

INVESTIGATION OF METHODS FOR OBTAINING COMPOSITION MATERIALS BASED ON POLYMER MIXTURES**Valiyev Vagif**- undergraduate,**Qasimov Ryad**- undergraduate

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Abstract

- Developed methods of chemical and physical modification of individual polymers, their mixtures to enhance the operational properties of composite materials; including the method of modification of polyethylene, which allowed to significantly increase its heat resistance in air and in vacuum, anticorrosive properties.

-Effectiveness of use in composite materials of oil-polymer resin SPP, intended for the production of products, operating under conditions of increased mechanical wear, temperature, pressure and deformation.

Solubility of interdynamic parameters of mixtures of polymers by the method of gas chromatography.
PARAMETERS OF MIXED POLYMER METHOD RECORDED

Keywords:

compatibility, tire molding, recycling, solubility parameter, chlorocarboxylate polyethylene (XCP), chlorinated polyethylene (XP), chlorosulfated polyethylene (XSPE), low and high pressure polyethylene (HPE), polyvinyl chloride (PVC), ethylene propylene rubber (EPR), polyurethane thermoplastic (PUTP), polyurethane (PU) methods of chemical modification of polymers, composition, technology, particle size

INTRODUCTION

The problem and its relevance. The problem of obtaining polymer materials with the necessary properties for operation in extreme conditions is currently being solved in two ways: by synthesizing new types of polymers and creating polymer compositions, where the properties of individual components additively complement each other[1-4].

The scientific and technological progress of production makes more and more stringent demands on polymer products, and the industry's demand for new materials is constantly growing. Therefore, the development of various polymer compositions that greatly simplify the technology of their production and processing and reduce the cost of obtaining materials with the required complexes of properties is very important in the existing technological conditions[5-8].

However, despite the great economic and technical advantages of the production of composite materials based on large-scale production of polyolefins and heterochain polymers, until recently, in Azerbaijan, as in other regions of the world, industrial production of individual polymers appeared: butyl rubber, polyvinyl chloride, chlorocarboxylated polyethylene, high-pressure polyethylene, polyurethane and others, which significantly reduced the efficiency of their use in the national economy of the country, export opportunities.[9-11].

This situation was caused by the fact that the theory of multicomponent polymer systems was still completely insufficiently developed, there were no scientifically grounded recommendations for the production, processing and use of such composite materials. [12-15]

Metodis

In order to impart optimal technological and physical-mechanical properties to mixtures, on the basis of PUTPE, the modifying role of HKPE, serving as a "carrier" for PVC incompatible with PUTPE, was investigated. Homogenization was carried out by experimental mixing of the components on two roller mixer at a temperature of 165 °C for 15 minutes, then the blades were cast, which after 7 days of exposure were subjected to rupture on a tensile R-0.5 machine according to GOST 270-75 with a drawing speed of 130 mm / min and a temperature 200°C Based on the literature data, the following parameters have been determined that are optimal for cast tires:

$d_v = 1.0 = 45.0 \text{ kN / m}$ - tear resistance

$d_\varepsilon = 1.0 = 375\%$ - relative elongation, where d_v and d_ε are functions of the desired factor.

The relationship between the desirability index y_1 and the desirability function is as follows:

$$d = e^{-(y_1)^n}$$

where n is an exponent, the value of which is determined by the requirement for the parameter.

By varying the desirability index from -4 to +4, we determine the form of the regression equation that connects the current value of the indicator under study with the desirability index, bearing in mind the equation:

$$Y_6 = a + y_1$$

where y_1 is the current value of the indicator.

As a result of the calculation, we have

$$y_{\varepsilon 1} = -8,42 + 0,0276$$

$$y_1 = 17,35 - 0,0356$$

We used a MIN-8 polarizing microscope equipped with a specially made photo attachment with a Zenit-TTL reflex camera, magnification $\times 480$, wedge-quartz $L = \frac{1}{2} \lambda$, polymer mixtures were investigated at a temperature of $298 \text{ }^\circ\text{K}$.

