PACS 536 + 539.2

ISSN 1729-4428

L.V. Baziuk, H.A. Sirenko

Thermophysical Properties of Metals and Polymer Compositions (Review)

Vasyl Stefanyk' Precarpathian National University, 57, Shevchenko Str., Ivano-Frankivsk, 76000, Ukraine

The dependence of enthalpy change, coefficient of thermal conductivity, coefficient of thermal capacity, linear coefficient of thermal expansion from temperature, serial number and radius of atom of metals has been analyzed and proved by correlation and regression analysis. Experimental investigation of thermophysical properties of composite polymeric materials based on polytetrafluorineetylene, aromatic polyamide and polyimide and fillers are explored.

Keywords: metals, polymers, polytetrafluoroethylene, aromatic polyamide, polyimide, thermophysical properties, enthalpy, coefficient of thermal conductivity, coefficient of thermal capacity, linear coefficient of thermal expansion, temperature, correlation analysis, regression analysis.

Стаття поступила до редакції 03.09.2012; прийнята до друку 15.12.2012.

The dependence of enthalpy change from temperature, serial number and radius of atom of metals has been analyzed and proved by correlation and regression analysis. Shown that the growth temperature enthalpy of metals growing. With the growth of the serial number of metal enthalpy decreases (Fig. 1). Established that growth between enthalpy and the radius of metal atoms no linear connection between a group IIA metals of periodic elements at temperatures 298.15, 400 and 900 K is close linear connection [1].

The dependence of coefficient of thermal conductivity from temperature, serial number and radius of atom of metals has been analyzed and proved by correlation and regression analysis. It is shown that with increasing temperature for most metals thermal conductivity decreases. In Figure 2 presents the dependence of thermal conductivity (λ) of copper, silver and gold on the temperature (T) in the temperature range 0-50 K (Fig. 2,a) and in the range 100 – 1300 K (Fig. 2,b). As can be seen from Figure 2, for gold (curve 3) observed a slight increase in the coefficient of thermal conductivity of $\lambda \approx$ 200 and $\lambda = 800 \text{ W/m} \cdot \text{K}$ with increasing temperature from ~ 0 K to T_{max} = 20 K. With further increase in temperature from T_{max} = 20 K to 50 K coefficient of thermal conductivity slightly decreases from $\lambda = 800$ to λ = 439 W/m·K. For silver and copper (Fig. 2, curve 1 and 2, respectively) observed a significant increase in the coefficient of thermal conductivity of $\lambda = \lambda = 4800$ to 10600 W/m·K (for silver) and from $\lambda \approx 500$ and $\lambda = 5000$ W/m·K (for copper) with increasing temperature from ~ 0 K to the temperature of the peak maximum of its value $(T_{max} = 8 \text{ K for silver and } T_{max} = 15 \text{K for copper})$. With

further increase in temperature from T_{max} to 50 K coefficient of thermal conductivity decreases sharply from $\lambda = 10600$ to $\lambda = 700$ W/m·K (for silver) and from $\lambda \approx 5000$ to $\lambda = 1500$ W/m·K (for copper). As shown in Figure 2,b, the coefficient of thermal conductivity of metals: copper (curve 1), silver (curve 2), gold (curve 3) with increasing temperature from T = 100 to T = 1300 K decreases linearly from $\lambda = 500$ to $\lambda = 320$ W/m·K (for copper), from $\lambda = 431$ to $\lambda = 381$ W/m·K (for silver) and from $\lambda = 343$ to $\lambda = 247$ W/m·K (for gold) and is independent of the atomic number of elements the metal.

Established that growth between coefficient of thermal conductivity and the radius of metal atoms no linear connection between a metals of periodic elements at temperatures 100, 200, 273, 300 and 900 K is close linear relationship [2, 3].



Fig. 1. Dependence of enthalpy change from temperature for: 1 - copper (Z = 29), 2 - silver (Z = 47), 3 - gold (Z = 79).







