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The Formation, Structure, and Properties of Epoxide Matrices for High-strength Composites

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The results of studies of the kinetics and thermodynamics of the formation, and the structure and properties, of epoxide cross-linked polymers, carried out in the last 7-8 years in the Institute of Chemical Physics of the Academy of Sciences of the USSR, have been reviewed. The molecular, topological, and supermolecular structures of epoxide polymers have been examined, and the relationship between the properties shown by these polymers in the vitreous and rubber-like states and their structure has been analysed. The progress made in the directed modification of the physicomechanical properties of epoxide binding agents have been discussed. The characteristic features of the structure and properties of epoxide polymers formed at the boundary with a solid surface have been examined.
The bibliography contains 136 references.

CONTENTS

I. Introduction 164
II. Structural organisation of the epoxide networks 164
III. Physicomechanical and relaxation properties 168
IV. The modification of epoxide binding agents 169
V. Characteristic features of the structure and properties of epoxide polymers at the boundary with a solid surface 169

I. INTRODUCTION

A central problem in the design and production of articles of composite materials is the need to choose a polymer matrix ensuring the maximum realisation of the possibilities provided by the high-strength reinforcing fibres. This problem has many facets; one of its most important aspects is the relationship between the structure of a polymer matrix and its properties on the one hand, and the relationship between the conditions of synthesis and the structure on the other.

The present review examines the principal results of work carried out under the general direction of N.S.Enikolopov and directed towards the solution of the above problems. Densely cross-linked epoxide polymers, whose applied and technological properties at present make them the most promising binding agents for high strength composites, were examined in these studies. Individual aspects of these studies have already been summarised in a monograph[1] and a number of reviews[2-15].

The structure of polymers is usually classified as molecular and supermolecular. In the analysis of the structure of cross-linked polymers, in contrast to linear polymers, it is necessary to introduce another level of structural organisation of polymers, which has been called the topological; it characterises the degree of connectedness of the elements of the polymeric system. The terms linear, branched, ladder, or cross-linked polymer characterise the topological level of its organisation, a quantitative measure of which is provided by the distribution function of the corresponding element of the structure of the polymer system: branching between the chains, rings, etc.

The different levels of structural organisation of a polymer determine its various properties. There is in principle no unique simple relationship between all the levels of structural organisation, but a change in structure at any of the levels considered may have a significant influence on the properties of a polymer.

For an understanding of the various physicomechanical properties of a polymer it is first necessary to have a detailed and adequate description of each of its levels of structural organisation, and the practical problems of present-day materials science require a quantitative description. Progress in theory makes possible in most cases a quantitative description of the molecular and topological levels of structural organisation, but unfortunately this usually cannot be done at the supermolecular level.

The possibility of a quantitative description of the molecular and topological structure of a polymer, however, does not eliminate serious difficulties, related primarily to the fact that the relationship between the micro-characteristics, which adequately describe the molecular structure and topology of the polymer, and the macroscopic properties of the material in many cases is unknown. This is characteristic chiefly of polymer matrices in the vitreous state, which is the main working state of the polymer in a composite. Thus the search for the regular features establishing this relationship is one of the most important directions in present-day studies in the field of polymers and composites based on them.

II. STRUCTURAL ORGANISATION OF EPOXIDE NETWORKS

1. Molecular Structure

It is first of all necessary to find the characteristics of the molecular structure of the original epoxide oligomers, which are usually synthesised by condensing epichlorohydrin and compounds containing a mobile hydrogen atom—phenols, alcohols, acids, amines, amides, etc.

The most widely encountered are epoxide oligomers based on diphenylolpropane, the output of which makes up more than 90% of the total production of epoxide resins. It is for this compound and corresponding model compounds that the most important regular kinetic features of the formation of epoxide oligomers have been studied, and the mechanism of the process established.

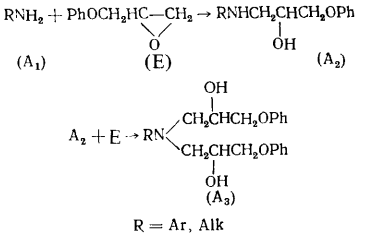
Epoxide oligomers are usually obtained by the reaction of epichlorohydrin with phenol; the epoxide ring of epichlorohydrin reacts with the phenolic hydroxyl group[16-18]. The reaction takes place by an ionic mechanism and is catalysed by bases. As a result of this reaction there is an increase in the molecular mass of the oligomer, and an excess of epichlorohydrin in the reaction system ensures the production of final oligomers which are bifunctional with respect to the epoxide groups. The main reaction, however, is always

accompanied by side reactions, involving mainly the consumption of epoxide groups in solvolysis and addition to internal secondary hydroxyl groups of the oligomers[19], leading to a change in the functionality and molecular structure of the final oligomer. The products sought are formed mainly in the first stage of the synthesis[20,21], whereas in the later stages an increasing contribution is made by side reactions[22,23].

