

Chapter 16

POLYURETHANEISOCYANURATE POLYMERIC MATERIALS

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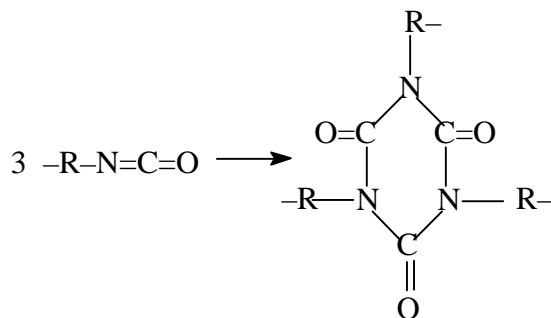
ABSTRACT

Polymeric materials based on Poly(oxypropyleneglycol), 2,4-toluenediisocyanate, and di-(3-chloro-4-aminophenyl)methane have been prepared. Materials mentioned above possess elastic behavior and its modulus of elasticity vary from 3.6 to 1250 MPa. It is evident that the polyurethaneisocyanurates prepared by us possess good physico-mechanical and physico-chemical.

Keywords: polyurethane isocyanurates, diisocyanate, isocyanurate ring, elasticity modulus, specific impact strength

Elastic polymeric materials derived from polyoxypropylene glycol, aromatic diisocyanates (MDI, TDI), and aromatic diamine possessing elasticity modulus in the range of 3.6 – 1,250 MPa were synthesized and studied [1 – 3]. The basis for the process of these networks synthesis is polycyclotrimerization of bifunctional monomer (diisocyanate) and an oligomer with end isocyanate groups. This reaction allows for formation of a network with trifunctional isocyanurate rings, produced in the interaction of three isocyanate groups:

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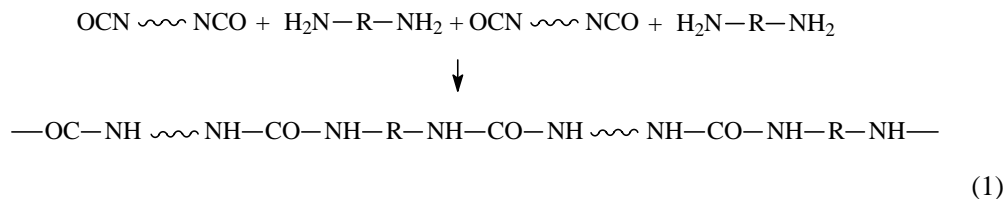


The reaction between macrodiisocyanate and aromatic diamine (di(3-chloro-4-aminophenyl)methane) was also used. Chemical structure of this network depends on the ratio between rigid bulky triisocyanurate crosslinked points and flexible linear fragments linking them. The products have different properties with respect to the ratio between crosslinked points and flexible chains.

Oligomeric diisocyanate (macrodiisocyanate) OEC was synthesized according to technique described in [2]. The progress of the reaction was controlled using IR-spectroscopy method by the band intensity at $2,280 \text{ cm}^{-1}$ and the bands of hydroxyl groups at $3,500 - 3,600 \text{ cm}^{-1}$ [4]. The quantity of isocyanurate groups (%) was estimated by their reaction with dibutylamine, which excess was titrated by an acid [5]. Resulting the reaction, formation of urethane groups absorbing in the range of $3,300 - 3,400 \text{ cm}^{-1}$ was determined from IR-spectrum [6]. OEC was synthesized as a viscous colorless liquid (at room temperature); $n_D^{30} = 1.4711$, $\rho = 1.057 \text{ g}\cdot\text{cm}^{-3}$.

For synthesizing polyurethane-isocyanurate networks possessing a wide controllable range of properties the methods of polycyclotrimerization and migration polymerization were applied. At the second stage of the process, OEC produced was mixed with variable TDI quantity, added with DMBA and ED-22 based amino-epoxide catalyst and variable quantity of diamine. As a result of catalytic interaction of isocyanate groups which enter into the composition of OEC and TDI, a 3D polyisocyanurate network structure representing a transparent gel, insoluble in acetone, was formed [2].

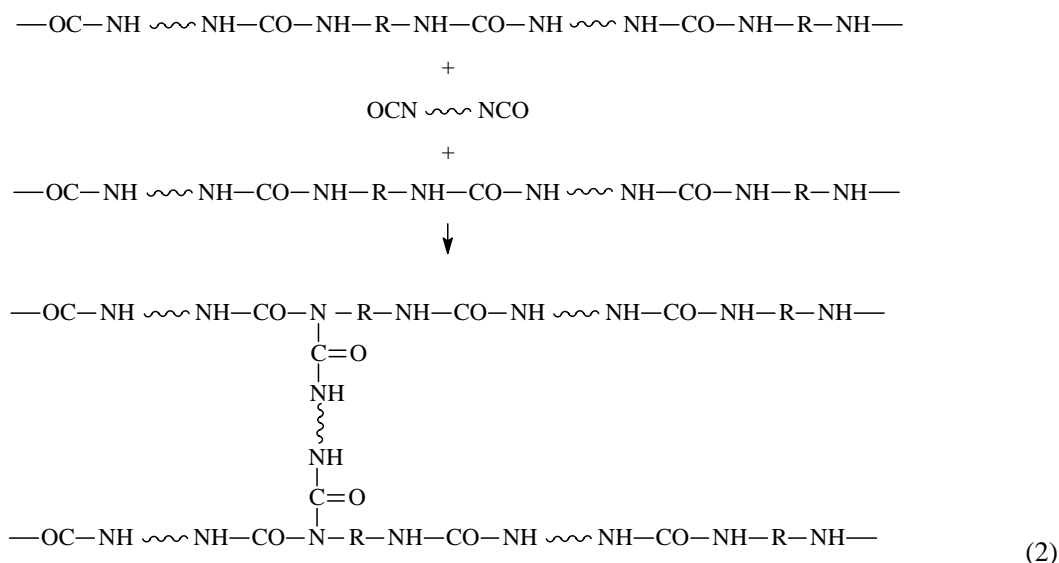
In its turn, MDC interaction with diamine first produced linear polyurethane urea, which was confirmed by spectroscopic data on the band intensity at $1,550 \text{ cm}^{-1}$ [6, 7]:



where $\sim \sim \sim$ is macrodiisocyanate molecule.

