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Ageing and stabilisation of polymers

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ABSTRACT. The most recent information on the kinetic mechanisms of the degradation of polymers and methods of stabilising different classes of polymer materials is presented. Progress in the field of thermal, thermooxidative, ozone, photo-oxidative, radiation, mechanically initiated, hydrolytic, and biological degradation of polymers is reviewed. The problems in predicting the stability of polymers, their blends, and certain composite materials during storage and use are discussed. New methods of studying degradation processes are described. The effect of the specific nature of the solid state on reactions in a polymer matrix is examined.

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I. Introduction

Problems concerning the ageing and stabilisation of polymers still constitute a vital question for research chemists and practical personnel working in the field of macromolecular compounds. Prolongation of the lifetime of polymer products during use and storage is equivalent to increasing the manufacture of these products and improving their quality. A sufficiently accurate prediction of the lifetime of reliable operation enables polymer products to be used to a greater extent without risk of failure.

Problems relating to protection of the environment from polymer waste products have assumed prominence at the present time. The scientific principles of the degradation of used polymers to monomers followed by their polymerisation or the pyrolysis of polymers to low-molecular-weight compounds with recovery of the products obtained have been developed for this purpose. Since up to the present time a significant proportion (in many countries the main part) of polymer waste products has been burnt in special furnaces or on dumps, questions relating to environmental protection have proved to be closely linked to problems in the pyrolysis and burning of polymers. The secondary processing of used polymers to new polymer products is also of considerable importance.

The use of degradation processes for the modification of polymer products in order to improve their performance (principally to change their surface properties) and also the production of polymers with a controlled "lifetime" have once again assumed vital importance.

The question of preventing the degradation of polymers was first raised in our country in the second half of the 1940s.[1–3] It was developed further in studies by M B Neuman, et al.[4–6] Subsequently a strictly quantitative approach was applied to it.[7,8] From 1966 to 1984 studies on this problem were directed in our country by Academician Emanuel',[9,10] who extended the scope of research and established international cooperation.[11,12]

II. Effect of intermolecular interactions on the kinetics of degradation processes in a solid polymer

It was demonstrated in the studies of N M Emanual', et al.[9,10] that a solid polymer has a number of properties that are mainly dependent on the mobility of the polymer chain. The concept of "polychromatic kinetics" of the reactions in the polymer matrix was put forward, where, in addition to the molecular-weight distribution, the dependence of the rate constants of the fundamental chemical reactions on the diffusion properties of the system, the accessibility of the reacting bonds, the optimum nature of the structure of the activated complex, etc., should be taken into account. "Polychromaticity" of the reaction kinetics is mainly caused by energetic factors (quite a wide scatter of values of the energy of activation for a given fundamental reaction).

In recent years a new model has been put forward,[12–15] according to which the polychromaticity of the kinetics of reactions in a polymer matrix is due to a change in the entropy term that forms part of the expression for the rate constant. The number and distribution of the various types of intermolecular bonds (donor-acceptor, electrostatic, Van der Waals, etc.) in a sample of polymer

determine the distribution of unassociated and associated monomer units along the blocks.

Starting from the theory of an activated complex, an expression was obtained for the rate constant of scission of a polymer chain

$$k=k_0 \exp\left[(\alpha_1-\alpha)n\right], \quad (1)$$

where k_0 is the rate constant of reaction without taking into account the change in flexibility of the chain, α and α_1 are coefficients representing the loss in flexibility of the unassociated section of the chain with a length of n monomer units in the initial and transition states respectively. The term $\exp(\alpha_1-\alpha)$ mainly depends on the entropy of the system since α and α_1 characterise the loss in flexibility of the chain.

The constant k_0 usually has a similar value to the rate constant of a reaction involving low-molecular-weight products. It follows from Eqn. (1) that the energy of activation does not depend on the length of the block—the pre-exponential term of the rate constant varies with a change in length of the block. In the initial state the entropy of the system is distributed according to the absence of free rotation of the chain units.

Since in practice there is a distribution of unassociated monomer units with respect to block length, the reaction kinetics can be polychromatic. They depend on the past history of the sample, since block distribution is determined by the conditions of synthesis, processing, and operation of the sample in a stationary but not equilibrium state. With an increase in temperature both the rate constants of the reactions taking place and the ratios of blocks of different lengths change. With these concepts it is possible to interpret in a new way the dependence, which has been recorded by many research workers, of the rate of the process and the apparent energy of activation on temperature.

When a block of unassociated monomer units reaches a given length in the system, there is a thermodynamic possibility of chain scission in the middle of the block. From this a different interpretation can be given to the change in the degradation process from scission at the chain ends (low temperatures) to "random" scission (high temperatures), which occurs in a number of cases, and to reactions in cross-linked polymers only starting from a given temperature.

III. Effect of the supermolecular structure of a polymer on thermooxidative processes

The question concerning the nature and role of the supermolecular structure of amorphous polymers is related to the physicochemical behavioural characteristics of polymer products. In recent years quite a large amount of information on the role of supermolecular structures in polymer reactions has been published.

A number of scientists[16–23] have advanced the theory of the role of structural microheterogeneity in chemical reactions that occur in a polymer matrix. A model of heterophase processes in the solid state has been developed. It has been proposed that a polymer consists of a large number of small entities and the reactions in a polymer occur on their surface.

The role of structural microheterogeneity in chemical reactions was examined in studies of a model polymer chain reaction involving benzoyl peroxide. It was demonstrated in the case of vitreous polycarbonate,[16] cellulose triacetate,[17] polypropylene,[18] and molten polyethylene[19] that conversion of the macromolecules may involve successively induced heterogeneous reactions that occur in two structural zones of globular aggregates—in a relatively dense shell and in a looser three-dimensional microphase (the "roe" model).

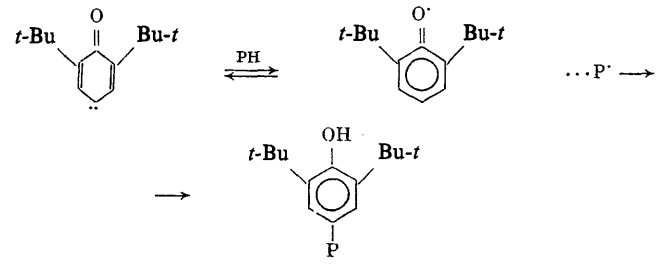
Studies on the oxidation of poly(ethylene oxide) showed that microheterogeneity predetermines the heterophase conditions for oxidation.[20,21] From the proposed structural kinetic model of reaction it was possible to find a kinetic equation that represents the change in concentration of hydroperoxide [ROOH]

$$d[ROOH]/dt = W_{max}^{ROOH}[ROOH]^{1/2}(C+[ROOH])^{-1/2} - aW_i k_{[ROOH][A]}[ROOH]\,t \quad (2)$$

and the corresponding integral expression for [ROOH]t, which is in agreement with the experimental data. In Eqn. (2) W_{max}^{ROOH} is the maximum rate of formation of [ROOH] attained at the moment of complete loss of the function as branching agent by hydroperoxide; C is a composite constant; W_i is the rate of initiation (initiation occurs by a heterogeneous mechanism at the interface of structural zones); $aW_i t$ is the concentration of aldehyde formed in the melt that reacts with ROOH and ensures that $[ROOH]_{max}$ is reached; $k_{[ROOH][A]}$ is the rate constant of the reaction between aldehyde and ROOH. This result is important in that it stimulates the interest of research workers in the elucidation of the role of supermolecular structures in the autooxidation of polymers. The theories relating to the role of microheterogeneity in the heterophase oxidation of polymers have so far not been recognised by the majority of specialists working in the field of thermooxidative degradation of macromolecules. However, there is clear evidence in favour of this hypothesis. If it is shown in future that the process in a polymer does occur precisely in this manner, it will be necessary to revise the considerable amount of quantitative data obtained previously. For example, many rate constants of processes in a polymer matrix may prove to be only apparent overall constants rather than true constants of the fundamental stage.

IV. A new method for studying features of the physical structure of polymer matrices

Davydov, et al.[24,25] have proposed a new method for studying the structure of polymer matrices using the reactions of triplet carbenes. These reactions occur in a polymer via the formation of intermediate radical pairs as a result of the transfer of a hydrogen atom from the C–H bond of macromolecules to a carbene followed by their recombination



where PH is a macromolecule of the polymer matrix.

The kinetics of the conversion of triplet carbenes reflect the features of the physical structure of a matrix at the level of the effective distances in radical pairs (of the order of 3–5 Å). The effect of an external magnetic field on the rate of this process at low temperatures has recently been detected.[24,25] In the case of poly(methyl methacrylate), for example, at a temperature of 77 K the maximum rate occurs at zero field and at a field of 5000 Oe (Fig. 1).[24] The magnetic effect may be attributed to structural features of PMMA,[24,25] if it is assumed that in this radical process two types of intermediate radical pairs differing in their geometric configuration are formed.

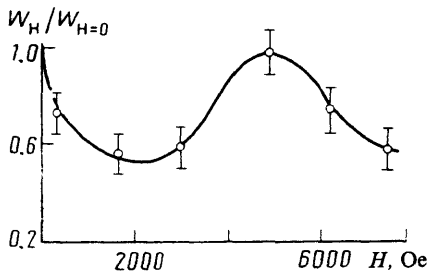


Figure 1. Dependence of the initial rate of conversion of carbenes in PMMA on the strength of the magnetic field.[24] $W_{H=0}$ is the initial rate when $H = 0$.