Studies carried out have established the molecular structure of epoxide oligomers, produced kinetic models of the processes involved in their synthesis, which describe the process quantitatively[24–27], and developed new methods for carrying out the synthesis, which make it possible to increase the proportion of the main reactions in the production of the structure and functionality of the oligomers and to decrease the rate of side reactions[28–31]. The establishment of the relationship between the molecular structure and the molecular-mass distribution (MMD) of the resulting oligomers and the conditions of the process has made it possible to control the process to obtain epoxide oligomers with a given molecular structure and given properties[32]. The method of carrying out the process developed by N.S.Enikolopov and co-workers has formed the basis of an industrial method for the synthesis of diane epoxide oligomers by a continuous technological scheme.

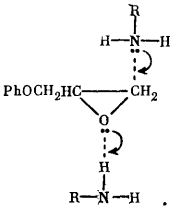
An extensive cycle of studies has also been carried out to establish the molecular structure of cross-linked epoxide polymers, obtained by hardening thoroughly purified and characterised epoxide oligomers and individual bifunctional monomers. In the course of these studies it has been possible not only to solve the principal problem being tackled, namely the production of binding agents with the required set of properties[1–12,33–36], but also to determine the principal regular kinetic features of the processes involved in the hardening of epoxide oligomers by various hardening agents[37–62], to establish a number of previously unknown details of the mechanism of these processes[7–12,36,39,41,44–52], to obtain a quantitative description of these processes and to determine the values of the thermodynamic and kinetic parameters[8,12,14,63–68], to establish the relationship between the reactivity and the chemical character of the reagents[50,69–71], to develop the principles of the rational choice of a hardening system and to control the molecular structure of the resulting three-dimensional network, and to establish scientifically based principles for selecting the hardening conditions to ensure intensification of the process and the production of materials with required properties[8,14,63].

In this cycle of studies, particular attention has been paid to the investigation of the kinetics and mechanism of the processes involving in the hardening of epoxide oligomers under the influence of amines, which are widely used in practice as hardening agents. The main reactions† taking place in this process can be represented by the following scheme:



† For simplicity, the reactions for the monofunctional compounds are given.

Before these studies, the mechanism of the opening of the epoxide ring under the influence of nucleophilic reagents was disrupted; it was not clear whether this reaction took place directly, or whether electrophilic cooperation was necessary. The studies[7,8,10,12,39] showed that the opening of the epoxide ring under the influence of nucleophilic reagents requires electrophilic cooperation, that is preliminary activation of the epoxide as a result of its reaction with some nucleophilic reagents. The idea of the need for activation is the key to the understanding of the regular kinetic features of the reaction of epoxide compounds with various nucleophilic compounds, including amines. This viewpoint makes it possible to understand the observed possibility of the non-catalytic reaction of epoxide compounds with primary or secondary amines and the second order of the reaction with respect to the amine[10,23,36]. In this case, one amine molecule acts as the nucleophile reagent, and the other as the proton donor. The transition state can be represented as follows:



A second important conclusion about the mechanism of the reactions studied is that the components of the reacting system, that is the starting materials and reaction products, are combined in hetero- and homo-complexes, characterised by different reactivities. The formation of these complexes may be both intermolecular and intramolecular; their existence has been reliably proved, and the thermodynamic parameters of complex formation determined[7,8,10,12,41,52,53,64,68].

It is only on the basis of ideas about complex formation in these systems that it is possible to understand such characteristic features of the kinetics of the reactions of epoxy-compounds with primary and secondary amines as the extremely unusual simultaneous reactions of self-acceleration and self-inhibition, the catalytic and inhibiting action of various solvents, the clearly defined *ortho*-effect of a number of substituents in aromatic amines, etc.[7–12,37,44,45,52,54].

The mechanism of the processes involved in the hardening of epoxide oligomers under the influence of amines is extremely complex; to a first approximation it can be described by a kinetic scheme which takes account of all the electron-acceptor interactions of the original reagents and the reaction products with one another. The kinetics of the processes of the hardening of epoxide oligomers under the influence of aromatic amines (at moderately high temperatures t < 150 °C) and the molecular structure of the resulting polymer are described almost completely by this scheme. At higher temperatures, condensation of the hydroxyl groups formed with unreacted epoxide groups and with one another also takes place, leading to the formation of additional cross-linking sites[59].