Excessive MDC not entering into the reaction induced the chain crosslinking. At such crosslinking and temperature increase above 100°C MDC was added by preliminarily formed

uric bonds, which are reactive enough in relation to diisocyanate groups. As a result, one more bond type – biuretic, occurred in crosslinked rubbers:



It is found that in spectra of polymers synthesized the bonds are present, typical of allophanate structures ($1,310 \text{ cm}^{-1}$) [6]. This testifies about high probability of the reaction between urethane group and isocyanate at temperature increase to $120 - 140^\circ\text{C}$ during synthesis of polyurethane isocyanurate materials under selected conditions.

The reactions of urea interaction with isocyanate and urethane group with isocyanate are very important for synthesis of polyurethane isocyanurate materials, because they induce formation of branched and crosslinked structures in polyurethanes. As is known, these structures are hard-wearing. These reactions are slowly proceeding (during 5 – 6 h), but are suitable because of required temperature level, equal to polyisocyanurate synthesis ($120 - 140^\circ\text{C}$), also usually applied in the industry.

The behavior of samples derived from polyurethane isocyanurate networks under conditions of thermomechanical and TGA analyses were considered. Figure 1a shows thermomechanical curves of seven samples containing different quantity of polyurethane (PU) component and TDI, also differing by the elasticity modulus values.

As found in previous observations [8], polyisocyanurate networks display two transitions with respect to their composition: the first is low-temperature transition associated with devitrification of the rubbery phase, and high-temperature related to devitrification of the glassy phase. Hence, both transitions are temperature-shifted towards one another, and the progress of such shift depends on the microphase composition. Therefore, Figure 1b presents separately thermomechanical curves of polyurethane isocyanurate samples related to the low-temperature area.

For a network polymer composed only by PU or containing the greater quantity of it (80 wt.%) (Figure 1b, curves 1 and 2), an increase of low-temperature transition temperature is insignificant, because the rubbery phase contains a small quantity of TDI residues. Vice versa, in a plastic sample with lower PU content or its full absence and consequently higher

TDI content, such shift is rather intensive. As a result, the low-temperature transition for the system containing no TDI is displayed at $\sim -50^\circ\text{C}$, whereas for the sample with 60 wt.% TDI (Figure 1b, curve 7) is occurs at $+50^\circ\text{C}$. Concerning the high-temperature transition, for the low-modular sample (Figure 1, curves 1, 2) it is observed at $150 - 190^\circ\text{C}$. Meanwhile, as TDI content in the sample increases (the content of polyisocyanurate – PIC – component increases), the transition happens at higher temperatures of about $320 - 330^\circ\text{C}$.

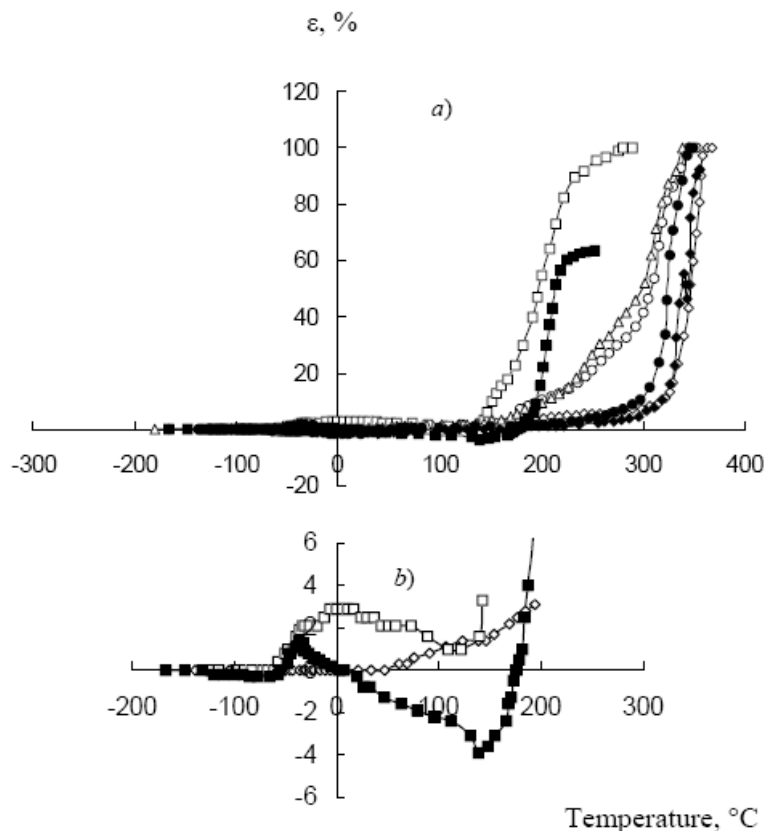


Figure 1. Temperature dependence of deformation of polyurethane isocyanurate polymeric materials. The material contains PU composites in amount of 100(1), 80(2), 60(3), 50(4), 40(5), 20(6), and 0 wt.%(7)

