Technical

New butyl polymer for curing bladders

Second of two parts

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Table II

In this design of experiment, there was good correlation or relatively high R^2 between predicted and actual values for a number of performance criteria for the bladder application.

The poorest correlation between the predictive model and actual response values was for tear properties; therefore they are not included for discussion.

Lambrinos

A probability, p-value in the Anova table less than 0.05 was used to determine the significance of the variable for inclusion in the regression model. Significant variables with this p-value level are highlighted.

The relative magnitude of the influence of an independent variable compared to the response in the model is indicated by (+) as a positive/increase to the equation or as (-) negative/decrease to the equation.

Variables with a p-value between 0.05 and p-value of 0.10 or less are still considered as variables of potential interest, important for consideration and are highlighted.

The analysis of performance characteristics offered insight to optimizing curing bladder. A look at hardness shows that the castor oil level has the largest influence on compound hardness. Surprisingly a reduction of one phr castor oil increases compound hardness by about one unit.

Fig. 3

One could consider this as an advantageous adjustment ingredient considering the relatively smaller effect on hardness from the resin level from the lowest to highest level evaluated. In this case resin plays a very small role over the 5.0 phr range evaluated.

A snapshot of 300 percent modulus shows similar trends with the castor oil levels having the largest influence on modulus, therefore it can be concluded that varying the castor oil level can be used as a method of fine tuning the compound modulus.

Upon hot air aging for 48 hours, the modulus at 100 percent elongation response was examined since an evaluation of 300 percent modulus could not be made, as there were some test combinations that could not attain 300 percent modulus after aging.

The results showed similar trends as in the unaged comparison. Once again the castor oil (-) and resin (+) are the main ingredients that impact modulus. As indicated earlier, the resin itself is a major contributor in the increase in compound modulus during aging.

The other finding of importance is that the interaction variable of low unsaturation polymer and resin also has a positive impact on aged modulus. In particular the higher amounts of resin tend to show a decreasing slope towards the high level of lower unsaturation polymer (i.e. lower amount of total unsaturation).

This is an advantage for bladder compounds since this trend implies a reduced impact of the resin with respect to further crosslinking due to the lower amount of total unsaturation in the formulation.

This supports the earlier remarks concerning the service hardening of the bladder with resin and residual unsaturation being the main players and one of the two routes for in-service hardening of bladders.

Fig. 4

Examination of the variables influencing the percentage increase or change in modulus from initial value to the after heat aging value shows that castor oil detrimentally increases modulus upon aging, as more of the ingredient is added in the formulation.

Even though castor oil has a high boiling point and is the most suitable oil to withstand the harsh operating temperature of curing bladder, the data suggests that at 180°C the castor oil still can be be depleted through volatilization over the service life of the bladder.

In a practical in-service perspective, castor oil should be tuned downward in the formulation if possible in order to stabilize the increase of the aged modulus. Once again the interaction effect of low unsaturation and (high) curing resin content show a decreasing favorable response to change in modulus of approximate 40 to 50 percent within the ingredient ranges used.

Fig. 5

The ultimate tensile strength also is strongly affected by the castor oil loading. **Fig. 6** shows the dependence of ultimate tensile strength on resin level and castor oil at a fixed polymer unsaturation level.

Unsaturation level does not have a significant effect on mechanical tensile strength, but changing the castor oil level from a high level to a low level results in an increase in ultimate tensile strength of about 50 percent.

Adjusting resin level between its low and high levels has a minor influence on tensile strength.

Fig. 6

The ultimate tensile strength properties after aging in hot air for two days at 180°C also were evaluated.

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Fig. 3. Compound physicals—hardness (Shore A).

