Application of modulus profiling to understand aging in rubber and plastic components

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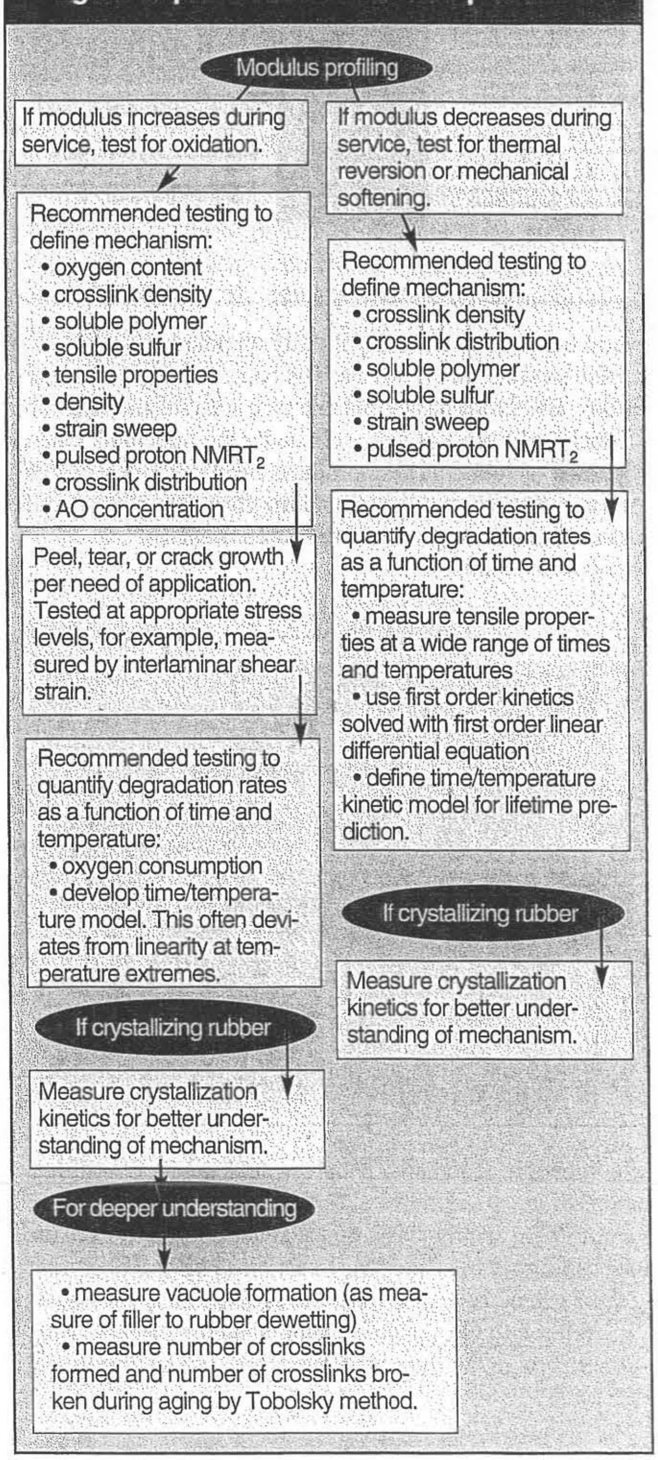
A series of controlled aging experiments (laboratory and service) were conducted on a variety of rubber and plastic components. After laboratory and service aging conditions, we studied the modulus changes using the modulus profiling technique pioneered by K. Gillen (refs. 1-3). The location and extent of aging was determined. The modulus changes in both the exterior and interior regions were quantified, thereby quantifying the location and extent of aging within the component. In earlier work, modulus profiling was applied to tire aging (ref. 6). Now, this technique is extended to other products, both rubber and plastic components. A variety of components was studied, including hose, v-belt, wiper blade, o-ring, rubber band, tread surface, cable jacket and polycarbonate. A rationale is presented in consideration of the concomitant changes in modulus due to effects of oxidation and mechanical energy. The technique has improved our understanding of aging in a wide variety of products.

