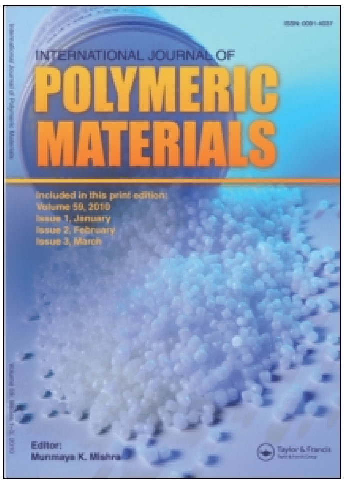

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The Current State of Polymer Aging and Stabilization

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Some investigations of problems of degradation and stabilization of polymers which were carried out at the Institute of Chemical Physics and other research centers in the USSR during the last few years are included in this paper.

The report includes the following topics. 1) The effect of intermolecular interaction on the kinetics of degradation processes in polymer mass. 2) The effect of submolecular structure on oxidation. 3) A new method for studying structural and physical peculiarities of polymeric matrices. 4) Problems of polymer stabilization during processing. 5) Interaction of nitrogen dioxide in the solid phase with macromolecules containing C═C bonds. 6) Ozone aging of raw rubbers and rubbers. 7) Photodegradation and light stabilization of some polymers. 8) The kinetics and the mechanism of oxidation of polymers under stress. 9) Radiation aging of polymers. 10) Hydrolytic degradation of some heterochain polymers. 11) Interaction of polymers with biomedia. 12) The problems associated with protecting metals with polymeric coatings. 13) Prediction of properties of polymeric articles and behavior of antioxidants. 14) Aging and stabilization of heat-resistant polymers. 15) Poly(vinyl chloride) aging with antistatic agents present.

KEY WORDS Polymers, aging, stabilization.

Today the problem of polymer aging and the search for ways of stabilizing polymers continue to remain central from the standpoints of both theory and practice. This is associated with major national economic problems that can be successfully solved by creating the scientific fundamentals of polymer aging processes under operating and storage conditions taking into account various factors related to environmental effect, i.e., heat, oxygen, ozone, light, penetrating radiation, corrosive liquid media, biologically active media, mechanical loads, and so forth.

The problem of preventing polymer degradation was first presented in the USSR as far back as the late 1940s by Prof. A. S. Kuz'minskii.[1–3] His studies covered mainly raw rubbers and rubbers. Using elastomers as examples, he showed some ways of improving the stability of polymeric materials, thereby bringing his developments to the practical introductory level.

Subsequently, in the late 1950s, the problem was undertaken by M. B. Neiman,[4–6] who introduced the quantitative kinetic method of investigation into the study of the aging processes (the research was performed largely on polyolefins). Meanwhile, the applied aspect of the problem was successfully being solved in the studies conducted by a number of institutes under the USSR Ministry for Petroleum

Industry and Ministry for Petrochemical Industry (K. B. Piotrovsky, B. M. Kovarskaya, E. N. Matveeva, E. P. Burmistrov, N. M. Zolotareva *et al.*).[7,8]

Since 1966, within the framework of the USSR Academy of Sciences and the Academy of Sciences of the Union Republics, the studies of the problem, "Aging and Stabilization of Polymeric Items" have been headed by Acad. N. M. Emanuel.[9,10] He began large scale studies; arranged the cooperation of the socialist countries, within the framework of the Academies of Sciences[11]; and supervised the creation of highly efficient stabilizers for polymers belonging to the class of the spatially hindered phenols—phenosanes (V. V. Ershov, A. A. Volod'kin, G. A. Nikiforov).

We point out the following features, which are presently among the practical applications of the polymer aging process:

- Extension of storage time and reliable operation of polymeric items as equivalent to an increase in output and improvement of quality (under large-scale production conditions, this becomes an important national economic target).
- Prediction of the lifetime of polymeric items when exposed to various environmental effects, creation of proximate prediction methods (this will enable to take the better advantage of the service lives of the items with no anxiety that the items will fail during operation).
- Secondary processing of polymeric items, secondary use of polymers (including monomer recovery due to pyrolysis and hydrolysis, and their subsequent polymerization.
- Burning of polymers, reduction of combustibility of polymeric materials.
- Environmental protection against polymeric waste (used polymeric items) including protection of the air basin against the combustion products of polymeric waste.
- Creation of polymers with predetermined lifetimes and subsequent decomposition into nontoxic, biologically assimilable products.
- Use of degradation as a method of modifying polymeric items and improving their service properties (primarily, the properties of the item's surface).

This paper provides data on the development of the theory of polymer degradation processes and the search for ways of stabilizing polymers as effected in the USSR mainly from 1985 to 1989, i.e., during the period between the 7th (Kazan) and the 8th All-Union Conferences on Aging and Stabilization of Polymers. These theoretical developments are required for solving the above-listed practical problems of polymeric materials technology.

1. THE EFFECT OF INTERMOLECULAR INTERACTION ON THE KINETICS OF DEGRADATION PROCESSES IN POLYMER MASS

The new model explaining the polychromatic kinetics of reactions in the polymeric matrix is advanced. Investigations conducted by Vaishstein[12–15] indicate that the number and location of the intermolecular bonds in the polymer specimen governs the lengthwise distribution of the blocks of the nonassociated and associated monomeric units. Based on the "activated complex" theory, the following expression was deduced for the constant of the chain break reaction rate:

$$K = K_0 \cdot e^{(\alpha_1 - \alpha) \cdot n} \qquad (1)$$

where K_0 is the reaction rate constant with flexibility change disregarded; α and α_1 are the coefficients characterizing the flexibility loss of the nonassociated chain section n-monomeric units long in the initial and transient states; $e^{(\alpha_1 - \alpha)}$ depends, for the most part, on entropy as α and α_1 are characteristics of the chain flexibility loss.

Usually, K_0 is close to the similar constant of the reaction rate in low molecular weight compounds. As may be seen from (1), the activation energy does not depend on the block length, whereas the pre-exponential term change follows that of the block length. When it is in the initial state, the entropy of the system changes due to the absence of "free rotation" of the chain units.

Since we deal with the lengthwise distribution of the blocks of the nonassociated monomeric units, the system may exhibit the polychromatic kinetics that depend on the past history of the specimen as the blockwise distribution is governed by synthesis, processing and operation of the specimen being in the stationary and not in the equilibrium state. The temperature rise is accompanied by both change in the constants of the rate of the proceeding reactions and the relationship between the different-length blocks that leads to explanation of the observed dependencies of the process rate and "observed activation energy" on temperature. As the block of the nonassociated monomeric units acquires a certain length, the thermodynamic possibility of a chain break in the middle of the block occurs that enables us to explain the observed transition of the destruction process from reaction at the chain ends (low temperature) to reaction by the "accidental law" (high temperatures) and origination of reaction in the cross-linked polymers starting from a certain temperature. At the temperatures at which the intermolecular interaction energy may be disregarded, the thermodynamically unstable "polymeric gas" is formed, which decomposes in an avalanchelike manner.

2. THE EFFECT OF SUBMOLECULAR STRUCTURE ON OXIDATION

The problem of the nature and importance of the permolecular structure for amorphous polymers has been raised time and again in connection with the physical and mechanical peculiarities frequently observed in polymeric items. Interest in the problem has also been stirred by the existence of incomplete data on the permolecular effects in polymeric reactions.

More or less consistently, the function of the structural microheterogeneity in the chemical reactions is covered in the course of the model polymeric chain reaction with benzoyl peroxide involved. In this case, the examples of the glassy polycarbonate and cellulose triacetate,[16,17] hyperelastic polypropylene[18] and melted polyethylene oxide[19] show that transformation of the macromolecules can proceed through the conjugated inhomogeneous reaction chains distributed between two structural zones of the globular aggregates, i.e., in the relatively dense sheath and in the more friable bulk microphase.

