

LOMONOSOV MOSCOW STATE UNIVERSITY

FACULTY OF CHEMISTRY

*POLYMER DEPARTMENT*

*Structural Engineering of  
Polymeric Materials*

*Introductory Remarks*

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**This textbook contributes to the Educational Course**

## **“SELECTED CHAPTERS OF CHEMISTRY”**

*Selected Chapters of Polymer Science*

**lectured for students of Faculty of Chemistry  
Lomonosov Moscow State University**

The principal idea of this textbook is to indicate the fundamentals of the design of modern polymeric materials and realization of this scientific background during processing. To advance in this multi-disciplinary field of knowledge, The *System Approach* was specified in terms of “*Structural Physico-Mechanics of Polymeric Materials*”. Polymeric material was considered as a system which consists of a sequence of subsystems or structural levels. Each structural level is characterized by the own microstructure and micromechanics. The final operating parameters of polymeric material are controlled by cooperative interaction between the above structural levels. From this standpoint, the production of polymeric material was considered as step-by-step structural design of each structural level: *Macromolecular Design, Supramolecular Design, and Suprapolymer Design*. Macromolecular design controls the chemical structure, configuration and molar mass characteristics of macromolecule. At the stage of Supramolecular Design, the aggregation of synthesized macromolecules forms a variety of the types of the supramolecular structure (crystalline phase, networks, oriented structure, suprasegmental and supramolecular clusters) in polymeric material based on the given polymer. As a result of Suprapolymer Design, two or more polymers are combined in complicated polymeric materials as blends, composites, *etc.* The above approach identified as “*Structural Engineering of Polymeric Materials*” allows one to represent the preparation of the modern polymeric materials as the interpenetrating scientific and technological problems.

*For students and post-graduated students who are specialized and/or interested in*  
**Polymer Science**

# CONTENT

<b>Introduction</b>	3
<b>Chapter 1. Macromolecular Design</b>	9
1.1. Amorphous Polymer Substances	11
1.2. Crystalline Polymer Substances	13
<b>Chapter 2. Supramolecular Design</b>	16
2.1. Rubbers (Elastomers)	16
2.2. Fibers	21
2.3. Plastics	25
<b>Chapter 3. Suprapolymer Design</b>	32
3.1. Blends (Alloys)	32
3.2. Block-Copolymers	35
3.3. Interpenetrating Networks	37
3.4. Composites	38
<b>Conclusion</b>	39
Appendix 1. <b>Industrial Synthesis</b>	40
Appendix 2. <b>Types of Commercial Elastomers</b>	51

## INTRODUCTION

Today's widening of the fields of application of modern polymeric materials is responsible for the growing of industrial demands for their operating properties. To advance in this area, the development of the fundamentals concerning the origin of the unique polymer properties followed by the appropriate technological realization of this scientific background is required.

From this standpoint, *Polymer Material Science* is considered as multi-disciplinary area and based on the penetration of chemistry, physics, physical chemistry, mechanics, engineering, and processing. To indicate the intrinsic relationship between the above fundamental and applied sciences, one should find the appropriate approach. To advance in this complicated problem, *System Approach* seems to be promising.

*System Approach* – the methodology which allows one to focus not on the particular aspects of the problem but on the relation between them.

In the framework of the System Approach, any phenomenon is conceived as a *System*.

*System* is hierarchically structures and consists of interacted and interconnected levels (subsystems). A given level of a System is constructed from the lower levels and constructs the higher level.

- The hierarchical principle allows one
- to conduct the detailed study of the behavior of a given level (subsystem);
  - to understand the behavior of the system as a whole in terms of cooperative interaction between different subsystems.

*Let us specify the above fundamentals of the System Approach in terms of Polymer Material Science*

**Polymer Material is a *SYSTEM***

**Each system is characterized by *STRUCTURE***

***STRUCTURE* is the hierarchy of structural sublevels.**

**A.** Each structural sublevel is constructed from the units of the previous sublevel and constructs the following sublevel.

**“monomer units” construct “segments” construct “macromolecules” construct “supra-molecular structural units” construct “macroscopic material”**

**B.** Each structural sublevel is characterized by the own physical and mechanical micro-properties or by the own physical and mechanical behavior.

**C.** Interconnection between structural sublevels controls the *STRUCTURE* of the physical body. The combination of the micro-properties controls exploitation behavior.

These ideas may be formalized in the framework of the “*Structural Physico-Mechanics of Polymers*”. The underlying principle of *Structural Physico-Mechanics* is the general correlation between structure and physico-mechanical behavior of the material.

***Physico-mechanical behavior*** is

- the combination of physical parameters (temperature of physical and phase transitions, sorption properties, *etc.*) and mechanical characteristics of the material (strength, Young's modulus, yield point, ultimate strain, *etc.*);
- the changes in the mechanical characteristics of the material with the changing of the operating parameters, primarily, temperature.

The structure of a material is a sequence of interrelated structural sublevels or structural subsystems. Each of these sublevels is quasi-independent and characterized by the micro-structural organization and corresponding micro-properties. The final macroscopic physico-mechanical behavior is controlled by the cooperative interaction between the above structural levels.

***From this standpoint,***

the objectives of “Structural Physico-Mechanics” are

- to understand the influence of structural organization on the final physico-mechanical parameters of the material;
- to find practical ways to control the final properties of the material via controlled design of structure at a certain structural level.

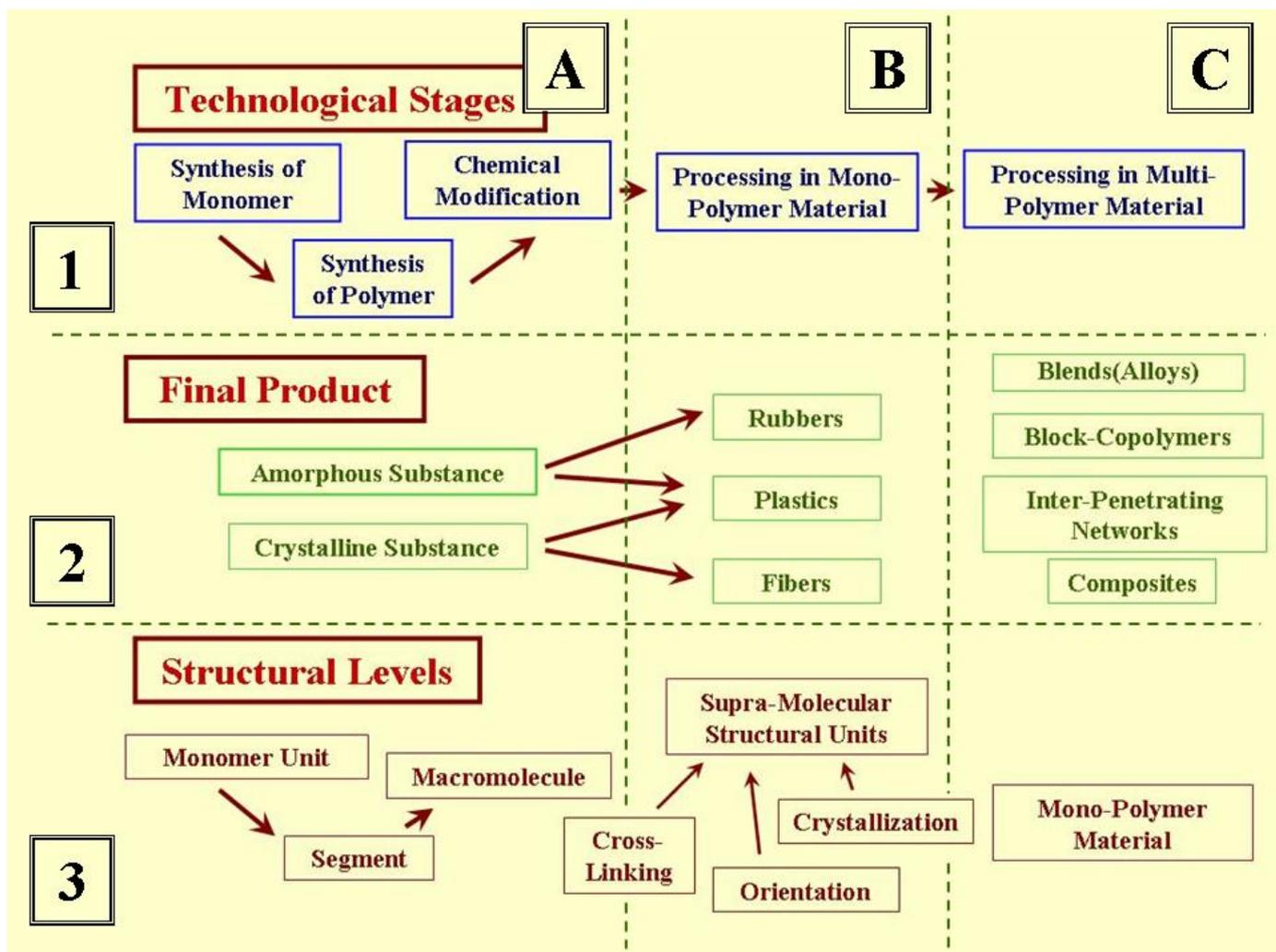
In the framework of the combination of System Approach and Structural Physico-Mechanics, the production of polymeric materials may be considered as shown in Scheme 1.

Technological stages (line 1, Scheme 1) involve synthesis (or choice) of the appropriate monomer (or monomers), their polymerization (or copolymerization) followed by the chemical modification when it is required. The aim of this stage is the synthesis of macromolecule with the desired chemical structure. Macromolecule is considered as a certain structural level (structural subsystem) of the final polymeric material (column A, line 3, Scheme 1). From this point of view, this stage (column A) may be identified as ***Macromolecular Design*** of a polymeric material. The final product of this stage is polymer substance (column A, line 2, Scheme 1) as the powders, granules, *etc.*

Polymer substances are processed in a “***mono-polymer material***” (passing from column A to column B, line 1, Scheme 1).

Monopolymer material is a material based on the only polymer substance.

*Scheme 1*



To obtain the required physico-mechanical characteristics mono-polymer material, the physical and physico-chemical modification is used. The aim of the modification is the generation of the supramolecular units (chemical and physical networks, domains, crystallites, and oriented structure) (column B, line 3, Scheme 1).

In connection with this, this stage (column B, Scheme 1) may be identified as the *Supramolecular Design* of a polymeric material.

The final products of this stage are the mono-polymer materials (or articles) with required shape and operating properties such as rubbers, plastics, and fibers (column B, line 2, Scheme 1).

The above ideas raise a *key problem*

Interrelation between terms

**“Substance”**

and

**“Material”**

**Substance**

*assemblage of macromolecules with the specified chemical structure and configuration*

**Material**

*assemblage of supra-molecular structural units*

For further improvement of the physico-mechanical properties of polymeric materials, mono-polymer materials are processed in multi-polymer materials (passing from column B to column C, line 1, Scheme 1).

Multi-polymer material is a material based on two or more mono-polymer materials.

The aim of this stage is the generation of the suprapolymer structures (mono-polymer separated phases) (column C, line 3, Scheme 1) in multi-polymer materials. From this standpoint, this stage (column C, Scheme 1) may be identified as the ***Suprapolymer Design***.

The examples of the final products of this stage are polymer blends (alloys), block-copolymers, interpenetrating networks, and composites (column C, line 2, Scheme 1).

The operating properties of the resulting multi-polymer material are controlled by the superposition of the physico-mechanical behavior of mono-polymer materials incorporated.

**Hence,**

the preparation of polymeric materials may be considered as the sequence of the controlled design of macromolecule, supramolecular and suprapolymer structures. These speculations may be formalized in terms of “**Structural Engineering of Polymeric Materials**”.

