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## X-RAY PHASE ANALYSIS OF METAL POLYMERS BASED ON AROMATIC POLYAMIDE

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**Summary.** This paper analyzes the structure of metal polymers studied by the method of X-ray analysis. It is shown that introducing metal into the polymer does not directly result in creating new crystallization centers but simply increases the efficiency of the existing ones by reducing the surface tension on the crystal - melt boundary. It has been established that X-ray degree of crystallinity of the developed metal polymers depends on particle size.

**Key words:** aromatic polyamide phenylone, aluminum, bronze, copper, nickel, titanium, metallpolymers, x-ray phase analysis

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**Problem statement.** Currently, there is a big amount of methods to do phase analysis. Radiographic method is most widely used due to the fairly well developed theory that has got some practical advantages. Given the fact that every ingredient is characterized by its lattice, specific chemical composition and distribution of the atoms, the diffraction pattern is a kind of a passport of a chemical compound, which can determine the kind of the previously known compounds that the diffractogram corresponds to. X-ray phase analysis method allows to obtain the most complete information about the substance state.

**Aim of the work.** The study the structure of developed materials by X-ray phase analysis.

**Objects and methods of research.** The aromatic polyamide phenylone, modification S-1 according to the TU 6-05-221-101-71 technical standard, was used as the polymeric matrix and fine powders of carbonyl nickel (PNK-2K10 according to GOST State Standard 9722-97), copper (PMS-1 according to GOST State Standard 4960-2009), aluminum (PA-1 according to GOST State Standard 6058-73), titanium (PTK-1(2) according to TU 14-22-57-92 standard), and bronze (Br O5Ts5S5 according to GOST State Standard 613-79) were used as filling materials [1]. The basic properties of the materials are presented in Table 1.

Table № 1

Basic properties of compacted powders

Symbol	Color	Density (kg/m <sup>3</sup> )	Apparent density (kg/m <sup>3</sup> )	Melting point (K)	Particle size (µm)
S-1	Pink	1350	200 – 300	543*	35-50
Ni	Gray	8900	≥ 1200	1726	12-21
Cu	Red	8960	1250-2000	1356	33-57
Al	Silver-white	2699	960	934	129-172
Ti	Silver-white	4505	2850	1933	158-284
Br.(Bronze)	Goldish	8800	3700 – 4700	1203 – 1373	43-90

\* Vicat softening point.

The following compacted powder compositions were used: phenylone S-1 + 5–20 wt % of a fine metallic filling material were prepared by mixing the components in a rotating electromagnetic field in the presence of ferromagnetic particles. The resulting mixtures were pelleted on a hydraulic press at room temperature and a pressure of 40 MPa; then, the pelleted samples were dried in an oven at a temperature of 473–523 K since the processing of undried phenylone impairs its strength properties and results in surface flaws. The dried and pelleted workpieces were subjected to compression molding at a temperature of 593 K and a pressure of 40 MPa for 10 min to manufacture products.

X-ray diffraction studies have been conducted at the URS-50IM set. Such a device is used for most tasks concerning ray diffraction analysis, particularly for determining the phase composition, the exact periods of the lattice, the block structure, for determining the characteristic temperatures.

A great advantage of the device is that it can significantly reduce the time required for obtaining X-ray and photometric curves. During the investigation MoK $\alpha$  - radiation (wavelength 0.710 Å) has been used.

To reduce the relative level of background in the diffraction diagram the combination of Johann's focusing monochromator explored by Lang has been used, located in front of Brittany Bragg counter for filming polycrystalline samples "on reflection". In this case, diffractometer conditions of the resolution depend on the first monochromator crack. The spectral range that is reflected by the monochromator does not depend on the crystal perfection, but is determined by slits and aberrations according to Johann method [1].

Qualitative X-ray analysis has been aimed at identifying crystalline phases based on the inherent values of interplanar distances  $d_{\text{HKL}}$ , calculated by Wulff – Bragg formula (1) and correspondent relative intensities.

