

UDC 620.22+539.26+531.424

**ORDERING AND DENSITY AMORPHOUS PHASE OF CARBON-FIBER
POLYMER-MATRIX PTFE-COMPOSITES**

**УПОРЯДОЧЕНИЕ И ПЛОТНОСТЬ АМОРФНОЙ ФАЗЫ ПОЛИМЕРНОЙ МАТРИЦЫ
КОМПОЗИЦИЙ ПТФЭ С УГЛЕРОДНЫМ ВОЛОКНОМ**

©**Kalistratova L.**,

*Omsk State Technical University,
Omsk, Russia, lfkalistr@yandex.ru*

©**Калистратова Л. Ф.**,

*Омский государственный технический университет,
г. Омск, Россия, lfkalistr@yandex.ru*

©**Kireev A.**,

*Omsk State Technical University,
Omsk, Russia, sashkir7@mail.ru*

©**Киреев А. П.**,

*Омский государственный технический университет,
г. Омск, Россия, sashkir7@mail.ru*

Abstract. We studied the application of a mathematical model for calculating the X-ray density of a pure amorphous-crystalline polymer, taking into account the degree of ordering, crystallinity and deformation of a crystalline cell in the amorphous phase, to carbon-fiber PTFE-composites. By comparing the theoretical densities (based on the developed software) of PTFE+CF-composites system with the results of experimental densities and X-ray structural parameters, it was shown that the degree of ordering and density of the amorphous phase of the polymer-matrix PTFE-composites linearly decrease as the content of the carbon-fiber increases. The change in the degree of ordering of the amorphous phase when filler application can be considered as one of the mechanisms of formation of supramolecular structure of composite materials on the basis of amorphous-crystalline polymers.

Аннотация. Изучается применение математической модели расчета рентгеновской плотности чистого аморфно-кристаллического полимера, учитывающей степени упорядочения, кристалличности и деформацию кристаллической ячейки в аморфной фазе, к композиционным материалам ПТФЭ с углеродным волокном. Путем сопоставления полученных с применением разработанных компьютерных программ теоретических плотностей композитов системы ПТФЭ+УВ с результатами экспериментальных плотностей и рентгенографических структурных параметров показано, что степень упорядочения и плотность аморфной фазы полимерной матрицы композитов ПТФЭ линейно уменьшаются при возрастании содержания углеродного волокна. Изменение степени упорядочения аморфной фазы при внесении наполнителя можно считать одним из механизмов формирования надмолекулярной структуры композиционных материалов на основе аморфно-кристаллических полимеров.

Keywords: model, density, structure, ordering, phase, polytetrafluoroethylene, filler.

Ключевые слова: модель, плотность, структура, упорядочение, фаза, политетрафторэтилен, наполнитель.

A priori it is considered that the supramolecular structure of the amorphous-crystalline polymers, prominent example of which is polytetrafluoroethylene (PTFE), consists of two phases: crystalline and amorphous, the boundaries between which filled the so-called interphase layer. In large objects (crystalites, fibrils, spherulites) of crystalline phase usually observed an the ideal crystal lattice, constructed of ideal elementary cells. The amorphous phase is represented by smaller crystal formations from polymer macromolecules in the form of globules, packets, domains or clusters [1–3]. Determining the mass fractions of the phases is a greatly difficult task.

For the theoretical calculation of the polymer–matrix density ρ_m in the two–phase model of amorphous–crystalline polymers, the following formula is used [3]:

$$\rho_m = \chi\rho_{cr} + (1 - \chi)\rho_{am} , \quad (1)$$

where:

ρ_{cr} and ρ_{am} — density of crystalline and amorphous phases, respectively;

χ — degree of the polymer crystallinity.

In the presence of the parameters values of the crystal cell, the value of ρ_{cr} can be easily calculated from the formula [13]:

$$\rho_{cr} = \frac{M}{N_A \cdot V_{cr}} \quad (2)$$

where:

M — polymer molar mass;

N_A — Avogadro's number;

V_{cr} — volume of the ideal crystalline cell, defined by its crystal structure (syngony).