Strategy for determining service life prediction

The guidelines shown in figure 1 serve as a strategy for establishing service life prediction in rubber and plastic products. The first step in this protocol is to establish the degradation mechanism. There are two key degradation mechanisms in rubber, namely oxidation and thermal reversion. Oxidation is the primary degradation mechanism in rubber products, and it is usually accompanied by an increase in the modulus of the product. The second major degradation mechanism is thermal reversion. When the service temperature is above 80°C, rubber products based on natural rubber experience significant rates of thermal reversion. Reversion is associated with loss of modulus and loss of polysulfidic bonds. Finally, there are other degradation mechanisms that could be important. These include mechanical softening, ultraviolet light, ozone and radiation. One of the most illustrative techniques to characterize the location and type of degradation is modulus profiling. Based on the modulus profile results, a different set of tests would be pursued to confirm the mechanism. After confirming the mechanism, a correlation to key physical properties would be determined. From this knowledge, a time and temperature model can be established for lifetime prediction. An outline of this service life prediction protocol is shown in figure 1.

The first step in this service life prediction protocol is the application of modulus profiling to begin to define the degradation mechanism. Modulus profiling has been illustrative to understand the key mechanism governing the degradation (refs. 3-6). Modulus profiling values agree with literature and measured modulus values by other measurement techniques (refs. 1-3). In this article, we have applied the technique to a wide range of rubber and plastic components to understand their aging mechanisms. This work includes hose, v-belt, wiper blade, o-ring, rubber band, tread surface, cable jacket and polycarbonate sheet. The results illustrate how modulus profiling directs the testing program

Figure 1 - protocol for service life prediction



for the predictive model, eliminates unnecessary steps, and quantifies the aging.

Effect of testing on automotive hose

The aging behavior of an automotive coolant hose was examined. Modulus profiling was completed on new and tested automotive coolant hoses to understand the effect of the circulation test on the hose. Automotive coolant hoses were profiled before and after testing. During the circulation test, fluid was circulated through the hose at 130°C for 400 hours. Three pieces from the hose were mounted in a holder, as shown in figure 2. The yellow dashed line in figure 2 indicates the approximate test location of the indentations. The modulus profiles were measured from inside to outside. The inner compound increased in modulus from 4.5 to 6 MPa during testing, and the outer compound increased in modulus from 7 to 11 MPa during testing (figure 3). Presumably, oxidation is the major degradation mechanism. Automotive coolant hose testing was accompanied by major property changes to the hose.

Figure 2 - optical micrograph of automotive hose

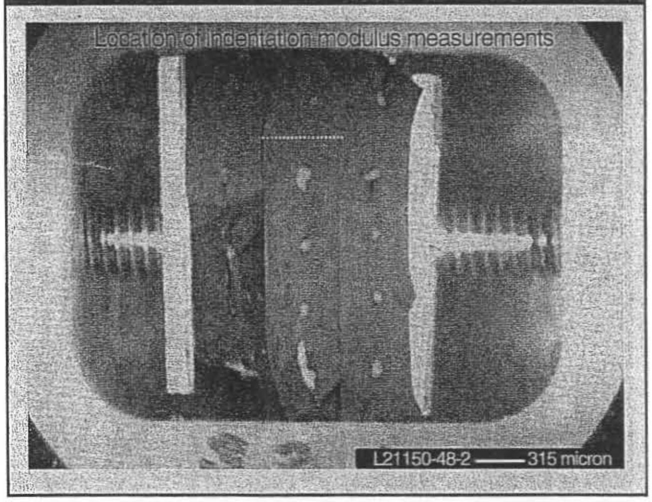
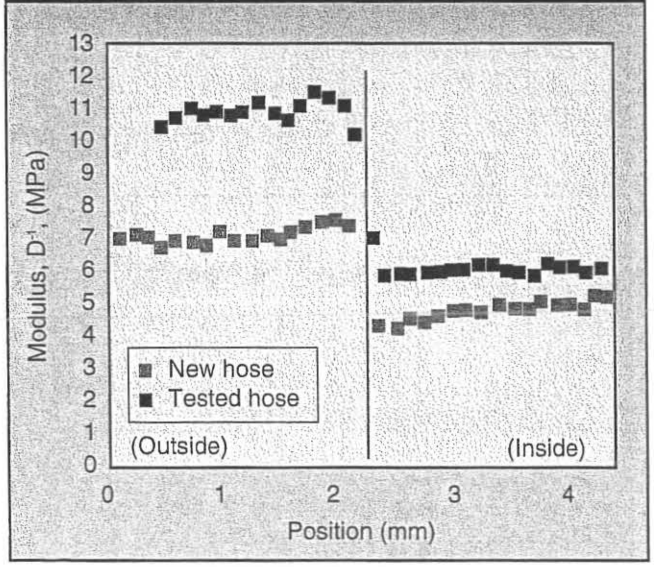