The comparative analysis of thermodynamic (Figure 1) and TGA curves (Figure 2) shows that for all samples, the initiation temperature of intensive thermal degradation falls in the range of $320 - 330^\circ\text{C}$. This means that for low-modular samples, high-temperature transition observed at $180 - 190^\circ\text{C}$ is not related to thermal degradation of the polymer. On the contrary, for high-modular samples, this transition is observed at the temperature, at which intensive thermal degradation proceeds. Therefore, it may be suggested that deformability of synthesized high-modular network systems is associated with degradation processes, proceeding in these systems at high temperatures. Therefore, in the systems such as high-modular polyurethane isocyanurates, heat resistance is limited by their thermal stability.

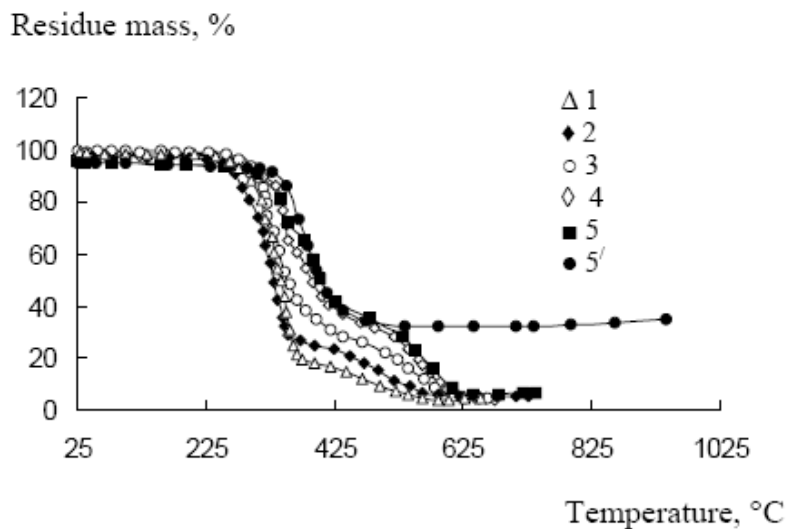


Figure 2. TGA curves for polyurethane isocyanurate polymeric materials in air (1 – 5) and in argon (5'). The material contains the following quantities of PU composites: 100 (1), 80 (2), 50 (3), 20 (4), and 0 wt.% (5, 5')

The increase of PIC concentration in the composite raises thermal stability of the polymer so higher, the higher TDI concentration is (Figure 2, curves 1, 5). Comparing with PU containing no TDI, the PIC composite with 60% TDI possesses temperature on intensive thermal degradation by 40°C higher. In the inert medium (argon), temperatures initiating weight decrease and intensive PIC degradation are not increased compared with degradation in the air (Figure 2, curves 5, 5'). However, degradation in argon gives much higher coke residue.

Thus, according to TGA and TMA data., it is possible to estimate the temperature interval, in which polyurethane isocyanurate polymers may operate without significant softening and degradation. For low-modulus polyurethane-isocyanurates, this range runs from –50 to 190°C, and for high-modulus composites it may reach 330°C.

We have also studied the influence of the PU/PIC ratio on physicomachanical properties of synthesized polyurethane isocyanurates. As would be expected (Table 1, n. 6), the highest specific impact viscosity (up to 12 kg×cm/cm²) is typical of a polymer, in which isocyanurate crosslink points of the network are linked by flexible polyurethane networks containing propylene oxide groups. Therefore, the higher PU concentration and, correspondingly, the lower TDI concentration is in relation to OEC in the initial composite, the higher specific impact viscosity is, or the material is not degraded at all, but bends during tests on “Dynstat” device. However, such indices as bending strength and elasticity modulus reach their minima. In its turn, the elasticity modulus reaches its maximum in the polymer with the maximal PIC concentration, which contains the maximal quantity of aromatic diisocyanate (Table 1, n. 1–3). Injection of different fillers to initial composites for the purpose of synthesizing polyurethane isocyanurate polymeric materials leads to changes in values of elasticity modulus, specific impact viscosity, and bending strength. For example, injection of 5 wt.% TiO₂ at 50 wt.% TDI concentration in the initial reaction mixture (Table 1, n. 2), specific impact viscosity is 5-fold increased. However, in the absence of TiO₂ and at 60 wt.% TDI

concentration specific impact viscosity is much lower (Table 1, n. 1). The injection of technical carbon in amount of 2 wt.% also 2-fold increases specific impact viscosity of the samples. The injection of the above-mentioned additives also increases elasticity modulus of the samples.