The question concerning the theoretical calculation of the size of the frames remains open. In addition, it is complicated by the fact that in the modern view of the structure of amorphous-crystalline polymers is more complex than described above. The proof of this is the emergence in the last decade of experimental work [4–6]. The results of which can assume the presence in the structure of the PTFE of the three phases: crystal and amorphous two phases, one of which has some degree of ordering.

For many years engaged in the study of the structure and properties of composite materials based on amorphous-crystalline PTFE radiographic method, the author of this work is also of the view that the presence of portions of the amorphous halo in the diffraction patterns of pure PTFE and carbon-fiber PTFE suggests that the amorphous phase of the polymer is characteristic of *a partial ordering*. We therefore propose the following formula to calculate the density ρ_{am} of the amorphous phase of the polymer frames [7]:

$$\rho_{am} = \alpha\rho_{am1} + (1 - \alpha)\rho_{am2} , \quad (3)$$

where ρ_{am1} – density crystalline formations *conventionally ordered* part of the amorphous phase with *deformed* crystal lattice, and ρ_{am2} – density *disordered* part, which is generally not characterized by the presence of the crystal lattice. The degree of ordering of α characterizes the ratio between the volumes of these parts. The separation of the concepts of *perfect* and *deformed* crystal cells enables calculation of the density of probation ordered parts ρ_{am1} by the formula similar to (2):

$$\rho_{am1} = \frac{M}{N_A \cdot V_{am}}, \quad (4)$$

where V_{am} – the average volume of the deformed crystal cell of a polymer in a *conventionally ordered* amorphous phase. As a result, for calculation of X-ray density of the matrix amorphous-crystalline polymer, depending on the degree of ordering of the amorphous phase and the crystallinity of the polymer-matrix provides a formula:

$$\rho_m = \chi \rho_{cr} + \alpha(1 - \chi) \rho_{am1} + (1 - \alpha)(1 - \chi) \rho_{am2}. \quad (5)$$

The basis of the theoretical calculation formula (5) is the presence of X-ray amorphous-crystalline polymer, which defines the basic quantities characterizing the structure of the polymer-matrix: the parameters of the crystal cell – a , b , c ; average interlayer distance in the amorphous phase – C_{am} ; the degree of deformation of the crystal lattice is – ϵ ; the degree of crystallinity – χ . In [7] presents all justification for the mathematical model described by equation (5), a computer program for calculating the density of ρ_m – in [8]. The analysis of theoretical dependences of $\rho_m = f(\alpha)$, $\rho_m = f(\chi)$, $\rho_m = f(C_{am})$ for pure PTFE, for which the ordering degree of the amorphous phase was equal to $\alpha = 0.5$ relative precision of 5% carried out in [9, 10]. The formula (5) can be applied to calculate the density of the composites based on amorphous-crystalline polymers.

The aim of this work is to study the effect of fibrous filler on the degree of ordering of the amorphous phase in the compositions of carbon-fiber PTFE. Calculations of the values of α are inverse solution of the formula (5), knowledge of the values of the X-ray structural parameters determined from conventional radiographs of the composite, the experimental values of density of the composites systems PTFE+CF and using computer programs.

Material and methods

The objects of study are composite materials based on carbon-fiber PTFE. The methods of obtaining samples of pure PTFE and carbon-fiber PTFE are described in detail in the monographs written under the General supervision of Professor, Ph. D., Mashkov Yu. K. [1, 2, etc.]. The content of hydrocarbons in the samples varied from 3 to 30 wt. % Values of the experimental densities of the composites of the system of PTFE+CF obtained by hydrostatic weighing, are given in [12]. The experimental carbon-fiber density $\rho_{CF} = 1.70 \text{ g/cm}^3$.

