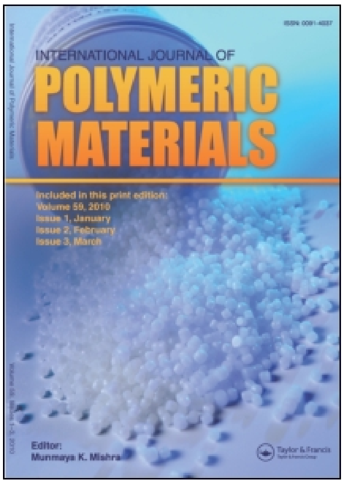

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PVC Wire Coatings: Part l-Ageing Process Dynamics

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PVC Wire Coatings: Part I-Ageing Process Dynamics

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PVC wire coatings represent a key element of aircraft structures. Considering that modern aircrafts contain tens of miles of wires and cables insulated with PVC coatings it is imperative to understand the degradation of these coatings in use. It is also essential that we develop methods which will enable us to predict as accurately as possible the lifetime of these systems. A review of current test methods shows that these methods are inadequate to achieve these objectives because they do not take into consideration the recent advances in polymer ageing and degradation. In this work we address these critical issues by first reviewing the dynamics of PVC ageing (Part I), while the second Part will deal with the prediction of actual life time of these systems.

Keywords: PVC; plasticized PVC; dehydrochlorination; PVC stability; ageing; degradation kinetics; plasticizer diffusion

INTRODUCTION

Polyvinylchloride-based polymers are widely used as insulating materials in wires and cables. Modern aircrafts contain tens of miles of wires and cables, and in some cases exploitation time of the aircrafts is controlled by the time of wire insulation lifetime.

Despite a number of undoubtful advantages, polyvinylchloride-based materials possess a limitation: they all are more or less subjected to ageing.

The limited resistance to ageing may cause serious consequences, so it requires the most accurate prognosis of the exploitation time of polyvinylchloride-based insulating material. The underestimation of the exploitation time leads to premature repair while the overestimation of use time can lead to accidents or costly repair.

The existing list of GOSTs and OSTs [1, 2] methods devoted to the problem of prognosis of lifetime is outdated and does not meet the modern requirements.

Recent polymer ageing studies allows us to work out techniques to predict the exploitation times of polyvinylchloride-based insulating materials for the aircrafts with the accuracy meeting current performance standards.

This article describes the mechanisms of plasticized PVC ageing which are used to develop methods of determination of the exploitation time of PVC insulated electric network in the aricraft.

AGEING OF POLYVINYLCHLORIDE

Ageing of polyvinylchloride on processing and exploitation has been the subject of numerous investigations. The majority of investigations is devoted to the study of dehydrochlorination of pure polymer in an inert atmosphere. PVC is most often used in plasticized form. The amount of plasticizers may reach 70% of the total mass. This makes the problem of PVC ageing very complex and requires consideration of all processes proceeding under conditions of processing and exploitation.

The following processes can proceed during ageing of plasticized PVC

- PVC dehydrochlorination
- Thermoxidative degradation of PVC and plasticizers
- Cross-linking
- Diffusional desorption of a plasticizer from an article.

1. DEHYDROCHLORINATION OF POLYVINYLCHLORIDE

The reaction of dehydrochlorination proceeds in PVC with a noticeable rate at high temperatures ($> 150^\circ C$) [3]:

$$\mathrm{CH_2{-}CHCl{-}CH_2{-}CHCl{-}CH_2{-}CHCl}$$

$$\xrightarrow{-\mathrm{HCl}} \mathrm{CH_2{-}CHCl{-}CH_2{-}CH{=}CH{-}CHCl}$$

(*β*-chlorallyl groups)

$$\xrightarrow{-\mathrm{HCl}} \mathrm{CH_2{-}CH{=}CH{-}CH{=}CH{-}CHCl} \rightarrow \text{etc.}$$

SCHEME 1

The presence of hydrochloride, the reaction product, and oxygen in the surrounding accelerates dehydrochlorination [4]. Therefore, it is necessary to consider the reaction of noncatalytic dehydrochlorination.

1.1. Noncatalytic Dehydrochlorination

Noncatalytic dehydrochlorination takes place when the rate of the diffusional desorption of hydrochloride from a sample exceeds significantly the rate of the reaction itself. For example, this condition is encountered with PVC powders or thin films when the experiments are carried out in vacuum or in inert gas.

The reaction is of the first order by the polymer. The correct data were obtained in solution [5]. In solid polymers their physical structure changes during dehydrochlorination leading to distortions of the reaction order [6].

The rate of noncatalytic dehydrochlorination (W^0) is calculated by the equation:

$$W^0 = \frac{\alpha}{t}; \quad \alpha = \frac{{}^{n}\mathrm{HCl}}{\overset{\infty}{{}^{n}\mathrm{HCl}}}. \qquad (1)$$

Here ${}^{n}\mathrm{HCl}$ and $\overset{\infty}{{}^{n}\mathrm{HCl}}$ are HCl amounts formed during time t and at complete polymer transformation, respectively. W^0 is constant until $\alpha = 0.3 - 0.5$ in dependence on reaction conditions.

HCl extraction is accompanied by formation of double bonds (polyene structures) in macromolecules. This is displayed through occurrence of characteristic absorption bands in UV-and visible spectrum parts. We can also observe a correlation between α and the optical density growth at low degrees of transformation [7].

The Process of Noncatalytic Dehydrochlorination

The process of noncatalytic dehydrochloridation consists of three main stages:

- Initiation of active centers
- Evolution of dehydrochlorination
- Termination of active centers.

Initiation

The initiation of dehydrochlorination can be induced randomly (β-chlorallyl group formation) or by active centers (defect structures) formed during synthesis and storage of PVC.

Starting from primary investigations on PVC degradation [3, 8, 9] and until present [10–13] it has been commonly accepted that the reason of low PVC stability as compared with low molecular chloralkanes is the existence of defect structures in macromolecules.

Double Bonds Activating action of double bonds is confirmed by the decrease of dehydrochlorination rate at soft PVC chlorination [14–15]. Double bonds may be identified and quantitatively determined by bromination followed by determination of the number of breaks, ozonolysis [16–18] and NMR technique [19]. The following results have been obtained in this case (see Tab. I)

TABLE I The amount of double bonds of different types in industrial PVC samples

Double bond types	*Amount per 1000 monomer units*
$-CH_2-CHCl-CH=CH_2$	0.7–2.2
$-CH_2-CHCl-CHCl=CH_2$ or $-CH_2-CHCl-CH=CH-CH_2-$	0 2.8
$-CH_2-CH=CCl-CH_2Cl$ or $-CH_2-CH=CCl-CHCl-$	0.6–2.7

A satisfactory correlation has been obtained between W^0 and the amount of terminal double bonds [4, 20, 22], as well as with the amount of internal double bonds [23–27].

Activating effect of internal double bonds has been discovered by Brown *et al.* [28] in investigations of dehydrochlorination of specially synthesized vinylchloride copolymers with phenyl acetylene.

Groups Possessing Tertiary Carbon Atoms Branched structures detach HCl much easier than normal chains do. Industrial samples contain from 5 to 7 such structures per 1000 monomer units [10, 29, 30]. The following structures were obtained with the help of the NMR technique (see Tab. II).

'Head-to-Head' Structure —CH_2—CHCl—CHCl—CH_2—. The content of the structures of this type does not exceed 6 per 1000 monomer units [31]. A special polymer has been synthesized elsewhere [32] that possessed the 'head-to-head' structure. The polymer had a lower temperature of dehydrochlorination initiation, but the maximum rate was reached at a higher temperature.

Stereoregularity Syndiotactic structures are less stable than isotactic ones [33–37]. The content of long polyenes increases at dehydrochlorination with the increase of syndiotacticity, however the number of active centers of dehydrochlorination decreases in this case.

Oxygen-containing Groups Compositions with double bonds can be oxidized, hence different oxygen-containing groups are present in PVC [38]. According to the data [39] PVC may possess ketoallyl groups, —$CH_2COCH{=}CH$—, in amounts 0.01–0.25 per 1000 monomer units. The presence of these groups is confirmed by polymer chain breaks in alkaline solution. Linear dependence of W^0 on ketoallyl group concen-

TABLE II The amount of branched structures of different types in industrial PVC samples [10]

Branched structure types	*Amount per 1000 monomer units*
Chloractylic	4–6
Chlorethylic	0.4–2.4
Butylic	0.4–1.6
Nonidentified longer ones	0.2–2.4

tration allowed the authors of those works to conclude on the most important role of ketoallyl groups at the initial stage of dehydrochlorination [40, 41]. However, the presence of ketoallyl groups in industrial polymers is considered doubtful by some authors [10, 12]. The presence of oxygen in the polymerization medium leads to the following reactions [42]:

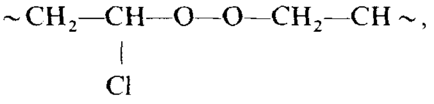
$$\sim CH_2—CHCl\sim + O_2 \rightarrow CH_2—CHCl—O—O^{\bullet}$$
$$\rightarrow CH_2O + HCl + CO + R^{\bullet}$$

Carbon oxide formed may copolymerize with vinylchloride forming structures with ketone groups [43]:

$$\sim CH_2—CHCl—CO—CH_2—CHCl,$$

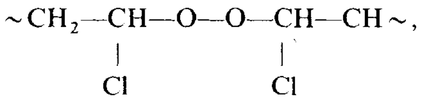
whose reactivity in dehydrochlorination is not yet clear.

Polymeric vinylchloride peroxides may be formed either during vinylchloride copolymerization with oxygen [44, 46]



$$\sim CH_2—\underset{\displaystyle Cl}{\underset{|}{CH}}—O—O—CH_2—CH\sim,$$

or at the cross break of peroxide macroradicals [47]



$$\sim CH_2—\underset{\displaystyle Cl}{\underset{|}{CH}}—O—O—\underset{\displaystyle Cl}{\underset{|}{CH}}—CH\sim,$$

or at the chain transfer to monomer [47]:

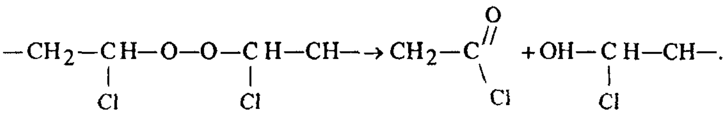
$$\sim CH=CCl—O—O—CH_2—CHCl\sim,$$

$$\sim CH_2—CHCl—O—OH.$$

Since the concentration of peroxide groups in PVC macromolecules is low, their direct experimental determination is difficult. Iodometry indicated 10^{-3} mole of peroxide per mole of VC for a polymer produced in oxygen, and 2.5×10^{-4} mole for a polymer processed under 0.15 Pa vacuum [48].

The proofs of the existence of peroxide groups are:

- Absorption in 850–900 and 1050–1080 cm^{-1} ranges of IR-spectra
- Absorption in 350–370 nm range of vv spectrum
- The decrease of PVC molecular mass at polymer processing by acids and alkali is caused by heterolysis of peroxide bonds in the presence of these substances



$$-CH_2-\underset{Cl}{CH}-O-O-\underset{Cl}{CH}-CH- \rightarrow CH_2-\overset{O}{\underset{Cl}{C}} + OH-\underset{Cl}{CH}-CH-.$$

Polyene Structures According to data from [39] polyene structures are absent in PVC, but other data [46] show their concentration to be about 0.4 per 1000 monomer units.