Table 1. Physicomechanical properties of polyurethane isocyanurate polymeric materials

No	PIC:PU, wt. %	Elasticity modulus (E), MPa	TDI content in the mixture with OEC in PIC composite, wt. %	Specific impact viscosity, kg·cm/cm ²	Bending strength, kg/cm ²
1.	PIC (without filler)	1185	60.0	1.04	771
2.	PIC (with TiO ₂)	1250	50.0	5.6	718.3
3.	PIC (with technical carbon)	1314	60.0	2.0	240.0
4.	80:20	517	48.0	3.9	232.5
5.	60:40	293	36.0	8.9	183.8
6.	50:50	127	30.0	12.0	30.0
7.	40:60	21.7	24.0	Does not degrade	27.8
8.	20:80	14.4	12.0	Does not degrade	12.8
9.	PU	3.9	0	Does not degrade	10.8

Note that polyurethane isocyanurate samples containing a great PU quantity and having elasticity modulus value falling in the range between polymeric glass and rubber, display elastic rather than viscoelastic behavior, which is typical of all known polymers present in the transition zone from the glassy to the rubbery state. In this connection, to analyze the type of mechanical behavior of synthesized polyurethane isocyanurate materials, relaxation curves for different values of elasticity modulus were calculated. The stress relaxation curves were composed in relative stress – time coordinates. The relative stress was calculated as σ_i/σ_0 , where σ_i is the current relaxing stress; σ_0 is the initial stress developed at the end moment of deformation setting. As observed from the Figure, currently synthesized polymeric materials show an abrupt stress reduction at the initial stage of relaxation with further transition to extremely low stress relaxation. It is also important that the composition of current materials is significant for the progress of relaxation curves of relative stresses, σ_i/σ_0 .

The estimation of water effect on synthesized polymeric materials (Table 2) indicated insignificantly higher water absorption and water absorption rate of low-modular polyurethane isocyanurate polymeric materials compared with high-modular ones. The oil resistance of high-modular samples reaches 0.15%. This value is so higher the higher PU concentration in the initial composite for the synthesis of polyurethane isocyanurates is.

Table 2. Physicochemical properties of polyurethane isocyanurate polymeric materials

No	PIC:PU wt.%	TDI content in the mixture with OEC in PIC composite, wt.%	Water absorption capacity ($B \cdot 10^4$), g/dm ²	Water absorption rate ($W \cdot 10^4$), g/dm ²	Oil resistance during 24 h, %	Fire resistance
1.	100	50	2.2	2.09	0.15	*
2.	80:20	40.0	2.35	2.12	0.34	The same
3.	60:40	30.0	2.40	2.27	0.65	The same
4.	50:50	25.0	2.67	2.45	1.6	The same
5.	40:60	20.0	2.73	2.55	2.85	**
6.	20:80	10.0	2.89	2.83	40	The same
7.	100	0	3.03	2.92	80	The same

* The sample weakly combusts longer than ¼ minute still.

** The sample highly combusts longer than ¼ minute still.

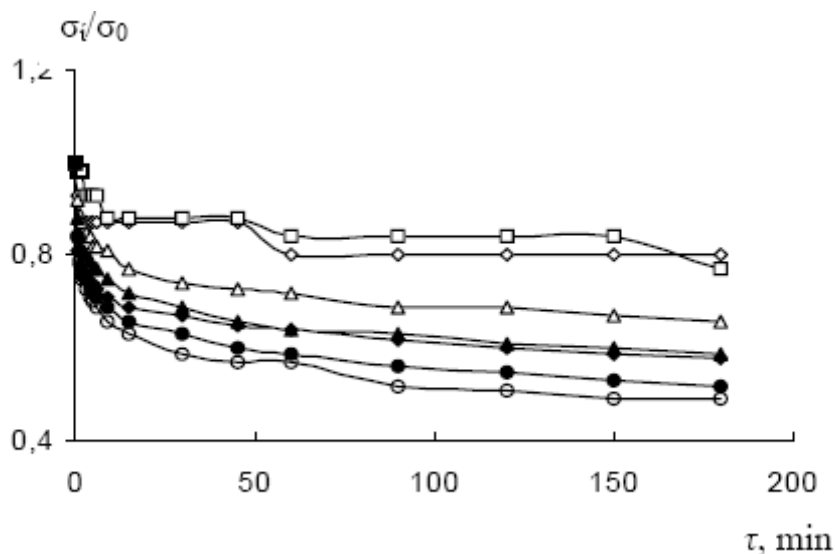


Figure 3. Relative stress relaxation curves for polyurethane isocyanurate polymeric materials. The materials contains PU composite in amounts: 100 (1), 80 (2), 60 (3), 50 (4), 40 (5), 20 (6), and 0 wt.% (7)

Finally, oil resistance of the elastic part reached 80%. After 24 h exposure to an oil product, low-modulus samples swell and crack. Fire resistance tests carried out by the technique described in [9, 10] showed their combustion time over 1/4 min.

Thus, thermal and heat resistance, as well as physicochemical and physicochemical properties of high-modulus and low-modulus polyurethane isocyanurates, synthesized by OEC and TDI polycyclotrimerization and migration MDC polymerization with diamine were studied. The influence of the ratio of these components on the mentioned properties is also studied. It is shown that polyurethane isocyanurates synthesized in the selective reactions of polycyclotrimerization and polymerization possess quite high physicochemical and physicochemical properties.

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Chapter 17

THE ESTIMATION OF OPPORTUNITIES OF LOW-TEMPERATURE DESTRUCTIONS OF SYNTHETIC RUBBERS IN SOLUTIONS IN RECEPTION OF HALF-FINISHED PRODUCT FOR FINISHING COMPOSITIONS

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ABSTRACT

The opportunity and expediency of use of catalytic and oxidizing destruction of synthetic rubbers in solutions reactionary compounds in quality of half-finished product are confirmed at reception with getting several finishing compositions. Many factors of influence on oxidative-destructive transformations of the various marks of rubbers, favorable for realizations of the specified opportunity are identified and characterized.

Keywords: Rubbers, Solutions, Reactionary Compounds, Catalytic Destruction, Oxidizing Destruction in Solutions, Finishing Compositions, Factors of Influence, Reception, Management of Process.

The oxidative-destructive transformations of synthetic rubbers (SR) in solutions allow to receive reactionary compounds with various qualitative and quantitative functional structures of products (Table. 1).