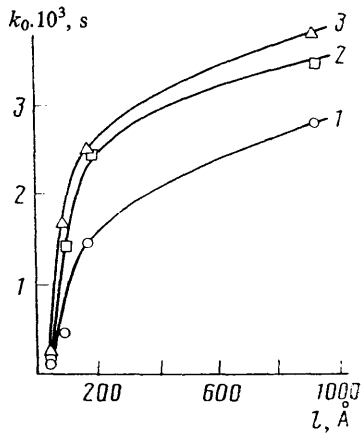


Figure 2. Dependence of the average rate constant for conversion of carbenes on the distance between Aerosil particles in filled PMMA at: *1*, 100; *2*, 113; *3*, 125 K.[25]

Modification of the physical structure of a matrix can be recorded from the change in kinetic parameters of the reaction of carbenes. For example, as the content of an inert filler (Aerosil) increases in PMMA to 65 wt.%, the rate constant of the thermal conversion of carbenes decreases by a factor of 10. The introduction of a filler modifies the physical structure of the polymer in the boundary layer. From kinetic analysis of this lattice reaction it is possible to determine the width of the boundary layer in filled polymers. It is clear from Fig. 2 that with a distance of less than 200 Å between the Aerosil particles, which corresponds to the apparent width of the boundary layer, there is a sharp fall in the rate of reaction.[25]

The method described here can be used to determine the structural features of composite materials (in this particular case—the width of the boundary layer). This has established its future potential.

V. Problems in the stabilisation of polymers during processing. Stabilisation at high temperatures

In recent years there has been increasing interest from research workers in questions relating to the stabilisation of polymer materials during processing, when the main factor causing degradation is mixing (in other words, a rapid shear deformation) of the melt.[11] Two types of stabiliser are recommended for use—amines of the class of sterically hindered piperidines and organic phosphites.[9]

These stabilisers reduce the degree of mechanical degradation processes in the polymers during their processing in an extruder and they considerably reduce the consumption of the principal stabiliser—the antioxidant that is introduced to prevent oxidative degradation of a polymer product during use and storage.

Currently the processing of polymers is being attempted in an inert atmosphere, which considerably reduces the problems related to mechanical oxidative destruction. Because of the high cost of the stabilisers the question has arisen concerning the reduction of their nonrational consumption in evaporation, washing out, bleeding, etc. As a result of this, researchers have shown greater interest in the problems of the solubility of stabilisers in a polymer and the diffusion of additives introduced into a polymer material.[7,26–30]

It was recently shown[27] that the solubility of antioxidants varies in accordance with temperature in a very complex manner and sometimes it even decreases as the tempeature increases. Phase transitions in the polymer constitute the reason for this; on passing through the melting point of the chemical added to the polymer, the heat of solution of the polymer changes and relaxation phenomena occur, leading to an irreversible change in polymer structure at high temperatures (above the glass-transition temperature T_g).

In recent years a property of the solution processes of additives (including stabilisers) such as the dependence of the solubility on the content of polar groups in aliphatic polyamides has been identified. On changing from polyethylene to polyamides-6 and -66 the solubility of the antioxidants usually passes through a maximum. With a small content of amide groups, increasing them leads to an increase in solubility, while when there is a high content, there is a decrease in solubility when they are increased. This is caused by the competition between the increase in solubility due to sorption of the antioxidant (phenol or amine) on the polar groups of the polyamide and its reduction because of the increase in the total compactness of the polymer that is cross-linked by amide–amide hydrogen bonds.[28]

Studies on the high-temperature stabilisation of polymers at $T >$ 200 °C are of considerable interest. Under these conditions conventional stabilisers (phenols, amines) are converted to initiators by thermal and thermooxidative degradation[8,9,11] because of the weakness of the PhO–H or Am–H bonds. Previously it was proposed to use salts of organic acids and metals of variable valence[31] as high-temperature stabilisers. These compounds, being

introduced into the polymer in advance, would decompose at high temperatures to metals or metal oxides in a lower oxidation state. Oxygen reacts with these thermolysis products much more rapidly than with the polymer. Thus, dispersed metals and their oxides protect the polymer from oxidation until they themselves reach a higher oxidation state. However, this method of stabilisation is not always effective, since the transition metal oxides can themselves be catalysts of thermooxidative processes.[8–11]

There may be greater future potential in certain stabilisers of a novel type[30]—polymeric or oligomeric compounds that degrade during oxidation to form free radicals that are free valence carriers. One of these stabilisers is poly(phenylenephenylstibine).[26]

Macroradicals that occur on the polymer chain are virtually immobile. That is why chain termination through recombination of macroradicals occurs extremely slowly even at elevated temperatures.[29,30] The introduction of low-molecular-weight radicals that are capable of migrating in the polymer matrix by diffusion leads to an increase in the rate of quadratic chain termination, i.e. a reduction in the rate of thermooxidative degradation. It is evident from Fig. 3 that small additions of the stibine $-[-C_6H_4Sb(C_6H_5)-]_n-$ reduce the rate of oxidation, whereas at high concentrations of the stibine this rate increases. If the rate of generation of the light radicals that mainly participate in chain termination is less than the rate of formation of the active macroradicals in the oxidation of the polymer, these light radicals will inhibit the reaction. However, an excess of light radicals assists oxidation as a result of their participation in chain propagation reactions. Antioxidants of this type only begin to be effective above a certain temperature—the so-called decomposition temperature.[26]

The proposed method for the stabilisation of polymers at high temperatures[30] is suitable not only during processing but also when heat-resistant polymers are being used.

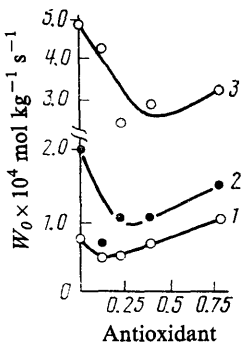


Figure 3. Variation in the rate of oxidation of poly(diphenylphenylene oxide) as a function of the concentration by weight of poly(phenylenephenylstibine) at: *1*, 653; *2*, 673; *3*, 693 K.[26]

Not only the chemical aspect of the reactions leading to inhibition of oxidation processes but also the physical factors related to the distribution characteristics of low-molecular-weight additives in the polymer matrix and the effect of these additives on the structure of the polymer melt have started to be taken into account recently. It is these effects that in a number of cases cause the acceleration of oxidation of a polymer when large concentrations of a reducing agent are introduced. Thus, the dependence of the induction period for the oxidation of polypropylene in the presence of gossypol (a sterically hindered phenol) on the concentration of dilauryl thiodipropionate (a polymer stabiliser) is shown in Fig. 4. The hydrocarbon heptadecane which simulates the hydrocarbon part of the dilauryl thiodipropionate molecule, behaves in a similar way to dilauryl thiodipropionate.[29] The physical aspect of this phenomenon is as follows. When the gossypol dissolves in the polymer its molecules are located in the so-called "potential holes". The number of these holes is limited by the solubility. Therefore, when another additive—dilauryl thiodipropionate (or heptadecane)—is introduced, some of the gossypol molecules are "knocked out" of the potential holes by these additives and are oxidised, resulting in an acceleration of the overall oxidation process.

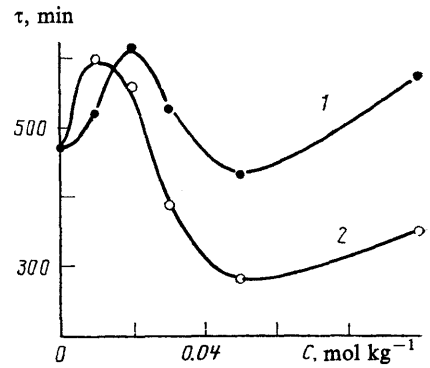


Figure 4. Dependence of the induction period for oxidation of polypropylene in the presence of 0.1 mol kg^{-1} of the natural stabiliser gossypol on the concentration of dilauryl thiodipropionate (*1*) and heptadecane (*2*) (T = 473 K, P_{O_2} = 300 mm Hg).[29]

An elucidation of the mechanism of the high-temperature inhibition of oxidation is one of the most important developments in studies of the chemistry of polymer degradation.[8] Although this process is very inconvenient to study as a considerable number of reactions are taking place simultaneously (several dozen reactions of this type have been identified up to the present time, including oxidation of the stabiliser itself),[32–36] practical requirements demand that increasing attention be given to high-temperature oxidation, since high temperatures are needed not only in polymer processing that is unavoidably accompanied by degradation but also in rapid methods of testing polymers for thermal and thermooxidative stability.

At the present time methods have been developed for the quantitative representation of the high-temperature inhibition of polymer oxidation.[32–36] For this purpose, the absorption of oxygen, accumulation of hydroperoxide (ROOH), and consumption of inhibitor (InH) are recorded and analysed throughout the whole induction period. By using a simple kinetic scheme[34,35] which includes kinetic chain transfer by the inhibitor radical (In$^{\cdot}$), it is

possible to represent the change in concentration of the three key reaction products—oxygen, hydroperoxide, and inhibitor.

Thus, a question that is important for the mechanism of inhibited oxidation of polymers—what happens (how complex do the kinetic mechanisms become) on changing from low temperatures, where the mechanism is quite simple and has already been established quantitatively,[37–42] to high temperatures[32–36]—has been resolved.