. 2. RESULT

There are a number of fundamental approaches to the manufacture of mixtures, of which the method of mixing thermoplastic polymers, carried out on an extruder or rollers, is favorably distinguished by the simplicity of the technology. Despite a number of limitations associated with the stability of the mixture throughout the entire preparation cycle according to this method, it was possible to obtain a number of mixtures of PUTEF with other thermoplastics. Thus, by mixing PUTEF with PVC, a material is obtained that combines the impact strength and abrasion resistance of PUTEF with the rigidity and high modulus of elasticity of PVC. Moreover, the resulting composite is cheaper than the "pure" PUTPE. After preparing the composition, the main properties were determined and the data obtained are shown in table 1 and 2

Table 1. Desirability function and desirability indices for tensile strength and elongation

$N_0 N_0$	$Y_i G_1$	$d_i G$	$Y_i \varepsilon_1$	$d_i \varepsilon$
1.	-2,78	0,01	4,78	1,0
2.	-3,40	0,01	0,37	0,45
3.	-2,97	0,01	-3,40	0,01
4.	-3,33	0,01	1,22	0,80
5.	-3,25	0,01	-3,23	0,01
6.	-3,67	0,01	0,81	0,61
7.	-2,99	0,01	-0,98	0,01
8.	-2,59	0,01	-1,73	0,50
9.	-2,84	0,01	-3,23	0,01
10.	-	-	-	-
11.	-3,84	0,01	-2,19	0,02
12.	-4,01	0,00	-3,01	0,01
13.	-3,01	0,01	-0,49	0,20
14.	-2,95	0,01	0,80	0,61
15.	-2,44	0,01	-2,69	0,01
16.	-2,74	0,01	-2,76	0,01
17.	-2,93	0,01	-2,41	0,01
18.	-3,16	0,01	-3,58	0,01

table 2 Physical and mechanical properties and enrichment of the desirability function of the composition

№№	Variables				Feedback			
	Inside -T	PVC	XKPE	SPP	Resistance break, MPa, Y1	Relates. elongation, % U2	Osta-exact lengthen., % U2	Generalized function desirability, D
	X0		X2	X3				
1a 1	100	5,0	5,0	0,55	20,4	354	57,5	0,1
1б 2	100	5,0	5,0	2,2	18,2	477	89,5	0,067
2a 3	100	5,0	12,5	0,588	19,7	583	89,6	0,01
2б 4	100	5,0	12,5	2,35	18,4	453	81,3	0,089
3a 5	100	5,0	20,0	0,626	18,7	578	89,8	0,01
3б 6	100	5,0	20,0	2,5	17,2	510	77,1	0,078
4a 7	100	7,5	5,0	0,562	19,6	515	90,5	0,032
4б 8	100	7,5	5,0	2,25	21,1	536	87,4	0,071
5a 9	100	7,5	12,5	0,6	20,0	578	102,1	0,01
5б 10	100	7,5	12,5	2,4	-	-	-	-
6a 11	100	7,5	20,0	0,638	16,5	549	91,5	0,014
6б 12	100	7,5	20,0	2,55	15,9	572	106,4	0,00
7a 13	100	10,0	5,0	0,576	19,5	501	91,5	0,045
7б 14	100	10,0	12,5	2,3	19,8	465	80,0	0,078
8a 15	100	10,0	12,5	0,612	21,6	563	91,5	0,01
8б 16	100	10,0	12,5	2,45	20,5	565	84,4	0,01
9 a 17	100	10,0	20,0	0,65	19,8	555	89,8	0,01
9 б 18	100	10,0	20,0	2,6	19,1	588	89,6	0,01

2.1. STUDY OF SOLUBILITY AND THERMODYNAMIC PARAMETERS OF POLYMER MIXTURES BY REVERSED GAS CHROMATOGRAPHY AND TURBIDIMETRIC TITRATION (IN A BLOCK AND SOLUTION)

Solubility parameters of substances characterize the relationship between mixing energy and mutual solubility. The value of the polymer solubility parameter is necessary to obtain valuable information on the behavior of the polymer when mixed with other polymers or low molecular weight substances.

