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RHEOLOGICAL PROPERTIES OF MELTS AND X-RAY METHOD OF STUDY OF CROSS-LINKED POLYETHYLENE

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Abstract. In the paper, the X-ray study of cross-linked polyethylene with isopropenyl styrene or acrylonitrile was carried out. It is shown that cross-linking leads to a significant decrease in the area of the exothermic peak, an increase in the resistance of the structured system to thermal oxidation. These data confirm that the increase in resistance to thermal aging of polyethylene cross-linked with acrylonitrile or isopropenyl styrene fraction.

Keywords: chemical bonds, polyethylene, vinyl monomer, IR spectroscopy, methylene groups, modification.

Introduction

Polyethylene is the cheapest polymer, which occupies the first place in the world polyolefin production. This unique material combines the most valuable properties and the ability to be processed by all high-performance methods that exist for thermoplastics.

Polyethylene is a plastic compound having good dielectric properties, increased shock resistance, low absorption capacity. It does not break, has a low gas and vapor permeability, physiologically neutral, odorless. Polyethylene is not susceptible to alkalis of any concentration, any salt solutions, carbonic, hydrofluoric and concentrated hydrochloric acids. Resistant to oil, vegetable juices, alcohol, water, gasoline. Destroyed by nitric acid, gaseous and liquid fluorine and chlorine. It does not dissolve, but only slightly swells in organic solvents. Resistant to vacuum heating, but collapses in air when heated at 353 K [1]–[12].

Polyethylene is frost-resistant (up to 333 K). Under the action of ultraviolet rays is subjected to photodestruction. It can be easily modified. Additional chlorination, sulfonation, bromination or fluoridation give polyethylene rubber-like properties, improve chemical and thermal resistance. Copolymerization with other polyolefins or polar monomers increases its transparency, elasticity, adhesion characteristics, as well as stress cracking resistance. Mixing polyethylene with different types of polymeric materials improves its other physical properties. Polyethylene is harmless to humans, substances that are hazardous to their health are not released from it [13]–[22].

Experimental Results

The rheological properties of polyethylene in a fluid state provide considerable information on the mechanical properties and processing behavior of polyethylene, which are necessary for calculating the manufacturing process and processing equipment, as well as at the establishment the optimum product performance. The most important characteristic of polyethylene is the melt viscosity.

In the research of the rheological properties of polymers are widely known the works of G. V. Vinogradov, G. M. Bartenev, E. E. Glukhov and others. In these works, a number of regularities

were established, in particular for high and low density polyethylene. These results are published in papers [1]–[5].

As for medium-density polyethylene (MDPE), the rheological characteristics of this polymer are studied extremely insufficiently. Taking into account the specific features of the MDPE macrostructure, then the study of the rheological properties of these polyethylenes acquires the substantive necessity.

Thus, the rheological study of MDPE is necessary not only to establish its various grades of flow, but also penetrate to the macrocosm to assess the internal forces acting in various bodies. Under the flow of the polymer imply the necessary shear deformation arising under the action of an external force [23]–[24]. Internal forces, i.e. the resistance to deformation forces, by counteracting external forces, determine the presence of an internal flow. And viscosity is nothing more than a measure of resistance, or the ratio of the shear stress to shear rate. Thus, under the effective viscosity of polyethylene understand [9], [11], [16]:

$$\eta = \frac{\tau}{\gamma}, \quad (1)$$

where η – is the share stress (dynes/cm²); τ – is the shear rate (s⁻¹); γ – is the viscosity (poise).

Polymer melts during flow are characterized by the following features: have high viscosity up to 6 poise or more; many of them exhibit pronounced anomalous properties, i.e. their flow does not obey Newton's law

$$\tau = \eta \cdot \gamma, \quad (2)$$

according to which viscosity is the coefficient of proportionality between the applied shear stress τ and the developing value of shear rate γ . Practically, the viscosity anomaly of polymers and is expressed in the fact that the values of η , measured at different τ and γ are different – with increasing τ , η of polymers decreases. The non-Newtonian behavior of melts is due to the peculiarities of supramolecular structures [15] (intermolecular interaction), as well as by the structure of macromolecules (chain character) [1], as a result, during the flow, the reversible structure destroying process and subsequential orientation of macromolecules develop, which lead to a steady fall [7]. The reversible process destruction of the supramolecular structures during the flow of thermoplastics is not accompanied by the destruction of molecules and can be repeated many times with high reproducibility. Such reversible changes occur at the moment of transition from highly elastic strain to steady flow under the condition of more or less significant γ [25]. With the flow of high molecular weight polymers, the heat of activation for the viscous flow process

$$E = R \cdot \left(\ln \cdot \eta \right) d \left(\frac{1}{T} \right) \quad (3)$$

does not depend on the degree of polymerization, indicating the independence of the elementary act of transfer in the flow process from the chain length of the macromolecule [26]–[28]. Therefore, only a small part of the macromolecule, the segment, participates in the elementary act of transfer. But nevertheless viscosity of polymer bodies depends on the total length of the macromolecule. This dependence is conditioned by the fact that to move a large molecule, as a result of the independent movements of its segments, is needed that the center of gravity of the entire macromolecule move. Furthermore, the viscosity significantly depends on the supramolecular structure of the polymers melt flow.