**System Approach**  
**for Polymer Material Science**  
**was formalized in terms of**

**Structural Physico-Mechanics of Polymers**

**the objectives of “Structural Physico-Mechanics” are**

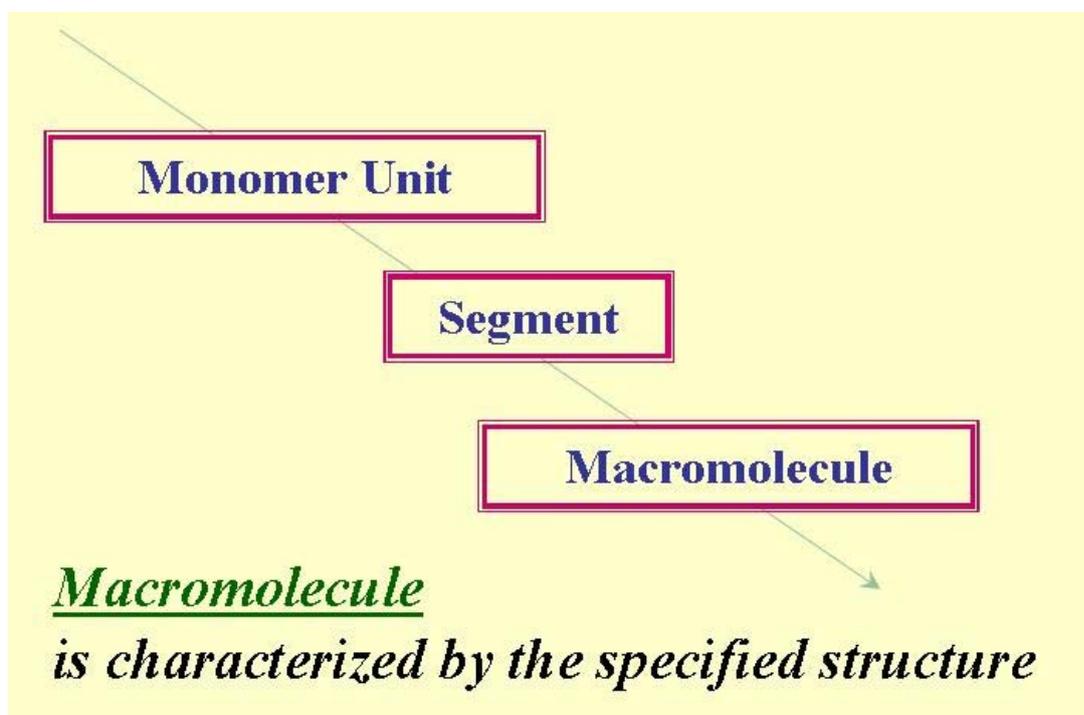
- to understand the influence of structural organization on the final operating parameters of the material;**
- to find ways to control the final properties of the material via controlled design of structure at a certain structural level.**

**Practically, to advance in this scientific and technological area**  
**Structural Engineering of Polymeric Materials**  
**was invoked**

## Chapter 1

# MACROMOLECULAR DESIGN

Macromolecular design (column A, Scheme 1) is associated with the synthesis of the macromolecule with controlled chemical structure. In macromolecule, one can recognize the following structural subunits. These are monomer unit and segment (column A, line 3, Scheme 1).



The chemical structure of monomer controls the chemical structure of monomer unit in macromolecule, that is, the *nature of chemical bonds of backbone (i) and chemical structure of side groups (ii)*.

These two factors are responsible for

- the energy of rotation of atomic groups around chemical bonds in the backbone;
- the size of segment;
- the resulting balance between flexibility and rigidity of macromolecule.

These speculations may be summarized in terms of *conformation* of macrochain.

**Conformation** is the spatial rearrangements of atomic groups in the macromolecule which are produced by the rotation around chemical bonds of the backbone as a result of applied thermal energy, mechanical stress, *etc.*

During polymerization, the mode of arrangement of monomer units to each other controls *configuration* of macromolecule.

**Configuration** is the spatial arrangements of atomic groups in the macromolecule which are not capable to be transformed to each other without the breakage of chemical bonds.

From this standpoint of configuration, macromolecules may be classified as regular and non-regular.

**Hence,**

the main problem of macromolecular design is the control for the

- balance between flexibility and rigidity;
- regularity of polymer macromolecule.

During synthesis of macromolecules, this problem is solved via application of different chemical mechanisms, initiators, catalysts, *etc.*

**Chemical structure of macromolecules as well as configuration and conformation of polymer chains are responsible for the following**

***DIVISION***

**of polymer substances**

**Crystalline Polymer  
Substance**

**Amorphous Polymer  
Substance**

### ***1.1. Amorphous Polymer Substances***

Amorphous polymer substances are used for production of rubbers and plastics (passing from column A to column B, line 2, Scheme 1). They exist in *glassy*, *rubbery*, and *viscous flow* physical states which are separated by *glass transition temperature*,  $T_g$ , and *flow temperature*,  $T_f$ .

The viscous flow physical state is the liquid state and is used for the processing of polymer substance in final polymeric material. Solid amorphous polymers exist in glassy and rubbery states.

For amorphous polymer solids, one of the important physical parameter is  $T_g$ .

Amorphous polymer substances with low  $T_g$  (generally, below  $0^\circ\text{C}$ ) serve for the production of rubbers. The amorphous polymers with  $T_g$  more than  $60^\circ\div 80^\circ\text{C}$  are used for the production of plastics.

The glass transition temperature is upper operating temperature for plastics and lower operating temperature for rubbers. From this point of view, the control for  $T_g$  is of prime importance.

The glass transition temperature is mainly controlled by the *flexibility* of macromolecules (i) and the free volume fraction in polymer body.

The higher both flexibility and free volume fraction, the lower  $T_g$  of the polymer.

To control the flexibility, one should control the ratio between the chemical bonds in backbone, around which the rotation is enhanced,

for example,  $-C-C-$  and  $-C-O-C-$  bonds

and the chemical bonds, around which rotation is hindered,

for example,  $-C=C-$ ,  $-CO-NH-$ , aromatic rings and cyclic groups

***via the synthesis (or choice) of appropriate monomers, copolymerization of appropriate monomers, and the following chemical modification.***

To increase the free volume fraction in polymer body, the monomers with bulk side groups are used. These bulk side groups prevent the close packing of macrochains, and, as a result, the fraction of free volume increases.

***Hence,***

Macromolecular Design allows one to control  $T_g$  of an amorphous polymer substance in the course of polymer synthesis.

***From the standpoint of Structural Physico-Mechanics,***

$T_g$  controls the occurrence of the segmental mobility in polymer chains and in final polymeric material.

In the rubbery physical state, at the temperature above  $T_g$ , appearance of the segmental mobility is responsible for the *high-elastic* reversible deformation.

In general, the mechanical behavior of polymers in rubbery state is *viscoelastic*.

Viscoelasticity is associated with the co-existence of reversible (elastic) and irreversible (flow) deformations.

Segmental mobility controls the high-elastic reversible portion of viscoelastic behavior. Displacements of macromolecular coils relative each other contribute to the flow irreversible part of viscoelastic deformation.

In the glassy physical state, at temperature below  $T_g$ , macromolecules do not possess segmental mobility. As a result, glassy polymers are much stiffer as compared with rubbers.

## 1.2. Crystalline Polymer Substances

Crystalline polymer substances are used for the production of plastics and fibers (passing from column A to column B, line 2, Scheme 1).

From the standpoint of *configuration*, crystallization is observed only for regular polymers chains which have not bulk side groups.

In general, for flexible polymers, crystallization, that is, formation of crystalline lattice proceeds via folding of macromolecules.

From this point of view, to provide crystallization, macromolecules should possess appropriate conformation.

The general structural feature of crystalline polymers is associated with the co-existence of amorphous and crystalline phases. These polymers are identified as *semi-crystalline* polymers. Quantitatively, the co-existence of these two phases is described by the *degree of crystallinity*, that is, the ratio between mass (or volume) of crystalline phase and total mass (or volume) of the sample. In other words, degree of crystallinity is the mass (or volume) fraction of crystalline phase.

The physical and mechanical properties of semi-crystalline polymers are controlled by the superposition of stiffness of crystalline phase and softness of amorphous phase.

Crystalline phase is characterized by *melting temperature*,  $T_m$ , and amorphous phase is characterized by  $T_g$ .

For semi-crystalline polymers, melting point is the upper operating temperature.

In general, the influence of the chemical structure on  $T_m$  is similar to that on  $T_g$ . The increasing of macrochains rigidity and the presence of the polar atomic groups favor crystallization and leads to the increase in melting point. The bulk side groups and side branches restrict the close packing of macromolecules, and  $T_m$  decreases.

The specific feature of semi-crystalline polymers is associated with the fact that the crystalline phase has a pronounced influence on  $T_g$  of the

amorphous phase. The crystallites hinder the mobility of *tie-chains* in amorphous phase, and, as a result,  $T_g$  increases. The influence of crystalline phase on  $T_g$  of amorphous phase depends, primarily, on the degree of crystallinity. The higher the degree of crystallinity, the higher  $T_g$  of amorphous phase. At the same degree of crystallinity,  $T_g$  of amorphous phase is controlled by the size and amount of crystallites, and, in general, by the crystallites size distribution.

*To summarize*

*The objectives of Macromolecular Design,  
that is,  
the synthetic aspects of Structural Engineering of  
Polymeric Materials:*

*to prepare polymers or polymer substances with  
controlled*

- **Chemical Structure;**
- **Configuration;**
- **Molar-mass characteristics;**
- **Branching**

**What factors hinder the solution of these problem**

**kinetics**

*incorporation of monomer molecules in growing macromolecule  
requires the overcoming of the potential barrier*

**thermodynamics**

*incorporation of monomer molecules in growing macromolecule  
seems to be not favorable because of decrease in entropy and requires  
noticeable exothermal effect*

To satisfy the above trends and requirements a variety of industrial techniques are used. The most important of them are discussed in *APPENDIX I*.

\* \* \*

The role of Macromolecular Design as the first stage of Structural Engineering of Polymeric Materials is of great importance because that is primarily responsible for the following Supramolecular Design via combination of various methods of chemical, physical, and physico-chemical modification (crystallization, orientation, cross-linking, plasticizing, impregnation, *etc.*).

These scientific and technological approaches allow one to produce polymeric materials with the desired exploitation parameters such as strength and impact strength, ductility, elasticity, operating temperature range, *etc.*

The possible ways of the solution of these problems are discussed in forthcoming chapter.

## Chapter 2

# SUPRAMOLECULAR DESIGN

Supramolecular Design (column B, Scheme 1) is associated with the preparation of the mono-polymer materials and final articles with required shape and operating characteristics. In general, mono-polymer construction materials can be classified as rubbers, plastics, and fibers (column B, Scheme 1).

### *2.1. Rubbers (Elastomers)*

According to ASTM D1566-90 rubber is defined as

“material that is capable of recovering from large deformations quickly and forcibly, and can be, or already is, modified to a state in which it is essentially insoluble (but can be swell) in solvent, such as benzene, methyl ethyl ketone, and ethanol toluene azeotrope”.

Commercial elastomers are defined as

“macromolecular material that returns rapidly to approximately the initial dimensions and shape after substantial deformation by a weak stress and release of the stress”.

In other words, an elastomer is considered as a rubbery polymeric material that can be or already is modified to a state which, after unloading, is characterized by rapid and complete strain recovery.

The most important types of commercial elastomers are listed in *APPENDIX II*.

### ***Required Physical and Mechanical Characteristics***

#### ***In practice,***

elastomers should satisfy the following requirements.

- Capability to be stretched to 100%;
- Capability to recover to within 10% of initial length within 5 min after stretching to 100%, holding for 5 min in stretched state, and releasing.

Hence, for commercial elastomeric material, required physico-mechanical behavior may be summarize as

well-pronounced high elastic reversible deformation with no noticeable irreversible plastic deformations within wide operating temperature range.

#### ***From the applied standpoint,***

preparation of elastomer for specific usage requires the control for the following mechanical and physical parameters.