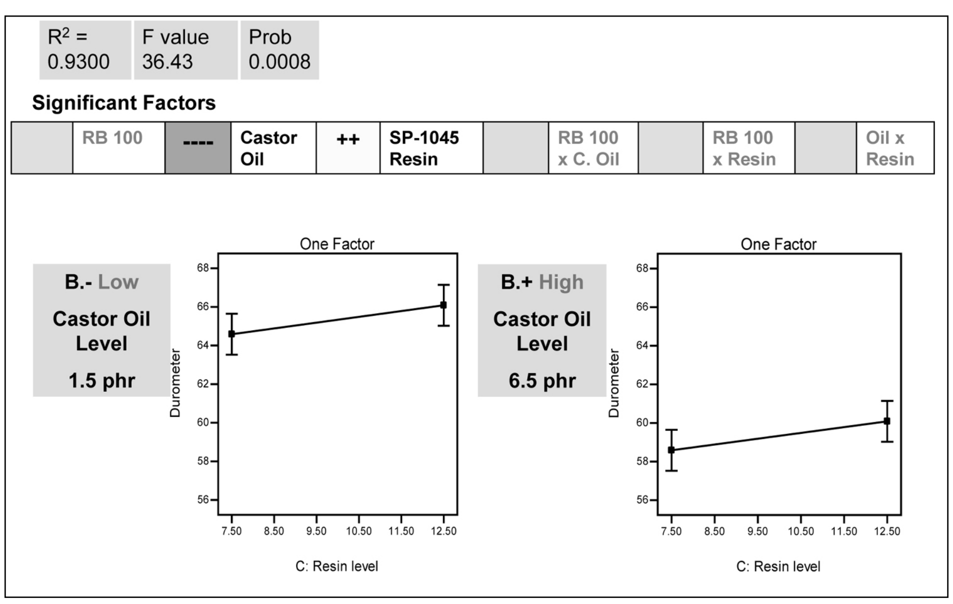

Fig. 4. Compound physicals—modulus at 100 percent (MPa) hot air aged.

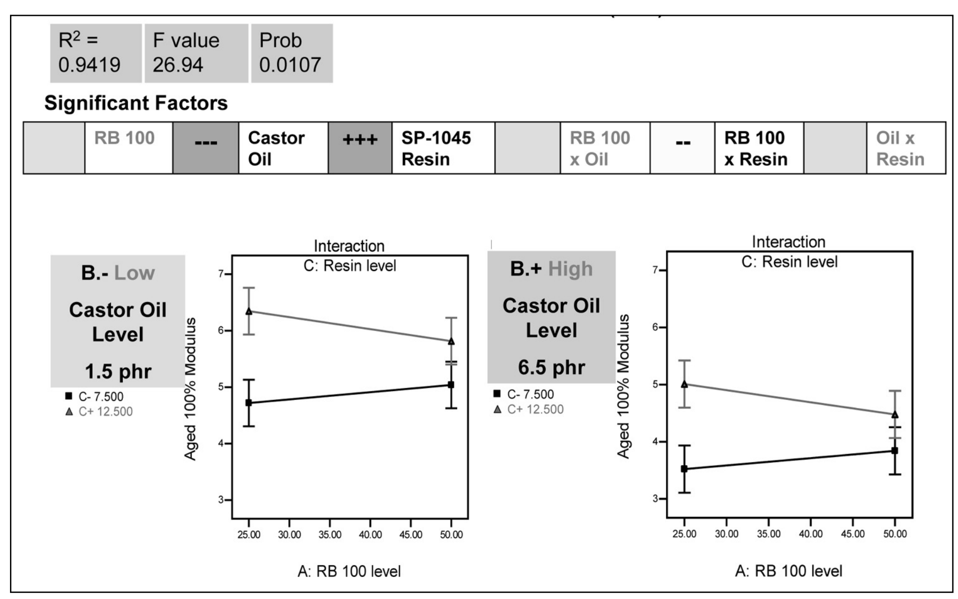

Fig. 5. Compound physicals—change percentage of 100 percent modulus.

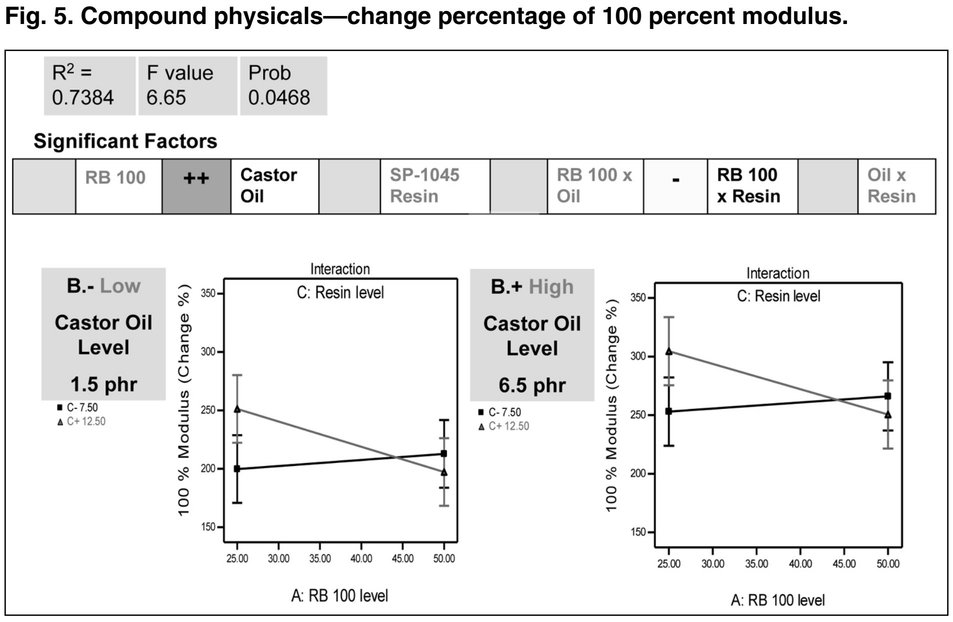

Fig. 6. Compound physicals—ultimate tensile strength (MPa).

