Естественные науки

УДК 544.72

I.M. Karzov,
Institute of New Carbon Materials and Technologies (Moscow, Russia)
Yu.G. Bogdanova,
Chemistry Department of Moscow State University (Moscow, Russia)
S.V. Filimonov,
Chemistry Department of Moscow State University (Moscow, Russia)
O.N. Shornikova,
Chemistry Department of Moscow State University (Moscow, Russia)
A.P. Malakho
Institute of New Carbon Materials and Technologies (Moscow, Russia)
Chemistry Department of Moscow State University (Moscow, Russia)
E-mail: ilya.k.inumit@gmail.com

Graphite laminated materials strength properties and energy characteristics of polymer binders

Annotation. *The approach which was proposed earlier for composite materials strength prediction using contact angle measurements was applied for graphite laminated materials. It was shown that the calculation of the work of adhesion to polar and non-polar model liquids can be applied to the choice of polymer binder.*

Key words: *wetting method, work of adhesion, tensile strength, prediction of strength properties, choice of polymer binder.*

INTRODUCTION

The mechanical properties of graphite laminates are highly determined by the strength of adhesion junction between graphite and laminated material. The strength of adhesion is the statistical value which depends on a shape and size of the samples, microstructure of adhesive layer and bonding defects [1]. The work of adhesion W_a is a thermodynamic measure of the strength of adhesion, which can be used for the prediction of graphite laminates strength properties. For the present article graphite laminates reinforced with stainless steel foil were chosen. The work of adhesion of graphite to polymer binder $W_{a(g)} = \gamma_1 + \gamma_2 - \gamma_{12}$ [2], where γ_1 and γ_2 are, respectively, specific free surface energy of polymer binder and graphite at boundary with air, and γ_{12} is the specific free surface energy of the graphite/polymer interface. The work of adhesion of stainless steel to polymer binder $W_{a(s)}$ can be described by similar equation: $W_{a(s)} = \gamma_3 + \gamma_2 - \gamma_{23}$, where γ_3 is free surface energy of stainless steel at boundary with air and γ_{23} is the specific free surface energy of the steel/polymer interface. The development of express techniques in order to determine these energetic characteristics of interface, to calculate the work of adhesion and to optimize the choice of polymer binder to the certain type of graphite laminate is the actual task for design of laminated materials. In [3] the new approach based on express wetting method measurements was proposed for the prediction of polymer composites tensile strength and optimization of polymer binder choice for ones creation. In present paper this approach was used for graphite laminated materials.

The specific free surface energies of solid materials being in contact with air or liquid can be determined by Young's equation for equilibrium contact angle (θ):

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}},$$

where γ_{SV}, γ_{SL} and γ_{LV} are surface energies of solid/vapor, solid/liquid and liquid/vapor interfaces respectively [2]. Experimental contact angle values of the test liquids with known surface tension dispersion and polar components (γ_{LV}^d and γ_{LV}^p) are usually applied to calculate the γ_{SV} and γ_{SL} values using the wetting molecular theory of Girifalco-Good-Fowkes-Young equations [4]. This approach allows to determine the dispersion and polar forces contribution in surface energy values (γ_{SV} and γ_{SL}). So the polymer binder adhesive properties can be determined using contact angle measurements.

It is clear that good mechanical strength properties of laminated materials can't be reached without sufficient level of adhesion. The simplest way to choose a polymer binder using (W_a) values is to determine its surface energy and surface energy of attached layer (γ_{V1} and γ_{V2} respectively) and ones dispersion and polar components (γ_{V1}^{d}, γ_{V2}^{p} and γ_{V1}^{d}, γ_{V1}^{p} respectively) and to calculate the work of adhesion value using eq.

$$W_a = 2\left(\sqrt{\gamma_{V1}^{p}\gamma_{V2}^{p}} + \sqrt{\gamma_{V1}^{d}\gamma_{V2}^{d}}\right) \qquad (1) \qquad [4, 5].$$

If laminate consists of several layers made of different materials it may be difficult to determine free surface energy of each material because of high complexity of that technique. Also it's a really complicated task for materials with rough surface, especially for perforated materials. There is another way to choose the optimal polymer binder which is based on calculation of the work of adhesion of polymer binder to model liquids with different polarity. Such approach based on technique developed by Ruckenstein [6] has been proposed for polymer composite strength properties prediction [3]. In present article this approach has been applied for graphite laminated materials.