The region of abnormal viscous flow is a permanent destruction of the supramolecular structure of the polymer, however, this region stretches in velocity and share stress by many decimal orders in the region of the completely destroyed structure (the lowest Newtonian viscosity cannot be achieved in the case of polymer melts).

In the works [1], [3], [5] established the temperature-invariant viscosity characteristic and its universality for a large number of polymers. This characteristic is the dependence of η / η on $\eta \cdot \gamma$.

Rheological results

To obtain the true results of rheological studies and to obtain invariant with respect to capillaries geometric dimensions, we measured the rheological parameters of medium-density polyethylene samples at different ratios of length of the diameter (D , mm) of the capillary. These data, calculated on the dependence of the shear rate $\dot{\gamma}$ on the shear stress τ , are shown in Fig.1. The values L/D used capillaries are given in Table 1.

Table 1

The rheological parameters of medium-density polyethylene samples

| Experiment No | MFI (g / 10 min) | L (mm) | D (mm) | L/D |
|---------------|------------------|----------|-------------------|-------|
| 1 | 7 | 8 | $1,18 \pm 0,015$ | 6,8 |
| 2 | | 16 | | 28,7 |
| 3 | | 48 | | 38,0 |
| 1 | 3,9 | 17 | $2,90 \pm 0,005$ | 5,5 |
| 2 | | | $2,090 \pm 0,015$ | 7,8 |
| 3 | | | $1,190 \pm 0,015$ | 13,6 |
| 4 | | | $1,00 \pm 0,025$ | 17,34 |
| 1 | 1,4 | 7 | $1,19 \pm 0,015$ | 5,9 |
| 2 | | 21 | $1,19 \pm 0,0191$ | 27,4 |
| 3 | | 43 | $1,29 \pm 0,015$ | 40,0 |

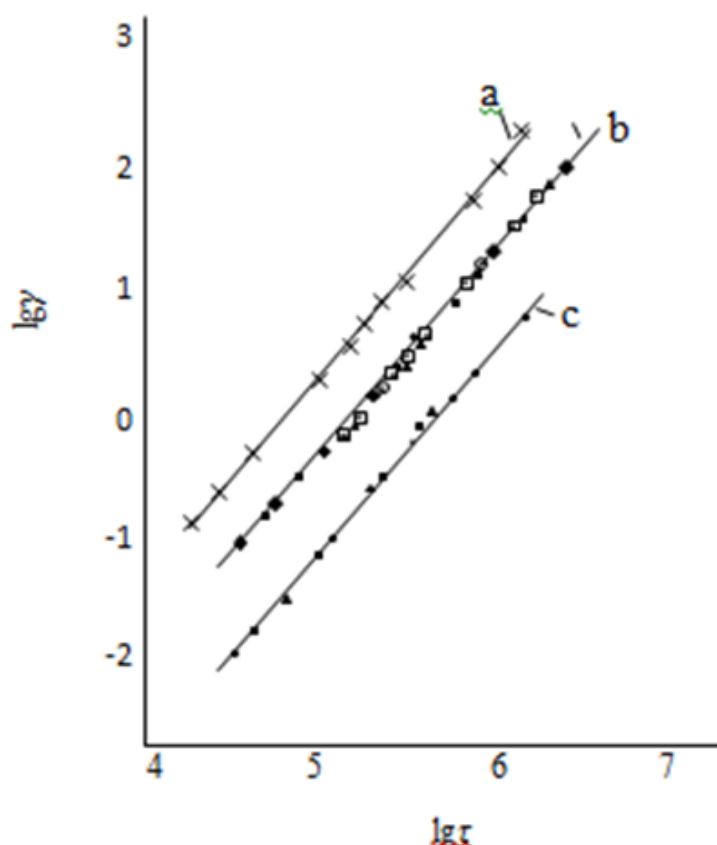


Fig. 1. Rheological flow curves of three grades of HDPE at temperature of 463K[^]

a (+, ×, ◆) – MFI-7.0; b (Δ, □, ◇, ⊙) – MFI-4.0; c (●, ▲, ■) – MFI-1,4

(the data obtained on the capillaries with different designations of L/D is given in Table 1)

The location of the flow curve is determined only by the brand of the homopolymer or by the magnitude of the MFI. The smaller the MFI, the larger the shear stress polymer flows. This pattern is

observed in a wide temperature range 408–573 K. The characteristic dependence of the share rate on the shear stress in the temperature range from 408 to 573 K for three grades of HDPE is shown in Fig. 2. The specific pressure, under the action of which the extrusion of the polymer melt through the capillary was carried out, was changed from 1 to 63 kgf/cm². Flow curves for HDPE with an MFI equal to 1,4; 4,0; 7,0 are presented in Fig. 2. It is evident that there is a certain temperature range inside which all the experimental data obtained in a fairly wide range of temperatures are located. For HDPE with MFI = 4.0, this area encompasses 433–513 K. The same areas were established for HDPE with MFI = 1,4 and 7,0. They were equal to 443–523 K and 433–523 K, respectively. In these temperature ranges effective viscosity vary slightly with temperature.