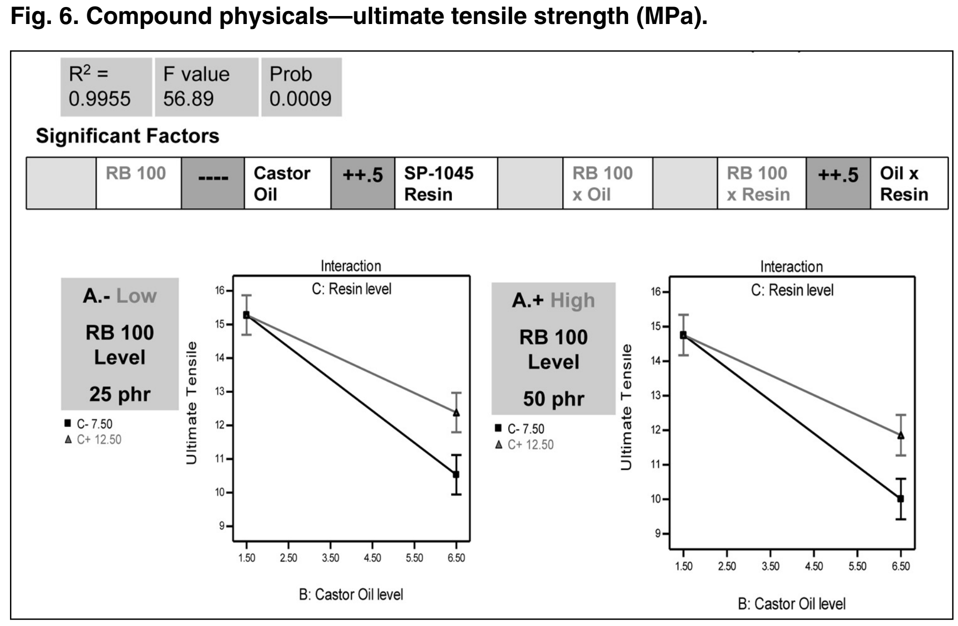

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Fig. 7

The left schematic shows aged tensile strength for the case of low castor oil level, and the right depicts the case for high level of castor oil. It can be seen that there is a slight interaction between the resin level and the unsaturation level since the curves are not parallel, but nevertheless the aged tensile strength follows the same trends observed in the original, unaged results. Castor oil level can be adjusted in compounding in order to retain the required tensile strength.

The ultimate elongation values give a relative representation for the elastic range of the compound, a property that is critical to maintain for curing bladder application in service. As would be expected, castor oil when added plays a significant role in increasing elongation and conversely increasing the resin results in a decrease in ultimate elongation values.

Fig. 8

Review of the data for the aged physicals indicates that the predictive model for aged elongation is not highly correlated, and the analysis must be understood to be a trend indicator only. From the values represented on the contour plot, in all instances the elongation values after two days of hot air aging are greatly reduced relative to the unaged values.

Fig. 9

The addition of resin plays the largest role in loss of elastic range from the initial elongation results. Castor oil has no impact in aged elongation as it helped increase elongation in the unaged results.

The contour plot in **Fig. 9** shows a good visual picture with regard to the impacts of the compounding ingredients. Of interest is the funnel shape that opens up when going to the higher RB 100 axis. In particular, if one were to draw across from left to the right side of the graph, decreasing total unsaturation level in the compound mitigates the effect of higher cure resin on aged elongation.

Another manner of looking at it observationally is that an increased cure state can be achieved without adverse effect on aged elongation. The contour plot opens up towards the right hand side of the graph where the total unsaturation is lower and shows more stable elongation within the resin ranges tested.

Ultimately there is a need for a functional level of resin, because resin is needed for mechanical property development but up to this point in the analysis, the addition of resin shows no incremental step changes for building mechanical properties.

Therefore, lowering the amount of resin compounded into the recipe should aid in stabilizing modulus increase and retaining elastic range (elongation) in service.

Resin content should be kept as low as possible in order to achieve the highest aged elongation result without compromising on other compounding attributes.

Crack growth was analyzed using the DeMattia flex fatigue to failure test with pre-cut specimens. The testing of hot air aged DeMattia flex specimens gives a good snapshot of dynamic flex requirement in bladder application.

