

FRACTOGRAPHY OF RUBBERY MATERIALS

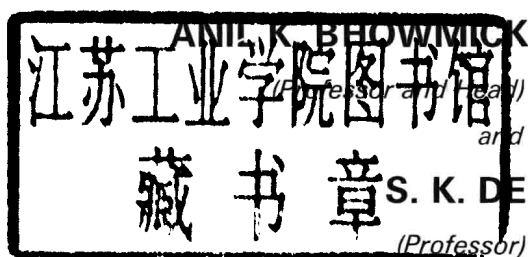


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FRACTOGRAPHY OF RUBBERY MATERIALS

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Preface

In spite of the best efforts of technologists, rubber components fail in service from time to time. In some cases replacement of a particular item serves the purpose, but in others the failure may lead to serious consequences involving financial loss, environmental contamination or loss of life. The fractographer is required to establish the root causes in terms of design, choice, and quality of material, and to determine the mechanism of failure based on the nature/details or appearance of fracture surfaces. It is the purpose of the present book to treat under a single title the morphology of fracture surfaces obtained from tear, fatigue, abrasion and combinations of these. The book attempts to analyse fracture surfaces of simple rubber and rubber components and to correlate the failure/strength properties with the morphology of fracture surface.

Although there is literature coming out from every corner of the world on fracture surface morphology, there is no single book devoted to this important class of material, namely rubber. Needless to say a similar attempt in the field of metallurgy has solved many intricate problems which are beyond the reach of simple mathematical analysis.

The first six chapters deal with simple rubber and rubber-based composites failed under controlled mode, namely, tensile, tear, fatigue, and abrasion. The remaining four chapters deal with the failure of rubber products and, hence, involve complicated analyses. As such, this book may serve as a guideline for further development of the subject in this field.

No edited book can be successful without the extensive, conscientious and patient cooperation and continuous understanding from the contributors. The Editors would like to thank them for their fine contributions and also Professor K. L. Chopra, Director, IIT.,

Kharagpur and C.E.P. cell of this Institute for their support. They acknowledge with thanks permission to reproduce illustrations from various journals. Finally, they would also like to extend their gratitude to their wives and families for their patient understanding and support during the preparation of the book.

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Rubber — science and technology with reference to fractography

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1 Introduction

A polymer is a class of material consisting of molecules of high individual molecular weights which may vary from a few thousands up to the tens of millions g/g mol. The overall molecular weight can only be expressed as a statistical average of the total number of molecular species. The molecules of each of these consist of a sequence of one or more basic units linked together in chains or networks of covalent bonds. The basic unit or units are called monomers and the corresponding network or chain of linked monomers is called a polymer.

Rubber is a polymer with some specific properties. The glass transition temperature of all rubbery polymers is well below room temperature. They are amorphous and the intermolecular force of attraction between the chains is low. As shown in Table 1, the glass transition temperature of natural rubber is -70°C , while that of styrene-butadiene-rubber is -50°C etc., and the molar cohesion value is of the order of 1–2 kcal/mol, much lower than those of fiber forming polymers. The physical properties of a few plastics and fibers are also shown in Table 1 for comparison. The glass transition temperature of plastic is well above room temperature, as shown for polystyrene. In the case of nylon fiber, the polyamide chains can exert powerful attractive

Table 1. Glass-transition and melting temperatures for various polymers.

Polymer	Glass-transition temperature T_g (°C)	Melting temperature T_m (°C)
Polyethylene	-125	137
Poly(<i>cis</i> -isoprene)	-70	28
Poly- <i>l</i> -octene, isotactic	-65	-38
Poly- <i>l</i> -pentene, isotactic	-40	70
Poly- <i>l</i> -butene, isotactic	-25	125
Polypropylene, isotactic	-20	165
Poly(4-methyl- <i>l</i> -pentene)	20	250
Polymethyl methacrylate, isotactic	45	160
Polymethyl methacrylate, syndiotactic	115	200
Polytetrafluoroethylene	-33	327
Polyvinyl chloride	87	212
Nylon-6, 10	40	227
Nylon-6, 6	50	265
Polyethylene terephthalate	70	267
Polyacrylonitrile	104	—
<i>Cis</i> -polybutadiene	-107	+ 3
Polychloroprene	-45	—
Styrene-butadiene-rubber	-50	—

forces towards each other; when such chains are oriented by cold drawing, these forces are strong enough to cause the oriented chains to crystallize into elongated crystals containing rigid chains which are responsible for their high strength. The glass transition temperature or the interchain forces can be changed by the incorporation of a special ingredient or by chemical modification. For example, polyvinyl chloride, a plastic, could be made rubbery by the addition of a plasticizer.

The choice of rubber for a particular application frequently results from one or more of the many benefits which can be offered by this class of material. These include:

- (1) Low density: the density of natural rubber is 920 kg/m^3 as compared to 2600 kg/m^3 of glass and 7860 kg/m^3 of mild steel.
- (2) Low price: in relation to many other materials, rubbers are competitive in cost terms when one looks at the special properties imparted.

