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CHEMISTRY, TECHNOLOGY AND PROPERTIES OF SYNTHETIC RUBBER

Tutorial

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Chemistry, technology and properties of synthetic rubber : tutorial / I.M. Davletbaeva, D.V. Beskrovniy, O.R. Gumerova; Ministry of Education and Science of Russian Federation, Kazan National Research Technological University. – Kazan : KNRTU Publishing, 2013. – 201 p.

The manual is intended for the 5th year students of the Polymer Faculty of 020015 "Chemical Technology" course. The manual reflects the current state of the elastomers science and production technologies. The focus is on technological methods, based on the scientific understanding of the chemistry in the synthesis of general-purpose and special rubbers, their properties and applications.

The content of the manual corresponds to the program of the course "Technology of Elastomers".

Published by the decision of the Editing and Publishing Board of Kazan National Research Technological University

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INTRODUCTION
1.1 Elastomers Classification

Generally speaking, elastomers are the polymers in the highly elastic state under normal conditions. Narrowly, they are constructional materials based on highly elastic polymers which have an extremely large significance in the development of technology.

The high flexibility of the polymer chains makes it possible to develop highly significant strain of elastomers under the influence of external mechanical forces, and the nature of strain depends on the structure of the polymer.

In view of relaxation processes, the connection between stress, strain and time for the polymers is complicated. In general, the total strain ε is made up of three components:

$$\varepsilon = \varepsilon_{el} + \varepsilon_{he} + \varepsilon_{pl}, \qquad (1.1)$$

where ε_{el}, ε_{he} и ε_{pl} – elastic, highly elastic and plastic strain respectively.

The elastic strain due to distortion of the bond lengths and bond angles (as in any solid), develops almost instantly and it is completely reversible. Highly elastic strain is associated with the changes in chain conformation and supramolecular structure of the polymer; it develops during time (relaxationally) and is reversible as well. Plastic strain is caused by the motion of macromolecules relative to each other, is irreversible (flow of the material), and its magnitude is proportional to the exposure time of external forces.

The basic component out of the three components of the total strain in elastomers is highly elastic strain ε_{he}, developing in time and completely reversible. However, in many cases the irreversible plastic deformation ε_{pl} can make a significant contribution. Naturally, such elastomers are not suitable for the common use as structural materials, since their products do not have the dimensional stability.

It should be considered as true elastomer the kind of the polymer, which is able only to reversible strains with highly flexible chains, which are unable to relative motion for some reason. The motion of macromolecules can be prevented in two ways: the

creation of a polymeric material with areas of intensive physical interactions (physical cross-linking) and transformation of a linear polymer into the cross-linked polymer (formation of system of intermolecular chemical bonds). In both cases, the flexibility of chains should remain.

Materials of the first type are called thermoplastic elastomers (TPE), since they behave as cross-linked elastomers at ordinary temperatures, and as linear thermoplastic polymers (plastics) at elevated temperatures. The destruction-recovery processes of the network of the material are completely reversible, associated only with temperature changes. Therefore, thermoplastic elastomers can be recycled, allowing waste and disabled goods recovering. The advantages of TPE are the simplicity of processing, an exception of vulcanization stage of the process. However, the operating temperature range of TPE is relatively narrow, and they are used only for the manufacturing of products, operating at normal temperatures (eg, footwear).

Much more common are cross-linked elastomers which polymer chains are connected by sufficiently strong chemical bonds. The main (traditional) way of obtaining such materials is vulcanizing of rubbers - linear, high molecular polymers in the highly elastic state. Initially, it was used exclusively natural rubber (NR) to obtain vulcanizates (often called rubbers). However, in the twentieth century, which was called as the age of the polymers by academician N.N. Semenov, synthetic rubbers have appeared (SR), and they gradually became the main raw material for the rubber industry. In the world consumption of rubber the ratio of SR:NR have been keeping at about 2: 1 for many years.