It has been found [1,2], that the structure of a final reactionary compound is a direct function of many conditions of carrying out oxidative -destructive transformations. In particular:

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- the nature of rubber (natural, butadiene rubber, styrene-butadiene rubber (SBR), methylstyrene-butadiene rubber (MSBR), isoprene rubber (IR), butyl rubber (BR), etc.);
- the nature of the solvent used (white-spirit, solvent, xylene, spirits, a mix of spirits and ketons);
- the conditions of preliminary reception of a solution and the contents of rubber in it (in a range of 5-15 % mass);
- the carrying out a full or partial dissolution SR directly in a reactor for oxidative-destructive transformations;
- the degrees of overlapping of dissolution SR and its oxidative-destructive transformations, and also duration of such a period;
- the nature, quantity and a phase condition of the catalyst or specially picked up catalytic systems;
- the type of the reactor used, the hydrodynamic conditions in it and the dynamics of change of the last in the course of the process;
- a temperature mode of a process carrying out (in most cases not isothermal);
- the organizations and quantitative characteristics of air bubbling or other kinds of contact of a reactionary compound with it;
- a choice of the moment of the oxidative-destructive process discontinuance and carrying out stabilization of the reactionary compound obtained;
- of some other individual factors in particular cases.

Table 1. The ranges of contents of the nonlimiting and oxygen-containing products in the final reactionary compounds, received at destructive oxidation SRS-30 in white-spirit at temperature $90 \div 105$ °C

Connections	A range of content in mole/kg of a initial firm rubber	A range of concentration in mole/kg of a reactionary compound
Peroxide	0,20÷0,50	0,01÷0,08
Nonlimiting	3,00÷23,00	0,25÷2,76
Carbonyl	0,50÷4,30	0,05÷0,45
Spirits	0,50÷9,00	0,05÷1,40
Acids	0,20÷0,68	0,01÷0,08
Epoxy	0,14÷0,23	0,02÷0,03
Hydrolyze	0,60÷8,80	0,03÷1,25

The examples of kinetic curves of change of a liquid phase viscosity and accumulation of the separate products of transformation are shown in Fig. 1 and 2. It is well seen, that the process mostly begins with some, sometimes a small induction period, removable by the period of the autoaccelerated development, achievement of the maximal speed and the subsequent fading. Thus as a rule there is a maximum on the kinetic curves of accumulation of functional groups, which time characteristics for separate functional groups are different. It allows to use time of the discontinuance of oxidative -destructive process as an important factor of management of the received products structure.

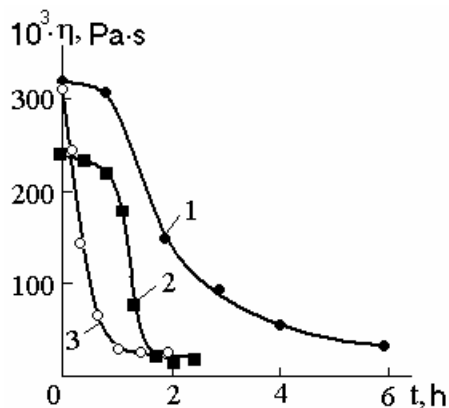


Fig. 1. Kinetic curve of changes of a reaction-ary compound dynamic viscosity at oxidative-destructive transformations (1,3) and catalytic destruction (2) of 13,7 % and 13 % solutions of SBR-30 in white-spirit at 100 °C in a reactor with pneumatic (1) and mechanical (2,3) hashing (1440 rev/min)

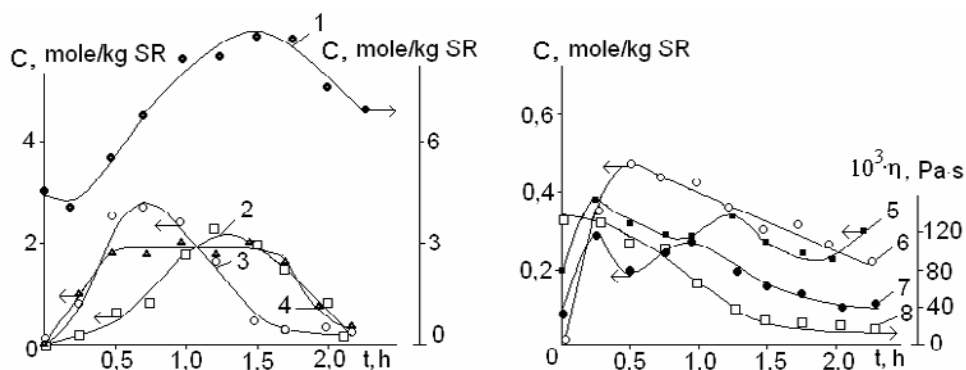
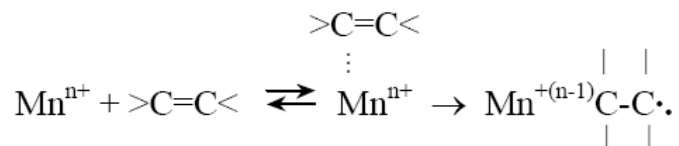


Fig. 2. The kinetic curve of accumulation of the nonlimiting (1), carbonyl (2), hydroxyl (3), hydrolyze (4), peroxide (5) and epoxy (6) connections, the sums of acids and per acids (7) related to unit of content of the nonvolatile components of the system (C , mole/kg SR) and also a change in time of a dynamic viscosity of a reactionary compound (8) at oxidative-destructive transformations of 12 % solution of SBR-30 in white-spirit at 100 oC, mechanical hashing (380 rev/min) and the discharge of air 0,2 l/min·kg at the presence 10-3 mole/kg of manganese (II) naphthionate as catalyst