References 20 and 21 use the oxidizable polyethylene oxide as an example to show that microheterogeneity predetermines the heterophase mode of oxidation. The advanced structural and kinetic model of reaction enabled the authors to find the theoretical kinetic equation of the change in the strength of hydroperoxide (Y)

$$dY/dt = W_{Y/\max}\cdot Y^{0.5}\cdot(C + Y)^{-0.5} - Q\cdot W_i\cdot K_{YA}\cdot Y\cdot t \qquad (2)$$

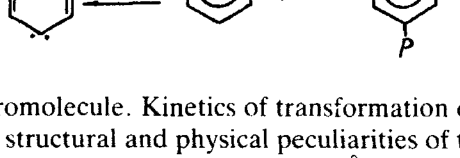
and the appropriate integral expression $Y(t)$ consistent with the experimental curves. In this equation $W_{Y/\max}$ is the maximum Y accumulation rate achieved at the instant hydroperoxide completely loses the branching agent function, C is the component constant, W_i is the initiation rate (initiation proceeds on the basis of the heterogeneous mechanism at the boundary of the structural zones), $(Q\cdot W_i\cdot t)$ is the strength of the aldehyde accumulated in the melt, reacting with ROOH and initiating $Y_{\max}\cdot K_{YA}$ as the constant of the rate of the aldehyde reaction with ROOH.

The result is important in that it stimulates the attention of the investigators to the function of permolecular structure in autooxidation of polymers. So far, the ideas of the function of microheterogeneity in the heterophase mode of polymer oxidation have not been recognized by the majority of specialists working in the field of thermal-oxidative degradation of polymers. This hypothesis, however, has a right to exist, and further accumulation of the facts will either validate or disprove it; modification of the hypothesis is likely.

3. A NEW METHOD FOR STUDYING STRUCTURAL AND PHYSICAL PECULIARITIES OF POLYMERIC MATRICES

The polymer oxidation processes depend largely on the structure of the polymeric matrix. Investigations conducted by D. Ya. Toptygin assisted by his co-workers[22,23] advanced the method of studying the structures of polymeric matrices using the reaction of the triplet carbenes.

Reactions of the triplet carbenes in the polymeric matrix proceeds through the stages of formation of intermediate radical pairs as a result of the hydrogen atom transfer from C—H bonds of the macromolecules to carbene and their subsequent recombination:

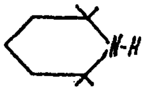


where PH is the macromolecule. Kinetics of transformation of the triplet carbenes take into account the structural and physical peculiarities of the matrix at the level of the effective distances in the radical pairs (3–5Å). The recent years witnessed the discovery of the external magnetic field effect on the rate of the process at low temperatures (77 K) in polymethyl methacrylate (PMMC). As seen from Figure 4, the maximum rate is observed in the zero field and the field of 5,000 oersteds. The magnetic effect can be explained by the structural peculiarities of polymethyl methacrylate with an assumption for this radical process of the formation of two types of the intermediate radical pairs distinguished by the geometric configuration (Reference Diagram):

The structural and physical modification of the matrix can be registered by the change in the kinetic parameters of the carbenes' reaction. Poly(methyl methacrylate) (PMMA) exhibits on addition of the inert filler (aerosol), a reduction of the carbenes' thermal transformation rate constant proportional to the increase of the filler content by 65 mass percent. The filler effect is determined by the modification of the polymer physical structure in change-over to the boundary layer state. The kinetic analysis of the considered cell reaction enables us to assess the thickness of the boundary layer in the filled polymers.

4. PROBLEMS OF POLYMER STABILIZATION DURING PROCESSING

In recent years, attention of the investigators working in the field of polymers aging and stabilization has been centered on the problems of stabilizing polymeric materials under processing conditions where the major factor causing destruction is the stirring of the melt (in other words, the shearing deformation). For this purpose, two types of stabilizers are recommended, i.e., the spatially hindered amines belonging to the class of the sterically hindered piperidine



and organic phosphites.

The stabilizers belonging to the classes above reduce the depth of the mechanical destruction of the polymers when processed in the extruder and considerably lower the consumption of the main antioxidant added for stabilization of the polymeric item in operation and storage.

Abroad, however, the trend is to process polymers in an inert atmosphere, which resolves the problems of the mechanical and oxidative destruction of the polymers.

The high cost of the stabilizers poses the added problem of reducing the irrational losses of the stabilizers due to their evaporation, wash-out, etc. In this context, the importance of the research efforts in the field of solubility, diffusion of the additives introduced into the polymeric material has increased significantly. The major contribution toward solving these problems was made by the investigations of Y. A. Shlyapnikov, S. G. Kiryushkin, and A. P. Mar'in.[7,24]

The solubility of the antioxidants changes with the temperature by very complicated laws, even undergoing an occasional decrease as the temperature rises.[25] The causes of the complex dependence are the polymer phase transitions; transition past the additive melting point at which the heat of solution changes; and the relaxation phenomena resulting in the irreversible change in the polymer structure at high temperatures (above the glass-transition temperature).

Among the peculiarities of the additives dissolution, as revealed in recent years, are the solubility dependence on the content of the polar groups in the aliphatic polyamides, i.e., in transition from polyethylene to polyamides 6 and 6,6 the solubility of the antioxidants passes a maximum, namely it increases at a low content of the amido groups and decreases at a high content thereof. The cause is the competition of the antioxidant sorption on the polar groups as leading to the growth of solubility and its decrease due to increase of the overall density of the polymer cross-linked with the amide–amide hydrogen bonds.[26]

A new type of stabilizer was detected, i.e., polymeric or oligomeric substances undergoing destruction under oxidation conditions associated with formation of free radicals as carriers of the free valency.

The macroradicals are practically at rest, hence the progress of the chain break due to recombination of the macroradicals is extremely slow. Introduction of low molecular weight radicals capable of transport due to diffusion into the system should result in a higher rate of the chain square break, i.e., the reduction rate. Antioxidants of this type become functioning only above a certain temperature of their decomposition.[24] As advanced by Y. A. Shlyapnikov, the new principle of stabilizing polymers at high temperatures is applicable not only to stabilization of the polymers when processed but, generally, to stabilization of heat-resistant polymers under conditions where classic stabilizers, i.e., phenols, amines, etc., change their function and transform into initiators (at a temperature over 200°C).

The investigations of recent years have begun to take into account not only the chemical activity of reactions resulting in oxidation process retardation but also the physical factors associated with the peculiarities of distribution of low molecular weight substances in the polymeric matrix and effect of the additives on the structures of the polymer melt.[27]

Identification of the high-temperature inhibited oxidation mechanism is one of the most important trends in research efforts in polymer degradation chemistry. On the one hand, this is a rather inconvenient object of study because it has already been proved that a large number of simple reactions proceed at the same time as several tens of reactions. On the other hand, practical requirements cause us to conduct such research now, since today polymers are not only being processed at high temperatures, with processing inevitably accompanied by aging of the material, but also in progress are thermal and oxidation stability accelerated tests in creation of the proximate methods for assessing the stability of polymers. The entire inhibitor mechanism undergoes a substantial change at high temperatures.

Unless the general concept of the mechanism exists, it is difficult to describe the high-temperature inhibited oxidation quantitatively. To produce the concept, the approach[28–30] based on the measurement and analysis of kinetics of three key products of polyethylene oxidation, i.e., absorption of oxygen, accumulation of hydroperoxide and consumption of the inhibitor (InH) during the induction period was realized.

Really, the simple kinetic system wherein provision is made for the reaction of the kinetic chain transfer by the inhibitor radical describes all three kinetics of change in the key oxidation products simultaneously, i.e., oxygen absorption, accumulation of hydroperoxides and inhibitor consumption.[31]

1. $R^{\cdot} + O_2 \xrightarrow{k_1} RO_2^{\cdot}$

2. $RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot}$

3. $ROOH \xrightarrow{k_3} RO^{\cdot} + {}^{\cdot}OH \xrightarrow[2O_2]{2RH} 2\ RO_2^{\cdot}$

6. $RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_6} \text{molecular products} + O_2$

7. $RO_2^{\cdot} + InH \xrightarrow{k_7} ROOH + In^{\cdot}$

8. $RO_2^{\cdot} + In^{\cdot} \xrightarrow{k_8} \text{inactive products}$

10. $In^{\cdot} + RH \xrightarrow[O_2]{k_{10}} \text{molecular products} + RO_2^{\cdot}$

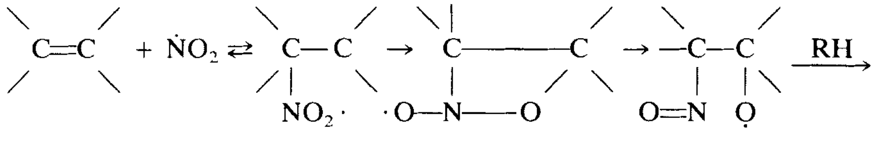
Thus the very important problem of the inhibition mechanism is solved, i.e., what occurs (kinetics complication) in the transition from low temperatures where the mechanism is sufficiently simple and already identified at the quantitative level to high temperatures where the mechanism is far from clear (the polymer and polymeric items are frequently exposed to the conditions above). The obtained data enable us to analyze the inhibitor behavior, for instance, in processing, measure the effective kinetic parameters and ascertain other important parts of the inhibition mechanism in terms of the dynamics of their change.