EXPERIMENTAL

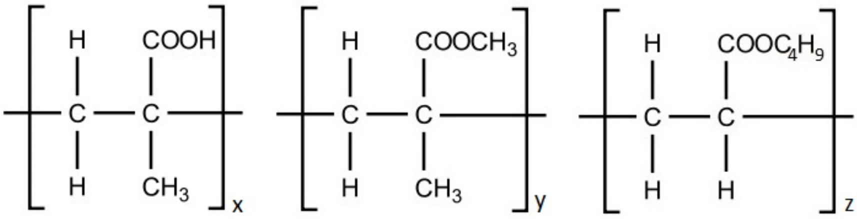
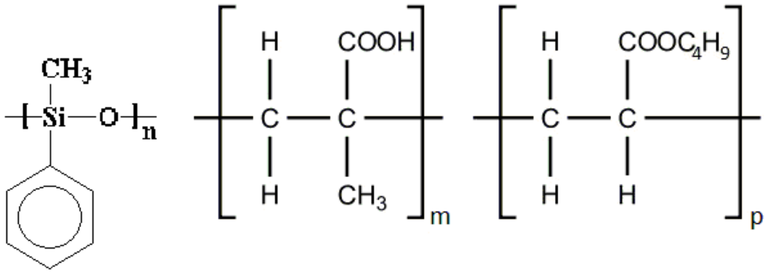
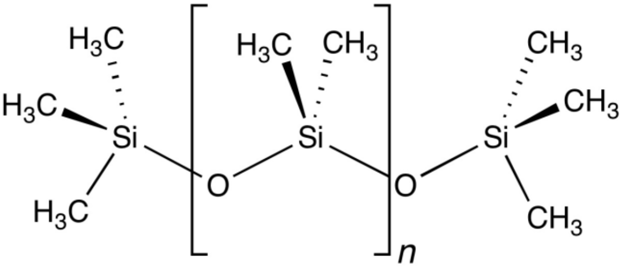
Three different polymer binders were used:

1) MBM-5C – acrylic copolymer emulsion in water,

2) VKT-2 – room temperature vulcanization silicone composition which consists of modified silicone resin and copolymer of butyl methacrylate and methacrylic acid.

3) Silicone resin based on silicone SKTN-A and catalyst K-18.

Table 1 – Structural formulas of components and fragments of polymer binders.

Composition	Formula
MBM-5C	
VKT-2	
SKTN-A	
K-18	$(C_5H_{11}COO)_2Sn(C_2H_5)_2$

Polymer coatings on alumina plate were dried in air atmosphere during 24 hours at the room temperature and placed at the closed chamber for contact angle measurements. The measurement accuracy of horizontal microscope was $\Delta\theta = \pm 1$deg. The droplet volume was (10÷20) μl. Contact angles of (7÷10) droplets were measured for each sample. The accuracy of surface energy calculation was $\Delta\gamma = \pm 1$ mJ·m^{-2}. The measurements were carried out at 20°C.

The γ_{SV} values for polymers, graphite foil and stainless steel were determined by two-liquid method (eq. 2, 3) using water and diiodinemethane as test liquids (table 2):

$$\begin{cases} (1+\cos\theta_{L1})\cdot\gamma_{L1} = 2\left(\sqrt{\gamma_{L1}^{d}\cdot\gamma_{SV}^{d}}+\sqrt{\gamma_{L1}^{p}\cdot\gamma_{SV}^{p}}\right) & (2), \\ (1+\cos\theta_{L2})\cdot\gamma_{L2} = 2\left(\sqrt{\gamma_{L2}^{d}\cdot\gamma_{SV}^{d}}+\sqrt{\gamma_{L2}^{p}\cdot\gamma_{SV}^{p}}\right) & (3), \end{cases}$$

where θ_{L1} и θ_{L2} – test liquids advancing contact angles at the polymer surface (Fig.1a), γ_{L1}^{p}, γ_{L2}^{p}, γ_{L1}^{d}, γ_{L2}^{d} are its polar and dispersion components respectively; γ_{SV}^{p}, where $\gamma_{SV} = \gamma_{SV}^{p} + \gamma_{SV}^{d}$, γ_{SV}^{p} and γ_{SV}^{d} are polar and dispersion components of polymer surface free energy [5].

Table 2. – The test liquids surface tension (γ_{LV}) and its dispersive (γ_{LV}^{d})and polar (γ_{LV}^{p}) components.