Quantitative analysis has been used to determine the X-ray degree of crystallinity (CD) by the formula (2), the shortest interatomic distance  $R_0$  by means of Hegel formula (3) and the size of crystallites (coherent scattering zones) by Selyakov - Scherrer formula(4).

$$2d_{\text{HKL}} \cdot \sin\theta = \lambda \quad (1), \quad R_0 = 0,615\lambda / \sin\theta \quad (3),$$

$$DC = \Sigma K \cdot 100\% / \Sigma K + A \quad (2), \quad L = \lambda / \beta \cdot \cos\theta \quad (4),$$

where  $d_{\text{HKL}}$  is interplanar distance;  $\theta$  is angle of dispersion;  $\lambda$  is wavelength; DC is the X-ray degree of crystallinity;  $\Sigma K$  is the sum of areas of crystalline phase; A is the area of the amorphous phase;  $\beta$  is the FWHM (full-width at half-maximum height).

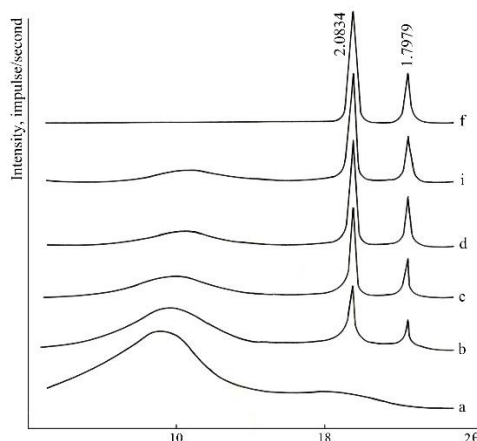
**Results and Discussion.** The introduction of fillers (FI) into the polymers leads to the emergence of a wide range of interactions (ranging from weak physical interactions to chemical ones) that occur at polymer - filler interface. The nature of these interactions depends significantly on the surface chemistry of the filler. Correspondence of different types of interactions that occur at the interface significantly affect the mechanical, physico-chemical and thermal properties of polymers and the filled system in general. Obviously, the surface chemistry of dispersed fillers is one of the most significant factors affecting the nature of the interaction at the interface and therefore the properties of the polymer [2].

Phenylone is an amorphous polymer that is obtained by means of polycondensation, a linear heterochain polar aromatic polyamide containing nitrogen and oxygen atoms in its main chain of macromolecules [3].

Diffraction of phenylone S-1 (Fig. 1, a) has got a broad amorphous halo ( $2\theta = 9^\circ$ ) and contains no crystalline reflexes, which is typical for amorphous polymers with rather rigid polymer chains and not very high molecular symmetry [4]. Amorphous polymers are disordered or badly ordered crystalline polymers. Their high deficiency, compared to crystals of substances

with low molecular weight is conditioned, on the one hand, by the structural features of the polymer crystals, i.e. the presence of folded conformation and, therefore, the appearance of defects in the bends of macromolecules. On the other hand, it is conditioned by the presence of various disturbances in the regularity of chains structure that disorder the crystalline lattice, forming the systems of the "forced" solid inclusions [5].

With the help of quantitative X-ray analysis it has been found that the shortest distance between atoms of phenylone is 0.56 nm, and the crystallite size is 1.77 nm (see table 2).

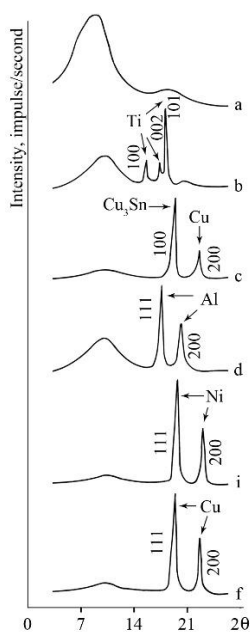


**Figure 1.** X-ray diffraction graphs of phenylone S-1 (a), of copper powder (f) and metal polymers containing 5 (b), 10 (c), 15 (d) and 20 wt % (e) copper as fillers

**Table № 2**

The results of quantitative analysis X-ray diffraction graphs of phenylone and metal polymers containing copper as fillers

Filler percentage (wt %)	–	5	10	15	20
The shortest interatomic distance, $R_0$ (nm)	0,56	0,54	0,51	0,48	0,47
The average crystallite size, L (nm)	1,77	1,81	2,20	2,82	2,18



**Figure 2.** X-ray diffraction graphs of phenylone S-1 (a) and metal polymers containing 15 wt %: (b) – Ti, (c) –  $\text{Cu}_3\text{Sn}$ , (d) – Al, (e) – Ni, (f) – Cu  $\text{Cu}_3\text{Sn}$ , tricopper stannide, is a binary intermetallic inorganic compound of copper and tin, characteristic for tinned bronze, as fillers