1. ***Tensile strength.*** Note that, in general, this operating parameter is not considered as a universal desired property because elastomers are not often used in tensile regime of loading. The importance of this parameter is associated with the fact that other desired properties of elastomer such as wear and tear resistance, resilience (elasticity and impact elasticity), cut resistance, stress relaxation, creep, flex fatigue, *etc.* correlate well and are improved with tensile strength. In other words, for a given elastomer, easily estimated tensile strength reflects the development of a set of physico-mechanical parameters and may serve as an indicator of a quality of material;
2. ***Ultimate strain;***

3. **Hardness** which is the index of the elastomer resistance to deformation under pressing a ball or blunt point onto the sample surface;
4. **Modulus**, that is, the ratio between stress (force per unit of original cross section) and a specified strain. For elastomers, modulus is usually estimated at strain of about 300 %, and this parameter has nothing in common with Young's modulus estimated, for solids, at the initial portion of stress-strain diagram. Under slight extension, elastomers are characterized by the rather low modulus which grows with extension in logarithm manner;
5. **Permanent set**, that is, deformation of elastomer which remains in unloaded sample after loading with a given stress for a given period of time;
6. **Compression set**, that is, deformation of elastomer which remains in unloaded sample after compression loading at either constant stress or strain for a given period of time;
7. **Flex fatigue** implies the elastomer fracture as a result of fluctuating stresses;
8. **Impact resistance**, that is, resistance of elastomer to abrading or cutting as a result of hitting with sharp object;
9. **Low-temperature properties** indicates a stiffening range and brittle parameters of elastomer;
10. **Tear resistance**, that is, the stress which is needed to maintain the rupture of elastomer sheet usually cut initially;
11. **Abrasion resistance**, that is, the resistance of elastomer to wear. This parameter is usually measured by the weight loss of material when a sample is in contact with a moving abrasive surface;
12. **Hysteresis** which denotes loss of mechanical work in loading cycle. The importance of this parameter is associated with the fact that, under cyclic loading, mechanical loss is converted into heat, and, in the case of poor heat removal, heating of the material may reach destructive temperatures;
13. **Heat build-up** indicates increasing temperature in elastomer material caused by hysteresis phenomena;
14. **Heat resistance**. In general, elastomers are not considered as heat-resistant materials. For them, heat resistance is estimated as the changes in tensile strength, ultimate strain, and hardness usually after 72 hours of keeping the sample at a given temperature;
15. **Flame resistance**;
16. **Ageing**. The desired properties of elastomers deteriorate markedly when chain growth and linkage (i) and chain rupture (ii) take place in the material under the action of sunlight, heat, oxygen, ozone,

moisture, and atmospheric nitrous oxide. The proceeding of the first type of the above chemical reactions in the material results in increasing hardness and tensile strength and decrease ultimate strain whereas chain rupture has the opposite effect. Note that some elastomers demonstrate hardening as a result of ageing, and others softens with time. In some cases, ageing of elastomers are characterized by initial hardening followed by softening;

17. **Radiation resistance.** Note that the effect of radiation on the elastomer properties is similar to that for ageing;
18. **Resistance to chemicals;**
19. **Gas permeability.**

Obviously, to realize the above physico-mechanical behavior and required specific properties, combination of molecular and supramolecular design is required. Let us discuss the possible ways to solve this problem.

### ***Ways of Solution***

Structural consideration of viscoelasticity of amorphous polymer substances in rubbery physical state suggests that the high-elastic reversible contribution to the viscoelastic deformation is controlled by the segmental mobility. The irreversible component of the viscoelastic deformation is associated with the mutual displacements (flow) of macromolecules. From this standpoint, to achieve the above most important requirement concerning the full strain recovery one should retain segmental mobility and suppress the mobility of macromolecular coils.

For rubbers, the operating temperature range is between  $T_g$  and  $T_f$ . Obviously, increasing  $T_f$  and decreasing  $T_g$  favors the widening of the required temperature range.

### ***Structural Engineering***

The increase in macrochains flexibility, the decrease in the energy of intermolecular interaction, and the increase in free volume favor the segmental mobility, and, as a result, enhance the the ability to high elastic deformation and decrease  $T_g$ , one should enhance segmental mobility via increasing flexibility of macrochain, decreasing the energy of intermolecular interaction, and increasing free volume. These problems

are related to formation of appropriate chemical structure at the macromolecular stage of design.

To suppress the irreversible displacements of macromolecules, the cross-linking (vulcanization) of rubbers is used. Cross-linking results in the formation of supramolecular structure, that is, chemical network (column B, line 3, Scheme 1). Note that the cross-linking also increases  $T_f$ . When the flow of macromolecular coils is suppressed completely,  $T_f$  is higher than the temperature of thermal decomposition of polymer. As a result, for vulcanized elastomers, the operating temperatures lies in the range from glass transition temperature to the temperature of thermal decomposition of material.

\* \* \*

**Hence,**

***At the stage of Macromolecular Design***

the problems concerning high flexibility of the polymer chains and low values of  $T_g$  are solved via choice of appropriate monomers and usage of appropriate synthetic techniques.

***At the stage of Supramolecular Design***

formation of the three-dimensional chemical network via vulcanization results in

- appearance of well-pronounced high-elasticity with no irreversible portion of strain in final elastomer;
- widening of operating temperature range up to the temperature of thermal decomposition of polymer.

***To satisfy special requirements*** (items 1, 3, 4, 7 – 11, 13 – 17)

a variety of physico-chemical methods of modification are used. They are associated with the plasticization and introduction of various fillers, stabilizers, and reinforcing agents in rubbery material.

In industry, to prepare the article with the desired characteristics the more sophisticated approaches are used. The prime example of this situation is the production of automobiles tires.

The tire is a composite material in which the rubbery matrix is reinforced by the organic and inorganic fibers (cords), steel plates, *etc.*

***Goodyear tire is a composite.***

**The preparation of this article requires the usage of**

*up to 12 types of rubbers  
several types of polymeric and metallic cords  
several grades of steel*

*In general, up to 60 raw materials*



## ***2.2.Fibers***

Polymer fibers are widely used in the various fields of application as individual monofilaments, reinforcing components in modern composite materials, for production of ropes, textiles, fabrics, *etc.*

The main advantage of polymer fibers is associated with their high strength (5 – 10 GPa) and high modulus (150 – 250 GPa) in combination with low density (0.95 – 1.5 g/cm<sup>3</sup>). The last parameter is of prime importance because allows one to decrease the weight of article without loss in mechanical characteristics. This trend dictates the high values of specific strength of polymer fibers, that is, the ratio between strength and density. For polymer fibers, this value lies in the range 3 – 10 (cm<sup>3</sup>GPa)/g. Note that the above mechanical characteristics of modern polymer fibers markedly exceeds those for steel.

## ***Required Physical and Mechanical Characteristics***

- high strength and modulus, that is, high resistance to applied loading;
- wide operating temperature interval.

## ***Ways of the Solution***

- suppression of both segmental and molecular mobility;
- increase in melting temperature.

## ***Structural Engineering***

At the stage of Macromolecular Design, to solve the above problems, one should increase the rigidity of macromolecules and the energy of intermolecular interaction via choice of appropriate monomers.

At the stage of Supramolecular Design, increasing stiffness and strength of the material is achieved by the formation of the supramolecular structures via *crystallization* and *orientation* (column B, line 3, Scheme 1).

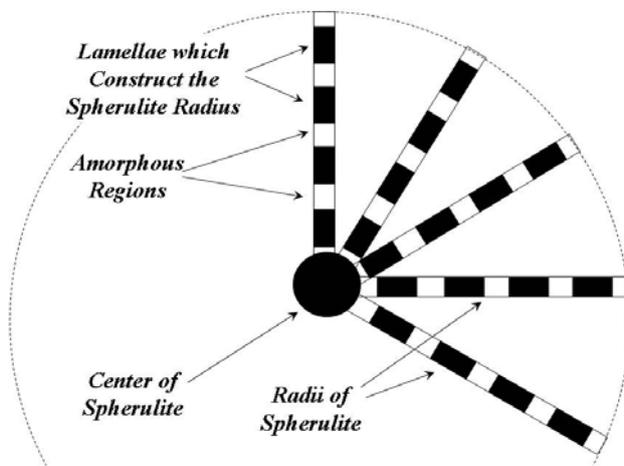
Crystallization is associated with the formation of supramolecular crystalline structure as a result of formation of crystallites. The aggregation of crystallites is accompanied by the formation of supracrystallite structures such as spherulites, dendrites, *etc.* In the crystalline phase, close packing of macromolecules with high energy of intermolecular interaction prevents slippage of macromolecules, and, as a result, resistance to applied deformation increases.

However, in semi-crystalline polymers, the above stiff crystalline phase coexists with amorphous phase. From this standpoint, macroscopic mechanical properties of semi-crystalline materials are also controlled by low resistance of amorphous phase to the applied loading. Obviously, to increase mechanical response of semi-crystalline polymer to applied stress, one should increase degree of crystallinity and the size of crystallites. Note that these factors are also responsible for the growth of melting temperature.

Both degree of crystallinity and size of crystallites are controlled by the time-temperature regimes of crystallization. The longer the time of crystallization and the closer temperature of crystallization to melting temperature, the higher both degree of crystallinity and size of crystallites.

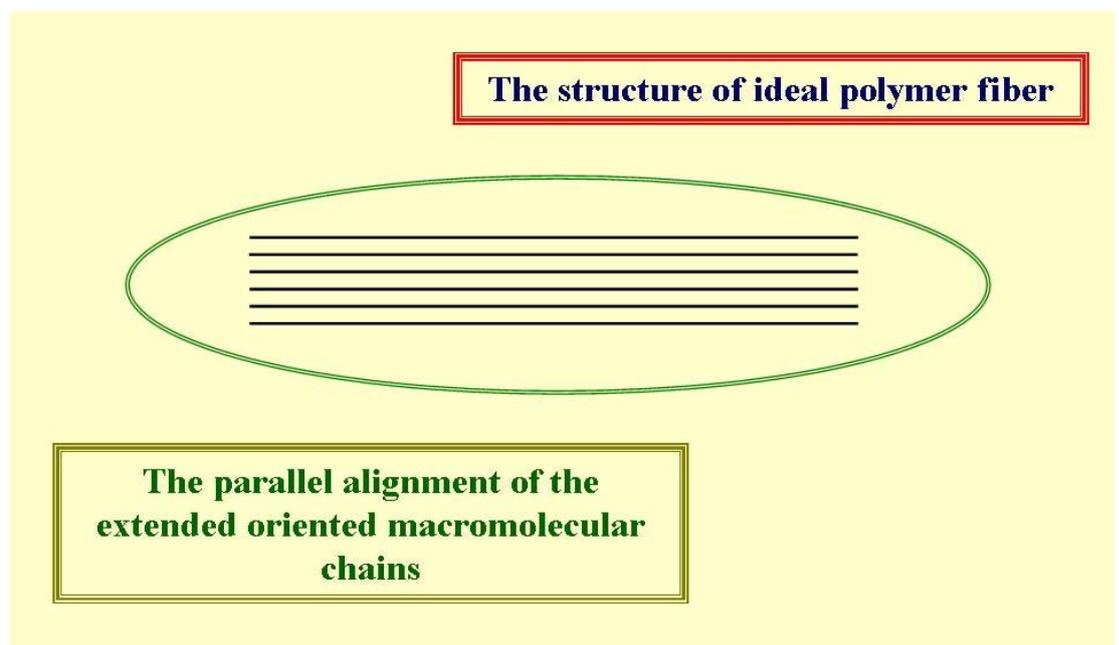
For as-prepared semicrystalline polymers, structural features of crystalline phase are associated with the folded structure of the individual

crystallites and random orientation of crystallites and supracrystallites (spherulites, as the prime example).



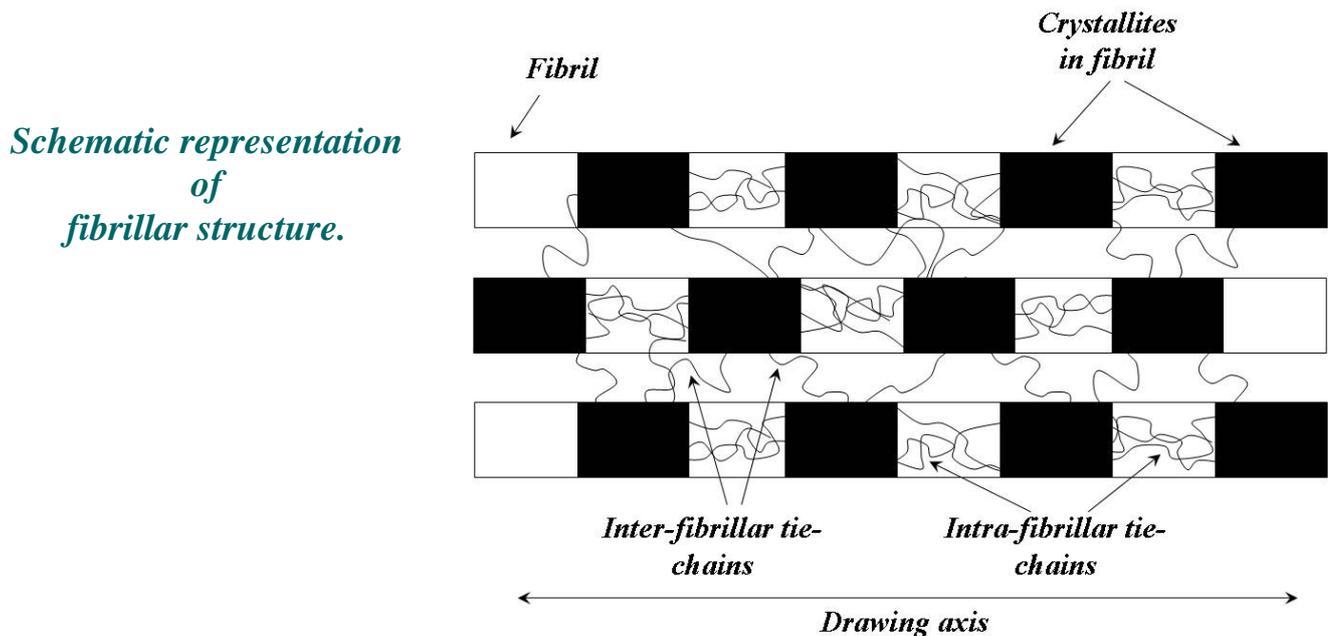
*Schematic representation of complicated structure of spherulite as the prime example of supracrystallite.*

To improve mechanical characteristics, one should attain parallel alignment of the macromolecules. In this case, during the deformation in the direction of the above alignment only strong covalent bonds are expected to resist to applied loading.