Cross-linked elastomers can be obtained by curing of *reactive oligomers with the terminal functional groups* ("oligomeric" technology) as well. Owing to the low molecular weight and consequently low viscosity of the oligomers, such technology makes it possible to strongly reduce energy use on the mixing and product forming processes. However, reactive oligomers are relatively expensive, only some products can be obtained in this way; therefore

oligomeric technology is used mainly in the industry of sealants, adhesives, coatings, etc. As an example, the reactive oligomers are urethane prepolymers, liquid Thiokol (polysulfides), liquid polydimethylsiloxanes.

Service conditions of elastomeric products are extremely varied, and as the technology develops the constructional materials requirements increasingly toughen. These requirements include: high elasticity retention at lower temperatures, providing of sufficient strength under the long-term exposure of corrosive mediums or high temperatures (often both of these factors), the significant effects of excess pressure (or vacuum), radiation and electrical fields, etc.

Nevertheless, a significant number of products run under the normal conditions, which mean the temperature range from -50 to 150°C, no contact with any corrosive liquids or gases, etc. Meanwhile, the main feature of rubbers is realized in elastomers - high elasticity, and of course, such general properties as strength, durability, etc. play the important role. Elastomers used in such conditions (as well as rubbers, from which they are derived) are called *general purpose elastomers (rubbers)*. They are primarily hydrocarbon rubbers: natural and synthetic isoprene, butadiene and butadiene-styrene (α-methylstyrene) rubbers. The main consumer of general purpose rubbers is tire industry, so just tire manufacturers who are the "trendsetters" with respect to this group of rubbers.

If the operating conditions are different from ordinary the rubber must have certain specific properties to maintain working capacity for the required period of time (*special purpose rubbers*). The range of special purpose rubbers is much wider, as a set of specific properties is quite large - above all, resistance to high (or low) temperatures, to the various corrosive liquids (primarily fuels, oils, solvents, etc.), light and radiation, etc. However, in terms of production volume, they are much smaller than general-purpose rubbers.

The special properties of elastomers are primarily associated with the chemical structure of polymer chains, so the carbon-chain special purpose rubbers for the most part are composed of some polar

atoms or groups, and many of them are heterochain or element-containing. The special purpose rubbers are chloroprene, butadiene-nitrile, acrylic, polysulfide (Thiokol), siloxane, urethane, fluorine rubber and many others. Some rubbers can be referred to any group, depending on whether the specific property plays a significant role in provision with the service properties of the product or not. For example, ethylene-propylene rubbers (EPR) are typical general purpose rubbers which are widely used as such. However, their rubbers offers highly resistance to atmospheric factors and dielectric properties, which allows to consider EPR as special purposes, such as insulating coatings of electric cables.

In addition, the properties of the final constructional material largely depend on the nature of intermolecular chemical bonds (method of vulcanization), formulation factors (type and amount of fillers, plasticizers, modifiers, etc.).

When choosing the special rubber for a particular application one should rely on the well-known structure–properties relations. For example, it is important for heat-resistant elastomers to have chemical bonds in the macromolecules and in the network junctions as strong as possible. Therefore, saturated polymers are more heat resistant than unsaturated ones, and fluorine rubbers and polysiloxanes are more highly efficient at elevated temperatures:

Type of rubber	Type of bonds in main chain	Peak temperature of continuous service, °C
Isoprene (peroxide cure)	C – C, C = C	90 ÷ 100
Ethylene-propylene (peroxide cure)	C – C	130 ÷ 150
Acrylate rubber	C – C	140 ÷ 160
Fluorine rubber	$-F_2C - CF_2-$	200 ÷ 250
Siloxane rubber	$-Si - O$	200 ÷ 250

When selecting rubber for cold-resistant rubbers you should primarily draw attention to the thermodynamic flexibility of its macromolecules, which can be estimated quantitatively by a factor of hindered internal rotation σ.