X-ray diffraction graphs of metal polymers (MP) containing copper as fillers (Fig.1, b – i) show two intense peak points characteristic for the cubic system which copper belongs to. The distance between the planes of lattice  $d_{\text{HKL}}$  are: 2.0834 (at  $2\theta = 19^{\circ}36'$ ) and 1.7979 (at  $2\theta = 22^{\circ}45'$ ), corresponding to the number  $d_{\text{HKL}}$  copper [6]. Also, they kept amorphous halo characteristic for phenylone, which has a lower intensity and is shifted towards larger angles by  $0^{\circ}18' - 1^{\circ}25'$ . This is caused by defects of type I which do not cause changes in the distribution of the intensity of correct reflection and therefore do not lead to the lines' expansion.

It is known [7] that in the process of shape change in order to manufacture details or semi-finished parts, the entire volume of the material or its surface layers can be influenced by external forces. These actions are accompanied by plastic deformation, which leads to a significant increase in the density of defects, such as dislocations, package faults, vacancies, inter-knot atoms, etc. Any defect can cause displacement of atoms from the lattice knots and the change of scattering ability of the  $n$ -th atom, leading to the weakening of the integrated intensity and the shift of reflexes.

On the other hand, reducing the intensity of diffraction lines is explained by the fact that the increased concentration of filler increases the number of metal particles that undergo X-ray action.

Table 2 shows that the increase of the fillers concentration leads to the decrease of the shortest interatomic distance, accompanied by the growth in the average size of crystallites, which indicates a specific effect of copper structure on phenylone. As it is shown in [5], introducing surfactants into the polymer does not directly result in creating new crystallization centers but simply increases the efficiency of the existing ones by reducing the surface tension on the crystal - melt boundary.

As for the influence of other dispersed metal fillers on phenylone structure, the situation does not significantly change (see Fig. 2). Metal polymers containing Ti show three intense peak points characteristic for the hexagonal crystal system which titanium belongs to, others show two intense peak points, like MP and copper.

Metal fillers lead to an increase in the average size of crystallites with simultaneous reduction of the shortest interatomic distance (see Table 3), with the biggest influence of carbonyl nickel, which is conditioned by its structure [8], while the smallest influence is that of aluminum.

**Table № 3**

The results of qualitative and quantitative analysis

Fillers	$r$ ( $\mu\text{m}$ )	DC (%)	$R_0$ (nm)	$L$ (nm)	Peak number	$d_{\text{HKL}}$ (nm)	I (%)
1	2	3	4	5	6	7	8
–	–	–	0,56	1,77	–	0,452	–
Ni	12 – 21	61	0,46	2,72	1	0,204	100
					2	1,770	50

1	2	3	4	5	6	7	8
Cu	33 – 57	55	0,47	2,27	1	0,208	100
					2	0,180	53
Br	43 – 90	48	0,49	2,40	1	0,209	100
					2	0,182	53
Al	129 – 172	34	0,50	1,85	1	0,233	100
					2	0,203	40
Ti	158 – 284	24	0,50	2,04	1	0,254	27
					2	0,234	20
					3	0,223	100

X-ray degree of crystallinity correlates with particle size ( $r$ , mcm) of the filler, which is conditioned by two factors. On the one hand, the decrease of particle size leads to the increase of the number of metal polymers in volume and as a result, in the area of monochromator crack. On the other hand, the area of polymer – filler interface is growing and the number of crystallization centers increases.

**Conclusions.** As a result of the research we have studied the effect of dispersed metallic fillers on phenylone structure. It is shown that metals specifically affect phenylone, increasing the efficiency of crystallization centers, with a more substantial impact of carbonyl nickel. It has been established that X-ray degree of crystallinity of the developed metal polymers depends on particle size.

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## **РЕНТГЕНОГРАФІЧНИЙ ФАЗОВИЙ АНАЛІЗ МЕТАЛОПОЛІМЕРІВ НА ОСНОВІ АРОМАТИЧНОГО ПОЛІАМІДУ**

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**Резюме.** З використанням рентгенографічного аналізу досліджено структуру металополімерів. Показано, що дисперсні метали наповнювачі активно впливають на полімерну матрицю на хімічному рівні, знижуючи поверхневий натяг на межі кристал – розплав.

**Ключові слова:** ароматичний поліамід фенілон, алюміній, бронза, мідь, нікель, титан, металополімери, рентгенографічний аналіз.

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