Liquid	γ_{LV}^{p}, mJ·m^{-2}	γ_{LV}^{d}, mJ·m^{-2}	γ_{LV}, mJ·m^{-2}
Water	50,8	21,8	72,6
Diiodinemethane	2,3	48,5	50,8
Octane	–	21,8	21,8

The test liquids surface tension ($\gamma_{LV} = \gamma_{SL}^{p} + \gamma_{SL}^{d}$) values were determined by Vilhelmy plate method; its polar (γ_{SL}^{p}) and dispersion (γ_{SL}^{d}) components were determined using experimental contact angle (θ) values of droplets at the Teflon-4 surface ($\gamma_{SV} = \gamma_{SV}^{d} = 18$ mJ·m^{-2} [7]) and Girifalco-Good-Fowkes-Young equation:

$$\cos\theta = \frac{2\sqrt{\gamma_{SV}^{d}\gamma_{SL}^{d}}}{\gamma_{LV}} - 1 \qquad [2].$$

The data obtained appeared to be aligned with literature data [8].

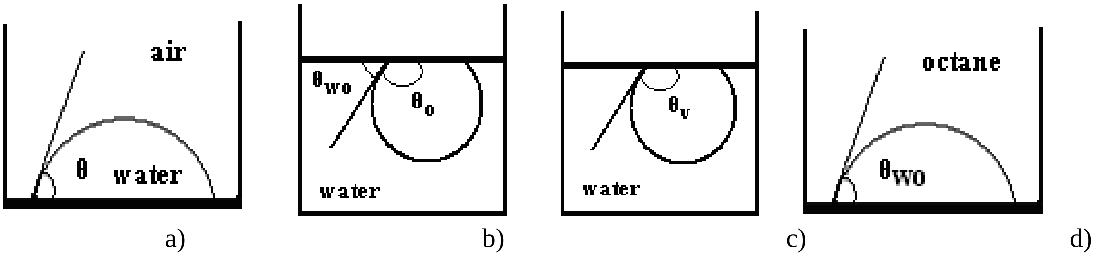
Water and octane were chosen as liquids simulating a polar and non-polar substrate respectively. The work of adhesion values of polymer binder to model liquids was determined calculated using eq. (3-4).

1) non-polar liquid $$Wdd = \gamma_{S} + \gamma_{O} - \gamma_{SO} \qquad (3)$$

2) polar liquid $$Wpp = \gamma_{S} + \gamma_{W} - \gamma_{S(W)W} \qquad (4)$$

The values γ_{SO}, $\gamma_{S(W)W}$ and $\gamma_{S(O)W}$ in eq. (3, 4) are equilibrium surface energy values at the polymer-octane, polymer-water and polymer (equilibrated with octane)-water interfaces respectively, γ_{SV} – polymer binder surface energy, γ_{O} и γ_{W} – octane and water surface tension values respectively.

In order to determine the γ_{SO}, $\gamma_{S(W)W}$ and $\gamma_{S(O)W}$ values technique developed by Ruckenstein [6]. Unlike other methods it takes into account the polymer chains mobility near the polymer/liquid interface. The polymer films were in contact with model liquids during 24 hours [6, 9]. Then the air bubbles and octane or water drops contact angles at the polymer surfaces were measured.



(a) – water droplet at the polymer surface in the air environment;

(b) – octane droplet at the polymer surface immersed in water (θ_O);

(c) – the air bubble at the polymer surface immersed in water (θ_V);

(d) θ_{WO} – the water droplet at the polymer surface immersed in octane.

Fig. 1 – The scheme of contact angle measurements

The contact angles were measured in accordance [10].
The following equations were used for calculations:

$$\gamma_{S(W)W} = \left(\sqrt{\gamma_{SW}^{p}} - \sqrt{\gamma_{W}^{p}}\right)^2 + \left(\sqrt{\gamma_{SW}^{d}} - \sqrt{\gamma_{W}^{d}}\right)^2, \qquad (5)$$

where γ_{SW}^{p} and γ_{SW}^{d} are equilibrium interfacial energy polymer/water polar and dispersion components;

$$\gamma_{SW}^{p} = \frac{\left(\gamma_W - \gamma_O - \gamma_{OW} \cdot \cos\theta_O\right)^2}{4\gamma_W^{p}}, \qquad (6)$$

where γ_{OW} = 50,8 mJ·m^{-2}– octane/water interfacial tension, θ_O – octane droplet contact angle at the polymer surface immersed in water (Fig1b) [10];

$$\gamma_{SW}^{d} = \frac{\left(\gamma_{OW} \cdot \cos\theta_O - \gamma_W \cdot \cos\theta_V + \gamma_O\right)^2}{4\gamma_O}, \qquad (7)$$

where θ_V is the air bubble contact angle at the polymer surface immersed in water (Fig1c) [6,9].