Figure 3 - effect of testing on automotive hose modulus profile



Effect of service on automotive v-belt

The aging behavior of an automotive v-belt was examined. The v-belts were Ford Motorcraft serpentine drive belts (JK6-967, XF2Z-8620-CB). The used belt had 77,773 miles on a 1999 Ford Windstar. Four pieces of v-belts were mounted in a holder, as shown in figure 4, for modulus profiling. There was more scatter in the modulus data associated with the presence of short fibers in the compounds. During service, the modulus decreased from 20 to 16 MPa (figure 5). Presumably, the dominant aging mechanism is mechanical softening.

Effect of service on automotive wiper blade

To understand the aging mechanism in automotive wiper blades, profiling was completed on new and used blades.

Figure 4 - optical micrograph of automotive v-belt

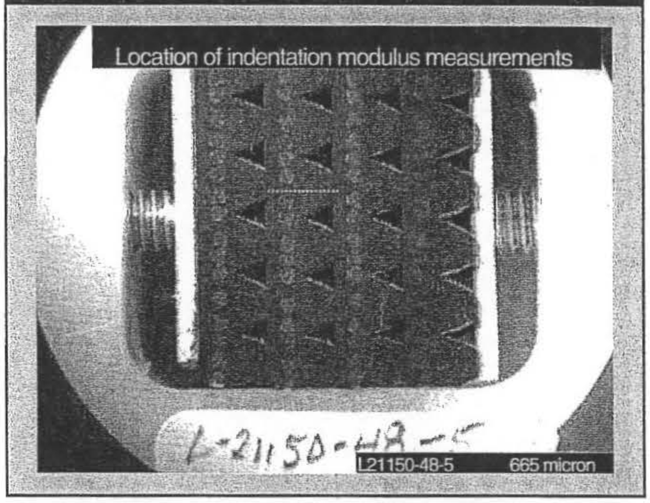
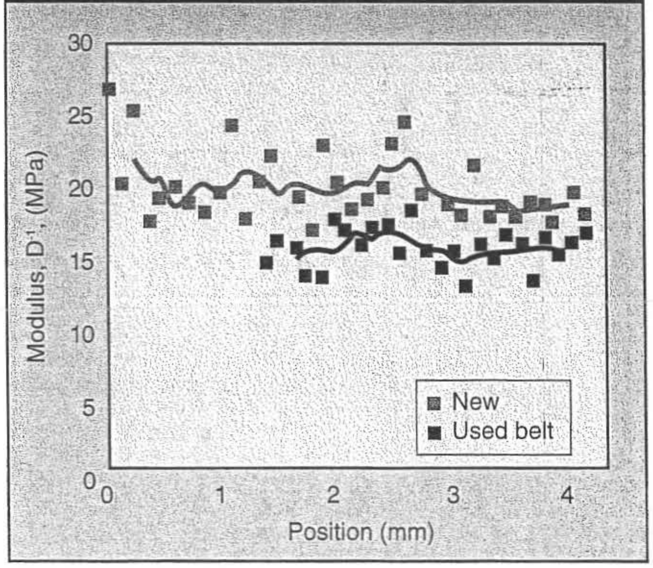


Figure 5 - effect of service on automotive v-belt modulus profile



The wiper blades were Anco Kwik Connect Federal Mogul 31-20 508 mm. The used wiper blade was in service for one year on a Ford Windstar in northeast Ohio. Three pieces of a wiper blade were mounted in a holder, as shown in figure 6. The surface of the new blade had higher modulus than the sub-surface, presumably from surface treatments used in manufacturing. During service, the modulus increased from 3.6 to 4.6 MPa (figure 7). Presumably, the dominant aging mechanism is oxidation.

