) for this property. From sorted parameter estimates the filler stood out as the most important factor influencing tensile strength. Using All pairs Tukey-Kramer analysis on tensile strength by the amount of peroxide it was concluded that the difference between the 1, 2, and 3% loadings were statistically insignificant. Similar results were obtained while doing the analysis on the paraffin oil plasticizer. Performing the analysis by the amount of filler it was concluded that the differences between the 15, 25, and 35% loading levels were statistically significant. The interaction profile for three factors on tensile strength is shown in Figure 10. It is interesting to see that the response is linear for the filler component.

Elongation at break is another key property. The model fit is in very good agreement with the actual data ($R^2 = 0.93$). From sorted parameter estimates the concentration of peroxide stood out as the most important factor. Using all pairs Tukey-Kramer analysis on elongation at break by the amount of filler it was concluded that the difference between the 15, 25, and 35% loadings were statistically insignificant. Similar results were obtained while doing the analysis on the paraffin oil. The interaction profile for

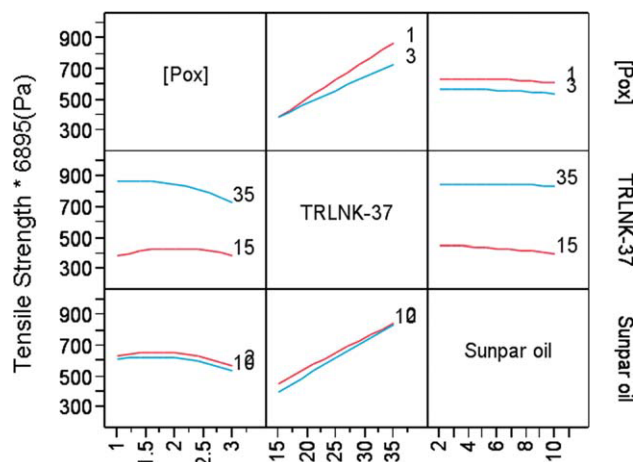


Figure 10 Interaction profile for three composition factors on tensile strength. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

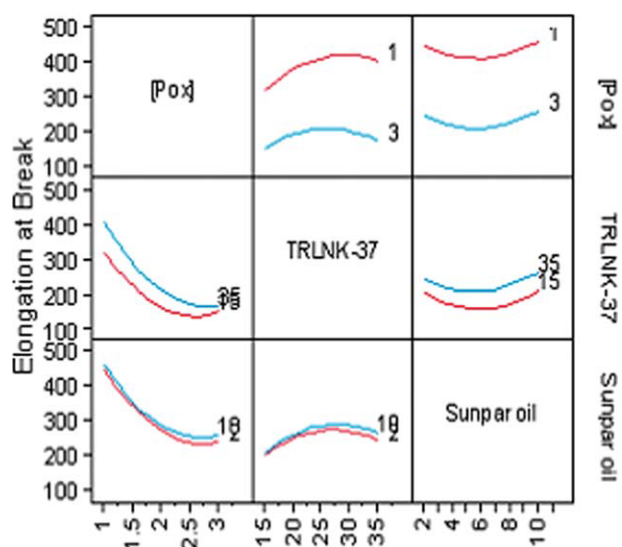


Figure 11 Interaction profile for three composition factors on elongation at break. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

three factors on elongation at break is shown in Figure 11. Curvature in all the profiles implies that the square terms are significant in the model.

For the Durometer Shore A, the model fit is in very good agreement with the experimental data ($R^2 = 0.98$). Sorted parameter estimates reveal all three factors to be important. Using all pairs Tukey-Kramer analysis on Shore A by the amount of filler it was concluded that the difference between the 15, 25, and 35% loadings were statistically insignificant. Similar results were obtained while doing the analysis on the paraffin oil. For different concentrations of

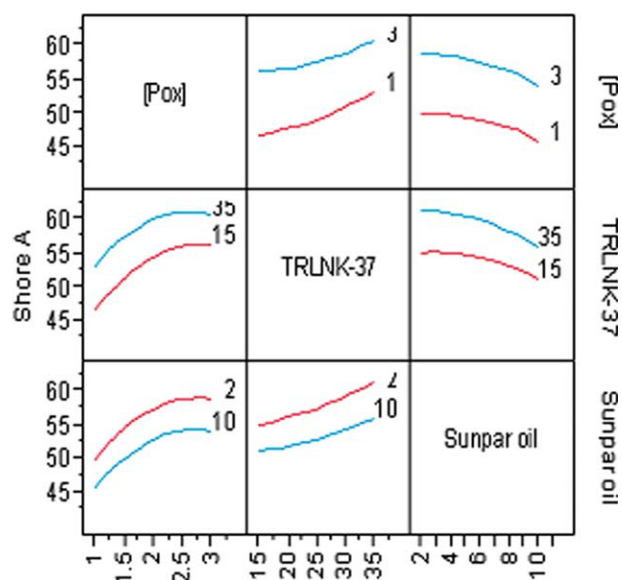


Figure 12 Interaction profile for three composition factors on shore A. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