The composites density of the PTFE+CF system can be calculated based on the formula:

$$\rho_c = n_1 \rho_m + n_2 \cdot \rho_{CF}, \quad (6)$$

where n_1 and n_2 – are the weight fraction of PTFE and CF, ρ_m and ρ_{CF} – density composite polymer-matrix and carbon-fiber density, respectively. When calculating the density of the composite ρ_c by the formula (6) density matrix ρ_m should be calculated according to the formula (5). The solution of the inverse problem of the formulas (2–6) the degree of ordering of α in its final form is defined as:

$$\rho_k = n_1 \rho_m + n_2 \cdot \rho_{CF}, \quad (6)$$

Processing of radiographs, obtained at an X-ray diffractometer DRON-3 in shooting mode at high angles, and calculation of the parameters characterizing the structure of the samples (i.e. values χ , C_{am} , ϵ and the constant of hexagonal crystalline cells) and the calculation of densities of ρ_m , ρ_{am1} and ρ_{am2} details are given in [7, 8].

The software is implemented in the computer algebra system Wolfram Mathematica, which finds wide application in computer, mathematical, engineering, scientific fields. The program includes three independent unit.

First block: data input.

The user is presented a form where you must enter the original data.

```
Text["Enter the data"];
[ТЕКСТ]
YV = 30;      Text["Carbon fiber,%"];
[ТЕКСТ]
Cam = 1.53;    Text["Average interlayer distance,nm"];
[ТЕКСТ]
e = 8.93;      Text["Degree of deformation of the crystal lattice,%"];
[ТЕКСТ]
X = 58;        Text["Degree of crystallinity,%"];
[ТЕКСТ]
Pkomp = 1.65;  Text["The experimental value of the density of the composite,g/m^3"];
[ТЕКСТ]
```

Second block: the calculation data.

```
Text["Calculation of results"];
[ТЕКСТ]
Pkomp =  $\frac{YV \cdot 1.7}{100}$ ; Text["The density of the matrix,the density of PTFE"];
[ТЕКСТ]
Pm =  $\frac{Pkomp}{1 - \frac{YV}{100}}$ ;
[ТЕКСТ]
Pam =  $\frac{Pm - \frac{2.69 \cdot X}{100}}{1 - \frac{X}{100}}$ ; Text["Amorphous phase density"];
[ТЕКСТ]
Pam1 =  $\frac{0.75}{6.02 \cdot 10^{23} \cdot 0.866 \cdot 0.564^2 \cdot 1.65 \cdot 10^{-24}}$ ; Text["The density of an ordered amorphous phase"];
[ТЕКСТ]
Pam2 =  $\frac{e}{100} \cdot 2.69$ ; Text["The density of a disordered amorphous phase"];
[ТЕКСТ]
alpha =  $\frac{Pam - Pam2}{Pam1 - Pam2}$ ; Text["Degree of ordering"];
[ТЕКСТ]
```

The third block: the output data obtained in block 2.

```
Text["Output of results"];
```

```
|текст
```

```
res = List[{"Pam1", "Pam2", "Pam", "Pm", "α"}, {Pam1, Pam2, Pam, Pm, α}] // TableForm
```

```
|список
```

```
|табличная фк
```

```
Pam1      Pam2      Pam      Pm      α
2.74097    0.240217   0.162789  1.62857  -0.0309618
```

Results and discussions

Scattering curves of carbon-fiber PTFE composites is given in [1], determined from radiographs of the parameters, characterizing the structure of the polymer-matrix PTFE composite, presented in Table.

Table.

X-RAY DIFFRACTION DATA AND DENSITIES OF THE PTFE+CF COMPOSITES PHASES

% CF	C_{am} , nm	ε , %	χ , %	ρ_c , g/cm ³	ρ_{am1} , g/cm ³	ρ_{am} , g/cm ³	ρ_m , g/cm ³	α
0	1.65	1.79	53	2.20	2.74	1.65	2.20	0.60
3	1.65	1.79	58	2.18	2.74	1.51	2.20	0.54
7	1.53	8.93	63	2.17	2.96	1.38	2.20	0.45
10	1.54	8.93	64	2.10	2.94	1.17	2.14	0.38
15	1.53	8.93	64	2.00	2.96	0.92	2.05	0.25
20	1.53	8.93	60	1.87	2.96	0.75	1.91	0.19
30	1.53	8.93	58	1.65	2.96	0.16	1.63	-
Column	1	2	3	4	5	6	7	8

With the introduction of the filler parameters of the crystal cell and its volume practically does not change within the error correspond to the values for pure PTFE ($a = 0.564$ nm, $C = 1.68$ nm, $V_{cr} = 0.472$ nm³).