Fig. 10

In the response analysis, the model equation is based on the natural logarithm determined to be the best fit. Optimum fatigue life occurs when resin content is low, oil content is high, and total unsaturation level is low. Increasing the castor oil provides compound lubricity and is reflected in favorable flex fatigue property development.

Conversely an increase in resin content effectively can reduce the cut growth resistance values to only a few thousand cycles. Significant care is needed in determining the optimum resin level for this application.

The last performance characteristic analyzed in this work was tension set property. This physical elastic property gives a relative correlation in regard to initial bladder dimensional stability and relative bladder growth in service.

Fig. 11

In the analysis of initial tension set, it is worth noting that all the independent variables and interaction variables show an effect on this dependent variable. As expected, an increase in castor oil content will increase the tension set, while increasing the resin decreases set.

Addition of a low unsaturation polymer has only a small effect in increasing the set property. For the aged tension set parameter **Fig. 12**, the linear regression correlation is low (R2 = 0.69) nevertheless only one variable, the resin level is significant in understanding the set property after hot air aging.

Whereas, a directional adjustment could be made with any of the compounding ingredients that have been identified for initial tension set requirement the aged analysis shows that resin level would be the ingredient that needs important manipulation to maintain overall tension set upon aging.

Increasing the resin level results in decreased aged tension set, which is desirable for minimizing dimensional growth in service. From a practical understanding, the building of an overall level of crosslinking network is essential to maintain set properties.

Optimization—Confirmation compounding

A mechanical blend of 25 phr of lower unsaturation polymer to 75 of higher unsaturation (1.85 mol percent) butyl polymer is still the best starting point. The design work also predicted that a 3.0 to 3.5 phr level of castor oil and a 7.5 phr level of resin were desirable for a good balance of properties to promote curing bladder service.

The confirmation study consisted of a comparison of the recipe with the original standard starting formulation versus an initial low 25 phr level of low unsaturation polymer recommendation with standard formulation ingredient loadings.

The third compound in this series was the "prediction" compound for best results at 3.0 phr castor oil level with 7.5 phr resin and the "prediction +" formulation with a 3.5 phr level of castor oil with 7.5 phr resin was the fourth compound.

The last compound in this compounding series included a 50 phr low unsaturation polymer addition rate "comparative" in order to obtain a broad understanding of trends and limits of low unsaturation polymer addition.

Fig. 7. Compound physicals—ultimate tensile strength (MPa) hot air aged.

R^2 =	F value	Prob
0.9967	597.95	<0.0001

Significant Factors

	RB 100	----	Castor Oil	+++	SP-1045 Resin		RB 100 x Oil	--	RB 100 x Resin		Oil x Resin

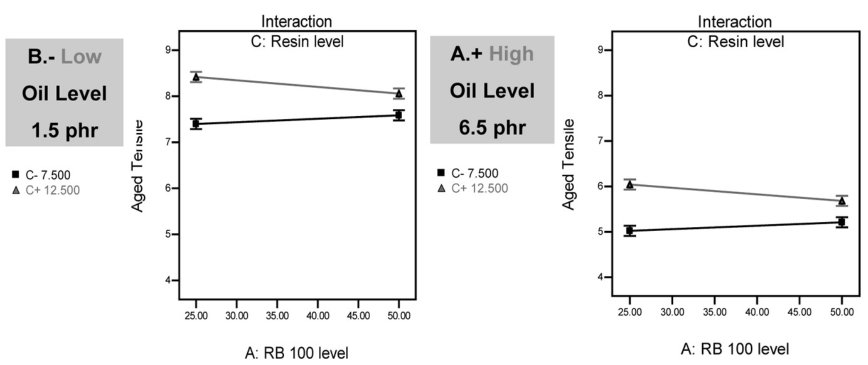

Fig. 9. Compound physicals—elongation (percentage) hot air aged.

R^2 =	F value	Prob
0.6579	6.13	0.0396

Significant Factors

	RB 100		Castor Oil	--	SP-1045 Resin		RB 100 x Oil		RB 100 x Resin		Oil x Resin

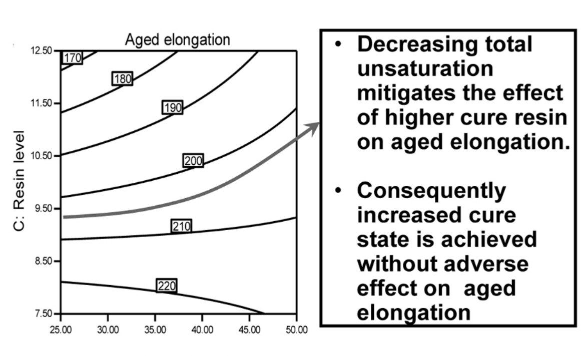

Fig. 8. Compound physicals—ultimate elongation (percentage).