To realize this situation, orientation drawing is used. The stretching of semi-crystalline fibers is accompanied by unfolding of the crystallites with the formation of new fibrillar supramolecular structure.

As compared with the initial supracrystalline structure, fibrillar structure is characterized by the partly elongated macrochains and folded crystallites oriented along the axis of drawing. As a result, the final mechanical parameters of oriented semi-crystalline polymer fibers exceed those of the isotropic material. Hence, the formation of new fibrillar supramolecular structure during orientation drawing controls the appearance of new mechanical properties of the material.



At the technological scale, it is necessary to work out the optimal regime to provide crystallization and orientation simultaneously just in the course of fiber processing (spinning) in the continuous way. At the present time, there are two basic spinning techniques: melt spinning and solution spinning.

Despite of a lot of differences between the above technological processes, the principal idea is the following. When polymer melt or solution is pushed out through the holes (spinnerets), solidification and crystallization take place because of cooling (melt spinning) or evaporation of solvent (solution spinning). Using the suitable wind-up devices, fiber is stretched to provide orientation simultaneously with the solidification (crystallization) of the cooling or drying fiber. In this case, orientation of fiber during processing results in the growth of packing density and enhances crystallization.

## To Summarize

### **Basic Requirements for Fibers**

1. High Strength
2. High Young's Modulus
3. Wide Operating Temperature Range, that is, High Melting Temperature,  $T_m$

$T_m$  – the upper exploitation temperature

### **Structural Engineering of Fibers**

#### **at the stage of Macromolecular Design**

1. Control for the balance between rigidity and flexibility of macromolecule
2. Increase in the energy of intra-molecular interaction
3. Increase in the energy of inter-molecular interaction

#### **at the stage of Supramolecular Design**

1. Orientation
2. Crystallization

## 2.3. Plastics

A wide variety of plastics makes the development of their all-purpose structural design difficult. Plastics are based on both amorphous and semi-crystalline polymers. They are classified as *thermoplastics*, when they soften with the heating, and *thermosets*, when with increasing temperature they harden because of chemical reactions. One may recognized basic plastics, engineering plastics and superengineering plastics with the different requirements for the final operating characteristics. Here, we outline the just general ideas concerning these polymeric materials.

### **Required Physicomechanical Characteristics**

- high strength and high impact strength;
- high modulus;
- wide operating temperature interval.

## ***Ways of the Solution***

### ***For plastics based on the semi-crystalline polymers***

the upper operating temperature is melting temperature.

### ***For amorphous plastics***

the upper operating temperature is glass transition temperature.

### ***For both these types of plastics***

the lower operating temperature is *brittleness temperature*.

Within this operating temperature interval, plastics are characterized by the well-pronounced ductility which contributes to the high impact resistance.

To attain the above combination of high strength and high impact strength, one should control the balance between stiffness and softness of these polymeric materials.

## ***Structural Engineering***

### ***For semi-crystalline plastics***

the balance between stiffness and softness is controlled by the co-existence of crystalline and amorphous phase. Crystalline phase contributes to the stiffness of the resulting material and increases its strength and modulus. In soft amorphous phase, pronounced molecular mobility provides the dissipation of applied mechanical energy as a heat and, as a result, prevents the brittle fracture. Note that, for amorphous polymers, molecular mobility appears at temperatures above glass transition temperature. From this standpoint, the compromise between strength properties and impact resistance is reached within operating temperature interval between glass transition temperature of amorphous phase and melting temperature of crystalline phase.

Obviously, the required balance between stiffness and softness of final plastic material is easily controlled by the degree of crystallinity. At the same degree of crystallinity, the above balance depends on the size and amount of crystallites, and morphology of the crystalline phase.

At operating temperatures below glass transition temperature of amorphous phase, the brittleness of semi-crystalline plastics increases, and, in general, the required mechanical properties are lost.

*Semi-Crystalline Polymer*

- Co-existence of crystalline and amorphous phases
- Macroscopic properties – superposition of micro-properties of crystallites and tie-chains which form the amorphous phase

*The Factors which Control Physical and Mechanical Behavior of Semi-Crystalline Polymer*

*at the level of crystalline phase*

- Degree of crystallinity
- Size distribution of crystallites
- Defects in crystallites

*at the level of amorphous phase*

- Physical state (glassy or rubbery state)
- Influence of crystalline structure on the behavior of tie-chains

*The Factors which Control the Micro-Mechanics of Crystallites*

- The size of crystallites or, to be more correct, the ratio between Surface and Volume
- Volume properties
- Molar mass and molar mass distribution
- Chemical structure of polymer
- The type of crystalline lattice.



*Control for the*

- Melting temperature
- Strength characteristics of plastic

*The Factors which Control the Micro-Mechanics of Amorphous Phase Composed from the Tie-Chains*

*«Direct» Factors*

- Molar mass and molar mass distribution
- Chemical structure of polymer (flexibility, energy of the intermolecular interactions)
- Temperature

*«Indirect» Factors*

- Degree of crystallinity
- Distribution of crystallites

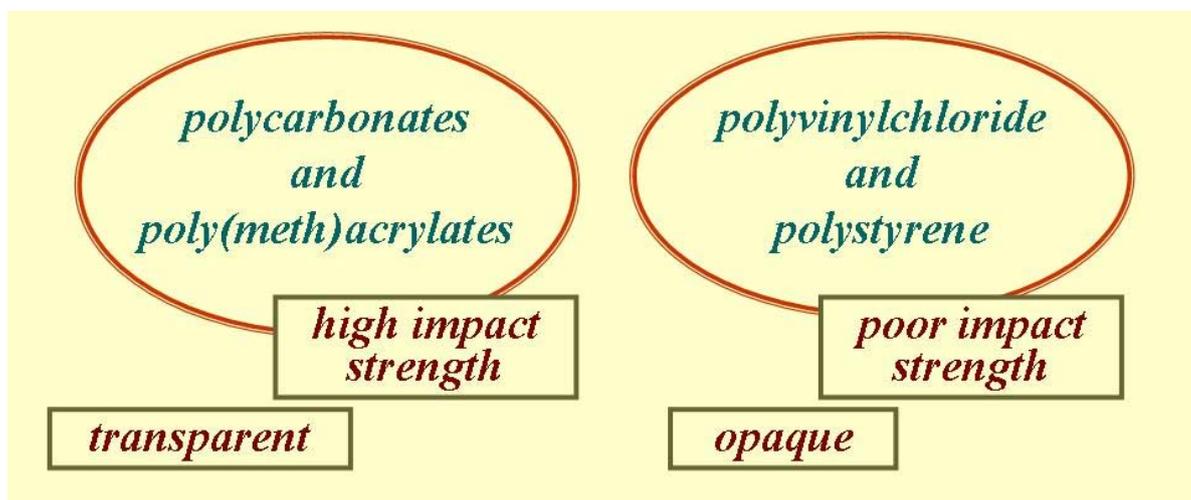


*Control for the*

- Brittleness temperature
- Elasticity (plasticity) of plastic

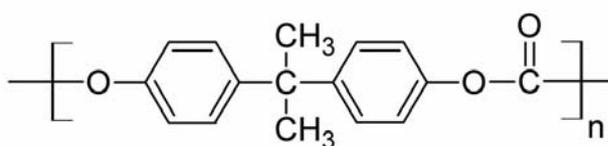
### *For amorphous plastics or polymer (organic) glasses*

Polymer glasses can be classified according to their construction properties, primarily, impact strength and according to their functional property – transparency.



At the *stage of Macromolecular Design*, the combination of strength properties and impact resistance is mainly controlled by chemical structure of these materials. Aromatic and cyclic atomic groups in the backbone contribute to the stiffness of final product whereas the chemical bonds, around which rotation is allowed, increase ductility.

As the prime example of this trend let us consider macromolecular design of polycarbonate family.



#### *Bisphenol A Polycarbonate*

The carbonate anomic group  $-\text{C}-\text{CO}-\text{C}-$  controls flexibility of the chain resulting in the appearance of “low-temperature” plasticity and high impact strength of the final material. Benzene groups provide rigidity of the macromolecule and, as a result, high strength and elastic modulus of the polymer.

Obviously, the final balance between the stiffness (high strength and high modulus) and elasticity (high impact strength) of the material is controlled by the ratio between carbonate anomic group  $-\text{C}-\text{CO}-\text{C}-$  and

“benzene” fragments as well as by the chemical structure of the “benzene” fragments.

The main disadvantage of polycarbonate materials is associated with the fact that to produce the new trademark of polycarbonate one need synthesize the new monomer (or monomers) and develop the technology of polymer synthesis as well as the processing of polymer substance to final article.

Hence, the production of new polycarbonate trademark requires elaboration of specific and whole technological scheme from the synthesis of monomer to preparation of final article.

At the *stage of Supramolecular Design*, the required operating characteristics can be achieved by the modification of commercial polymer using the following modification methods – orientation and cross-linking.

Note that polymethylmethacrylate (PMMA) is mostly prone to the above modification techniques. Let us discuss the possibilities of the above modification methods using PMMA as example.

### ***But***

in the majority of the cases a given modification technique results in the improvement of some parameter of the material while the other characteristics deteriorate.

### ***For example***

#### ***Cross-linking***

*results in increase in thermal stability and decrease in impact strength*

#### ***Orientation***

*results in increase in impact strength and decrease in thermal stability*

### ***The problem***

simultaneous improvement of all required parameters.

### ***The reason of decrease in thermal stability as a result of orientation***

entropic temperature-induced recovery of extended macromolecules.

## To increase thermal stability of oriented PMMA

It is necessary to embed the extended oriented macromolecules in isotropic polymeric matrix characterized by high viscosity

### *Technology proposed*

- *Bulk polymerization of monomer to 80% conversion*
- *Orientation*
- *Polymerization of residual monomer and cross-linking*

### *As compared with the conventional technology to produce oriented PMMA*

- *Bulk polymerization of monomer to 100% conversion*
- *Orientation*

The final product prepared using the proposed technology can be considered as oriented PMMA embedded in isotropic PMMA matrix or, in other words, *self-reinforcing* PMMA.

***Hence,***

the combination of orientation and cross-linking of polymerizing systems with conversion less than 100 % allows one to produce transparent PMMA with desired impact properties and thermal stability.

\* \* \*

### *To summarize*

Macromolecular Design of polymeric materials followed by the Supramolecular Design allows one to prepare mono-polymer materials with controlled physico-mechanical behavior. The limitation of this approach is associated with the fact that, for each mono-polymer material, only a well-defined set of physico-mechanical parameters may be attained.

To widen the areas of polymeric materials application, the superposition of the sets of operating parameters of mono-polymer materials is achieved via combination of the corresponding polymers in one multi-polymer material. These problems are discussed in the forthcoming chapter.

## Chapter 3

# SUPRAPOLYMER DESIGN

At the stage of Suprapolymer Design (column C, Scheme 1), mono-polymer materials are processed to multi-polymer materials (column C, line 1, Scheme 1) such as polymer blends, block copolymers, interpenetrating networks, and composites (column C, line 2, Scheme 1).

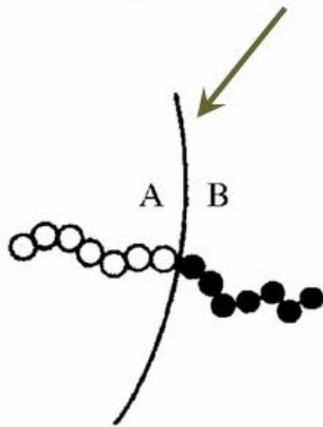
From the structural standpoint, preparation of multi-polymer material is associated with the controlled formation of suprapolymer structures (column C, line 3, Scheme 1).