The different behavior of the structural parameters C_{am} and χ of the amorphous phase of the polymer-matrix to the authors of works [1, 11] allowed to Express an opinion on the existence of the composites are quite different structures of the polymer-matrix: the minor (up to 10 masses. %) the content of hydrocarbons in it there is a structure of type I and high (more than 15 masses. %) the content of the carbon-fiber structure of the type II.

Compare the above comments on structural types of the PTFE+CF system composites with estimated densities of all phases. Compare the above comments on structural types of the PTFE+CF system composites with the estimated densities of the phases. For all compositions, the density of the crystalline phase think almost the same and equal to $\rho_{cr} = 2,69$ g/cm³.

Completely different CF affects the density of the amorphous phase. The transition of the structural type matrix composites from type I to type II is characterized by an abrupt increase in the relative deformation ε of the crystal cell in a relatively orderly part of the amorphous phase of the matrix about 5 times. This leads to the same increase of density of the disordered part of the amorphous phase of the matrix from the values $\rho_{am2} = 0,048$ g/cm³ in structural class I, to the values of 0.24 g/cm³ in structural class II. In addition, under the same conditions, a decrease in the average

interlayer distances C_{am} leads to a small increase in the density ρ_{am} conditionally orderly part of the amorphous phase of PTFE is only 7.7%. Total influence of changes of these values with increasing content of hydrocarbons leads to a systematic linear decrease in the density of the amorphous phase frames (Table, Column 6) in the whole range of studied concentrations of hydrocarbons.

The density of the polymer matrix of ρ_m composites is almost constant in the region of existence of the structural organization of type I, and in the structural organization of type II, starting with concentrations of 10 wt. % CF, the density ρ_m , as well as the density of the composites ρ_c decreases with increasing content of hydrocarbons already due to the large content of the fibrous filler, the density of which is much less than the density of PTFE (Table, Column 7).

With regard to the degree of order α , then it is, regardless of the types of structural organizations decreases linearly from its maximum value $\alpha_{max} = 0.60$, characterizing of pure PTFE, to almost zero (Figure).