When primary or secondary aliphatic amines or aromatic amines with a nitrogen-containing heterocyclic ring are used as hardening agents, the polycondensation reactions are accompanied by anionic polymerisation of the epoxide oligomers under the influence of tertiary amines[10,12,36,46–49]. This gives a polymer which has the chemical structure of a simple polyether and which contains as terminal groups

double bonds of the vinylidene type, hydroxyl and alkyl groups, or a tertiary amino-group. These terminal groups are obtained by the decomposition of the active growing centre—the quaternary ammonium alkoxide—in several directions and subsequent secondary initiation[12,46-48].

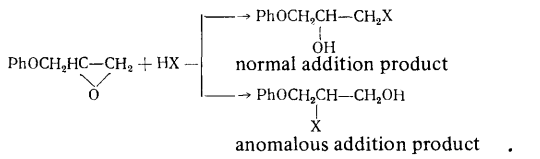
If the tertiary amine used is a nitrogen-containing heterocyclic compound such as pyridine and its derivatives, a new reaction takes place, leading to opening of the pyridine ring[46-48]. In this case the resulting polyene structure becomes a fragment of the polyether chain. The molecular structure of the polymer obtained is very complex; nevertheless, it can be reliably predicted if the detailed reaction mechanism is studied and the kinetic characteristics of the elementary stages of the process determined.

Analogous investigations directed towards the study of the kinetics and mechanism of the reactions and in the final analysis the establishment of the molecular structure of the resulting epoxide polymers are now being carried out with other hardening agents—phenols, alcohols, carboxylic acids, acid anhydrides, etc.[16-29,33,56,57]

The first results obtained in these studies confirmed the basic ideas about the important role of complex formation and the need for electrophilic cooperation in the reactions of nucleophilic addition of reagents to an epoxide ring. In contrast to amines, however, in a number of cases the reaction can also take place by an ionic mechanism.

A characteristic kinetic feature of the condensation of phenols and carboxylic acids with epoxides is that the product of the addition of a second molecule of the epoxide compound to the hydroxyether can be formed not only in succession, but also in parallel, by the direct reaction of two molecules of the epoxide–phenol (or carboxylic acid) complex[56,57].

Finally, new data on the determination of the direction of the opening of the epoxide ring are of considerable interest. A detailed study carried out by different NMR methods[33,36] showed that, contrary to the widespread view that normal addition takes place preferentially in nucleophilic attack at the epoxide ring, an appreciable proportion (up to 50%) corresponds to the anomalous addition of the nucleophilic residue X:



A number of studies have been devoted to the determination of the stability of epoxide polymers to the action of high temperatures and atmospheric oxygen. A detailed study of the thermal[72] and thermo-oxidative[73] degradation of cross-linked polymers based on the diglycidyl esters of diphenols with aromatic and aliphatic amines has been carried out by field mass spectrometry. Analysis of the products of the thermal and thermo-oxidative degradation of low-molecular-weight compounds[74] modelling the structure of the polymers studied showed that the weakest are the bonds $C^{\beta}-C^{\alpha}N$ in the hydroxypropylene bridge HC–CN in the aliphatic amine and $C-C_6H_4$ in the diphenylolpropane part of the chain, and the entire degradation process is described by a radical-chain mechanism. The process is initiated by the oxidation of the aliphatic parts of the polymer by atmospheric oxygen and the subsequent decomposition of the hydroperoxides formed. Chain transfer to heteroaliphatic parts of the polymer gives aminyl, alkyl, and aroxyl macro-radicals, whose decomposition gives derivatives of phenols, acetaldehyde, acetone, formaldehyde, and $H_2C{=}NCH_3$.[75]

With longer exposure to oxygen there is a decrease in the temperature of the appearance of those degradation products which are identical to the products of the thermal decomposition of the polymers in a vacuum. The thermo-oxidative degradation gives a large quantity of heavy products with masses 1.5–2.5 times the mass of the original model compound. The oxidation of secondary NH groups, which have not reacted with the epoxide, in the derivatives of aromatic amines gives stable aminyl and nitroxyl radicals, which inhibit the degradation, and in the derivatives of aliphatic amines gives the aminyl radical $\sim CH_2CH_2\dot{N}CH_2CH_2(OH)\sim$, which is actively involved in chain transfer. The dehydration process is the highest-temperature process both under conditions of the action of oxygen and in the subsequent degradation of the polymer in a vacuum.