Scheme 1

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

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

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

$$RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_4} \text{molecular products} + O_2,$$

$$RO_2^{\cdot} + InH \xrightarrow{k_6} \text{inactive products},$$

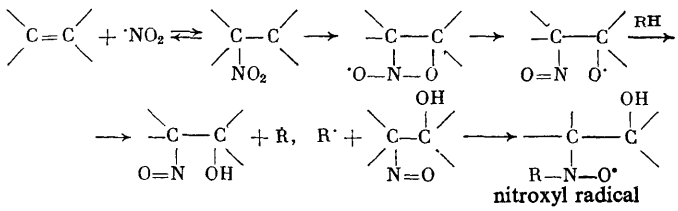
$$In^{\cdot} + RH \xrightarrow{k_7} InH\ (\text{molecular products}) + RO_2^{\cdot}.$$

VI. Reaction between polymers and atmospheric contaminants

In recent years quantitative studies on the effect of components that contaminate the environment on the degradation of polymers have started to appear in the literature. Particular attention has been given to a study of the reaction between nitrogen and sulphur oxides and polymers.[43–46] The kinetics and mechanism of reactions involving nitrogen oxides have been studied in the greatest detail. It has been shown, in particular,[44–46] that the reaction of nitrogen dioxide with the double bonds of macromolecules (including rubbers and vulcanised materials) may be one of the most important ways of initiating the free-radical reactions of polymer ageing in an atmosphere contaminated by industrial waste gases.[44–46]

The reaction between NO_2 and macromolecules containing  bonds has been studied by many methods—EPR, UV and IR spectroscopy, and others. It has been found that nitroxyl radicals are amongst the main reaction products. Usually the two-stage scheme adopted for reactions in solution (the formation of a nitroxyl radical, its conversion to an α-nitro-β-nitroso compound, and acceptance of a second nitroxyl radical by the latter) cannot explain the formation of $(R)_2-NO^{\cdot}$ radicals in the solid state.[44]

A mechanism has now been proposed in which the occurrence of successive "pseudolattice" reactions that have a minimum steric migration of the free valence and which form $(R)_2-NO^{\cdot}$ radicals is assumed.[45]



An $R^{\cdot}$ radical is formed in the immediate vicinity of the nitroso group $(R)_2-N-O^{\cdot}$ and a dialkylnitroxyl macroradical can be a product of the lattice reaction. The formation of $(R'-C=O)-(NO^{\cdot})-R$ radicals in poly(methyl methacrylate) in the presence of NO_2 indicates the decomposition of alkyl macroradicals that is accompanied by cleavage of ester groups with elimination of $(C=O)-OCH_3$.

The reaction of NO_2 with macromolecules containing double bonds is formally given by the kinetic equation[46]

$$\frac{[NO_2]_0}{[NO_2]_t} - 1 = k_{app}t\,, \qquad (3)$$

which reflects the properties of solid-state reactions. The reaction of rubbers with NO_2 is accompanied by a decrease in concentration of C–H groups and the formation of nitro $(R-NO_2)$ and nitrate $(R-O-NO_2)$ groups.

Thus, it has been demonstrated[43–46] that the formation of $(R)_2-NO^{\cdot}$ radicals in reactions between NO_2 and polymers containing double bonds is a free-radical lattice process in which an alkoxyl radical is formed as an unstable intermediate, being highly active in transfer and decomposition reactions with scission of the polymer chain. This leads to ageing of the polymer material.

VII. Ozone ageing of rubbers and vulcanised materials

At the present time considerable progress has been recorded in a kinetic representation of processes involving the ozone cracking of elastomers.[47–50] By improving experimental methods it has been possible to identify the reason for the divergence in experimental results recorded earlier and to elucidate the kinetic mechanisms of the growth of cracks and stress relaxation in samples.[47]

The curves of the dependence of the specific surface area of growing cracks (S_τ) on time τ at difference concentrations of ozone have a similar shape to the well-established characteristics of the rate of autooxidation of hydrocarbons[8] and elastomers.[9] However, in contrast to oxidation by oxygen the ozone ageing of rubbers and vulcanised materials is known to have the characteristics of a nonchain reaction[50] and it does not require an induction period. The chemical reactions that are responsible for its occurrence have molecular mechanisms. The apparent induction period of the dependence of S_τ on τ results from the phenomenon of surface restoration, as first detected by Rzumovskii, et al.[48] In this case the chains ruptured by ozone "escape" towards the interior of the product while the elastomer polymer chains that have not been degraded by ozone appear on the surface. The kinetics of the growth of cracks are satisfactorily represented by the equation for a straight line that is displaced from the origin. From an analysis of kinetic data it was possible to determine the analytical relationship between the surface of the cracks and the experimental parameters at any given moment of time.[49]

$$S_\tau = a + d\,[O_3]^m \left\{\tau - \frac{\gamma\left[\diagup C{=}C \diagdown\right]}{V_r([O_3]_0 - [O_3]_e)}\right\}, \qquad (4)$$

where S_τ is the specific surface of the cracks; a, d, and m are empirical constants; γ is the coefficient of surface restoration; V_r is the rate of introduction of the gaseous mixture into the reaction

volume; $[O_3]_0$ and $[O_3]_e$ are the concentrations of ozone at the entry and exit of the experimental chamber respectively.

A study of the kinetics of the decrease in strength in a sample on ozonisation of different types of rubbers showed[48] that the growth of cracks and stress relaxation essentially constitute two nonconcurrent processes. Induction periods are absent from the curves of the decrease in strength and the rates of decrease in strength are highest at the start of the process, whereas the rates of growth of cracks, on the other hand, increase with time.

It is now generally assumed[47] that the decrease in strength of a sample is a process involving two components—volumetric and surface. The first is dependent on the decrease in cross-sectional area of the sample from the growing cracks. This process is appreciable at the advanced stages of ageing. The second component is related to cleavage of the C=C bonds in the macromolecules of the surface layer. This process predominates at the early stages of reaction.[49]

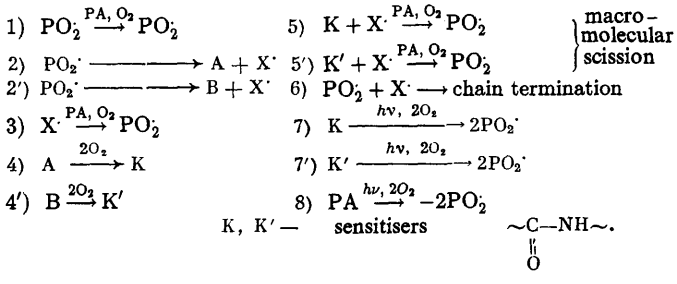
The quantitative data obtained on ozone ageing of elastomers can be used to improve the accuracy of predicting the lifetime of reliable operation of rubbers and vulcanised materials in an atmosphere of ozone.[11]

VIII. Photodegradation and light stabilisation of a number of polymers

In the field of photodegradation and light stabilisation new data have been obtained on the mechanism of the photoconversion of polyamides,[51–56] and the mechanisms of the principal reactions for photoconversion of polymers such as poly(vinyl chloride) (PVC)[57] and cellulose and its derivatives[58,59] have been established. The effects of physico-structural factors and the acid-base properties of the medium on the light stability of polymers have been analysed in the case of the photooxidation of cellulose.[58]

Recent experimental data have made it possible to amplify and generalise the previously proposed mechanism of the photooxidation of aliphatic polyamides (PA). The general mechanism, as depicted below in Scheme 2, is based on the following arguments. The photooxidation of PA is a chain process whose development is governed by a specific succession of reactions involving peroxide macroradicals $PO_2^{\cdot}$ and low-molecular-weight radicals $X^{\cdot}$ (these would appear to be $HO_2^{\cdot}$ or $^{\cdot}O_2^{-}$).[51] An important route in the conversions of $PO_2^{\cdot}$ radicals is the elimination from them of light $X^{\cdot}$ radicals.[52] In this case an unstable intermediate A (or B) is formed, which is readily oxidised by atmospheric oxygen and converted to a ketoimide (K) and its kinetic analogue (K′) which are kinetic chain carriers and can act as photoinitiators of oxidation.[53]

Scheme 2



A maximum optical absorption at 360 nm is characteristic of a ketoimide. The nature of its kinetic analogue, which absorbs light in the region of 313 nm, is still unclear. Products K and K′ readily react with $X^{\cdot}$ radicals, which results in macromolecular scission and propagation of the kinetic chain.[54] Chain termination occurs when $PO_2^{\cdot}$ and $X^{\cdot}$ radicals recombine.[55] Chain initiation is achieved by photolytic reactions of products K and K′, the inherent amide groups of the polymer, and the sensitiser introduced into it, the contribution of which varies according to the wavelength of light.[56]

With this proposed mechanism it is possible to represent quantitatively the photooxidation of PA on exposure to UV and longer wavelength radiation. The correlation between the calculated and experimental values of the rate of photooxidation of PA (W_{O_2}) is shown in Fig. 5.

