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Analysis of Steelcord-Rubber Interface by SEM/EDX; Controlled Experiments

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Prologue

The subject of adhesion of brass-plated steelcord to rubber has been investigated and addressed by a number of rubber scientists and metallurgists. The chemistry of the bonding mechanism and the chemical reactions taking place preceding and during the vulcanization process are truly complex. Of all the proposed mechanisms, the van Ooij model is generally accepted by researchers as best explaining the intricate chemistry of the process from rubber chemical, electrochemical and metallurgical standpoints.

Additionally, detailed research has been conducted on liquid (squalene and squalane) systems, e.g., Hamed et al., in order to study compounding variables and the effects of compounding ingredients on the rubber to metal bond. Using the squalene/squalane systems, elemental depth profiles from TOF-SIMS in controlled lab experiments have been used to confirm the van Ooij model and verify the bonding layers formed *in situ* at the rubber/brass interface during the vulcanization process.

Tire manufacturers' development departments have been engaged in materials evaluations and compound development of steelcord skimstocks long before the steel belted radial tire became an OEM commercial product in the early 70's in the United States. The focus of the development compounding effort then and now has traditionally been on empirical experimentation, test tire evaluations principally on indoor high speed and endurance tests as screening tests for candidate formulations. Production formulations have been the end result of exhaustive laboratory, indoor dynamometer, outdoor fleet, commercial fleet and field testing experience and evaluation. The empirical approach has been directed toward optimization of recipes suitable for intended use, i.e., the development testing process involves building and testing tires to failure under a variety of conditions: high speed, overload, underinflation, fatigue, impact, accelerated aging, exposure to ozone, salt water and other environments, besides anticipated conditions encountered in varieties of vehicles and roadway surfaces, temperatures, loads, speeds, inflation pressures and other factors.

Empirical evaluations of steelcord adhesions are commonly obtained by controlled experiments utilizing ASTM Method D 2229. This requires the use of a control steelcord and a benchmark generic control rubber compound. Prepared unvulcanized and vulcanized specimens are subjected to a variety of agings and environmental exposures depending on the compounder and his company's development philosophy. This methodology is the most broadly used technique used to screen materials prior to larger scale development tests.

A lesser amount of scientific work has been conducted on steelcord/rubber specimens removed from steel belted radial tires. Conventional measurements of the residual bond strength between tread plies can be obtained by cutting tire sections and obtaining ply adhesions between belts and adjoining layers. Testing is conducted at room temperature and elevated temperature, typically 100°C. These measurements do not, however, directly reflect the residual rubber/brass bond strength unless the exposed tear surfaces are along the rubber-to-brass interface, which is extremely rare. Most often, variations in both adhesive and cohesive tear patterns are observed in ply adhesion tests. In order to obtain information on the brass-rubber bond, more sophisticated classic means of examination are required.

Of late, there have been numerous allegations made by tire failure analysts that the classic belt separation pattern (Tread and #2 belt totally or partially thrown off the casing along the belt ply interface) observed in failed steelbelted radial tires is *prima facie* evidence of a manufacturing or design defect, or both, in the failed product. Further, it has been alleged that even in tires failing after 50,000 miles of wear, examination of cord filaments from the failed tire allegedly reveal conditions indicating that either no bond or an insufficient bond was formed in the manufacturing process, thus rendering the product "defective".

These arguments rely on a combination of visual observation and SEM/EDX information obtained on a few millimeters of cord filament samples taken from the failed tire, often months after failure. Most of the work performed by these analysts suffers from improper or incomplete sampling, improper use of the SEM/EDX tool, inadequate benchmarking, or misinterpretation of the data. Nonetheless, their resultant opinion of manufacturing defect is typically based on one of four arguments: 1.) The evidence of residual brass on steelcord exposed on portions of failed tires is evidence of incomplete vulcanization, (The Brassy Wire Theory) 2.) A bright, brassy appearance on exposed steelcord indicates little or no bond formed between the rubber and the brass during the vulcanization process, (The Bright Brassy Wire Theory), 3.) SEM/EDX evidence of little or no sulfur on the exposed brass-plated steelcord is evidence of inadequate, i.e., little or no bonding between the rubber and the brass during vulcanization, 4.) Separation at or along an interface is conclusive evidence of contamination or some condition on the rubber surface which has prevented proper bonding.

These analysts rarely, if ever, consider the possibility of bond deterioration or the effects of tire abuse as a causative or a contributing factor in tire failure, the visual appearance of the failed product, or the microscopic condition of the brass/rubber bonding layer post-failure.

The subject of bond deterioration is generally recognized in the tire development compounding community, and that bond deterioration is an irreversible phenomenon. The principal cause of bond deterioration is hysteretic heat and age, exacerbated in combination. As indicated earlier, In order to evaluate the sufficiency and efficacy of a steelcord skimstock compound, tire manufacturers' technical teams conduct many different types of tests intended to evaluate the effects of heat deterioration and age on the bonding layers, including effects of heat and age on the dynamic properties of the compounds.

