

# Supramolecular structure of polymer binders and composites: targeted control based on the hierarchy

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**Abstract.** The article discusses the problem of targeted control over properties by modifying the supramolecular structure of polymer binders and composites based on their hierarchy. Control over the structure formation of polymers and introduction of modifying additives should be tailored to the specific hierarchical structural levels. Characteristics of polymer materials are associated with structural defects, which also display a hierarchical pattern. Classification of structural defects in polymers is presented. The primary structural level (nano level) of supramolecular formations is of great importance to the reinforcement and regulation of strength characteristics.

## 1. Introduction

Despite the rapid development of polymer science, the problem of targeted control over the supramolecular structure in manufacturing tailored polymer and composite materials still remains unsolved. We need to determine, which methods and techniques of impact on the structure of the material and composite are preferable and efficient under various technological conditions and during operation. These pending problems, as well as the others, reduce the performance capabilities of engineering polymeric materials and composites, reduce their efficiency and ultimately hinder the widespread introduction of novel advanced materials into the building practice.

Progress in the development of building polymer composite materials is feasible under condition of understanding the mechanisms of structure formation and the role of supramolecular structures in the resulting set of material properties, as well as upon identifying the effective tools for regulation and control over the supramolecular structure. This knowledge is indispensable in designing building materials with desired set of properties, in development of modern production technologies for polymer-based composite materials [1, 2]. Determination of the basic patterns in the design chain for engineering polymer composites: “composition – structure/modification – manufacturing technology for materials or products – properties – application” defines the objective and content of the present work.

## 2. Literature View

*Structural and defect hierarchy as a prerequisite for the level-based structure modification of polymers and composites*

The structure of polymeric materials is commonly interpreted as the spatial positioning of structural elements – macromolecules, units, and clusters that form a macroscopic polymeric substance. According



to modern concepts, the organization of polymer matter should be considered as a set of progressively complexified structures. Thus, the polymer substance has a certain hierarchy of supramolecular structures represented by successively increasing multi-molecular formations and complexified structural elements of these formations. The levels of supramolecular structures and their structural elements can be classified according to the following criteria: 1) geometric; 2) thermodynamic (stability in a given specific system); 3) kinetic (time of transition from one structural state to another and the lifetime of a structural element).

Changing the structure of one subsystem is associated with changes in properties and behavior of other structural formations; that is why the discrete behavior pattern of complex hierarchically-structured polymeric material went unnoticed for so long and does not always clearly demonstrate itself [3]. In the process of operation, a polymeric substance is modified under the influence of external factors and its supramolecular structure is rearranged. Separate hierarchical levels of the structure are rearranged rather independently. When the capability of one structural level is completely exhausted, the subsequent levels are reorganized. Discreteness of structural rearrangement is confirmed by data on the deformation fractures values observed and described by G. M. Bartenev [4].

Studies of the fracture micromechanics in polymeric materials by small-angle X-ray scattering method have demonstrated that sub-microcracks of up to 10 nanometers length develop rapidly in weak spots of the structure under load. This coincides with the dimensions of primary molecular structures. However, even numerous sub-microcracks are not as destructive and hazardous as large microcracks, which expand, spread and merge together, resulting in the final destruction of the material.

According to Peterlin [5], the microcrack nuclei are associated with the boundaries of primary structures and defects located at the joints of the subsequent structural levels. These are the weakest sites of supramolecular structures. The discrete spectrum of sub-microcracks and microcracks dimensions (length) was identified and described by G. M. Bartenev and other researchers [6, 7].

The relatively ordered structure of amorphous thermosetting polymers is evidenced by measurements of mechanical, electrical and other properties. Measuring the characteristics of macroscopic properties of non-crystalline polymers suggests that both the elements with dimensions in the tens of angstroms, and substantially larger structural formations and elements are retained in their structure [8].

### 3. Results and Discussion

We have consistently observed a discrete pattern of modifying characteristics of polymer materials and composites in the study of mechanical properties as a function of the rate of loading material. Under a slow and gradual increase of the loading rate, a discrete (stepwise) pattern of modifying characteristics was established in samples in ultimate tension and compression strength test series. We attribute this feature to the manifestation of discrete deformation of the structural elements at various macromolecule packing levels and the associated certain structural defects.

