

## Technical

## Examining functionalized butyl rubber

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Many industrial rubber applications are subjected to cyclical stress or deformations, which can cause cracks to initiate and propagate, leading to failure of the rubber article. The fatigue process involves the formation of cracks due to naturally occurring flaws or the aging process.

As minimizing the propagation of cracks is critical for many applications in their service life, improving fatigue is a major challenge for dynamically loaded rubber products.

Many types of polymers, fillers, and vulcanization systems are used in rubber applications (all of which are known to influence fatigue behavior)<sup>1-2</sup> in order to achieve a wide range of mechanical properties.

Ionomers are polymers that contain a small amount of covalently bound ionic functionality dispersed in a nonpolar matrix. They are an important class of polymers as ionic interactions produce large changes in physical, mechanical and rheological properties compared with polymers that do not contain ionic groups.<sup>3-8</sup>

Ionomers are microphase-separated materials, where the ionic groups aggregate into domains, which act as reversible crosslinks, strongly influencing the polymer behavior.

The ionic clusters affect the viscoelastic response with an increase in modulus,

## Executive summary

X\_Butyl I4545P is a new butyl-based material that has been developed by Lanxess and contains a persistent ionic charge attached to the butyl backbone. In addition to the properties of traditional butyl rubber (impermeability and low temperature flexibility), this new butyl ionomer displays many unique physical and dynamic properties, including excellent green strength, improved polymer-filler interaction and the formation of stable pellets.

Incorporation of the butyl ionomer in an bromobutyl inner liner compound formulation has been shown to provide improved green strength leading to greater dimensional stability needed during extrusion and calendaring processes.

The final cured article shows significant improved crack growth resistance and adhesion to carcass compounds without impacting the other compound properties. Such properties may lead to longer lasting tire inner liners, which can be of benefit for off-the-road tire manufacturing and retreading operations.

melt viscosity and relaxation time. The solubility behavior and the glass transition temperature also can be affected by ionic associations.<sup>3-8</sup>

Relaxation of the ionic groups is thought to proceed through a mechanism of "ion hopping" where ion pairs hop to another aggregate, allowing the stress of the polymer chain segment containing the ion group to relax.<sup>7-9</sup>

Butyl ionomer is a new class of butyl polymer that has been developed by the generation of permanent ionic groups bound to the polymer backbone.

In addition to the properties of traditional butyl rubber polymers (impermeability and low temperature flexibility), the ionic

interactions allow for improved green strength and polymer-filler interactions as well as the formation of stable pellets.<sup>10-14</sup>

In Fig. 1, the butyl ionomer is characterized through its rheological properties and is evaluated in a halobutyl-based rubber compound to demonstrate the performance attributes of this new material.

## Raw polymer characterization

Fig. 2 displays the storage ( $G'$ ) and loss ( $G''$ ) modulus mastercurves of high Mw brominated butyl rubber (BIIR-h) and butyl ionomer at a reference temperature of 20°C.

Time-temperature-superposition was successful for the ionomer due to the large difference between the entanglement and ionic relaxation times. A small amount of ionic functionality (0.4 mol percent) gave rise to large changes in the polymer's viscoelastic properties.

An expected increase in the plateau modulus,  $G_N$ , is observed for the butyl ionomer as ionic aggregates act as physical crosslinks.

Here,  $G_N$  is estimated from the  $G'$  at the frequency of the  $G''$  minima. The  $G_N$  of  $3.0 \times 10^5$  Pa obtained for BIIR-h is similar to that of reported values for polyisobutylene between  $2.9 \times 10^5$  Pa to  $3.2 \times 10^5$  Pa,<sup>15-17</sup> while the butyl ionomer was found to be  $3.8 \times 10^5$ .

This increase in modulus is useful in butyl applications where an increase in elasticity is desired or where greater cohesive strength is required, such as for adhesives.