2. Topological Structure

Analytical methods for describing the topological structure of cross-linked polymers suffer from the significant disadvantage that they do not make it possible to take account of the existence in the networks of rings of different size and complexity[1]. It is this feature, however, that determines the topological structure of the polymer network. Ring formation has a significant influence on the proportion of elastically active chains, which determine the mechanical behaviour of the polymer networks above the vitrification temperature. Allowance for this feature in different versions of the kinetic theory of high elasticity is usually made by introducing an empirical parameter—the front factor[1]. These difficulties have been successfully overcome by the development of a statistical topological model of the structure of cross-linked polymers, which has made it possible to establish a quantitative relationship between the chemical structure of the starting materials, the mechanism and conditions of the process of network formation, and the topological structure and various mechanical properties of networks in the highly elastic state[1,6-8,60,61,76-80].

The model of the structure of a densely cross-linked polymer was based on the view of a network as a set of randomly connected rings with a certain size distribution. The ring, that is a minimal closed contour in the network structure, was taken as the elementary structural unit. This approach made it possible to make specific the problem of describing the topology of the network structure and to reduce it to the determination of the distribution of the rings with respect to size. The process of formation of the network structure by the condensation of bifunctional molecules of diepoxide and tetrafunctional molecules of diamine was modelled on a computer by the Monte Carlo method. The scheme for the model process took account of intramolecular cross-linking (ring formation) both in the pre-gel region and in the later stages of the reaction, beyond the point of gel formation. The algorithm of the calculation made it possible to examine the influence on the kinetics of formation and topology of the network of such factors as monocyclisation, different ratios of the original reagents, differences in the reactivities of the functional groups of the reagents, and the change in reactivity during the reaction. Experimental analysis of the gel and sol fractions of the hardened systems confirmed the adequacy of the model of a real network system[78].

Berling and Oshmyan[81] were the first to describe the regular kinetic features of network formation; in particular, they predicted and detected a decrease in the reaction rate constant in the kinetic range in the later stages of the hardening reaction as a result of the high topological complexity of the system. The increase in the topological complexity of the system during the process leads finally to a non-trivial

physical effect. In stoichiometric mixtures, the reaction in principle does not go to completion, in spite of the presence in the system of a sufficient number of functional groups, capable of reacting. This limit of the reaction (yield < 100%), called the topological limit[77], appears because the reactive groups, which during the process have entered different topological formations in the network, cannot meet and react with one another even in the complete absence of diffusion restrictions.

The statistical model developed made it possible to carry out a quantitative analysis of the equilibrium elasticity of a network polymer in the rubber-like state. Because of the small dimensions of the chains between the nodes in the systems studied, this analysis could not be carried out within the framework of the traditional concepts of the kinetic theory of high elasticity. In the rubber-like state, the equilibrium elasticity of the network is determined by the elasticity of the chain between the nodes and by the topology of the network polymer. It has been shown[79] that by applying a mechanical stress to the boundaries of a model polycyclic network it is possible, by a numerical method on a computer without the use of any empirical parameters, to find the distribution function of the stresses in the chains between the nodes and the equilibrium modulus of elasticity of the network with allowance for the details of its molecular structure. Experimental verification of the theory showed excellent quantitative agreement between the results of the calculation and the experimental data, that is the proposed model provides an adequate description of the structure and equilibrium elastic properties of the networks. The observed agreement in the values of the modulus of elasticity indicates that all the non-uniformity of a real network lies within the limits of the statistical scatter. Spatial non-uniformity in the distribution of the reagents, for example as a result of micro-synergesis, would obvious lead to a decrease in the value of the equilibrium modulus of high elasticity E_∞. This conclusion is confirmed by an analysis of the topological structure and the equilibrium elasticity of the network systems, which show a conformational tendency to undergo monocyclisation reactions[60,61].

The topological model of a network polymer has been used successfully in a theoretical analysis of the durability and the nature of the breakdown of the network in the highly elastic state[79]; the undoubted advantage of this model for solving this problem lies in the possibility of taking account of the non-uniform character of the unloading of the chains between the nodes as a result of the topological non-uniformity of the network. Numerical modelling also made it possible to obtain information on the conformational characteristics of the short chains between the nodes in densely cross-linked networks. The dependence of the elasticity of the short chains on the elongation is stepped in character, and their conformational behaviour differs significantly from the generally adopted approximations of Langevin and Gauss[80].

In addition to the creation of the above statistical topological theory of the formation of polymer networks, work has continued on the development of traditional statistical methods for describing network polymers by means of the mathematical apparatus of the theory of branching processes[82-85]. In particular, a new parameter of the theory has been proposed—the probability of the termination of the chain of network development—whose magnitude determines not only the kinetics of the process of gel formation but also the topological structure and hence the properties of the cross-linked polymer in the highly elastic state; information on the structure of the gel can be obtained from the sol fraction of the polymer, which is easily analysed experimentally. When side reactions causing network growth to stop take place, the sol fraction contains the products of these reactions, including the monocyclisation reaction.