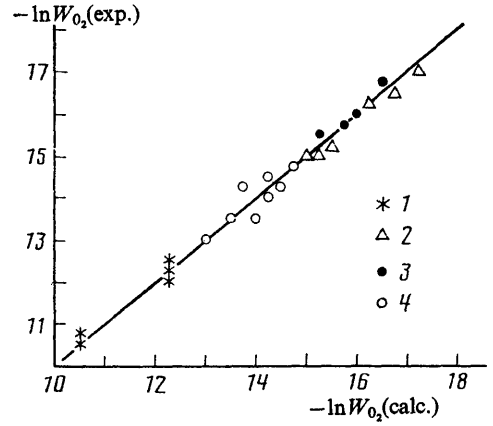


Figure 5. Correlation between experimental and calculated values of $-\ln W_{O_2}$ in the photooxidation of polyimide exposed to light radiation with wavelength: *1*, 254; *2*, 365; *3*, 313 nm; and *4*, in photosensitisation of the process with benzophenone.[51]

Equations have been obtained by Vichutinskaya, et al.[56] which can be used to determine the concentrations of $PO_2^{\cdot}$, K and K′ (the suffices of the rate constants correspond to the numbers of the reactions, W_0 is the rate of chain initiation):

$$[PO_2^{\cdot}] = \sqrt{\frac{k_3}{k_{2'}k_6} k_7 [K] W_0}, \quad (5)$$

$$[K] = \frac{k_2 k_3}{k_{2'} k_5} \frac{k_4}{(k_4 + k_{4'})}, \quad (6)$$

$$[K'] = \frac{k_2 k_3}{k_{2'} k_{5'}} \frac{k_{4'}}{(k_4 + k_{4'})}. \quad (7)$$

Directed research into new light stabilisers is being conducted on the basis of this mechanism. This task continues to be quite urgent as even the best of the known light stabilisers cannot reduce the rate of photooxidation by more than a factor of 5.

Currently it is not completely clear why the overall process according to the scheme given above can be represented in terms of the kinetics of conventional homogeneous reactions. So far no

characteristics of the system related to its solid state nature have been detected, although they evidently must exist.[8] Only in recent studies on chemiluminescence[51,52] were certain charcteristics suggesting the heterogeneous nature of photooxidation identified.

The role of such factors as the structure, molecular mobility, and pH of the medium in the ageing of polymers were revealed in studies on the photoageing of cellulose.[58,59] It was first shown that the rate of photoageing of cellulose is proportional to the content of the accessible amorphous phase. This means that photooxidation does not occur throughout the whole amorphous phase but only in that part which is accessible for low-molecular-weight compounds. On reducing the content of the accessible amorphous phase from 30 to 0%, the rate of photoageing decreases by a factor of 14.[59]

Another important factor in ageing is the molecular mobility. It can vary, for example, by plasticising cellulose with water. An increase in the content of water from 0 to 50% leads to a decrease in the rate of ageing by a factor of 6. This effect, according to Margolin, et al.,[58,59] is due to a sharp increase in the rate of radical recombination (i.e. termination of the oxidation chains) on increasing the molecular mobility of the macromolecules. Another possible explanation[9] is the decrease in reactivity of the peroxide radicals in chain propagation rections when they are hydrated with water molecules ($PO_2^{\cdot}\cdots H_2O$).

The third factor in the photoageing of cellulose—the pH of the medium—is of very considerable significance. It was found[58] that the rate of photodegradation of cellulose can vary by a factor of 10^2-10^3 according to the pH of the medium, and the minimum rate occurs in the region of pH 5. This is due to the catalytic nature of the reactions of radicals and products at the chain propagation stage of the oxidation process.

By varying the structure, molecular mobility, and pH of the medium, it is possible to achieve an increase in the light stability of cellulose by a factor of 100–1000. This indicates what practical significance there is in the application of these factors.

Despite the large number of studies on the degradation and stabilisation of PVC,[60] a solution to the question of its photodegradation and light stabilisation still remains very remote. In recent years the basic principles of the photodehydrochlorination and photooxidation of PVC—the main processes that occur during photoageing of this polymer—have been established.[57]

According to a mechanism put forward recently, photodehydrochlorination of PVC is a photochain process with a kinetic chain length of several tens of units, in which chain propagation occurs by photochemical conversion of alkyl and polyene radicals (Scheme 3).

Scheme 3

$$X \xrightarrow{W_0} P^{\cdot} \text{ – chain initiation}$$

$$P^{\cdot} \xrightarrow{k_1} P_1^{\cdot} \text{ – chain propagation}$$

$$\begin{cases} P_1^{\cdot} \xrightarrow{\alpha\varphi k_{app}} P_2^{\cdot} + HCl \\ \cdots\cdots\cdots\cdots \\ P_1^{\cdot} \xrightarrow{k_{app}} P_n^{\cdot} + (n-1)HCl \end{cases}$$

$$\begin{cases} P_1^{\bullet} \xrightarrow{k_{1,1}} P_1 + P^{\bullet} \\ \cdots\cdots\cdots \\ P_n^{\bullet} \xrightarrow{k_{n,n}} P_n + P^{\bullet} \end{cases}$$

$$P_1^{\cdot} \xrightarrow{k_r} \text{inactive products}$$

$$P_1^{\cdot} \xrightarrow{k_{r,1}} \text{inactive products}$$

where W_0 is the rate of initiation, α_i is the probability of new radicals being formed, k_{app} is the apparent rate constant of reaction:

$$k_{app} = \varphi\varepsilon I. \tag{8}$$

Here φ is the quantum yield of radical conversion, ε is the extinction coefficient of radical absorption, I is the intensity of light.

From this kinetic scheme for the photodehydrochlorination of PVC, an expression can be readily obtained[57] from which the rate of dehydrochlorination can be calculated from known kinetic parameters.

$$W_j = \gamma\eta\alpha_j W_0, \tag{9}$$

where

$$\eta = \frac{k_1 k_{app}}{k_r + (k_1 + k_r)k_{r,1}k_{app}^{-1}}, \tag{10}$$

$$\gamma = \sum_{j=1}^{n}[\dot{R}_j]_{pl} \Big/ \sum_{j=1}^{n}[\dot{R}_j]_{rig}. \tag{11}$$

In this case the subscripts "pl" and "rig" refer to plasticised and rigid PVC respectively.

According to the proposed mechanism, the key parameters are the values of the extinction coefficient ε, the quantum yield φ of radical conversion, and also the intensity of light I. Moreover, with a knowledge of the proportion of the rigid regions in plasticised PVC, where radicals R_j are stable, the dependence of the rate of dehydrochlorination on the content of plasticiser can be given.

The photooxidation of PVC occurs as a process with a very short chain length and formally linear termination.[57] The possibility of migration of the free valence for considerable distances in solid PVC has been demonstrated by means of low-molecular-weight radicals. The results suggest the possibility of using light-stable antioxidants and also quenchers of excited states for the light stabilisation of PVC, which opens up new ways of increasing light stability.

In recent years a considerable number of studies have been published on the photoradical ageing of polymers,[61–67] namely, on the change in functional composition and structure of high-molecular-weight compounds as a result of the chemical reactions of electronically excited radicals and radical ions.

A considerable amount of data has been obtained on the quantum efficiency of photochemical reactions of macroradicals in various carbon-chain and heterochain polymers and on the effect of photon energy on the quantum efficiency of these reactions.[68–77] The efficiency of photodissociation processes of macroradicals can be represented satisfactorily in terms of a free-volume model. The mechanism and kinetics of the photoradical ageing of polycaproamide and poly(acrylic acid) at 77 K have been studied in detail. It has been established that the principal route of the reactions of electronically excited radical anions in these polymers is the ejection of an electron, the quantum yield of which increases with an increase in photon energy. Neutral macroradicals (median and terminal) are active sites of the photoradical ageing of poly(acrylic acid) and polycaproamide. In this case excited median macroradicals only undergo dissociation. Photoradical chain reactions involving median macroradicals have been identified in the degradation of a large number of different polymers, including poly(acrylic acid) and polycaproamide. In the case of poly(acrylic acid), for example, photodecomposition of median radicals can occur by two routes—with scission or without scission of the main polymer chain.

The second of these two reactions, which is the photochemical stage of chain propagation, is also accompanied by efficient rupture of the functional groups and the formation of a product (a ketene) whose subsequent reactions cause cross-linking of the polymer chains.

$$\sim CH_2\dot{C}(COX)CH_2\sim \xrightarrow{h\nu} \begin{cases} \longrightarrow \sim CH_2C(=C=O)CH_2\sim + X^{\cdot} & (I) \\ \longrightarrow \sim CH_2\dot{C}(COX)\dot{C}H_2 + \dot{C}H_2(COX)CH_2\sim & (II) \end{cases}$$

$$X^{\cdot} + \sim CH_2CH(COX)CH_2\sim \longrightarrow \sim CH_2\dot{C}(COX)CH_2\sim + HX, \quad (III)$$

$$\sim CH_2C(=C=O)CH_2\sim \longrightarrow \sim CH_2\ddot{C}CH_2\sim + CO. \quad (IV)$$

The quantum yields of these reactions have been determined.

By using the above results together with the experimentally determined apparent rate constants for macroradical recombination, it was possible to represent with considerable accuracy the kinetics of the change in concentration of the initial, intermediate, and final products of the photoradical ageing of poly(acrylic acid).[61–67]

An important fact which is consistent with the scheme given above has been established experimentally: by changing the dose of absorbed light radiation it is possible to produce a directed change in the molecular weight distribution of the polymer in which median macromolecules occur. With small doses the molecular weight distribution is determined by reaction (II), while with large doses it is determined by reaction (IV) and the subsequent formation of cross-links as a result of reactions involving the ketene.