Another difference in the butyl ionomer rheology is seen in the decrease in the mid-frequency ( $10^{-2}$  to  $10^1$  rad/s)  $G''$ , which is normally identified with the relaxation of the non-functionalized polymer chain through reptation, contour length fluctuations and constraint release mechanisms as described by the tube model.<sup>18-20</sup>

Conversely, for the butyl ionomer, relaxation after the entanglement time,  $T_e$ , (Rouse time of the chain segment between entanglements) proceeded through the "hopping" of ionic aggregates to reduce the stress as well as relaxation through reptation.<sup>7,21,22</sup>

A maximum in  $G''$  was detected for the butyl ionomer at approximately 10 rad/s and is attributed to the relaxation of ionic aggregates, with  $T$  representing the average duration of an ion pair multiplet. The "ion hopping" relaxation mechanism subsequently hindered reptation and imparted a much greater terminal

Fig. 2.  $G'$  (solid symbols) and  $G''$  (open symbols) mastercurves at a reference temperature of 20°C.

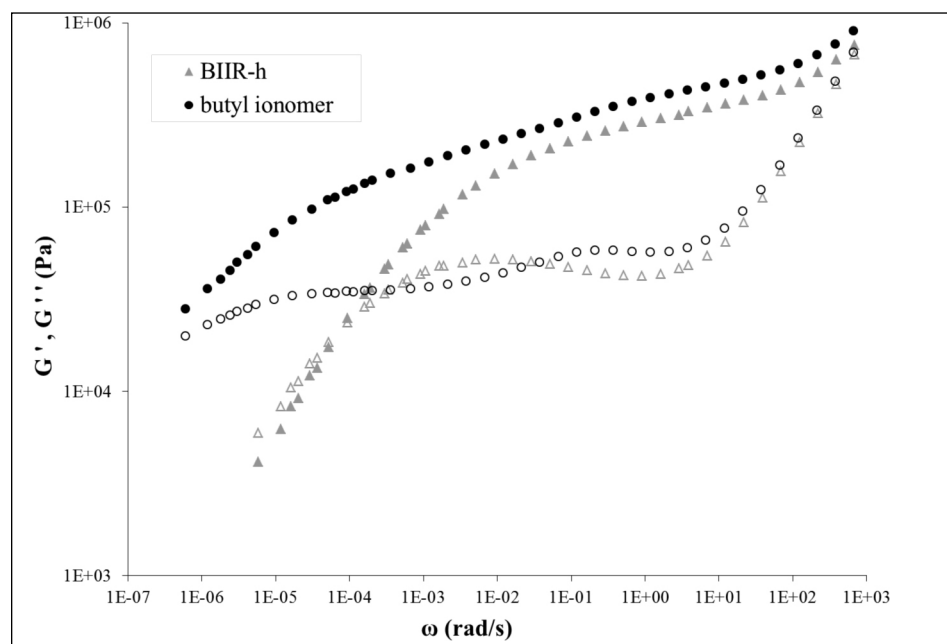


Fig. 3. Temperature dependence of the shift factors.

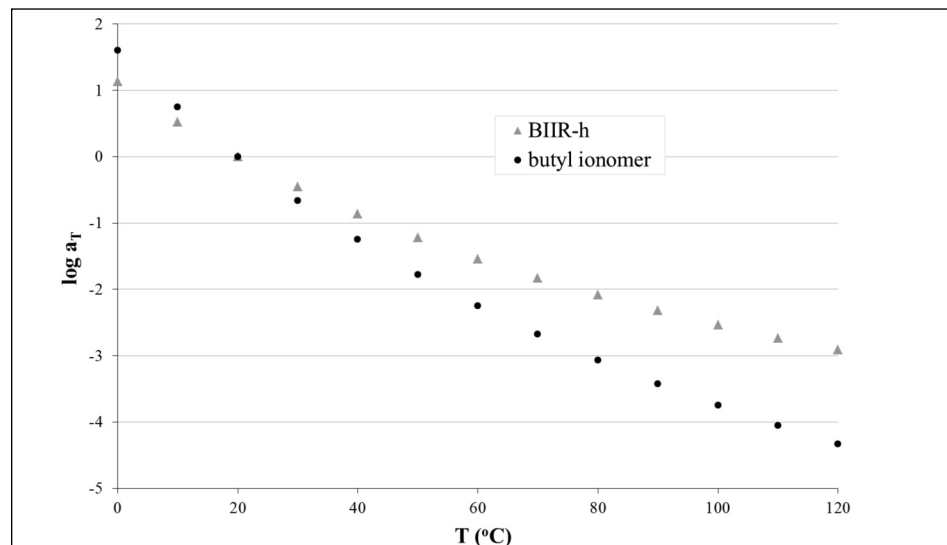
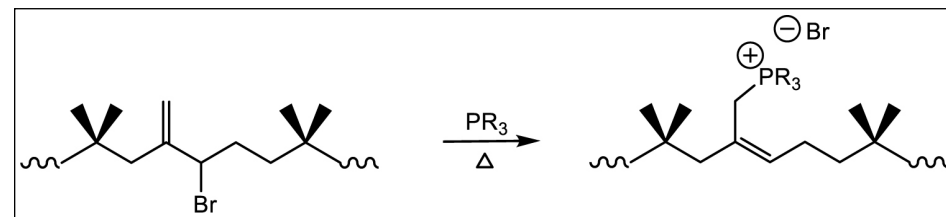


