White paper

ExxonMobil

Why tire air retention matters now more than ever

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In a recent incident, a tractor-trailer crossed into the opposite lane and crashed head-on into a bus on Interstate 40 in New Mexico.[1] Seven passengers on the bus lost their lives. Authorities believe steer tire blowout caused the crash, and in news camera images, the suspected steer tire shows signs of being underinflated before it blew out. According to an industry expert, creeping air loss causes 80% of tire blowouts. Just 5 psi lower air pressure in a steer tire can change a truck's fate from reaching its destination safely to ending up in a tragic mess.[1,2]

As we enter a new phase of mobility, led by the growing presence of electric vehicles, which make greater demands on tires due to their heavier weight and instant torque, proper inflation becomes even more critical. Unfortunately, most consumers think that tire pressure remains constant – that radial tires are leak-proof. In truth, they continuously lose air. The percentage of air lost by a tire in a month is referred to as the inflation pressure loss rate (IPLR). The monthly average IPLR is 2.4%.[3] In continuous dynamic on-road conditions, it's double that amount.[4] That's 42% air lost in a year. See the problem?

Tire inflation impacts performance

The safety risks of underinflated tires are clear. Underinflation can lead to poor fuel efficiency, sluggish handling, longer stopping distances, high uneven tire wear, increased component stresses within the tire and subsequent heat buildup.[5] This buildup can cause the tire to fail prematurely or even catastrophically (such as belt separation or blowout). A study by the U.S. National Highway Traffic Safety Administration (NHTSA) revealed that 16% of tire-related crashes were due to tires that were underinflated by 10% or more.[6]

Looking beyond safety, consider performance. The tire industry spends billions of dollars every year on research and development to meet or exceed the growing regulatory and performance expectations of tires regarding fuel efficiency, traction, braking, noise, comfort, mileage, durability, wear and chip/chunk resistance. However, the effect of all these improvements can be realized in a meaningful way only if the tire retains its full recommended inflation pressure.

The issue of underinflation is worsening due to extended service intervals caused by advances in engine technologies and synthetic lubricants. The longer we can go without having our vehicles serviced, the longer the time between tire pressure checks. With the radical changes in mobility happening now (and with many more on the horizon), we need, more than ever before, maintenance-free tires with the lowest possible air-loss rates.

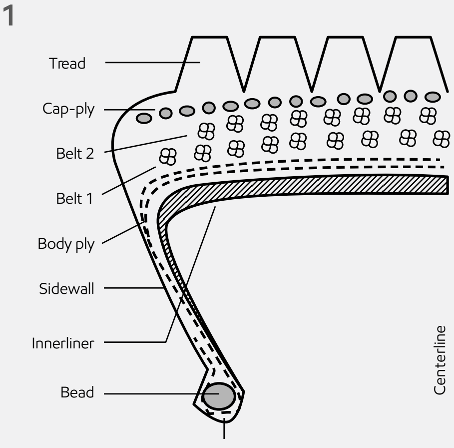
Finding solutions

Air retention is primarily governed by the thin innermost layer of the tire often referred to as the "innerliner."[7] To effectively design tires with low air-loss rates, we must consider the three main factors affecting air retention:[7]

1. Innerliner compound permeability
2. Innerliner thickness
3. Innerliner end point

Permeability is the rate at which molecules pass through a material at a given pressure and temperature. Low innerliner permeability, high innerliner thickness and low innerliner end point-to-toe distance will lead to better air retention. Studies done by ExxonMobil show that the biggest contributor to air-loss reduction is permeability. While decreasing innerliner end-to-toe distance by 50% (from 20 mm to 10 mm) improves IPLR by 10%, reducing the permeability coefficient by 40% improves IPLR by 30% (**Figure 1**).[7]