Comparison of new and used o-rings

To understand the aging mechanism in a 90 durometer fluorocarbon elastomer 0.275 inch diameter o-ring, profiling was completed on new and used o-rings. The used o-ring was in service for 16 years. Pieces of o-rings were mounted in a holder, as shown in figure 8. The surface modulus of the new o-ring had higher modulus than the sub-surface. The 16-year-old o-ring had lower modulus than the new o-ring, 20 MPa and 13 MPa, respectively (figure 9). The background on the compounds and changes to the compound over 16 years would need to be verified before making conclusions on the aging mechanism in this o-ring. There could have been compound and/or production changes in combination with the aging effects in this comparison.

Figure 6 - optical micrograph of automotive wiper blade

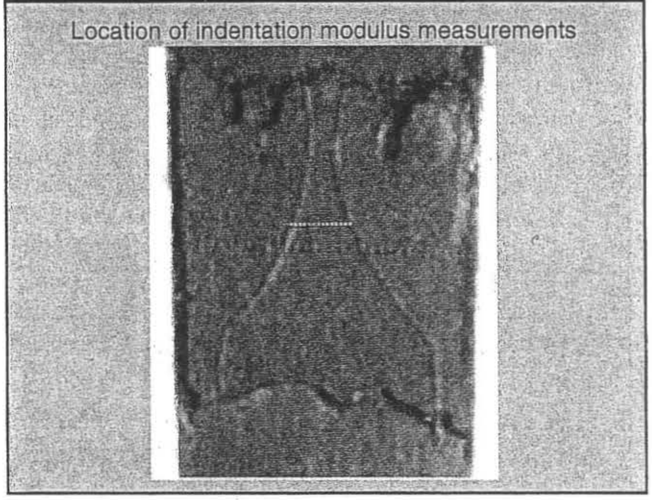
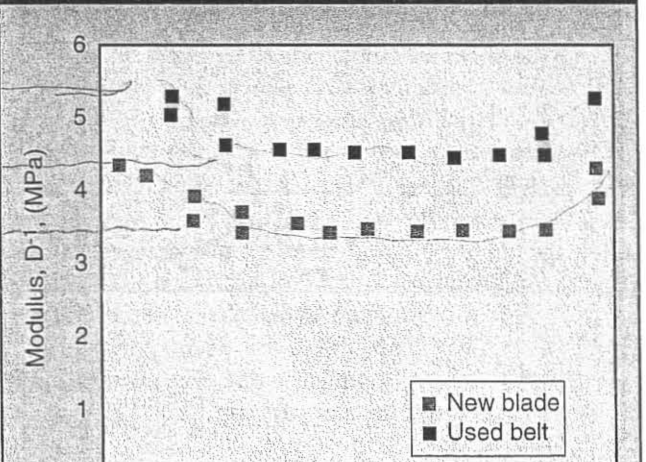


Figure 7 - effect of service on automotive wiper blade modulus profile



913

623

493

Modulus

.008 ,016 ,024 ,032 ,040 ,044

INCHES

Effect of outdoor exposure on rubber bands

To understand the aging mechanisms in rubber bands, profiling was completed on new, tested and used rubber bands. The new and tested rubber bands were OfficeMax brand rubber bands. The used rubber band had aged on an asphalt road in Tennessee for at least one year. Seven pieces of a rubber band were mounted in a holder, as shown in figure 10. During outdoor exposure, the surface modulus dramatically increased (from 2 to about 10 MPa) (figure 11). In comparison, no modulus change was observed after oven aging at 50°C for five weeks, indicating field conditions were more severe. Presumably, oxidation in the presence of ultraviolet light was the predominant aging mechanism in the field.