### ***3.1. Blends (Alloys)***

The most simple way to combine the properties of two or more polymers is their blending in appropriate ratio. Most polymer *blends* are immiscible, and, as a result, in these materials phase separation occurs. To increase compatibility between the polymeric components of the blend a variety of compatibilization techniques are used. Such compatibilized blends are sometimes identified as polymer *alloys*.

***Compatibilization*** of the polymeric components of the blend is achieved by incorporation of compatibilizers in materials. As the most popular compatibilizers block- or graft copolymers are used. The basic principle of compatibilization can be represented as follows.

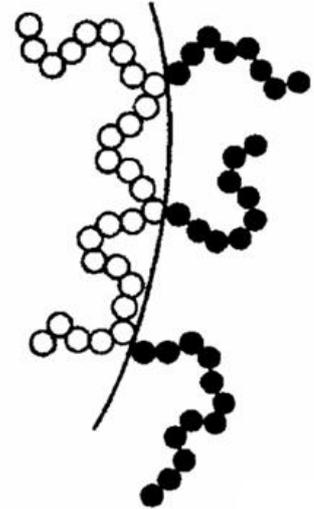
**The boundary between  
polymer A phase and polymer  
B phase**



**Compatibilization  
with diblock  
copolymer**



**Compatibilization  
with triblock  
copolymer**



**Compatibilization  
with graft  
copolymer**

The “white” blocks of copolymers are miscible with the polymer of type A, and the “black” blocks – with the polymer of type B. As a result, adhesion between A and B phases is markedly improved. Note that the compatibilizers also affectively reduce the surface energy her unit area.

**The morphology** of polymer blend depends mainly upon the composition of the material.

In general, when the concentration of a given polymer component of a two-phase blend is rather low this component forms approximately spherical droplets dispersed throughout the matrix.

The size of these droplets depends on

- the nature of polymers;
- molar mass and molar-mass distribution;
- the regime of preparation of the blend and conditions of processing;
- the presence or absence of compatibilizers.

With increasing content of a given polymer component up to *phase-inversion concentration* dispersed phases become continuous giving the so-called *co-continuous morphology*.

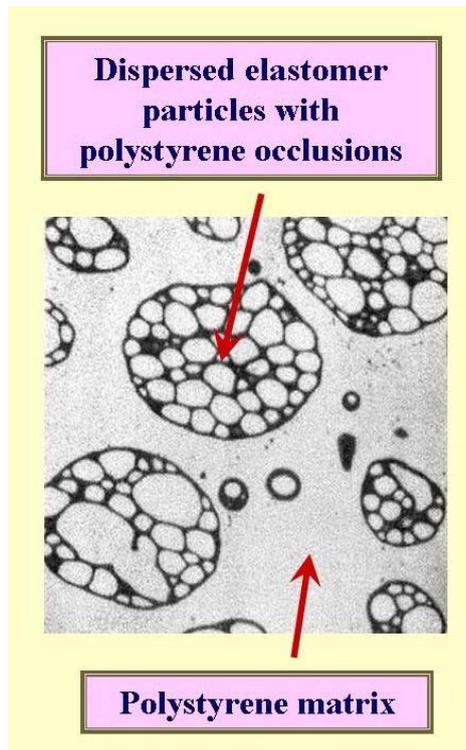
### ***Properties and fields of application of polymer blends***

Blending is widely used to improve mechanical characteristics of polymeric materials such as impact strength, strength and modulus. The prime example of this approach is the production of *high-impact polystyrene* (HIPS).

As mentioned in chapter 2.3 polystyrene is characterized by poor impact strength. To increase this parameter rubbery particles are incorporated in polystyrene matrix via dissolving about 4 % of polybutadiene in styrene and further polymerization of solution. The final product contains 94 % of polystyrene and 6 % of the styrene-butadiene graft copolymer which contains about 30 % of styrene units.

HIPS consists of a matrix of polystyrene containing spherical particles of rubbery polybutadiene. The dimensions of these inclusions are in the range  $1 \div 30 \mu\text{m}$  and are controlled by the composition and polymerization techniques.

Another type of rubbery-toughened blends is acrylonitrile-butadiene-styrene (ABS) plastic. This material is based on the styrene-acrylonitrile block copolymers toughened with either polybutadiene or polystyrene-polybutadiene copolymers.



### ***Hence***

At the stage of Suprapolymer Design, increasing impact properties of polymer glasses is achieved by the inclusion of rubber particles in glassy matrix. The mechanism of rubber toughening is associated with the fact that, under impact loading, as compared with glassy matrix, rubbery phase deforms easier, and dissipation of the localized stress takes place.

These events prevent the propagation of the cracks and contributes to the impact resistance of polymeric material. The final impact properties are controlled by the mechanical properties of both glassy matrix and incorporated rubbery material, volume fraction and size distribution of rubbery inclusions. Macromolecular Design and Supramolecular Design are responsible for the physicomechanical behavior of the components of the blend. The main objective of suprapolymer design is to combine

appropriately the separated polymer phases in the final multi-polymer material.

### 3.2. Block-Copolymers

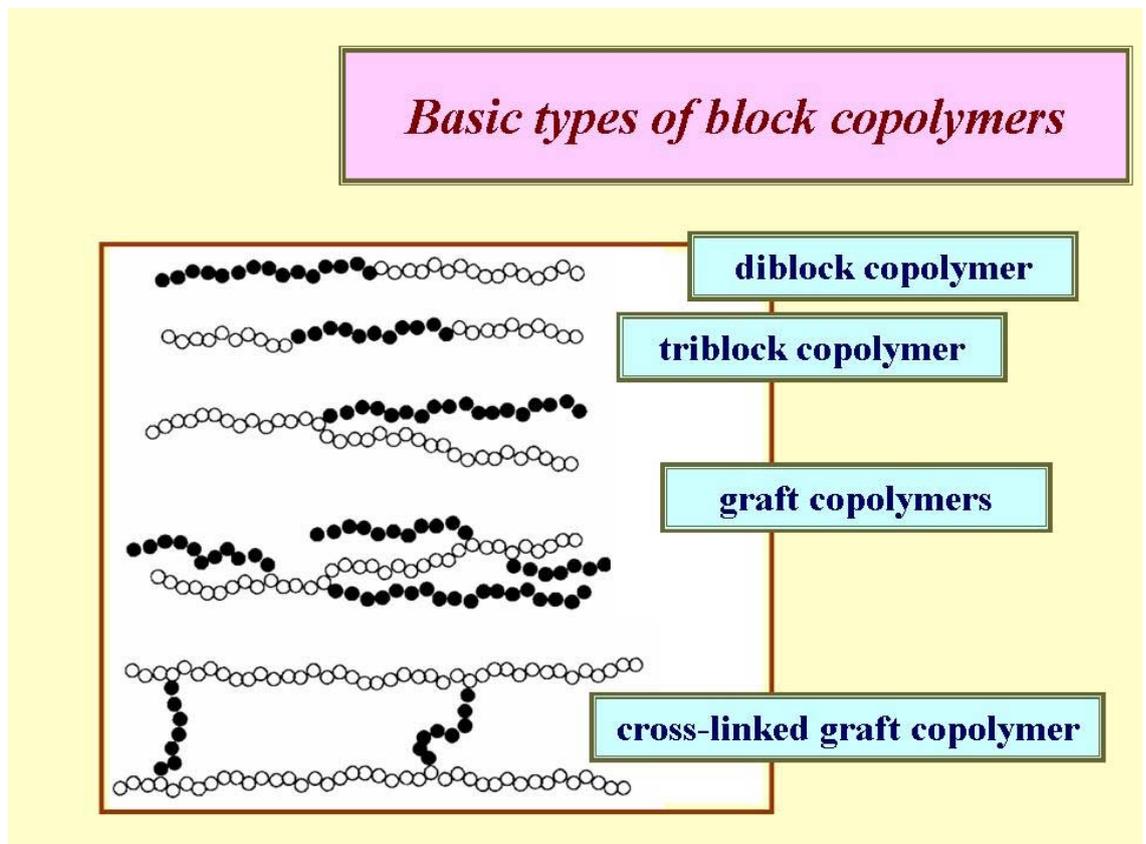
*For these polymeric materials,*

immiscible polymers are incorporated in one polymer chain.

In this case, each block forms its own phase, and microphase separation takes place. As compared with the polymer blends,

for block copolymers, the separated phases are covalently linked with each other.

Structural Engineering of these polymeric materials is based mainly on the influence of the length of block on the size and morphology of the corresponding phase.



At the volume fraction of the block not more than 20 %, it forms spherical phase. These spherical particles are regularly included in polymer matrix which is formed by the other block. At the approximately equal volume fractions, the resulting material is characterized by the lamellae suprapolymer structure. Cylindrical morphology of included blocks is observed when the fraction content of the block is intermediate between the above cases.

The above suprapolymer design provides the appearance of specific physico-mechanical behavior. For example, block copolymers have two glass transition temperatures which are close to those for the corresponding homopolymers. Each block is characterized by the own set of physico-mechanical and physico-chemical properties.

Block copolymers are widely used as compatibilizers (see Section 3.1). Another important field of application of triblock ABA copolymers is associated with the production of *thermoplastic elastomers* or *elastoplastics*.

***ASTM D 1566 defines thermoplastic elastomers as***

“a family of rubberlike materials, that unlike conventional vulcanized rubbers, can be processed and recycled like thermoplastic materials.”

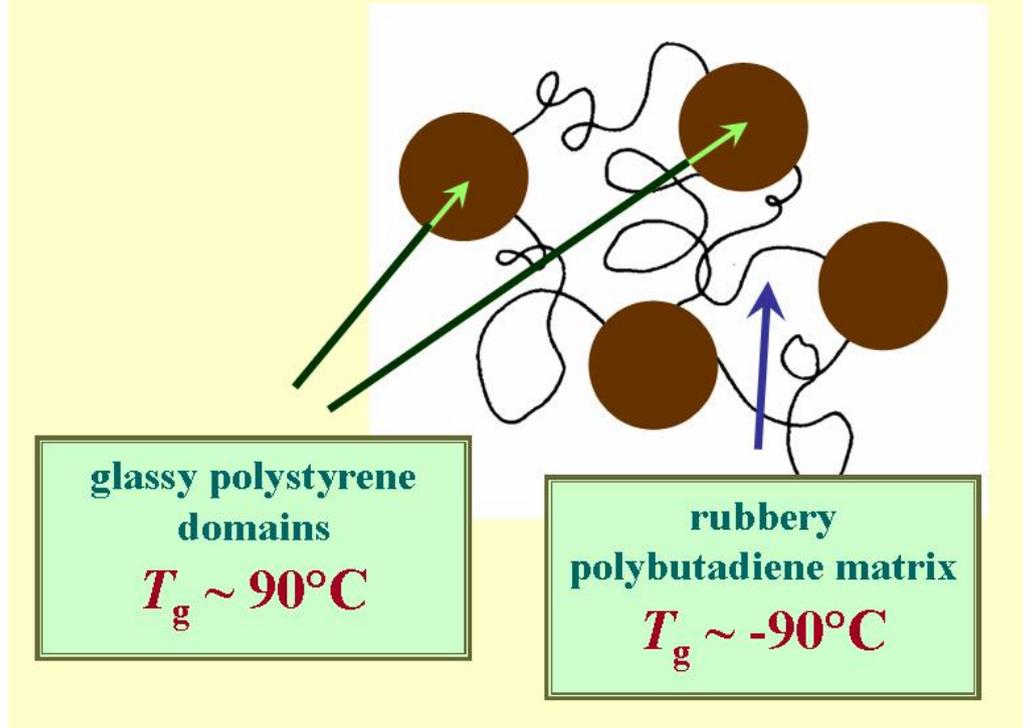
In other words, thermoplastic elastomers demonstrate operating performance similar to that of commercial thermoset vulcanized rubbers, but they can be fabricated, processed, and recycled as conventional thermoplastics.

***The principal idea of Suprapolymer Design to produce thermoplastic elastomers***

Triblock ABA copolymer is copolymerized using glassy A blocks and rubbery, elastomeric B block. The typical examples of these materials are styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) triblock copolymers with styrene volume concentration of 10 ÷ 20 %.