The macromolecular substance can not be perfect in structure, due to the bulkiness of the macromolecules as such, and their packing failures caused by a number of reasons. The supramolecular polymer structure has many defects and these are different at different structural levels.

Thus, taking into account the hierarchical organization of the polymer matter and the relative independence, i.e., discreteness of the structural elements levels, it becomes obvious that structural defects of the system also follow the law of hierarchy. In other words, there is a hierarchy of structural defects in polymers [3].

When the operating polymeric materials are exposed to external factors, we have to deal with the destruction of weak or defective structural elements with the hierarchical pattern and dependence. It can be argued with high probability that different external impacts keep with the weaknesses of different structural levels, i.e., hierarchy-specific structural defects.

If we turn to classifying structural defects, their hierarchy can be represented as follows:

1. Defects of the short-range order (nano scale) associated with failed conformations in the arrangement of separate fragments of the polymer chain and its primary packing, the asymmetry and gaps in spatial mesh nodes formation; these defects range in dimensions from one to tens nanometers and are

comparable with the structural elements of the initial (primary) structural-level of macromolecule packing.

2. Defects of the globular order emerge under the packing failures of globules (folded into conglomerates or coils of long sections of polymer chains) and their mutual arrangement. These defects tend to concentrate at the boundaries of globular elements, are formed mainly by the chain ends, free (unpacked) parts of macromolecules belonging to the transit chains and low molecular weight macromolecules. Dimensions of these defects are comparable with those of the globules and can range from tens to hundreds nanometers.

3. Defects related to the asymmetry and failures of cluster associates, packs, domain and other 3-D structures of the higher level, resulting from inherent stresses, as well as defects at the boundaries between the polymer binder and the filler. Defectiveness (i.e., deviation from the crystallographic order) in the pack or the domain is very high. Dimensions of these defects can be estimated in tenths of microns.

4. Structural macro defects of the composite or the entire product are macropores, foreign inclusions, macro cracks, etc. Dimensions of these defects are even greater and can reach tens and hundreds of microns.

Structural defects can derive from various causes; they can be formed by different conditions, in the same way as the structural elements:

- 1) geometry, for example, steric constraints, spatial disorder; in these cases, geometrical defects can have different dimensions depending on the structural hierarchy level;
- 2) thermodynamics, due to thermodynamic instability of formations (groups and clusters) and fluctuations at different structural levels. The higher hierarchical level of the structure (of a more long-range order) is the more defective, due to the accumulation and summation of defects;
- 3) kinetics – in the case when the rate of relaxation processes is less than the rate of structural elements formation.

The basic concept or idea in designing durable polymeric materials and composites with enhanced operational properties should consider the hierarchy of structural levels in polymers, as well as the hierarchy of structural defects.

Actions aimed at reducing the structural defectiveness, or any effects on the structural packing of the polymer macromolecules should be undertaken purposefully, with consideration to its hierarchy and depending on the defective structure level to be controlled or “cured”. When designing tailored composite materials, it needs to be coordinated with a specific destructive impact factor using the structure modifiers effective at a given hierarchical level (see *Table*).

With view of these findings, the primary structural level (nano level) of supramolecular formations gains particular importance, since it (i.e., its defectiveness) determines the further macromolecule packing and the defectiveness of the subsequent structural elements. This level has long been neglected in the studies concerned with structure modification of polymeric materials. The situation has changed with the development of nanotechnology and its methods, because the nano scale supramolecular organization can be addressed only by nanotechnology methods, i.e., by nano dimensional particles. Here, the related problem of their dispersion and distribution in the mass of polymeric material comes to the foreground.

Formerly conventional modifiers of the polymer structure – rubbers and elastomers, ordinary powdered solids are inappropriate for nano structural modifications, due to the large size of their particles. Oligomeric systems (rubbers and elastomers) are extremely hard (almost impossible) to be dispersed properly and to be distributed uniformly in the cubic content of the polymer matrix, in order to ensure their action at the nano scale level.