Fig. 3. Dependence of the thermal capacity from temperature for: 1 - copper (Z = 29), 2 - silver (Z = 47), 3 - gold (Z = 79): a) in the temperature range 0 - 200 K; b) in the temperature range 200 - 1300 K

The dependence of coefficient of thermal capacity from temperature, serial number and radius of atom of metals regression analysis. It is shown that with increasing temperature for most metals thermal capacity increases. Established that growth between coefficient of thermal capacity and the radius of metal atoms no linear connection between a metals of periodic elements at temperatures 100, 200, 273, 298 and 700 K is close linear relationship [4, 5].

In Figure 3 shows the dependence of coefficient of thermal capacity (c_p) metal-subgroup of group Periodic system - copper, silver and gold - the temperature (T) in the temperature range 0-200 K (Fig. 1a) and in the range 200-1200 K (Fig. 1b). As shown in Figure 1a, for gold (curve 3) an increase in the coefficient of thermal capacity of $c_p = 6 \cdot 10^{-6}$ to $c_p = 0,123$ kJ/kg·K, for silver (curve 2) a significant increase from $c_p = 7.2 \cdot 10^{-6}$ to $c_p = 0,225$ kJ/kg·K for copper (99.99%) (curve 1) Sun rises sharply from $14 \cdot 10^{-6}$ to 0.356 kJ/kg·K with increasing temperature from

~ 0 K to T = 200 K. The coefficient of thermal capacity with increasing atomic number of elements decreases. As shown in Figure 1b, the coefficient of thermal capacity of metals: copper (curve 1), silver (curve 1)

2), gold (curve 3) with increasing temperature from T = 200 to T = 1200 K increases linearly from $c_p = 0.356$ to $c_p = 0.502$ kJ/kg·K (for copper), from $c_p = 0.225$ to $c_p = 0.267$ kJ/kg·K (for silver) and from $c_p = 0.123$ to $c_p = 0.142$ W/m·K (for gold), depending on the serial number of elements the metal.

The dependence of linear coefficient of thermal expansion from temperature, serial number and radius of atom of metals has been analyzed and proved by correlation and regression analysis. It is shown that with increasing temperature for most metals linear coefficient of thermal expansion increases.

In Figure 4 shows the dependence of the linear coefficient of thermal expansion α of the metals subgroup of the periodic system elements - copper, silver and gold – from the temperature (T) in the temperature range 0 - 200 K (Fig. 4,a) in the temperature range 200 - 1250 K (Fig. 4,b) and in the range from 0 to 1250 K (Fig. 4,v). As shown in Fig. 4,a, linear coefficient of thermal expansion of metals with increasing temperature from ~ 0 K to T = 100 K rapidly increases from $\alpha = 0,008 \cdot 10^{-6}$ to $\alpha = 10,45 \cdot 10^{-6}$ (for copper), from $\alpha = 0,026 \cdot 10^{-6}$ to $\alpha = 11,5 \cdot 10^{-6}$ (for gold). Further increase in



Fig.4. Dependence of the linear coefficient of thermal expansion of the metal from the temperature: 1 - copper (Z = 29), 2 - silver (Z = 47), 3 - gold (Z = 79).

temperature from 100 K to 200 K leads to a slight increase in α . As the Fig. 2,b in all three cases, linear coefficient of thermal expansion α increases linearly, from $11,5 \cdot 10^{-6}$ to $19,5 \cdot 10^{-6}$ for gold (curve 3), $\alpha =$ $10,45 \cdot 10^{-6}$ to $\alpha = 24,4 \cdot 10^{-6}$ for copper (curve 1) and from $\alpha = 14,7 \cdot 10^{-6}$ to $\alpha = 28,1 \cdot 10^{-6}$ for silver (curve 2) with increasing temperature from 100 K to T = 1250 K. As shown Fig. 2, v with increasing temperature from ~ 0 K to 100 K linear coefficient of thermal expansion of Cu, Ag and Au intensively growing. In the range of high temperatures there is a slight increase in the linear coefficient of thermal expansion with increasing temperature in all three cases. Dependence $\alpha = f(T)$ is described by logarithmic equation with linear expansion coefficient does not depend on the serial number of elements.

Established that growth between linear coefficient of thermal expansion and the radius of metal atoms is linear connection between a metals of periodic elements at temperatures 100, 200 and 300 K, at temperature 800 K– no linear connection. Established that growth between linear coefficient of thermal expansion and the serial number of the metal atoms is linear connection between a metals

of periodic elements at temperatures 100, 200 and 800 K, at temperature 300 K- no linear connection [6].