Figure 8 - optical micrograph of o-ring

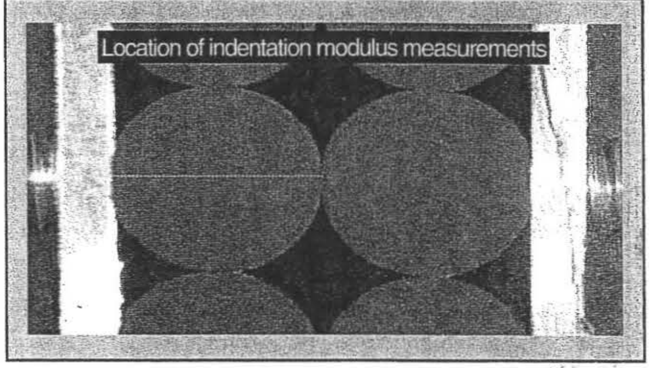
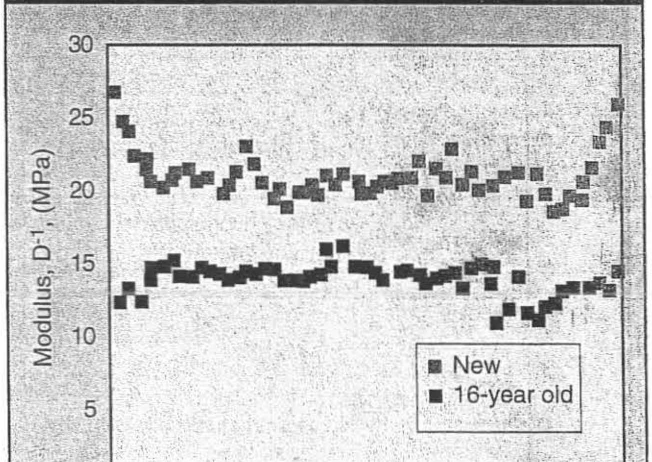


Figure 9 - effect of service on o-ring modulus profile



Worn passenger tire tread surface

To understand the aging mechanisms in passenger tire treads, profiling was completed on new and worn tires. We examined the tread surface of passenger tires to understand their degradation mechanism. The first tire was a Goodyear Regatta 2 P215/75R15 tire. The worn tire had 1.3 years of service and 23,410 miles on the right front position of a 1999 Ford Windstar. Worn surfaces were mounted face to face in a holder, as shown in figure 12. During service, the tread sub-surface modulus increased from 3 to about 4.3 MPa, depen-ding on lug position. The tread surface increased from 3 to about 4.8 MPa, depending on lug position (figure 13). The second series of tires were BFGoodrich Touring T/A P197/ 65R15 tires with various service histories. One worn tire had three years of service and 23,199 miles. A second worn tire had five years of service and 51,392 miles. The new tire had a thin (about 0.1 mm) high-modulus layer on the tread surface. During service, the tread sub-surface modulus in-creased from 5.5 to 6.5 MPa in three years, and then to 7.6 MPa after five years. During service, the tread surface modulus increased from 6 to 8 MPa in three years, and then to 9 MPa after five years. The dominant aging mechanism is oxidation. Presumably, the tread surface oxidizes faster than the sub-surface because mechanical scrubbing and higher temperatures during treadwear accelerate oxidation (figure 14).

Effect of service on cable jacket

To understand the aging mechanism in the small polyolefin component of a power plant cable, profiling was completed on new and used cables. The cables were Rockbestos RSS-6-104 with polyolefin jacket material. The used cable was from a nuclear power plant. The cable consists of multiple layers. The jacket layers included an outer wrap, a polyolefin layer and center polyolefin layer. Pieces of cable were