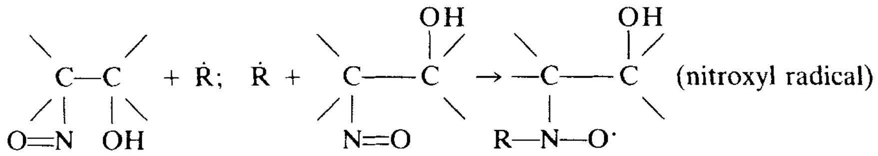
5. INTERACTION OF NITROGEN DIOXIDE IN THE SOLID PHASE WITH MACROMOLECULES CONTAINING $>C{=}C<$ BONDS

Recent years have witnessed the appearance of quantitative studies associated with the effect of environmental pollution components (mainly, the atmosphere) on the polymer degradation process.

Investigations conducted by D. Ya. Toptygin and his co-workers[39,40] demonstrate, in particular, that the reaction of nitrogen dioxide with the double bonds of the macromolecules can be one of the most important ways of initiating the free-radical reactions of polymer aging in an atmosphere polluted with industrial waste.

The interaction of nitrogen dioxide (NO_2) with the macromolecules containing $>C{=}C<$ bonds has been investigated using the methods of electron paramagnetic resonance and ultraviolet and infrared spectroscopy in solid poly(methyl methacrylate), wherein 0.3 mol/kg of the middle bonds (I) was accumulated during photolysis and in raw rubbers. The PMMC synthesis of radicals (Z—C=O) − (NO˙) − R indicates the decomposition of the alkyl macroradicals with breakdown of the ester groups with radical·(C=O) − OCH_3 splitting off:





R˙ is formed in the immediate vicinity of the nitroso group R_2—N—O˙ and, in the cell reaction, may lead to formation of the dialkylnitroxyl macroradical.

As shown by the results of the ultraviolet spectrometry, absorption of NO_2 by the double bonds I, II, III is described by the formal-kinetic equation

$$[NO_2]_o/[NO_2]_t - 1 = K_{exp} \cdot t$$

featuring the reactions proceeding in a solid phase.

As is shown by the results of infrared spectrometry, reaction of the raw rubbers with NO_2 is accompanied by the reduction of the concentration of C—H bonds, and formation of nitro (R—NO_2) and nitrate (R—O—NO_2) groups.

Thus, it is shown that formation of R_2—NO˙ in reaction of NO_2 with the double bonds of the polymers occurs as a result of the free-radical cell process, wherein formed in the intermediate unstable state is the alcoxyl radical, it being highly active in the reactions of transfer and decay associated with the polymeric chain break and causing aging of the polymeric materials.

6. OZONE AGING OF RAW RUBBERS AND RUBBERS

Recent years have witnessed appreciable progress in the kinetic description of the processes associated with the ozone cracking of elastomers. Improvement of experimental methods has eliminated the formerly present spread of the results, and has identified the regularities in the kinetics of the growth of cracks and relaxation of tension in the specimens.[41–43]

The quantitative results obtained for elastomer ozone aging enable us to improve the accuracy of predicting the time of the reliable operation of raw rubbers and rubbers in the ozone atmosphere.[43]

7. PHOTODEGRADATION AND LIGHT STABILIZATION OF SOME POLYMERS

As regards the field of photodegradation and light stabilization of polymers, data are obtained on the mechanism of phototransformation of polyamides,[44–46] and mechanisms of the main reactions associated with phototransformation of such seemingly investigated polymers as poly(vinyl chloride) (PVC) are identified.[47] The effect of the structural and physical factors as well as the acid–base properties of a medium on the polymer light resistance[48] are analyzed using cellulose photooxidation as an example.

New experimental data enables us to complement and generalize the earlier advanced mechanism of photooxidation of aliphatic polyamides (PA). The essence of the generalized mechanism is represented in the diagram and is as follows. The PA photooxidation is essentially the chain process whose progress is determined by the specific alternation of the reactions of peroxide macroradicals $PO_2^{\cdot}$ and low molecular weight radicals r' (presumably $HO_2^{\cdot}$ or $^{\cdot}O_2^{-}$). The important trend of transformation of radicals $PO_2^{\cdot}$ is the elimination of light radicals r'. The thus-formed unstable intermediate product A is easily oxidized by the air oxygen, and is transformed into the new products K and K', which are the kinetic chain carriers capable of playing the role of oxidation photoinitiators. Product K is essentially ketimide and exhibits maximum optical absorption at 360 nm. The nature of its kinetic analogue K' absorbing light in the region of 313 nm is so far unknown. K and K' react easily with radicals r', which leads to the breaks of macromolecules and continuation of the kinetic chain. The chain breaks at recombination of $PO_2^{\cdot}$ and $r^{\cdot}$. Depending on the light wavelength, the chain is initiated by various contributions of the photolysis reactions of products K and K', the intrinsic polymer amido groups and sensitizers introduced therein.

1. $PO_2^{\cdot} \xrightarrow{PA,\ O_2} PO_2^{\cdot}$

2. $PO_2^{\cdot} \rightarrow A + r^{\cdot}$

2′. $PO_2^{\cdot} \rightarrow B + r^{\cdot}$

3. $r^{\cdot} \xrightarrow{PA,\ O_2} PO_2^{\cdot}$

4. $A \xrightarrow{2O_2} K$

4′. $A \xrightarrow{2O_2} K'$

$$[PO_2^{\cdot}] = \sqrt{\frac{k_3}{k_2' k_6}}\, k_7[K]I_o$$

$$[K] = \frac{k_2 k_3}{k_2' k_5}\,\frac{k_4}{(k_4 + k_4')}$$

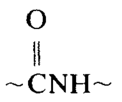
$$\left.\begin{array}{l} 5.\ K + r^{\cdot} \xrightarrow{\text{PA, O}_2} \text{PO}_2^{\cdot} \\ \\ 5'.\ K' + r^{\cdot} \xrightarrow{\text{PA, O}_2} \text{PO}_2^{\cdot} \end{array}\right\} \text{breaks } [K'] = \frac{k_2k_3}{k_2'k_5'}\frac{k_4'}{(k_4 + k_4')}$$

$$6.\ \text{PO}_2^{\cdot} + r^{\cdot} \longrightarrow \text{chain break}$$

$$7.\ K \xrightarrow{h\nu,\ 2\text{O}_2} 2\text{PO}_2^{\cdot}$$

$$7'.\ K' \xrightarrow{h\nu,\ 2\text{O}_2} 2\text{PO}_2^{\cdot}$$

$$8.\ \text{PA} \xrightarrow{h;\nu,\ 2\text{O}_2} 2\text{PO}_2^{\cdot}$$



$K, K', S \sim\overset{\overset{\displaystyle O}{\|}}{C}NH\sim$ are sensitizers.

Based on the mechanism above, the directed search for new light stabilizers is now in progress. The task is currently central, as even the best of the known photostabilizers do not enable us to reduce the photooxidation rate more than five times.

The outstanding remaining problem is that the entire process according to the presented system is described within the framework of routine homogeneous kinetics. The solid-phase features of the system do not reveal themselves for some reason. Only recently, have the investigators[44–46] studying chemiluminescence encountered indications pointing to the heterogeneous nature of the oxidation process. Research efforts continue. The authors expect that these efforts will provide new data on the mechanism and, conceivably, new approaches to light stabilization.

The problems of identifying the function and effective range of such polymer aging factors as the structure, mobility of molecules and medium pH are covered by the recently conducted cellulose photoaging investigation.[48] The latter shows that the cellulose photoaging rate is proportionate to the content of the available amorphous phase. This implies that cellulose photooxidation does not cover the entire amorphous phase but is confined to the phase part accessible to low-molecular weight substances. Decrease of the content of the available amorphous phase from 30 to 0% results in the 14-time reduction of the photoaging rate.

Other aging factors, i.e., mobility of the molecules, can be changed, for instance, by plasticizing cellulose with water. The increase of water content from 0 to 50% results in the 6-time reduction of the photoaging rate. This effect is governed by the drastic increase of the radicals recombination rate as the molecular mobility increases.