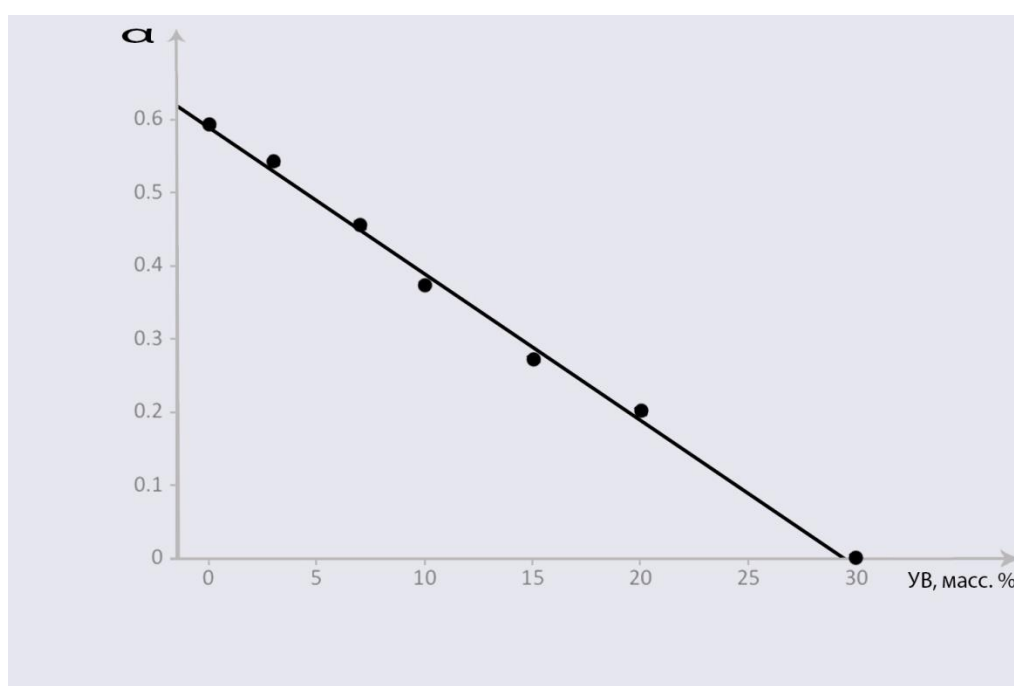


Figure. The concentration dependence of the degree of ordering of the amorphous phase of the matrix in the PTFE+CF composites system

Thus, the fibrous filler in the amorphous and crystalline polymer contributes at high concentrations of filler disordering of the amorphous polymer-matrix and its transition in two-phase state with fully disordered amorphous phase.

Conclusions

1. The degree of ordering of the amorphous phase of the supramolecular structure of the polymer-matrix of pure PTFE is equal to 0.6.
2. The increase in the content of the fibrous filler resulted in a linear decrease in the degree of alignment and density of the amorphous phase of the matrix of the composites regardless of the type of structural organization of the polymer-matrix.
3. Complete loss of ordering of the amorphous phase observed in the compositions with a high content of fibrous filler (more than 25 mass. %) is likely related to the amorphous phase of crystalline formations of PTFE macromolecules.

4. The change in the degree of ordering of the amorphous phase while making filler can be considered as one of the mechanisms of formation of supramolecular structure of composite materials on the basis of amorphous-crystalline polymers.

Special thanks and appreciation to Professor O. V. Kropotin for providing the experimental of PTFE+CF composites systems density.

References:

1. Mashkov, Yu. K., Ovchar, Z. N., Surikov, V. I., & Kalistratova, L. F. (2005). Composite materials based on polytetrafluoroethylene. Moscow, Mashinostroenie, 2005. 240. (in Russian)
2. Mashkov, Yu. K., & Kalistratova, L. F. (2016). Methodological aspects of the theory of synthesis and the evolution of the structure of PTFE-composites. *Materialovedenie*, (4), 39-44. (in Russian)
3. Surikov, V. I., & al. (2014). Viscoelasticity and relaxation properties of modified polytetrafluoroethylene. Omsk, Izd-vo OmGTU, 140. (in Russian)
4. Antipov, E. M., Ignatieva, L. N., & al. (2010). X-ray phase analysis of polytetrafluoroethylene. *Kristallografiya*, 55, (4), 651-655. (in Russian)
5. Kozlov, G. V., & Novikov, V. U. (2001). A cluster model for the polymer amorphous state. *Physics-Uspekhi*, 44, (7), 681-724
6. Lebedev, Yu. A., & al. (2010). X-ray phase analysis of the polytetrafluoroethylene. *Kristallografiya*, 55, (4), 651-656. (in Russian)
7. Kalistratova, L. F., & Egorova, V. A. (2017). Methods of determination of density of amorphous-crystalline polymers based on mathematical models based on radiographic parameters. Moscow, OFERNiO. Electronic resource.
8. Kireev, A. P., & Kalistratova, L. F. (2017). Computer program for theoretical calculation of X-ray density polytetrafluoroethylene. *Konferentsiya "Rossiya molodaya: peredovye tekhnologii - v promyshlennost": materials*. Omsk, Izd-vo OmGTU, (1), 332-336. (in Russian)
9. Kalistratova, L. F., & Kireev, A. P. (2017). Effect of structural parameters on the theoretical X-ray density for amorphous and crystalline polymers for example, PTFE. *Konferentsiya "Teoriya i praktika sovremennogo nauchnogo znaniya. Problemy. Prognozy. Resheniya": materialy*. St. Petersburg, 121-127. (in Russian)
10. Kalistratova, L. F., & Egorova V. A. (2017). Methods of determining the density of the composites based on amorphous-crystalline polymers subject to radiographic parameters. Moscow, OFERNiO. Electronic resource.
11. Kropotin, O. V., Akimenko, S. S., Gorbunov, V. A., Stishenko, P. V., & Fefelov, V. F. (2014). Vliyanie mezhfaznogo vzaimodeistviya v grafitonapolnennom politetraforetilene na plotnost matritsy. *Omskii nauchnyi vestnik*, (1). 22-26. (in Russian)
12. Mirkin, L. I. (1961). Handbook of X-ray diffraction analysis of polycrystals. Moscow, Gos. Izd-vo fiz.- mat. lit., 863. (in Russian)