3. Supermolecular Structure

The next level of structural organisation of a polymer, reflecting the relative arrangement of its chain in space, must be characterised by the type of intermolecular interaction of the chains and their degree of ordered character. The first characteristic influences the magnitude of the free volume and the density of packing, which reveals itself in the morphological characteristics of the polymer[1,3,4,6].

Extensive systematic studies of the morphology of densely cross-linked (>10^{21} nodes cm^{-3}) epoxide polymers[1,3,4,6] have shown that the typical structural elements in these systems, which can be detected by electron microscopy, are globules. An important characteristic of these systems is that any attempts to change the nature of the globular structure by varying the chemical structure of the original epoxide oligomers and hardening agents, by changing the hardening conditions, or by the action of thermal and mechanical fields on the already formed network polymer did not lead to any significant change in the morphology of the system; in all cases it remained globular, and only the size of the globules changed.

These studies indicated that the fairly widespread view that globules are more highly cross-linked formations than the cross-linked polymer in the space between the globules is in general incorrect. Thus theories in which the variations in the mechanical properties of cross-linked polymers in the vitreous state are attributed to differences in the density of cross-linking of the globules cannot be correct.

The difference in the densities of the globules and the polymer in the space between the globules was extremely small, ~0.1%.[86] The physicomechanical characteristics of epoxide cross-linked polymers show extremely little sensitivity to the preliminary action of thermal, mechanical, and electromagnetic fields on the prepared polymer over a wide range of conditions. The variation in the properties of the polymers in this case does not exceed 20%. At the same time, even slight changes in chemical structure lead to fairly marked changes in the physicomechanical characteristics of the polymer.

These results are fundamental, since they show that the topological and supermolecular structures of the polymer, formed during the hardening process, are fixed by the three-dimensional network and cannot subsequently be changed by conformational rearrangement of the chains between the nodes without the rupture of chemical bonds.

The above observations led to the important conclusion that densely cross-linked polymers are characterised by a closer relationship between the different levels of their structural organisation, compared with linear polymers. The higher levels of the structure—topological and supermolecular—are determined to a considerable extent by the primary molecular structure of the polymer[1,3,6]. As a result, different external preliminary treatments of the prepared polymer, capable of producing radical changes in the properties of linear polymers, have a much less significant influence on the properties of densely cross-linked polymers, which to a large extent are determined by their molecular structure[87-98].

Studies of the density of epoxide polymers in the vitreous state have shown that the coefficient of molecular packing was unexpectedly high (K = 0.71–0.72), and appreciably higher than that for vitreous linear polymers[6,87,91]. This means, on the one hand, that the formation of chemical cross-linkages does not impose any kinetic restrictions on

the packing of the elements of the network, and on the other hand that the chains between the nodes, in spite of their considerable length (8–12 framework atoms), have a flexibility sufficient for closest packing to be produced. Subsequent experimental studies of the molecular mobility of epoxide polymers completely confirmed this conclusion.

Interesting and important results were obtained in an experimental and theoretical study of the kinetics and mechanism of the formation of the supermolecular structure of epoxide polymers[1,43,51,86].

An extremely general mechanism of the production of the supermolecular organisation of an amorphous polymer has been formulated, taking account of the kinetic characteristics of the process of its formation and its molecular mobility, and a mathematical model of the process has been developed. In this model, the size of the polymer cluster formed is greater, the greater the self-acceleration factor of the hardening process (irrespective of its specific mechanism) and the lower the molecular mobility of the polymer[98].

III. PHYSICOMECHANICAL AND RELAXATION PROPERTIES

Another important problem is the establishment of the relationship between the properties of cross-linked epoxide polymers in the vitreous state and the characteristic features of their structure. As indicated above, the equilibrium mechanical properties of cross-linked epoxide polymers in the rubber-like state is described completely by their topological structure and the conformation characteristics of the chains between the nodes. On going to the vitreous state, however, the situation changes radically[1,3–6,91,97]. The polymer matrices in high-strength composites are used at temperatures below the vitrification temperature, so that the study of the properties of epoxide polymers under these conditions is of particular interest; moreover, in general the properties of polymers in the vitreous state represent one of the least studied fields of polymer physics.

In view of the practical aspects of the application of polymer matrices, it is natural that the mechanical properties of these polymers were studied first. A cycle of studies carried out with epoxide cross-linked polymers with different chemical structures investigated the static and dynamic mechanical properties, the relaxation of stress, creep, various problems of the durability and breakdown and the relationship between these properties and the molecular and topological structures of the epoxide networks[1,3–6,71,87,88,94,96,99–107].