Fig. 1. BIIR-based phosphonium ionomers.



## The authors

Kevin Kulbaba is the technical marketing manager for NAF-TA-focused butyl rubber at Lanxess Inc., located in London, Ontario. His work focuses on business development for butyl rubber materials and applications.

Kulbaba has more than 17 years of experience in the field of polymer science, including 12 years with elastomers and rubber compounding.

He studied chemistry at the University of Western Ontario and obtained his doctorate in inorganic polymer chemistry at the University of Toronto.

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Dana Adkinson is a senior research scientist at the Research and Development Center for Lanxess in London. She focuses on the development of new butyl-based materials geared toward expanding the application scope of butyl rubber.

She received her doctorate in chemistry from the University of Western Ontario in 2005. Her work has resulted in more than 12 patent applications.

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He leads the physical and dynamic material research laboratory in support of the development of new butyl-based materials, focusing on expanding the application scope of butyl rubber.

He received his degree in physics from the University of Waterloo in 1996 and accepted a position at Lanxess (then Bayer) in 2000.



Adkinson



Bielby

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relaxation time or disentanglement time,  $T_d$ , on the polymer to such an extent that it is not measurable in the experimental window.

This indicates that the butyl ionomer may be more difficult to handle than BIIR-h in certain industrial processes.

The temperature dependence of the experimental shift factors,  $a_T$ , used to construct the viscoelastic mastercurves obeyed the Williams, Landel and Ferry equation:<sup>15,23</sup>

$$\log a_T = \frac{-c_1(T - T_0)}{c_2 + T - T_0}$$

While polyisobutylene is known for its weak temperature dependency,<sup>24,26</sup> the shift factors were influenced strongly by ionic functionality as the temperature dependence was greatest for butyl ionomer at higher temperatures in comparison to the reference.

The greater temperature dependence is due to the large separation in ion hopping and entanglement relaxation mechanisms. The shift factors are plotted against temperature in **Fig. 3**.

A vertical shift of the modulus was performed according to the expression,<sup>27,23</sup>

$$G(T_0) = \frac{G(T)}{b_T}$$

with

$$b_T = \frac{\rho(T)T}{\rho(T_0)T_0}$$

**Fig. 4** shows the temperature dependence of butyl ionomer compared with BIIR-h. The effect of the relaxation of the ionic network is clearly seen as the butyl ionomer has a significantly higher elastic modulus at lower temperatures, but has a similar modulus at 120°C.

The reduction of the elastic modulus with increasing temperature compared with BIIR-h is due both to ionic relaxation and the difference in Mw as BIIR-h is a higher Mw polymer.

These temperature dependent properties can be exploited to improve the processing behavior of the butyl ionomer.

Viscous flow ( $G'$  slope = 2,  $G''$  slope = 1) was not observed within the experimental window of the mastercurves for either of the polymers studied. There-

fore, creep testing was employed to determine the terminal response, with the zero shear viscosity being calculated:

$$\eta_0 = \frac{(t - t_0)}{J_N(t)}$$

where  $J_N(t)$  is the Newtonian creep compliance.<sup>27</sup>

**Fig. 5** displays the shear creep curves of BIIR-h and butyl ionomer. The creep response validated the impact of only a small amount of ionic content towards the rheological properties as the creep of the butyl ionomer is greatly reduced.

