10.10 Rubber Analysis

10.10.1 Types of Rubber

Ethylene-propylene-terpolymer rubber (EPDM): Terpolymer of ethylene, propylene, and a diene with the residual unsaturated portion of the diene in the side chain. Contains large number of ethylene and propylene groups with an occasional nonconjugated diene. Most commonly used diene is ethylidene norbornene.

Styrene-butadiene rubber (SBR): Majority of synthetic rubber production.

Polybutadiene rubber (BR): Major component is cis-1,4-polybutadiene. It is utilized almost entirely in tires, blended with SBR and natural rubber.

Butyl rubber (IIR): A copolymer of isobutylene and isoprene in its most common form. Also known as isobutene-isoprene rubber.

Polyisoprene rubber (IR): Known as isoprene synthetic rubber. It is similar to natural rubber in that it is high in cis-1,4-polyisoprene.

Polychloroprene rubber (CR): Known as neoprene. Chloroprene (2-chloro-1,3-butadiene).

Nitrile rubber (NBR): Known as nitrile-butadiene rubber. It is a copolymer of acrylonitrile and butadiene with compositions ranging from as low as 15% acrylonitrile to about 45%.

Natural Rubber (NR): Consists of more than 98% cis-1,4-polyisoprene, plus a small amount of trans-1,4-polyisoprene.

Specialty Elastomers:

- Acrylics: Primarily ethyl-, butyl, or methoxy and ethoxy ethyl acrylates. Major uses are in seals, gaskets, and hoses. Major producers are American Cyanamide, DuPont, and B. F. Goodrich.
- Chlorosulfonated polyethylenes: Crystalline polyethylene that is modified by chlorine and sulfonyl groups. Major uses are as wire and cable coverings, roofing, automotive parts, pond liners, hoses, and belting. Major producer is DuPont.
- Copolyester ethers: Polymers result from condensation of polybutylene terephthalates and polytetramethylene ether glycol terephthalate. Major uses are as hose, wire, and cable coverings, as well as in various automotive parts. Major producers are DuPont, GAF, and General Electric.
- Epichlorohydrins: Homo- and copolymers of epichlorohydrin. Major uses are in automotive products such as gaskets, hoses, and motor mounts. Major producers are B. F. Goodrich and Hercules.
- Fluorinated polymers: Fluorine-containing polymers, made of C2 and C3 fluoro-olefins. Major uses are in seals, gaskets, and hoses. Major producers are DuPont, Ethyl, and 3M.

10.10.2 Rubber Terminology

Accelerator: Speeds cross-linking of rubber by sulfur. Example: 2,2'-dithiobis (benzothiazole).

Acrylate Rubber: A class of elastomers based on acrylate esters.

Activator: Renders accelerators more potent. Example: zinc oxide with stearic acid. Alternatively, a secondary accelerator that is an accelerator in its own right but is more often used with others. Examples: thiurams, dithiocarbamates, and guanidines.

Antioxidant: Protects cured rubber products against oxidative degradation in service. Examples: N-isopropyl-N1 -phenyl-p-phenylenediamine, which is also anantiozonant, and octylated diphenylamine, which is not. Antioxidants that protect synthetic rubbers from production through processing are called stabilizers.

Antiozonant: Protects cured rubber products against ozone. Examples: waxes, which migrate to the surface to form a physical barrier, and N,N1-bis (1,4-dimethylpentyl)-1,4-phenylenediamine, which protects by chemical reaction.

Atactic Polymer: A polymer type in which substituents on the polymer chain are arranged randomly. Opposite of isotactive polymer.

Block Copolymer: A polymer consisting of two or more separate chain sequences, each with properties similar to those that a homopolymer would have if it were the chain alone.

Blooming: Unwanted migration of substances like sulfur to rubber surfaces to produce discoloration.

Bonding Agent: Enhances rubber adhesion to fabric or fiber. Example: resorcinol plus hexamethylenediamine.

Carbon Black: Powdered elemental carbon used to reinforce elastomers.

Coagulation: The process of converting dispersed particles of latexes into large coherent particles of elastomer. Coagulation is caused by both physical and chemical changes in the latex.

Crystallinity: Degree of orientation of polymer molecules in repeating patterns; influences properties such as stiffness and heat resistance.

Cure: Cross-linking of rubber polymer chains to impart elastomeric properties. Also called Vulcanization.

Cure Time: Time needed for rubber compounds to reach maximum viscosity or modulus at a given temperature; the sum of the scorch time and cross linking time.

Elastomer: A polymeric material that can recover its shape after removal of a deforming force. In general, this term means a synthetic polymer. By contrast, the term rubber usually means the natural product.

Emulsion Polymerization: A process in which monomer particles are emulsified with a soap in water and polymerized.

Gross Rubber: The total weight of salable product, including elastomer, carbon black, extender oils, and other compound materials.

Gutta-percha: A type of natural rubber which is high in trans¬polyisoprene; by contrast, normal Hevea-type natural rubber is high in cis-polyisoprene.

Hard Rubber: Rubber cured with 15% to 40% of added sulfur.