Experimental

A simple controlled experiment was conducted to evaluate several obvious factors that might affect or are alleged to affect the steelcord/rubber bond: moisture on the steelcord prior to calendaring, accelerated heat aging, and exposure of the steelcord/rubber composite to moisture (tap water) and to a corrosive liquid (salt water).

A suitable test recipe was chosen based on a combination of personal experience, formulations available from the literature, and from compositional analyses of various manufacturers' tires:

Benchmark Steelcord Skim Formulation

Ingredient		PHR
Natural Rubber		100.00
HAF Carbon Black*		50.00
Silica		10.00
Zinc Oxide, French Process		8.00
Stearic Acid		1.50
Naphthenic Process Oil		1.50
B19S Resin		3.50
Cobalt Salt		1.50
Insoluble Sulfur (80%)		5.00
DCBS		0.75
HMMM		2.00
	Total:	183.75

*Black weighed into 2 bags

The two batches of the skimstock compound were mixed in a Farrel 'B' Banbury® internal mixer; the batches were mill-blended and tested for rheological properties. The mixing specification was as follows:

Mixing Specification

77rpm rotor, 40psi ram, 60°C MB, 38°C Final
Mixed and blended 2 batches.

Masterbatch

Time	Addition
0'	NR, 2/3 Black, ZnO
2'	1/3 Black and all other except DCBS, HMMM, Sulfur
4'	Sweep
5'	Sweep
6'	Dump, weigh

Mill @ 60°C, 3 cuts each side, 3 end passes, sheeted to cool; cooled 4 hours before mixing Final batch.

Final

Time	Addition
0'	½ MB, DCBS, Sulfur, HMMM, ½ MB
1'	Sweep
2'	Dump, weigh

Mill @ 60°C, 3 cuts each side, 3 end passes, set grain 2 minutes, sheeted; rested compound 2 hrs. @ RT before rheometer. Rheometer @ 142°C. Adhesion Pads cured 60' @ 142°C.

A new sample of desiccated certified production steelcord wire, 2+2X0.25mm (64.70% copper content), was obtained from Bekaert Corporation for this experiment. The steelcord was used "as received." Wires were cut to length and were handled only at the cut ends with special lint-free gloves.

Adhesion pads were constructed in accordance with ASTM D 2229-99 and cured 60' @ 142°C. Adhesion pad test variables are listed below:

ADHESION PAD DESIGNATIONS

Group	Designation	Feature
Benchmark	Control	Bare steelcord as received;
A	Unaged	Cured pad, no aging or immersion;
B	UnagedRH	Steelcord aged 4 hrs. in 100% relative humidity prior to building and curing adhesion pad;
C	HA24	Pad air oven aged 24 Hrs. @ 70°C;
D	HA72	Pad air oven aged 72 Hrs. @ 70°C;
E	HA168	Pad air oven aged 168 Hrs. @ 70°C;
F	HA336	Pad air oven aged 336 Hrs. @ 70°C;
G	72H20	Tap water immersed 72 Hrs. @ R.T.;
H	72H20RH	Same, steelcord aged 4 Hrs. in 100% relative humidity prior to building and curing adhesion pad;
I	168H20	Tap water immersed 168 Hrs. @ R.T.;
J	72 NaCl	Immersion in 10% NaCl for 72 Hrs. @ R.T.;
K	72NaClRH	Same, steelcord aged 4 Hrs. in 100% relative humidity prior to building and curing adhesion pad;
L	168NaCl	Immersion in 10% NaCl for 168 Hrs. @ R.T.

Adhesion Pad Sample Preparation and Testing

All pads were trimmed flush to the pad base with wire cutters; approximately 85mm of bare wire extended above the top of each pad. Fifteen wires are cured into each pad. For air oven aging, the ASTM pads were suspended individually in the center of an ASTM Type II calibrated circulating air oven for the times noted. For immersion aging, each pad was totally immersed to a point 25.0mm above the top of the pad so that the cut wires at the base of the pad as well as the 25mm of wire above the top of the pad were immersed in the subject solution for the prescribed period.

Each adhesion pad was pulled in the same calibrated tensile tester by the same operator in accordance with ASTM D 2229-99. The percent rubber coverage of the pulled-out cords was estimated subjectively, results as follows:

Designation	% Rubber Coverage (Subjective)
Control	Not Applicable
Unaged	75%
UnagedRH	75%
HA24	75%
HA72	75%
HA168	75%
HA336	75%
72H20	75%
72H20RH	75%
168H20	75%
72 NaCl	75%
72NaClRH	75%
168NaCl	50%

Adhesion Pad Data Analysis (See Tables)

Adhesion data was analyzed using Statmost for Windows® statistical software to obtain general statistical data and tests of hypotheses, i.e., tests for significant difference at the 95% confidence level. Steelcord specimens that broke while being pulled out were excluded from the statistical analyses; this amounted to a maximum of two wires per pad. A half-matrix table was used to summarize the statistically significant differences among the test pad variations. The general statistical data analysis and the half-matrix of significant differences are appended.