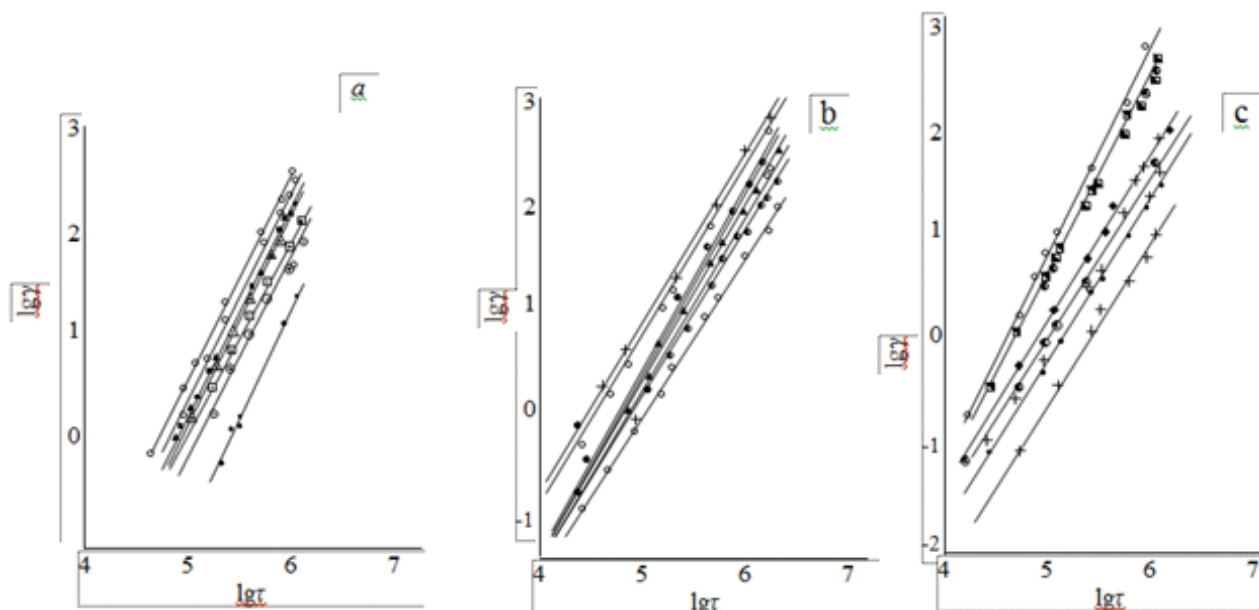


Fig. 2. Rheological flow curves of three grades of HDPE at different temperatures

Another characteristic property of the HDPE melt flow is the subordination of the ratio (τ/γ) to the flow of power law over the entire temperature range considered.

To consider the temperature dependence of the melt viscosity of HDPE, the experimental data obtained were processed in accordance with the accepted method [4] and provided as a dependency $\lg \eta$ on τ , where $\eta = \tau/\gamma$. In Fig. 3 (a, b, c) these dependences are given for HDPE samples with the magnitude of the MFI = 1.4, 4.0, and 7.0, respectively.

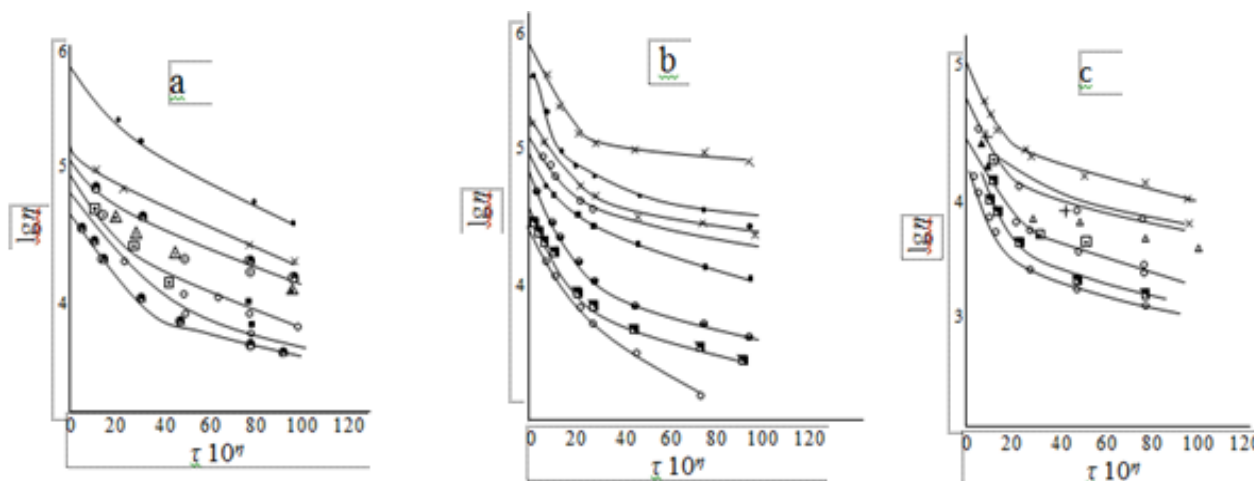


Fig. 3. Dependence of effective viscosity of melt grades on shear stress at various temperatures

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Using the method of determining the value of the melt viscosity, published in studies [12]–[24], the highest melt viscosity values of three HDPE samples were calculated in a wide temperature range. The results showed (Fig. 4) that for HDPE there are three temperature ranges, each of which is characterized by certain values of apparent heat of activation for viscous flow ΔH .