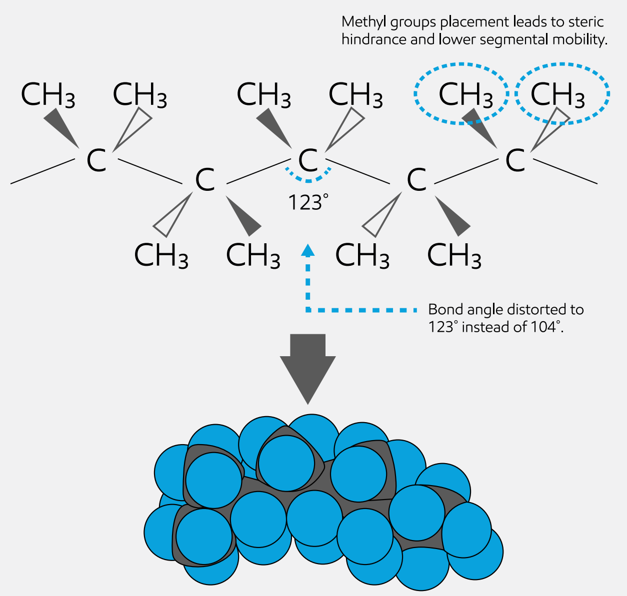
Figure 1



To make tire innerliners, rubbers with low permeability have to be compounded with other ingredients to impart strength and processability and to enable crosslinking. The type and amount of these ingredients directly affect permeability. For the past six decades, the polymer of choice for innerliners has been halogenated isobutylene-isoprene elastomers (halobutyl) – namely bromobutyl and chlorobutyl. Almost all the other layers (carcass, belts, sidewalls, overlays, sub-tread and tread) use either natural rubber (NR), styrene butadiene rubber (SBR), butadiene rubber (BR) or a combination of these polymers. These ingredients all have much higher permeability than halobutyl polymers.

The contribution of these other layers to tire air retention is almost insignificant because natural rubber and styrene butadiene rubbers have carbon-carbon bonds at 109° (the classic tetrahedral bond angle).[8] In butyl, the angle is stretched to 123° due to placement of the methyl groups, thereby leading to lower segmental mobility. The closer the angle between the carbons is to 180°, the flatter it is. In this way, it enables the packing of more polymer chains, and the oxygen molecules will have to struggle more to escape (**Figure 2**).

Figure 2



Chain straightening in polyisobutylene results in effective packing.

The high packing density of isobutylene chains enables ultra-low permeability. However, if the polymer consists of only isobutylene, then it cannot be crosslinked into a hard rubber. The presence of low amounts of isoprene in the main chain enables crosslinking to other unsaturated elastomers and to itself (i.e., it can be cured). The halogen substitution (such as bromine or chlorine) enhances bonding to the inside of the tire carcass layer, facilitating manufacture of tubeless radial tires.

In innerliner compounds, fillers (carbon blacks) are used to render strength and processability. Resins, tackifiers and secondary polymers (like natural rubber) are used to achieve the right viscosity, improve processability and provide sufficient green tack and good adhesion to adjoining layers. Small amounts of clays are used to improve barrier characteristics and green tack. Curing agents (zinc oxide, stearic acid sulfur and accelerators) are used to achieve the desired crosslink density in a desired time frame.

Generally speaking, permeability is reduced by minimizing low molecular weight materials, such as oils, and eliminating secondary polymers, such as natural rubber. However, these modifications undermine processability and productivity, and manufacturers must find the right balance. If the limits of these ingredients have been reached, then the only way to reduce air loss further is by using a polymer with lower permeability.

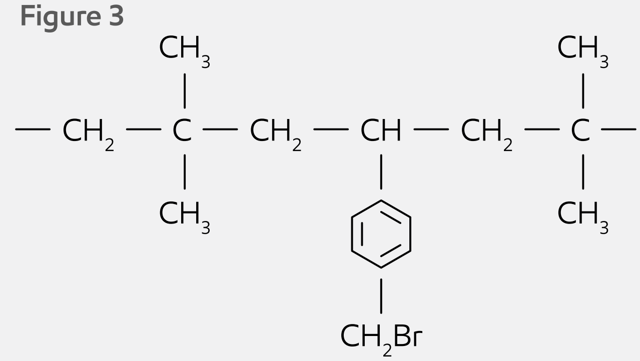
It is also worthwhile to note that tires run hot. Due to unsaturation in the molecular backbone (i.e., carbon-carbon double bonds, from isoprene in the backbone), halobutyl polymers are prone to oxidation via heat and ozone (via cleavage of the double bonds). This tendency can lead to cracking and innerliner split problems during running conditions. Hence, it would be valuable to have a new polymer, not only with an intrinsically lower permeability than halobutyl, but one containing a fully saturated backbone.