R^2 =	F value	Prob
0.8823	13.00	0.0302

Significant Factors

	RB 100	+++	Castor Oil	-	SP-1045 Resin		RB 100 x Oil		RB 100 x Resin		Oil x Resin

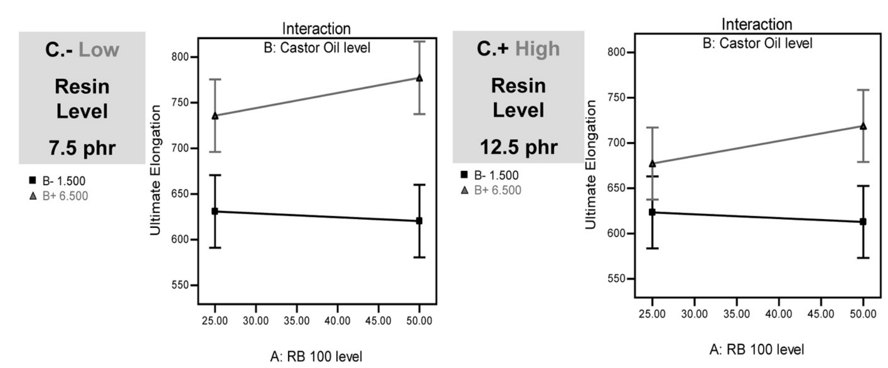

Fig. 10. Compound physicals—DeMattia (pre-cut) to 600 percent crack growth hot air aged.

R^2 =	F value	Prob
0.8865	13.5	0.0287

*equation = natural logarithmic (De Mattia)

Significant Factors

	RB 100	++	Castor Oil	--	SP-1045 Resin		RB 100 x Oil		RB 100 x Resin		Oil x Resin

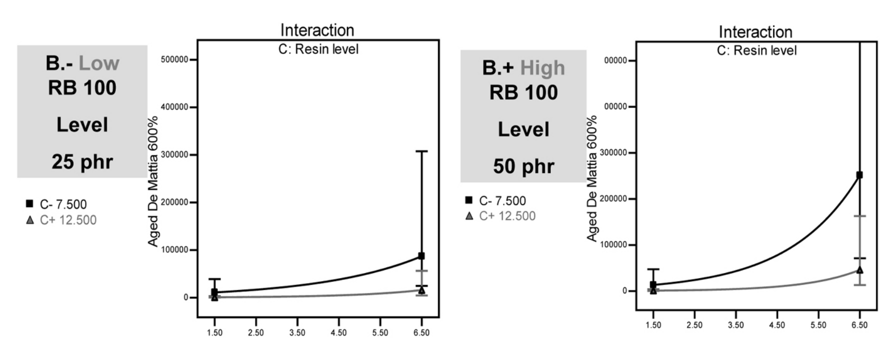

Table III

The Mooney scorch in the "predicted" and "predicted +" data suggests that the viscosity is higher than the standard control formulation with the reduction in oil and possibly the lower resin might be contributing to the increase.

The scorch safety is improved by more than 10 percent, and this should aid the molding process. The rheology cure characteristics indicate that improved processing safety is not achieved at the expense of cure rate.

The overall t90 values for all compounds appear to be in the same range as the standard control compound and the "predicted +" recipe is the closest to the standard formulation.

Table VI

The analysis of 100 percent and 300 percent modulus results in **Table VII** again confirms the beneficial impact of adding the low unsaturation polymer (see initial vs. standard). As predicted by the prior designed studies, there is also an additional reduction of the percentage change in modulus when the castor oil and resin are decreased.

Relative to the addition of low unsaturation polymer alone "initial" there is an additional step change improvements in the later subsequent "predicted," "predicted +" and "comparative" iterations. It is seen in **Table VII** that the "predicted+" compound shows the least change in modulus upon hot air aging.

Table VII

Table VIII shows the results on ultimate tensile and elongation.

From this compounding work, it can be observed that the compounds develop tensile strength equivalent to or better than the standard compound, and thus the compounds with an overall lower level of unsaturation are all within the target level for ultimate tensile strength.

The "predicted" and "predicted+" compounds show a small increase in tensile strength with the lower oil addition. Advantageously, the tensile strength is retained after hot air aging.

The "predicted +" recipe represents the longest elongation result after aging.

Table VIII

Even though the DOE gave a poor predictive correlation for Die C Tear testing, it was included in the analysis of the optimization compounds as it is a design parameter of significant interest for bladder compound development.

Table IX shows that the original Die C Tear tested at room temperature conditions shows that the addition of lower unsaturation polymer results in a reduction in tear strength, but this might be an acceptable small tradeoff in balancing performance in bladder.