The third aging factor (i.e., the medium pH), which was understood earlier, is of utmost importance, as is now evident. It was found that the medium pH causes the cellulose photoaging rate to change by the order of 2 to 3 and in doing so the minimum photoaging rate is observed in the region of pH = 5. The pH effect on photoaging is explained by the catalysis of the reactions of radicals and products in the stage of the oxidation chain continuation.

Thus, variation of three factors, i.e., the structure, mobility of molecules and medium pH, may enable us to increase the cellulose light stability 100 to 1,000 times. This indicates the importance of future use of the above factors in the practice of light stabilization.

Despite the large number of papers dealing with PVC degradation and stabilization, the problem of photodegradation and light stabilization in the above polymer is still very far from being solved. The major regularities of PVC photodehydrochlorination and photooxidation have recently been established, i.e., the main processes running as the above large-capacity polymer[47] undergoes photoaging.

According to the new advanced mechanism, PVC photodehydrochlorination is essentially the photochain process with the kinetic chain of several tens of links long, wherein the chain continuation is enabled by the photochemical transformation of the alkyl and polyphenyl radicals. Within the framework of new ideas, the single explanation covers such features of dehydrochlorination as the synergistic effect of the long-wave light to which the polymer is not directly exposed as well as the drastic decrease of the rate on adding the photochemically inert plasticizer.

The PVC photooxidation proceeds as a process featuring a very small length of the chain[47–49] and a formally linear break of a chain. The possibility of the valency migration in a solid PVC by large distances using the low molecular weight radicals is proved.

The obtained data indicate the possibility of using light-resistant antioxidants as well as excited-state extinguishers for PVC light stabilization, thus opening new avenues of improving PVC light resistance. The results related to PVC photoaging as obtained by V. Y. Shlyapintokh and V. B. Ivanov[47,49] largely complement the results obtained by K. S. Minsker[50] in the field, and enable the investigative efforts to be presented in strictly quantitative terms.

Recent years have witnessed the highly active research efforts of the group of investigators at the chemical kinetics chair of the Moscow State University chemical department.[51–56] The area of their interest in examination of polymer aging processes is the so-called photoradical aging process, i.e., the change in the functional composition and structure of the high molecular weight compounds, occurring as a result of the chemical reactions of the electron-induced radicals and ion radicals. They have obtained the data array related to the quantum efficiency of the photochemical reactions of the macroradicals in various carbon-chain and heterochain polymers, the effect of the photon energy on the quantum efficiency of these reactions. It is shown that the efficiency of the photodissociation processes of the macroradicals can be satisfactorily described within the framework of the unconfined-space model. Studied in detail are the mechanism and kinetics of the photoradical aging of polycaproamide and polyacrylic acid at 77 K. It is established that the basic direction of the reactions of the electron-induced anion-radicals in these polymers is the electron ejection whose quantum output increases following the photon energy increase. It is shown that the active centers of the photoradical aging of the polyacrylic acid and polyacrylamide are the neutral macroradicals, i.e., mid-radicals and terminal radicals. It is proved that the induced mid-macroradicals enter only into the dissociation reactions. Discovered is the proceedings of the photoradical chain reactions with their participation in the polyacrylic acid and polyacrylamide. It is established that the photodecomposition of the mid-macroradicals in the polyacrylic acid follows two directions, i.e., with the main polymeric chain breaking and unbreaking. The last of the reactions above being the photochemical stage of the chain continuation, it is accompanied by the effective breakdown of the functional groups and formation of the product (ketane) whose subsequent reactions cause the cross-linking of the polymeric chains.

$$\sim CH_2\dot{C}(COX)CH_2\sim \xrightarrow{h\nu} \begin{cases} \sim CH_2C(=C=O)CH_2\sim + \dot{X} & (1) \\ \sim CH_2C(COX)CH_2 + \dot{C}H(COX)CH_2\sim & (2) \end{cases}$$

$$\dot{X} + \sim CH_2CH(COX)CH_2\sim \rightarrow HX + \sim CH_2\dot{C}(COX)CH_2\sim \qquad (3)$$

$$\sim CH_2C(=C=O)CH_2\sim \rightarrow \sim CH_2\underset{\cdot}{\dot{C}}CH_2\sim + CO \qquad (4)$$

The obtained values of the quantum outputs of the reactions (1), (2) and (4) in the case of polyacrylic acid are $\Phi^1_{313} = 0.1$, $\Phi^2_{313} = 0.015$, $\Phi^4_{313} = (2.0 \pm 0.4)\cdot 10^{-2}$, respectively. Using the above-specified data along with that determined by experiments, it is found that effective constants of the macroradicals recombination rates enable the kinetics of change in the initial, intermediate and final products of the polyacrylic acid photoradical aging to be described with adequate accuracy. An important experimentally discovered fact is that the change in the dose of the absorbed light can directionally influence the change in the molecular mass distribution (MMD) of the polymer, wherein produced are the mid-macroradicals (at low doses, the MMD change is determined by reaction (2), whereas at high doses, it is determined by reaction (4) with subsequent formation of the cross-links as a result of the ketene reactions). In addition to the already well-known effect of the kinetic nonequivalence as was observed earlier by the authors[57] in the photoradical processes in various polymers, detected for the first time is the leveling effect of the photon energy on the kinetic nonequivalence of the sulfonyl macroradicals.

Evidently, the most interesting trends in the years to come in the field of polymer photoradical aging should be considered to be the research efforts as regards the photochemistry of the macroradicals in the forbidden transition regions (substantial expansion of the spectral sensitivity area is likely) and investigation of the photoradical chain reactions and, primarily, the spatial distribution of the reaction products.

8. THE KINETICS AND THE MECHANISM OF OXIDATION OF POLYMERS UNDER STRESS

The cycle of the research efforts covering the study of stress effects on the structure, dynamics and reactivity of polymers enables us to obtain the following results.[58–61]

The structural stresses of the energy-induced nature cause the chemical reaction rate either to increase or decrease exponentially, depending on the change in the reaction center's linear dimension with the reaction in progress:

$$\ln \frac{k_\sigma}{k_0} = \frac{\gamma \cdot \sigma}{RT} \tag{1}$$

where K_σ and K_0 are the constants of the polymer chemical reaction rate in the stressed and limp states; σ is the stress; and γ is the stress sensitivity factor equal to the product of two quantities, i.e., γ_a as the constant characteristic of each specific reaction and factor β taking into account the irregularities of the bondwise load distribution ($\beta \geqslant 1$).

Establishment of the quantitative rate constant-and-stress dependence enables various chemical reactions to be classified in terms of their sensitivity to the effect of forces. It also enables the investigation of the permolecular structure of the polymers.[58,59,61]

In terms of sensitivity to strain, all chemical reactions are divided into three types:

1. Processes insensitive to the effects of strain. As regards these processes, factor $\gamma_a = 0$.
2. Chemical reactions exhibiting high sensitivity to loads ($\gamma_a \geqslant 0.5$ to 1.10^{-29} m^3). This type includes the processes accompanied by the break of the main macrochain, for instance, hydrolysis of polyamides, processing of the published data using equation (1) produces assessment value $\gamma_a \approx 2.10^{-29}$ m^3.
3. Reactions displaying low sensitivity to strain ($0 < \gamma_a < (0.5$ to $1))^{10-29}$ m^3.

These include the reactions of ozone with the saturated macromolecules-polyolefins ($\gamma_a = 0.33 \cdot 10^{-29}$ m^3) and polyamidoimides ($\gamma_a \approx 0.05 \cdot 10^{-29}$ m^3).

Investigation of the permolecular structure of polymers using equation (1) enables the production of the quantitative assessment of the bondwise load distribution irregularity in the oriented polyolefins, i.e., polyethylene of high density and polypropylene ($\beta = 2$ to 6).

This method enables the particularly detailed study of the permolecular structure of the isotropic polyamidoimides containing the fluorenic cycle (PAI-1), nitrile group (PAI-2) and paraphenylene group (PAI-3). Factor β varies over the range of from 40 to 120, depending on the polyamidoimide chemical structure. The most ordered structure is formed by the PAI-1 for which is identified the minimum β value and the minimum density of the specimens, thus providing the best possibility of forming the intermolecular hydrogen links.

The irreversible reconstruction of the permolecular structure (PMS) influences the dependence of the ozone oxidation rate on the load.[61] The particularly considerable effect of the PMS reconstruction is observed during ozone oxidation of the oriented polyolefins exposed to the action of the tensile loads in the stress relaxation mode. The additional orientation of the specimens results in improvement of the fibrillar structure and reduction of the ozone oxidation rate.