Their action is manifested at the micro level at best, which is quite sufficient for certain (small) improvements of physical and mechanical characteristics. But this would not affect significantly the physical, chemical and mechanical properties. Hence, numerous attempts to achieve a greater effect by nano modification of polymeric materials were unsuccessful

**Table 1.** Hierarchy of structure, defect levels of polymer matrices and composites, and associated properties

Structural level	Modifiers	Characteristics of structural levels and structural defects	Associated characteristics and properties
I. Submicroscopic level (molecular or nanolevel)	Monomolecular substances or nanoparticles dispersed by nanotechnology methods	Chains and chain fragments of polymers. Structure is determined by packing and stacking of individual chains and fragments with dimensions up to tens of nanometers (nanostructure). Dimensions of defects – nanometers	Chemical and radiation resistance, aging, resistance to thermal-oxidative degradation
II. Mesoscopic level (topological or cluster)	Alloying micro additives and oligomers injected by liquid-phase methods	Globular formations, interglobular boundaries, contact zones between chain-packed structures of the polymer, mesopores, sub-microcracks. Dimensions of defects up to 0.1 microns	Hardness, microresistance, diffusion properties, heat resistance, bio stability
III. Supramolecular level (formation of associates, domains and packs)	Micro-sized particles and additives, fillers, polymers, elastomers, rubbers, etc.	Polymeric substance with inclusions between domains and packs of microparticles (cement, mineral dust, “aerosil”, microsphere, etc.). Dimensions of defects can reach tens of microns	Modulus of elasticity, modulus of shear, brittleness, creep, water absorption, low temperature resistance
IV. Macroscopic level (composite or finished building product)	Powdered fillers and additives introduced by a common method. The structure is largely determined by the product technology and introduction of additives	Polymer composite with inclusions of filler grains, micro- and macropores and microcracks with dimensions of 0.01–1.0 mm. the Characteristic dimension of structural defects is comparable with that of grain size, macro- and micropores	Mechanical properties: strength, wear resistance, resistance to static and dynamic loads, shocks, abrasion, etc.

From the standpoint of the above described representations, the mechanism of reinforcing rigid polymer matrices by rubber modifiers becomes obvious and clear, since it improves mechanical characteristics of elasticized (rubber-modified) plastics and resins.

Rubbers form an independent phase in the thermo set (e.g., epoxy) matrix and thus prevent merging and spreading “large” microcracks responsible for mechanical destruction of the polymer. According to G. M. Bartenev [4], dimensions significant for the mechanical destruction of micro-cracks, are at least  $\sim 30 \cdot 10^{-4}$  mm, which corresponds to the third structural level of the hierarchy structure presented in our table. Dimensions of defects and cracks (matching with the data of G. M. Bartenev) are large enough and can be “cured” by macromolecules of rubbers and oligomers. Cracks (microcracks) of the second level are  $\sim 1\text{--}3 \cdot 10^{-4}$  mm. The first, i.e., the initial level (sub-microcracks) has dimensions of  $\sim 0.3\text{--}0.2 \cdot 10^{-4}$  mm, which corresponds to the primary structural level, and, accordingly, modifiers with the same particle size, i.e., nanoparticles are required. The discrete spectrum of cracks in polymeric systems was recorded by a number of researchers [6-9, 11].

At the same time, there have been very successful attempts to improve significantly the properties of polymeric materials by nanomodifying with carbon nanoparticles, fullerenes, and similar nano modifiers. [12-14].

Thus, it became obvious that strengthening and protection of the molecular structure at the nanoscale level needs nanostructural modifiers, i.e., chemical compounds and substances that can be spread within

the polymer nanostructure. This is a great challenge. For example, these requirements are met by nanoparticles of liquid molecular organosilanes and siloxanes (subjected to ultra dispersion, for example, using the ultrasound) [15-17].