Although the initial tear is somewhat reduced, it should be noted that after 48 hours of hot air aging, the standard as well as all other compounds with lower total unsaturation show equivalent tear properties.

Table IX

Hot Die C tear at 100°C was examined and was demonstrated to have a different outcome compared to the room temperature testing. In this case the original standard compound experienced the lowest initial hot tear.

The addition of the lower unsaturation polymer and reduction in castor oil and resin resulted in an initial hot tear improvement.

The "predicted +" iteration has the highest observed result.

The "comparative" recipe appears to have good hot tear, but the actual tear strength value was not determined since the specimen exceeded the stroke limit of environmental chamber before rupture.

Hot Die C tear strength for specimens aged after 48 hours aging in hot air, illustrates that all of the compounds in this series have equivalent or better tear strength values as that of the original standard formulation.

Elevated temperature testing might be a better indicator of bladder in service conditions.

The DeMattia flex fatigue results shown in **Table X** are as predicted.

Table X

All of the confirmation compounds containing a mechanical blend of low unsaturation butyl and the higher 1.85 mol percent butyl show improvements in crack growth propagation compared to the standard formulation. With regard to the aged DeMattia flex test results, there is evidence of a two-step improvement. The first improvement stems from the use of the mechanical polymer blend, and the second stems from the optimization of the cure resin and the castor oil plasticizer dosage.

The results in **Table X** show that the "comparative" formulation, containing the highest dosage of low unsaturation gives an enormous improvement in crack growth, but as previously stated and as expected, there is a definite detrimental increase in tension set. (see also **Table XI**)

For the compounds containing the optimized cure and plasticizer dosage, as well as the polymer blend, ("predictive" and "predictive+") a significant increase in the number of cycles to reach 600 per-

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Fig. 11. Compound physicals—initial tension set percentage (300 percent strain).

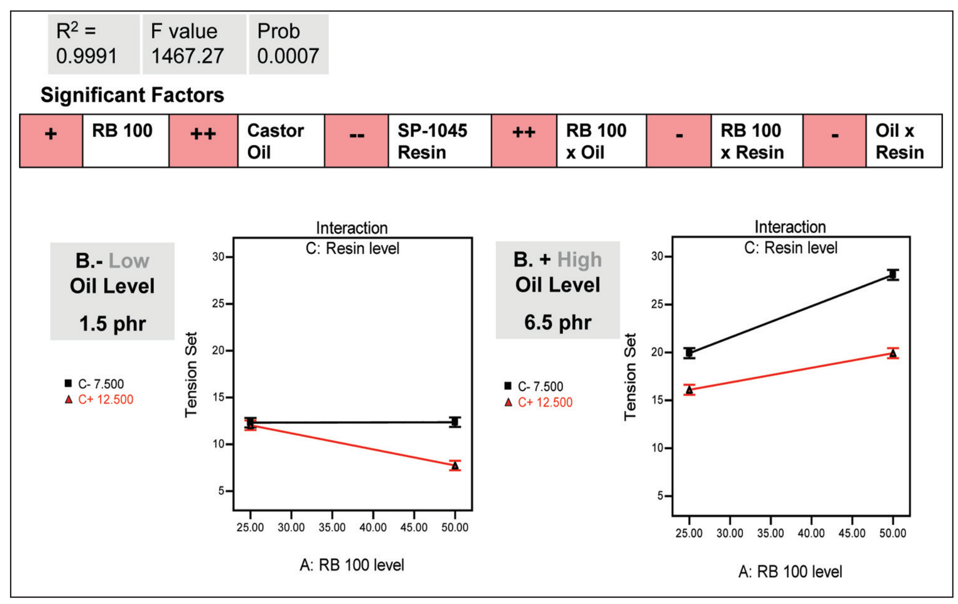

Fig. 12. Compound physicals—tension set percentage (100 percent extension) hot air aged.