Direct determination of the heat of vaporization and, consequently, the solubility parameters of polymers is impossible due to their non-volatility. At present, the most widely used methods for determining the cohesion energy of polymers, based on the study of the interaction of a polymer-solvent with known solubility parameters.

In [1-6], the swelling of cross-linked polymers was studied and it was found that swelling is maximal in solvents having the same cohesion energy density as the polymer. Bristow and Watson [7] obtained the solubility parameters of polymers from viscosity measurements in a number of solvents using the Flory Huggins X12 interaction parameters. Moreover, the polymer solubility parameter was taken equal to the solvent solubility parameter, in which the limiting viscosity is maximum.

Small derived the additive molar attraction constants for various molecular groups from vapor pressure measurements of volatiles and used these values to calculate the solubility parameters of polymers. Subsequently, these constants were revised by Hoy and Van Krevelen.

Sokh and Clarke proposed to determine the energy density of cohesion from the data of turbidimetric titration (TDT) of solutions with poly-precipitants. The solubility parameters of polystyrene and poly-o-chlorostyrene determined by them are in good agreement with the known values obtained from swelling measurements.

Ito and Gillett showed that using polymers as a stationary phase and various sorbates with known solubility parameters, the method of reverse gas chromatography can be used to determine the solubility parameters of polymers.

Both of the latter methods for determining the solubility parameters of polymers are characterized by a diametrically opposite state of the "polymer - solvent" system, namely, in the TDT method, the polymer solubility parameter is

determined under conditions corresponding to the “infinite” dilution of the polymer in the solvent, which can be denoted as δ_{20} . In the case of using inverse gas chromatography, the solubility parameter is determined by “infinite” dilution of the low molecular weight substance in the polymer and the maximum interaction between the polymer molecules. The solubility parameter is correctly designated as δ_0 .

Thus, taking into account the presence of strong specific intermolecular interactions in polar polymers, an increase in the difference between δ_{20} and δ_0 of solvents and precipitants, solvents and precipitants, should be expected as the strength of intermolecular interaction increases.

Based on the theory of Hildebrand - Scatchard and Flory, provided that the volume remains unchanged upon mixing, the parameter X is related to the solubility parameter by the ratio:

$$X = V_1 / RTx (\delta_1 - \delta_2) + X_5 \quad (1)$$

Where V_1 is the molecular volume of the solvent; δ_1 and δ_2 are the parameters of the solubility of the solvent and polymer, respectively; R, T - gas constant and absolute temperature; X_5 is the entropy contribution to the interaction parameters.

Expanding the brackets and dividing the variables, we have:

$$\delta_{12} / RT - X / V_1 = 2 \delta_2 / RT x \delta_1 - (\delta_{22} / RT + X_5 / V_1) \quad (2)$$

Equation (44) is a linearized form of equation (2)

As established by Gray, the contribution of the X / V term for good solvents (having the smallest value for X of a particular polymer) is insignificant and for these sorbates the linearization $\delta_{12} / RT - X / V_1$ relative to δ_1 is not very different from the parabola.

Thus, the polymer solubility parameter δ_i can be found from the slope of the linear dependence $\delta_{12} / RT - X / V_1$ relative to a number of sorbates. The quantities included in the left-hand side of equation (2) can be found from the condition that samples in the vapor state with infinite dilution behave like an ideal gas.

Then,

$$\delta_1 = H_v - RT) / V_1] 0.5$$

Here, the values of the molar volume of the solvent V_1 and the heat of vaporization H_v are easily determined or are available in the literature [8].