Rubber	σ	Floor temperature of continuous service, °C
Styrene-butadiene rubber (SKS-30)	~1,8	–40 ÷ –50
1,4-*cis*-Isoprene (NR, SKI-3)	1,7	–50 ÷ –60
1,4-*cis*-Butadiene (SKD)	1,5	–90 ÷ –100
Syloxane	1,3	–50 ÷ –90

The behavior of elastomers in contact with organic liquids is determined by the affinity between them, which can be seen from the values of cohesive energy density (CED) and the solubility parameter $\delta=(CED)^{1/2}$. In most cases, similar values of these parameters ($\delta_1 \approx \delta_2$) indicate a significant swelling of the elastomer in the liquid. The comparative data for the resistance of rubbers of different rubbers to some organic media (on a 5-point scale; rubbers and liquids are arranged in order of the polarity growth) is given below:

	R u b b e r s					
	NR	BSK	Butyl rubber	PH	BNK	Thiokol
Hydrocarbons Aliphatics	1	1	1	3	5	5
Hydrocarbons Aromatics	1	1	1	2	3	5
Fats, vegetable oils	2	2	5	4	5	-
Ketones, alcohols	3	3	1	1	1	-

Unfortunately, not all of the specific properties have the explicit link with the chemical structure of the elastomer, so you often have to rely on experimental data and find some empirical relations.

Historically the main form of commercial rubbers are the briquettes. For the processing of rubber it is required heavy and energy-intensive equipment, which is the most likely to be of periodic action. Therefore, besides the economic, environmental, sanitation, etc. problems there are difficulties with ensuring the consistency of product.

The plastic processing industry which occurred later had to deal immediately with the polymers in the form of granules and powders and it offered continuous processes, which are much easier to automate and robotize. The use of these advanced technologies applied to rubbers is complicated by the fact that under normal conditions, the polymer is in a highly elastic state. This can lead to aggregation of the particles during storage and transportation, which is unacceptable for the successful operation of process equipment. Therefore, production of rubber in the form of granules is limited, and it is suitable for the most hard rubbers - chloroprene, ethylene-propylene, thermoplastic elastomer (TPE), etc.

Last years the interest in powdered mixtures of rubber with fillers (especially with carbon black) has grown again. Such stable free-flowing powders are suitable for the use in continuous

processes, but they can be successfully applied when working on the standard stirrers. Getting a mixture of latexes (including natural), it simplifies the process of selection of rubber for unnecessary coagulation, mechanical dewatering, drying the polymer at high temperatures, pressing briquettes. The use of rubber-filler mixtures is the most appropriate way in large recycling processes, for example, in the tire industry, so this commodity form is promising for the general-purpose rubbers.

Part of the rubber is produced in the form of commercial latexes, which find wide application for obtaining some of the products from elastomers (latex technology), as the basis of adhesives, paints and coatings, impregnation of the reinforcing parts, as well, etc. Mainly the synthetic rubber of the emulsion polymerization (synthetic latex) is produced in the form of latexes, but it is also possible to derive latexes from elastomers obtained by other methods (artificial latex). Natural rubber latex, its types, properties and applications are not considered in this book.

A very small amount of rubbers can be produced in the form of solutions, in those cases where the further use of rubber requires its dissolution (eg, for subsequent modification, or as the basis for coatings, etc.).

1.2. Structural Characteristics of Elastomers and Their Properties

When establishing the correlation between the molecular structure of elastomers and their properties it should be kept in mind that synthetic rubber is a raw material for the rubber industry (tires, various technical rubber products, shoes, etc.). During the processing the rubber is mixed with various ingredients to get the rubber compounds ("raw", ie, not vulcanized). The property package associated with the behavior of rubbers and raw rubber compounds at various stages of the processing cycle, is combined into concept of *technological properties of rubbers*. First of all, these include

plasticity, viscosity (Mooney), hardness (Defoe), recoverability, as well as more specific properties - millability, calenderability, extrudability, cold flow, shrinkage, and tackiness.

The most important technological properties of rubber are associated with its processability on rubber mixing and molding equipment. The cost of energy on mixing, processing temperature, and even the possibility of its implementation are due to the *plasto-elastic parameters of rubber*. They are determined for raw rubbers, and the most important characteristic is the value of the effective viscosity for a particular strain mode and shear rate.

The most common measurement is Mooney viscosity. Compare the values of shear rate (γ), typical for the different processing of rubber compounds, as well as realizable in the Mooney type viscometers when determining the viscosity of the material:

Table 1.