Список литературы:

1. Машков Ю. К., Овчар З. Н., Суриков В. И., Калистратова Л. Ф. Композиционные материалы на основе политетрафторэтилена. М.: Машиностроение, 2005. 240 с.
2. Машков Ю. К., Калистратова Л. Ф. Методологические аспекты теории синтеза и эволюции структуры ПТФЭ-композитов // Материаловедение. 2016. №4. С. 39-44.
3. Суриков В. И. и др. Вязкоупругость и релаксационные свойства модифицированного политетрафторэтилена. Омск: Изд-во ОмГТУ, 2014. 140 с.

4. Антипов Е. М., Игнатьева Л. Н. и др. Рентгенографический фазовый анализ политетрафторэтилена // Кристаллография. 2010. Т. 55. №4. С. 651- 655.
5. Kozlov G. V., Novikov V. U. A cluster model for the polymer amorphous state // *Physics-Uspekh*. 2001. Т. 44. №7. С. 681-724.
6. Лебедев Ю. А. и др. Рентгенографический фазовый анализ политетрафторэтилена // Кристаллография. 2010. Т. 55. №4. С. 651-656.
7. Калистратова Л. Ф., Егорова В. А. Методика определения плотности аморфно-кристаллических полимеров на основе математической модели с учетом рентгенографических параметров. М.: ОФЭРНиО, 2017. Электронный ресурс.
8. Киреев А. П., Калистратова, Л. Ф. Компьютерная программа для теоретического расчета рентгеновской плотности политетрафторэтилена // Конференция «Россия молодая: передовые технологии - в промышленность»: материалы. Омск: Изд-во ОмГТУ. 2017. №1. С. 332-336.
9. Калистратова Л. Ф., Киреев А. П. Влияние структурных параметров на теоретическую рентгеновскую плотность аморфно-кристаллических полимеров на примере ПТФЭ // Конференция «Теория и практика современного научного знания. Проблемы. Прогнозы. Решения»: материалы. СПб., 2017. С. 121-127.
10. Калистратова Л. Ф., Егорова В. А. Методика определения плотности композитов на основе аморфно-кристаллических полимеров с учетом рентгенографических параметров. М.: ОФЭРНиО, 2017. Электронный ресурс.
11. Кропотин О. В., Акименко С. С., Горбунов В. А., Стищенко П. В., Фефелов В. Ф. Влияние межфазного взаимодействия в графитонаполненном политетрафторэтилене на плотность матрицы // Омский научный вестник. 2014. №1 (127). С. 22-26.
12. Миркин Л. И. Справочник по рентгеноструктурному анализу поликристаллов. М.: Гос. Изд-во физ.- мат. лит., 1961. 863 с.

*Работа поступила
в редакцию 16.12.2017 г.*

*Принята к публикации
20.12.2017 г.*

Cite as (APA):

Kalistratova, L., & Kireev, A. (2018). Ordering and density amorphous phase of carbon-fiber polymer matrix PTFE-composites. *Bulletin of Science and Practice*, 4, (1), 137-144

Ссылка для цитирования:

Kalistratova L., Kireev A. Ordering and density amorphous phase of carbon-fiber polymer matrix PTFE-composites // Бюллетень науки и практики. Электрон. журн. 2018. Т. 4. №1. С. 137-144. Режим доступа: <http://www.bulletennauki.com/kalistratova> (дата обращения 15.01.2018).