Hevea: The most common and largest-volume natural rubber tree genus from which the latex is taken.

Isotactic Polymer: Polymer structure with repeating asymmetric atoms. Opposite of atactic.

Latex: Water emulsion of rubber polymer, used as is for coating or dewatered for making solid parts.

Lubricant: Eases flowing of rubber in molding or extrusion.

Masterbatch: The mixture of elastomer or natural rubber and other materials such as carbon black and fillers used to make the compounded rubber for final fabrication.

Mastication: Preliminary physical and chemical breakdown, usually of natural rubber, in a mill or mixer to reduce viscosity for further processing.

Natural Rubber: Rubber is formed in a plant, most often the tree Hevea brasiliensis.

New Rubber: All rubber, synthetic or natural, produced or used for the first time; excludes all reclaimed or scrap rubber.

Oil Content: Hydrocarbon oils added to polymer as an extender or processing aid.

Peptizer: Promotes chemical breakdown of rubber during mastication; also called plasticizer. Example: pentachlorothiophenol.

Phr: Parts-per-hundred rubber; the number of parts by weight of substance added to 100 parts of rubber.

Plantation Rubber: Crude natural rubber from cultivated rubber trees in contrast to rubber from wild trees.

Plasticizer: A peptizer, an oil, a monomeric ester softener, or an extender. Example: bis(butoxyethoxyethyl) glutarate.

Retarder: Lengthens time before onset of curing. Example: phthalic anhydride. Sulfenamide-type retarders have acquired the separate name of prevulcanized inhibitors. Example: N-cyclo-hexylthiophthalamide.

Reversion: Decrease in rubber modulus or viscosity caused by overworking.

Ribbed Smoked Sheets: Plantation-natural rubber sheets that have been passed through a ribbing mill, washed, and then hung on racks in a smokehouse.

Scorch: Premature curing.

Scorch Time: Safety margin of time that a rubber compound can be worked at a given temperature before curing begins.

Soft Rubber: Rubber cured with 0.5% to 8% of added sulfur.

Stabilizer: Antioxidant that protects rubber from polymerization through curing. Example: tris (nonylphenyl) phosphite.

Staining: Blue or purple coloration of rubber surfaces due to oxidation of p-phenylenediamine-type antioxidants and antiozonants.

Sulfur Donor: Organic polysulfide that replaces some elemental sulfur in rubber compounds and promotes curing mostly by monosulfide cross-links in a process called efficient vulcanization. Example: tetramethyldithiuram disulfide.

Thermoplastic Rubber: An elastomer that can be repeatedly softened by heating and hardened by cooling; not vulcanized but shows properties similar to vulcanized rubber.

Vulcanization: Process for cross-linking polymer chains, causing an elastomer to become less plastic and more elastic. Often restricted to cross-linking with sulfur; by contrast, the term curing covers other cross-linking methods.

Vulcanizing Agent: Cures rubber by forming cross-links among polymer chains. Examples: sulfur, organic peroxides, and phenolic resins.

10.10.3 Minimum Standards & Controls

10.10.3.1 Definitions

Blank: an analysis performed on a laboratory-prepared sample which includes all components of the unknown sample except for the material of interest. All reagents, preparatory steps and analysis conditions will be identical to that used on the unknown sample.

Control: a test performed on a known sample under identical conditions as that used on the unknown sample.

Verification: a test performed on a known sample as a check of an instrument's output.

Minimum Standard of Analysis: the minimum required analytical tests to be performed in order to report a conclusive finding.

Preliminary Test: an analytical procedure that yields information about a sample but by itself cannot be used as a basis for a conclusive finding.

Confirmatory Test: an analytical procedure that will specifically identify an unknown sample.

Standards File: a collection of spectra or chromatograms of known materials to be used as a reference for comparison to an unknown sample.

Reagent: any substance used in a reaction for the purpose of detecting, measuring, or analyzing other substances.

10.10.3.2 Instrumentation

10.10.3.2.1

Blanks must be run at the same conditions as the samples. A blank will be run if the preceding instrument run was a positive result.

10.10.3.2.2

All instrument data generated from case exhibits must contain the case number, exhibit number, analyst's initials and date.

10.10.3.2.3

Pertinent instrument parameters used for an analysis must be documented in the procedures manual or in the case record.

10.10.3.2.4

All verification or calibration data must be documented and contain the analyst's initials and date.

10.10.3.2.5

Identification or classification made by comparison to other than in-house standards must be noted in the case record.

10.10.3.2.6

Identification or classification made via computer search must be confirmed by visual comparison to computer's standard and noted in the case record.

10.10.3.2.7

Pyrolysis Gas Chromatography

10.10.3.2.7.1

Blank of the cleaned sample boat or tube will be run immediately prior to each sample. The blank can be done using a five-minute isothermal run at the program maximum temperature.

10.10.3.2.7.2

Control: A standard rubber sample will be run each day case samples are run. This will be retained in the laboratory.

10.10.3.2.7.3

The blank run will be filed in the case record.

10.10.3.2.7.4

The instrument parameters used for an analysis shall be documented in the procedures manual or in the case record.