The values of shear rate (γ) for the different processing of rubber compounds

Process	γ, sec^{-1}
Measurement of Mooney viscosity	~1,5
Press molding	$1 \div 10$
Calendering	$10 \div 10^2$
Extrusion	$10^2 \div 10^3$
Diecasting	$10^3 \div 10^4$

As it can be seen from data given above, Mooney viscosity may be used only as indicative or comparative characteristic, but it cannot be used in the calculation of processing of the elastomer.

More information about the viscous properties of rubbers can be obtained from flow curves representing the dependence of the shear rate on stress (σ_F). For liquids obeying the Newton's viscosity, this dependence is linear. The liquids that flow faster than the Newtonian are called pseudo-plastic, and almost all rubbers and rubber compounds are belong to this group.

In most cases the flow curve can be described by a law equation of Ostwald de Vila:

$$\sigma_F = K \cdot \gamma^n , \qquad (1.2)$$

Where K and n are rheological constants of material

The constant *n*, called the flow index, in this equation characterizes the deviation of flow from Newtonian one, as for the last *n* = 1. For elastomers *n* is a few tenths and it depends on molecular weight, molecular weight distribution, chains branching, the concentration of filler in rubber, as well as on temperature.

Despite the greater information value of the rheological constants their determination requires a fairly long experiment, and there are used mainly the Mooney viscosity to characterize the technological properties of rubbers. This index for linear polymers is related to their molecular mass characteristics: Mooney viscosity increases with increasing of average molecular weight and decreases with increasing of polydispersity index. The presence of branched macromolecules with long lateral branches also leads to an increase in Mooney viscosity in comparison with linear polymers of the same molecular weight and polydispersity. Thus, technological properties of the rubbers are etermined by their molecular structure, which, in turn, is associated with the specific synthesis of elastomers.

The molecular weight of most of the rubbers is in the range from 10^5 to 10^6. The formation of natural rubber as a result of biochemical reactions does not allow to adjust the length of the macromolecules, so before processing NR is subjected to mastication to reduce the molecular weight and improve the technological properties. When obtaining the synthetic rubber the molecular weight is easy to adjust in the process of synthesis, and, as a rule, the same type of SR is produced in the form of various grades which vary in viscosity.

All synthetic rubbers and even oligomers are polydisperse namely a mixture of macromolecules of different molecular weight. Polydispersity of polymers is quantitatively described by the polydispersity index (*f*) or a function of molecular weight distribution

(MWD). Practically, it is more likely to use the values of the polydispersity, quantitatively equal to the ratio average and number average molecular weight of the polymer: $f = M_w/M_n$. For monodisperse substance $f = 1$, for polydisperse – $f > 1$, so the higher the value of this coefficient for the real rubber, the greater the polydispersity. The molecular weight distribution function is the dependence of the relative number or weight fraction of macromolecules with particular molecular weight of the value M.

The molecular weight distribution function of the macromolecules depends on the conditions of synthesis of rubber, mainly on the nature of the used catalyst system or the initiator.

The peculiarities of the structure of the active center in ionic polymerization determine the ratio of the rates of elementary reactions of the polymerization process - initiation, growth, chain termination, and the dependence of these rates on the length of the chain. Thus, in the anionic polymerization of diene monomers the active center is highly stable, which nearly rules out the possibility of such reactions as limiting the growth of macromolecular chains, deactivation or transfer of the kinetic chain to the monomer and polymer. Derived polydiene rubbers are characterized by a narrow molecular weight distribution and their polydispersity index verges to one. When using the Ziegler-Natta catalysts the reactions of chain transfer to monomer, to catalyst complex or to its components could take place that leads to extension of MWD function and increasing the values of f respectively.

The processes of polymerization by a radical mechanism are even more complicated by numerous reactions of chain transfer and deactivation of active centers.