- (3) Less energy intensive fabrication: derived from the lower processing temperature and better automation.
- (4) Amenable to high speed production.
- (5) Resistance to corrosion and related electrochemical action.
- (6) Low thermal and electrical conductivity: the high resistivity of many rubbers is exploited as electrical insulators.
- (7) Design flexibility: processing technology available for fabrication of rubber items makes it possible to produce a variety of shapes at low cost.
- (8) Wide range of properties: the mechanical properties of rubbers can vary considerably according to the type of rubber and form of modification adopted. Thus, for example, they may be soft and resilient and they may also have high strength and stiffness. It is this versatility which enables the selection of rubber for such a wide variety of end uses. The chemical properties vary according to the chemical composition of rubber. Some are solvent resistant while some are heat resistant. Some give good tear and abrasion properties and a few others are biocompatible.

2 Types of Rubber

There are various types of rubber with different chemical structures. They may consist of organic or inorganic chains, and, accordingly, they are known as organic or inorganic rubber. A few examples of various types of rubber are given in Table 2. The structure, stereoregularity, glass transition temperature, etc., determine the properties a particular rubber can impart. For example, nitrile rubber is oil resistant because of the acrylonitrile group, whereas EPR is heat resistant because of the absence of a double bond. Silicone rubber can be used at a very low temperature (down to -100°C), and at the same time at a very high temperature (up to 250°C), since it has a low glass transition temperature indicating the flexibility of the molecules at just above T_g and also the Si—O bonds are more heat resistant than the —C—C— or —C—S bonds. Good regularity of polymer chains makes it possible for many rubbers to crystallize when stretching and hence result in high strength properties. An example is natural rubber. However, the double bonds in any diene rubber are susceptible to oxidation. Of the various structures given in the table, some rubbers consist of a homopolymer chain, i.e. the repeat unit is the same, while the others consist of two or three monomer

Table 2. Types of conventional rubber

Type	Basic unit and structure	
Natural rubber	<i>cis</i> 1,4 isoprene $ \begin{array}{c} \text{CH}_2 \qquad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H}_3\text{C} \qquad \text{H} \end{array} $	
Polyisoprene rubber	<i>cis</i> -1,4 isoprene $ \begin{array}{c} \text{CH}_2 \qquad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \qquad \text{H} \end{array} $	
Polybutadiene	$ \begin{array}{c} \text{H}_2\text{C} \qquad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \qquad \text{H} \end{array} $ <i>cis</i> -1,4 butadiene	
Styrene-butadiene-rubber	Styrene	$\text{Ph}-\text{CH}=\text{CH}_2$
	and Butadiene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
Nitrile rubber	Butadiene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
	and Acrylonitrile	$ \begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{CN} \end{array} $
Butyl rubber	Isobutylene	
	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{CH}_3 \end{array} $	
	and a few per cent of isoprene $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	

Table 2 — *contd.*

Type	Basic unit and structure	
Ethylene-propylene-diene rubbers	ethylene	$\text{CH}_2=\text{CH}_2$
	propylene	$\text{CH}_3-\text{CH}=\text{CH}_2$
	and a few per cent of diene	
Neoprene	Chloroprene (2-Chlorobutadiene)	
		$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \\ \text{Cl} \end{array}$
Polysulfide elastomers (Thiokol)	$(\text{RS}_x)_n$	
Silicone rubbers	Silanols,	$\begin{array}{c} \\ -\text{Si}-\text{O} \\ \end{array}$
Urethane polymers	Polyether/polyester	
	$\text{HO}[-\text{R}-\text{O}-]_n\text{H}/\text{HOR}'\text{O}[-\underset{\text{O}}{\underset{ }{\text{C}}}-\text{R}-\underset{\text{O}}{\underset{ }{\text{C}}}-\text{OR}'\text{O}-]_n\text{H}$	
	and diisocyanate	
	$\text{O}=\text{C}=\text{N}-\text{R}-\text{N}=\text{C}=\text{O}$	
Fluoro carbon rubber (Viton)	Vinylidene fluoride $\text{CH}_2=\text{CF}_2$ and hexafluoropropylene $\text{CF}_2=\text{CF}$ $\begin{array}{c} \\ \text{CF}_3 \end{array}$	

units. The latter class is called copolymers. Styrene-butadiene rubber is a copolymer of styrene and butadiene.

All the above types of rubber (Table 2) have one feature in common — they are all vulcanized before being made into any rubber component. However, polymer developments during the past two decades have provided new materials that need no vulcanization and that bridge the gap in property between conventional rubbers and plastics. These are thermoplastic elastomers that have the physical properties of elastomers, that is long range reversible extensibility, but can be processed like thermoplastic at high temperature into fabricated products. They generally have a two-phase structure — the hard phase constituting the pseudo-crosslink or tie points may be glassy or crystalline