Improving permeability

ExxonMobil has developed a class of fully saturated specialty elastomer by the carbocationic polymerization of isobutylene and para-methyl styrene (pMS) followed by halogenation, thereby completely eliminating isoprene. These elastomers were known as brominated isobutylene-co-paramethylstyrene (BIMSM) and have been commercialized under the trade name Exxpro™ specialty elastomers (**Figure 3**).[7]

Exxpro specialty elastomer has several advantages over halobutyl polymers, including a fully saturated backbone, which enables exceptional chemical and oxidation stability. The elastomer also has increased chain stiffness and better packing density with benzylic bromide groups in the chain. This structure creates a

Figure 3



much more tortuous path for oxygen molecules, enabling much lower permeability than halobutyl polymers. Since crosslinking occurs via substitution of the benzylic bromide groups, these systems can be cured sulfur-free.[9]

Exxpro™ specialty elastomer is used in many industrial applications, including pharmaceutical stoppers, curing bladders, envelopes, high-temperature-resistant inner tubes, hoses (covers and tubes), adhesives and some industrial rubber components.[10] However, use of Exxpro in innerliners has been very limited for several reasons. Because Exxpro was initially developed for high heat resistance, the focus was not on permeability. For Exxpro to offer step-change innerliner performance, its permeability needed to be significantly decreased and hence its content increased, which took a toll in engineering, manufacturing and finishing.

The viscosity of the commercialized Exxpro grades was higher than those generally used for innerliner applications. This higher viscosity added complexity to continuous manufacturing (due to sticking and agglomeration). Several process and engineering modifications were required to achieve the desired balance of permeability improvement and viscosity. After five industrial trials and close to a thousand formulations, the right formulation with a low viscosity that simplifies the innerlinner process was achieved. It's called Exxpro™ 3563.

Exxpro 3563 specialty elastomer[7]

The benefits of this specialty elastomer as an innerliner material are evident from its compound characteristics. When comparing it with bromobutyl, three main aspects – **processability, consistency and performance** – need to be considered.

Processability. For this comparison, two main compound indicators – green strength and shrinkage – were evaluated. Green strength is a measure of the force required to stretch the uncured compound (not crosslinked yet) to a certain length. For good processability, innerliner compounds are expected to have the highest green strength, which indicates better resistance to stretching and application on the tire-building drum. Exxpro 3563 shows ~30% higher green strength than bromobutyl (**Figure 4a**). When the innerliner is calendared or extruded to form a sheet, it tends to shrink in the machine direction, affecting its dimensional stability. Exxpro 3563 demonstrated approximately one-third less shrinkage than bromobutyl (**Figure 4b**).

Consistency. Advanced imaging techniques (in this case, bimodal atomic force microscopy) were used to study the distribution of the carbon black filler in innerliner systems. Exxpro 3563 enabled much better dispersion and smaller sizes of carbon black particles than bromobutyl (**Figure 5**), indicating better consistency, which is an indicator of better product quality and uniformity.