In addition to the already well-established phenomenon of kinetic nonequivalence which was observed previously[57] during photoradical processes in different polymers, the levelling effect of the photon energy on the kinetic nonequivalence of sulphonyl macroradicals has recently been detected.[52,53]

A study of the photochemistry of macroradicals involved in forbidden transitions (the possibility exists for considerably extending the region of spectroscopic sensitivity) and an investigation of photoradical chain reactions, in particular the steric distribution of their products, should evidently be considered the most interesting developments of future research into the photoradical ageing of polymers.

IX. Kinetics and mechanism of oxidative reactions of stressed polymers

Studies of the effect of mechanical stresses on the structure, dynamics, and reactivity of polymers led to a number of unexpected new results.[78–83]

Structural stresses of an energetic nature increase or reduce the rate of a chemical reaction depending on the change in linear dimensions of the reaction site during reaction.[79]

$$\ln \frac{k_\sigma}{k_0} = \frac{\gamma\sigma}{RT}, \quad (12)$$

where k_σ and k_0 are the rate constants of the chemical reaction of the polymer in stressed and unstressed states respectively: σ is the stress; γ is the coefficient of sensitivity of the reaction to stress, equal to the product of a constant γ_a, which is inherent to each specific reaction, and a coefficient β, which takes into account the nonuniform distribution of stress on the bond ($\beta \geqslant 1$).

By establishing a quantitative relationship between the rate constant of reaction and the stress it was possible to classify different chemical reactions according to their sensitivity to the application of stress and also to study the supermolecular structure of the polymers.[78,79,81,82]

All chemical reactions can be divided into three groups in accordance with their sensitivity to deformational stresses.

1. Processes that are insensitive to applied stress; for these $\gamma_a = 0$.

2. Chemical reactions that are highly sensitive to stress; these have $\gamma_a \geqslant (0.5-1.0) \times 10^{-29}$ m^3. These include processes that are accompanied by scission of the main macrochains, for example, the hydrolysis of polyamides. Treatment of the results of Popov[79] using Eqn. (12) gives an estimated value of $\gamma_a \approx 2 \times 10^{-29}$ m^3.

3. Reactions having low sensitivity to stresses; for these $0 < \gamma_a < 0.5 \times 10^{-29}$ m^3. These include reactions of ozone with saturated polyolefins ($\gamma_a = 0.33 \times 10^{-29}$ m^3) and polyaminoimides ($\gamma_a = 0.05 \times 10^{-29}$ m^3).

By studying the supermolecular structure of polymers using Eqn. (12), it was possible to determine quantitatively the nonuniform distribution of stress on the bonds in oriented polyolefins—low- and high-density polyethylene and polypropylene ($\beta = 2-6$).

The supermolecular structure of isotropic polyamidoimides containing a fluorene ring (PAI-1), a nitrile group (PAI-2), and a *para*-phenylene group (PAI-3) were studied in particular detail with this method. In this case the coefficient β varies from 40 to 120 according to the chemical structure of the polyamidoimide. PAI-1 has the most ordered structure, and it is characterised by the lowest value of β and the lowest density, which provides the greatest opportunity for the formation of intermolecular hydrogen bonds.

Irreversible rearrangement of the supermolecular structure of polymers affects the dependence of the rate of their ozone oxidation on stress.[81] A particularly marked effect of this type of rearrangement occurs in the ozone oxidation of oriented polyolefins subjected to tension under conditions of stress relaxation. The additional orientation leads to an improvement in the fibrillar structure and a decrease in the rate of ozone oxidation.[82]

The physical and performance properties of polymers and the rate and mechanism of the chemical reactions occurring in them are determined to a considerable extent by the relaxation properties of the macromolecules and the mobility of low-molecular-weight additives,[78] since polymer products are generally used under conditions of mechanical stress and by the effects of temperature and oxidation. In order to resolve many scientific and practical problems, it is important to elucidate the effect of these factors on the molecular mobility of oriented polymers.

At the initial stage of stretching previously oriented samples (ε is about 6% for polyethylene and about 10% for polypropylene), the molecular mobility of the chains in the amorphous regions increases, with the magnitude of these changes depending on the molecular weight distribution, degree of orientation stretching, and degree of oxidation.[79] Deformation of samples with an average molecular weight and narrow molecular weight distribution at high degrees of stretching is accompanied by a decrease in molecular mobility.

Ozone oxidation produces a considerable increase in the rigidity of the amorphous regions,[81] which leads (at low degrees of oxidation) to an improvement in the mechanical properties of the polymer material.

A study of the effect of the orientation temperature (T_{or}) on the structure and strength of films of mixtures of polypropylene and high-density polyethylene (HDPE) showed that when T_{or} is higher than the melting point of the crystallites of HDPE, considerable changes occur in the polymer matrix. A new crystalline modification of PE is formed, the tensile strength decreases sharply, and the

melting point of the crystallites of PE and its degree of crystallinity are reduced. The combined experimental data suggest that the T_{or} of polyolefins should be close to the melting point of the more readily melting component of the mixture but should not exceed it.[78]

Ozone-oxygen oxidation of polymers substantially alters such characteristics of the physical structure of a polymer matrix as the melting point of crystallites of components of the polymer mixture, the polydispersion, and degree of crystallinity of the components.[82,83] As a result of oxidation there is a small decrease in the melting point and an increase in polydispersion of polyethylene and also a substantial decrease in melting point and polydispersion of polypropylene. When a mixture of polypropylene and polyethylene is treated with ozone, only the crystalline structure of the former is rendered amorphous to the extent of complete loss of crystallinity.[79]

Recently, unexpected effects relating to the action of mechanical stresses on the kinetics of oxidation of polyolefins have been revealed.[60] The oxidation of oriented polyethylenes, and particularly oriented and stressed polyethylenes, occurs in separate spatial zones of the reaction. The number of the latter and the characteristics of their distribution in space provide a basis for the assumption that they are formed around particles of contaminants that initiate the oxidation of the polymer.[82] Products of the conversion of polymerisation catalysts present in trace amounts in the polymer and also metal ions that have penetrated the polymer as a result of corrosion of the equipment (the polymerisation reactor, for example) can act as these particles. This in particular governs the variable thermooxidative stability of the same polymer synthesised using different catalytic systems.[8,9]

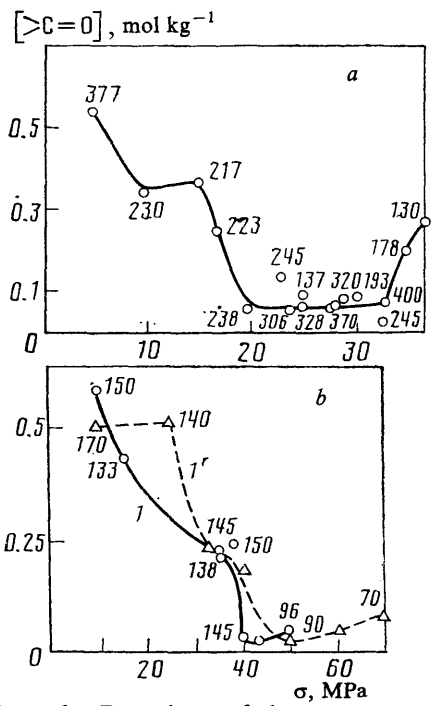


Figure 6. Dependence of the average concentration of carbonyl groups formed up to the moment of sample fracture on stress in the oxidation of oriented polypropylene: *a*, degree of stretching λ = 7.5, temperature of oxidation 120 °C; *b*, λ = 8.5, temperature of oxidation 130 °C.[78]

Mechanical stresses during oxidation primarily alter the permeability of the matrix. With low stresses the rate of translational diffusion of the low-molecular-weight radicals that are carriers of free valence from initiation "points" through the matrix falls (Fig. 6).[78] This leads to a marked decrease in the overall rate of oxidation under load. However, on increasing the stress above a given limit, mechanical radical initiation that is distributed throughout the polymer much more uniformly than initiation on contaminants starts to predominate.[82] At the same time the rate of oxidation of the polymer starts to increase again. With an increase in mechanical stress, not only the rate but also the oxidation conditions are altered. There is a change from a branched-chain process to a nonchain oxidation of the terminal macroradicals. These effects have the result that the criterion of rupture as a fixed average concentration of scissions or terminal oxygen-containing groups is not applicable to stressed polyolefins undergoing oxidation.[78]

Models for the rupture of stressed polyolefins undergoing oxidation which can be used in a number of cases to predict the longevity of various grades of polymers under various operating conditions have been proposed.[78–84] Analytical expressions that relate the longevity of a polymer to the number of initiation sites in samples and their growth rate have been obtained. The number of sites depends on the conditions of polymerisation, purity, and formation and their growth rate depends on the polymer structure and the oxidation conditions. All this makes it possible to develop new principles for increasing the stability of polymers without the use of traditional stabilisers. Careful removal of contaminants, increasing the degree of initial stretching, etc., are required for this purpose.

X. Radiation ageing of polymers

Bykov, et al.[85–87] have studied in detail the phenomena of shrinkage and cracking in polyolefins, in particular polyethylene, during radiative oxidation.