At these concentrations, styrene blocks form spherical glassy inclusions in rubbery butadiene matrix. Styrene glassy inclusions act as cross-links and contribute to reinforcement of the final polymeric material. Polybutadiene chains between cross-links are responsible for the high elastic deformations.

## Schematic structure of SBS thermoplastic elastomer



This multipolymer material operates as monopolymer chemically cross-linked rubber. The main advantage of triblock rubber is its thermoplastic behavior. Styrene inclusions work as cross-links at operating temperatures below glass transition temperature of polystyrene. At temperatures above  $T_g$ , softening of the material allows its processing in article and recycling. Obviously, these procedures can not be carried out for the vulcanized rubbers.

### 3.3. Interpenetrating Networks

#### *Interpenetrating polymer network*

multi-polymer material which comprises two or more networks interlacing on a molecular scale without covalent bonding to each other. These networks cannot be separated unless chemical bonds are broken.

In general, *preparation of interpenetrating networks* is based on the *in situ* polymerization of a given monomer in a given polymer matrix. The most simple procedure involves swelling of cross-linked polymer matrix in the mixture of monomer, initiator, and cross-linking agent

followed by the polymerization of incorporated monomer and cross-linking of the resulting polymer. After that, as-obtained two interpenetrating networks may be linked via appropriate chemical reactions, for example, transfer reactions. Interpenetrating networks may be fine dispersed or may form separate phases.

Interpenetrating networks are widely used in pharmaceutical, medical and biomedical industry due to their enhanced biological and physical characteristics such as biodegradability, biocompatibility, stability, swelling capacity, mechanical strength, *etc.* These materials play a significant role for preparation of carrier systems for controlled drug delivery.

### 3.4. Composites

Composites are based on the combination of two or more materials and exhibit the properties which are not observed for individual incorporated components.

The prime example of these materials is *fiber-reinforced composites*.

In this case, high modulus and high strength oriented fibers with length-to-diameter ratios more than 100, that is, monopolymer material obtained at the stages of Macromolecular Design and Supramolecular Design are embedded in polymer matrix. The reinforcing component of composite (fibers) contributes to the strength properties of the material and matrix provides bulky properties and dimensional stability.

For these composites, the final operating parameters are provided by the

- properties of individual polymers incorporated,
- volume ratio between them,
- interaction between them,
- mode of the reinforcing components arrangement in the matrix.

Suprapolymer Design controls the last three terms.

Note the wide possibilities of the design of composite material. Composites may be based not only on polymeric material and involve inorganic fibers and metals as the reinforcing components.

## **CONCLUSION**

Combination of System Approach and “Structural Physico-Mechanics of Polymeric Materials” allows one to train and study in the multi-disciplinary “Polymer Material Science” in terms of “Structural Engineering of Polymeric Materials”.

The approach proposed is based on the sequential structural design of macromolecule, supramolecular structure, and suprapolymer structure.

## Industrial Synthesis

### Gas-Phase Polymerization

Gas-phase polymerization is widely used for production of several types of polyethylene.

Gaseous ethylene is polymerized according to radical mechanism at high pressure (150 ÷ 300 MPa) and temperature (200 ÷ 260°C) with oxygen or peroxides as the initiators. The final product contains a large number of side groups (branches) which hinder crystallization, reduce density, and lower final mechanical parameters. This type of polyethylene is referred to as low-density polyethylene (LDPE) or high-pressure polyethylene (HPPE).

Ziegler-Natta catalysts allow polymerization of polyethylene at ambient pressure (0.1 ÷ 2 MPa) and temperature (120 ÷ 150°C). In this case, relatively linear polyethylene with higher density and crystallinity is produced, and this type of polyethylene is identified as high-density polyethylene (HDPE) or low-pressure polyethylene (LPPE). Characteristics of LDPE and HDPE are listed in Table .

*Table 1*  
**Characteristics of Different Types of Polyethylene**

	<b>LDPE</b>	<b>HDPE</b>
<i>Density, g/cm<sup>3</sup></i>	0.910 - 0.925	0.941 - 0.965
<i>Degree of Crystallinity, %</i>	60 - 70	80 - 95
<i>Branching, equivalent CH<sub>3</sub> groups per 1000 carbon atoms</i>	15 - 30	1 - 5
<i>Melting point, K</i>	380 - 390	400 - 416
<i>Tensile Modulus, N/m<sup>2</sup></i>	0.97-2.6 × 10 <sup>8</sup>	4.1-12.4 × 10 <sup>8</sup>
<i>Tensile Strength, N/m<sup>2</sup></i>	0.41-1.6 × 10 <sup>7</sup>	2.1-3.8 × 10 <sup>7</sup>
<i>Hardness, Shore D</i>	41 - 46	60 - 70

## ***Bulk Polymerization***

Bulk (or mass) polymerization is the simplest and most direct way for commercial production of polymers which are dissolved in their monomers via radical polymerization mechanism. The polymerizing system involves monomer and monomer-soluble initiator, and, under appropriate temperature control, polymerization proceeds till complete monomer exhaustion.

***The main difficulties*** of industrial bulk polymerization are associated with the specific features of radical polymerization.

When polymerization proceeds, the viscosity of polymerizing system increases markedly. As a result, well-pronounced *gel effect* and distinct acceleration of the rate of polymerization take place. Taking into account the exothermic effect of radical polymerization, gel effect is responsible for the increasing temperature of polymerizing system. Increasing temperature favors the further acceleration of reaction and so on.

Note that the polymers and, in general, organic systems are characterized by the low heat capacities and thermal conductivities. These factors control the poor removal of the heat released as a result of reaction. High viscosity of polymerizing system prevents the enhancement of heat removal via convenient stirring. Hence, the intrinsic feature of bulk polymerization is the *well-pronounced overheating* of polymerizing system.

“if a complete rapid polymerization of a reactive monomer in large bulk is attempted, it may lead to loss of apparatus, the polymer or even the experimenter” (C.E. Schildknecht, *Polymer Processes, Interscience, New York, 1956, p. 38*).

If we manage to avoid the above serious problems, bulk polymerization is accompanied by the localized overheating which leads to localized destruction of polymer chains, decreasing molar mass and widening the molar mass distribution of the final polymer. This localized overheating is also responsible for the loss in optical properties and appearance of noticeable internal stresses which degrades the operating parameters of the resultant polymeric material. In connection with this, industrial bulk polymerization requires very precise control for the reaction temperature.

Actually, bulk polymerization is performed at lower temperatures to provide low polymerization rate and effective dissipation of a heat.

***From the thermodynamic viewpoint,***

decreasing reaction temperature is advantageous because of decreasing the equilibrium monomer concentration in polymerizing system and resultant amount of residual unreacted monomer in final polymeric material.

***From the kinetic viewpoint,***

polymerization is accompanied by the increasing the glass transition temperature of polymerizing system. As a result, at a given temperature, polymerization proceeds with noticeable rate till glass transition temperature of polymerizing system attains temperature of polymerization. Solidification of polymerizing system prevents the diffusion of monomer molecules to the reactive ends of growing macrochains, and polymerization is terminated.

In connection with this, temperature regime of bulk polymerization involves polymerization at moderate temperatures up to conversions not above 40 - 50 %, careful increasing temperature above glass transition temperature of polymerizing system followed by the careful cooling.

Despite the above difficulties bulk polymerization is widely used for production of a variety of polymeric materials. The prime examples of them are plexiglass polymerized from methyl methacrylate and a various types of acrylic and methacrylic organic glasses which are widely used in automobile and aircraft industry because of their high optical quality and mechanical parameters.

***The main advantages of bulk polymerization are the following:***

1. The highest possible purity of final polymer because initial polymerizing system consists of only monomer and initiator;
2. After completion of the reaction, the resultant polymer has the shape of the mold where bulk polymerization was performed. In connection with this, bulk polymerization allows direct preparation of final polymeric material with required shape without following processing;
3. As compared with the other industrial synthetic techniques, bulk polymerization is characterized by the highest polymer yield close to 100 %.

## ***Precipitation Polymerization***

For polymers which are insoluble in their monomers, primarily, poly(vinyl chloride), poly(vinylidene chloride), and polyacrylonitrile, bulk polymerization is characterized by the following specific features.

During polymerization, the solubility of growing macrochains decreases, and they precipitate out of solution as swollen gel-like particles. In this case, reactive end groups of the growing macromolecules are mainly buried in the particles, and further polymerization involves diffusion of monomer molecules to the above reactive end groups. Obviously, this factor decreases the rate of polymerization.

Inside the swollen particle, polymerization is similar to bulk polymerization when gel point is reached, and gel effect controls the autoacceleration of the reaction and noticeable release of the heat. However, as compared with bulk polymerization, the macroscopic viscosity of the polymerizing system as a whole is not high enough. This is the reason of the effective heat removal.

## ***Solution Polymerization***

In solution polymerization, ***polymerizing system consists of***

- monomer dissolved in appropriate solvent,
- initiating agents.

Initiating agents may be soluble in solvent or exist as a suspension.

The solvents used are required

- not to react chemically with initiators,
- to have low transfer constants to provide sufficiently high degree of polymerization.

Polymerization in solution allows one to avoid the above difficulties of the bulk polymerization. Obviously, in this case, *heat dissipation from polymerizing system is much enhanced*. To prevent gel effect because of increasing viscosity, the monomer concentration in solution should not exceed 20 %.

For these polymerizing systems, *effective stirring* may be applied to improve heat removal and avoid localized overheating. In connection with

this, solution polymerization requires more easy control for the process and makes it possible to regulate molar mass and molar mass distribution of the resulting polymer.

When the resultant polymer is insoluble in solvent, spontaneous precipitation simplifies polymer separation from polymerizing system. When polymer is soluble in solvent, it is separated from solution via adding of the precipitants, evaporation of the solvent, *etc.* On the other hand, polymer solutions obtained via solution polymerization can be used directly for, as an example, coating of a various substrates.

The most of ionic polymerizations including Zeigler-Natta mechanism are performed in industry in solution. This method is used for commercial production of

- stereoregular poly(*cis*-1,4-isoprene),
- polybutadiene,
- polypropylene,
- block- and random copolymers of butadiene and styrene,
- poly(ethylene-*co*-propylene),
- high-density polyethylene,
- polystyrene,
- poly(methyl methacrylate),
- polyacrylamide,
- poly(acrylic acid),
- polyacrylonitrile, *etc.*

***The main disadvantages of solution polymerization are the following:***

1. For this process, expensive, flammable, and often toxic solvents are used. After completion of polymerization, they should be regenerated via additional technological stage;
2. Separation and purification of the polymer obtained are required;
3. According to the theoretical kinetic scheme, both rate of polymerization and degree of polymerization are proportional to monomer concentration. From this standpoint, polymers synthesized in solution are characterized by the lower molar masses as compared with those obtained via bulk polymerization. Additional decreasing degree of polymerization takes place when the solvent acts as transfer agent;

4. Using the inert solvent in polymerizing system lowers the yield of polymer and capacity of the process.

## ***Suspension Polymerization***

As discussed above, for bulk polymerization, ***the main problem is associated with the effective heat removal*** from the polymerizing system.

To facilitate heat removal, the most simple way is the decreasing volume of the reaction zone.

This situation is successfully realized in suspension polymerization when the monomer with initiator are dispersed as the droplets with the diameter from 0.01 to 1 mm in inert liquid (water, in the most cases). Usually, the monomer-water volume ratio is from 0.25 to 0.5. When the droplets are formed, temperature is increased to the required polymerization temperature.

These droplets may be considered as *isolated reactors in which usual bulk polymerization proceeds*, and their small dimensions provides easy heat removal to low-viscosity suspension medium. To maintain stability of the suspension during polymerization, suspending agents and agitation are used.

As suspending agents, “protective colloids” (i) or insoluble inorganic compounds (ii) are used. Protective colloid (water-soluble polymer such as gelatin, poly(acrylic acid), poly(vinyl alcohol), *etc.*) is added to suspension medium (water) to increase its viscosity and hinder hydrodynamically the coalescence of monomer droplets. Inorganic compounds such as  $\text{MgCO}_3$ ,  $\text{MgO}$ ,  $\text{Al(OH)}_3$ , silicates, *etc.* stabilize suspension via adsorption at the droplet-water interface.

During suspension polymerization, to prevent coalescence of the droplets, effective stirring of the polymerizing system is particularly required when conversion of polymerization is between 20 and 70 %. At conversions below 20 %, monomer phase is sufficiently fluid to re-disperse after coalescence. When conversion is higher than 70 %, the droplets become solid enough to avoid agglomeration.