The Flory - Huggins interaction parameter is calculated using the equations proposed by Patterson and his colleagues

$$= 273.2 xR / P_{01} x V_g 0 x M_1 - P_{01} / RT x (B_{ii} - V_1)$$

$$X_{12} \infty = - (V_1 / V_2) - 1 + M_1 + v_1 / M_2 + v_2$$

where M_1 , P_{01} , V_1 , v_1 - molecular weight, saturated vapor pressure, molar and specific volumes of the solvent at temperature T, respectively; B_{ii} is the second virial coefficient; M_2 , v_2 - segment molar weight and specific volume of polymer at T; $V_g 0$ - the characteristic retention volume reduced to 2730 K is obtained in the usual way [9].

In turn, the X value in the case of titration with two different precipitants, one of which has a lower δ_1 (XCL) value, and the other has a higher δ_1 (XCh) value will be [9]

$$X_{CL} = V_{mL} (\delta_2 - \delta_{mL}) 2 Ch / RT \quad (3)$$

$$X_{Ch} = V_{mh} (\delta_{mh} - \delta_2) Ch / RT + (X_s) Ch \quad (4)$$

Here the indices m_L and m_h refer to the mixture of solvent and precipitant at the turbidity point. Equating both expressions (3) and (4) to each other, taking $(X_s)_{CL} = (X_s)_{Ch}$ for a low polymer concentration in solution and solving with respect to δ_{20} , we have

$$\delta_{20} = \sqrt{V_{mL} x \delta_{mL} + \sqrt{V_{mh} x \delta_{mh}} / \sqrt{V_{mL} + \sqrt{V_{mh}}}$$

where

$$V_m = V_1 x V_2 / \Phi_1 V_3 + \Phi_3 V_1$$

$$\delta_m = \Phi_1 \delta_1 + \Phi_3 \delta_3$$

Here F_1 and F_3 are the volume fractions of the solvent and the precipitant in the solvent; δ_1 and δ_3 are the solubility parameters of the solvent and precipitant; $V_1 x V_3$ are the molar volumes of the solvent and precipitant.

Thus, the values of δ_{20} and $\delta_{2\infty}$ can be determined from the experiment and, using the extrapolation method of reducing to one temperature, can be compared.

We investigated industrial samples of polymers, which were subjected to additional purification by reprecipitation from a weight% solution in an appropriate solvent into a precipitant - a standard, with a solvent: precipitant ratio of 1:10.

Organic liquids of various chemical structures, chemically pure grade were used as sorbates, solvents, and precipitants. or purified according to the methods described in [11].

Investigations by the WGC method were carried out on a Tsvet-100 gas chromatograph with a flame ionization detector. Nitrogen was used as a carrier gas. The silanized support ChromatonN –AW-DMCS with a particle diameter of 0.20–0.25 mm served as a solid support.

The packing was prepared by the evaporation method. The following solvents were used: in the case of (SRE PT), carbon tetrachloride; in the case of chlorocarboxylated (CSPT), chlorinated PE (XPE), PVC, and P U, tetrahydrofuran. The percentage of stationary phase in the packing was determined by serial weighing after extraction of the polymer for 1 week in a Soxhlet extractor. Used stainless steel columns with a length of 1.0 m, which were filled with packings with a polymer content of 10-12 wt.%.

The characteristics of the columns are listed in Table 3.

Table 3

Column characteristics

Polymer	Column packing weight, g	Polymer content in the packing, %	Polymer weight in the column, g
XSPE	5,750	10,0	0,575
XPE	4,520	10,1	0,558
PVC	5,750	10,3	0,592
PU	6,300	10,0	0,630
SREP	4,802	10,7	0,514

The experiments were carried out at 353, 373, 393 °K, which is higher than the glass transition temperature of all polymers. The volume of the sorbate sample was 0.02 0.5 µL. The value of the retention time “b” and “interaction” was determined from gaseous methane.

Equilibrium values of the retention volumes were obtained by extrapolation to zero flow rate of the carrier gas.