Explain the properties can be found as follows. During the solidification of metals (such as in the cooling melt) while the huge number of small crystals, which interfere with each other to grow and acquire the correct form. Therefore, any metal product has polycrystalline structure consisting of a large number of small crystals the so-called crystallites, or grains, which, unlike the well-polished single crystals of other inorganic substances have irregular shape and different spatial orientation. For this reason, in the crystal structure of metals occurring defects that significantly affect the physical properties of metals.

Thermophysical behavior of polyimide composites filled with graphite and carbon fibers have been studied in a wide temperature range. The influence of the concentration of fiber (carbon fiber fabric with THN-2m) filler on the thermal properties of antifriction materials based on polyimide PM-69 (Fig. 5). Found that when injected in the composition of the carbon fiber fabric THN-2m in amounts up to 40 wt. % Of the observed linear increase in thermal conductivity of the material



Fig. 5. The dependence of the thermal conductivity of composite materials based on aromatic polyimide PM-69 and graphite fiber fabric with THN-2m from temperature: 1 - 0% carbon fiber; 2 - 10% carbon fiber; 3 - 20% carbon fiber, 4 - 30% carbon fiber, 5 - 40 % carbon fiber.

temperature. In Figure 5 clearly shows that the thermal conductivity increases linearly with increasing concentration of graphite fibers. This dependence increases with temperature tests. Two characteristic ranges have been revealed on concentration dependence: $\varphi < 20 \%$ vol and $\varphi > 40 \%$ vol. Composite behavior has been found differ essentially beyond the limits indicated [7].

Experimental investigation of thermophysical properties of composite polymeric materials based on polytetrafluorineetylene, aromatic polyimide and fillers are explored. The regularities of thermal capacity and thermal conductivity of composite materials on the basis of polytetrafluorineetylene, based on dependency upon temperature and concentration of ingredients of the filler were discovered. When checking the adequacy of the models revealed that the dependence of thermal capacity c_p from temperature T for composite materials PTFE

		Calculated thermal conductivity (W/m·K) by the				Experimental
	Volumetric	formulas				thermal
Filler	filler	Maxwell-	Odelevsky	Nielsen	Dulnev	conductivity
<u> </u>	content, %	Eiken			2 4 4 4	(W/m·K)
Graphite C–1	20,0	0,42	0,41	0,83	0,46	0,82
Titanium carbide /d = $1-2$ мкм/	23,0	0,45	0,45	0,44	0,49	0,40
Carbon fibers (GC; LM; $E_B = 37 \Gamma\Pi a, \sigma_B = 0.54$ $\Gamma\Pi a T_K = 1120K$)	26,7	0,49	0,49	0,45	0,49	0,39
Coke + Carbon fibers (GC; LM; $E_B = 37 \Gamma\Pi a, \sigma_B = 0.54$ $\Gamma\Pi a T_K = 1120K$)	15,0 + 7,0	0,35	0,35	0,37	0,35	0,47
$Coke + Carbon fibers (GC; LM; E_B = 36 \Gamma\Pi a, \sigma_B = 0,49 \Gamma\Pi a T_K = 2670K)$	15,0 + 7,0	0,37	0,38	0,37	0,38	0,69
Coke + Carbon fibers (PAN; HM; $E_B = 270$ $\Gamma\Pi a, \sigma_B = 2,2 \Gamma\Pi a T_K = 2670$ K)	15,0 + 7,0	0,63	0,29	0,36	0,39	0,49
Powder copper + molybdenum disulphide	28,0 + 2,6	0,52	0,52	0,64	0,56	2,6
Powder nickel + molybdenum disulphide	28,0 + 2,6	0,52	0,52	0,63	0,56	0,82

The thermal conductivity of composites based on PTFE-4 for temperature 298K

Table 1

+5% PI +15% UTM-8, PTFE + 8% PI + 8% UTM-8, PTFE +10% PI + 15% UTM-8, PTFE + 15% PI + 5% UTM-8 corresponds to the linear model $c_p = a + b \cdot T$ (for temperature range 50 - 175°C). The dependence of the thermal conductivity λ of the temperature T for the same composite material not only meets the model $\lambda = a + b \cdot T$, but also an adequate model $\lambda = a \cdot T^2 + b \cdot T + c$ (for the range of temperatures 50 - 200°C). [8].