The physical and mechanical properties of the polymers and the rate and mechanisms of the chemical reactions proceeding therein are largely governed by relaxation properties of the macromolecules and dynamics of the low molecular weight additives.[58] As the polymeric articles are operated, as a rule, under conditions of stress, temperature and oxidation effect, it is important to identify the effect of these factors on the molecular dynamics in the oriented polymers so as to solve many scientific and practical problems.

As shown by the conducted investigations, the initial stage of the preoriented specimens tension (ε up to $\approx 6\%$ in polyethylene and $\approx 10\%$ in polypropylene) shows that the molecular mobility of the chains in the amorphous regions grows, and in doing so, the intensity of such changes depends on the molecular-mass polymer parameters, the extent of the orientation drawing, and the oxidation level. The results obtained indicate that deformation of the specimens exhibiting the mean molecular mass (MM) (narrow MMD) and high extents of drawing is followed by retardation of the molecular mobility.

Ozone oxidation leads to considerable growth of stiffness of the amorphous regions, thus resulting (at low oxidation levels) in better mechanical properties of the polymeric material.

The effect of the oxidation temperature[59] on the structure and strength of high-density polypropylene-polyethylene mixture films is investigated. It is shown that the polymeric matrix of the mixture undergoes major changes at the orientation temperatures above the melting point of high-density polyethylene (HDPE) crystallites. The results are the appearance of a new crystal modification of polyethylene (PE), the breaking strength experiences the drastic drop, and the melting point of PE crystallites and the extent of PE crystallinity also drop. The experimental data indicate that the orientation temperature of polyolefins should be close to the melting point of the mixture component that exhibits the lower melting point, but should not exceed the melting point.

It is established that ozone-oxygen oxidation brings about substantial change in the structural and physical characteristics of the polymeric matrix, i.e., the melting point of the crystallites of the components being part of the polymeric mixture, polydispersion, extent of crystallinity of the components. Detected are the minor change of the melting point and the increase of polydispersion of the polyethylene during oxidation as well as the substantial reduction of the melting point and polydispersion of the polypropylene (PP) crystallites in the oxidized specimens as compared to those that are unoxidized. It is established that ozone renders amorphous only the crystal structure of polypropylene in the mixture down to its complete disappearance in some mixed compounds (low content of polypropylene in the mixture).

Recently, investigations conducted by N. Ya. Rapoport[58,60] have revealed the effects of stresses in the oxidation kinetics of polyolefins.

It is disclosed that oxidation of the oriented and, in particular, the oriented prestressed polyolefins occurs on the spatially separated nucleation sites for a reaction whose number and location in space provide the grounds to assume that they emerge around the particles of the foreign inclusions which initiate oxidation of the admixtures. The function of such particles can be performed by the traces of the polymerization catalysts transformation products. This governs various oxidation stability of one and the same polymer synthesized using various catalytic systems.

The stress increase brings about change not only in the rate but also in the oxidation reaction conditions, i.e., from the branched chain process to the nonchain oxidation of the terminal macroradicals.

The effects above result in that the *oxidizing prestressed polyolefins are denied the destruction criterion as the fixed mean concentration of breaks or terminal oxygen-containing groups*.

The models of destruction of the oxidizing prestressed polyolefins are advanced, enabling in some cases the prediction of longevity of various brands of the polymer under various operating conditions. The advanced models are constructed on a basis of computer-aided design and analytical expressions have been obtained which relate longevity to the number of initiation centers in the specimens and their growth rate. The first expression depends on conditions of polymerization, cleaning and moulding, whereas the second expression depends on polymer structure and oxidation conditions. This makes it possible to put forward some principles of improving stability of polymers without using conventional stabilizers, i.e., thorough cleaning so as to dispose of contamination, higher extent of predrawing, and so forth.

9. RADIATION AGING OF POLYMERS

Investigated are PE shrinkage and cracking effects during radiation oxidation.[62,63] It is established that thick layers (plates, cable insulation) exposed to the diffusion-controlled oxygen supply exhibit formation of the marked sandwich structure comprising the external oxidized layer and the internal radiation-protective layer. In this case, the interior of the material experiences stresses causing the material to crack down to the depth of the oxidized layer. Thickness of the oxidized layer and, accordingly, the depth of cracks depend on the ionizing radiation power.

No cracking occurs in the thin films experiencing the uniform oxidation in thickness, but shrinkage evidently associated with accumulation of the polar groups with oxidation in progress is observed.

Shrinkage of thin films and cracking of thick films are governed by one and the same structural reconstruction process: cracking starts at the instant when shrinkage reaches a certain critical level.

As regards both investigated effects, i.e., shrinkage and cracking, post-effect not associated with post-radiation oxidation is detected. The structural reconstruction processes governing shrinkage and cracking exhibit delay as compared to oxidation. The characteristic time delay is about one month.

The kinetic model enabling production of the single description of shrinkage and cracking effects as consequences of radiation oxidation is constructed. The procedure for estimating the guaranteed service time of the PE cable insulation has been elaborated on a basis of the model above and is being tested at present in the cable industry.

10. HYDROLYTIC DEGRADATION OF SOME HETEROCHAIN POLYMERS

All heterochain polymers that react with water are subjected to destruction. The hydrolytic reaction is catalyzed by acids and bases. In the diluted solutions of acids and alkalis (pH region), the rate increases in proportion to the increase in concentration of the solvated H^+ and OH^- ions. In more concentrated solutions of acids and alkalis, dependencies of the hydrolysis rates on the medium composition exhibit the more complicated nature.[63,64] Thus, for instance, as regards amides, the hydrolysis rate increases following the higher concentration of $H_5O_2^+$, reaches the maximum value at about 15% solution of H_2SO_4 as regards the aliphatic amides (about 50% solution of H_2SO_4 as regards the aromatic amides) and undergoes the subsequent reduction. Reduction of the destruction rate is related to formation of the nonreactive protonated form of the amido bond. In this context, it is presumed that solutions of polyamides in concentrated sulphuric acid are stable.[62] As has recently been shown,[65] however, the constants of the destruction rates as regards aliphatic and aromatic polyamides decrease to 99.5% solution of H_2SO_4 with only subsequent drastic increase following the acid concentration rise to 100%. The observed change in the reactivity is unrivaled in the chemistry of low molecular weight amides. Conceivably, this is associated with the fact that the polymeric state of a substance brings about high local concentrations of protonated amido bonds in a solution, which causes the change in the medium properties when directly exposed to polycation. The results obtained are important for the chemistry of aromatic fiber-forming polyamides as the concentrated sulphuric acid is the only available solvent for these polymers.

Recently, the function of mineral acids as catalysts of polycyclodehydrotation of poly-*o*-oxyamides in a solution has been shown at the quantitative level.[65]

The data obtained represent an undoubted interest in predicting stability of poly-*o*-oxyamides in aggressive media. The data also look promising from the standpoint of synthesizing these polymers to considerably lower cyclodehydrotation.

11. INTERACTION OF POLYMERS WITH BIOMEDIA

Recently, the structure and properties of segmented polyesterurethanes intended for medical purposes have been subjected to comprehensive analysis.[66–69] Use of block copolymers as artificial organs (ventricles of the heart, valves, catheters, and so forth) dictates the need for creation of a scientifically validated system of requirements placed on the material and articles made thereof intended for solving a specific practical task. The target of the comprehensive analysis of some domestic and foreign segmented polyesterurethanes is to obtain reliable information on their structure, morphology, sorption characteristics and some other properties, with subsequent assessment of such important characteristics of the articles as serviceability and hemocompatibility.

Stemming from the possibilities of identifying the physical and chemical parameters and properties of the polymers on a basis of segmented polyesterurethanes using the group of spectroscopic and diffusion methods, the comprehensive approach to investigation of materials and articles intended for use as coatings, diaphragms and other elements of the artificial heart is elaborated on.

It is established that the studied polymers are essentially the complex multiphase system with the microphase separation, whose extent is governed by the kinetic factors and process conditions required for material preparation. As regards some domestic materials, i.e., Vitur-0533 (Silurem), the existence of crystal formations whose content depends on conditions of synthesis and processing is shown. As regards the materials Vitur RM, Gemotan and their foreign analogue Biomer, partial microphase separation is observed without noticeable formation of crystallites. Shown for the first time is the existence, virtually in all materials, of the intermediate (composite) phase comprising polyester and polyurethane fragments, which are largely responsible for the complexity of the physicochemical and mechanical properties of the material (article). The correlation between the extent of the structural heterogeneity and the adsorption properties of the surface of polyesterurethanes with respect to blood plasma proteins is established. The correlation obtained seems to be extremely important in connection with the specific conditions of operating the articles. The comprehensive approach to investigation of the kinetics of adsorption of blood plasma proteins on the surface of block copolymers is advanced, which includes the diffusion-kinetic model of the process, the procedure for determination of the physical and chemical parameters of the polymer-protein system and prediction of the composition and structure of an adsorption layer as a decisive factor in assessment of the thromboresistant properties of the segmented polyesterurethanes.