Figure 10 - optical micrograph of rubber band

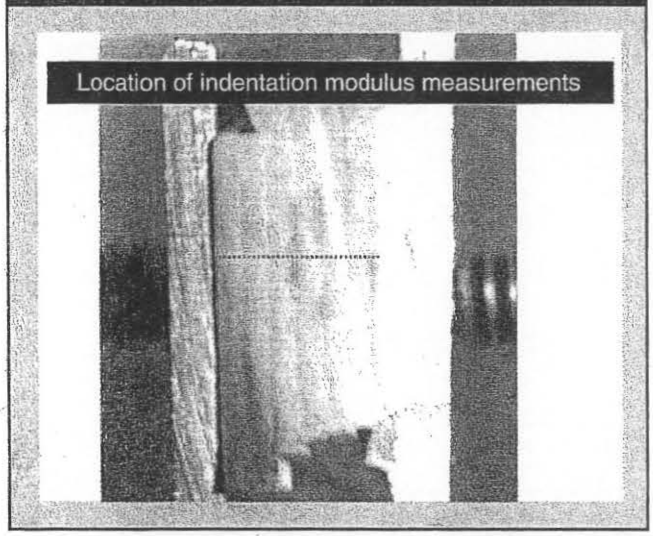


Figure 11 - effect of service on rubber band modulus profile

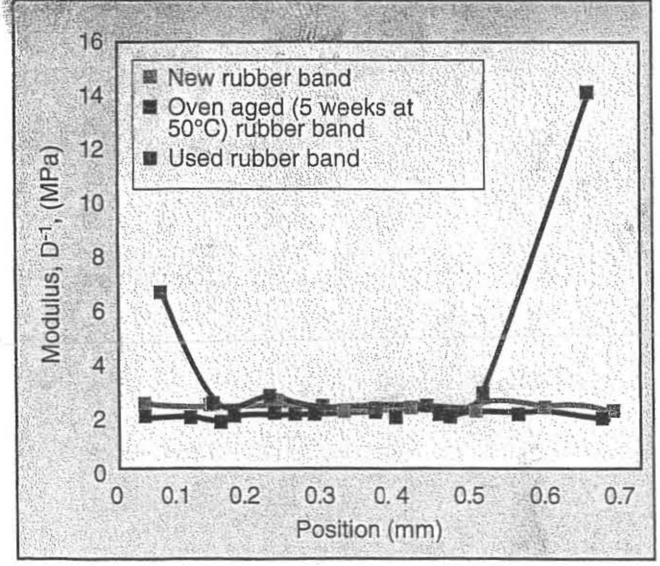


Figure 12 - optical micrograph of worn tread surfaces

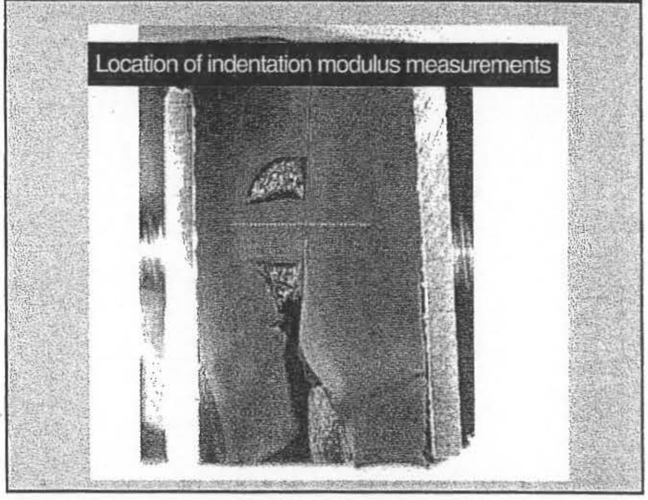
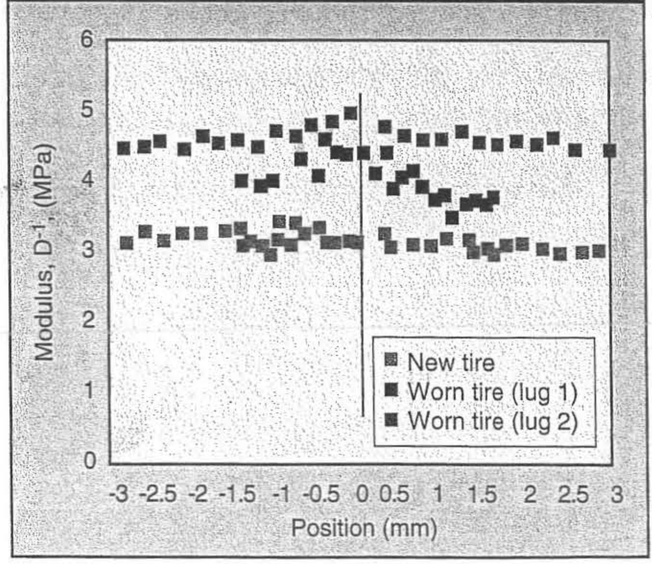


Figure 13 - effect of service on tire tread surface



mounted in a holder, as shown in figure 15. During service, the polyolefin modulus increased from 80 to 105 MPa. Presumably, the dominant aging mechanism was oxidation.