The oxidative -destructive transformations, the liquid-phase oxidation of olefins, the oxidizing and catalytic destructions proceed in accordance with chain radical mechanism with origin of chains with the participation of the catalyst. One of variants of the latter is the reaction between the manganese-containing heterogeneous catalyst and olefins, having trailer double bond [1]:



The following values of speeds of chains origin have been received by a method of inhibitors for catalytic destruction of 7 % solution of SBR-30 in white-spirit at 95 °C at the presence of 10^{-3} mole/kg of manganese (II) salts in a metal reactor at mechanical hashing (1440 rev/min) [3]: $(0,6\div 4,0)\cdot 10^{-6}$ mole/l·s (for resinate at use quinone and hydroquinone); $(0,8\div 5,0)\cdot 10^{-6}$ mole/l·s (for naphthionate at use quinone and hydroquinone); $(0,4\div 5,0)\cdot 10^{-6}$ mole/l·s (for benzoate at use quinone and hydroquinone); and for catalytic destruction of 10 % a solution of butyl rubber (BR) in white-spirit in the same conditions: $4,4\cdot 10^{-6}$ mole/l·s (for stearate manganese at use quinone). The following values of speeds of chains origin have been received for oxidative-destructive transformations of 10 % solution of SBR-30 in white-spirit at 90 °C at the presence of 10^{-3} mole/kg of manganese (II) salts in a metal reactor with rabble (380 rev/min) and the charge of air 0,25 l/min·kg: $(1,4\div 2,6)\cdot 10^{-6}$ mole/l·s (for resinate at use quinone); $(2,6\div 4,2)\cdot 10^{-6}$ mole/l·s (for resinate at use hydroquinone); $(1,4\div 2,0)\cdot 10^{-6}$ mole/l·s (for resinate at use of iodine); $(2,0\div 3,4)\cdot 10^{-6}$ mole/l·s (for benzoate at use quinone); $(2,8\div 4,0)\cdot 10^{-6}$ mole/l·s (for benzoate at use hydroquinone); $(2,0\div 2,5)\cdot 10^{-6}$ mole/l·s (for benzoate at use of iodine). They are in good conformity with the data, available in the literature for modeling reactions, considered type [4-6].

The optimum interval of temperatures for the considered oxidative-destructive transformations is 90÷105 °C. The growth of viscosity of a solution affects at lower temperatures, that results in different reduction of process speed. At higher temperatures (120÷130 °C) the catalyst loses activity as a result the intensive system dehydration with partial loss by salts of their crystallized waters, and also as a result the transition of the basic salts in average, in particular as a consequence of oxidation of system reducers by manganese (III) and (IV) salts. The waterless manganese (II) salt dissolved better in tens times. In a result more often more active in considered systems the heterogeneous catalyst of destruction disappears and concentration of the homogeneous catalyst more effective already for polymerization processes grows.

Qualitative and quantitative comparison of the kinetic characteristics of the processes of catalytic destruction butyl rubber (BR), SBR-30, butadiene rubber and isoprene rubber (IR) in solutions of white-spirit at the presence of manganese (II) salts has been carried out [3]. Many analogies take place in the qualitative plan, but quantitative characteristics are predetermined by nature SR in the greater degree. SBR-30, butadiene rubber, IR destroy easiest. Destruction BR, which is characterized by the least compared by the contents in a polymeric molecule of isolated multiple bonds, proceeds with the least speed.

In the course of process of catalytic destruction SR in solutions there are strong changes of molecular-mass distributions of destruction products, that through respective alterations of structure of a reactionary compound affects its physical characteristics. In most cases kinetics of viscosity changes has been submitted monotonously decreasing curve (fig. 1), though there are variants linear (SBR at rather low quantities of the catalyst), step (BR) and even extreme (with a minimum) character. It is a consequence of that in considered system processes of condensation develop alongside with destruction, and competing ability of these chemical transformations in the course of process can vary in very wide limits. In case of catalytic oxidative-destructive transformations there are even more essential changes in functional structure of reactionary compounds as a result of the parallel with destruction courses of liquid-phase oxidation of destruction products.

Influence of the nature and quantity of the catalyst, and also concentration SR in an initial solution on duration of process and structure of products in reactionary compound has been appreciated. Examples in this plan are submitted on Fig. 3 and in Table. 2 [1].