The diffusion method and the isotope H-D exchange method elaborated specifically for this class of polymers have enabled their important service properties to be determined, i.e., sorption capacitance as regards water, and diffusion and permeability coefficients, which should be taken into account in storage and operation of the materials. For the first time, the permeability method has enabled it to be established that transfer of organic acids in the segmented polyesterurethanes capable of microphase separation is effected in the polyester phase. Should the microphase separation be partially effected, the interaction of the diffusing molecules with the urethan groups results in retardation of diffusion. Transfer of the acids over the hydrophobic areas contributes to the selective effect likely to involve the separation of the flows of the lipophylous and lipophobic components as observed, for instance, in the case of the mixture of organic and inorganic acids.

Based on the results obtained, the complexity of the methods for determining the physical and chemical characteristics of segmented polyesterurethanes as required for quality control in the stages of synthesis, processing of the material and the production process of the article has been recommended for pilot-scale production.

Kinetic regularities of the transfer processes in the system containing the polymer, solvent and low molecular weight additives are obtained.[66] The topicality of the theoretical and experimental investigation of the processes involving the joint transfer of the solvent and low molecular weight substances in the polymeric materials is influenced, for instance, by the creation of the prolonged-action medicinal depots[67] of the matrix and reservoir type, capable of performing their service functions in contact with the physiologically active medium. To solve this problem, it appears that the equilibrium and kinetic regularities of the interaction of the polymeric materials with such specific solvents as water and aqueous solutions of low molecular weight compounds should be studied.

Classification of high molecular weight compounds is advanced in terms of the extent of hydrophily, based on thermodynamic functions (parameters of solubility) and the data on the mechanism of water transfer in the polymers. Developed and supported by the experimental results are the mathematical models of water sorption and transfer in the hydrophobic materials using the example of fluoroplastics and polyethylene of low density. The possibility of water transfer in the hydrophobic matrix in the form of the associates is shown for the first time, and the method for designing the physical and chemical parameters of the water-hydrophobic polymer system is advanced. A polyamide was used as an example for consideration of the principle regularities of transfer of inorganic and organic acids in moderately hydrophylic polymers.[68] The developed diffusion model takes into account the peculiarities of the aggressive medium transfer in the amorphous and mesamorphous regions of the structurally heterogeneous polymer. The physical and chemical parameters of transfer in the investigated systems are determined. The model of the structural $\gamma \rightarrow \delta$ transition in crystals under conditions of acid sorption by the polymer is suggested.

The methods for experimental investigation and mathematical modeling of the transfer processes in the polymer-water-drug system are elaborated.[69] Shown is the efficiency of using the advanced methods in liberation of antibiotics from the matrix-type depot based on the copolymers of poly-*N*-vinylpyrrolidone and the therapeutic systems of the reservoir type. The decisive effect of the chemical composition, structure of the polymeric composition as well as the geometry of the specimen on the mechanism and physicochemical parameters of the drug liberation has been established. Thus, as the polymer hydrophily extent decreases, the transition from limiting the process of liberation by the water sorption stage (displaying in many cases the anomalous-nondiffusing nature) to purely diffusive liberation in moderately hydrophylic and hydrophobic materials is observed.

The results obtained enable us to predict the kinetics of liberating the drugs from the polymeric articles exhibiting arbitrary geometry on the edge conditions approximating the real conditions.

Recent years have witnessed emergence of the problem at the junction of mechanics, biology and some medical sciences, i.e., creation of the substitutes of various biotissues and systems. Along with other substitutes, most frequently used are the polymeric materials.[70–76]

When implanted into a living organism, polymeric material is exposed to the joint action of the physiologically active medium and stress, i.e., the biomechanical effect.

Along with biological compatibility, it is very important for the polymeric implant to be rheologically compatible. Rheological incompatibility, i.e., disagreement of the biomechanical properties of the implant and reconstructed organ or tissue, results in emergence of excess concentrations of stress at the junctions of the implant and the biological tissue. Hence, in creating synthetic materials used for medical purposes, the following problems exist: prediction of their deformative, strength, structural characteristics; and assessment of these properties following prolonged exposure to the aggressive medium under conditions of continuous cyclic stress. Most frequently, the polymer is exposed to biomechanical effects when it is used in endoprosthetics of the locomotor system, for instance, endoprosthetics of the hip joint, and plasty of the ligaments and tendons.

Polyethylene terephthalate (PETP) exposed to the biomechanical effect in plasty of ligaments and tendons[70–73] has been investigated. Use is made of woven bands of PETP fiber exhibiting mutually perpendicular interweaving of the filaments. The initial specimens and those removed in the patients in various implantation stages have been investigated. Kinetic experiments in the model media have also been conducted. The stay of the PETP fibers in an organism leads to minor changes in the material's structural characteristics. A change in the orientation characteristics is noted, even in the specimen that stayed in the organism for only three months, thus indicating the displacement of macromolecules in the polymer amorphous regions.[70] Also noted is a certain redistribution of the microheterogeneities as a result of the smaller contribution of the minor pores. The specimen that stayed in the organism for eight years does not exhibit further orientation change, whereas the nature of porosity varies in the same direction as in the initial implantation period (the contribution of the minor pores undergoes further reduction). The number of fine surface pores could decrease either due to an increase of their size in the surface PETP hydrolysis or to the invasion of pores by the organism's collagen tissues. Minor changes in the structure of the fibers, however, influence creep flow. The ultimate creep flow figure experiences a noticeable increase during the three-month stay of the material in the organism. This increase of creep flow most likely occurs due to tissue fluid sorption. As a result to the fluid sorption at the constantly active load (the ligament work in a living organism), PETP fiber orientation hardening occurs.[71] In later implantation stages, the ultimate creep flow figure varies little (that is also proved indirectly by the data presented in paper).[72]

Investigations conducted earlier[69,71] enable us to provide the approximate prediction of the likely changes in the lavsan substitutes of the ligaments and tendons. According to the equation suggested in this paper

$$P = P_0(1 - k_{ef} \cdot t/d_0 \cdot \rho)^2$$

where P_0, P are the tensile strengths (initial and present), k_{ef} is the effective constant of the destruction process rate, t is time, d_0, d are the mean diameters (initial and present) of the PETP filament, and ρ is density of the PETP fiber, one may approximately estimate the time during which the substitutes of the ligaments and tendons lose 50% of their strength. As estimated, the time is (30 ± 2) years.

Thus, the data of the conducted investigations have shown that implants made of woven PETP bands are sufficiently stable when used during eight years. It is assumed that adsorption[73] and sorption of the tissue fluid and jointly active stress are followed by orientation hardening of the PETP fibers. Furthermore, these research efforts enable us to provide the approximate prediction of the likely changes in the lavsan substitutes of the ligaments and tendons at more prolonged periods of stay in the organism, and in doing so, their functioning time is determined by about 30 years.

In the light of the biotechnology works, of interest is the trend associated with the use of biodestructible polymers in devices associated with the controlled liberation of drugs.[77] Unlike in the use of bioinert polymers, the use of biodestructible polymers does not require their removal from the organism. Biodestructible polymers are usually employed in the form of implants or are circulated in the blood channel by microparticles introduced by injection. With polymer surface erosion in progress, liberation of a drug occurs as a rule (according to the zeroth-order law). This is in compliance with the therapeutic requirements for application of drugs. V. S. Livshits, E. F. Vainshtein and Zaikov[78] elaborated on the kinetic fundamentals of the process associated with liberation of drugs from bioeroded polymers, and reviewed the importance of the initial polymer molecular mass distribution for the kinetic parameters of liberation. Also considered from the standpoint of kinetics is the case where drug fragments are linked to the polymeric chain. Integral kinetic equations are derived, enabling all required kinetic parameters to be attained. Also shown is the possibility of nonuniform liberation caused by formation of the soluble products of biodestruction covering the entire polymer volume.