The zero shear viscosity was found to increase by more than a decade from  $3.6 \times 10^8$  Pa-s for BIIR to  $4.2 \times 10^9$  Pa-s for butyl ionomer. Lower Mw brominated butyl rubber (BIIR-I), with a  $\eta_0$  of  $1.82 \times 10^8$  Pa-s is also shown in the figure for comparison.

Whereas the long relaxation time may be an issue with some processing conditions, a small amount of butyl ionomer may show improvements in others, with its enhanced melt strength and reduced cold flow.

### Inner liner compounds

Rubber compounds outlined in **Table I** were mixed on the laboratory scale using a 1.5-liter internal mixer, refined on a cold 10x20" two roll mill where the curatives were incorporated into the compound. The final batch was then sheeted out from which test specimens were cut.

A standard tire inner liner formulation using commercially available bromobutyl rubber was used as a control formulation (BB-CTRL) to compare the effect of blending bromobutyl with incremental amounts of the butyl ionomer (BB-ION10 and BB-ION20).

There is no impact on the final state of cure or on the rate of cure when the butyl ionomer is incorporated into the compound (refer to **Table II**).

The presence of residual allylic bromide groups and isoprene groups in the butyl ionomer allows the polymeric modifier to be cured into the network without reducing the effective chemical crosslink density of the cured article.

As mentioned previously, the ionic aggregates depicted in **Fig. 1** can impart significant changes in the physical and dynamic properties of a polymer. The properties inherent to the butyl ionomer translate directly into improved physi-

cal properties for the blend compounds.

**Table II** outlines the change in Mooney viscosity and Mooney scorch of the halobutyl blend compounds relative to the control. The 10 percent increase in Mooney viscosity can be attributed to improved filler dispersion and the presence of low concentrations of ionic aggregates at such temperatures.

**Table II** also highlights the change in green strength relative to the mill shrinkage of the compounds.

Significantly, the blends shows a 40-90 percent improvement in green strength (peak stress) with no negative impact on the mill shrinkage, thereby resulting in an enhancement in dimensional stability of an uncured compound without significantly increased nerve, which is desirable for extrusion or calendaring operations.

**Table III** compares the resulting tensile properties of the BB-ION10 and BB-ION20 blends relative to the BB-CTRL compound. The higher modulus for the resulting butyl ionomer blend compounds shows significant reinforcement relative to the control.

This effect may be attributed to improved filler dispersion resulting in a higher degree of reinforcement in the cured article.

There is no impact on the permeation properties when butyl ionomer is incorporated into the carbon black filled tire inner liner formulation.

As expected, the barrier properties inherent to the butyl rubber base polymer are maintained for the butyl ionomer blends. There was a slight increase in tear strength observed.

The ionic aggregates act as reversible physical crosslinks, which may be increasing the energy required to initiate a crack. This effect is diminished in the butyl ionomer blend compounds, but nonetheless is still observable.

There is however, a significant increase in adhesion to an NR/BR carcass compound. It is difficult to assign the exact mechanism of this increased adhesion; however the increased polarity of the butyl matrix in the butyl ionomer blend compound may be a contributing factor.

When the cured samples are subsequently aged (100°C for one week), there is a slight reduction in modulus relative to the control compound. Such an effect would be of benefit during retreading operations to prevent hardening of the tire

inner liner with repeated heat cycles.

Crack propagation was determined using a DeMattia flex tester on samples that were aged for one week at 100°C. The results show that the rate of crack propagation for the BB-ION10 blend was comparable to the control formulation while the crack propagation for the BB-ION20 compound was enhanced (refer to **Fig. 6**).

Since the physical crosslinks due to the ionic interactions are reversible, the incorporation of the butyl ionomer into the polymer matrix appears to impart self-healing properties, whereby the ionic aggregates break and re-form.

Thus, a substantial reduction in the fatigue properties of the cured rubber article could be realized once again with the addition of low levels of the butyl ionomer.