Dependence between size of components filler, its form and distribution for sizes, concentration, degree of the grafitation, thermal conductivity of components of the filler and thermal conductivity of composite material based on polytetrafluorineetylene and aromatic polyamide are explored. Theoretical analyze of results calculations of thermal conductivity of composite materials with different fillers using Maksvel-Eiken, Odelevsky, Dulnev and Nilsen's formulas are made [9, 10]. Introduction spherical fillers in composites with carbon fibers broad distribution in length leads to an increase in thermal conductivity of composites (Table 1). A significant increase in thermal conductivity of composites is observed with the introduction of metal

powders (Fig. 6). This is due to the fact that the filler content 20 vol. % or more, the role of surface phenomena at the interface of phases, as most of the substance enters the state boundary surface layers. Interaction of metal particles with macromolecules of the polymer prevents hlobuloutvorennyu and shifts the mobility of interstitial segments in the boundary layer. This process involves the formation of aggregates of macromolecules of the polymer, which in turn is a consequence of the formation of donor-acceptor bonds between the metal particles and macromolecules of the polymer at the interface phases. This facilitated enerhoobminni processes and thus increases the thermal conductivity of the composite. Note that for materials with low conduction matrix and high conductive filler metal powder at concentrations 25 -28 ob.% Thermal conductivity of the composite decreases with increasing temperature. This phenomenon is due to the dominant role of the metal particles in vysokonapovnenyh polymer systems, for which the behavior of the composite in thermal repeats dependence of thermal conductivity of metal temperature. Analysis of the results of calculations of thermal conductivity of



Fig. 6. The dependence of thermal conductivity from temperature composites based PTFE-4 with fillers: 1 – 25.4 % vol. carbon fiber, 2 – 28 vol.% nickel powder + 2.6 vol % powdered molybdenum disulfide, 3 – 20% vol. ARV graphite powder; 4 – 28vol.% copper powder + 2.6% vol. powdered molybdenum disulfide.



290 020 040 070 050 420 440 470 450 U.R. Fig. 7. Dependence of thermal conductivity from temperature for compositions based on aromatic polyamide: 5 - with minimal graphite content (2.31 mass fraction);7 - with a maximum content of carbon fiber (34.99 mass fraction), graphite (22.99 mass fraction) and basalt fiber (49.61 mass fraction); 11-Containing 28.59 mass fraction carbon fiber, 18.8 mass fraction graphite, 13.2 mass fraction basalt fiber; 12 - Containing 28.59 mass fraction carbon fiber, 6.5 mass fraction graphite, 39.88 mass fraction basalt fiber; 13 - Containing 28.59 mass fraction carbon fiber, 6.5 mass fraction graphite, 13.2 mass fraction basalt fiber;14 - Containing 9.81 mass fraction carbon fiber, 18.8 mass fraction graphite, 39.88 mass fraction basalt fiber; 15 - Containing 9.81 mass fraction carbon fiber, 18.8 mass fraction graphite, 13.2 mass fraction basalt fiber; 16 -Containing 9.81 mass fraction carbon fiber, 6,5 mass fraction graphite, 39.88 mass fraction basalt fiber.

composites with different fillers Maxwell-Eiken, Odelevsky, Nielsen and Dulnev formulas leads to the conclusion that the slightest deviation from the calculated thermal conductivity is observed for the experimental formula Nielsen (Table 3). But the greater thermal conductivity of composite fillers, the greater the deviation of empirical data from experimental. Steels Nielsen equation taking into account the ratio of thermal conductivity fillers and polymer shape of the filler particles, Poisson's ratio of the polymer matrix. However, the dependence of the thermal conductivity of the composite on the temperature of heat treatment of carbon fibers and the distribution parameters of particles and fibers in size equation Nielsen ignores.