With narrow MWD and in the absence of branching the rubbers are processed poorly, often exhibit a high cold flow, making them difficult to transport and long-term storage. Rubbers with wide MWD have the best technological characteristics. The presence of high fractions creates a "frame", which prevents from flowing at low shear stresses (and prevents cold flow). At the same time the low

molecular weight fractions existing in rubber act as a plasticizer to facilitate the flow at high shear stresses (during the processing). A small branching also creates a "frame" and helps to reduce the cold flow of rubber, but also increases the tendency of polymers to mechanical degradation.

Rubbers are characterized by statistical branching of macromolecules, which has a quantitative measure as the density of branching ρ, equal to the ratio of the number of nodes to the total number of branching units in the polymer chain. Due to the statistical nature of branching the average number of branch points in the macromolecules is proportional to their molecular weight. The main reason for the branching of the macromolecules during their formation is the transfer reaction of the active center to the polymer chain. Owing to occurrence of additional active centers in this macromolecule it is often observed the acceleration of its growth and the increase of the probability of further branching. As a consequence, the branching process leads to expansion of the molecular weight distribution, and the highest molecular fractions contain the highest number of branches. If the density of branching reaches some critical value ρ_{cr} there are supramolecular particles arising in the system, and then the macroscopic particles, which represent three-dimensional spatial structures. The formation of such structures is shown in the sharp increase in viscosity of the system during polymerization in bulk, and in the appearance of a gel in rubber solutions.

Thus, the synthetic rubber is a polymer system with a complex molecular *(topological) structure,* which determines not only the technological properties of elastomers, but also the service properties of rubbers obtained from them.

The ability of raw rubber mixtures to vulcanize describes the group of *vulcanization characteristics,* the most important among them are the cure rate and the maximum attainable spatial cross-link density. Vulcanization characteristics of mixtures are determined increasingly by the composition of vulcanizing group, i.e. mixtures

with different vulcanizing activity can be prepared on the base of the same rubber. However, the variation of the composition and the structure of macromolecules of rubber can also affect this group of properties. Thus, as the reactivity of double bonds and the mobility of hydrogen atoms in the polymer chains increases, the rate of sulfur vulcanization enhances. The ratio of links of different structure (1,2-, 3,4-, 1,4-*cis,* 1,4-*trans)* strongly influences the curing activity of chloroprene rubber. The incorporation of the carboxyl groups in macromolecules of rubber enables the metal oxides vulcanization. Halogenation of butyl rubber is one of the ways to increase its cure rate. However, the main methods of regulating the curing activity of rubber compounds are formula factors.

The properties of rubber as a structural material are often called as **technical (or service).** Depending on the application of rubber priorities may be different, but in nearly all cases required properties are high strength, elasticity, time consistency.

It is possible to obtain vulcanizates with the highest tensile strength only on the basis of rubber with sufficiently high molecular weight (about $250 \div 600$ thousand). The molecular structure of rubber, which ensures good processing characteristics of mixtures and at the same time allows obtaining the rubber with high mechanical properties, demands various, often opposite requirements. Thus, the best physical and mechanical properties have rubber-based rubber with regular structure, high molecular weight and narrow molecular weight distribution. As a result of vulcanization of such rubbers there are less defective network structures, which are also characterized by a narrow distribution of molecular weights of network links. However, the rubbers of such structure have poor technological properties.

Therefore, for each specific application of rubber there should be considered the required service characteristics and processing conditions. For example, in the case of butadiene rubber in the tire industry, the polymer with a molecular weight $(3 \div 3,5) \cdot 10^5$ and polydispersity index equal to $2,5 \div 3,0$ satisfies the technological and

physical-mechanical properties. At the same time, for the producing of industrial rubber products, butadiene rubber with such MWD is unacceptable, it requires more enhanced MWD (f = 4,0÷5,0).

The main difference of elastomers from other types of macromolecular compounds is that their temperature range of high elasticity occurs in the region of temperatures, the most important for the practical use of the material.

To show a high elasticity of the polymer it is needed that the macromolecules are long, continuously fluctuating statistical coiled chains. The polymer chain can take such conformations only if it has sufficient internal mobility, which is provided primarily by the rotation of the separate fragments of the chain around the single bonds (C-C in the case of carbon-chain rubber). The smaller size of this fragment, the higher conformational mobility (thermodynamic flexibility) of chain and, consequently, the higher the high elastic properties of the polymer.