For the solubility parameter of polymers by the TDT method, solutions with a concentration of 0.05 g / dL were prepared. The precipitant was slowly added to 15 ml of the polymer solution while stirring the solution.

The change in the optical density of the solution was recorded on a FEK-M photoelectric calorimeter, after which the concentration of the precipitant corresponding to the onset of polymer precipitation (turbidity point) was determined by extrapolation to zero optical density. To titrate polymer solutions at 298 °K two different precipitants were used - one with a higher solubility parameter, the other with a lower solubility parameter.

As expected, polar and non-polar chlorine derivatives of hydrocarbons turned out to be good solvents for HPE and CCPE.

For PU, polar chlorine derivatives of hydrocarbons and ketones turned out to be good solvents, and non-polar compounds for EPDM. It is interesting to note that tetrahydrofuran and chloroform turned out to be good solvents for all studied polymers at temperatures of 353 – 393°K. It is known [12] that halogen (or oxygen) atoms activate the hydrogen atom and it becomes capable of forming hydrogen bonds, which are weakly implemented between homogeneous molecules, which makes such compounds universal solvents for polymers. This is also facilitated by the small size of the molecules, which facilitates diffusion into the bulk of the polymer. (Table 4)

Table 4

Contribution of $X_{12\infty}/V$ to $\delta/RT - X/V_1$ of the sorbates used, the value of which varies with temperature

Polymer	$\delta_{2\infty}$				298 °K
	393°K	373°K	353°K	Payment 298°K 0K	
SREPT	6,750,31	7,260,49	7,750,33	9,160,36	9,860,35
XPE	7,110,49	7,530,56	7,930,44	9,060,50	9,910,35
PU	7,060,57	7,500,41	8,050,65	9,490,55	12,070,35
SREP	7,110,15	7,360,57	7,590,11	8,250,28	8,550,35
PVC	7,110,51	7,520,56	7,910,98	9,140,42	9,890,35

The contribution of $X_{12\infty}/V$ to $\delta/RT - X/V_1$ is different for a number of used sorbates, the value of which also changes with temperature.

Thus, according to the criterion of the contribution X/V_1 , we selected for CCPE -7 sorbates, PU -7 sorbates, HPE -6 sorbates, and SREP-7 sorbates, which were used to calculate $\delta_{2\infty}$.

As can be seen, all values of $\delta_{2\infty}$ are a decreasing function of temperature, which allows extrapolating the obtained results to 469 °K with sufficient reliability [12-13].

The obtained value $\delta_{2\infty} = 8.250.28$ for EPDM turned out to be in fairly good agreement with $\delta_{2\infty}0.11$ obtained by the WRC method [13], taking into account the influence of the nature and composition of the polymer on its solubility parameter.

It should be noted that the measurement error increases with an increase in the number of functional groups in the macromolecule, reaching the maximum value for PU.

It was shown [14] that in all cases the δ_{20} values obtained from titration data in aliphatic solvents are more widely scattered and consistently lower than the values obtained from titration data in aromatic solvents. Hildebrand showed [15] that good agreement with experiment can also be obtained for hydrocarbons if it is assumed that the values of their solubility parameters are 0.6 higher than those calculated from the evaporation energy. However, in practice, a correction to δ_1 of about 0.3 was required. This introduces an uncertainty in the value of δ_{20} for aliphatic solvents, leading, however, to an error in determining δ_{20} , no more than 0.35. This error value was taken for all determinations of polymer solubility parameters by the TDT method.

1V.CONSLUSION

Thus, an experimental comparison of the values of the solubility parameters of polymers obtained by the two WRC and TDT methods, characterized by an extremely opposite state of the polymer with respect to the solvent, showed a significant difference in the solubility parameters for polymers with strong specific interactions between macromolecules, which requires attention when using the theory of parameters solubility to predict the compatibility of polymer pairs to the method by which the value used is derived. Obviously, for crystallizing polymers, there should also be a difference in the solubility parameters.

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