Study of the $\sigma-\varepsilon$ (elongation, compression, shear) diagrams has shown that in most epoxide polymers, in spite of the presence of a high concentration of chemical cross-linkages, at temperatures more than 100 K below T_g and moderate rates of deformation, plastic (induced-elastic) deformation is realised, and the frequently observed brittleness of specimens is due to their macroscopic defect character[1,3,6,91]. The limiting deformations at breakdown may be extremely high (10–15%). This conclusion is important, since it refutes the extremely widespread view that systems with such a high density of cross-linking cannot show plasticity.

Measurements of Young's modulus and the shear modulus, and also the yield limit, have shown that these important mechanical properties are practically independent of the topological characteristics of the network (the density of the nodes, the concentration of mono-rings[1,3,6,91,97]); only the strength was found to be sensitive to the concentration of mono-rings[1,3,95,97]. At the same time, as noted above, the mechanical properties of the networks in the highly elastic state are determined completely by their topological structure[1,6,8,60,61,78,79].

These results are fundamental, since they show that the properties of cross-linked polymers in the vitreous state must be related to the characteristic features of their packing[1,6,89,91,93,108], that is that the behaviour of networks, even when densely cross-linked, does not differ in this sense from that of linear polymers. The liquid–glass transition during the production of the network has a significant influence on the physicomechanical properties of the resulting polymer[91,97]. The slower the vitrification of the polymer during hardening (at low temperatures), the better its mechanical properties in the vitreous state, in spite of the lowered values of the degree of conversion at low hardening temperatures. At the same time, the values of the coefficient of molecular packing for specimens of a given polymer with appreciably different mechanical properties were found to be similar[91,97].

A possible explanation for these facts may be that the properties of a vitreous polymer are determined not only by the total fraction of the free volume in it but also by the nature of its distribution in the specimen. Direct measurements of the dependence of the free volume for epoxide systems on the concentration of chemical cross-linkages provides evidence in support of this suggestion[1,3,89,93,108].

The characteristics of the deformation and breakdown of epoxide polymers in the vitreous state have been studied[99–105]. In spite of the high density of chemical cross-linkages, in epoxide polymers, as in linear polymers, when a crack is propagated through the material, appreciable plastic deformations, irreversible under the given conditions, are observed in the opening of the developing crack. It is these deformations, preceding the rupture of chemical bonds, that to a large extent determine the stability of the material to the propagation of cracks, and hence its strength. These observations indicate that the extremely short bonds between the nodes in epoxide polymers are sufficiently flexible, and are able to undergo conformational rearrangements under deformation conditions.

The size of the plastic zone along the axis of elongation for films of densely cross-linked polymers (plane-stressed state) is equal to the thickness of the film, and this made it possible to formulate criteria for their breakdown[104].

The deformation of densely cross-linked polymers at values of the deformation close to or equal to the yield limit is accompanied by the rupture of chemical bonds[99–102]. This local breakdown of bonds during deformation long before the breakdown of the entire specimen is apparently due primarily to the short length of the chains between the nodes and the non-uniform distribution of stresses in the chains between the nodes. This mechanical degradation may be one explanation for the effect of the "anomalous" relaxational and deformational strengthening of densely cross-linked polymers, detected by various workers[3,99–102]. The essential feature of the phenomenon is that in contrast to linear polymers, during the successive relaxations of the stress or during deformation, the relaxation properties of the densely cross-linked polymers improve (the relaxation time decreases).

The practical result of the studies carried out was the development of epoxy-amine binding agents with record values of the modulus of elasticity (600–700 kg mm^{-2}) and yield limit (17 kg mm^{-2}) at room temperatures and ordinary rates of loading[3,6,91,96].

One of the most important characteristics of a binding agent is its heat resistance. A series of studies[1,3,6,34,35,89,91,109,110] established that the vitrification temperature T_g is determined unambiguously by the molecular and topological structures of the epoxide network. T_g for an epoxide polymer can be increased by high-temperature treatment (>150 °C) as the result of the reaction of unreacted (as a consequence of the topological limit) epoxide groups with

hydroxyl groups of the chains between the nodes[59]. This method of increasing the heat resistance of epoxide matrices for composites is hardly a promising technological technique, because the increase in the thermal stability and a definite but small increase in the value of the Young's modulus are accompanied by a marked increase in the brittleness of the polymer is also observed.

The unique relationship between the molecular structure of the network polymer and T_g makes it possible to use the method of increments to calculate *a priori* T_g for polymers with different chemical structures. This approach made it possible to propose and later to synthesise a number of highly heat-resistant epoxide binding agents.

The study of the vitrification temperature and mechanical behaviour of epoxide networks led to a non-trivial result of practical importance. It was found that important characteristics of the binding agents, such as the heat resistance and the mechanical properties, are determined by different structural parameters, in the first case by the chemical structure of the network, and in the second case by the packing of the chains in the polymer glass. This makes possible the directed and to some extent independent control of these properties of polymer binding agents.