A well-defined sandwich structure consisting of an external oxidised layer and an internal unoxidised layer will be formed in thick films (plates, cable insulation) as a result of the diffusion-controlled flow of oxygen. The oxygen-containing compounds formed in the oxidised layer alter the conformation of the initial molecules. In this case mechanical stresses develop, leading to cracking of the polymer to the depth of the oxidised layer. The thickness of the oxidised layer and hence the depth of the cracks depends on the strength of ionising radiation.

In thin films that are oxidised to a uniform depth (oxygen permeates a sample quite rapidly) cracking does not occur, but shrinkage that is related to the accumulation of polar groups during oxidation is observed. The shrinkage of thin films and the cracking of thick films are governed by the same structural reorganisation processes—cracking starts at the moment when shrinkage reaches a given critical magnitude.[85–87]

A post-effect that is not related to post-radiative oxidation is characteristic of both the phenomena studied—shrinkage and cracking. The structural reorganisation processes that give rise to shrinkage and cracking are delayed relative to oxidation. The characteristic time lag is ~1 month.[88]

A kinetic model was developed, making it possible on the basis of common arguments to represent the phenomena of shrinkage and cracking as the result of radiation oxidation.[85–88] Using this model a

method was developed for determining the guaranteed operating lifetimes of cable insulation made of polyethylene. At the present time this method is being tested in the cable industry.

XI. Hydrolytic degradation of heterochain polymers

All heterochain polymers undergo degradation by reacting with water.[89–91] The hydrolysis reactions are catalysed by acids and bases. In dilute solutions of acids and bases (the so-called pH region) the rate of these reactions increases in proportion to the concentration of solvated H^+ and OH^- ions.[89] In more concentrated acid and base solutions the dependence of the rate of hydrolysis on the composition of the medium is more complex. Thus, for example, the rate of hydrolysis of amides increases with an increase in concentration of $H_5O_2^+$ ions and reaches a maximum value for aliphatic amides when the concentration of H_2SO_4 is 15% (for aromatic amides this occurs at about 50% H_2SO_4) and then decreases. The decrease in the rate of degradation at higher concentrations of sulphuric acid is related to the formation of an unreactive protonated form of the amide bond.[91] Because of this, the view was expressed[89] that solutions of polyamides in concentrated sulphuric acid should be stable.

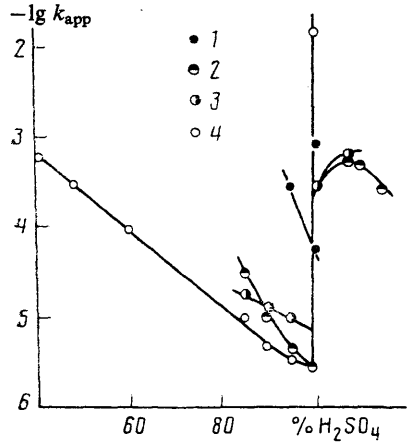


Figure 7. Dependence of the rate constants for degradation of polyamide on the concentration of H_2SO_4 at 80 °C:[89] *1*, polybenzamide; *2*, poly(*p*-phenylene terephthalamide); *3*, poly(*m*-phenylene terephthalamide); *4*, polycaproamide.

However, it was recently shown[90,91] (Fig. 7) that the rate constants for degradation of aliphatic and aromatic polyamides decrease as the content of H_2SO_4 increases up to 99.5%, while when it rises further to 100% they increase sharply. This change in reactivity has no analogies in the chemistry of low-molecular-weight amides. This is believed[91] to occur because the polymer state of the material assists the development of high local concentrations of protonated amide bonds in solution, with the result that the properties of the medium are changed in the immediate vicinity of the polycation.

The results obtained are important for the chemistry of aromatic fibre-forming polyamides since concentrated sulphuric acid is the only readily available solvent for these polymers.

It was recently demonstrated at a quantitative level that mineral acids act as catalysts of the polycyclodehydration of poly(*o*-hydroxy-amides) in solution. When mineral acids (hydrochloric, sulphuric, phosphoric) are introduced into a mixture containing poly(*o*-hydroxyamides) in dry *N*-methyl-2-pyrrolidone, two reactions—hydrolysis and cyclodehydration—occur simultaneously.[91] By changing the conditions of the reaction it is possible to direct it along a given route. With these data it is possible to predict the stability of poly(*o*-hydroxyamides) in aggressive media. They are of potential benefit in terms of the synthesis of these polymers, since they can be used to alter the reaction conditions (reduce the temperature, for example) so as to direct it on the cyclodehydration route.

Similar results have been obtained for a large number of polyamides, polyimides, polybenzoxazoles, and other polymers.[90,91]

XII. Interaction of polymers with biological media

Recently a complex analysis of the structure properties, and stability of poly(ether–urethanes) for medical use was carried out.[92–95] The use of block copolymers for the manufacture of artificial organs (cardiac chambers, cardiac valves, etc.) and a number of medical products (for example, catheters) makes it necessary to develop a scientifically based system of requirements to be imposed on these materials. A comprehensive approach has been developed for studying materials and products used as membranes, diaphragms, and certain other elements of an artificial heart, involving the application of a number of spectroscopic and diffusion methods.[92]

In virtually all of the materials of this type there is an intermedite (mixed phase) that consists of polyether and polyurethane residues, and this is responsible to a considerable extent for a whole set of physicochemical and mechanical properties of the material (and products made from it).[93] A correlation has been established between the degree of structural heterogeneity and the adsorption properties of the surface of poly(ether–urethanes) relative to blood plasma proteins (formation of blood clots on the polymers),[94] which is extremely important in relation to the specific conditions of using the products.

A comprehensive approach has been suggested[95] for studying the kinetics of adsorption of blood plasma proteins on the surface of the block copolymers, including the development of a kinetic diffusion model for the process, a method of determining the physicochemical parameters of the system polymer–protein, and a prognosis of the composition and structure of the adsorbed layer as a factor that is of definite significance in determining the thrombosis-resistant properties of segmented poly(ether–urethanes).[92–95]

A diffusion method and an H–D isotope exchange method specially developed for this class of polymers were used to determine their essential properties (water adsorption capacity, coefficients of diffusion and permeability) which it was necessary to take into account during use and storage of the materials.[94]

In recent years a new problem concerning the production of substitute materials for various biological tissues and systems has arisen on the borderline between mechanics, biology, and medicine. Polymer materials are increasingly being used for this purpose.[96–101]

For a polymer implant, not only the biological compatability but also the rheological compatibility is of considerable importance. Rheological incompatibilty, i.e. a lack of correspondence between the biochemical properties of the transplant material and the redesigned organ or tissue, results in very severe stresses developing at the points where they are connected. Therefore, in developing synthetic materials for medical application, the question of predicting their deformations and strength and structural characteristics is a vital one as is a determination of these properties after prolonged exposure of the material to an aggressive medium under conditions of continuous cyclic stress.

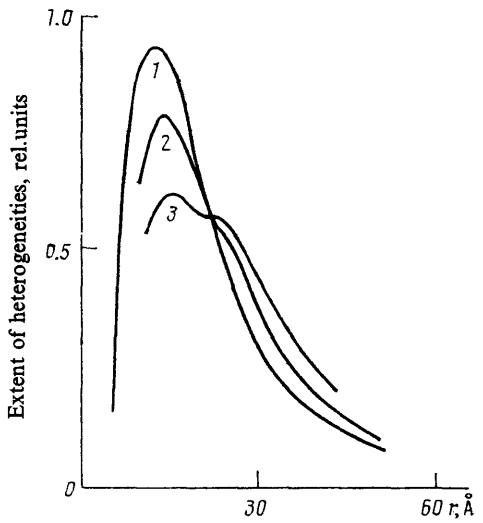


Figure 8. Distribution by size of microheterogeneities in PET fibres at different periods of implantation:[96] *1*, initial material; *2*, 3 months; *3*, 8 years.

In this connection studies were made on poly(ethylene terephthalate) (PET) that was subjected to biomechanical stresses in the transplantation of ligaments and tendons.[96–99] Braided tissue bands made of PET fibres were used with perpendicular interweaving of filaments. The residence of such fibres in an organism leads to irreversible changes in the structural characteristics of the material (Fig. 8), for example, a redistribution of microheterogeneities (the proportion of small pores decreases).[96] The number of small pores on the surface can decrease through an increase in their size as a result of the hydrolysis of PET[89] and also through penetration of the pores by collagen tissues of the organism.[97]

The change in structure of the fibres has an effect on their creep, which increases as the residence time of the PET material in the organism increases (Fig. 9).[97] The increase in deformation mainly occurs because of sorption of tissue liquid by the material.[97] As a result of the sorption of liquid under a continuous load (for example, the operation of a ligament in a living organism, an orientation strengthening of PET fibre occurs.[98]

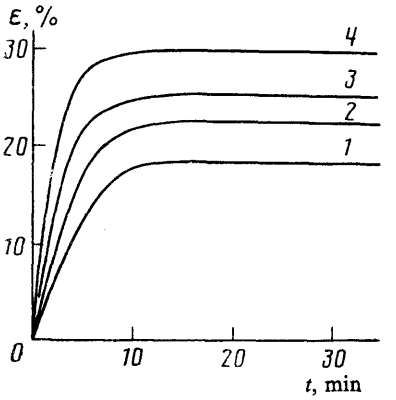


Figure 9. Creep of PET fibres at different periods of implantation:[97] *1*, initial material; *2*, 3 months; *3*, 1 year; *4*, 8 years.