### Conclusions

The physical and rheological behavior of Lanxess X\_Butyl I4565P (butyl ionomer) was compared with brominated butyl rubber. The butyl ionomer was found to have an increased plateau modulus, which would be beneficial for cohesive strength in adhesives and a longer relaxation time that may be a processing issue if utilized in high phr levels in the compound.

Viscoelastic shift factors showed a greater temperature dependence of the butyl ionomer due to a relaxation of the ionic aggregates at higher temperatures, which can be taken advantage of in melt processing.

Also, creep testing exhibited an improvement in cold flow resistance for butyl ionomer.

The butyl ionomer has been evaluated in a standard tire inner liner compound formulation based on 100 phr of bromobutyl. The green strength of the butyl ionomer blend compounds was significantly higher than the control but with negligible change in the mill shrinkage of the compound.

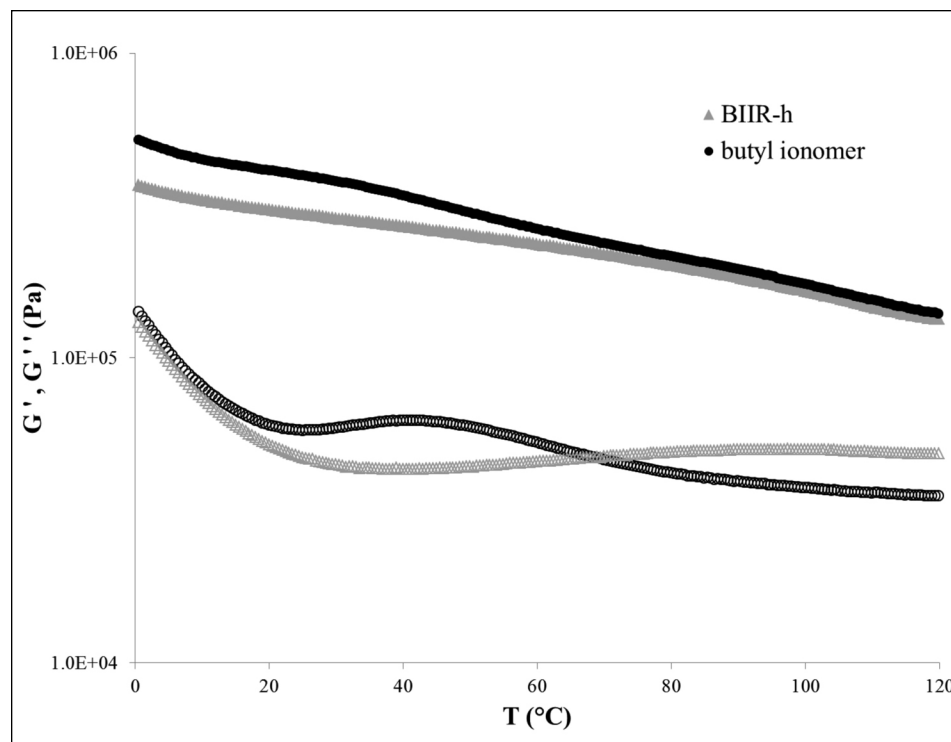
This effect allows for improved shape retention of the uncured compound during processing, which is desirable for extrusion and calendaring operations.

The cured compounds showed improvements in reinforcement (modulus) and reduced compound hardening during heat aging.