$$\gamma_{S(O)W} = \gamma_{SW}^{p} + \left(\sqrt{\gamma_{SO}^{d}} - \sqrt{\gamma_{SW}^{d}}\right)^2, \qquad (8)$$

where solid/octane equilibrium interfacial energy dispersive component value $\gamma_{SO}^{d} \approx \gamma_{S}^{d}$ [6,9];

$$\gamma_{SO} = \gamma_{SO}^{d} + \gamma_{SO}^{p} + \gamma_O - 2\sqrt{\gamma_{SO}^{d}\gamma_O}, \qquad (9)$$

where γ_{SO}^{p} – solid/octane equilibrium interfacial energy polar component

$$\gamma_{SO}^{p} = \frac{\left(\gamma_{OW} \cdot \cos\theta_{WO} + \gamma_W - \gamma_O\right)^2}{4\gamma_W^{p}}, \qquad (10)$$

where θ_{WO} – contact angle of the water droplet at the polymer surface immersed in octane (Fig1d) [6,9].

Equilibrium values of interfacial energies γ_{SO}, $\gamma_{S(W)W}$ were compared with interfacial energies "polymer-octane" γ^*_{SO} and "polymer-water" γ^*_{SW} which were calculated using polar and dispersion components of polymer binders according to eq. (11)-(12):

$$\gamma^*_{SW} = \gamma^p_{SV} + \gamma^d_{SV} + \gamma_W - 2\sqrt{\gamma^d_{SV}\gamma^d_W} - 2\sqrt{\gamma^p_{SV}\gamma^p_W} \quad (11),$$

$$\gamma^*_{SO} = \gamma^p_{SV} + \gamma^d_{SV} + \gamma_O - 2\sqrt{\gamma^d_{SV}\gamma_O} \quad (12).$$

Strength of adhesion of graphite/steel laminate was calculated by measuring a force of graphite circle pull-out from a laminated sample using «Tinius Olsen H5KS».

Tensile strength (P) of graphite laminates was determined using apparatus «Tinius Olsen H5KS». Every sample was measured 8-10 times. The magnitudes of tensile strength were calculated on the cross-section area of laminated material.

RESULTS

Results of free surface area measurements are presented in table 3. Graphite foil is non-polar material with $\gamma^d >> \gamma^p$. It's well known [11], that steel is a polar material with high value of specific free surface energy which exceeds 1000 mJ·m^{-2} and depends on chemical composition. As far as it can't be determined by the wetting method, *Wpp* value was used for understanding of the difference in adhesion level between various polymer binders and stainless steel.

Table 3 – Specific free surface energy of graphite foil, steel and polymer coatings

Material	γ^d, mJ·m^{-2}	γ^p, mJ·m^{-2}	γ, mJ·m^{-2}
Graphite foil	45	1	46
MBM-5C	29	32	61
VKT-2	24	5	29
SKTN-A + K18	21	2	23

VKT-2 and SKTN-A + K18 are silicone polymer binders with small value of free surface energy which is typical for silicones. It seems that the modification of silicone resin by copolymer of butyl methacrylate and methacrylic acid increases a contribution of polar component γ^p and γ for VKT-2. Butyl methacrylate and methacrylic acid are also copolymers of MBM-5C which appeared to be a high energy polymer composition with strong contribution of polar component $\gamma^p \approx \gamma^d$. As far as increase in γ^p and γ^d leads to the growth of W_a according to equation 1, and polar and dispersive components increases in the series SKTN-A + K18, VKT-2 and MBM-5C it can be concluded that 1) the highest values of the work adhesion to graphite and stainless steel should be provided by MBM-5C, 2) work of adhesion of VKT-2 to graphite and stainless steel should be higher that SKTN-A + K-18. So it can be supposed that graphite laminated materials with MBM-5c should be superior in strength of adhesion and tensile strength as well.

Calculated values of work of adhesion *Wa* of polymer binders to graphite foil, *Wpp, Wdd,* strength of adhesion and tensile strength are presented in table 4. *Wa, Wpp, Wdd* values are higher for MBM-5C than for silicone based polymer binders. It means that MBM-5C is better coupling agent for polar and non-polar phases including graphite foil and stainless steel. Higher strength of adhesion and tensile strength values (table 4) confirm the prediction based on wetting method measurements.