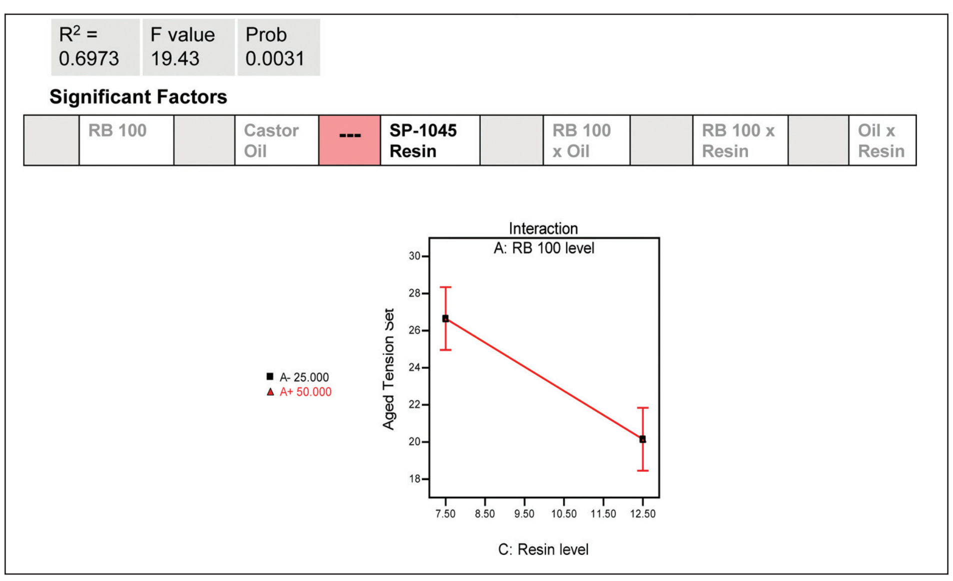

Table V. Physical properties initial and aged in hot air of butyl blends.

300% MODULUS					
Isoprene(mol%)	1.85	1.61	1.38	1.14	0.90
300 % Modulus (Orig.) (MPa)	4.2	3.8	3.00	3.1	1.8
Aged in Air 24 hrs 180 °C (MPa)	10.2	8.8	8.2	7.8	6.8
Aged in Air 48 hrs 180 °C (MPa)	-	7.8	7.0	6.9	6.2
ELONGATION (%)					
Isoprene (mol%)	1.85	1.61	1.38	1.14	0.90
Elongation (Orig.) (%)	778	765	855	786	895
Aged in Air 24 hrs 180 °C (%)	350	390	398	391	401
Aged in Air 48 hrs 180 °C (%)	266	300	310	322	347

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cent crack growth can be seen. In the case of the 48-hour aging, the improvement relative to the standard compound exceeds 500 percent.

The tension set results are presented in **Table XI**. While the use of a high dosage of low unsaturation butyl polymer without other optimization "comparative," show unacceptable tension set values, the optimized compounds "predicted" and "predictive+" give only slightly higher tension set values compared to the standard formula, but these are believed to be within an acceptable range and are expected to have comparative results for bladder dimensional stability in service.

Table XI: Conclusions

In conclusion, the addition of low unsaturation in a mechanical blend with traditional polymer provides an opportunity to impart an improved balance of properties through the stabilization of modulus increase attributable to resin reactivity during aging, through improved elongation retention and through better flex fatigue properties over the service timeline of bladder.

In addition, use of the low unsaturation polymer reduces the opportunity for bladder reactivity with migrant tire curing ingredients, especially sulfur in the tire bead area. Tension set values slightly increased but are considered acceptable when comparable to the standard recipe 1.85 percent unsaturation polymer.

Castor oil is needed in the formulation for compound lubricity and cannot be eliminated entirely. These studies show positive improvements to flex properties upon addition of oil. From the design of experiment, it was determined that the most desirable combination would be a reduction in the castor oil since excess amounts of castor oil promotes increases in modulus.

The downward adjustment to tune the modulus can be made without compromising flex properties. The downward adjustment in castor oil also facilitates in optimizing tensile strength, aged tensile strength, and initial tension set decrease. This work suggested that a 3.5 phr level of castor oil is desirable for a good balance of tire curing bladder properties.

Resin is important to develop overall properties, but care is needed in understanding the level required for optimizing elongation and flex properties, the final level is critically determined by requirement of set properties. A level of 7.5 resin was determined the best to achieve overall bladder optimization.

References

1. Bayer Polysar Technical Centre, 1992, Butyl and Halobutyl Compounding Guide for Non-Tyre Applications, Continental Printing, Antwerp

2. W. Hopkins, J.G. Neilsen, "New Insights into the Cure and Aging of Resin Vulcanized Butyl Curing Bladder Compounds" presented to ACS Rubber Division, Orlando, Fla. (September 1999)

Acknowledgements

Lanxess personnel: Lionel Cho-Young and Ezio Campomizzi for their experience and discussions with regard to this application.

Table VI. Optimization—process characteristics - rheology data.

		Standard	Initial	Predicted	Predicted +	Comparative
Compound		1	2	3	4	5
BUTYL RB 100		-	25	25	25	50
BUTYL RB 301		88.6	63.6	65.2	65.2	40.2
Castor Oil		5	5	3.0	3.5	3.0
SP-1045		10	10	7.5	7.5	7.5
Mooney Viscosity (1 + 4) @ 100 °C	MU	77	75	82	82	78
T3 Scorch @ 125 °C	mins	22.4	26.7	25.0	26.4	27.4
Rheology(180 °C,1°Arc,30 mins.)	Mh	16.3	15.7	16.3	15.9	15.6
	Mh-Ml	12.3	11.8	12.2	11.8	11.5
	ts2	2.3	2.2	1.9	2.0	2.0
	t90	20.0	21.1	20.7	20.5	21.3

Table VII. Optimization—modulus at 100 percent and 300 percent.