Table 3. Examples of thermoplastic rubbers

Sl. No.	Thermoplastic material	Shore hardness (°)	Density (g/cm ³)
A.	1. Thermoplastic natural rubber (TPNR)	70A–60D	0.91
	2. Olefinic thermoplastic rubber (TPO)	65A–60D	0.89
B.	1. SBS and SIS copolymers	40A–95A	0.94
	2. TPNR grafts (TPNR-G)	40A–95A	0.94
C.	1. Polyurethane thermoplastic rubbers (TPU)	70A–75D	1.25
	2. Copolyester thermoplastic rubbers (TPCP)	40D–72D	1.25

and the soft phase is rubbery in nature. The ionic bonds in an elastomeric matrix may also be used to make thermoplastic elastomers. Table 3 gives a few examples of these thermoplastic elastomers. The development of this class of material is very rapid and hence the example of a few polymers gives only an indication of these materials. Most important are the styrene–diene block copolymers, the thermoplastic polyurethanes and the copolyesters. The structure of these elastomers decides their properties. For example, the strong points of polyester thermoplastic elastomers are as follows: low temperature properties, resistance to oils and chemicals, heat resistance, UV radiation resistance, abrasion and flex-fatigue resistance. Details of various rubbers and thermoplastic elastomers are given in several other publications.^{1–4}

3 Brief Outline of General Preparation

Polymerization reactions are either condensation reactions or addition reactions.⁵ The polymer formation in condensation polymerization proceeds stepwise, the various intermediates, dimer, trimer, etc., existing as stable molecules until the next reaction step. Small molecules like water are split off at each step of the reaction. Addition polymerization is characterized by the fact that the reaction from monomer to polymer occurs without the elimination of by-products. A form of addi-

tion polymerization is co-polymerization in which two or more different monomers, linked together either at random or in alternate sequence, form one single co-polymer chain or network.

In the polycondensation method the reactants are brought together in appropriate reaction vessels and mixed with the catalyst. The condensation is started by heating the reaction mixture and the reaction is continued under close temperature control until the desired degree of polymerization is reached.

There are two ways in which addition polymerization can be carried out:

- (1) In a homogeneous phase in which the monomer is a gas, a liquid or a solid (bulk polymerization) or in which the monomer is completely dissolved in a solvent (solution polymerization).
- (2) In a heterogeneous phase in which the monomer is emulsified in an aqueous medium (suspension polymerization).

Natural rubber can be isolated from more than 200 different species of plants, even including such surprising examples as dandelions or goldenrod. However, only one tree source, *Hevea Brasiliensis*, is commercially significant. Other varieties of rubber are made synthetically. For example, styrene-butadiene-rubber is made by emulsion polymerization as well as by solution polymerization. Polybutadiene is prepared by polymerization in emulsion or in solution. Segmented polyester-polyether block copolymers are prepared by melt transesterification.

4 Compounding of Rubber

Compounding is the art or science of selecting the right materials for a rubber compound for a particular end-use application. Rubber, as such, is never used without containing compounding ingredients. These materials impart the desired physical and processing properties. They also protect diene-containing rubber and of course, in conventional rubber, are used for network formation. A general outline of compounding of rubber is given below, though it will vary from material to material.

4.1 Conventional Rubbers

The materials utilized by a rubber compounder can be grouped as follows:

Elastomers: this is the basic component chosen on the basis of the physical properties of the final product. They may be single rubber, blends, reclaimed rubber or rubber-black masterbatches. The selection of other ingredients will depend very much on the nature of elastomers. Table 2 lists the names of some common elastomers.

Processing Aids: these are the materials used to modify rubber during the processing stage, i.e. mixing, calendering, extrusion or molding operations. For example, zinc salt of pentachlorothiophenol or oil soluble sulfonic acids are used as peptizing agents in natural rubber.

Vulcanizing Agents: these materials are necessary for chemical cross-linking without which no improvement in physical properties can occur. Sulfur is a common vulcanizing agent for diene rubbers. However, metal oxides such as zinc oxide can also be used for vulcanization as in the case of polychloroprene rubber.

Accelerator and Accelerator-Activators: accelerators increase the rate of vulcanization in combination with vulcanizing agents and improve the mechanical properties of rubbers. One such example is cyclohexyl benzthiazole sulfenamide. There are many others, the activity of which will depend on the chemical structure.

Accelerator-activators are used to increase the rate of vulcanization and physical properties further. In natural rubber zinc oxide in combination with stearic acid are used for this purpose.

Age resisters: rubbers containing double bonds deteriorate in the presence of oxygen, ozone, light, heat, radiation, etc. Antioxidants and antiozonants are used to prevent the ageing process in vulcanizates. There are three general types: secondary amines, phenolics and phosphites. *N*-isopropyl *N*-phenyl *p*-phenylene diamine is a common age-resistor for tyre compounds.

Fillers: these materials are used to reinforce rubber, reduce cost, improve processing or modify physical properties. Carbon blacks of various particle size (20–350 nm) are common reinforcing fillers. The level of reinforcement depends upon the particle size and surface area. Particles of 20–30 nm size impart excellent tensile properties to styrene-butadiene-rubber. The activity of the chemical groups on carbon black will also influence the reinforcement properties. The loss of active sites by heat treatment of carbon black to a temperature 1600–3000°C in nitrogen has a most profound effect on the mechanical properties. Silica, china clay, whiting, talc, etc., are also used as fillers in rubber compounds.