Dependence between thermal conductivity and temperature of composite materials based on aromatic polyamide with different fillers is explored. The largest thermal conductivity are compositions containing the maximum amount of graphite, the lowest thermal conductivity are compositions containing a minimal amount of graphite. The effect of temperature is most noticeable in the compositions of the maximum and minimum content of carbon fiber, graphite and basalt fibers (Fig. 7, curve 7, Fig. 8, curve 10. In Figure 3 shows a linear relationship between the thermal conductivity and temperature with a minimum content of carbon fiber, graphite and basalt fibers (Fig. 3, curve 10), and with increasing temperature the thermal conductivity decreases. For minimum and maximum content of basalt fibers (Fig. 3, curves 8,9) and in the absence of combined filler (Fig. 3, curve 17) observed a linear increase in the coefficient of thermal conductivity on temperature. For most components of the combined ratio filler composite thermal conductivity decreases with temperature, passing through a minimum [11].

Influence of nature of dispersion fillers (graphitise) on thermophysical properties of aromatic polyimide in dependency upon temperature are explored. Using Maxwell-Aiken, Odelevsky, Dulnev and Nielsen's formulas theoretical analyze of results calculations of thermal conductivity of composite material with dispersion graphite filler are made [12]. The effect of high concentrations (graphite C-1) filler on the thermal properties of antifriction materials based on polyimide PM-69 (Fig. 9). Found that when injected into the



Fig. 8. Dependence of thermal conductivity from temperature for compositions based on aromatic polyamide: 8 - with a maximum content of basalt fiber (49.61 mass fraction); 9 - with minimal basalt fiber (4.00 mass fraction); 10 - with minimal carbon fibers (3.4 mass fraction), graphite (2.3 mass fraction) and basalt fiber (4.00 mass fraction); 17 - in the absence of fillers.

composition structure of graphite C-1, the thermal conductivity initially increases linearly with increasing filler content (up to 30% by mass), and then when the content of graphite C-1 more than 30% by mass, this figure increases dramatically, which can be explain the formation of conductive channels at a given concentration of graphite. Accordingly, it has returned linear approximation equation

l = 0,0009T + 0,0615 for curve 1 (a = 0%); (1)

I = 0,0008T + 0,286 for curve 2 (a = 10%); (2)

l = 0,0016T + 0,3173 for curve 3 (a = 20%); (3)

l = 0,0012T + 0,6867 for curve 4 (a = 30%); (4)

l = 0,0043T + 0,582 for curve 5 (a = 40%);. (5)

The total error ranged from 1.5 - 6.99% when the temperature T = 298 - 473 K and the concentration of graphite C-1 C = 0 - 40\%.

The influence of concentration of carbon fiber, graphite and basalt fiber on thermal conductivity and wear of composite material based on aromatic polyamide is researched using methods of mathematics planning of experiment and search of optimal decisions [13 - 15]. Found that the intensity of wear on the first and second stages with limited lubrication concentration has a significant impact basalt fiber. Values of the intensity of wear without lubrication is much higher than with



Fig. 9. Dependence of the thermal conductivity and confidence intervals for composite materials based on aromatic polyimide PM-69 and graphite C-1 the temperature at a concentration of graphite (% by mass): 1 - 0, 2 - 10, 3 - 20, 4 - 30, 5 - 40.

limited lubrication. Thermal conductivity at temperatures of 473 and 373K increases with increasing content of carbon fiber and graphite. Gradual growth basalt fiber content leads initially to reduce thermal conductivity values, and then to increase them.

The intensity of wear on the first stage with a limited lubrication affects the concentration of carbon fiber. With increasing content of carbon fiber composition decreases the intensity of wear, ie wear resistance of the material increases. The intensity of wear on the second stage with a limited lubrication affects the concentration of basalt fiber: the greater the fiber content in the composition, the higher the intensity of wear, that material has greater abrasive properties. With increasing content of carbon fiber intensity wear during friction without lubrication decreases. Intensity wear during friction without lubrication is much higher than the intensity of wear on the first and second stage with limited lubrication. 4. The coefficients of thermal conductivity at temperatures of 373 and 473 K depending on the content of carbon fiber and graphite and do not depend on the content of basalt fibers: the thermal conductivity increases with increasing content of carbon fiber and graphite

The maximum intensity of wear on the first stage with a limited lubrication observed at low content of carbon fiber. The intensity of wear on the second stage with a limited lubrication affects the concentration of carbon and basalt fiber: with increasing content of basalt fibers and a decrease in carbon fiber intensity of wear on the second stage increases. The intensity of wear at low graphite content is less than high. Intensity wear during friction without lubrication increases with increasing content of basalt fibers and the reduction of carbon fiber. Values of the intensity of wear without lubrication is much higher than with limited lubrication. Thermal conductivity at 473K depends on the concentration of carbon fiber and is not dependent on the concentration of basalt fiber. The higher content of carbon fiber, the higher thermal conductivity. The value of thermal conductivity at 473K and value of thermal conductivity at 373K with minimal graphite less than the maximum.