The solution of these problems also made it possible to shed light on various general fundamental problems of the theory of the vitreous state of a substance. In particular, a fluctuational theory of vitrification[111] and a diffusion model of the volume relaxation of glasses have been developed. It was proved experimentaly for the first time[112] that the relaxation of the free volume in polymer glasses takes place not only by a local elasticity mechanism but also by a diffusion mechanism, which is revealed in two new non-trivial effects: the scale effect of the density of epoxide films and the scale effect of their rate of annealing.

A new effect, not yet understood, has also been detected, namely that the relaxation of the free volume in polymer glasses, taking place by a diffusion mechanism, is accompanied by ordering of the structure of the surface layers of the polymer[113].

Important information on the structure of network epoxide polymer glasses has been obtained in studies of their molecular mobility[1,3,6,64,87–95,106,108–110,114–123]. The use of a wide range of methods—mechanical and dielectric relaxation, dilatometry, thermally stimulated depolarisation, NMR, EPR, and calorimetry—established that in densely cross-linked epoxide polymers there is the entire spectrum of molecular movements characteristic of linear polymers. At the same time the molecular movements in these systems are characterised by a number of important features[1,3,6,89,90,92,109,110,114,119]:

1) the chemical units of the epoxide networks (their type and concentration) have no significant influence on the kinetic parameters of the local movements of all types;

2) the half-widths of the α-transitions in cross-linked polymers are usually much smaller than those in linear polymers;

3) the activation energy of the segmental mobility is always lower than that for linear polymers, and decreases with increase in the density of the cross-linkages, whereas the vitrification temperature increases.

The last two facts indicate on the one hand that there is a more uniform distribution of the segments with respect to length in a cross-linked polymer, and on the other hand that they are less extensive than the segments of linear polymers. Direct experimental measurements confirmed this conclusion, and showed that the segment in a network formed from individual diepoxides and diamines is a chain between two neighbouring chemical units[123].

IV. THE MODIFICATION OF EPOXIDE BINDING AGENTS

One of the traditional methods for producing a directed change in the properties of binding agents is by their chemical and physical modification. A series of studies[3,6,71,88,94,95,106,107,110–121,124–129] investigated the physicomechanical and relaxational properties of epoxide compositions over a wide range of chemical structures of the epoxide oligomers and hardening agents. Studies have been made of the properties of epoxide compositions whose chemical structure had been changed in directed fashion by carrying out copolycondensation reactions or by simultaneously carrying out reactions in the hardening system involving the polycondensation and polymerisation of a monomer or monomers of different kinds, or by other methods. Particular attention was paid to the study of the physicochemical modification of epoxide binding agents by the addition of low-molecular-weight rubbers[3,107,124–128]. This method made it possible to increase by almost two orders of magnitude the value of the effective surface energy of breakdown of the epoxide binding agents; this is extremely important for increasing their resistance to impact[107]. Extensive thermodynamic and kinetic studies of the production of the phase structure of epoxide polymers with inclusions of rubbers of different chemical character are making it possible to approach an understanding of the relationship between the chemical nature of the components and the conditions of the preparation of compositions and the phase structure of the composition material.

The phase equilibrium in the original epoxide–rubber systems is described satisfactorily by the Flory–Huggins theory[128]. A thermodynamic analysis of the change in the phase state of hardening epoxide–rubber systems showed that during hardening, the thermodynamic affinity between the epoxide polymer and the rubber decreases, leading finally to the exhaustion of their mutual solubility.

The kinetic condition of the production of the phase structure of epoxide–rubber compositions are determined by the ratios of the rates of the chemical reaction of hardening and the mutual diffusion of the components[124–128]. On the basis of these studies, ideas were developed about the mechanism of the production of the phase structure of epoxide–rubber compositions, a characteristic feature of which is the growth of the nuclei of the new phase under conditions of constantly changing coefficients of mutual diffusion of the components. The ideas developed make it possible to explain why the original thermodynamic compatibility of the components and the width of the distribution of the particles of the dispersed rubber phase with respect to size change in the opposite sense. They also make it possible to understand the frequently observed polymodal distribution of the particles of the dispersed phase with respect to size.

The proposed[124–128] model of the production of the phase structure is apparently of general value for any dispersed-reinforced polymer compositions, whose formation is related to the phase separation of the initially homo-phase mixture of the original components, and makes it possible to influence their phase structure, and hence their useful properties, in directed fashion.

