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Passenger tires inflated with nitrogen age slower: Part 2 of 2

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Results and discussion

As stated in the introduction, the wedge rubber is one of the most important components of the tire construction related to durability. One of the more useful ways to analyze the change in properties of the wedge rubber is to utilize the data analysis method of Ahagon and co-workers, which correlates the strain ratio at break with the modulus at 100-percent strain.[8,9,10]

This approach is particularly useful in distinguishing between different aging mechanisms. By plotting the log of the strain ratio at break vs. the log of the modulus at 100-percent strain, a straight line with a slope of -0.75 is indicative of the aerobic aging of rubber. This approach was arrived at by taking one compound with different levels of sulfur and measuring the stress-strain data. The same compound (at one level of sulfur) was then oxidatively aged and it was shown that the stress-strain data behaved identically to the compounds with increased sulfur. Thus, the mechanism of oxidative aging was inferred to consist of increased crosslink formation. High temperature aerobic (defined as Type III aging) or possibly anaerobic aging (defined as Type II aging) of the rubber results in data deviating from the straight line.

It is important to realize that the slope of -0.75 is an empirically derived number and more than likely dependent on the aging characteristics of the individual compound being studied. Careful reading of the referenced studies does not yield a ``first principles'' reason for the slope to be any particular value. Fig. 2 is a representation of how data for the various aging types would look in graphic form. Aerobically aging NR typically stress hardens, leading to lower elongation, which yields a prediction of a negative slope, given the data treatment shown.

Fig. 3 shows the results for the tires in the present study plotted in the manner described above. The nitrogen concentrations in the tire cavity at the beginning of oven aging for the four filling gas conditions were (in ascending order): 56 percent (the 50/50 N2/O2 inflation blend with 1 atmosphere of air present), 78 percent (air inflation), 96 percent (99.9 percent nitrogen with 1 atmosphere of air present), and 99.9 percent (99.9 percent nitrogen with the 1 atmosphere of air purged). The tires were aged at 60°C for three to 12 weeks. As can be seen in Fig. 3, the wedge rubber of the tires containing more than 95 percent nitrogen experienced almost no change in stress-strain properties, even after 12 weeks in the oven, while tires filled with air or 50/50 N2/O2 experienced a substantial change after only three weeks of oven aging. The changes seen in the data for tires inflated with more than 95 percent nitrogen are consistent with completion of curing of the new tire, not oxidative aging. The excluded points on the graph are for tires with air and the 50/50 N2/O2 mixture at 12 weeks in the oven. The mechanism of aging has been affected by loss of oxygen due to permeability over that time and the oxidation of the wedge rubber has become limited by diffusion.

An additional method used to analyze the data was to plot the normalized strain ratio at break vs. residence time in the ovens at 60°C (Fig. 4). Normalized strain ratio at break is determined by dividing the strain at break of a tire aged in the oven for time t (e(t)) and dividing it by the strain at break for a new, unaged tire (e(0)). The results in Fig. 4 show that for tires inflated with more than 95 percent nitrogen there is an initial drop in strain at break. The reason for that again could be that new tires generally are undercured and the continuation of cure was completed during the first three weeks in the oven.

After the first three weeks, the results are unchanged for the durations tested, except for the point at 12 weeks oven duration and 96 percent nitrogen concentration. It may be that the oxygen concentration present in the tire took that long to reach the wedge in concentrations large enough to affect the strain at break properties. Again, tires filled with air or 50/50 N2/O2 experienced a substantial change after only three weeks of oven aging and continued that trend out to 12 weeks.

One conclusion that is inescapable from this initial work is that the oxidation of the steel belt rubber truly is driven from the contained air pressure inside a normal passenger or light truck tire. Granted, the rate of degradation would be much higher if no halobutyl innerliner was present, but the presence of innerliner and antioxidant packages only slows the rate of degradation, not eliminating it.