Effect of oven aging on polycarbonate sheet

To begin to characterize the aging mechanism in polycarbonate sheet, profiling was completed on new and oven aged sheets. The samples were unfilled polycarbonate Sheffield Plastics, Bayer. Hyzod polycarbonate sheet. The sheet was aged for various times at 100°C. Two pieces of polycarbonate sheet were mounted in a holder, as shown in figure 17. During oven aging, the modulus did not change. Hyzod polycarbonate did not significantly change under these aging conditions.

Conclusions

In the determination of aging mechanism(s) in rubber and plastic components, modulus profiling was able to provide significant insight. Modulus profiling identified key degradation mechanism(s), quantified the degradation and provided an approach to lifetime prediction modeling.

Multiple aging behaviors were found in rubber and plastic components by modulus profiling. A preliminary determination of the aging mechanism was made in each case. In two examples, oxidation led to hardening in the sample (hose and wiper blade). In one sample, surface oxidative hardening was presumably induced by UV radiation exposure (rubber band). Passenger tire treads had surface oxidative hardening possibly catalyzed by mechanical scuffing and heat during treadwear. In v-belts, mechanical softening was probably the dominant aging mechanism. In one case, oxidative hardening was observed in polyolefin plastic cable jacket.

The dominant degradation mechanism appears to depend heavily on the service conditions and compound.

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Figure 14 - effect of service on tire tread surface