Dependence of ΔH on temperature for three HDPE is represented in Fig. 5. The figure shows that in the temperature range 408–433 K in the values of ΔH for the specified polyethylene samples, there is a sharp decrease in ΔH .

The latter effect may be due to the destruction of ordered regions in the polyethylene melt, therefore at 428–433 K occurs the transition of the structure of the melt polyethylene to a new state in which the sizes of the kinetic units are such that the value of heat of activation equal to 0.6–0.7 kcal/mole is already sufficient to move them under the action of thermal motion.

At temperatures above 523 K, melt viscosity of the HDPE begins to decrease sharply, which is obviously associated with the onset of the process of its intense thermal destruction. The accompanying process of the destruction of macromolecules leads to an increase in the amount of the apparent heat of activation for viscous flow. Thus, apparently, a significant part of the thermal energy supplied to the initial polymer is expended mainly on the thermal oxidative destruction of macromolecules. Accordingly, the value ΔH in the temperature range above 523 K, should be presented as the total activation heat of two main and simultaneously occurring processes of viscous flow and thermaloxidative destruction per mole of chain segments.

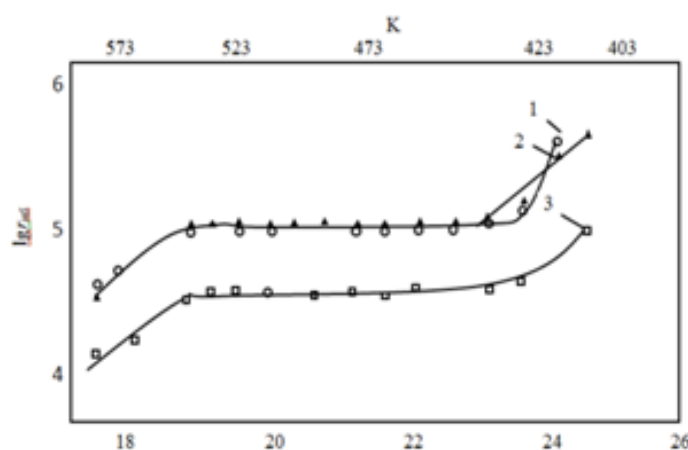


Fig. 4. The dependence of the melt viscosity of different HDPE grades on temperature: 1 – MFI-1.4; 2 – MFI-4.0; 3 – MFI-7.0

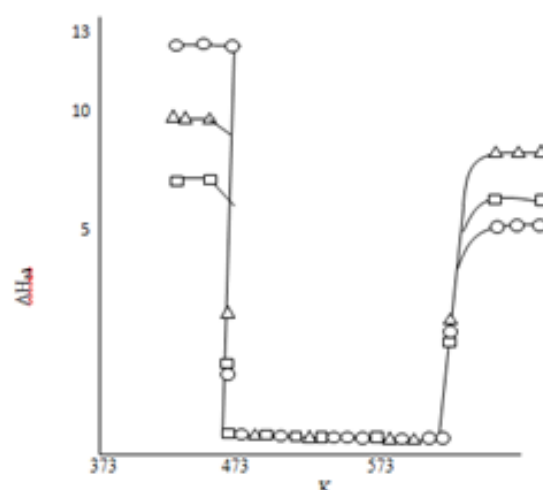


Fig. 5. Dependence of the apparent heat of activation for viscous flow (ΔH^*) of different HDPE grades on temperature: 1 – MFI-1.2; 2 – MFI-4.0; 3 – MFI-7.0

A generalized representation of the viscosity properties of polymer melts in $\dot{\eta}/\eta_0 - \gamma\eta_0$ coordinates is particularly important for base samples. A generalized characteristic of HDPE samples is illustrated in Fig. 6. Here, two solid lines indicate the allowable universal scope of the temperature-invariant viscosity characteristic of linear polymer melts. The dots 1 and 2 (Fig. 6) are experimental data for three samples of HDPE in the temperature range 408–573 K.

X-ray study of polyethylene cross-linked with different content of isopropenyl-styrene fraction

As illustrated in Fig. 5 the generalized dependency describes quite satisfactorily the flow of HDPE.

At present, radiographic determination of the degree of crystallinity of polyolefins is widely used [1], [2].

The issue of availability of a chemical bond between polyethylene and vinyl monomers was clarified by IR spectroscopy, X-ray diffraction and differential thermal analyzes [11], [24]–[28].

By the method of X-ray structural analysis it was determined that in the modified polyethylene the crystal structure is preserved (Fig. 6). However, with an increase in the degree of cross-linking, there is a slight decrease in the degree of crystallinity [5].