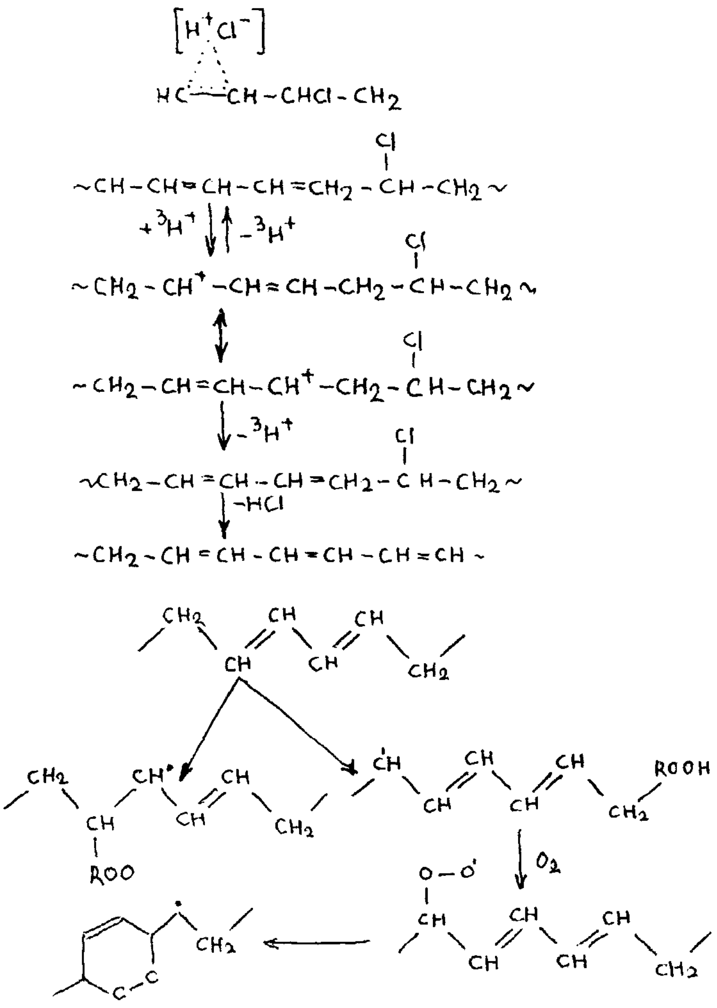
Admixtures Industrial PVC samples contain a large amount of various admixtures: metals, solvent residues, emulsifiers, initiators. Many of them can accelerate PVC dehydrochlorination. This is indicated by the increase of polymer stability (by 30%) on its complete purification [4,49,50]. Among admixtures the influence of initiators on dehydrochlorination rate is studied most. For example, W^0 grows with the increase of 1,1'-azo-bis-isobutyronitrile concentration in PVC (from 10^{-2} to 1 mol%) [51,52].

Thus a great number of various defect structures is known, capable of initiating PVC dehydrochlorination. There are several types of defect structures present in industrial polymers, so it is difficult to find a correlation between W^0 and a definite defect concentration. This point is confirmed by the data of the work [53].

Development of Dehydrochlorination and Active Center Termination

Development of dehydrochlorination proceeds with HCl detachment from β-chlorallylic group (allylic activation mechanism) or from the chain fragments with the above mentioned defect structures. Double bonds formed, in turn, activate HCl detachment from the neighbour

$\sim CH_2$—CHCl$\sim$ groups (see the Scheme 1), that finally leads to the formation of polyene structures.



By comparing the rate constants of dehydrochlorination in model PVC compositions with different amounts of double bonds we find that the introduction of each double bond increases K^0_{eff} value by approximately two orders of magnitude in both gas and liquid phases (see Tabs. III and IV).

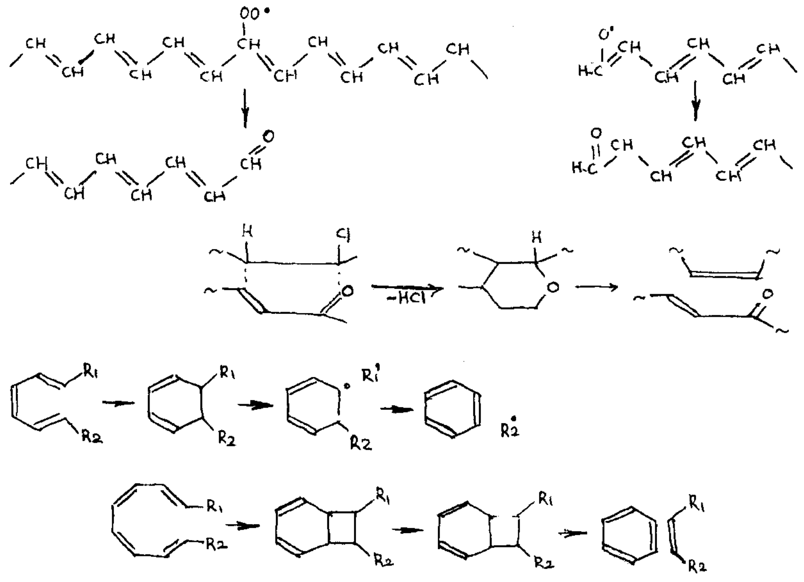


TABLE III Kinetic parameters of dehydrochlorination reaction of model PVC compositions in the gas phase

Model composition	*Temperature range, °C*	$K_{177°C} \times 10^{11}, s^{-1}$	*E, kJ/mol*	$lg A, s^{-1}$
2-chlorbutane	347–394	3.6	206	13
2,4-dichlorpentane	347–397	3.3	206	13
2,4,6-trichlorheptane	346–386	3.4	214	14
4-chlorpentene-2	296–345	859	172	12
6-chlorheptadien-2,4	302–347	45900	147	10

TABLE IV [58]

Model composition	*Temperature range, °C*	$K_{177°C} \times 10^{11}, s^{-1}$	*E, kJ/mol*	$lg A, s^{-1}$
8-chlor-hexadecane	236–284	1	151	10.5
8-chlor-tri-decene-6	165–196	10^3	105	8.1
4-chlor-dodecene-2	156–180	8×10^2	125	6.9
7-chlor-nonadyene-3,5	70–96	4×10^5	81	8.0
6-chlor-octadyene-2,4	87–113	3.2×10^5	75	7.1

The process of dehydrochlorination may, therefore, be considered as set of consecutive reactions where the first reaction controls the rate of the entire process.

Polyene structures formed usually contain from 4 to 10 double bonds [54–56]. This shows that an active center is destroyed after formation of several double bonds and that the dehydrochlorination does not proceed along the whole molecule. Therefore, the concentration of polyene structures is comparatively low in this case.

The mechanism of the active center destruction is not yet clear. It is possible that the active center is destroyed by formation of cyclic structures [59, 60].

Polyvinylchloride Stability

Stability of PVC in noncatalytic dehydrochlorination is most often estimated by W^0 value. The data obtained by different authors for the process of noncatalytic PVC dehydrochlorination under vacuum are successfully described by the Arrhenius equation (Fig. 1). The activation energy value is 134 ± 8 kJ/mol. The following equation [61–63] can be used for calculations in 90–230°C temperature range:

$$W^0 = (2 \pm 1) \times 10^9 \exp\left(-\frac{134 \pm 8}{RT}\right)(\mathrm{s}^{-1}). \qquad (2)$$

Two questions relative to PVC stability determination need to be addressed.

1. How does W^0, obtained for a polymer, differ from that for model compositions in the liquid state?
2. What difference exist for W^0 obtained for different industrial polymers?

Table V shows W^0 values for PVC and chloralkanes in the liquid phase at 177 and 200°C.

It is seen that W^0 for PVC and chloralkanes in the liquid phase falls in the same range. The agreement between the rate constants of dehydrochlorination is improved with the increase of chlorine amount in model compositions. However, we have to consider these data very carefully, because the influence of the solvent on the dehydrochlorination rate should be taken into account while estimating the reactivity of chloralkanes [65].

Table VI shows W^0 values for different industrial polymers [42].

Industrial polymers from different countries display small differences in W^0_{eff}, and its average value is $(7.8 \pm 0.9) \times 10^{-7}\mathrm{s}^{-1}$.

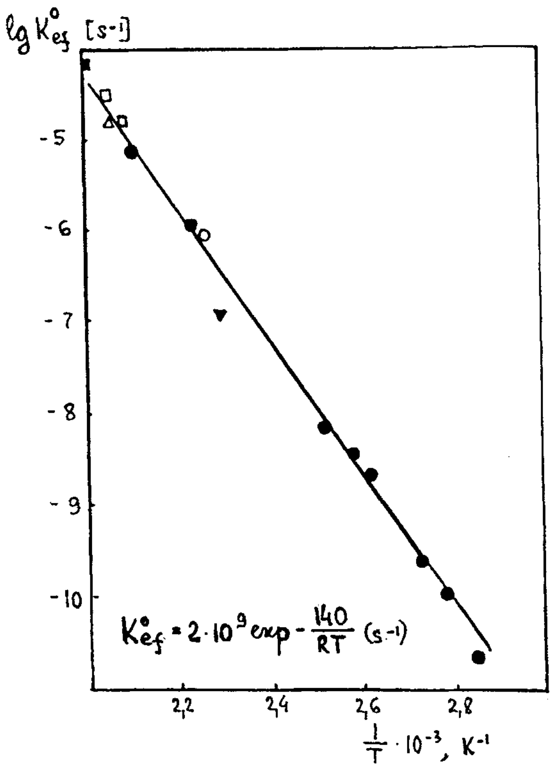


FIGURE 1 The dependence of the rate constant logarithm of noncatalytic dehydrochlorination on reverse temperature.

TABLE V Values of W^0 for PVC and chloralkanes in the liquid phase

Compound	$W^0_{177}{}^{\circ} \times 10^7, s^{-1}$	$W^0_{200}{}^{\circ} \times 10^6, s^{-1}$
PVC	6–9	2–4
8-chlorhexadecane	1	1
2,4-dichlorpentadecane	17	5
1,4,7-trichlorheptane	6.5	3
1,4,9-trichlornonane	6.0	4

On the basis of above data and results reported in the work [60], we can conclude that the stability of industrial PVC for dehydrochlorination is determined mainly by the structure of the elementary chloralkyl unit. The defect structures may exist in these polymers either in nearly equivalent amounts or may have no significant role.

TABLE VI W^0_{eff} values for different industrial polymers at 177°C and 10^{-2}Pa

Trade mark	*State*	$\bar{M}_r \times 10^{-3}$	$W^0_{eff} \times 10^7, s^{-1}$
S-70	Russia (former USSR)	138	8.2
S-68	Russia (former USSR)	104	7.2
S-55	Russia (former USSR)	70	10.3
Sircon 548 PM	Italy	143	7.1
Ravinyl PP 100/70P	Italy	136	7.0
TK-1300	Japan	163	6.8
B/III-8000	Japan	139	6.1
Nicavinyl-1300	Japan	132	7.1
Vestolit S 7064	Germany	130	6.9
Vestolit S 6051	Germany	90	8.8
Hostalit M-VP 3067	Germany	108	9.2
Lucovil-1150	France	133	9.0
Revicon R-45	Sweden	125	8.0
Solvic 223	Belgium	65	7.9

Since the process of dehydrochlorination is complex and includes several consecutive reactions, the attempts have been made to determine the kinetic parameters of these reactions.