10.10.3.2.8

Fourier Transform Infrared Spectrometer (FTIR)

10.10.3.2.8.1 Preparations

- Pellet press and die.
- Compression cell with Diamond windows and salt plates.
- 2 mm KBr and/or NaCl Disks (plates).
- Fine-tip tweezers.
- Fine-pointed needles or probe.
- Scalpel.
- Liquid Nitrogen
- Polystyrene Calibration Standard
- Microtome

10.10.3.2.8.2 Instrumentation

- Stereomicroscope
- Fourier Transform Infrared Spectrometer (FTIR). A microscope accessory is preferred.
- FTIR Collection Parameters
    - Parameters must be adjusted to provide sufficient intensity and resolution for spectra comparison or classification.
    - The use of the microscope will require:
        - Change in scan speed.
        - Use of external mirror.
        - Use of MCT Detector.
        - Increase number of scans.
        - Proper adjustment of apertures with the same setting for sample and background collection.

10.10.3.2.8.3 Procedure or Analysis

- Samples must be prepared so the thickness is between 3 to 15 microns for transmittance operation.
- Samples may be prepared by any method which allows for a sample thin enough for transmission:
    - Use a scalpel to slice a thick piece of rubber.
    - Use glass slide as a guide and cut a thin cross section of the rubber.
    - Compress sample between two salt plates in a compression cell or diamond windows in the compression cell.
    - Place sample on KBr die and use pellet press.
    - Use microtome for cross section
- Place sample on a salt plate. It may be retained in the compression cell during analysis.
- Set instrument parameters.
- Run polystyrene calibration standard.
- Place sample on microscope stage and adjust apertures to area of interest.
- Run sample.
- Move off sample and run background.
- Perform comparison and/or classification.
    - Documentation must meet standards and controls requirements.
    - Run a polystyrene calibration standard each day the instrument is in use.
    - Blanks: A blank or background of any cell or salt plates used will be run before each sample.
    - IR Spectra must include case number, exhibit number, date, analyst's initials, resolution, number of scans, sample type (KBr pellet, liquid, vapor, etc.), frequency range and mode (absorbance or %T).
    - All IR Spectra of case exhibits must be preserved in the case record.

10.10.3.2.8.4 Documentation

- All exhibits/containers must be marked with case number, exhibit number, date, analyst's initials.
- Worksheets
    - State all tests performed and their results.
    - All non-routine tests will be fully detailed.
    - An accurate description of the evidence will be recorded.
    - If the sample is consumed in analysis, a notation will be made.
    - An accurate description of how the evidence is repackaged should be noted.

10.10.4 Safety Considerations

This protocol involves hazardous materials, operations, and equipment. This protocol does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this protocol to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Proper caution should be exercised and the use of personal protective equipment should be considered to avoid exposure to dangerous chemicals. Consult the appropriate MSDS for any chemicals used prior to use.

10.10.5 References

Kauffman, G.B.; Seymour, R.B. "Elastomers I. Natural Rubber"; Journal of Chemical Education, 1990, 67, 5, 422-425.

Kauffman, G.B.; Seymour, R.B. "Elastomers II. Synthetic Rubbers"; Journal of Chemical Education, 1991, 68, 3, 217-220.

Seymour, R.B.; Kauffman, G.B. "Elastomers III. Thermoplastic Elastomers"; Journal of Chemical Education, 1992, 69, 12, 967-970.

Yust, J. "E.P.D.M. (Ethylene, Propylene, Diene, Terpolymer) Rubber Roofing"; Fire and Arson Investigator, 1992, 43, 2, 59-62.

Osland, R.C. J.; Price W.J.; A.H. Devenish. "Infrared Techniques in the Analysis of Rubber"; American Laboratory, 1978, 10, 111-120.

Blackledge. "Examination of Automobile Rubber Bumper Guards by Attenuated Total Reflectance Spectroscopy Using a FTIR"; Journal of Forensic Sciences, 1981, 26, 554-556.

Pouchert, C. "The Aldrich Library of FT-IR Spectra"; Vol 1, 2, 1st ed., Aldrich Chemical Co, 1985.

Sadtler. "The Infrared Spectra Atlas of Monomers and Polymers"; Sadtler Research Laboratories, 1980.

Parybyk A.E.; Kobus, A. "The Characterization of Plastic Automobile Bumper Bars Using Fourier Transform Infrared Spectroscopy (FTIR), Pyrolysis Gas Chromatography (PGC), and Energy Dispersive X-Ray Microanalysis Combined with a Scanning Electron Microscope (SEM-EDX)"; Journal of Forensic Sciences, 1990, 35, 281-292.

Lennard, C. J.; Margot, P.A. "The Analysis of Synthetic Shoe Soles by FTIR Microspectrometry and Pyrolysis-GC. A Case Example"; Journal of Forensic Identification, 1989, 39, 239-243.

Duncan, W. P. "Use of GC-IR-MS and Pyrolysis for Polybutadiene Characterization"; American Laboratory, 1988, 20, 40-46.