V. CHARACTERISTIC FEATURES OF THE STRUCTURE AND PROPERTIES OF EPOXIDE POLYMERS AT THE BOUNDARY WITH A SOLID SURFACE

The relationship between the physicomechanical properties of epoxide binding agents in the vitreous and rubber-like states and the different levels of their structural organisation was examined above. The processes involved in the

hardening of binding agents in a composite material, however, often taken place in thin layers, in close contact with the filler surface. A large number of studies have shown that a filler may have a significant influence on a matrix, and so-called "boundary layers" are formed in it, with properties different from those of the block polymers[131,132]. The production of these boundary layers is usually attributed to the chemical influence of the solid surface of the filler on the production of the binding agent, the selective sorption of the components of the reaction system, the orienting influence of the surface on the molecules of the reagent and reaction product, etc. The large thickness of the boundary layers (up to tens and even hundreds of microns), however, can hardly be explained in terms of existing thermodynamic concepts.

Published data on this topic are extremely contradictory, apparently because there are kinetic factors, not previously taken into account, which are decisive in determining the observed changes in the properties of the matrix formed on the solid surface.

Various model experiments[133-136] have indicated that this decisive factor may be the internal stresses produced directly during the formation (hardening) of the polymer matrix in the composite. The internal stresses (shrinkage and thermal) arise unavoidably during the hardening of the binding agent in the composite. An important role in the production of composite materials may be played by other sources of internal stresses: 1) stresses produced by the relaxation of the volume of the previously deformed filler, and 2) stresses produced by a change in volume as a result of a phase transformation in the filler. The last two types of stress are easily modelled. Thus the appropriate experiments have been extremely informative from the viewpoint of the determination of the role of internal stresses in the production of composite materials with an epoxide matrix.

Studies involving the extensive use of various relaxation methods and the photoelasticity method have made it possible to investigate the kinetics of the production of internal stresses, their spatial distribution close to the boundary of an inclusion, the gradient of properties (T_g) of the matrix close to an inclusion, and the influence on these parameters of the nature of the adhesion interaction between the matrix and an inclusion, the conditions of hardening, and other factors. A distinct correlation has been noted between the observed gradient of the properties of a matrix at a previously deformed inclusion and the gradient of the developing stresses. Analogous results have been obtained in other model experiments. These data indicate a clearly defined causal relationship between the changes in the properties of a matrix formed on a solid surface and the internal stresses produced.

In addition to the decrease in T_g of a polymer produced in a field of mechanical forces, this polymer also shows an increase in the proportion of the sol fraction, a decrease in the equilibrium modulus of high elasticity, and the production in the specimen of structural stresses, that is residual stresses which are not annealed under any conditions. All these changes in the matrix are greater, the greater the stresses operating in the hardening process.

The observed changes in the properties of the matrix can readily be understood if it is assumed that the process of hardening of the matrix is accompanied by mechanodegradation of the chains of the network[134,135]. The data obtained lead to the following picture of the processes involved in the mechanodegradation of hardening polymer systems under the influence of mechanical stresses. In the range of pre-critical degrees of transformation, when the hardening system remains liquid and has a low viscosity, the applied stress relaxes. In the range of gel formation, when the viscosity of the system increases sharply, the rate of relaxation decreases, and although the stresses operating are extremely weak, they may nevertheless be comparable with the destructive stresses, since the number of elastically active chains, that is chains "holding" the load, in the network in the range of gel formation is also small, and the strength of this system is low. After the point of gel formation, the number of elastically active chains and hence the strength of the polymer increase sharply, and the system can now withstand a load (external or internal) without breakdown.

Thus during the formation of a cross-linked polymer there is a narrow range of degrees of transformation, close to the point of gel formation, in which the cross-linked polymer is very vulnerable to mechanical loads. The degree of damage to the polymer evidently depends on the level of stresses operating and on the kinetics of the hardening process, which determine the time for which the forming polymer is in the "danger" zone.

Although the qualitative picture appears quite satisfactory, quantitative agreement is not observed. Calculations show that the number of degraded chains between the nodes, required to explain the observed changes in the vitrification temperature of the polymer, is one hundred times that determined experimentally by the inhibitor method. Additional studies are therefore necessary to reach a final conclusion about the mechanism of the influence of internal stresses on the structure and properties of polymer matrices in a composite.

Nevertheless, it has already become clear that it is kinetic factors (the nature of the production and relaxation of internal stresses and the excess free volume) that are decisive in determining the observed changes in the properties of polymer matrices produced in contact with a solid surface. An understanding of these regular features is extremely important for the directed control of the properties of composite materials.

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To summarise this extensive cycle of studies, it can be stated that they essentially form the basis of a branch of the physical chemistry of macromolecular compounds which is of practical importance but which has not been developed theoretically, namely the field of densely cross-linked polymer systems.

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