Statistic HCl detachment from chloralkane chains

$$\frac{d[\mathrm{HCl}]}{dt} = K_c[\mathrm{ChA}], \tag{3}$$

here K_c is the rate constant of dehydrochlorination at HCl detachment from chloralkane groups; [ChA] is the concentration of chloralkane groups in polymers.

The rate of this reaction is most often determined by the accumulation of breaks in PVC macromolecules on ozonolysis [17, 18], and less frequently by NMR method by accumulation of internal double bonds [66]. The kinetic parameters of this reaction were calculated in the work [67]:

$$K_c = 10^{11 \pm 0.5} \exp\left(-\frac{160 \pm 40}{RT}\right) \mathrm{s}^{-1}. \tag{4}$$

Values of the pre-exponential and the activation energy are close to the correspondent parameters for 8-chlorhexadecane (see Tab. IV).

HCl detachment from chloralkane chains by means of activation by β-chlorallyl or ketoallyl groups

$$\frac{d[\mathrm{HCl}]}{dt} = K_I\,[\beta - \mathrm{ChA}]. \qquad (5)$$

Here K_I is the rate constant of dehydrochlorination activated by β-chlorallyl; [β-ChA] is the concentration of β-chlorallyl groups.

K_I values can be estimated from the data described elsewhere [14]. K_I values at 150, 170 and 220°C equal 7.5×10^{-5}, 2×10^{-4} and $1.2 \times 10^{-4}\,\mathrm{s}^{-1}$, respectively.

$$K_I = (5 \pm 2) \times 10^9 \exp\left(-\frac{115 \pm 8}{RT}\right)\mathrm{s}^{-1}. \qquad (6)$$

Kinetic parameters of dehydrochlorination initiated by ketoallylic groups were determined in the work [41]. Attempts were made to obtain general kinetic equations, which would take into account the initiation of dehydrochlorination by different defective structures. Thus, for example, the concept on the most important role of ketoallyl groups was developed in [40] and corresponding equation was deduced. However this equation does not explain the experimental fact: the invariability of dehydrochlorination rate until transformation reaches 0.3–0.5. Since the ketoallyl groups should be spent very fast because of their high reactivity, the dehydrochlorination rate should decrease, which is not the case.

The Mechanism of Noncatalytic Dehydrochlorination

Presently there is no general opinion on the mechanism of noncatalytic dehydrochlorination [3, 61]. Ideas were proposed favoring the molecular-ionic, as well as, the radical-chain mechanism.

The molecular-ionic mechanism explains HCl detachment from a chloralkane group according to one of three different pathways [68].

1. Monomolecular mechanism (E_1)

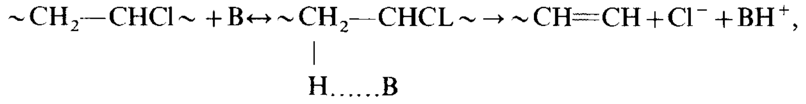
$$\sim\mathrm{CH_2{-}CHCl}\sim\;\leftrightarrow\mathrm{CH{-}\overset{+}{C}H}\sim + \mathrm{Cl^-}\quad \text{(slowly)}$$

$$\sim\mathrm{CH{-}\overset{+}{C}H} + \mathrm{S} \rightarrow \mathrm{CH{=}CH} + \mathrm{SH^+}\quad \text{(rapidly)},$$

where S is a solvent.

Usually this mechanism is realized in polar solvents, and there is no reason to suppose any probability of such a mechanism proceeding in a polymer matrix with the dielectric constant ~ 4.

2. Bimolecular mechanism (E_2)



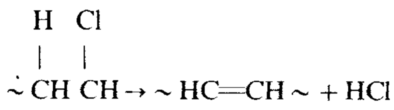
$$\sim CH_2{-}CHCl\sim + B \leftrightarrow \sim \underset{\underset{H\ldots\ldots B}{|}}{CH_2}{-}CHCL\sim \rightarrow \sim CH{=}CH + Cl^- + BH^+,$$

where B is a base.

According to this mechanism the detachment proceeds in the presence of strong bases. Realization of such a mechanism is of a very low probability in industrial polymers.

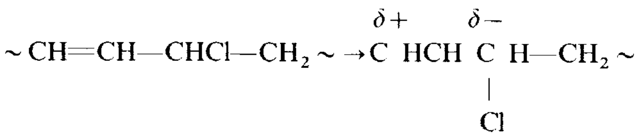
3. Cyclic mechanism

Cyclic detachment is a monomolecular single-stage process (contrary to the mechanism E_1), where the detached chlorine atom extracts β-proton with it when yields.



$$\sim \overset{\overset{H}{|}}{C}H\;\overset{\overset{Cl}{|}}{C}H \rightarrow \sim HC{=}CH\sim + HCl$$

This process is not ionic because it does not proceed through formation of ions in a free state. But in some cases we may put forward an analogy with ionic processes. For example, pyrolysis of alkylhaloids displays the same dependence of reactivity on the composition structure as in the mechanism E_1. This means that the transition state resembles an ionic pair R^+Cl^-. For example, we can imagine that HCl detachment from chlorallyl group proceeds through formation of an allyl zwitterion:



$$\sim CH{=}CH{-}CHCl{-}CH_2\sim \rightarrow \overset{\delta+}{C}\;HCH\;\underset{\underset{Cl}{|}}{\overset{\delta-}{C}}\;H{-}CH_2\sim$$

Therefore, the cyclic mechanism appears to be the most suitable to describe the noncatalytic dehydrochlorination of PVC.

The radical-chain mechanism includes formation of free radicals and their further dehydrochlorination by direct detachment of HCl or formation of Cl atom. For the first time this mechanism was suggested in the works [69, 70].

The following arguments are usually put forward for the benefit of the molecular-ionic mechanism:

- The absence of radical reaction products (H_2, Cl_2, etc.)
- HCl catalysis
- The absence of the influence of radicals' inhibitors
- The decay of low molecular chloralkanes according to the molecular-ionic mechanism [71–73].

To confirm the radical-chain mechanism of dehydrochlorination we can present data on the ^{3}H- and ^{14}C-labeled toluene introduction into a polymer chain and on correlation of the transformation degree of this reaction with the degree of PVC dehydrochlorination.

Recently the ion-radical mechanism of PVC dehydrochlorination was suggested [74]. This process includes C—Cl-bond ionization in a polymer segment with the formation of an ion pair with cyclic chloronium ion, electron transfer and macroradical formation which initiates dehydrochlorination. We believe that this mechanism is confirmed by the influence of thiols, dihydroanthracene and other proton donors on chain dehydrochlorination.

1.2. Catalytic Dehydrochlorination

Hydrogen chloride plays a very important role in PVC ageing. It was found that HCl catalyzes dehydrochlorination. PVC catalytic dehydrochlorination proceeds when the diffusion rate of formed hydrogen chloride is comparable with the rate of noncatalytic dehydrochlorination, or the reaction proceeds in the hydrogen chloride atmosphere.

Hydrogen Chloride Solubility in PVC

Hydrogen chloride is soluble in PVC, that is confirmed by kinetic data showing that the rate of catalytic reaction is proportional to a polymer volume [75]. However attempts to obtain quantitative data by gravimetric technique (McBain scales) so far failed.

Hydrogen chloride solubility in a polymer is determined in [76] by the manometric technique, namely, by the decrease of HCl pressure in a vessel possessing volume V_0, which contains a definite mass of polymer (m). The solubility coefficient σ was determined by the following equation:

$$\sigma = \frac{P_0 V_0 - P_1(V_0 - V)}{P_1}, \tag{7}$$

where P_0 and P_1 are initial and terminal (after polymer introduction) pressures of HCl, respectively; $(V_0 - V) = \Delta V$ is the system volume change.

The solubility obtained ($\sigma_{20} = 6.6$) is, apparently, overestimated, because in the case of the PVC powders adsorption should prevail. Specific surface of the PVC powders is in the range from 0.3 to 1.6 m^2/g [77]. Nevertheless, the data obtained in this study [77] are of a great interest, because they show that HCl solubility increases during degradation:

$$\sigma = \sigma_0(1 + \beta \times \alpha), \tag{8}$$

where the coefficient of proportionality $\beta = 63$ at 20°C.

Active Centers of Catalytic Dehydrochlorination

In general case chloralkane, β-chlorallyl and ketoallyl groups may be active centers for PVC catalytic dehydrochlorination.

Chloralkane Groups The role of chloralkane groups as active centers for the catalytic dehydrochlorination is not yet clearly established. Pocker [78] has found that HCl is a strong electrophilic catalyst in media with low dielectric constant, and it increases significantly the rate of tert-butylchloride dehydrochlorination in these media.

β-Chlorallyl Groups are π-bases capable to bind HCl. The existence of β-chlorallyl group-hydrogen chloride complexes was for the first time demonstrated by Schlimper [79] and Onozuka *et al.* [80]. The investigations of the role of these complexes in the catalytic dehydrochlorination showed that the rate of 4-chloro-2-hexene dehydrochlorination increases with the increase of the solvent polarity (the condition favorable for the complex formation).

TABLE VII Rate constants of 4-chloro-2-hexene dehydrochlorination in different solvents in the presence of 0.8 ml^{-1} of HCl at 60°C

Solvent	*Dielectric permeability*	*$K \times 10^4 min^{-1}$*
Methanol	32.6	8
1,2-dichlorethane	10.3	3.5
Tetrahydrofuran	7.2	0
Dioxane	2.2	1.0
Heptane	2.0	0.8
Ethyl-2-hexyl	11.0	1.5

The most important proofs of β-chlorallyl group activity in the catalytic dehydrochlorination were obtained by the ozonolysis and subsequent counting of the number of breaks in PVC after dehydrochlorination [81].

If β-chlorallyl groups are the active centers for the catalytic dehydrochlorination, then $\bar{M}_n$ of the samples subjected to degradation in the presence or in the absence of HCl must be the same, because the detachment of polyene fragments will not affect the $\bar{M}_n$ value (the lengths of polyene fragments are much shorter than that of PVC fragments, which include nonreacted chloralkane groups).

If chloralkane groups are active centers of the reaction, $\bar{M}_n$ of PVC samples should change in the process degradation in the presence of HCl, as formation of double bonds in the PVC molecules will proceed by the random law.

The experiments performed at ambient temperatures showed that the time dependence of breaks in PVC samples subjected to degradation in the presence or in the absence of HCl is practically equal. This indicates that under these conditions the reactivity of β-chlorallyl groups is much higher than that of chloralkane groups.

Groups with tertiary carbon atoms are n-bases and, consequently, may be active centers for dehydrochlorination. Structures possessing the general formula $R_1R_2R_3CCl$ with tertiary C—Cl bond and substituents R_1, R_2 and R_3, which contain polyene fragments capable to conjugate with α-carbonic atom [82], should be the most basic ones.

Macrokinetics of PVC Catalytic Dehydrochlorination

The general equation of catalytic dehydrochlorination is the following:

$$\frac{dc_{\text{HCl}}}{dt} = \frac{dc_{=}}{dt} = \sum_i K^k_{\text{eff}}\, c_{\text{HCl}} c_{(\text{a.c.})}. \qquad (9)$$

Here c_{HCl} is the HCl concentration in the polymer; $c_{=}$ is the concentration of double bonds formed; $c_{(\mathrm{a.c.})}$ is the concentration of active centers in the polymer.