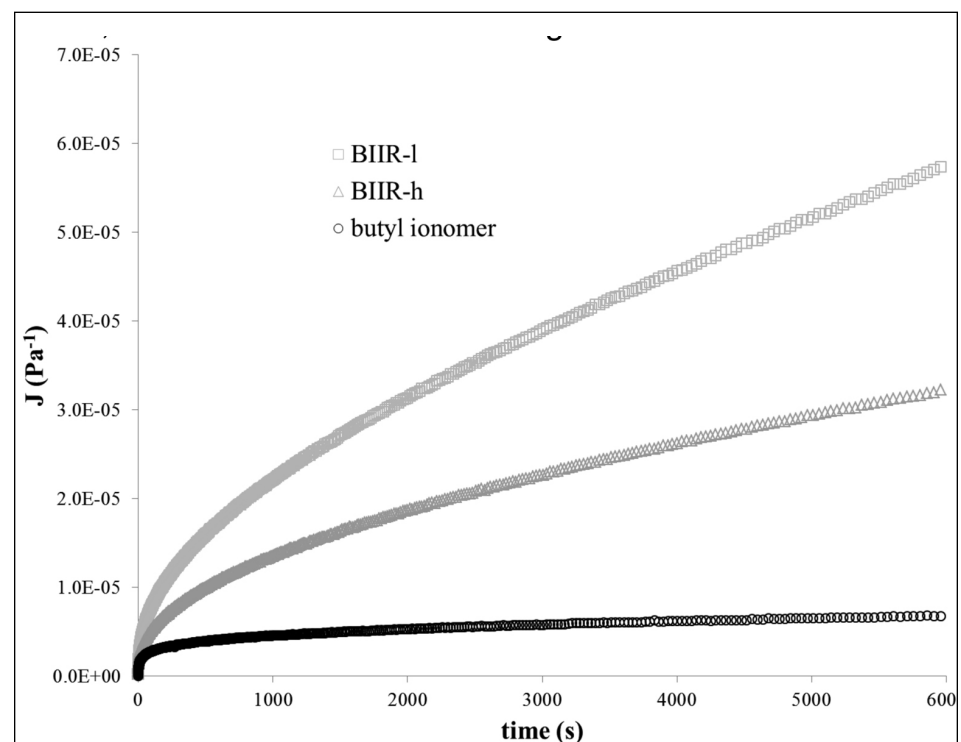
Most significantly an increase in the flex fatigue resistance and adhesion to a

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**Fig. 4. Temperature dependence of the modulus.**



**Fig. 5. Creep compliance of at 20°C.**



## Products

**Dow Automotive Systems** has launched Specflex Activ, the first viable amine emission-free polyurethane foam formulation for interior applications. This technology enables automotive seat pad foamers to meet the most stringent industry requirements, Dow Automotive said, such as the German original equipment manufacturer specifications including ultra-low emissions.

Traditional polyurethane foams require amine catalysts to promote reaction between polyols and water with the isocyanate component (the gelling and blowing reactions), Dow Automotive said. Previously, these added catalysts have contributed to amine emission issues with polyurethane foams and negatively impact physical and mechanical properties.

Specflex Activ has been tested and validated in an industrial setting by Faurecia, one of the leaders in automotive seating.

The Specflex Activ product includes a

new Dow Automotive additive polyol with high and specifically balanced catalytic activity. This formulation allows foam manufacturers to eliminate catalysts and amine emissions when manufacturing polyurethane foam.

For more information, go to [www.dow-automotive.com](http://www.dow-automotive.com).

**Synchro L.L.C.** has launched SyncAlert, a real-time notification and escalation software that enables manufacturing teams to quickly notify the right resource about problems and enable a rapid response, while tracking the results and minimizing costly downtime.

SyncAlert is an add-on designed to run in tandem with SyncOperations, a workflow engine and data historian for smart monitoring and synchronization, and SyncView software, a visual factory information system.

Features of SyncAlert include: Commu-

nicates alerts in real-time; mobilizes resources based on standard operating procedures; automatically escalates issues; views resources assigned to the escalation and the status; and captures and exports data including actual response time, escalation rates and machine-level problems.

SyncAlert software is part of the Synchro Demand-Driven Manufacturing Platform. For more information, including a video of the Platform, go to [www.synchro.com](http://www.synchro.com).

**Henkel Corp.** has introduced Loctite MR5898 foaming polyurethane for hydraulic roof support equipment used in longwall mining.

Loctite MR5898 foaming polyurethane is a pour-in-place foam material designed to bond to pockets and hydraulic cylinders. By foaming up to fill cavities and adhering to edges, this foam blocks out debris, particulates, teeth or tools

that might damage the equipment, Henkel said, yet is flexible enough to allow free movement of the hydraulic leg.

Loctite MR5898 foaming polyurethane replaces precut foam inserts that allow debris to get into cavities through gaps between inserts and equipment edges. This self-extinguishing, low-odor foam is intended for use underground and in confined spaces. The two-part formula begins to foam a few minutes after mixing, Henkel said, and becomes tack-free within minutes of pouring. The flexible cured foam can be cut or trimmed using a serrated blade, the company said.