A general prediction of the possible changes that occur in Lavsan (PET) substitute materials for ligaments and tendons can be made (Fig. 10).[89,96–98]

$$P = P_0(1 - k_{app} t d d_0^{-1} \rho^{-1})^2, \quad (13)$$

where P_0 and P are the initial and continuing tensile strengths respectively; k_{app} is the apparent rate constant for degradation; t is the residence time in the organism; d_0 and d are the initial and continuing average diameters of a simple filament of PET; ρ is the density of the PET fibre. This equation can be used to determine the average time taken for the ligaments and tendons to lose 50% of their strength. This time is estimated to be 30 ± 2 years.[96]

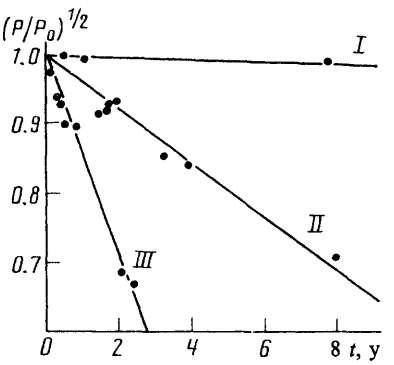


Figure 10. Dependence of the relative tensile strength of materials made of PET on the residence time of an implant in the human organism (*I*, PET ligaments and tendons, *II*, PET gauze) and rabbit (*III*) PET gauze.[98]

There is considerable interest in recent studies[99,100] related to the use of polymers subject to biodegradation in equipment for the controlled release of drugs. Drugs are released in proportion to the

surface erosion of these polymers. This usually occurs with zero-order kinetics, which corresponds to the therapeutical requirements of the supply of drugs to the organism.

The kinetic principles for representing the process of drug release from polymers undergoing bioerosion have recently been developed.[99,100] The molecular weight distribution of the initial polymer affects the kinetic parameters of drug release. The case where residues of a drug are connected to a polymer chain has been examined in terms of the kinetics. From the integral kinetic equations obtained it is possible to determine all of the required kinetic parameters. There is also the possibility of the nonuniform release of drugs due to the formation of soluble biodegradation products throughout the whole polymer.[100]

In general the following processs can occur in biodegraded polymer products:[89]

– adsorption of substances present in tissues of a living organism or of microorganisms on the surface of the material;

– destruction of the material either as a result of the specific action of living organisms that can use the polymer material as a nutritional source or by the action of an aggressive medium, including the action of metabolic products from microorganisms.[101–106]

When the first process occurs, the chemical structure does not change as a rule; the material acts as a support on which the adhesion and growth of colonies of microrganisms occur or collagen-like capsules are formed (when the material is used as an implant).

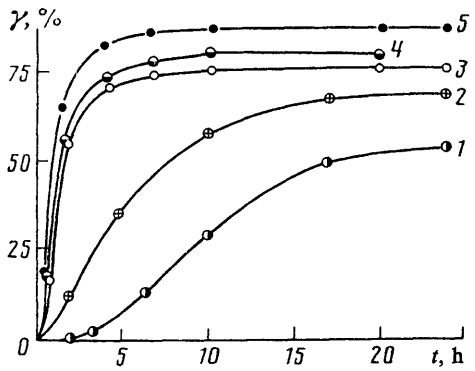


Figure 11. Kinetic curves for adhesion of colonies of spores of *Aspergillus niger* to the surface of different polymers: *1*, polyethylene; *2*, epoxy resin; *3*, poly(methyl methacrylate); *4*, cellophane; *5*, acetylcellulose (25 °C, 90% relative humidity).[105]

The second process leads directly to ageing of the polymer material through the action of chemically active agents. In this case the "bulk" operating properties are changed.

The kinetics curves of adhesion are satisfactorily given by the equation[105]

$$\ln(\gamma/\gamma_0) = -kt, \qquad (14)$$

where γ and γ_0 are respectively the proportion of particles remaining on the polymer surface after adhesion over a period t and the proportion of particles irreversibly adhering under these conditions; k is the rate constant for formation of adhesive bonds between the spores of microorganisms and the surface of the material.

The kinetic curves for the growth of biomass are satisfactorily given by the exponential function[106]

$$m/m_\infty = 1 - \exp(-kt), \qquad (15)$$

where m and m_∞ are respectively the continuing and final quantities of biomass on the surface of the polmer. In this case m_∞ is greater, the higher the solubility of water in the polymer. To illustrate this, the kinetic curves for adhesion and growth of biomass on different polymers that have been plotted according to Eqns. (14) and (15) are shown in Figs. 11 and 12.

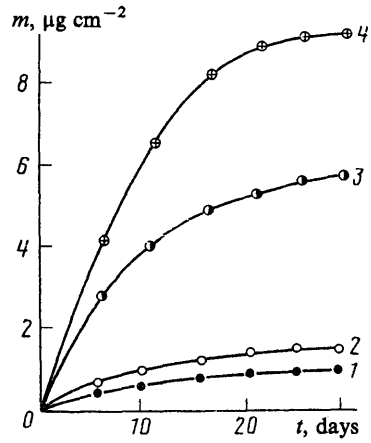


Figure 12. Dependence of the accumulation of biomass consisting of spores of *Aspergillus niger* on residence time on the surface of different polymer films (25 °C, relative humidity 90%): *1*, polyethylene; *2*, fluoropolymer; *3*, poly(ethylene terephthalate); *4*, cellulose.[106]

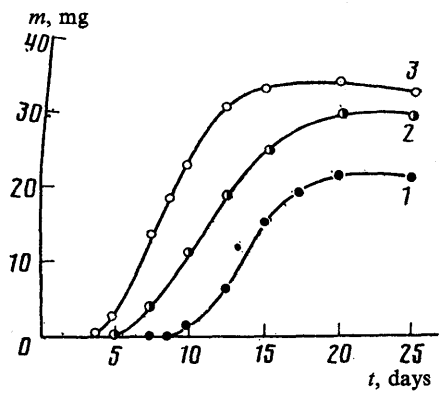


Figure 13. Kinetic curves for growth of *Aspergillus niger* biomass on canvas subjected to thermal humid ageing.[106] Ageing time, h: *1*, zero (initial material); *2*, 400; *3*, 1000 (25 °C, relative humidity 90%).

Under real conditions, degradation and biodegradation of the polymer material can occur simultaneously. The kinetic curves for the accumulation of biomass on canvas consisting of flax and cotton that has undergone thermohumid ageing followed by the growth of fungal spores are given in Fig. 13. It is clear that an increase in the time of ageing leads to an increase in the growth of biomass.[106]

Thus, the biological stability of a polymer material is governed by a combination of complex physicochemical processes involving adhesion, biological growth, and biodegradation which occur under certain external conditions.

XIII. Protection of materials with polymer coatings

One of the methods of protecting materials from the effect of aggressive media is to deposit protective polymer coatings on their surface. However, since the polymer coating itself is also degraded on contact with aggressive media, its service life is finite if it is a question of protecting a metal, and the aggressive medium, on reaching the metal surface, causes it to corrode.[9,11,89,91,94] Therefore, there is still considerable interest in studying ways of reducing the rate of penetration of aggressive media through protective polymer coatings.

A method of protection that is related to the introduction of additives which absorb oxygen and thus inhibit its participation in the thermooxidative degradation of polymers[107] is effective if the concentration of the aggressive medium (ozone, oxygen) is of the order of thousandths of a percent.[11] When the pressures of the aggressive medium are close to atmospheric, this method of protection is ineffective.

An experimental study of the efficiency of binding fillers such as oxides of beryllium, cadmium, magnesium, calcium, and alkaline earth metals and alkali metal hydroxides in the inhibition of diffusion of solutions of hydrochloric, hydrofluoric, and nitric acids in foamed plastics, polyarylate, polypropylene, and other polymers showed that the inhibitory effect depends in a complex manner on the nature of the polymer and the acid as well as on the concentration of the aggressive medium.[108]

The simplest model of the inhibitory effect of protective additives involves two possible mechanisms.[108] A diffusing molecule A binds with additive B in the polymer either reversibly as in

$$A + B \overset{K_e}{\rightleftharpoons} (AB),$$

where K_e is the equilibrium constant, or irreversibly as in

$$A + B \xrightarrow{k_1} (AB),$$

where k_1 is the rate constant of reaction. In both cases the diffusion coefficient (D_0) of molecules A in the initial polymer decreases after introduction of the additive as a result of these reactions, which immobilise a proportion of the diffusing molecules. Specially introduced low-molecular-weight compounds as well as certain functional groups of macromolecules, such as amide and amine groups in a polyamide, can act as additives in relation to diffusing HCl and H_2O molecules.[109]

The calculated curves for distribution of the diffusing component A throughout the coating at the same moment in time with reversible and irreversible binding and in the absence of binding are shown in Fig. 14, while the kinetics of formation of the "free" diffusing component A at the polymer–metal interface are displayed in Fig. 15. In this case the inhibitory effect with irreversible binding is equal to 30, while with reversible binding it is equal to 5.

The calculations demonstrate that under certain conditions the introduction of absorbents into the polymer can slow down the progress of the front of an aggressive medium towards a metal surface by a factor of several tens.