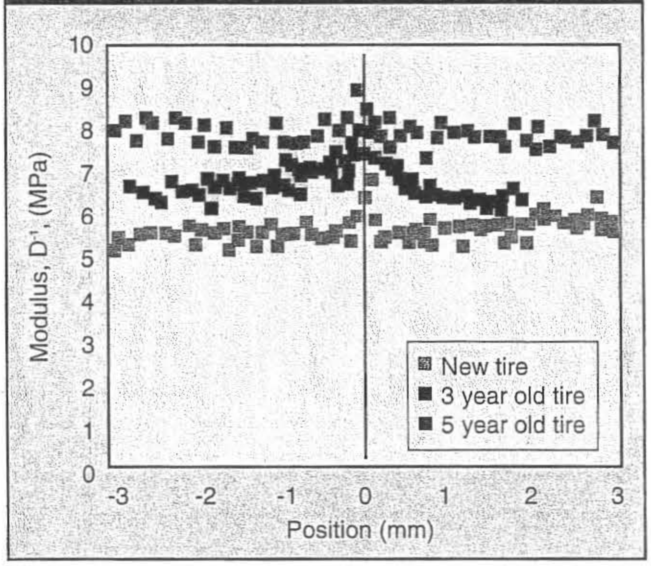


Figure 15 - optical micrograph of power plant cable

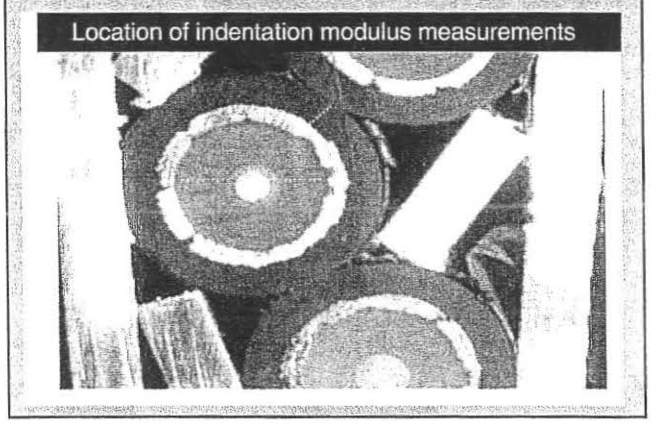


Figure 16 - effect of service on cable jacket

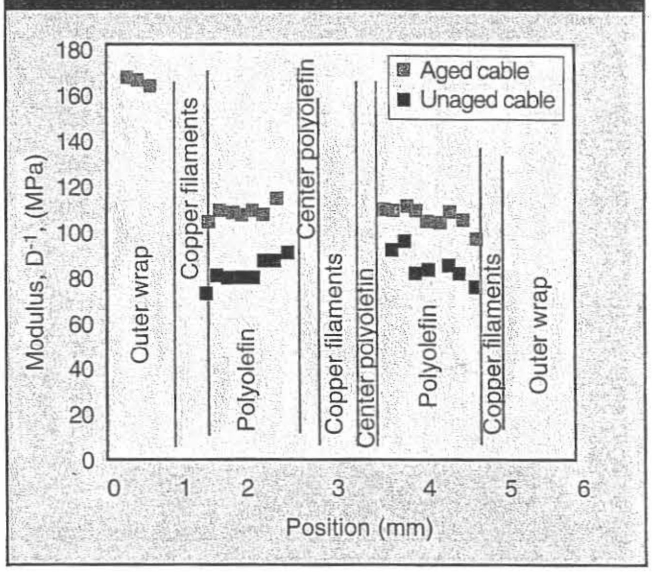


Figure 17 - optical micrograph of polycarbonate sheet

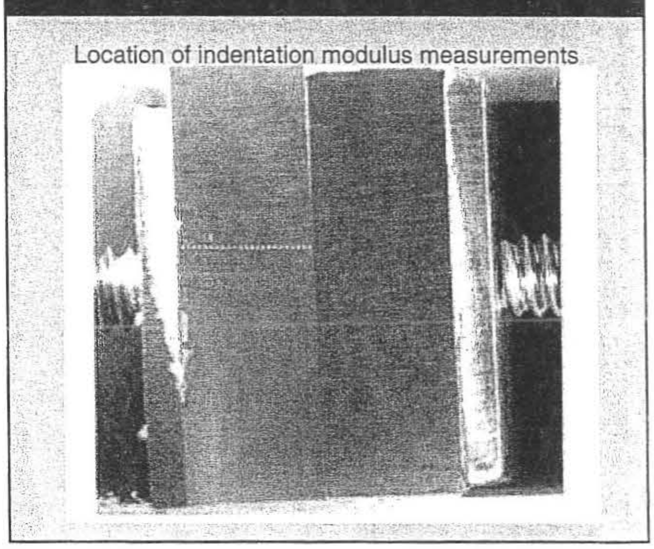
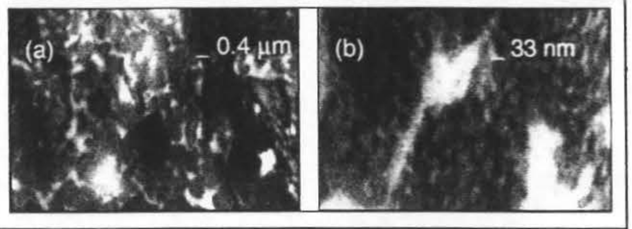


Figure 9 - TEM morphology of STP-65 with different magnification (a) x 23,164 and (b) x 287,910



scale for a STPV is similar to that of a CTPV. However, the STPV has the subtle difference of nano phases (PS multi-junction) dispersed within the micro domains. This dual rubber phase network morphology with micro and nano scale rubber phases is likely to increase crosslink density and elasticity of the rubber phase. This dual network morphology could explain the excellent long term compression set consistency (elastic recovery) and solvent resistance. One can conclude that the nano domain is a fairly unique feature of the STPV morphology when compared with a conventional TPV.

Conclusions

The development of a styrenic TPV (STPV) as shown in this article had great success. The STPV was shown to have excellent stable long-term compression set and improved hot oil resistance at 125°C compared to conventional PP/EPDM TPVs. Also, the developed STPV in comparison to the conventional TPV had a well-balanced mechanical profile that can be readily molded and recycled. These excellent long-term properties are explained by the dual rubber phase network generated by a modified HSBC.

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Modulus profiling

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Figure 18 - effect of oven aging on polycarbonate sheet modulus profile