Use of Loctite MR5898 foaming polyurethane ensures proper functioning of equipment, reduces downtime and prevents costly component replacement, Henkel said. The foaming polyurethane product is available in kit sizes.

For additional information, visit [www.henkelna.com/mining](http://www.henkelna.com/mining).

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carcass compound were observed for the BB-ION blend compounds, which should provide advantages for off-road tire applications where delamination and cracking can occur under high stresses.

These effects were observed without any detriment to the air retention or tear strength of the final cured articles.

In addition to the bromobutyl-based

inner liner compound, incorporation of 10-25 phr of the butyl ionomer has shown similar advantages with other polymers, including regular butyl, chlorobutyl, natural rubber, EPDM, SBS and blends thereof, allowing for the use of this novel polymer in both current butyl applications as well as new applications.

#### References

1. Lake, G.J.; Lindley P.B. *Rubber Journal*, 1964, 11:30.

2. Mars, W.V.; Fatemi, A. *Journal of Rubber Chemistry and Technology*, 2004, 77:391.

3. Earnest, T.R.; MacKnight, W.J. *Journal of Polymer Science, Polymer Physics Edition*, 1978, 16:143.

4. Eisenberg, A.; King, M. *Ion containing Polymers: Physical Properties and Structure*. New York: Academic Press, 1977.

5. Makowski, H.S. et al. *Ions in Polymers*. Washington: Adi Eisenberg, 1980.

6. Tant, M.; Wilkes, G.J. *Macromolecules*, 1988, C28: 1.

7. Lieber, L. et al. *Macromolecules*, 1991, 24:4701.

8. Vanhoorne, P.; Register, R.A. *Macromolecules*, 1996, 29: 598.

9. Tierney, N.K.; Register, R.A. *Macromolecules*, 2002, 35: 2358.

10. Parent, J.S. et al. *Journal of Polymer Science, Part A: Polymer Chemistry*, 2005, 43:5671.

11. Parent, J.S. et al. *Polymer*, 2004, 45:8091.

12. Parent, J.S. et al. *Macromolecules*, 2004, 37: 7477.

13. Parent, J.S. et al. (to Lanxess Inc.) U.S. Patent 7,238,736, July 3, 2007.

14. Adkinson, D.K. et al. (to Lanxess Inc.) International Patent Application No. PCT/CA10/000158, 2010.

15. Ferry, J.D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York (1980).

16. Fetters, L.J. et al. *Macromolecules*, 24, 3136 (1991).

17. Santangelo, P.G. et al. *Macromolecules*, 32, 1972 (1999).

18. de Gennes, P.G. *J. Chem. Phys.*, 55, 572 (1971).

19. Doi, M.; Edwards, S.F. *The Theory of Polymer Dynamics*; Clarendon: Oxford (1986); Likhtman, A.E.; McLeish, C.B. *Macromolecules*, 35, 6332 (2002).

20. Kim, J. et al. *Macromolecules*, 27, 6347 (1994).

21. Colby, R.H., et al. *Phys. Rev. Lett.*, 81, 3876 (1998).

22. Williams, M.L., et al., *J. Am. Chem. Soc.*, 77, 3701 (1955).

23. Plazek, D.J. et al. *Macromolecules*, 25, 4920 (1992).

24. Ngai, K.L., Plazek, D.J., *Rubber Chem. Tech. Rubber Rev.*, 68, 376 (1995).

25. Kunal, K. et al., *J. Poly. Sci. Part B: Poly. Phys.*, 46, 1390 (2008).

26. Ninomiya, K.J., *J. Phys. Chem.*, 67, 1152 (1963).

Table I: Tire inner liner formulations.

Compound	BB-CTRL	BB-ION10	BB-ION20
X_Butyl™ BB2030	100	90	80
X_Butyl™ I4565P	0	10	20
Stearic Acid	1	1	1
Resin SP1068	4	4	4
Sunpar 2280	7	7	7
N660 Carbon Black	60	60	60
Sulfur	0.5	0.5	0.5
MBTS	1.3	1.3	1.3
Zinc Oxide	3	3	3

Fig 6. Comparison of aged (168 h @ 100°C) flex fatigue properties of tire inner liner compounds.