At temperatures close to ambient, β-chlorallyl groups present in the polymer act as active centers as the noncatalytic dehydrochlorination proceeds with a very low rate.

At low degree of transformation and constant HCl pressure the reaction system fits the equation:

$$\alpha = K_{\mathrm{eff}} t, \tag{10}$$

where $K_{\mathrm{eff}} = K^{k}_{\mathrm{eff}} c^{0}_{\mathrm{HCl}} c^{0}_{\mathrm{a.c.}}$.

This equation was applied to describe experimental data on catalytic dehydrochlorination of thin PVC films (no diffusional limits) in HCl and in hydrochloric acid vapours at 60°C [75].

In [50, 83–85] the reaction of catalytic dehydrochlorination was performed in a closed volume at high temperatures. The reaction was monitored by the increase of the hydrogen chloride pressure in the system. Noncatalytic dehydrochlorination proceeds with noticeable rate at temperatures above 185°C, and the concentration of active centers (β-chlorallyl groups) should increase during the reaction.

Thus, autocatalytic character of PVC dehydrochlorination is stipulated by two reasons: the increase of the hydrogen chloride concentration in a polymer and increase of number of the active centers for catalytic dehydrochlorination.

General kinetic equation displays a complex form [75], however, the experimental data obtained in works [50, 83–85] at low transformation degrees are succesfully described by the following equation (see the Fig. 2):

$$\lg\frac{\alpha}{1-\alpha} = \lg\alpha_0 + 0.434 K^{k}_{\mathrm{eff}} c^{0}_{a.c.} t, \tag{11}$$

where α is a parameter connected to HCl pressure in the system.

Expressions $K^{k}_{\mathrm{eff}} c^{0}_{\mathrm{a.c.}}$ calculated for different initial HCl pressures for the process of the PVC powder dehydrochlorination at 210°C are shown in Table VIII.

The $K^{k}_{\mathrm{eff}} c^{0}_{\mathrm{a.c.}}$ change with the P^{0}_{HCl} increase may be due to inapplicability of the Henry law or a change of the active center-HCl complex concentration with the increase of HCl concentration in the polymer.

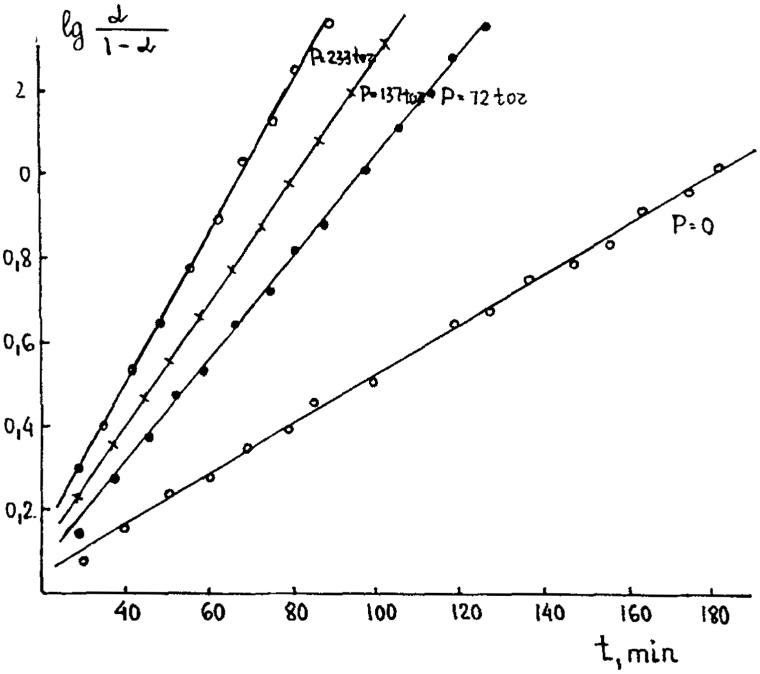


FIGURE 2 Treatment of the experimental data of HCl pressure influence on kinetics of dehydrochlorination at 200°C in accordance with the equation (11).

TABLE VIII Values of $K^{k}_{\text{eff}}c^{0}_{\text{a.c.}}$ calculated by equation (11) for the process of the PVC powder dehydrochlorination at 210°C

P^{0}_{HCl}, torr	0	72	137	233
$K^{k}_{\text{eff}}c^{0}_{\text{a.c}} \times 10^{4}$, s^{-1}	1.0	2.0	2.3	2.8

In accord with the data [48, 81] the presence of HCl in the atmosphere catalyzes just the detachment of hydrogen, making no influence on the length and distribution of polyene structures.

Kinetic regularities of PVC film dehydrochlorination at simultaneous proceeding of noncatalytic and catalytic reactions were considered in works [82, 83].

The change of HCl concentration in a polymer in diffusional-kinetic range during dehydrochlorination can be described by the following equation:

$$\frac{\partial c_{\text{HCl}}}{\partial t} = D\frac{\partial^{2} c_{\text{HCl}}}{\partial x^{2}} + K^{0}_{\text{eff}} + K^{k}_{\text{eff}}\, c^{0}_{\text{a.c.}}\, c_{\text{HCl}}, \tag{12}$$

where D is coefficient of HCl diffusion in a polymer.

The equation has an analytical solution if we assume that the concentration of the active centers at catalytic dehydrochlorination is constant ($c_{\text{a.c.}} \approx c^0_{\text{a.c.}}$). Then, the equation (12) has the following solution:

$$c_{\text{HCl}} = -\frac{2K^0_{\text{eff}}}{\pi}\sum_{n=1}^{\infty}\frac{1-\cos n\pi}{n\left(K^k_{\text{eff}}c^0_{\text{a.c.}} - Dn\frac{\pi^2}{e^2}\right)}$$

$$\times\left[1-\exp t\left(K^0_{\text{eff}}c^0_{\text{a.c.}} - Dn\frac{\pi^2}{e^2}\right)\right]\sin\frac{n\pi x}{l}, \qquad (13)$$

here l is the film thickness.

The amount of HCl diffused through the specific surface during dt equals

$$dm = -D\left[\frac{dc_{\text{HCl}}}{dx}\right]_{x=l} dt = \frac{2DK^0_{\text{eff}}}{l}dt\sum_{n=1}^{\infty}\frac{(1-\cos\pi n)\cos n\pi}{\left(K^k_{\text{eff}}c_{\text{a.c.}} - Dn^2\frac{\pi^2}{l^2}\right)}$$

$$\times\left[1-\exp t\left(K^k_{\text{eff}}c_{\text{a.c.}} - Dn^2\frac{\pi^2}{l^2}\right)\right]. \qquad (14)$$

Final solution for the transformation degree α is as follows:

$$\alpha = \frac{2DK^0_{\text{eff}}}{l^2 m_{\infty}}dt\sum_{n=1}^{\infty}\frac{1-\cos\pi n}{\left(K^k_{\text{eff}}c^0_{\text{a.c.}} - Dn^2\frac{\pi^2}{l^2}\right)^2}$$

$$\times\left[\exp t\left(K^k_{\text{eff}}c^0_{\text{a.c.}} - Dn^2\frac{\pi^2}{l^2}\right) - t\left(K^k_{\text{eff}}c^0_{\text{a.c.}} - Dn^2\frac{\pi^2}{l^2}\right) - 1\right], \qquad (15)$$

where m_{∞} is the theoretical amount of HCl that may be extracted from a specific polymer volume.

Analysis of the equation (15) shows that there are two limiting cases:

1. $K^k_{\text{eff}}c^0_{\text{a.c.}} \gg D\pi^2 l^{-2}$, dehydrochlorination proceeds in the autocatalytic regime, and a sharp increase of the process rate is observed:
2. $K^k_{\text{eff}}c^0_{\text{a.c.}} < D\pi^2 l^{-2}$, no acceleration of dehydrochlorination is observed, and the maximum rate is reached at the time when the exponential term of the equation becomes negligibly small.

Figure 3 shows a typical change of the transformation degree α with time for dehydrochlorination of the PVC samples of different thickness. As it is seen from the data shown in the Figure 3 the process rate increases with the growth of the sample thickness. Pudov [85] was the first who introduced the idea of the critical sample thickness, i.e. the value l at which the degradation transforms from the stationary regime to autoaccelerated one. The critical value l_{cr} is determined from the following condition:

$$\frac{\pi^2 D}{l_{\text{cr}}} = K^k_{\text{eff}} c^0_{\text{a.c.}}. \tag{16}$$

Table IX shows values of $K^k_{\text{eff}} c^0_{\text{a.c.}}$ and D obtained by different authors.

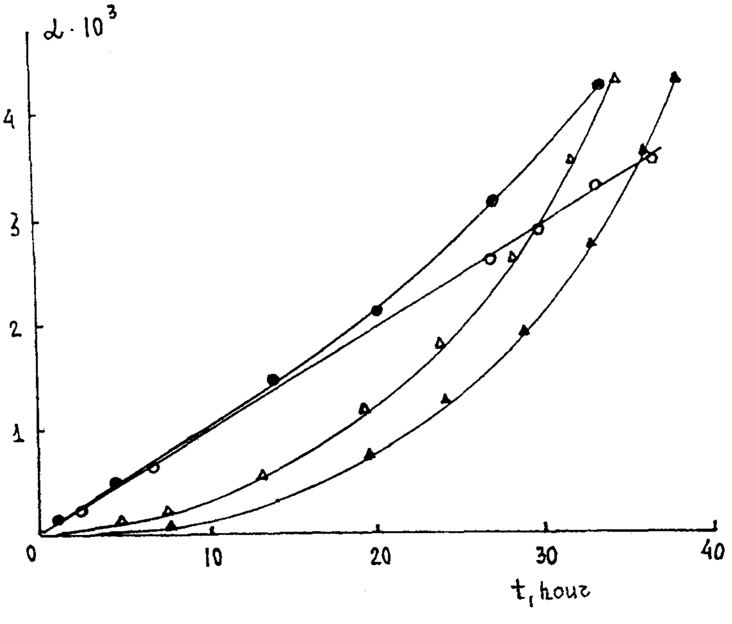


FIGURE 3 The dependence of the transformation degree of hydrogen chloride on time of dehydrochlorination of PVC disks or different thickness: ○ –0.05 cm; ● –0.1 cm; Δ –0.2 cm; □ –0.4 cm at 140°C.

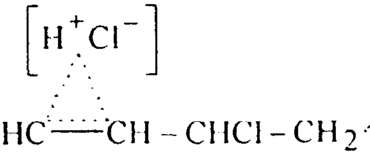
TABLE IX Values of $K^k_{eff}c^0_{a.c.}$ and D obtained for different temperatures

t, °*C*	$K^k_{eff}c^0_{a.c.} \times 10^4, s^{-1}$	$D \times 10, cm^2 s^{-1}$	*References*
120	0.075 ± 0.005	3.5 ± 0.5	87
130	0.190 ± 0.020	5.5 ± 0.5	
140	0.440 ± 0.020	7.5 ± 0.5	
180	1.000		88
185	1.100		84
200	1.700	33	86
210	1.700		20

The activation energy of the catalytic dehydrochlorination is 117 ± 8 kJ/mol [86].