Базюк Л.В. – викладач кафедри неорганічної та фізичної хімії, магістр

Сіренко Г.О. – доктор технічних наук, професор, завідувач кафедри неорганічної та фізичної хімії.

- [1] G.O. Sirenko, L.V. Bazjuk, N.V. Meshherjakova. Fizika i himija tverdogo tila 12(1), 197 (2011).
- [2] L.V. Bazjuk, G.O. Sirenko, N.I. Bertolon. Visnik Prikarpats'kogo nacional'nogo universitetu imeni Vasilja Stefanika, Serija Himija HIII, 102 (2011).
- [3] L.V. Bazjuk, G.O. Sirenko. Fizika i himija tverdogo tila 12(4), 1026 (2011).
- [4] L.V. Bazjuk, G.O. Sirenko. Fizika i himija tverdogo tila 13(1), 244 (2012).
- [5] L.V. Bazjuk, G.O. Sirenko. Visnik Prikarpats'kogo nacional'nogo universitetu imeni Vasilja Stefanika, Serija Himija HIV, 130 (2012).
- [6] L.V. Bazjuk, G.O. Sirenko. Fizika i himija tverdogo tila 13(2), 528 (2012).
- [7] V.P. Sviders'kij, L.V. Karavanovich. Visnik Prikarp. un-tu. Ser. Himija 2, 70 (2002).
- [8] L.V. Karavanovich. Visnik Prikarp. un-tu. Ser. Himija 4, 67 (2004).
- [9] G.O. Sirenko, V.P. Sviders'kij, L.V. Karavanovich. Fizika i himija tverdogo tila 5(3), 557 (2004).

[10] L.V. Bazjuk, V.P. Sviders'kij. Visnik Prikarp. un-tu. Ser. Himija V, 47 (2008).

[11] G.O. Sirenko, L.V. Bazjuk, V.P. Sviders'kij, S.M. Taranenko. Fizika i himija tverdogo tila 6(3), 486 (2005).

[12] G.O. Sirenko, V.P. Sviders'kij, L.V. Bazjuk. Polimernij zhurnal 27(4), 272 (2005).

[13] G.O. Sirenko, L.V. Bazjuk, V.P. Sviders'kij, L.Ja. Midak. Fizika i himija tverdogo tila 7(2), 357 (2006).

[14] G.O. Sirenko, L.V. Bazjuk, V.P. Sviders'kij, S.M. Taranenko. Polimernij zhurnal 28(3), 214 (2006).

[15] G. O. Sirenko, L.V. Bazjuk, L.Ja. Midak. Voprosy himii i himicheskoj tehnologii (3), 107 (2006).

Л.В. Базюк, Г.О. Сіренко

Теплофізичні властивості металів та композиційних матеріалів (огляд)

Прикарпатський національний університет імені Василя Стефаника, вул. Шевченка, 57, м. Івано-Франківськ, 76025, Україна

За літературними даними вивчено, проаналізовано методами кореляційної та регресійної аналізи та обґрунтовані залежности коефіцієнта теплоємности, теплопровідности, лінійного коефіцієнта теплового розширення та зміни ентальпії від температури, порядкового номера та радіусу атома металів. Вивчено експериментальні дослідження теплофізичних властивостей композиційних полімерних матеріалів на основі політетрафторетилену, ароматичного поліаміду, полііміду та наповнювачів.

Ключові слова: метали, полімери, політетрафторетилен, ароматичний поліамід, поліімід, теплофізичні властивості, ентальпія, коефіцієнт теплоємності, коефіцієнт теплопровідності, лінійний коефіцієнт теплового розширення, температура, радіус атома металів, порядковий номер, кореляційна аналіза, регресійна аналіза.