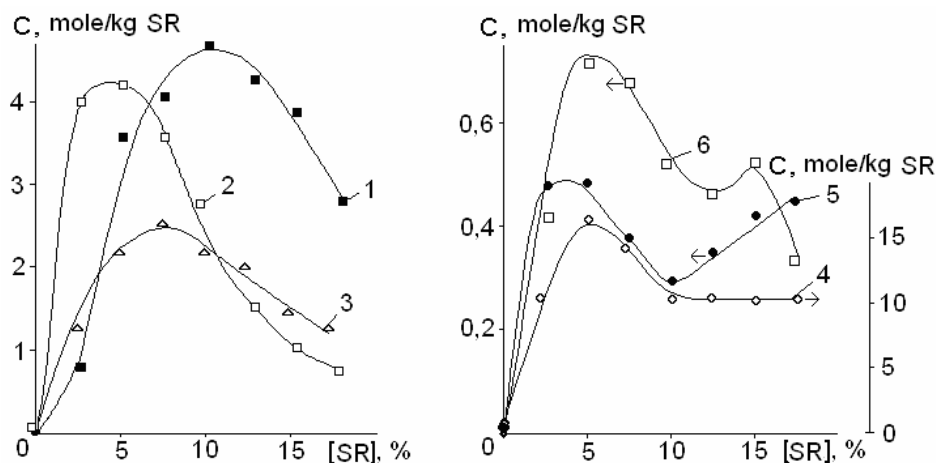


Fig. 3. The maximal yield of the hydroxyl (1), carbonyl (2), hydrolyze (3), non-limiting (4) and peroxide (5) connections, the sums of acids and per acids (6) related to unit of content of the nonvolatile components of the system (C, mole/kg SR) depending on mass content of SBR-30 in initial loading at its oxidative-destructive transformations into a solution of white-spirit at 100 °C, mechanical hashing (380 rev/min) and the discharge of air 0,33 l/min·kg at the presence 10^{-3} mole/kg of manganese (II) stearate as catalyst

Table 2. As many as possible achieved yields of the basic products of oxidative-destructive process in dependence upon nature used for creation catalytic systems of transitive metal salts

A salt of a transitive metal besieged from the water environment	A maximal yield of the products, mole/kg SR			
	Nonlimiting connections	Spirits	Carbonyl connections	Hydrolyze connections
manganese stearate	22	9,0	1,4	7,0
manganese resinate	18	5,1	1,1	7,3
manganese benzoate	20	2,8	4,0	7,6
manganese naphthionate	10,0	3,4	3,0	5,0
copper stearate	10,5	5,0	1,4	8,8
cobalt resinate	22	9,0	1,2	8,0
cobalt naphthionate	21,5	6,0	4,0	6,0
lead resinate	23	3,4	3,3	2,2

On the basis of results of preliminary executed research, some final reactionary compounds, representing solutions, a mix of the limited soluble in each other solutions or rather proof emulsions of products of destructive and oxidative-destructive transformations SR into hydrocarbonic solvents has been offered to use as target finishing compositions and half-finished product for them without additional operations concentration, divisions. Thus, in particular, technologies of reception have been developed:

- butyl-rubber drying oils and paints through a stage of destructive oxidation butyl rubber in a solution of white-spirit [7];
- oil-butyl-rubber drying oils and paints through a stage of joint oxidation at $95\div 105$ °C oxidized of butyl rubber, sunflower oil and terpene oils in the ratio on dry substance 1:0,5:1,5 [8];
- oil-rubber siccative-free drying oils, paints and enamels by one-phasic joint oxidation SR such as SBR, MSBR, butadiene rubber, IR in solvent with terpene oil and sunflower oil in the ratio on dry substance 1:1,5:0÷0,5 in an interval of temperatures $90\div 105$ °C [9];
- rubber varnishes for rubber footwear through a stage of catalytic destruction of SBR-30 solution in white-spirit in an interval of temperatures $90\div 105$ °C [10].

The operational experience gained has allowed to formulate recommendations on the storage of the obtained film-forming bases. The degree of destruction is one of the major factors, determining their safety. The reactionary compound representing a solution or a mix of solutions of products of transformation in hydrocarbonic solvents, in which are metal-containing the connections, capable to sedimentation at upholding, as suspension, are most stable. And the quantity gone into a solution metal-containing connections should be as small as possible, as further they favour development and course of processes of structurization. At big degrees of oxidative-destructive transformations the reactionary compound from a solution passes in emulsion, i.e. becomes a less stable system. Hence, it is possible to count a degree of destruction limited, predetermining transition of system from solution to emulsion. It means, that the duration of a process is the way of management not only functional structure and consumer properties, but also stability of obtained final reactionary compounds.

Strong deviations from an optimum mode of course of reception of film-forming bases processes result in reception of unstable compositions, while being stored inclined to spontaneous polymerization with capture of all solvent of system and rubbery compound formation.

On the whole the determined ways of management of destructive and oxidative-destructive processes have considerably facilitated the rational decision of a problem of processing of waste products of manufacture of mass purpose SR by reduction of their molecular mass and change of functional structure with the purpose of optimization of properties of received film-forming and others half-finished product for finishing compositions of a different special-purpose designation.

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Chapter 18

**TEMPERATURE TRANSITIONS IN
POLYCARBONATE –POLYTETRAMETHYLENOXIDE
BLOCK COPOLYMER RESINS**

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ABSTRACT

The main temperature transitions in polycarbonates and polycarbonate – polytetramethylenoxide block copolymer resins, obtained by acceptor-catalytic polycondensation in solution, were studied by the method of differential scanning calorimetry.

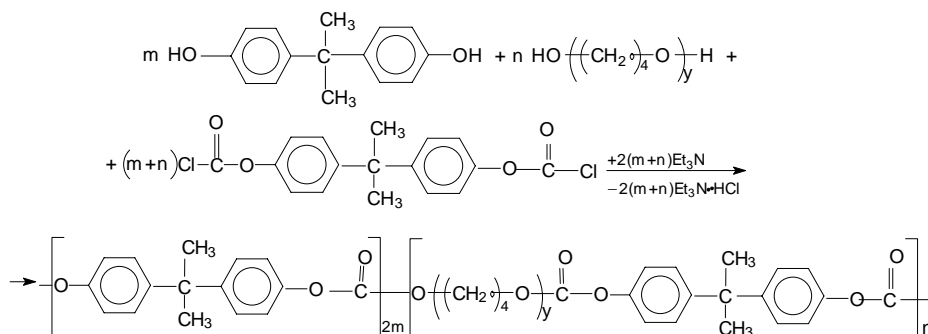
Key words: polycarbonate, polycarbonate –polytetramethylenoxide block copolymer resins, acceptor-catalytic polycondensation, vitrification temperature, melting temperature, crystallinity.