Figure 4a

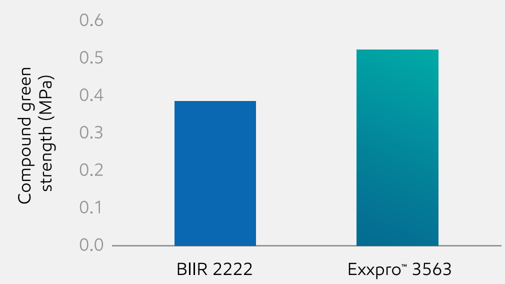


Figure 4b

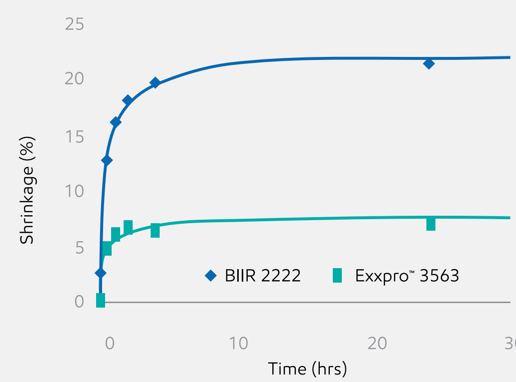
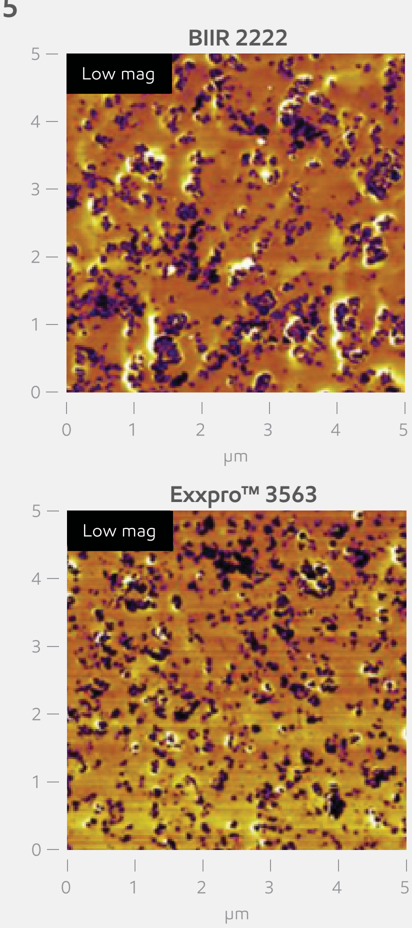


Figure 5



Performance. When innerliner compounds are heated for long periods of time (after curing), cleavage of double bonds causes halobutyl polymers to degrade (called reversion). While bromobutyl shows some reversion, Exxpro™ 3563 shows none (**Figure 6a**).

The permeability of Exxpro 3563 compounds is ~20–30% lower than bromobutyl (**Figure 6b**). Tires with Exxpro-based innerliners showed an overall 15% lower inflation pressure loss rate (**Figure 7**) leading to lower pressure build-up in the carcass area. In tires with superior innerliner systems, fewer oxygen molecules permeate through the innerliners into the belt edge regions. In other words, the rubber around the belt ends oxidizes less, reducing belt edge cracking, which leads to longer tire life and enhanced safety.

Figure 7

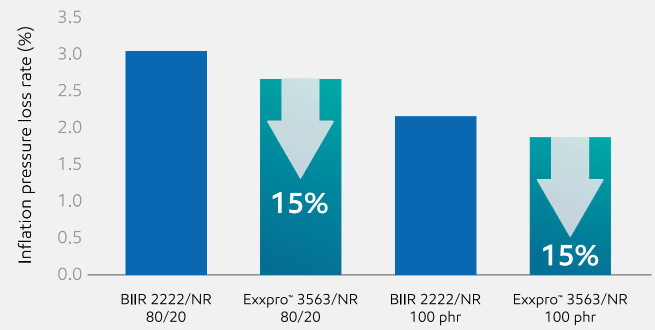


Figure 6a

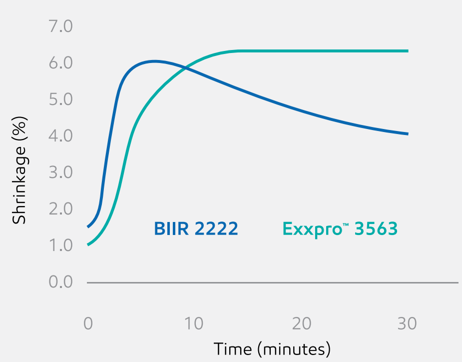
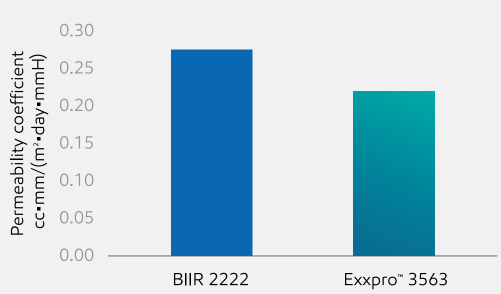


Figure 6b



Conclusion

ExxonMobil internal surveys have shown that consumers typically do not maintain their tires very well. To help mitigate personal injury or even loss of life, we, as an industry, must provide the consumer with tires that hold air better. Air retention helps sustain true tire performance and improve vehicle handling. As the mobility sector shifts to more electric and autonomous drive systems, which make greater demands on tires, maintaining consistent in-use performance is more important than ever.

Exxpro 3563-based innerliners provide a solution. They can provide as much as 46% improvement in IPLR over current industry standard blends, reduce wear and rolling resistance, and improve vehicle handling.

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To learn more about Exxpro 3563™ specialty elastomer, contact us at **www.exxonmobilchemical.com/contactsujith**.

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