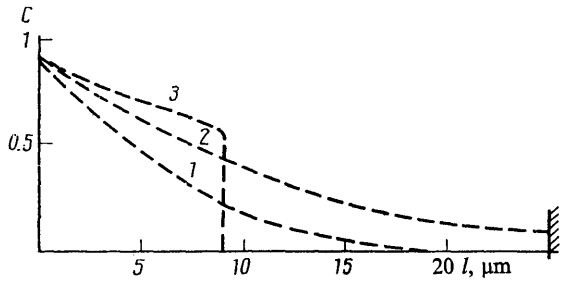


Figure 14. Calculated curves for distribution of the diffusing species throughout the coating 2 min after diffusion has started when $D_0 = 7 \times 10^{-13}$ m^2 s^{-1}:[109] *1*, reversible binding; *2*, absence of binding (no additives); *3*, irreversible binding.

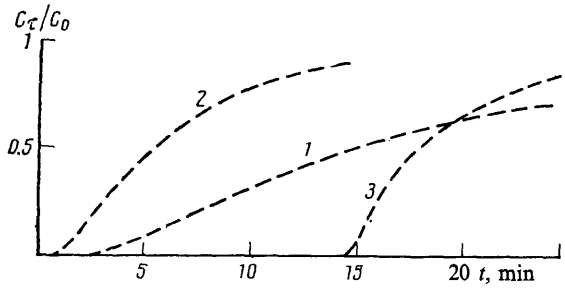


Figure 15. Accumulation of "free" diffusing species at the polymer–metal interface[109] (C_0 is concentration of diffusing species at the interface between coating and medium, C_τ is the continuing concentration of diffusing species at the metal interface: *1*, reversible binding; *2*, absence of binding (no additives); *3*, irreversible binding.

XIV. Predicting the properties of polymer products

The problems of polymer ageing are inseparably linked to a prediction of the change in their properties under real operating conditions.[9–11,89,91] It has been demonstrated in practice that predictions based on exiting rapid test methods frequently give erroneous results, since the mechanisms that are typical of real operating conditons are not reproduced during rapid testing. In order to determine to what extent the effects are equivalent, it is first of all necessary to make a detailed study of ageing mechanisms under natural climatic and artificial conditions.[110–122]

In order to conduct systematic studies on polymer materials for ageing under natural conditions in a warm humid climate, an experimental unit was developed and produced for determination of

molecular mobility, relaxation and phase transitions, viscoelastic properties, and the structure of polymers based on the use of current high-sensitivity methods.[110–122]

The information already collected at this stage can be used to classify the mechanisms of physicochemical reactions of different classes of polymers during atmospheric ageing in a moist subtropical zone. Data are currently being collected on the link between the physicochemical reactions and the change in macroscopic properties of the polymers and on the role of individual climatic factors in the ageing of polymer materials. An interactive information system that is designed for processing the results of kinetic tests and predictions has been developed.[123–126] In order to represent data, the user can select a suitable function from a suggested library of standard models. Unknown parameters are determined by maximum probability based on prior information. Statistical treatment of the results with determination of the accuracy of the parameter estimates and a check of the statistical hypotheses are carried out. Provision is made for planning the experiment, transforming the results using different anamorphisms, and presenting the results in the form of graphs, tables, and storing them. This program forms the basis of the first machine-readable standard in the country.

A method for predicting the photochemical response to a given polychromatic effect on a polymer with an unknown spectroscopic sensitivity has recently been developed.[123,124] The necessary and sufficient conditions for correctness have been determined and an original regularisation method has been developed. The results are presented in the form of a corridor of admissible response values.

The proposed method has already found practical application in solving problems in applied photochemistry, and it can be used to determine much more effectively the photosensitivity of polymer materials being used under real conditions. A package of computer programs has already been developed for putting this method into effect. An investigation of the mechanism of action of classical inhibitors such as phenols and amines is in progress, in order to provide a prediction of their efficiency as stabilisers for polymers.[127,128]

carbonised polyimides (Fig. 16) with a maximum coking value is achieved with a quasi-isothermal heat regime, a statistical inert atmosphere, a relatively high content of nitrogen atoms in the main polyimide chain, and by orientation of the sample.[130]

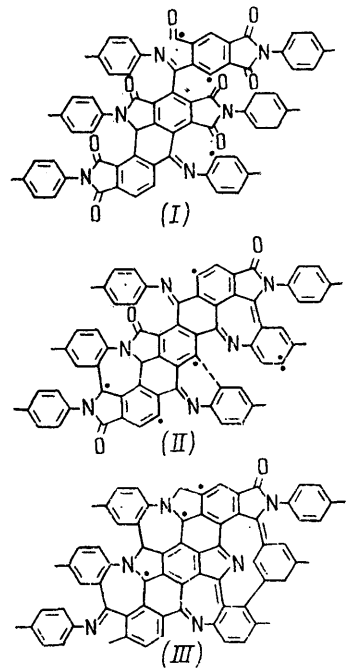


Figure 16. Structural scheme for carbonisation of polypyromellitimide at: *I*, 525; *II*, 575; *III*, 625 °C.[129]

XV. Ageing and stabilisation of heat-resistant polymers

The ageing and stabilisation of heat-resistant polymers can be suitably studied at temperatures above 300 °C, and in a number of cases above 400 °C.[127–139] Polyimides constitute the best known examples of this class of polymers. Two approaches to the stabilisation of heat-resistant polymers have already been examined above in Section V.[26,30,31]

Recently there has been a considerable growth of interest in studying thermochemical reactions that occur at temperatures of 500 °C and above. This is related not only to the problems of thermal and thermooxidative stability of polymers but also to research into their combustion processes, the primary stage of which is pyrolysis of the polymer to gaseous products.[140] At these temperatures thermal degradation is characterised by substantial rearrangement of the whole macromolecular structure (of the polyimide in this case) with the formation of carbonised products that are more or less ordered and mainly consisting of condensed aromatic and heterolytic species.[127,128] One of the aims of these studies is to establish the optimum conditions for obtaining polyimide materials that have a maximum "cooking value" and at the same time acceptable mechanical properties. The preparation of

An effective way of stabilising heat-resistant polymers, in particular polyimides, is to refine their methods of synthesis[131] with the aim of substantially reducing the cyclisation temperature of the prepolymers. This trend, which is not related to classical stabilisation methods,[132] can be used in a number of cases to perfect the structure of the polyimides and improve their thermal stability and other important properties.[133]

The use of polyimides for the heat stabilisation of other so-called large-tonnage polymers should be regarded as having future potential.[134] The use of a polyimide in combination with poly(vinylpyrrolidone), furfuryl alcohol, and epoxy resins results in the formation of composite materials in which the polyimide structure acts as a unique heat-resistant framework, substantially increasing the heat stability of polymer fillers.[135–139] According to thermal analysis data,[134–139] the heat resistance increases by 100–150 °C in the case of poly(vinylpyrrolidone) and by approximately 200 °C for furan and epoxy resins. The second component in turn imparts a number of valuable properties to the polyimide such as thermohydrolytic stability and high-temperature adhesion to metals and graphite materials.

At the present time this is the most promising development in research into ageing processes and in seeking ways to stabilise heat-resistant polymers.

XVI. Conclusion

The ageing of polymers and the stabilisation of polymer materials remains, as before, a vital problem. At the present time the accent of research has shifted from individual polymers to polymer blends and composites.[121] The transition to multicomponent systems complicates the task, since in this case additivity does not usually occur. It was demonstrated back in the 1960s that even in the co-oxidation of two hydrocarbons,[142] each of which is separately oxidised under given conditions, cases are possible where only one compound (R_1H) is oxidised in the mixture, and the other (R_2H) is not oxidised. In essence this occurs because hydrocarbon R_2H is regenerated by R_1H according to Scheme 4.

Scheme 4

$$R_1H + O_2 \longrightarrow R_1^{\cdot} + HO_2^{\cdot}$$
$$R_1^{\cdot} + O_2 \longrightarrow R_1O_2^{\cdot}$$
$$R_1O_2^{\cdot} + R_1H \longrightarrow R_1OOH + R_1^{\cdot}$$
$$R_2H + O_2 \longrightarrow R_2^{\cdot} + HO_2^{\cdot}$$
$$R_2^{\cdot} + R_1H \longrightarrow R_2H + R_1^{\cdot}$$
$$R_2^{\cdot} + O_2 - \times \longrightarrow$$

Investigations are continuing into the specific nature of the polymer state with regard to the reactivity of interacting species in the polymer matrix[143,144] and the mobility of molecular chains and low-molecular-weight compounds in polymers under different conditions. Particular attention is being given to the effect of structural relaxation of vitreous polymers on the kinetics of chemical reactions. A model that has been proposed[143,144] can be used to represent qualitatively the majority of known kinetic effects of structural relaxation of vitreous polymers.

There is no doubt that studies to establish cases of synergism and antagonism in the stabilisation of polymers in the presence of several stabilisers and other chemical additives will be continued. Multifunctional stabilisers that contain a number of functional groups in the same molecule, acting by different mechanisms and thus creating a synergistic effect, are of increasing interest. The application of polymeric stabilisers for the stabilisation of polymers operating at high temperatures is expanding. At high temperatures they are quite mobile (and therefore effective), while at the same time they are not washed out and do not bleed like low-molecular-weight stabilisers. The development of new, more sensitive methods has been proposed[145] for studying polymer degradation processes that would allow the conditions of testing to approximate to real operating conditions and hence markedly increase the accuracy of predicting the lifetime of reliable operation and preservation of polymer products.

Degradation processes are starting to be used more extensively for the modification of polymer products in order to improve their properties.

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