Physical-chemical properties of polymers, and particularly block copolymer resins (BCR) are determined by their phase state and phase morphology to a significant degree [1]. That is why these characteristics of polymers are very important for understanding a number of processes, taking place in their treatment and use.

It is known that macromolecules of polycarbonate (PC) are characterized by a great rigidity, limited by the rotation of aromatic nuclear and due to this reason they are weakly tend to crystallization. Industrial PC is a vitreous polymer which has both short and long range ordering areas. The degree of crystallinity does not usually overcome 10-15 %, and it can reach 30-40% only after special treatment of specimens [2].

Evaluation of physical structure of BCR is of a great interest. It is known from special literary resources that the character of phase separation and phase morphology in BCR depends on the chemical structure of blocks, molecular weight and the sequence of blocks in macromolecules, the crystallinity capability of the constituent blocks, and also on the prehistory of the specimen [3,4].

Temperature transitions in polycarbonate –polytetramethylenoxide (PC PTMO) block copolymer resins, obtained in solutions by the method of acceptor – catalytic polycondensation are studied in the scheme:



The method of differential scanning calorimetry (DSC) was used to define temperature transitions and evaluate the phase state of blocks in PC PTMO. Investigations of PC and PC PTMO block copolymer resins were carried out with the help of scanning calorimeter DSK-2 (by the firm “Perkin-Almer”) in the temperature interval from 173 to 523 K at the heating speed 40° a minute. The measurement accuracy was 1-2 degrees. After the first scanning the specimen was quenched up to the primary temperature and the hardened specimen was scanned again.

The calorimetrical curves of PC and PTMO were taken for comparison. On the thermogram for PC there was only one change at 417 K, corresponding to the its vitrification temperature. The transition, connected with PC melting was absent, i.e. polycarbonate film had a liquid –like structure. However, as it has already been pointed out, according to the literature data, PC crystallizes in certain conditions and its melting temperature varies in the interval from 493 to 503 K [2].

For PTMO with the molecular weight 2000 and terminal hydroxyl groups the following temperature transitions are found: $T_v=192$ K, $T_m= 300$ K, $Q_m= 21,4$ cal./g.

To analyze the data, obtained with the help pf DSK for PC PTMO block copolymer resins, it was synthesized a model polymer, consisting of PTMO blocks with $MM=2000$, elongated with the help of bischloralformate bisphenol A. It turned out that temperature transitions of this model differ from transitions in PTMO with hydroxyl groups: $T_m=294$ K, $Q_m=23,2$ cal./g., $T_{\text{cryst.}}= 268$ K.

Polycarbonate –polytetramethylenoxide block copolymer resins were investigated in the form of films, obtained by the method of sprinkling from the solution, and in the form of powders. As the specimens had different prehistory, all of them were brought into similar conditions by heating up to 57 K and quenching (320 degr./min) to 153 K.

Calorimetrical investigations showed that PC and PTMO blocks in such block copolymer resins are partially combined. The dependences of temperature transitions are shown in Table.

Table. The main temperature transitions in PC PTMO block copolymer resins

Structure of PK-PTMO block copolymers, % mass.	T _g PK phase, K	T _g PTMO phase, K	T _m PK phase, K	T _m PTMO phase, K
100:0	422	-	493	-
90:10	415	-	-	294
80:20	403	-	-	293
70:30	395	-	-	295
60:40	343	189	493	291
50:50	338	191	494	290
40:60	323	195	493	289
0:100	-	192	-	294

As it was shown, the mean temperatures of vitrification, which are different from T_v of homopolymers, are observed for all the specimens in a high temperature area. With the increase of content of PTMO blocks the meanings of T_v move to the area of a low temperature. Moreover in BCR, containing up to 40% PTMO blocks, a partial combination of PC and PTMO blocks take place and T_{v1} of plasticized PC phase and T_{m2} PTMO phase is observed for them only. If contents of PTMO blocks in BCR is more than 30% of its weight, a more complex apportionment into separate phases, which are characterized by their vitrification temperatures (T_{v2}) and melting (T_{m2}), is observed.

Simultaneously, the melting temperature of crystallite PC phase (T_{m1}) develops. Temperature T_{v1} is still lowering and this fact testifies the partial compatibility of PC and PTMO blocks and in the area of BCR constituents.

The melting degree of the crystallinity phase formed of PC blocks, and the degree of crystallinity rise with the increase of contents of PTMO blocks. The maximal degree of crystallinity (about 16%) in the studied line is achieved under containing PTMO blocks at about 60% of its weight. It is found out that PC PTMO block copolymer resins are sensitive to the change of the regime heating-cooling. For instance, the repeated processes of heating-cooling lead to lowering of T_{v1} up to 5-7 degrees. We may suppose that the observed phenomenon is connected with the partial thermal – oxidative degradation of BCR, and with the reaction of interchain exchange. Both of them should lead to improving compatibility of PC and PTMO blocks. Under the repeated heating-cooling process of BCR, besides the lowering of T_{v1} , a lowering of the melting temperature is observed. The melting temperature of the PC phase does not change significantly.

The obtained results show that a microphase separation of hard and elastic blocks is observed in PC PTMO block copolymer resins. As PC and PTMO blocks can crystallize, both vitrification temperature and melting temperature of different phases is fixed.

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