Our experience has shown that small quantities of organosilanes and organosiloxanes have good compatibility with most polymers in melts or solutions. Saturated silanes and siloxanes are chemically inert and generally do not react with molecules of the polymer binder. During formation of the supra molecular structure, they are expelled to the disorder zones and get localized in structural defects. In the case when the modifier particle size is within the nanometer dimension, these substances can settle at the primary nano structural level of polymer matter. This level is the least defective; it is responsible for chemical and physical-chemical processes of polymer destruction, i.e., ageing, thermal oxidative degradation, photo destruction, resistance to aggressive gaseous media, chemical factors, etc.). The number of structural defects at the initial hierarchical level is estimated by the fraction of a percent and does not exceed 0.5-1.5%. Stabilizing additives, antioxidants, ageing retarders, UV adsorbers, etc. are introduced into polymers in the same proportions (with a small margin allowing for the uneven distribution). The action of stabilizers is performed at the level of polymer macromolecules, i.e., within the primary structural level. Structural modifiers for “curing” the nano scale defects should be introduced approximately in the same quantities as stabilizing additives, i.e., from 0.5 up to 1,5% or slightly more.

The problem of detailed structure of polymers, which are traditionally viewed as amorphous, is still under discussion but the possible existence of ordered structural formations at different hierarchical levels in amorphous polymers is conclusively established.

Until recently, irregular and unstructured mass of heavily entangled coils (globules) with the excess free volume served as the conventional model of amorphous polymers. The physical properties of such systems are described by a single-phase statistical coil model. This model played an important role in the development of the theory of high elasticity, because the entanglement of molecules explains satisfactorily the expansion of the area of high elasticity against the increasing molecular weight, while the excess free volume – high values of coefficients of gas diffusion in amorphous vs. crystalline state. However, this model can not explain the irreversible plastic flow and the overestimated density values in amorphous polymers, as compared with those derived from the same model. The disadvantage of this model is that it does not provide for the presence of the experimentally observed regions of regularity, namely, structural aggregates of 50-100 Å in size [2, 3].

We have studied the effect of liquid organosilicon modifiers on the supra molecular structure of the epoxy binder. Alternating ordered formations of globular-type particles were detected with a scanning electron microscope in ED-20 dieneoligomer epoxy matrix consolidated with PEPA (polyethylene polyamine) amine hardener at room temperature (Fig.). The photomicrographs presented below demonstrate the epoxy matrix modification by organo siloxane, which leads to the formation of a more ordered structure containing significantly less pores and voids.

Distribution of organosiloxane particles and low molecular weight heat-resistant siloxane synthetic rubber across the matrix is clearly visible in the photomicrographs (see figure 1). Large particles are localized in the epoxy matrix as an independent phase; fine particles are distributed between the globules of epoxy macromolecules and in some cases form chained clusters, which corresponds with the above mentioned notions on the hierarchy in the supra molecular polymer structure.

In our view, structural organization of polymers (including those cross-linked or thermo setting) can be subdivided into at least three hierarchical levels and, consequently, include at least three types of ordered supra molecular structures. Accordingly, the polymer substance includes at least three hierarchical levels of structural defects.