Table 4 – Work of adhesion of polymer binders to graphite foil, steel, model liquids and tensile strength of graphite laminated materials

Polymer binder	Strength of adhesion, kPa	Work of adhesion of polymer binder to graphite, mJ·m^{-2}	*Wpp,* mJ·m^{-2}	*Wdd,* mJ·m^{-2}	Tensile strength, MPa
MBM-5C	64	84	132	57	21
VKT-2	59	70	101	50	15
SKTN-A + K-18	26	64	87	45	7

Table 5 – Free surface energy of polymers on the interface with water and octane, *-values were calculated using eq. (11)-(12) [γ]= mJ·m^{-2}

Polymer binder	γ_{SO}^{*}	γ_{SO}	γ_{SW}^{*}	$\gamma_{S(W)W}$
MBM-5C	33	25	3	1
VKT-2	5	1	24	1
SKTN-A + K-18	2	0	33	9

The long-time contact of polymer films with model liquids led to the decrease of free surface energy on the interface with water and octane (table 5) what points to the fact of polymer chains mobility.

The work of adhesion of VKT-2 to graphite and model liquids is higher than for SKTN-A + K18, so it should provide stronger binding in laminated material. According to experimental results using VKT-2 instead of SKTN-A + K18 composition leads to significant decrease of adhesion strength and tensile strength. Delamination occurs when graphite and stainless steel sheets are connected with SKTN-A + K18. This fact demonstrates that polymer binder with $\gamma \leq 23$ mJ/m^2 is not able to provide sufficient adhesion to both surfaces of stainless steel and graphite foil.

CONCLUSION

The approach which was proposed earlier for composite materials strength prediction using contact angle measurements was applied for graphite laminated materials. It was founded that the strength of adhesion and tensile strength is connected with the work of adhesion to graphite foil, stainless steel and model liquids. The calculation of the work of adhesion to polar and non-polar model liquids can be applied to the choice of polymer binder. It was shown that MBM-5C provides the highest level of tensile strength among tested materials.

ACKNOWLEDGEMENTS

The work was carried out with a financial support of The Ministry of Education and Science of Russian Federation (Agreement 14.579.21.0028, Unique handle of the agreementRFMEFI57914X0028)

REFERENCES

1 Kerber M. L., Vinogradov V. M., Golovkin G. S., et al. Polymer Composites: Structure, Properties and Technology: Training Manual Ed., A. A. Berlin, St.–Petersburg Professiya, 2008. P. 556. [in Russian].

2 Adamson A.W., Gast A.P. Physical Chemistry of Surfaces, A Wiley-Interscience Publication, 1997.

3 Bogdanova Y. G., Dolzhikova V. D., Karzov I. M., Alentiev, A. Y. A New Approach to the Determination of Adhesion Properties of Polymer Networks // In Macromolecular Symposia, 2012. – Vol. 316. – No. 1. – P. 63–70.

4 Van Oss C.J., Good R.J., Chaudhury M.K. The role of van der Waals forces and hydrogen bonds in "hydrophobic interactions" between biopolymers and low energy surfaces // J. Colloid Interface. Sci., 1986. – Vol. 111. – P. 378–392.

5 Vojtechovska J., Kvitek L. Surface energy – effects of physical and chemical surface properties // Acta Univ. Palacki. Olomuc, 2005. – Chemica 44. – P.25–48.

6 Ruckenstein E., Gourisankar S.V. Environmentally induced restructuring of polymer surfaces and its influence on their wetting characteristics in an aqueous environment // J. of Colloid and Int. Sci., 1985. – Vol. 107. – P.488–502.

7 Summ B.D., Goryunov Yu.V. Physico-Chemical Fundamentals of Wetting and Spreading, Chemistry, Moscow, 1976.

8 Lee L.H. Correlation between Lewis Acid−Base Surface Interaction Components and Linear Solvation Energy Relationship Solvatochromic α and β Parameters // Langmuir, 1996. – Vol. 12. – P.1681–1687.

9 Ruckenstein E., Gourisankar S.V. Preparation and characterization of thin film surface coatings for biological environments//Biomaterials, 1986. – Vol. 7. – P.403–422.

10 Ruckenstein E., Lee S.H. Estimation of the equilibrium surface free energy components of restructuring solid surfaces // J. of Colloid and Int. Sci., 1987. – Vol. 120. – P. 153–161.