The decrease in the degree of crystallinity is caused by the appearance of cross-links between the molecules of polyethylene and vinyl monomer and as the degree of hardening of polyethylene increases, a decrease in the degree of crystallinity of the polymer is observed [8].

With increasing of styrene content in the composition, the amount of chemically unbound polystyrene increases and polyethylene decreases [10]. When constructing a graphical dependence of the content of free polyethylene and polystyrene on the initial amount of styrene in the composition, the best indicators of structured polyethylene fall on the content of unbound polyethylene and polystyrene in it within 4 % [7]. These conditions are achieved at an initial weight ratio of polyethylene and styrene in the composition of 1:0.45 and at the highest yield of the insoluble fraction of the cross-linked polyethylene (94 %). X-ray diffraction analysis data are in good agreement with the results of differential thermal analysis.

Results of differential thermal and thermogravimetric analysis

Fig. 7 provides the curves of differential thermal and thermogravimetric analyzes, showing that the area of the endothermic peak, which characterizes the softening temperature of cross-linked polyethylene, is slightly less than for the initial polyethylene. This fact testifies a decrease in the degree of crystallinity (8-10 %) of structured polyethylene, which is characteristic of cross-linked polymers.

The taken thermograms not only confirm the facts of changes in the degree of crystallinity of polyethylene during cross-linking, they show the thermal effects of softening and oxidation of samples of the initial and modified polyethylene.

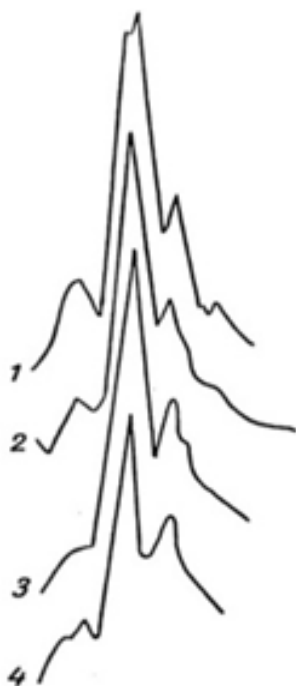


Fig. 6. Radiographs of the initial (1) and polyethylene cross-linked with different content of isopropenyl-styrene fraction (2, 3, 4): 2 – 20 mass fraction; 3 – 40 mass fraction; 4 – 100 mass fraction of the isopropenyl styrene fraction per 100 mass fraction of polyethylene and 1.3 mass fraction of tert-butyl peroxide

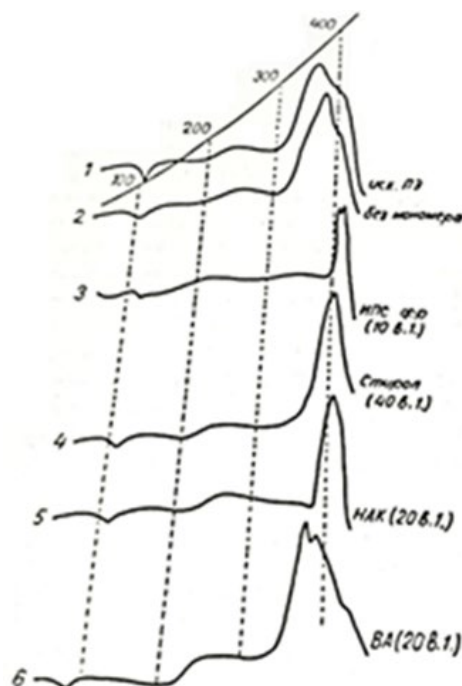


Fig. 7. DTA curves of polyethylene cross-linked with various vinyl monomers

The normal melting peak, characteristic of non-crosslinked high-density polyethylene, appears at a temperature of 378-381 K (Fig. 7, curve 1). The positions of the melting peaks on the thermograms of

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cross-linked polyethylene (Fig. 7, curves 2–6) are practically unchanged. The latter is consistent with the literature data.

The thermograms shown in Fig. 7 indicate that the cross-linking of polyethylene with vinyl monomers increases the resistance of the polymer system to thermal oxidation according to the nature of the monomer.

The analysis of thermograms (Fig. 7) shows that when cross-linking polyethylene with vinyl acetate or in the presence of only an organic peroxide, there is a slight increase in the oxidation temperature of the polymer from 623 K for the initial polyethylene (curve 1) up to 648 K for the above systems (curves 2, 6). The decrease in sample weight at the oxidation temperature is 38 % for the initial polyethylene (curve 1), and for polyethylene cross-linked with vinyl acetate or only an organic peroxide 36.4 % (curve 5) and 46.7 % (curve 2), respectively.

Cross-linking of polyethylene with acrylonitrile (Fig. 7, curve 5) or with styrene (Fig. 2, curve 4) raises the oxidation temperature of the polymer to 673–683 K. This temperature accounts for 13.6 % (Fig. 7, curve 4) and 23 % (Fig. 2, curve 3) mass loss, respectively.

Structuring polyethylene with isopropenyl styrene fraction shifts the peak of polymer oxidation towards higher temperatures (683–693 K).