Mechanisms of Catalytic Dehydrochlorination

At present time there are several approaches to the mechanism of PVC catalytic dehydrochlorination. Generally accepted is the one of participation of polyene sequences in catalytic dehydrochlorination of PVC [88], and in this case it is assumed [89] that π-complex is the reactive particle:



$$\overset{[H^+Cl^-]}{HC{=}CH}-CHCl-CH_2\sim$$

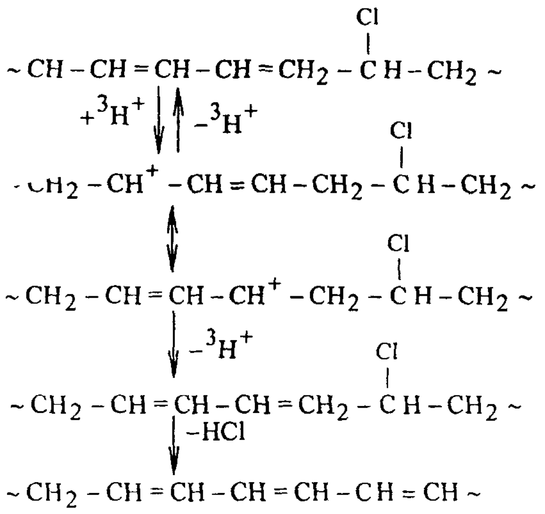
Such π-complex forms no carbonium ion, but promotes HCl detachment from the neighbour chloralkane group.

The mechanism of the chain dehydrochlorination via a polyene-cation system was suggested [90, 91] basing on the rapid isotopic exchange between PVC and ^{3}HCl present in the atmosphere:

Plasticizer Effect on Dehydrochlorination

A plasticizer in PVC can exist in several forms:

- The solvent
- The adsorptional layer on the surface of the overmolecular structures



- The Quazi-free phase in the free space between the super molecular structures.

Various forms of a plasticizer can be identified, for example, by DTA [92] or NMR [93] techniques. It should be expected that a plasticizer existing in different forms will differently affect the rate of dehydrochlorination; in turn, the chemical nature and the concentration predict a ratio between plasticizer forms.

Figure 4 shows a typical picture of dehydrochlorination K^0_{eff} change from an infinitely diluted PVC solution in a plasticizer to a pure polymer [94]. The proportion between K^0_{eff} and the polymer concentration is in the range of diluted solutions (< 100 g/l). The range of concentrated polymer solutions does also show the increase of W^0 with the PVC concentration growth. In the range of intermediate concentrations some cases of W^0 independence on the polymer concentration changes were observed [95].

From the investigations in diluted solutions we can obtain information on the plasticizer influence on PVC dehydrochlorination on the molecular level. The data show that the nature of the plasticizer affects significantly the rate of dehydrochlorination, the W^0 value decreases, with the solvent polarity [95–98].

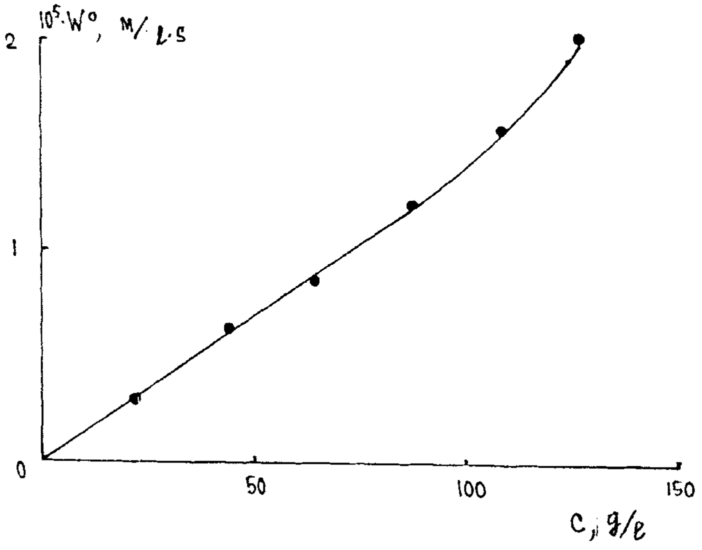


FIGURE 4 The dependence of the rate of PVC dehydrochlorination in dioctylphthalate solution on polymer concentration at 212°C.

Figure 5 shows the dependence of the relative rate logarithm on the reverse dielectric permeability for PVC dehydrochlorination in eight solvents [95, 98]. Two of the solvents (benzophenon and decalin) do not fit the present dependence. It is interesting that the increase in solvent polarity causes no increase of the activation energy as it should based on the compensation effect. It actually decreases from 134 kJ/mol for PVC to 95 kJ/mol for benzyl alcohol. This induces the supposition that the medium polarity is not the only factor that influences the dehydrochlorination rate. The solvent acidity is also expected to play an important role. This is observed in practice [97]. These are the bases from which the medium influence on attachment of hydrogen chloride to olefins is considered [99].

Apparently, plateau on the dependence W^0-c_{PVC} in the range of concentrated solutions is associated with the formation of a quazi-free plasticizer phase. In addition, the plasticizer molecules located in the free space between super molecular structures does not significantly influence the dehydrochlorination rate.

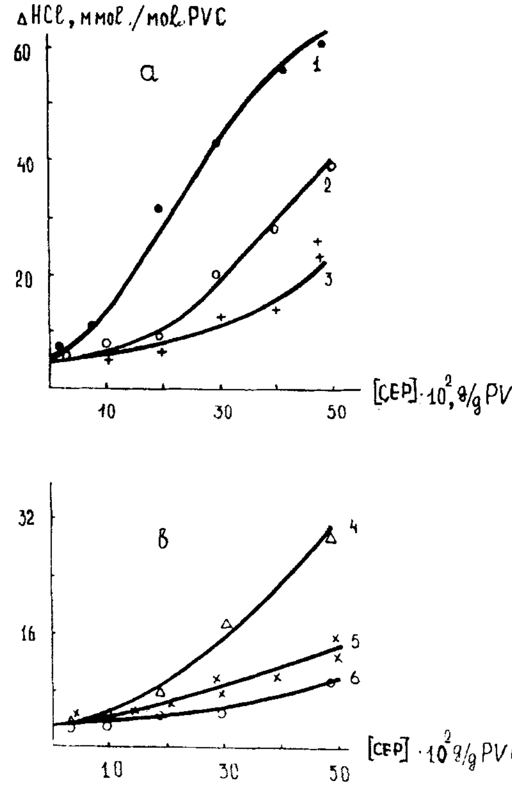
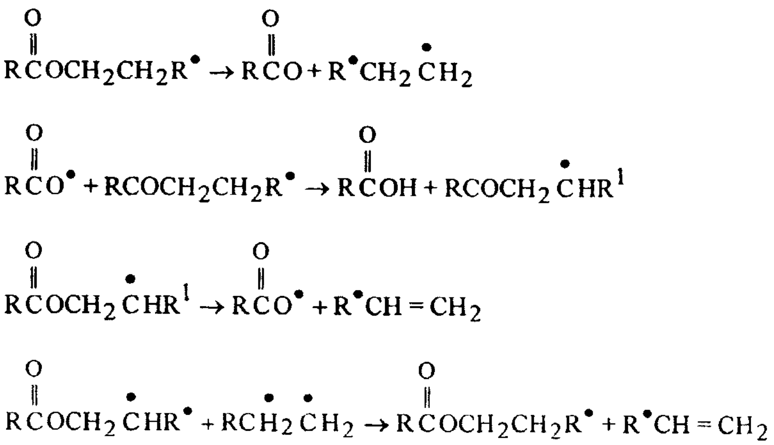


FIGURE 8 The dependence of hydrogen chloride amount yielded during 60 min on concentration of a complex-ester plasticizer (CEP) at thermodegradation of PVC (175°C) in O_2 (a) and in air (b): 1, 4 – DOS; 2, 5 – DOA; 3, 6 – DOP.



$$R\overset{\overset{\displaystyle O}{\|}}{C}OCH_2CH_2R^\bullet \rightarrow R\overset{\overset{\displaystyle O}{\|}}{C}O + R^\bullet CH_2\overset{\bullet}{C}H_2$$

$$R\overset{\overset{\displaystyle O}{\|}}{C}O^\bullet + RCOCH_2CH_2R^\bullet \rightarrow R\overset{\overset{\displaystyle O}{\|}}{C}OH + RCOCH_2\overset{\bullet}{C}HR^1$$

$$R\overset{\overset{\displaystyle O}{\|}}{C}OCH_2\overset{\bullet}{C}HR^1 \rightarrow R\overset{\overset{\displaystyle O}{\|}}{C}O^\bullet + R^\bullet CH=CH_2$$

$$R\overset{\overset{\displaystyle O}{\|}}{C}OCH_2\overset{\bullet}{C}HR^\bullet + RC\overset{\bullet}{H}_2\overset{\bullet}{C}H_2 \rightarrow R\overset{\overset{\displaystyle O}{\|}}{C}OCH_2CH_2R^\bullet + R^\bullet CH=CH_2$$

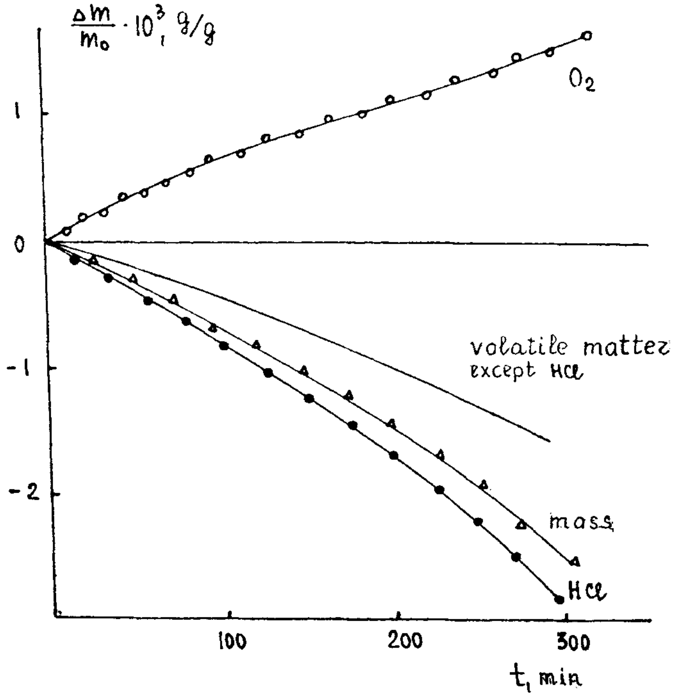
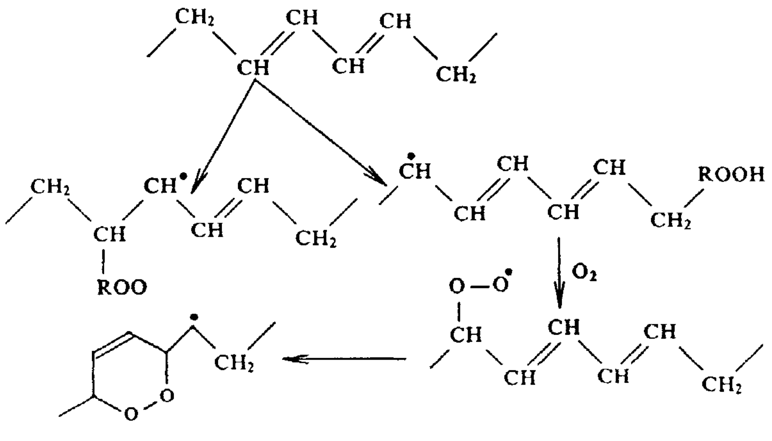
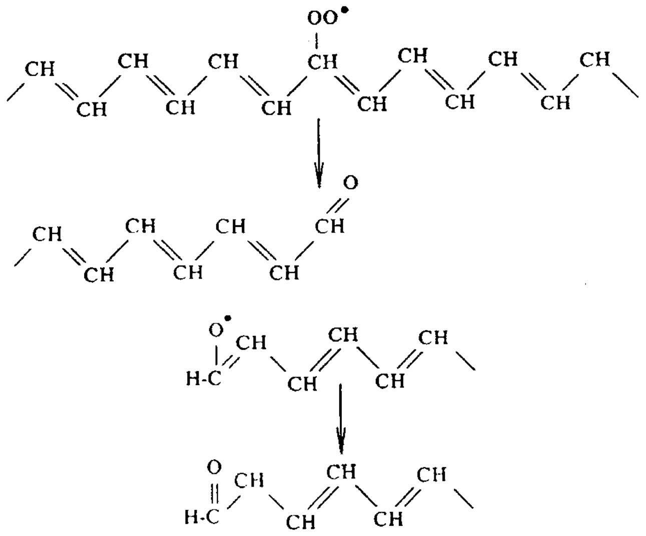