Peel strengths of the steel belt composites also were evaluated. The peel strength is a measure of the force required to separate the two steel belts and is a simple way to measure tearing energy.11 Fig. 5 shows the results of the normalized peel strength vs. log time. Normalized peel strength is determined by dividing the peel strength of a tire aged in the oven for time t (p(t)) and dividing it by the peel strength for a new, unaged tire (p(0)).

As opposed to the results for the strain at break of material obtained from the wedge region of the tire, the peel strength of rubber from the much thinner skim region does degrade with time for all inflation media used in the study. The results in Fig. 5 also show, however, that the tires inflated with more than 95 percent nitrogen degrade at a much slower pace than tires inflated with air or 50/50 N2/O2. The fact that tires inflated with either 96 percent or 99.9 percent nitrogen degrade almost identically leads one to believe that either oxygen is reaching the belt skim rubber from the outside of the tire or that the change in peel strength is due to a change in the crosslink density distribution not detected in the wedge material properties. Both mechanisms are being investigated and will be reported in future work. Oxygen uptake measurements are being taken on the skim stock to determine whether oxygen is reaching the area from another source and crosslink distribution measurements are being made to determine if any sulfur rearrangements have occurred.

The data shown in Fig. 5, however, all appear to be changing according to the same mechanism. If that is true, then one should be able to shift the data according to a time-pressure superposition method to determine the acceleration of the degradation mechanism present. Ferry has shown that ultimate properties can be analyzed using reduced variables and shifted with respect to temperature or pressure.12 In this case, the partial pressure of oxygen is different between the four conditions analyzed.

Fig. 6 is a graph of the normalized peel data whereby the data for tires inflated with air or 50/50 N2/O2 are shifted along the x-axis to line up with data from tires inflated with more than 95 percent nitrogen. The data shifts overlap and appear to have an excellent fit to a logarithmic regression. This fact suggests that the change in the peel strength for nitrogen-inflated tires is caused by oxidation in the skim rubber, not by changes in the crosslink distribution.

One could infer from the shift factor between air and nitrogen inflation that tires inflated with nitrogen would take twice as long to deteriorate as air-inflated tires would. While this may be true at 60°C, the magnitude of improvement may be lessened if the data were shifted down to temperatures that tires operate at normally. The discrepancy would be caused by possible diffusion limited oxidation effects at 60°C vs. ambient temperature. The concentration of oxygen diffusing into the tire may be sufficiently low enough in the oven so that it never reaches the wedge and only small amounts reach the skim because at elevated temperatures the oxygen reactivity is increased. At ambient temperature, however, more oxygen may reach the skim and perhaps even reach the wedge. This is not to say that tire oxidation is not driven by the inside air pressure, just that in the absence of inside air pressure, oxidation in the wedge and skim regions may occur from outside air and the rate could be higher than what is reported at 60°C. Nonetheless, it is perhaps a fair assumption to say that there would be some improvement in tire durability if nitrogen was used as the inflation media, but it is too soon to speculate as to how much of an improvement it would be.

Conclusions

The overall conclusion of the study is: When N2 is used as the inflation media, the change in rubber properties is slowed down significantly or even halted. From a practical standpoint it is important to note that the presence of 1 atmosphere of air in the 96 percent nitrogen-inflated tires did not significantly affect the results, as compared to the 99.9 percent nitrogen-inflated tire. This is important for the average consumer because the need to purge existing tires completely of air before filling with nitrogen may not be necessary.

Another conclusion is that the oxidation of the steel belt rubber truly is driven from the contained air pressure inside a normal passenger or light truck tire. The skim region may be oxidized slightly from outside the tire when filled with nitrogen, but the rate of degradation is significantly lower than when the tire is filled with air. The wedge rubber, on the other hand, is in a sufficiently thick part of the tire, and is not nearly as susceptible to oxidation from the outside. The converse of this conclusion, therefore, is that oxidative aging can be accelerated by the use of oxygen enriched filling gases in the tire cavity without changing the mechanism of degradation in the tire's internal components.

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