The weight loss of the sample is 12% of the spatial grid of the polymer, resulting in increased resistance of the polymer to the effects of temperature. Our research showed that in many cases there is no need for complete thermodynamic combination of components in polymer-polymer systems, since the specified properties of the composition are often achieved precisely because the system is incompatible. We have proved this regularity from the standpoint of thermodynamic compatibility, and especially the colloid chemical one represented in disperse systems.

The study of the IR spectrum of non-cross-linked and cross-linked polyethylene

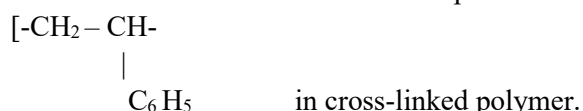
These studies were conducted with the aim of cross-linking polyethylene with acrylonitrile or styrene. In this case we used the most modern research methods. The issue of the presence of a chemical bond between polyethylene and vinyl monomers was clarified by IR spectroscopy, X-ray diffraction and differential thermal analyzes.

The IR spectra of films with the thickness up to 100 μm were recorded using VR spectrometer with NaCl and LiF prism in the region 700 cm^{-1} . X-ray analyzes (plate $1.5 \times 2.5\text{ mm}$) were carried out with a URS-50 IM apparatus with ionization registration.

Thermal analysis of samples ($1 \times 2\text{ mm}$ crumb) was performed on F.Paulik – J.Paulik – L.Erdey derivatograph system in the temperature range 298–6273 K and the heating rate (degree/min) using platinum crucible.

The presence of a chemical bond between polyethylene molecules of vinyl monomer can be judged by the spectra taken from the extracted samples of the cross-linked polymer (Fig. 8).

In the spectrum of polyethylene cross-linked with styrene (Fig. 9), the appearance of additional absorption bands at 750; 840; 908; 1028; $1600\text{--}1940\text{ cm}^{-1}$ should be classified as the methylene groups of the aromatic series. These bands in the spectrum indicate the presence of structures



As it can be seen in Figs. 8–9, in the spectra the band at 730 cm^{-1} , which is usually used to assess the crystalline state of polyethylene in the spectra of cross-linked polyethylene, retains its intensity.

In Fig. 10 in the spectrum of polyethylene cross-linked with isopropenyl styrene fraction, intense absorption bands in region of $886\text{--}892\text{ cm}^{-1}$ belong to the isopropyl group, and the absorption bands in the region of $1600\text{--}1900\text{ cm}^{-1}$ to the methylene groups of the aromatic series.

The study of the spectrogram of polyethylene, cross-linked with acrylonitrile (Fig. 11) shows the appearance of absorption bands in the region $1070\text{--}2246\text{ cm}^{-1}$ which are characteristic, respectively

deformation stretching vibrations of $C \equiv N$ bonds [2], [4] allowing to continue the presence of groups in structured polyethylene.

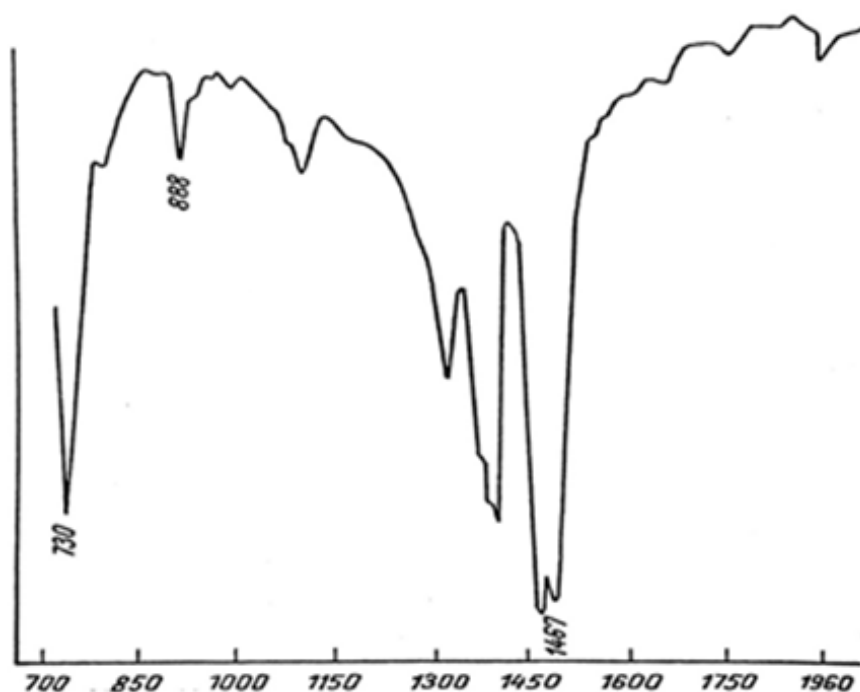
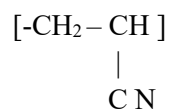