In suspension polymerization, final polymer is obtained in the form of pearls and is called pearl polymer. In general, the size of pearls is controlled

by the nature of monomer, suspending system, and efficiency of stirring. After polymerization, pearls are filtered or centrifuged, washed with water to remove protective colloid or rinsed with appropriate solvents to decompose inorganic compounds.

Suspension polymerization is applied for monomers with poor solubility in water. For monomers which are slightly more soluble, electrolytes are added to suspension medium to salt monomer out. The prime example of polymer obtained via suspension polymerization is polystyrene. As compared with bulk polymerization, polymers prepared via suspension polymerization are less pure because of residues of suspending agents adsorbed at the pearls surfaces.

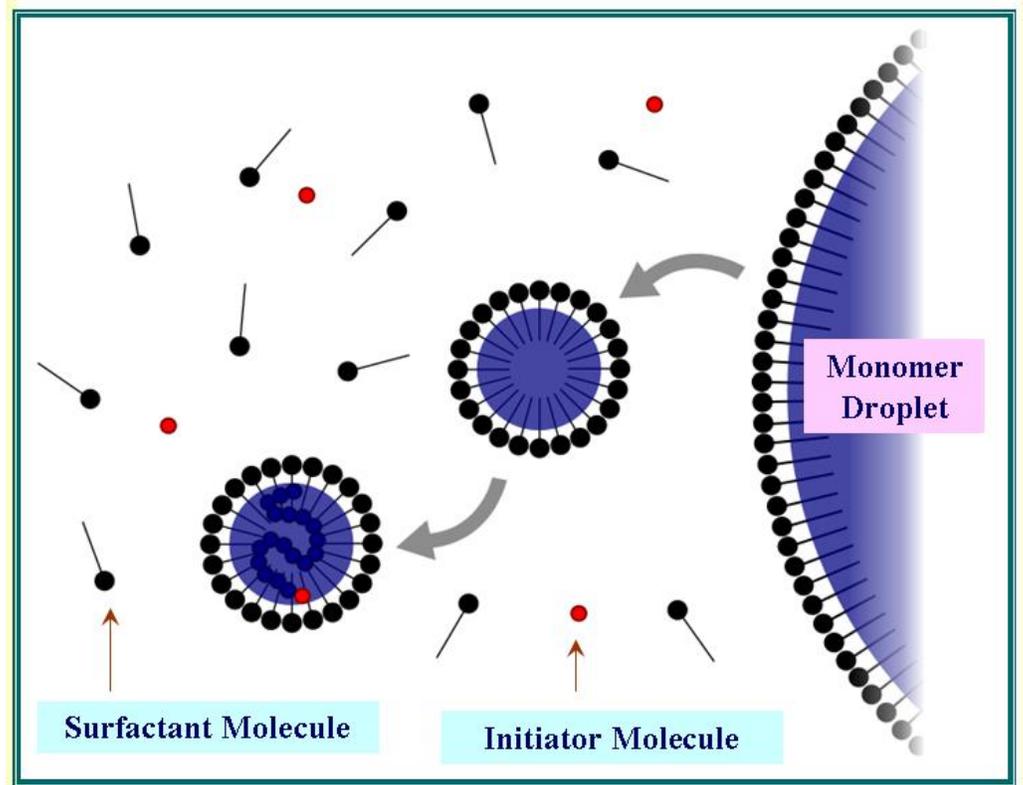
### ***Emulsion Polymerization***

Moderate modification of suspension polymerization such as adding a detergent in a system and using water-soluble initiator results in dramatic changes in the polymerization mechanism.

For emulsion polymerization, polymerizing system contains

- droplets of the monomer stabilized by the detergent,
- continuous water phase which involves initiator and is saturated with monomer and detergent,
- detergent micelles with incorporated monomer molecules.

In this industrial method initiation and propagation start in the aqueous phase. When macrochain grows, its hydrophobicity increases, and growing macromolecule tends to pass from water to more suitable media - monomer droplets or micelles. Note that, despite their smaller mass fraction, the total surface of the micelles is larger than that for the monomer droplets for several orders of magnitude. As a result, all growing chains are practically gathered in micelles. Diffusion of monomer molecules into micelles controls the growth of macrochains inside micelles, increase in their size, and exhaustion of monomer in the water phase. To compensate the decreasing saturated monomer concentration in water, the slow dissolution of monomer droplets occurs, and polymerization continues via gradual transport of monomer from droplets to micelles.



In parallel, new polymer chains are initiated in the aqueous phase and incorporated into micelles. When the second macroradical enters the same micelle, termination occurs immediately because of high local concentration of macrochains in small micelle. In this micelle, further polymerization is possible when the new growing macroradical is incorporated and proceeds till the entrance of the next macroradical and so on.

This unusual mechanism of radical polymerization controls the specific kinetic features of emulsion polymerization.

At any moment, in polymerizing system, polymerization proceeds in a certain fraction of micelles while no polymerization takes place in others.

*In connection with this,*

- Concentrations of both monomer and initiator do not influence on the rate of polymerization which depends mainly on the number of micelles and, in its turn, concentration of detergent.

$$V \approx [Detergent]$$

- Degree of polymerization is controlled by the average time of growth of macrochain within micelle till termination by the macroradical entered from aqueous phase. Hence, degree of polymerization is reciprocal to frequency of the new radical entries in micelles which is proportional to the initiator concentration.

$$\bar{P}_n \approx \frac{1}{[Initiator]}$$

Note that, for bulk polymerization, the rate of polymerization is proportional and degree of polymerization is reciprocal to the square root of initiator concentration.

At the present time, emulsion polymerization is the most popular industrial method for conducting radical chain polymerization.

*The prime examples of commercial polymers produced via emulsion polymerization are*

- polystyrene,
- poly(vinyl chloride),
- poly(methyl methacrylate),
- poly(vinyl acetate),
- polyacrylonitrile,
- copolymers of the above monomers with butadiene.

The resultant polymer is produced in the form of fine powder - latex with particles size 0.05 0.15  $\mu\text{m}$ .

Obviously, emulsion polymerization is easily controlled because the viscosity of polymerizing system is much less as compared with that for the true solution of comparable concentration and, as a result, heat removal is much enhanced.

In emulsion polymerization, polymers with high molar mass are produced with the high rate under appropriate balance between concentration of initiator and detergent.

***The disadvantage of the process is associated with***

the purification of the final polymer from detergent and residual monomer. However, the extremely small size of latex particles provides very effective removal of monomer and detergent molecules from the polymer by steam stripping, for example.

***Stepwise Reactions***

In industry, stepwise reactions is most frequently performed *in the monomers melt* at temperatures above 200°C in an inert atmosphere to prevent destruction and secondary reactions. After completion of the process, the system is evacuated to remove low-molar-mass products of the reaction, and resultant polymer is comminuted for the further processing. When stepwise synthesis requires moderate temperatures, stepwise reactions are conducted *in the solutions of monomers*.

A variation of solution stepwise reactions, that is, *interfacial polycondensation* is performed at the interface between two immiscible liquid phases. Each monomer of a condensation pair is dissolved in its own liquid phase, and resultant polymer is not soluble in both liquids. In this case, monomers diffuse to the interface where they react with formation of polymer film. Within this polymer film, for one monomer of the condensation monomer pair, the probability to meet an opposite monomer and start new chain is very low as compared with that to be incorporated into existing chains. As a result, the molar mass of the resultant polymer is higher than for other polycondensation reactions.

The film obtained is gradually withdrawn from the interface, and new portion of polymer forms providing, thus, continuous conducting of the process up to complete exhaustion of the monomers.

Commercially, it is much easy to stir the phases together to provide interfacial polycondensation in emulsion. Under appropriate conditions, this process is used for continuous production of polymer fibers.

***The main advantages of the interfacial polycondensation are associated with***

the high molar mass of resultant polymers, and high speed of reaction which easily proceeds at room temperature and normal pressure as compared with long duration of other types of polycondensation reactions which require elevated temperatures and vacuum.

The need to separate and recycle solvents and unreacted monomers is responsible for the drawbacks of the process.

## Types of Commercial Elastomers

### *Natural Rubber*

At the present time, the major part of natural rubber is produced from the *Hevea brasiliensis* tree. To produce natural rubber, the tree is tapped, and free-flowing latex is coagulated with an acid and coagulant, milled and creped to reduce the moisture, and carefully dried.

#### *From the chemical viewpoint,*

natural rubber is stereospecific 1,4-*cis*-polyisoprene. This regular *cis*-configuration of the natural polymer is responsible for high elastic properties of resulting material. The presence of double bond controls the possibilities for cross-linking of natural rubber with appropriate curing agents to produce cross-linked (vulcanized) commercially available types and grades of natural rubber.

Elastomers based on natural rubber are characterized by

- high tensile strength,
- resilience,
- tear and wear resistance,
- good resistance to acids and bases,
- good electrical-insulation properties.

As compared with synthetic elastomers, natural rubber possesses rather poor sunlight, oxygen, and ozone resistance. However, the application of special compounding and modification allows noticeable improvement of these characteristics. Natural rubber is not also satisfactory in resistance to oils from petroleum, vegetable, and animal origin.

The ageing properties of natural rubber are not so good as those for synthetic elastomers. However, the changes of properties of natural rubber with time are opposite to those for synthetic elastomers - natural rubber becomes softer with time while synthetics harden.

Elastomers based on natural rubber are widely used in tires and mechanical goods.

## ***Synthetic Elastomers***

### ***Carbon-Chain Elastomers***

#### ***Elastomers Based on Dienes***

Polymerization of diene monomers with the general chemical structure



proceeds with the appearance of the mixture of the following configuration isomers:

- 1,4-*cis*- and 1,4-*trans*-isomers;
- 1,2- and 3,4-vinyl isomers.

The usage of diene monomers to synthesize and produce synthetic elastomers became possible when the stereospecific polymerization techniques were discovered and developed. These synthetic advance allowed one to control the configuration isomerism of resulting polymers and, as a result, their final physicomechanical behavior.

In dependence of the chemical nature of *R* side group, the following types of monomers and corresponding polymers are generally used for production of this type of elastomers:

- isoprene and polyisoprene ( $R = \text{CH}_3$ ),
- chloroprene and polychloroprene ( $R = \text{Cl}$ ),
- butadiene and polybutadiene ( $R = \text{H}$ ).

#### ***Polyisoprene Rubbers***

The successful stereospecific synthesis of 1,4-*cis*-polyisoprene in 1956 provided a basis to develop and produce synthetic equivalent of natural rubber. Infrared analysis of both natural rubber and synthetic polyisoprene shows the similar high content of 1,4-*cis*-isomers in them. This similarity of the chemical structures is responsible for the similarity of the final operating parameters and fields of application of these two natural and synthetic materials.

## *Neoprene Rubbers*

Neoprene is the generic name for polymers based on chloroprene. Neoprene was one of the first commercial synthetic rubber manufactured since 1930s.

From the chemical standpoint, commercial neoprene polymers are characterized by the following approximate content of configuration isomers:

- |                       |         |
|-----------------------|---------|
| • 1,4- <i>trans</i> - | 88-92 % |
| • 1,4- <i>cis</i> -   | 7-12 %  |
| • 1,2-                | 1.5 %   |
| • 3,4-                | 1 %     |

High content of extended 1,4-*trans*-isomer is responsible for crystallization of resulting polymer, and degree of crystallinity can be easily controlled by the change of the content of this isomer in material. Note that 1,2-addition results in the appearance of chlorine atom in allylic form. High lability of chlorine in this position provides the principal sites for vulcanization of neoprenes. To vulcanize these rubber materials, metallic oxides (primarily, zinc oxide and magnesium oxide) are used. The reaction of metallic oxides with chlorine atoms provides the cross-linking of polymer chains with oxygen-containing bridges. When the acceleration of curing is required, accelerators (ethylene thiourea, as a prime example) can be used. Red lead ( $Pb_3O_4$ ) is used as vulcanizer when high water resistance is required.

Neoprene rubbers are characterized by good resistance to oxidative chemicals, and their weather- and ozone-resistance are close to those for natural rubber. Among the other synthetic rubbers, neoprenes are considered as moderately oil-resistant materials. Crystalline nature of neoprenes controls their high tensile strength and wear properties. The presence of polar chlorine atoms in chemical structure decreases neoprene electrical-insulation properties as compared with non-polar natural rubber. However, chlorine contributes to the excellent flame resistance of neoprenes which are, actually, self-extinguishing.