Biodamage to the polymeric materials may occur as they contact the living organisms, and results in changes in their service properties.[79-81]

In the general case of biodamage, the following processes may take place:

- adsorption on the material surface of the microorganisms or substances existing in the tissue of the living organism.[82]
- material failure either as a result of the specific action (the living organism employs the polymeric material as a supply source) or under effects of the products of metabolism.

With the first process in progress, as a rule, the polymer chemical structure does not change, and the material acts as a substrate whereon adhesion and growth of colonies of microorganisms (bioovergrowing) or formation of the collagen-type capsules in using the material as an implant are observed. Adhesion of microorganisms is the initial stage of bioovergrowing of the materials, predetermining all subsequent pattern of bioovergrowing of and biodamage to polymeric materials. In the stage of bioovergrowing, of high interest is determination of the biomass on the surface of the polymeric material as the amount of the biomass influences the "surface" service properties, i.e., optical, adhesive, and so forth.

The second process directly results in aging of the polymeric material under the action of the chemically active substances. In this case, the "volumetric" service properties, both mechanical and dielectric, etc., will change.[83,84]

Thus, biostability of the polymeric material can be characterized as a combination of the complex physical and chemical processes of adhesion, bioovergrowing and biodamage, running under environmental conditions.

12. THE PROBLEMS ASSOCIATED WITH PROTECTING METALS WITH POLYMERIC COATINGS

One of the methods for protection of metals against attack by corrosive media is application of protective polymeric coatings to the surface. However, due to the fact that polymeric coating proper fails in contact with aggressive media, its service life ends and the aggressive medium reaching the metal surface starts to cause its corrosion. Thus, of interest is the search for ways of retarding the rate of aggressive media penetration through protective polymeric coatings.

The method of supplying the polymer with the additives fixing the aggressive medium and, thus decreasing its effective diffusion coefficient is not novel. For instance, reference 85 provides the approximate analysis of efficiency of action of the additives absorbing oxygen, thus preventing its participation in the oxidation destruction of polymers. It is shown that such a protection method is efficient provided the aggressive medium concentration (i.e., that of ozone, oxygen) is confined to the thousandth fractions of percent in the air atmosphere. At aggressive medium pressures close to the atmospheric pressure, such a method of protection displays low efficiency. The paper by A. L. Shterenzon *et al.*[86] provides an experimental study of the efficiency of binding fillers, i.e., oxides of beryllium, cadmium, magnesium, calcium; oxides of the alkaline-earth metals, hydroxides of alkali metals in the processes associated with retardation of diffusion in the solutions of the hydrochloric, hydrofluoric and nitric acids in a foam plastic, polyarylate, polypropylene. It is shown that the retardation effect exists and its extent depends in a complex manner on the nature of the polymer and acid as well as the aggressive medium concentration.

The simplest model of the retardation action of protective additives includes two possible mechanisms[87,88]:

1. Either diffusing molecule A is added in the polymer to the additive in a reversible manner:

$$A + B \xrightleftharpoons{K_p} (AB); \qquad \text{(I)}$$

2. Or in the irreversible manner:

$$A + B \xrightarrow{k_1} (AB). \qquad \text{(II)}$$

In both cases, the diffusion coefficient of molecules A in the polymer in the absence of additives D_0 will undergo reduction as reactions (I) and (II) proceed and render some diffusing molecules immobile. The role of the additives can be played by both the low molecular weight substances added to the polymer for this purpose and some functional groups existing in the macromolecules, for instance, —CONH— and —NH_2 groups in polyamide relative to diffusing molecules HCl and H_2O.

Disclosed below are the theoretical results showing the qualitative and quantitative differences in efficiency of action of the additives on the rate of transfer of molecules *A* inside the polymer, as regards the cases of reversible and irreversible binding of the diffusant molecules. All curves are obtained numerically by the computer-aided solution of the appropriate diffusion-kinetic equations on the assumption of constancy of the boundary conditions and the diffusion coefficient as well as in the absence of polymer swelling. The analyses included selection of a coating thickness of 25 μm, diffusion coefficient $D_0 = 7.10^{-9}$ cm^2/s and corresponds approximately to the coefficient of water in the polycaproamide.

The disclosed results of the analysis indicate that under certain conditions addition of absorbents to the polymer can impede the advance of the aggressive medium front toward the metal surface several tens of times. This is, so to speak, a purely diffusive effect. Really, the change in the metal corrosion rate on adding the retardation additives to the protective coating can be assessed only by solving the diffusion equation with the boundary condition at the polymer-metal interface, taking into account the proceeding of the electrochemical corrosion reactions.

13. PREDICTION OF PROPERTIES OF POLYMERIC ARTICLES AND BEHAVIOR OF ANTIOXIDANTS

The problem of polymer aging is inextricably associated with the task of predicting the properties under actual service conditions. Practical experience shows that the predictions obtained on a basis of the existing methods of the accelerated tests frequently lead to erroneous results. As it is known, this is because the accelerated tests do not reproduce the mechanisms characteristic of the actual service conditions. To create such equivalent effects, it is essential first of all to investigate in detail the aging mechanisms under the natural climatic and artificial conditions.

The Batum Branch of the All-Union Institute of Aviation Materials conducts the system tests of polymeric materials for aging under the natural conditions of the warm humid climate. The tests include active investigation of the processes of physical and chemical transformations. For this purpose, the complexity of the experimental equipment intended for investigations of the molecular mobility, relaxation and phase transitions, viscoelastic properties and structure of the polymers on a basis of the sensitive methods of present day, i.e., the dynamic mechanical analysis, dielectric spectroscopy, ultraviolet and infrared spectroscopy, linear dilatometry, and so forth, was developed and manufactured. The data on the unique assemblies of the installations, measurement techniques and methods for obtaining the information on the physical and chemical transformations in the polymers were published in references 89–91.

References 92–101 present specific examples of identifying aging mechanisms in artificial[92,93,95,96] and natural[89,92,97–100] climatic conditions, under the extravehicular activity conditions,[101] thin polymeric films,[92-96] block thermosoftening plastics,[89,97,101] and polymeric composites.[98-100] The above-mentioned papers provide the experimental evidence that in the course of the complex measurement of the polymer's physical characteristics over the wide temperature range, it is possible to identify such effects as oxidation, destruction, disorientation, cross-linking, plasticization, change in the structural heterogeneity in the amorphous, crystal cross-linked polymers, and to detect the areas of localizing such effects at the reliable qualitative level and, in some cases, at the quantitative level. For instance, the relaxation processes and viscoelastic properties of low-density polyethylene may exhibit a noticeable change in the initial aging stage at concentrations of the oxygen-containing groups less than 10^{-2}–10^{-3} mol/kg and stable strength due to the fact that oxygen reacts with the weak lines of the macromolecules, thus breaking the chains and facilitating reconstruction of the crystal structure[92,93,95,96]; the chemical reactions are localized in the less-ordered intercluster domains of the amorphous polymers or in the amorphous and paracrystal phases on the partially crystal polymers[92-97]; as shown by the example of the low-density polyethylene, the cross-linking processes activated by the solar radiation[92] play an important part in the physical and chemical transformations of polyolefins under the climatic aging conditions. Anisotropy of the mechanical properties and thermal expansion of the oriented thermosoftening plastics in the course of the climatic aging increases.[95] The loss of deformability, strength, and impact elasticity of the block thermosoftening plastics in aging is governed mainly not by the extent of the physical and chemical transformations in the polymer volume but by the nature of the material's surface damage. On reaching the critical level of damage, the surface layer exhibits the change in the nature of failure (from elastic to brittle). Removal of the damaged surface layer results in practical restoration of the mechanical properties to the initial values.

Even in the present stage the accumulated body of information enables the systematization of the regularities of the physical and chemical transformations in various classes of polymers during atmospheric aging in the humid subtropical zone. It is assumed that further accumulation of the information will cover the relation between the physical and chemical transformations and the change in the macroscopic characteristics of the polymers, the part played by certain climatic factors during climatic aging.

A similar approach would be preferable for use in investigation of polymer aging and in other climatic zones as well as in the course of the accelerated tests.

With the complexity of the prediction problem duly taken into account, achievement of the new qualitative success in its solution is impossible without participation of a wide team of specialists with their joint efforts in the target-oriented complex programs.

14. AGING AND STABILIZATION OF HEAT-RESISTANT POLYMERS

The problems of aging and stabilization of heat-resistant polymers should be reviewed now over the temperature range above 300°C and, in some cases, even above 400°C. The most investigated representative of this class of polymers are the polyimides whose structure and destruction during the last two decades have been studied in many works by V. V. Korshak and M. M. Kotton. A list of their works could be the subject of an individual bibliography.