Fig. 8. IR spectra of non-cross-linked polyethylene

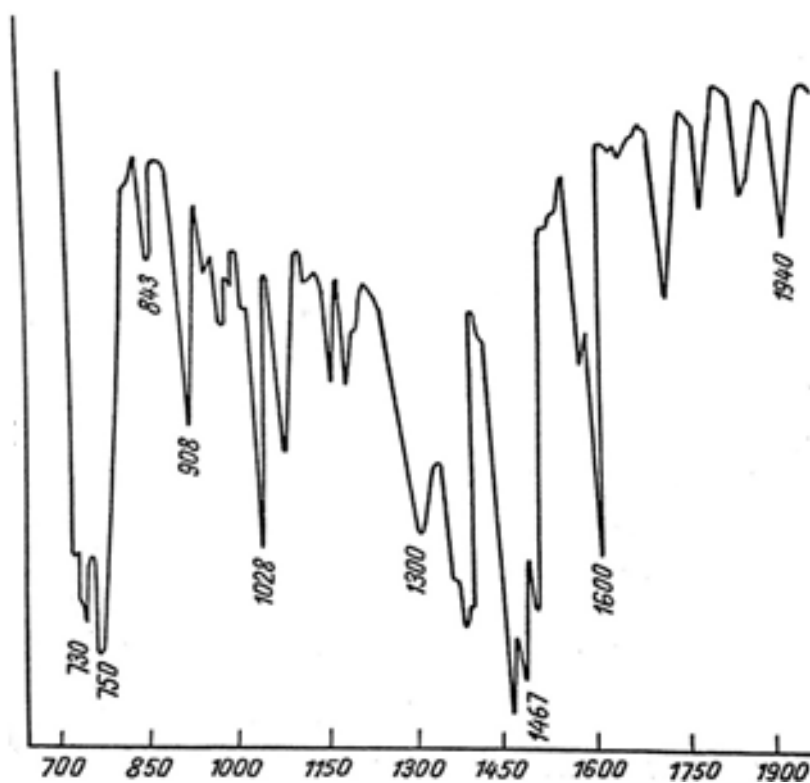


Fig. 9. IR spectra of polyethylene cross-linked with vinyl monomer fraction. Composition: PE – 100 mass fraction, styrene – 40 mass fraction, tert-butyl peroxide – 1.3 mass fraction

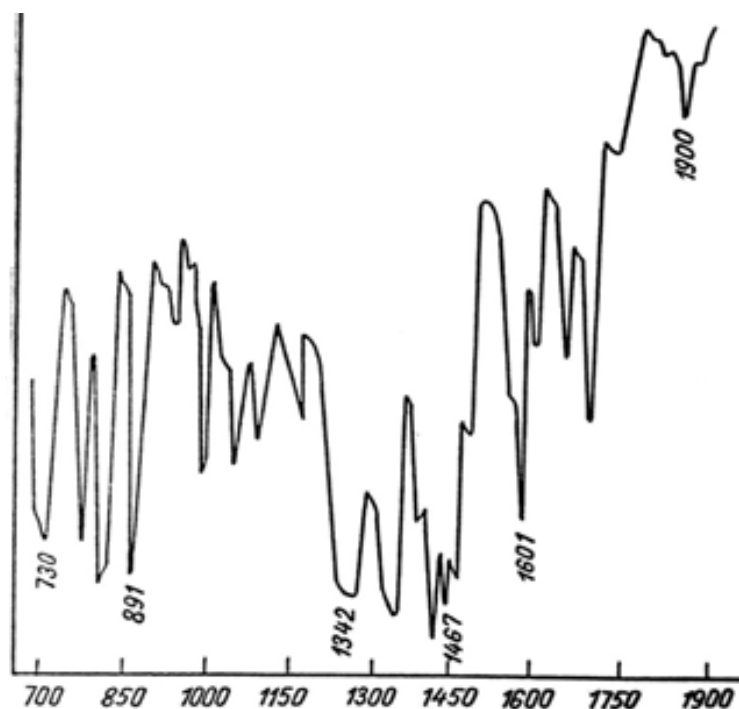


Fig. 10. IR spectra of PE cross-linked with vinyl acetate. Composition: PE – 100 mass fraction, vinyl acetate – 20 mass fraction, tert-butyl peroxide – 1.3 mass fraction

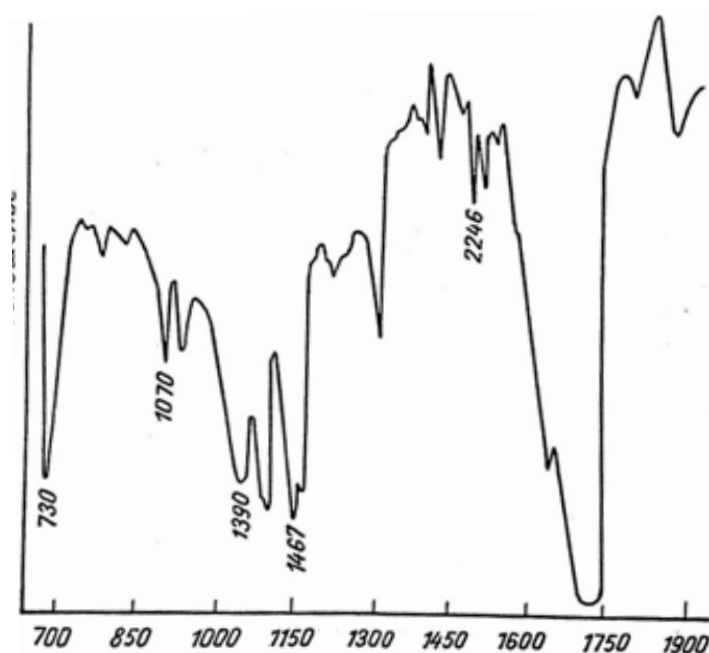
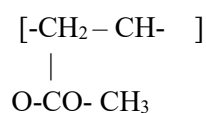