FIGURE 6 Relative change of polymer mass at oxygen absorption, extraction of HCl and other volatile products during thermoxidative degradation of PVC at 180°C and 1 atm O_2.

state is a spin-prohibited event. Oxidation proceeds via the stage of the peroxyradical interaction with the polyene structures with further formation of hydro-and cyclic additives:



Decomposition of polyene radical proceeds with the formation of a carbonyl compound and an oxyradical, the latter transforming into an allyl radical:



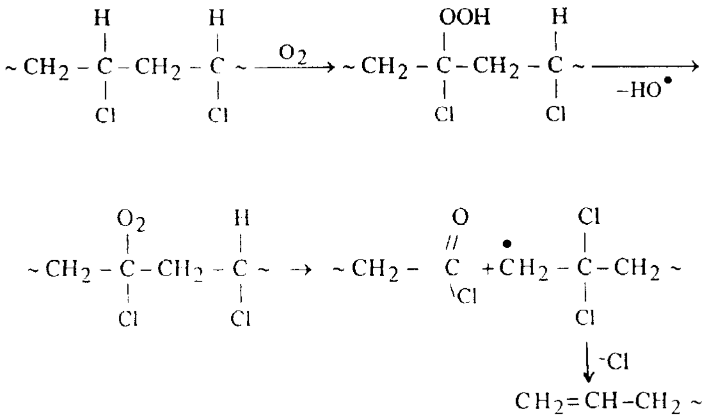
From the presented scheme it could be seen that products are formed in the reactions of isomerization and polyene peroxyradical decomposition, which contain smaller amount of double bonds. This has been confirmed by several investigations [54, 55, 106, 107].

The rate of the oxygen absorption is determined by means of the equation:

$$W_{O_2} = a[A]\sqrt{W_i}\frac{K_2}{\sqrt{K_6}} + \sqrt{W_i}\frac{K_x}{\sqrt{K_6}}, \tag{17}$$

where $[A]$ is the concentration of polyenes; W_i is the initiation rate; K_2 and K_6 are the rate constants of propagation and break of the chains, respectively. $K_x/\sqrt{K_6}$ characterizes the relative reactivity of a polyene peroxyradical in the reactions of decomposition and isomerization.

The PVC chain decomposition, probably proceeds by the following scheme:

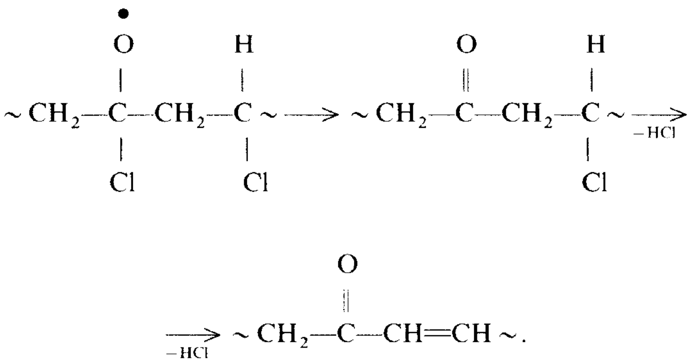


$$\sim CH_2-\underset{Cl}{\overset{H}{C}}-CH_2-\underset{Cl}{\overset{H}{C}}\sim \xrightarrow{O_2} \sim CH_2-\underset{Cl}{\overset{OOH}{C}}-CH_2-\underset{Cl}{\overset{H}{C}}\sim \xrightarrow[-HO^{\bullet}]{}$$

$$\sim CH_2-\underset{Cl}{\overset{O_2}{C}}-CH_2-\underset{Cl}{\overset{H}{C}}\sim \;\rightarrow\; \sim CH_2-\overset{O}{\overset{//}{C}}\backslash Cl + \overset{\bullet}{C}H_2-\underset{Cl}{\overset{Cl}{C}}-CH_2\sim \xrightarrow{-Cl} CH_2=CH-CH_2\sim$$

2.2.2. Oxygen Effect on Dehydrochlorination

Dehydrochlorination is significantly accelerated in the presence of oxygen [108]. This is connected with formation of oxygen-containing groups, which initiate dehydrochlorination:



$$\sim CH_2-\underset{Cl}{\overset{\overset{\bullet}{O}}{C}}-CH_2-\underset{Cl}{\overset{H}{C}}\sim \longrightarrow \sim CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\underset{Cl}{\overset{H}{C}}\sim \xrightarrow[-HCl]{}$$

$$\xrightarrow[-HCl]{} \sim CH_2-\overset{O}{\overset{\|}{C}}-CH=CH\sim.$$

Figure 7 shows the change of the transformation degree α with time in the argon/oxygen mixture. The kinetic curve of the HCl yield is described by the formal equation [109]:

$$\frac{d\alpha}{dt}=(K_S+K_\alpha)\left(1-\frac{\alpha}{\alpha_\ell}\right), \tag{18}$$

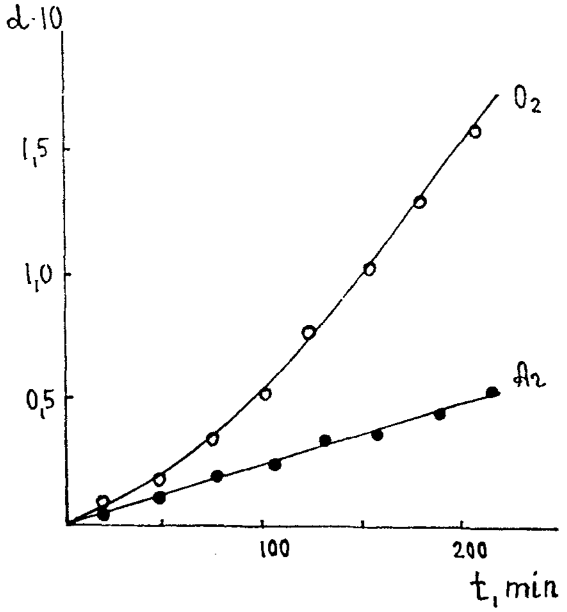


FIGURE 7 HCl yield from PVC powder during degradation at 200°C at 1 atm O_2 and 1 atm Ar.

where K_s is the rate constant of the initial part of the kinetic curve; K_α and α_∞ are formal constants.

Values of K_s at different temperatures are determined from the following equation:

$$K_S = 9 \times 10^8 \exp\left(-\frac{126}{RT}\right) s^{-1}. \tag{19}$$

2.2.3. Effects of Plasticizers on Thermoxidative Degradation

Introduction of plasticizers accelerate the thermoxidative degradation of PVC [110–112].

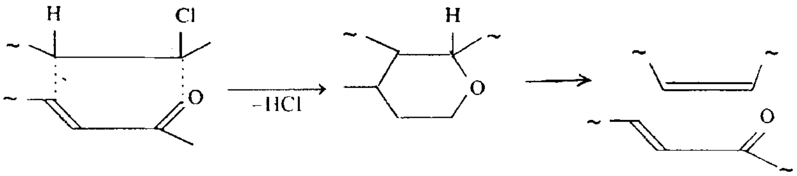
Figure 8 shows the kinetic curves of dehydrochlorination for PVC containing different amounts of a plasticizer.

The autocatalytic character of PVC dehydrochlorination is bound with oxidation of plasticizers themselves and the influence of the oxidation products on dehydrochlorination.

Acids and olefins are formed in the process of thermodegradation of complex-ester plasticizers:

Beside acids compositions with peroxide, carbonyl and hydroxyl groups are formed in the presence of oxygen. They are the groups which initiate PVC dehydrochlorination. The mechanism of this process is not, however, quantitatively described.

It is known that unsaturated ketones activate dehydrochlorination according to the following scheme:



3. CROSS-LINKING OF POLYVINYLCHLORIDE

Cross-linking of the PVC macromolecules proceeds under the same conditions as dehydrochlorination. The formation of cross-links and three-dimensional net structure leads to the increase of the molecular mass and the decrease of solubility (gel-fraction formation). Occurrence of gel-fraction happens after the induction period, the value of which depends on temperature (see the Fig. 9).

The process of cross-link bond (C) formation may be presented as follows:

$$\frac{dC}{dt} = K_{\mathrm{cr.l.}} c^n_{\mathrm{a.c}}, \tag{20}$$

where $K_{\mathrm{cr.l.}}$ is the rate constant of cross-linking; $c_{\mathrm{a.c.}}$ is the concentration of active centers in macromolecules; n is the reaction order.

The concentration of the cross-links at the moment of gel-formation (τ_2) is:

$$C_{\mathrm{cr.}} = K_{\mathrm{cr.l.}} c^n_{\mathrm{a.c.}} \tau_2. \tag{21}$$

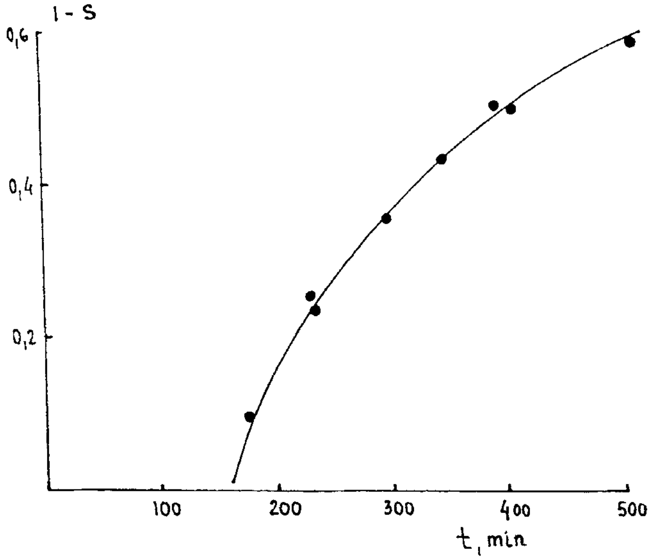


FIGURE 9 Kinetic curve of gel formation during PVC thermoxidative degradation at 180 C in O_2. '1 - S' is the mass part of gel.