100 % Modulus

	Standard	Initial	Predicted	Predicted +	Comparative
Compound	1	2	3	4	5
100% Modulus (Orig.) (MPa)	1.8	1.8	2.1	2.0	2.0
Aged in Air 24 hrs 180 °C (MPa)	5.1	4.8	5.1	4.9	4.8
Aged in Air 48 hrs 180 °C (MPa)	5.1	4.6	4.9	4.3	4.5
Change %	+183%	+156%	+133%	+115%	+125%

300 % Modulus

Compound	1	2	3	4	5
300% Modulus (Orig.) (MPa)	5.1	5.0	6.2	5.8	5.3
Aged in Air 24 hrs 180 °C (MPa)	-	10.1	11.4	10.7	10.2
Aged in Air 48 hrs 180 °C (MPa)	-	-	-	-	-
Change %		+102%	+84%	+84%	+92%

Table VIII. Optimization—tensile elongation properties.

Ultimate Tensile

	Standard	Initial	Predicted	Predicted +	Comparative
Compound	1	2	3	4	5
Ult. Tensile (Orig.) (Mpa)	13.3	13.4	14.3	14.1	12.9
Aged in Air 24 hrs 180 °C (Mpa)	10.3	10.4	11.4	11.2	10.7
Aged in Air 48 hrs 180 °C (Mpa)	7.3	7.4	8.0	8.2	7.8
Change %	-45%	-45%	-44%	-42%	-40%

Elongation

Compound	1	2	3	4	5
Elongation (Orig.) %	732	759	659	702	683
Aged in Air 24 hrs 180 °C	284	315	303	314	317
Aged in Air 48 hrs 180 °C	189	225	220	274	250
Change %	-74%	-70%	-67%	-61%	-63%

Table IX. Optimization - tear properties.

Tear Strength (RT @ 23 °C)

	Standard	Initial	Predicted	Predicted +	Comparative
Compound	1	2	3	4	5
Tear Die C (Orig.) (kN/m)	47.4	43.3	41.2	41.7	40.5
Aged in Air 48 hrs 180 °C (kN/m)	28.1	29.6	29.1	28.2	29.7
Change %	-41%	-32%	-29%	-32%	27%

Hot Tear Strength (@ 100 °C)

Compound	1	2	3	4	5
Tear Die C (Orig.) (kN/m)	29.9	32.3	34.7	39.7	*
Aged in Air 48 hrs 180 °C (kN/m)	16.8	18.1	18.5	16.9	17.4
Change %	-43%	-44%	-47%	-57%	*

* specimen exceeded limit of environmental chamber before rupture

Table X. Optimization—DeMattia crack growth (unaged and hot air aged).

De Mattia (pre-cut) Unaged

	Standard	Initial	Predicted	Predicted +	Comparative
Compound	1	2	3	4	5
Crack Growth 300% (Orig.)(Kc)	46.8	156.6	147.7	117.7	>250
Crack Growth 600% (Kc)	180.3	>250	>250	>250	>250

De Mattia(pre-cut) Aged 24 hrs @ 180°C

Compound	1	2	3	4	5
Crack Growth 300% (cycles)	700	1,200	1,200	1,750	16,800
Crack Growth 600% (cycles)	2,500	5,600	4,300	8,400	55,000

De Mattia (pre-cut) Aged 48 hrs @ 180°C

Compound	1	2	3	4	5
Crack Growth 300% (Orig.) (cycles)	700	1,000	1,300	2,500	12,000
Crack Growth 600% (cycles)	2,700	4,100	3,900	19,000	55,500

Table XI. Optimization— tension set—unaged, hot air aged and hot tension set.

	Standard	Initial	Predicted	Predicted +	Comparative
Compound	1	2	3	4	5
Tension Set (Orig.) 300 % strain 10 mins., relax 10 mins. (%)	10.0	10.7	10.0	10.7	16.0
Aged in Air 24 hrs 180 °C, 200% strain 10 mins., relax 10 mins. (%)	25.3	26	24.7	24.0	26.7
Aged in Air 48 hrs 180 °C, 100% strain 10 mins., relax 10 mins. (%)	20.0	21.3	23.3	23.3	23.3
Tension set @ 100 °C 300% strain 10 mins., relax 10 mins. (%)	18.0	23.3	20.0	21.3	31.3