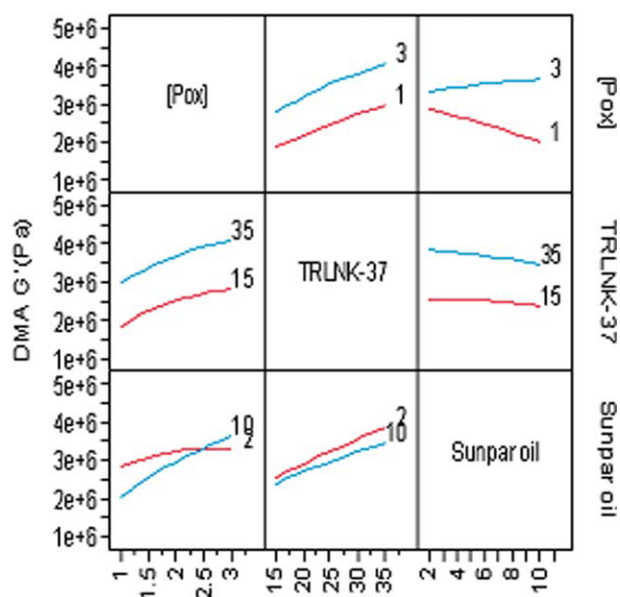


Figure 13 Interaction profile for three composition factors on the DMA equilibrium shear modulus at 200°C (DMA G'). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

peroxide it was found that there was no statistical difference between 2 and 3 wt %, although the response of 1 wt % peroxide was statistically significantly different from the rest. The interaction profile for three factors on Shore A is shown in Figure 12. Curvature in all the profiles implies that the square terms are significant in the model.

The equilibrium shear modulus at 200°C (DMA G') as measured by DMA was used as an indicator of the level of crosslinking. Unfortunately, the model predictions (Fig. 13) are not as good as the other factors ($R^2 = 0.62$ when plotted against actual data). The most important factor affecting DMA G' was found to be the filler level. It was also found that the differences in response due to the varying levels of peroxide and plasticizer oil were statistically not significant enough. From the interaction plots shown in Figure 10 it appears that the level of filler is more or less linearly correlated.

Dielectric strength

The dielectric strength is an important quantity to assess the compound insulation characteristic for use in electrical cable coating applications. However, this property could not be modeled based on simple linear and two degree terms. As discussed previously filler has an important role to play in this regard. However, within the limits of variation for this DOE study no difference could be discerned. Also the data suggest that this property behaved independently of changes in all the three composition factors. Hence it is concluded that within the

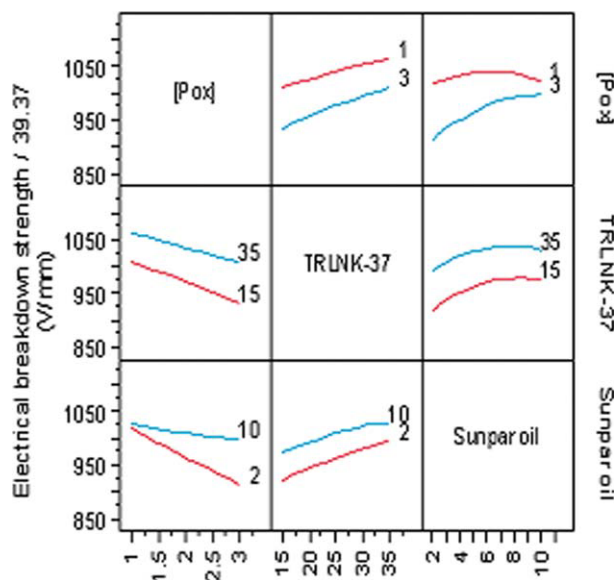


Figure 14 Interaction profile for three composition factors on the electric breakdown strength. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DOE formulation space the breakdown or dielectric strength is just dependent on the base resin and although some trends can be seen among the three factors studied, they are not statistically significant as suggested by the data in Figure 14. Detailed studies, which are outside the scope of the current work, on impact of other properties such as morphology on the dielectric strength need to be conducted to fully understand the behavior.

CONCLUSIONS

This study was conducted to understand the key variables and interactions controlling cure kinetics and final properties of a peroxide cured, filled EPDM system containing clay and oil. It was found that for mechanical properties, the tensile modulus was affected mostly by the filler and peroxide levels (extent of cure). The filler level also impacted strongly the tensile strength and the high temperature modulus as well, while the elongation was strongly affected by the extent of cure. The Shore A hardness was not impacted by one single variable, but all three parameters investigated appear to be equally important. For the electrical breakdown strength, although individual formulation components, especially the filler, showed a non-negligible

impact on this property, within the formulation design space, this property appears to be more characteristic of the base resin. Finally, on the cure kinetics it was found that Isayev's model showed a good correlation with the experimental data. Kinetic parameters calculated for the model were found to be in good agreement with existing literature data for these systems. Although, level of cure was suppressed on increasing the proportion of oil in the unfilled formulations, cure rate did not seem to be impacted by the oil to filler ratio. In the filled formulations, the oil increased the cure level, possibly due to passivation of the filler surface to prevent acid-catalyzed decomposition of peroxide. Though performance of some of these four-component formulations was adequate, the reduced cure in some of the compositions underscores the importance of additional components, such as acid scavengers, in commercial formulations.

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