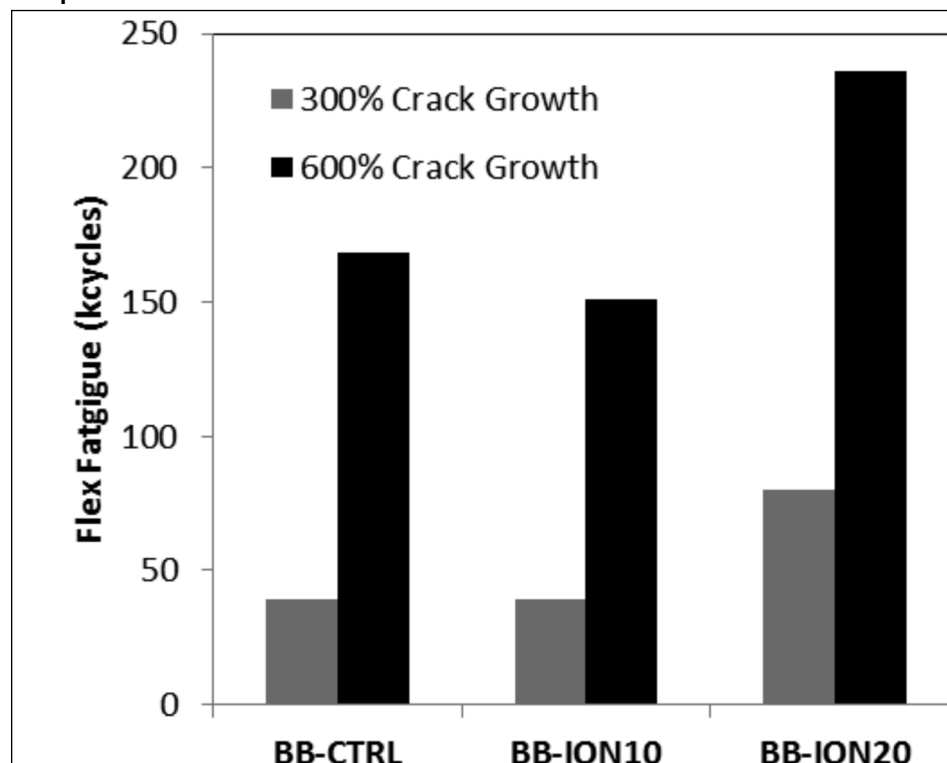


Table II: Compound properties for tire inner liner.

	BB-CTRL	BB-ION10	BB-ION20
M <sub>H</sub> (dNm @ 160°C)	9	10	10
M <sub>L</sub> (dNm @ 160°C)	2	3	3
M <sub>H</sub> -M <sub>L</sub> (dNm @ 160°C)	7	7	7
Mooney Viscosity (MU, ML 1+4 @ 100°C)	57	61	63
Mooney Scorch (min)	9	10	11
Green Strength			
Peak Stress (MPa)	0.27	0.35	0.45
Mill Shrinkage (%)	21	20	22

Table III: Selected properties for tire inner liner.

	BB-CTRL	BB-ION10	BB-ION
Unaged			
Shore A Hardness (Pts)	51	49	51
Ultimate Elongation (%)	713	688	739
Ultimate Tensile (MPa)	10.9	11.1	11.8
M25 (MPa)	0.6	0.7	0.7
M50 (MPa)	0.8	0.9	1.0
M100 (MPa)	1.2	1.4	1.5
M300 (MPa)	4.9	5.5	5.6
Permeability	185	186	189
Tear Strength (kN/m)	35	38	39
Adhesion to Carcass (kNm)	6	15	10
Aged (168 h @ 100°C)			
Ultimate Elongation (%)	457	539	590
Ultimate Tensile (MPa)	10.6	10.5	10.6
M25 (MPa)	1.0	0.9	0.9
M50 (MPa)	1.5	1.4	1.4
M100 (MPa)	2.8	2.5	2.5
M300 (MPa)	8.6	7.9	7.6