Fig. 11. IR spectra of polyethylene cross-linked with acrylonitrile. Composition: PE – 100 mass fraction, acrylonitrile – 20 mass fraction, tert-butyl peroxide – 1.3 mass fraction

In the spectrum of polyethylene cross-linked with vinyl acetate (Fig. 12), the appearance of a characteristic absorption band in the region 1720-1730 cm^{-1} should be attributed to stretching vibrations of the C=O containing groups [6]. This allows to suggest that in the process of polyethylene cross-linking occurs cross-linking of structures with the polymer chain.



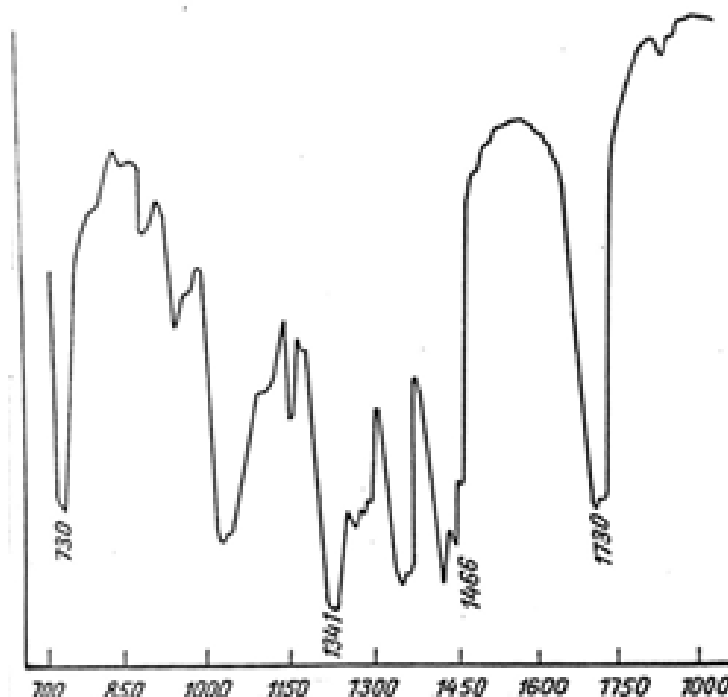


Fig. 12. IR spectra of PE cross-linked with vinyl acetate. Composition: PE – 100 mass fraction, vinyl acetate – 20 mass fraction, tert-butyl peroxide – 1.3 mass fraction

The Table 2 indicates the optical density of the characteristic absorption bands of cross-linked polyethylene, depending on the content of monomer composition.

Table 2

The change in the optical density of the characteristic absorption bands of cross-linked polyethylene, depending on the content of monomer composition

| Monomer content in mass fraction per 100 mass fraction of polyethylene | Absorption bands in polyethylene cross-linked with monomers at the respective frequencies: cm ⁻¹ | | | | | | | |
|--|--|------|------|------------------------|------|---------------|------|------------------|
| | Styrene | | | Isopropenyl styrene | | Acrylonitrile | | Vinyl acetate |
| | 908 | 1028 | 1600 | 891 | 1600 | 1080 | 2246 | 1720-1730 |
| 10 | 0,08 | 0,10 | 0,15 | 0,20 | 0,31 | 0,10 | 0,14 | 0,56 |
| 20 | 0,12 | 0,17 | 0,27 | 0,38 | 0,46 | 0,11 | 0,38 | 0,69 |
| 40 | 0,21 | 0,28 | 0,47 | 0,44 | 0,47 | 0,13 | 0,39 | 0,80 |
| 60 | 0,22 | 0,33 | 0,60 | 0,46 | 0,78 | 0,15 | 0,37 | 0,98 |
| 80 | 0,31 | 0,43 | 0,80 | 0,54 | 0,81 | 0,12 | 0,40 | 1,21 |

Conclusions

The analysis of the infrared spectra of the cross-linked samples testifies that the interaction between polyethylene macromolecules and vinyl monomers in the presence of tert-butyl peroxide leads to a chemical reaction, resulting in monomeric units chemically bonded to polyethylene losing the ability to dissolve in appropriate solvents and give characteristic absorption bands. These studies were performed in order to crosslink polyethylene with acrylonitrile or styrene. At the same time we used the most modern research methods. In our studies it was determined that in many cases there is no need for a complete thermodynamic combination of components into polymer-polymer systems, since the specified properties of the composition are often achieved precisely because the system is incompatible. We have proved this regularity from the standpoint of thermodynamic compatibility and especially colloid-chemical,

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represented in disperse systems. The question of the presence of a chemical bond between polyethylene and vinyl monomers was clarified by IR spectroscopy, X-ray diffraction and differential thermal analysis.

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