## ***Polybutadiene Rubbers***

Mentioned above discovery of stereospecific solution polymerization of isoprene in 1950s advanced the possibilities for the synthesis and production of stereoregular diene polymers. Taking into account the high cost of isoprene, the efforts were devoted to development of elastomers based on the more cheap butadiene. Development of the catalyst systems which allowed one to regulate the ratio between *cis*-, *trans*-, and *vinyl*-isomers provided a basis for the preparation of butadiene rubbers with required operating properties. Production of polymers ranging from 100 per cent *cis*, 100 per cent *trans*, and 100 per cent *vinyl* isomers, and any combination became possible.

Note that the *trans*-polybutadiene is a tough elastomer with high hardness, poor hysteresis, *etc.* In contrary, *cis*-polybutadiene is characterized by excellent resilience, low hysteresis, excellent dynamic properties and abrasion resistance. To control the combination of the above operating parameters, one should change the ratio between *cis*- and *trans*-isomers via selecting the appropriate catalyst systems. Polymers with the *cis* content in the range 40 - 85 % are amorphous materials with intermediate properties.

## ***Elastomers Based on Butadiene Copolymers***

To control the physicommechanical behavior of butadiene-based elastomers, copolymerization of butadiene with appropriate comonomers is widely used. At the present time, this type of commercial elastomers involves poly(styrene-*co*-butadiene) and poly(acrylonitrile-*co*-butadiene).

The commercial production of styrene-butadiene rubbers (SBR) was started in 1940s to substitute natural rubber, and up to now this material is considered as the most important and the most widely used synthetic rubber. In general, copolymerization of styrene and butadiene results in dispersion of styrene monomeric units and styrene monomeric units in three possible configurations, that is, 1,4-*cis*, 1,4-*trans*, and *vinyl*. In dependence on the manner of distribution of these comonomers in polymer chain, random, block-, and graft-copolymers may be prepared. To control the ratio between monomeric units and the type of distribution the different polymerization techniques are used.

SBR prepared via emulsion copolymerization usually contains about 23 % of styrene dispersed randomly with butadiene in the polymer chain. The configuration content of butadiene units is about 18 % of *cis*, 65 % of *trans*, and 17 % of *vinyl* isomers. Solution copolymerization provides copolymers with lower *trans*, slightly lower *vinyl*, and higher *cis* contents of butadiene units as compared with emulsion SBR. Note that solution copolymerization allows preparation of both random and block-copolymers.

Obviously, to control the final physical and mechanical properties of material, one can change the ratio between styrene and butadiene units in copolymer.

Vulcanization of SBR proceeds under the action of the same curing agents (primarily, sulfur) as for natural rubber and other unsaturated hydrocarbon polymers. Vulcanization of SBR requires less vulcanization agent for curing than natural rubber. However, SBRs are slower curing than natural rubber because of their lower unsaturation and require more acceleration.

As mentioned above, the original purpose of SBR was to replace natural rubber. However, as compared with natural rubber, SBR lacks in tensile strength, elongation, resilience, hot tear, and hysteresis. The main advantages of this type of elastomers are associated with its low cost, cleanliness, and better heat ageing and wear.

Poly(acrylonitrile-*co*-butadiene)s are known by several generic names. The most popular of them is Nitrile Rubber which is considered as one of the most widely used elastomer. For Nitrile Rubbers the same vulcanization agents are used as for SBR and natural rubber.

Because of the presence of polymer *CN* groups, Nitrile Rubber is above neoprene in polarity and is characterized by poor electrical insulation. The physical and mechanical properties of these elastomers are comparable to those for SBR except the much better heat resistance. The main advantage of Nitrile Rubber is associated with its overall excellent resistance to oils, fuel, and solvents than any other polymer. However, it lacks in weathering and ozone resistance.

## *Elastomers Based on Olefins*

### *Ethylene-Based Rubbers*

The excellent combination of physical and mechanical properties such as

- electrical and chemical resistance,
- resistance to ozone and weathering,
- high flexibility,
- well-pronounced ductility,
- adaptability to processing, *etc.*

as well as low cost makes polyethylene very attractive for a variety of industrial application including rubber industry.

To use polyethylene-based materials as elastomers, one should to solve the following general problems:

- to convert initial thermoplastic polyethylene to thermoset material via cross-linking of polymer chains;
- to suppress well-pronounced spontaneous crystallization of polymer.

To solve the above problems, at the present time, the following approaches are used.

For production of elastomers based on *chemically cross-linked polyethylene*, the general vulcanization reactions can not be applied because of low reactivity of this saturated polymer. To cross-link polyethylene, active peroxides or high energy radiation are used. Note that high energy radiation may be applied only to materials with thin cross-section. Chemical cross-linking with peroxides is adaptable to materials with any geometry and shape, and, in connection with this, this vulcanization technique is more widely used.

The chemical fundamentals of polyethylene cross-linking involves the decomposition of peroxide (dicumyl peroxide, as a prime example) with formation of free radicals, These free radical agents react with polyethylene chains with abstraction of hydrogen from polymer and appearance of free

radical on polymer backbone. Recombination of two polyethylene chains with free radical sites on the backbone results in chemical cross-linking.

To prevent crystallization of polyethylene, one should select branched polyethylene, for example, LDPE. Another approach to control degree of crystallinity of polyethylene is associated with the copolymerization of ethylene with propylene. The distribution and ratio of comonomers which can be varied in the wide range is responsible for the development of crystalline structure and, as a result, for final physicomechanical properties of the material. For example, the most alternative distribution of monomeric units in poly(ethylene-*co*-propylene), provides the most amorphous polymers or polymers with very low crystallinity because of distortion of regularity of polymer chain. Note that this copolymerization is carried out using Ziegler-Natta coordination catalysts.

At the present time, *ethylene-propylene rubbers* are commercially available in two types:

- *ethylene-propylene copolymers* (EPM),
- *ethylene-propylene terpolymers* (EPDM).

Both of them were commercialized in 1960s and, up to now, are widely used in industry because of a good combination of physical and mechanical parameters characteristic for ethylene-based rubbers.

EPM elastomers are vulcanized with the same peroxide agents which are used for preparation of chemically-cross-linked polyethylene. For EPDM, incorporation of the small amount of aliphatic or cyclic non-conjugated diene units in polymer chain allows preparation of sulfur-vulcanizable elastomers.

Chlorosulfonation converts polyethylene to amorphous HYPALON® synthetic rubber introduced in industry in 1950s. This chemical treatment of polyethylene is responsible for appearance of reactive alkyl chloride groups and small amount of sulfonile chloride junctions. To vulcanize the resulting polymer, metallic oxides, sulfur bearing organic compounds, and epoxy resins in various combination are used. In dependence on the nature of curing system, cross-linking takes place through sulfonyl chloride junctions with the formation sulfonate salt bridges or through alkyl chloride groups with the appearance of sulfur cross-links.

From the operating viewpoint, HYPALON® is close to neoprene. However, over neoprene, HYPALON® is characterized by improved heat and ozone resistance, electrical properties, colour stability, and chemical resistance. For example, light-coloured neoprene darkens with time when HYPALON® does not.

### ***Butyl Rubbers***

Butyl rubbers are produced by copolymerization of isobutylene with small amounts (1.5 ÷ 4.5 %) of isoprene. In addition to the conventional grades, chlorinated butyl rubber is also available. Chlorination of butyl rubber increases polarity of polymer and provides the wide possibilities for its chemical modification.

Butyl rubber's outstanding physical properties are

- low air permeability (about 20 % of that of natural rubber),
- high energy-absorbing qualities.

These elastomers are characterized by

- excellent weathering and ozone resistance,
- excellent resistance to corrosive chemicals, dilute mineral acids, vegetable oils, *etc.*,
- excellent flexing properties,
- good low temperature flexibility,
- excellent heat resistance,
- tear resistance about that of natural rubber,
- tensile strength about that of SBR,
- very good insulation properties.

However, it has very poor resistance to petroleum oils and gasoline.

## *Acrylic Elastomers*

Acrylic elastomers are generally based on ethyl acrylate and butyl acrylate or their combination. For these polymers, completely saturated backbone nature is responsible for their excellent heat resistance and require special curing agents. To improve curability, acrylic monomers are copolymerized with 2-chloroethyl vinyl ether, 2-chloroethyl acrylate, acrylonitrile or methacrylonitrile, vinyl chloroacetate, methacrylic or itaconic acids. The original polyacrylates cure with long chain amines. For the above copolymers, the choice of curing system depends on the composition of rubber and final results required.

The chemical nature of original polyacrylate as well as the composition of copolymers have a noticeable influence on the properties of the rubber. For example, transition from poly(ethyl acrylate) to poly(butyl acrylate) is accompanied by the decreasing both brittleness temperature and oil resistance because of increasing the length of side alkyl group. For copolymers, incorporation of acrylonitrile, chloroethyl vinyl ether, or chloroethyl acrylate monomeric units results in decreasing low temperature properties of material and increasing oil and heat resistance.

*The main advantage* of application of acrylic elastomers is associated with their saturated backbone and choice of curing system. Note that the oils for hot applications often contain sulfur-bearing chemicals. In some systems such as automotive transmissions, this sulfur reacts with a variety of elastomers used (for example, nitrile rubber) and hardens the material. Acrylic rubbers are not affected by hot sulfur-modified oils and, in conjunction with transmission oils, work up to 150°C. In connection with this, they are usually used in hot-oil application. As compared with nitrile rubber, acrylic rubbers are characterized by higher heat, oil, and ozone resistance and poorer low-temperature properties.

## *Fluoroelastomers*

This type of elastomers is based on fluorinated carbon-chain polymers and their copolymers (fluorocarbon elastomers) and fluorinated silicone polymers (fluorosilicone elastomers). Vulcanization of fluorocarbon rubbers is initiated by basic substances, primarily, metallic oxides via elimination of hydrogen fluoride at relatively low temperatures. The resulting unsaturation provides sites for the following vulcanization with difunctional amines.

Fluorine groups contribute to high-temperature stability of these elastomers. Fluoroelastomers are valuable in automotive use because their extreme heat and oil resistance which is much higher than that for acrylic rubbers. They have weathering properties superior to those for neoprene and satisfactory physical and mechanical properties about those for SBR. Fluoroelastomers resist most of lubricants, fuels, and hydraulic fluids used in aircrafts and missiles, various corrosive chemicals, and chlorinated solvents.

## *Elementoorganic Elastomers*

### *Polysulfide Elastomers*

Polysulfide elastomers are prepared via reaction of organic dihalides, primarily, ethylene dichloride and dichloroethyl formal with sodium polysulfides, for example, sodium tetrasulfide. In the case of reaction between ethylene dichloride and sodium tetrasulfide, the linear polysulfide is obtained.

Vulcanization of the resulting polymer proceeds under the action of a variety of oxidizing agents.

Polysulfide elastomers are characterized by

- excellent weathering properties,
- resistance to hydrocarbons, aliphatic liquids, chlorinated solvents, the common alcohols, ketones, and esters used in paints, varnishes and inks.

In connection with this, these elastomers are widely used in solvent-carrying hose, printers rolls, and newspaper blankets. As compared with nitrile rubber, they are characterized by poorer tensile strength and abrasion resistance, and high creep under strain.

## *Silicone Elastomers*

Silicone elastomers are based on the polymers with backbone which consists of silicon and oxygen. The prime example of these materials is poly(dimethyl siloxane).

Because of the fact that *silicon is more stable element than carbon*, silicone elastomers are characterized by extremely wide operating temperature range from  $-70 \div -80$  to  $250 \div 300^{\circ}\text{C}$ .

Note that the chemical modification of silicone elastomers provides a wide possibility to control their physical and mechanical characteristics. For example, in poly(dimethyl siloxane), substitution of a fraction of methyl groups by phenyl groups result in the shift of the lower operating temperature down to  $-100^{\circ}\text{C}$  and improvement of radiation resistance. Incorporation of vinyl side groups is accompanied by the improvement of compression set characteristics and enhances vulcanization of polymer. Inclusion of fluorine-containing groups (see *fluoroelastomers*) increases markedly oil resistance.

Vulcanization of silicone rubbers is carried out with organic peroxides activated by heat similar to general procedures used in rubber industry. Note that they are also adaptable to room temperature vulcanization with special curing agents. In this case, silicone elastomers may be used as adhesives, sealants, impregnating materials, *etc.*

In addition to mentioned above extreme heat resistance, silicone elastomers are characterized by resistance to oxidation, ozone, good compression set properties and tear resistance. On the other hand, for them, tensile strength is rather low.