11 Deyev G.F. Surface Phenomena in Fusion Welding Processes. CRC Press. – 2005. – P. 222.

СПИСОК ЛИТЕРАТУРЫ

1 Кербер М.Л., Виноградов В.М., Головкин Г.С. и др. Полимерные композиционные материалы: структура, свойства, технология: учеб. пособие / Под ред. А.А. Берлина. – СПб.: Профессия, 2008. – С. 556.

2 Adamson A.W., Gast A.P. Physical Chemistry of Surfaces, A Wiley-Interscience Publication, 1997.

3 Bogdanova Y. G., Dolzhikova V. D., Karzov I. M., Alentiev, A. Y. A New Approach to the Determination of Adhesion Properties of Polymer Networks // In Macromolecular Symposia, 2012. – Vol. 316. – No. 1. – P. 63–70.

4 Van Oss C.J., Good R.J., Chaudhury M.K. The role of van der Waals forces and hydrogen bonds in "hydrophobic interactions" between biopolymers and low energy surfaces // J. Colloid Interface. Sci., 1986. – Vol. 111. – P. 378–392.

5 Vojtechovska J., Kvitek L. Surface energy – effects of physical and chemical surface properties // Acta Univ. Palacki. Olomuc, 2005. – Chemica 44. – P.25–48.

6 Ruckenstein E., Gourisankar S.V. Environmentally induced restructuring of polymer surfaces and its influence on their wetting characteristics in an aqueous environment // J. of Colloid and Int. Sci., 1985. – Vol. 107. – P.488–502.

7 Сумм Б.Д., Горюнов Ю.В. Физико-химические основы смачивания и растекания. Химия. Москва, 1976.

8 Lee L.H. Correlation between Lewis Acid–Base Surface Interaction Components and Linear Solvation Energy Relationship Solvatochromic α and β Parameters // Langmuir, 1996. – Vol. 12. – P.1681–1687.

9 Ruckenstein E., Gourisankar S.V. Preparation and characterization of thin film surface coatings for biological environments//Biomaterials, 1986. – Vol. 7. – P.403–422.

10 Ruckenstein E., Lee S.H. Estimation of the equilibrium surface free energy components of restructuring solid surfaces // J. of Colloid and Int. Sci., 1987. – Vol. 120. – P. 153–161.

11 Deyev G.F. Surface Phenomena in Fusion Welding Processes. CRC Press. – 2005. – P. 222.

ТҮЙІН

И.М. Карцов,
Жаңа технологиялар институты (Мәскеу, Ресей)
Ю.Г. Богданова,
ММУ химиялық факультеті (Мәскеу, Ресей)
С.В. Филимонов,
ММУ химиялық факультеті (Мәскеу, Ресей)
О.Н. Шорникова,
ММУ химиялық факультеті (Мәскеу, Ресей)
А.П. Малако
Жаңа технологиялар институты (Мәскеу, Ресей)
ММУ химиялық факультеті (Мәскеу, Ресей)

Гарифитті ламинадталган заттардың мықтылық қасиеттері және полимерлі байланыстырушылардың энергетикалық сипаттары

Бұрышты өлшеуді қолдану арқылы бұрын гарифитті ламинадталған заттардың беріктілік қасиеттері болжау үшін көрсетілген жол. Полярлық және полярлық емес агдезияның үлгілі сұйықтармен жұмыстарының есебі көрсетілген.

Түйін сөздер: *сулау әдістері, агдезия жұмыстары, созылыңқылықтың кернеуі, беріктілік қасиеттерін болжау.*

РЕЗЮМЕ

И.М. Карцов,
Институт новых углеродных материалов и технологий (Москва, Россия)
Ю.Г. Богданова,
Химический факультет МГУ (Москва, Россия)
С.В. Филимонов,
Химический факультет МГУ (Москва, Россия)
О.Н. Шорникова,
Химический факультет МГУ (Москва, Россия)
А.П. Малако
Институт новых углеродных материалов и технологий (Москва, Россия)
Химический факультет МГУ (Москва, Россия)

Прочностные свойства графитовых ламинированных материалов и энергетические характеристики полимерных связующих

Предложенный ранее подход для прогнозирования прочности композитных материалов с использованием измерений угла контакта применялся для ламинированных графитом материалов. Показано, что расчет работы адгезии с полярными и неполярными модельными жидкостями может быть применен к выбору полимерного связующего.

Ключевые слова: *метод смачивания, работа адгезии, напряжение растяжения, прогнозирование прочностных свойств, выбор полимерного связующего.*