In the last few years, interest in the study of thermochemical reactions proceeding at a temperature above 500°C and characterized by intense reconstruction of the entire structure of the polyimide macromolecule, leading to formation of carbonized products exhibiting a higher or lower degree of order and comprising mainly the condensed aromatic and heterocyclic formations has substantially quickened. The objective in this field is to identify the mechanism of transformations of polyimides over the temperature range of from 500 to 1,000°C. From a practical point of view, the objective is to determine the best conditions for producing the polyimide materials exhibiting the maximum "coking value" (a rather popular term for characterizing products of the high-temperature treatment of polymers), acceptable mechanical characteristics and specific electrical properties.

The first results of these studies were published.[102-107] As indicated in the abovementioned papers, production of the carbonized polyimides with maximum "coking value" is ensured by quasi-isothermic heat treatment conditions, existence of a static inert atmosphere, higher content of relative quantities of nitrogen items in the main polyimide chain and degree of the polyimide article orientation. From the point of view of mechanics, the polyimide fibers offer advantages. As regards the electrical characteristics, reduction of the specific electric resistance down to 0.1–10 ohms^{-1} cm^{-1} is attained. The progressive trend in this field of research can be represented by the differentiated directed thermolysis involving the use of radiant energy.

Stabilization of polyimides and other heat-resistant polymers may include methods for improvement of their synthesis, enabling the temperatures of cyclization of their prepolymers to be substantially decreased. This trend is purely synthetic and is not related to classic stabilization methods but in some cases this enables the structure of polyimides, their thermal stability and other valuable characteristics to be substantially improved. An example of work in this field is the use of such compounds as triphenylphosphate, imidazole, benziimidazole and other heterocyclic compounds[108-110] which act as stereospecific catalysts of the solid-phase cyclodehydrotation of polyamidoacids. Polyimides produced in the presence of such catalysts exhibit higher heat stability and flexibility as compared to conventionally produced polyimides.

The use of polyimides for heat stabilization of other so-called large-capacity polymers holds much promise. Even the first works in this field[113,114] have shown that the use of polyimide in combination with polyvinylpyrrolidone, furfuryl alcohol, and epoxy resins results in formation of composite polymers, wherein the polyimide structure plays the part of a peculiar thermostable frame that substantially increases the thermal stability of the polymeric fillers. As indicated by thermal analysis data, this growth of thermal stability is 100–150°C for polyvinylpyrrolidone, about 200°C for furan resins and approximately the same for epoxy resins. The second component, in turn, provides polyimides with some valuable properties such as an increase in thermohydrolytic stability, high-temperature adhesion to metals and carbon–graphite materials. Development of this trend is at present the most promising in the field of research efforts associated with aging and stabilization of heat-resistant polymers.

15. POLY (VINYL CHLORIDE) AGING WITH ANTISTATIC AGENTS PRESENT

As regards most industries of the national economy, i.e., electronic, radio engineering, instrument-making, medical, shipbuilding, petrochemical, petroleum-refining, aviation industries, computers, television and radio centers, construction engineering, required only are the antistatic polymeric materials eliminating the detrimental effect of static electricity.

Static electricity causes the essential process interference, explosion and fire hazard in the case of spark discharges, lowers labor productivity, increases the amount of the rejected products, and produces the unfavorable medical and biological effects on the human organism. The static electricity discharges are likely to initiate destruction of the polymers, and thus are capable of substantially affecting their service time. This factor should be taken into account in solving the problem of aging and stabilization of polymers. Hence, the problem of producing polymeric materials and articles exhibiting antistatic properties is of high importance. The important production target of creating antistatic polymeric materials is to ensure the required level of antistatic properties and their stability in time under service conditions.

The empirical attempts of elaborating the procedures for production of the nonelectrifiable polymeric materials are being undertaken in two major directions: (1) Creation of current-conducting and semiconductor polymeric materials by adding current-conducting fillers, i.e., commercial-grade carbon, graphite, carbon–graphite fibers, metallic powders, changing the structure of the polymers at the temperature of decomposition or dehydrohalogenation, directed synthesis of polymers containing long chains with conjugate links; (2) Creation of antistatic polymeric materials using surface-active substances applied to the surface of the polymeric material or added to volume.

Tested are the antistatic properties of PVC materials with additives of all practically known nonionogenic and ionogenic surface-active substances added to the material volume (totaling more than 60 substances).[115–118]

The important part of the problem of producing antistatic materials is ensuring their high thermal stability.

References 115 and 117 disclose that the surface-active substances preventing accumulation of static electricity in PVC materials contribute to accelerated polymer decomposition of high temperatures. Thus, at a temperature of 200°C a considerable amount of hydrogen chloride, i.e., 38–62%, is liberated from PVC containing SAS during 2 h. A particularly drastic increase of the dehydrochlorination rate is observed in the presence of the effective nitrogen-containing antistatic agents. It is established that the processes of dehydrochlorination and accumulation of the double bonds and carbonyl groups run in the polymer in a parallel manner.

With PVC decomposing in the presence of the antistatic agents: 1) the amount of hydrogen chloride splitting out of PVC is about two orders higher than in the case of the splitting out of the initial polymer; 2) the HCl split-out rate remains practically unchanged during a long time, though the amount of splitted-out HCl considerably (20–100 times) exceeds that of the antistatic agent added to the polymer. This indicates catalysis of the PVC dehydrochlorination by antistatic agents. The catalytic contribution of antistatic agents to the PVC decomposition process is observed both in closed space and under dynamic conditions (provided HCl is continuously removed from the system).

Established is the retardation effect of decomposition of PVC with the nitrogen-containing antistatic agent in the presence of the compound containing hydrogen hydride as caused by saturation of carbcations with hydride ions. This indicates the ionic mechanism of the process of catalytic dehydrochlorination of PVC with the nitrogen-containing antistatic agent.

Dehydrochlorination of PVC in the presence of the nitrogen-containing antistatic agent involves two catalytic processes: one process with participation of hydrogen chloride, whereas the second process, with participation of the antistatic agent. There are grounds to believe that both processes run according to the close mechanisms including formation of active centers-carbcations. The difference is in the initiation stage, i.e., participation of hydrogen chloride or amine (amide). This is proved by the fact that in both cases the retardation action is demonstrated by dienophiles, for instance, maleic anhydride interacting with polyene sections of the polymer following the pattern of the Diels–Alder reaction.

Established is the high thermal stability of the effective nitrogen-containing SAS-antistatic agents, thus preventing the catalytic contribution of antistatic agent decomposition products to the PVC decomposition process.

Established is the accelerating effect of oxyethyl groups in the nitrogen-containing antistatic agent on the PVC dehydrochlorination. This is proved by decomposition of PVC with polyoxyethylene glycol (POEG) of different molecular mass (MM).[117] The acceleration effect of PVC decomposition depends on the molecular mass of POEG, i.e., the smaller the molecular mass, the lesser the effect. These data indicate the stabilizing effect of the hydroxyl groups which, conceivably, reduce the catalytic effect of the oxyethyl groups.

The total rate of HCl splitting out of PVC is the presence of antistatic agents can be expressed as follows:

$$W_{\mathrm{HCl}} = W_0 + KC_1 + K_a \cdot A$$

where W_0 is the HCl catalytic formation rate, K is the HCl catalytic split-out rate constant, C_1 is the HCl concentration in the polymer, K_a is the rate constant of the HCl splitting-out under the action of the antistatic agent, and A is the antistatic agent concentration in PVC.

It is established that in the closed system, the process of PVC dehydrochlorination in the presence of the antistatic agent is always self-accelerated, whereas the amount of the splitted-out HCl under these conditions exceeds this value for pure PVC the following number of times:

$$\left\{1 + \frac{K_a \cdot [A]}{W_0 \cdot [K_a/K \cdot (1 + V_2/V_{1 \cdot \sigma})]} + 1\right\}$$

where V_1 is the polymer specimen volume, V_2 is the system volume, and σ is the coefficient of HCl solubility in the polymer.

The possibilities of neutralizing the negative effect of the antistatic agents on the PVC thermal stability have been studied.

Established is the retardation effect of stearates of some metals belonging to groups I, II and IV of the periodic system on dehydrochlorination of PVC with the nitrogen-containing antistatic agent.

O. N. Sheverdyaev worked out the effective stabilizing system for PVC with the nitrogen-containing antistatic agent, including the stabilizers severing the kinetic chains and breaking down hydroperoxides without formation of the free radicals, and a HCl acceptor.

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