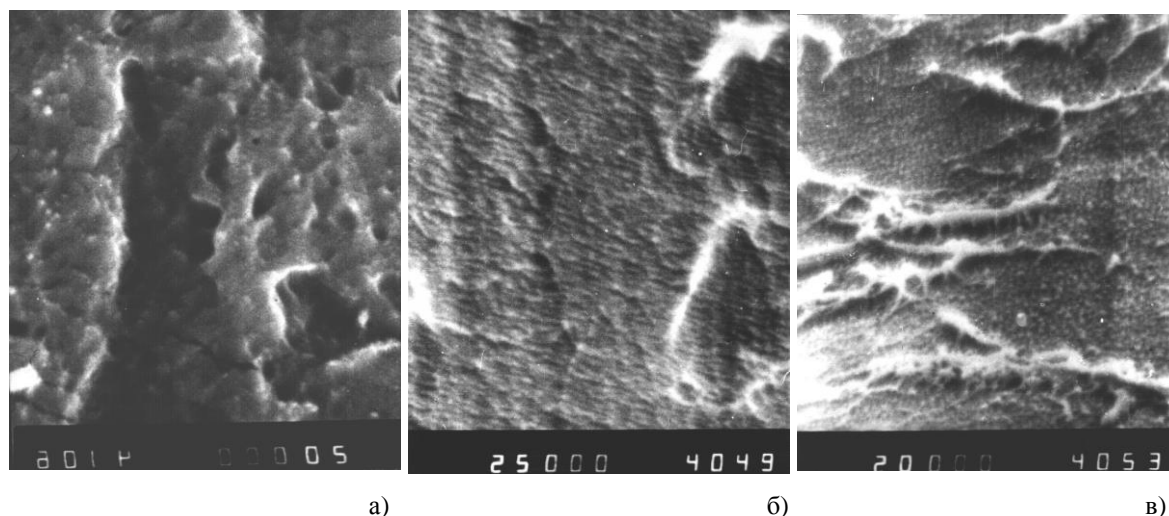


Figure 1. Electron photomicrographs of supramolecular structures in ED-20 polyethylene polyamine epoxy matrix: a) initial (unmodified), X 20,000; b) organosiloxane-modified (1 % wt.), X 25,000; c) heat-resistant siloxane rubber-modified, X 20,000.

Certain physic -chemical and physic -mechanical (including strength) characteristics of the polymer substance, performance properties of the finished product are associated with defects in supra molecular, micro- and macrostructure and are determined by them. We have identified the following hierarchical structural levels:

- 1) Primary level (micro level or nano level) features a short-range order in the arrangement of chains fragments and macromolecules. Within the small spatial regions, groups of atoms and chain fragments are more or less ordered. The degree of disorder (defectiveness) at this level probably ranges from 0.5 to 2.5 % depending on technological parameters.
- 2) Meso level (or cluster) – pseudo crystals, packs and clusters, which are more often formed at above plasticization temperature, can emerge and disappear, due to fluctuations. These structural formations reveal a permanent dimensional distribution pattern. The degree of defectiveness at this level probably ranges from 10 to 20-30 %, i.e., is approximately greater by an order of magnitude; it depends mainly on the kinetic conditions of formation and the defectiveness of the preceding level.
- 3) Supramolecular level – associates of clusters and packs. The degree of defectiveness is even higher and is comparable with the degree of order but can as well exceed it (40-60 %). The structural defectiveness at this level depends on the defectiveness of the preceding levels and is associated with the external environmental factors.
- 4) The composite structure of the finished product is mainly determined by its manufacturing technology. The result of structure formation is a macrostructure of the finished composite or product, which depends on the entire set of technological factors, external impacts, as well as the internal conditions preceding its formation.

#### 4. Conclusions

The above discussed features of the polymorphic and hierarchical structure of polymeric substances and structural defects yield several important implications.

First, the structural and physical heterogeneity creates a non-uniform distribution of reagents in the polymer matrix. Thus, low-molecular substances (oxygen, oxidation products, monomolecular stabilizing additives, etc.) are concentrated mainly in the sites where the initial order is absent, i.e., amorphous or defective zones of the polymer structure. The most reactive elements of macromolecules (oxidized groups, unsaturated bonds, etc.) are also located there. Local concentrations of chemical reagents in these zones may significantly differ from the average values.

Second, structural micro heterogeneity leads to widespread regions of various molecular motions within the polymer resulting in a broad set of kinetic constants and activation energies of elementary chemical reactions and physicochemical interactions occurring in different regions.

Third, structural-kinetic heterogeneity of polymers and the respective localization of reagents lead to the spatial localization of chemical reactions, i.e., to the formation of unique “microreactors”, where the intensive processes of the polymer oxidation and destruction develop.

Modification of the structure of polymeric materials and composites, “curing” its defects should be tailored to specific hierarchical levels.

The above discussed theoretical principles concerning the discreteness and hierarchy of supramolecular structures, the hierarchy of structural defects, as well as special importance of primary structural formations (nano levels) to improve the operational properties of composite materials, methods of their modification and “curing” defects have been confirmed for various classes of materials, thermoplastic and thermosetting (epoxy and polyester polymer composites), and many others [3,18–20].

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