The critical concentration of the cross-links required for gel formation is determined by the known Flory expression:

$$C_{\text{cr.}} = \frac{1}{\bar{P}_{w^0}}. \tag{22}$$

Taking into account that most polymers have $(\bar{P}_W/\bar{P}_n) \approx 2$, we obtain the following expression for $K_{\text{cr.l.}}$:

$$K_{\text{cr.l.}} = \frac{1}{2c^n_{\text{a.c.}}\tau_2\bar{P}^0_n}. \tag{23}$$

PVC cross-linking is the second order reaction ($n = 2$) in both concentrated solutions in inert atmosphere and in a solid polymer under vacuum. The temperature dependence of the solid polymer cross-linking is described by the following equation:

$$K_{\text{cr.l.}} = (1 \pm 0.2) \times 10^7 \exp\left(-\frac{125}{RT}\right) \text{s}^{-1}. \tag{24}$$

The activation energy of cross-linking in solutions is ~ 100 kJ/mol [5].

Some authors [5, 115, 116] consider cross-linking as the process proceeding independently on dehydrochlorination, some other [42, 116, 118] think that cross-linking is a secondary reaction with active centers presented by preliminarily formed polyene structures, and the reaction proceeds according to the Dyllce-Alder dyene synthesis.

In the presence of oxygen, cross-linking proceeds simultaneously with the degradation of macromolecules [119–121]. The following equation is used to describe these reactions [122]:

$$S + \sqrt{S} = \frac{W_d}{W_{\text{cr.l.}}} + \frac{1}{W_{\text{cr.l.}} \bar{P}_n^0} \times \frac{1}{t}, \tag{25}$$

here S is a soluble polymer fraction; W_d and $W_{\text{cr.l.}}$ are the reaction rates of degradation and cross-linking of macromolecules, respectively.

Figure 10 shows experimental data of the PVC transformation in Ar and O_2, treated in accordance with equation (25). It is clearly seen that in inert atmosphere the reaction of macromolecule degradation does not take place. The value of W_d in the O_2 atmosphere at 180°C is found $(2\text{–}20) \times 10^{-8}\text{s}^{-1}$ for various industrial PVC samples, and $W_{\text{cr.l.}}$ is $(5\text{–}35) \times 10^{-8}\text{s}^{-1}$ [121].

4. FORMATION OF VOLATILE PRODUCTS AT THERMODEGRADATION

Volatile product yielding at thermodegradation of PVC starts up at temperatures > 210°C. It was shown that the following products are formed: benzene, naphthalene, styrene, toluene, methylnaphthalene [123–125]. The first four compounds are formed in intramolecular reactions, whereas toluene and methylnaphthalene are the products of intermolecular reactions with the transfer of one or two H-atoms.

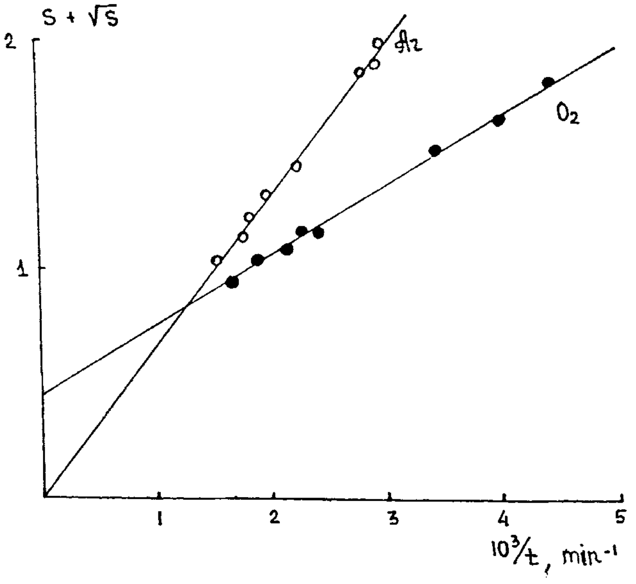
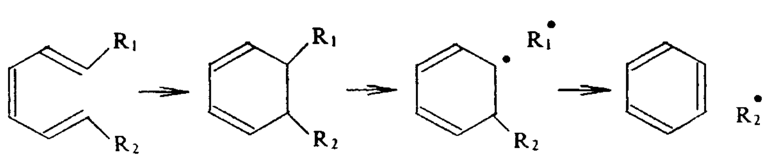
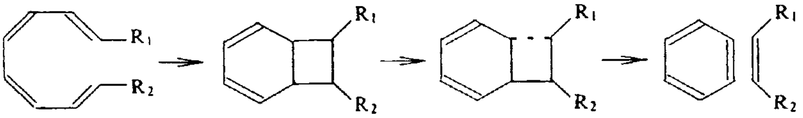


FIGURE 10 Experimental data of gel formation at PVC degradation in Ar and O_2 at 180°C treated in accordance with the equation (25).

Benzene formation is the most well-studied reaction. Figure 11 shows the kinetic curve of this reaction at 180°C in air. The rate of benzene formation is $2.6 \times 10^{-8} s^{-1}$. There are two mechanisms suggested for this reaction [10, 126]:



Then the R_1 and R_2 radicals recombine:



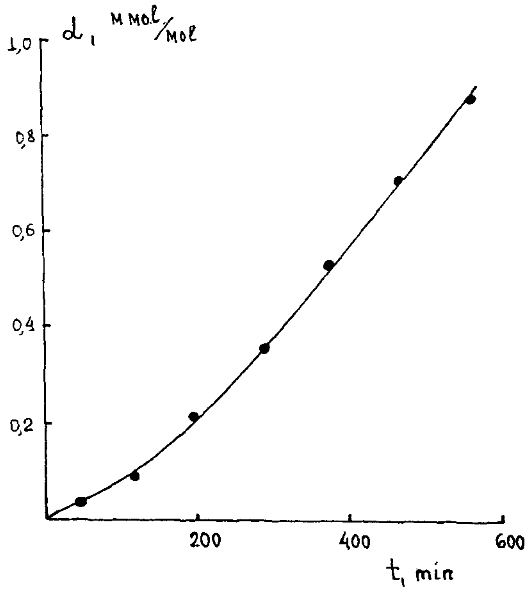


FIGURE 11 Kinetic curve of the benzene formation at PVC degradation in Ar at 180°C.

5. DIFFUSIONAL DESORPTION OF PLASTICIZERS FROM ARTICLES

Processes of a plasticizer diffusional desorption from plasticized PVC have not yet been studied. This should be due to the fact that under real conditions these processes proceed with low rates, dependent on geometrical sizes and construction of an article as well as on its history. It is obvious that these circumstances complicate the comparison of data from different works. We consider it advisable to discuss the existing data according to the following three aspects:

- The dependence of the plasticizer diffusional desorption on the concentration and type of the plasticizer
- The time dependence of the plasticizer diffusional desorption
- The changes of the PVC-plasticizer properties at ageing.

5.1. The Dependence of Plasticizer Diffusional Desorption on Concentration and Type of Plasticizer

The diffusion coefficients of different plasticizers were determined by the gravimetric technique in vacuum [127, 128]. Subsequently, the data were substantiated with the help of the refraction technique, because a correlation ratio exists between the plasticizer concentration and the refraction index [128]. Table X shows the values of the diffusion coefficients of plasticizers at different concentrations and temperatures. Table XI shows the values of the activation energy and constant D_0. It is clearly seen that the diffusion coefficient as well as the diffusion activation energy depend on the plasticizer concentration.

Attempts to derive a quantitative correlation between the value of the evaporized plasticizer and its vapour pressure gave no satisfactory results [129]. In the case of high plasticizer yields it should be due to the controlling role of the diffusion rate of the plasticizer in the polymer [129]. At the same time the comparison of different plasticizers shows

TABLE X Diffusion coefficients of plasticizers in PVC (m^2/s)

Temperature °K	*Average plasticizer concentration, mass %*	*Tri-octyl phthalate*	*Di-octyl phthalate*	*Di-butyl phthalate*	*C_7-C_9 The ester of adipic acid and alcohols*
298	80	3.8×10^{-23}	6.4×10^{-13}	1.9×10^{-12}	–
	60	3.0×10^{-13}	6.2×10^{-14}	4.1×10^{-13}	–
	40	5.0×10^{-14}	–	2.9×10^{-14}	–
313	80	6.5×10^{-12}	1.7×10^{-12}	3.1×10^{-12}	–
	60	1.6×10^{-12}	2.8×10^{-13}	1.3×10^{-12}	–
	40	1.8×10^{-13}	2.4×10^{-14}	2.1×10^{-13}	–
	10	–	–	–	2.1×10^{-15}
333	80	1.3×10^{-11}	3.2×10^{-12}	8.1×10^{-12}	–
	60	4.1×10^{-12}	1.1×10^{-13}	3.8×10^{-12}	–
	40	9.1×10^{-13}	1.1×10^{-13}	1.7×10^{-12}	–
	10	–	2.4×10^{-14}	2.4×10^{-15}	3.0×10^{-14}
353	80	1.8×10^{-11}	6.7×10^{-12}	1.6×10^{-11}	–
	60	6.4×10^{-12}	3.3×10^{-12}	1.3×10^{-11}	–
	40	1.3×10^{-12}	6.1×10^{-13}	3.3×10^{-12}	–
	10	8.7×10^{-15}	6.1×10^{-15}	4.0×10^{-14}	1.3×10^{-13}
373	80	3.0×10^{-11}	1.4×10^{-11}	3.2×10^{-11}	–
	60	1.2×10^{-11}	9.0×10^{-12}	2.3×10^{-11}	–
	40	5.6×10^{-12}	2.1×10^{-12}	1.2×10^{-11}	
	10	5.3×10^{-14}	5.6×10^{-14}	2.6×10^{-13}	7.3×10^{-13}

TABLE XI Diffusion activation energy and diffusion coefficients of plasticizers in PVC

Plasticizer	*Average plasticizer concentration, mass %*	*E, J/mol*	*D_0, m^2/s*
Tri-octylphthalate	80	24.28	7.3×10^{-8}
	60	37.26	2.0×10^{-6}
	40	50.52	4.3×10^{-4}
	10	100.50	5.6×10^{-4}
Di-octylphthalate	80	36.43	1.7×10^{-6}
	60	56.52	6.8×10^{-4}
	40	74.53	5.9×10^{-2}
	10	126	2.3×10^{-4}
Ester of adipic acid and alcohols C_7-C_9	80	36.01	3.5×10^{-6}
	60	47.73	1.1×10^{-4}
	40	65.31	1.7×10^{-2}
	10	85.41	6.2×10^{-1}

the existence of a correlation between the pressure of their vapours and their evacuation from PVC-plasticate [130, 131] (see Tab. XII).

It was stated that the dependences of mass losses (%) vs. the reciprocal of film thickness for certain time periods are follow linear relationships [130, 131].

The character and degree of different plasticizer migration from PVC-plasticates into insulating rubber vulcanisate at room temperature during 26 months were investigated in the work [132]. The results obtained allowed to conclude that better volatile plasticizers migrate easier (see Tab. XIII).

It is seen that the migration of the plasticizer mixture is not an additive value, but is smaller than the one calculated according to the additivity rule.

A quantitative correlation between the effectiveness and mobility of a plasticizer was derived in the work [129]. Plasticizers possessing

TABLE XII

Plasticizer	*Vapour pressure, mm. Hg × 10^6*	*Mass loss after 100 hour exposure at 60°C, %*
Tri-crezylphosphate	8.2	0.6
Di-butylphthalate	1720	26.3
Di-octylphthalate	15.8	1.4
Di-butylsebacynate	326	15.0
Di-octylsebacynate	2.8	0.5

TABLE XIII

Plasticizer	*Migration into rubber vulcanisate, mg/dm²*	*Volatility, mg/dm²*
Di-butylphthalate	390	228
Mesamol	255	169
DOP + DBP (3:1)	215	91
DOP	180	72
TCP + DBP(1:1)	123	72
TCP	0	0

higher effectiveness (decreasing vitrification temperature to higher degree) are characterized by higher mobility (higher diffusion coefficient) in the PVC-plasticates (see Fig. 12).