In the case of elastomers high thermodynamic flexibility of isolated macromolecules combines with relatively weak intermolecular interactions in the polymer. Quantitative criterion of these interactions is the cohesive energy density (CED), which has the physical meaning of energy required to separate molecules in a volume unit of substance (for low-molecular liquids, it coincides with the energy of evaporation). Typically, the value of CED is expressed in MJ/m^3 or equivalent units - MPa. Equivalent intensity characteristic of interactions is the solubility parameter $\delta = (CED)^{0.5}$. The ability of polymers to dissolve or swell in liquids of different nature, to combine with each other and with the plasticizers, the properties associated with the cohesion of polymer chains (primarily mechanical properties, gas and water resistance, etc.) depend on the value of CED (or δ).

The chemical structure of polymer chains uniformly influences the intra- and intermolecular interactions, i.e. with increasing polarity of the polymer both the potential barrier of rotation (which makes the conformational transformations in

polymer chains complicated) and the cohesive energy density increase. Here are the values of cohesive energy density of some common polymers:

Polymer	CED, MPa	Polymer	CED, MPa
Polyethylene	265	Polystyrene	328
Polypropylene	275	Polyvinyl chloride	384
Polyisoprene	275	polyethylene terephtalate	483
Polybutadiene	298	Polycaproamide	780
Polychloroprene	328	Cellulose	1025

Comparing these data with the mechanical properties of polymeric materials, we can conclude that the polymers with the lowest values of CED are the most low-modulus (elastomers). The higher the intensity of intermolecular interactions, the harder the polymer - the maximum values of CED are in fiber-forming polyamide and cellulose. It is also clear that the elastomers with low values of CED are not oil- and petrol-resistant, as the nonpolar hydrocarbons have similar values of the intensity of intermolecular interactions.

Cohesive energy density determines the correlations between the rates of molecular rearrangements and the rates of cooling or heating the polymer samples. Molecular mobility and free volume associated with the cohesive interactions are responsible for the transition temperature of polymers to the glassy state (T_g). Thus, the increasing CED weakens the segmental motion and thus T_g increases. In addition, the glass transition temperature is significantly affected by the thermodynamic flexibility of the polymer chains, which depends on their chemical structure and composition. At T_g the elastomer loses its high elastic properties completely, so it is always below the lower usage temperature limit of elastomeric materials. Depending on the chemical nature and structure of the

monomer units the glass transition temperatures of the different elastomers is between minus 130 and 0°C (Table 2).

In the processing of rubber mixtures their cohesive strength has often a great importance, i.e. the ability of the unvulcanized blends to stand the relatively high strain without breaking (up to 1 MPa) under significant deformations (~400%). The problem of increasing the cohesive strength of the blends is particularly burning for general-purpose rubbers, as they have the lowest values of the CED, and the most large-tonnage products are produced on their base.

The chemical structure of the elastomers specifies their supramolecular organization, which may show itself in three varieties. First, this is a certain kind of order and heterogeneity caused by morphology in the amorphous polymer. Secondly, the regularity of the macrochain structure can cause the formation of various crystalline structures. Finally, almost all the block copolymers, and in some cases in statistical copolymers, due to the incompatibility of chemically dissimilar fragments of the polymer chains, there are segregated areas of microscopic or submicroscopic size (domains).

Table 2.
The glass transition temperature of some rubbers

Raw rubber	T_g, °C
Siloxane ACT	123
Trans-polipentenamer	-105 ÷ -100
1,4 - *cis*-butadiene (SKD)	-110 ÷ -105
Butadiene (SKDL)	-90 ÷ -60
Polybutadiene emulsion	№ 80);
1,4 - *cis*-isoprene (NR, SKI-3)	-70 ÷ -68
Isoprene lithium (SKIL)	-69 ÷ -66
Styrene-butadiene emulsion SKS-30	-64 ÷ -59
Styrene-butadiene emulsion SKS-10	72
Styrene-butadiene solution DSSK	-78 ÷ -75