Light Optical microscopy

The adhesion pads and the individually labeled wires were photographed using an Olympus SZ-60 light/dark field Zoom Stereo Optical Microscope (10-125X) with attached B&B Microscopes, Ltd. EKE twin Fiber-Optic illumination, interfaced to a Polaroid DMC-ES digital camera. Macro images, as applicable, were obtained using a Navistar Zoom 7000® macro lens. Photomicrographs were printed on an EPSON ProStylus® 700 color printer. Digital photomicrographs were acquired with Polaroid PhotoDirect® computer software and images were enhanced for brightness and contrast with Paintshop Pro® (Version 4.14) computer software as necessary to best illustrate the true microscopic image.

Color digital images, when obtained, were verified for true color by the use of a neutral gray card and Corel Color Matrix® correction software.

Scanning Electron Microscopy (SEM) and Electron Dispersive X-ray (EDX)

1. Sample Preparation

The steelcord pullout samples were prepared by isolating only the area that was embedded in the rubber and mounting ~ 12mm length of the entire steelcord bundle on a carbon planchette with colloidal carbon adhesive. The carbon planchette was then mounted on an aluminum pin mount, and any exposed aluminum surfaces were coated with the colloidal carbon.

2. Analysis

Photomicrographs at various magnifications were taken of the samples using a Cambridge S4-10 scanning electron microscope (SEM) interfaced with a Polaroid camera. Secondary electron imaging was used to obtain surface detail, and backscattered electron imaging was used to facilitate analysis using atomic number contrast.

Backscattered electron imaging utilizes differences in atomic number contrast with lower atomic number elements such as carbon being relatively darker than higher atomic number elements such as iron and zinc which would be visualized as being relatively lighter than the lower atomic number elements. Backscattered electron imaging is also useful in visualizing surface coatings that may have slightly different atomic number composition than the substrate material. The electron beam energy of 20KV penetrates the surface of the material to a depth of approximately 1.6 microns to 7 microns (depending on the density of the substrate).

Secondary electron imaging is useful in giving more information about surface structure of the material being analyzed. The electron beam energy of 10KV only penetrates the surface to a depth of about 0.2 microns to 1.5 microns (again, depending on the density of the substrate), therefore, near surface information can be obtained.

3. EDX Analysis

The samples were analyzed using a Cambridge S4-10 SEM interfaced with an EDAX PV9800 X-ray detector. The Backscatter Detection (BSD) mode was used for imaging. Energy Dispersive X-ray (EDX) analysis was done on elements above Sodium (Na) in the periodic table in the energy range from 0 KeV to 20 KeV. If no elements are present above 10 KeV the plotted spectrum will represent those elements found in the 0-10 KeV range. Results are reported as being semi-quantitative, however, it should be kept in mind that only an area approximately 0.003 mm^2 is being analyzed and the sample may not be homogenous over a larger area. The beam energies used were 10 and 20KV, which penetrate the surface to a depth of anywhere from 0.16 microns to 7 microns depending on the density of the substrate (rubber or brass).

4. Discussion

A total of 120 light optical microscope photos, 98 SEM photos, and 117 EDX spectra were obtained and analyzed. Representative examples are appended. EDX data was obtained at both 20KV and 10KV. Results of the EDX elemental analyses are appended.

Comparative Industry Data

The results of the SEM/EDX data were compared to results obtained on steelcord filaments removed from new and used steel belted radial passenger tires from a variety of manufacturers. (See data tables appended)

Conclusions

1.) Statistically significant differences were observed in the ASTM D 2229-99 adhesions:

  a.) The pads heat-aged 72, 168 and 336 hours were progressively worse than the unaged control pad. The 24 hour heat-aged pad was equal to the control;
  b.) The 72 hour salt-aged pad containing 4-hour 100% R.H. pre-exposed cords was worse than the unaged control;
  c.) The 168 hour salt-aged pad was worse than the unaged control.
  d.) The unaged pad built with the 4-hour 100% R.H. pre-exposed cords was worse than the control (95.8 lbf v. 87.6 lbf)

2.) The sulfur levels and the Cu/Zn levels detected at 20KV are consistent with results obtained on steelcord samples obtained from the industry sampling.

3.) EDX data obtained on K-shell X-ray emissions at 10KV is not always reliable; the Zn atoms present may or may not be detected at this level of energy.

4.) Useful comparative information on the steelcord/rubber bonding layer(s) can be obtained at 20KV provided that sample orientation and other operator-controlled variables are optimized.