5.2. Time Dependence of Diffusional Desorption of Plasticizers

Early attempts to develop a quantitative correlation of plasticized of PVC mass loss with ageing failed. For example, the calculation per-

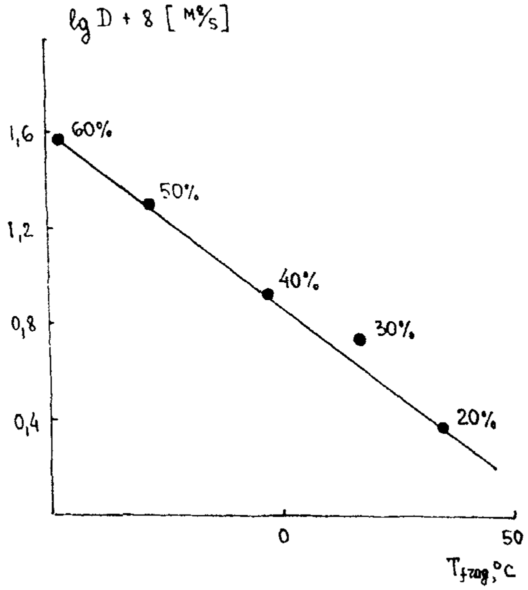


FIGURE 12 Temperature dependence of plasticized PVC embrittlement on diffusion coefficient of tri-crezylphosphate.

formed by Read and Connor [130] that gave 1/4 decrease of dibutylphthalate mass during 500 days of exploitation is disproved by the exploitation practice.

Systematic study of the process of di-octylphthalate diffusional desorption from plasticized PVC at its contact with different soils are shown in works [133–136]. By solving the second Fick equation under the supposition that the stationary flow with the constant concentration gradient is set at a certain time, the dependence of the plasticizer amount desorbed from the covering on time t was obtained:

$$m=\frac{Kd(12Dt-d^2)}{24D}+\frac{4Kd^3}{D\pi^4}\exp\left(-\frac{\pi^2 Dt}{d^2}\right)(\mathrm{mg/cm^2}), \qquad (26)$$

here K is a constant value dependent on the nature of the low molecular plasticizer and the covering material; D is the diffusion coefficient (mg/dm^2); d is the covering thickness (cm).

The expression obtained describes quite well the kinetics of the desorption process for comparatively long times. The process rate is low under soiling conditions: after 10 years in the soil the double-layered PVC covering displayed 2–3% of the plasticizer (DOP) loss in the upper layer (in contact with the soil). The layer in contact with the metal (pipe subjected to insulation) showed no change of the plasticizer amount.

The work [137] describes another attempt to establish the time dependence of the plasticized PVC mass loss, induced by the diffusional desorption of the plasticizer by solving the second Fick equation at border condition $c=0$. However, as the supposition that $D=\mathrm{Const}$ is not correct in this case, the results obtained are in contradiction with the actual data. For example, exploitation times until a definite loss of the initial resistance to cold differ by an order of magnitude.

5.3. Changes of Plasticized PVC Properties with Ageing

The change of plasticized PVC properties at ageing is reflected by the Boyer scheme [129] (see Fig. 13). Many studies are devoted to the investigation of changes in electrical, mechanical and thermal properties of plasticized PVC-plasticates during use under different conditions [138–147].

It was shown [138] that the mechanical characteristics and resistance to cold abruptly decrease during use of articles having plasticized PVC as insulating material.

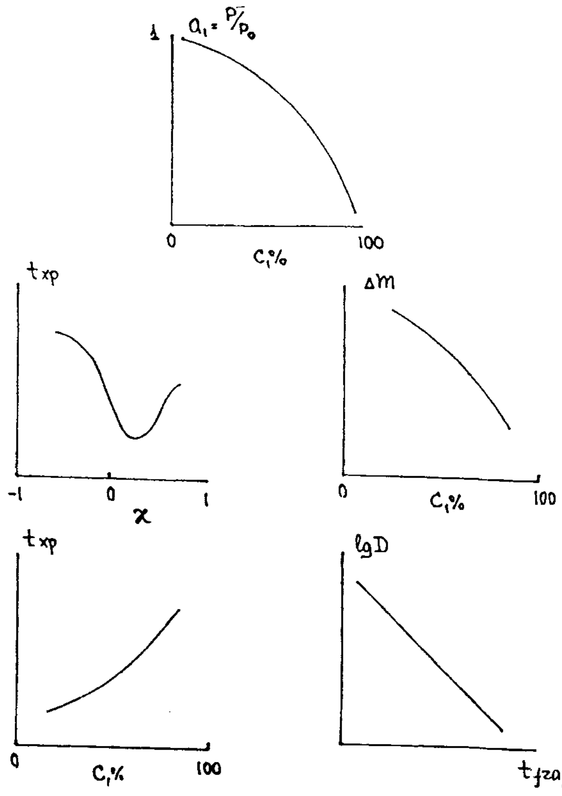


FIGURE 13 The connection between compatibility, effectiveness and mobility of plasticizer.

Similar results are shown in the work [139]. Unfortunately, the authors of works [138–139] limited consideration by phenomenology only, and did not perform the analysis of plasticizer content and changes in PVC.

The work [140] stated that at polyethylene contact with plasticized PVC the process depends on initial concentration of plasticizer in the system. The dependence of migration on plasticizer concentration is of S-form with its linear part in the range of 15–35% of plasticizer concentration. Such character of dependence is explained by authors by partial plasticizer solvation by highly filled polymer. The migration value decreases with the growth of polyethylene crystallinity [141].

When plasticized PVC is in contact with liquid media, the extraction of plasticizers is considered, although two processes of interdiffusion proceed in this case.

General view of mathematical description of such a process was given in the work [142]. High effectiveness of low masses was obtained in investigation of extraction of DBP and DOP plasticizers by different oils. In this case larger amounts of oils diffuse into the plasticized polymer containing DOP plasticizer than DBP [143]. Similarly to the effect of the diffusion coefficient increase with plasticizer concentration growth the increase of the extraction rate with plasticizer concentration growth is observed.

Similar investigation of food oils applied to extraction of DBP and DOP from PVC-plasticate composition [144] allowed to obtain their effectiveness growth in the sequence as follows: olive oil < cotton oil < soy-bean oil. It was found that DOP is extracted faster than DBP.

The following empyric dependence of plasticizer extraction degree was obtained for this case,

$$\alpha^a = \sqrt{C_n^{\infty} M b^{-1}}, \tag{27}$$

here α is the extraction degree; C_n^{∞} is the limit plasticizer concentration; M is plasticizer molecular mass; a and b are coefficients.

The resistance of PVC composites to benzene [129], diesel petrol [146] and other media [147] have also been investigated.

The following empiric dependence of vitrification temperature change during ageing of plasticized PVC in contact with soils was proposed in the work [133]:

$$T_{\text{vitr}} = \frac{RT}{(a - C_0)} \times \frac{Kd\left(12.182\pi^4 d^2 - \pi^4 d^2 + 87.6 d^2 \exp\left(-\frac{\pi^2 Dt}{d^2}\right)\right)}{24.36\pi^4 D m_0}, \tag{28}$$

here a and C_0 are constants.

The process of cracking as the terminal stage of PVC ageing was considered following the ideas proposed by Zhurkov. The following equation was suggested for the rate of crack growth when the material reaches vitrification state:

$$V = \eta A \exp\left(-\frac{B - c\sigma}{RT_{\text{vitr}}}\right), \tag{29}$$

here η, A, c are constants; σ is total tension in the sample; T_{vitr} is temperature of the surrounding equal to vitrification temperature.

The time for a complete crack to form in the covering is determined by the following formula:

$$\tau = \frac{d}{\eta A \exp\left(-\dfrac{B - c\sigma}{RT_{\text{vitr}}}\right)}, \tag{30}$$

here d is the material thickness at which the catastrophic growth of crack is initiated.

It follows from the above mentioned data that the main result of the change of plasticizer concentration in plasticized PVC during ageing is the increase of vitrification temperature.

6. RADIATION AGEING OF POLYVINYLCHLORIDE

The treatment of polyvinylchloride with ionizing radiation induces dehydrochlorination accompanied by cross-linking and degradation [148]. At low temperature single-unit double bonds are formed. At room temperature, however, the dehydrochlorination displays a chain character and, as a result, conjugated double bonds are formed.

Degradation degree is lower at radiation treatment in vacuum than in air [149–150]. Radiation-chemical yield of the cross-linking of polyvinylchloride is found higher at polymer radiation in some solvents than in solid state. At radiation in air [151] degradation in nonplasticized polymer proceeds faster than in plasticized one. Apparently, this is connected with the difficulty in polymer radical recombination in more rigid nonplasticized material. Some plasticizers (tri-creotylphosphate, phenyl-di-creotylphosphate) display protective effect on polyvinylchloride at radiation treatment.

If nonsaturated monomers of complex polyesters are introduced, the yield of radiation-chemical linking increases [152]. Adding of tri-allyl ester of cyanuric acid to polyvinylchloride abruptly decreases radiation dose required for obtaining materials with higher thermoresistance and resistance to solvent influence [153]. Radiation doses required for formation of nonsoluble fraction in polyvinylchloride mixture with tri-allylcyanurate (the ration is 90 mass parts to 10 mass parts) decrease from 30 to 0.5 mrad if compared with the initial polyvinylchloride.

Some plasticized PVC become more rigid under radiation influence, their modulus of elasticity increases [154–156], where the relative change of strength at elongation proceeds in the same way as in nonplasticized polymer. The structure of compositions significantly influences their sensitivity to radiation. At radiation treatment of polyvinylchloride plasticized by di-2-ethylhexylphthalate in presence of different stabilizers the stability to break in tension and relative elongation decrease monotonously, and at 78 mrad dose it reaches one half of the initial value. In this case gel-fraction content reaches 55%. Significant difference in actions of different stabilizers was not found [157]. However, tin-containing stabilizer was found more effective filler in presence of $CaCO_3$ comparing with cadmium or barium compounds [158].

Changes in mechanical and electrical properties of plasticized polyvinylchloride of different types were investigated in [159].

It was found that the resistance to break is significantly decreased in the dose range between 5 and 50 mrad, and the elongation at break monotonically decreases in the entire investigated dose range. The changes in resistance to break become larger with compositions containing large amounts of plasticizers. The volume resistivity is also very sensitive to radiation dose. At 150 mrad, it is reduced to 3–37% of its initial value in dependence of the plasticized compositions. Water absorption of plasticized PVC increases markedly in the radiation doses between 1–40 mrad. This is attributed to chemical changes of polymer involving oxidation caused by ionizing radiation in the presence of oxygen [159].

CONCLUSION

The background presented in this article allows us to select a set of characterization techniques required to follow the chemical and physical changes in plasticized PVC which take place in use. These data in turn are required for predicting the lifetime of plasticized PVC wire coatings and articles made with this polymer system. Similarly, the residual lifetime of plasticized PVC articles which have been in use for sometime can also be determined. The methodology which we developed for this purpose will be presented in the second part of this article.

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