Eurasian Chemico-Technological Journal 18 (2016) 311-316

Graphite Laminated Materials Strength Properties and Energy Characteristics of Polymer Binders

I.M. Karzov*, Yu.G. Bogdanova, S.V. Filimonov, O.N. Shornikova, A.P. Malakho

Lomonosov Moscow State University, GSP-1, Leninskie Gory, Moscow, 119991, Russia

Article info

Received:
05 March 2016

Received in revised form:
23 April 2016

Accepted:
17 June 2016

Abstract

The approach for graphite laminated materials strength properties prediction using contact angle measurements was proposed. The tensile strength of laminated materials made of graphite foil and stainless steel with acrylic and silicone adhesives was measured. It was shown that tensile strength depends on energy characteristics of polymer binders, which can be determined by simple and express wetting method. It was found that the highest values of tensile strength, strength of adhesion and the work adhesion to graphite and stainless steel were provided by acrylic adhesive MBM-5C. The delamination occurred when graphite and stainless steel sheets were connected with low surface energy silicone resin, $\gamma = 23$ mJ/m^2, what was not able to maintain sufficient adhesion level to the both types of attached surfaces: polar steel and non-polar graphite. It was demonstrated that the calculation of the work of adhesion to polar and non-polar model liquids (water and octane respectively) can be applied to optimize the choice of polymer binder and design of laminated materials. It's quite important that the proposed technique doesn't require to determine free surface energy for each type of sheet material which is especially difficult and complex task if laminate consists of several different layers.

1. 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^d_{LV} and γ^p_{LV}) are

---

*Corresponding author. E-mail: ilya.k.inumit@gmail.com 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

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

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.

2. Experimental

Three different polymer binders were used (Table 1):

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.

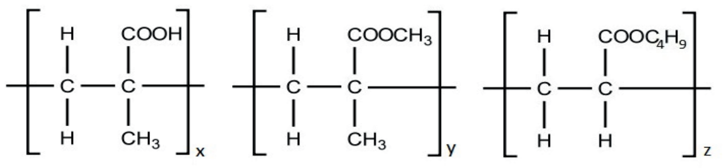
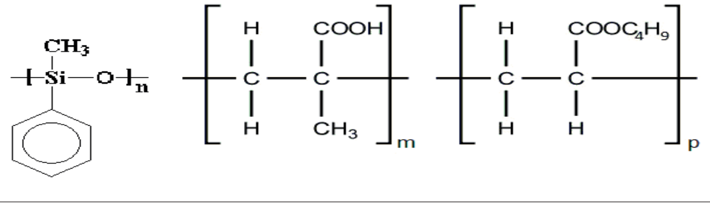
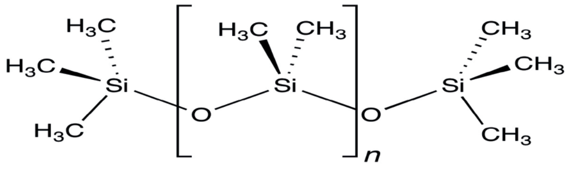
3) Silicone resin based on silicone SKTN-A and catalyst K-18.

Polymer coatings on alumina plate were dried in air atmosphere during 24 h 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 (Eqs. 2, 3) using water and diiodinemethane as test liquids (Table 2):

Table 1

Structural formulas of components and fragments of polymer binders

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

$$\left(1+\cos\theta_{L1}\right)\cdot\gamma_{L1}=2\left(\sqrt{\gamma^{d}_{L1}\cdot\gamma^{d}_{SV}}+\sqrt{\gamma^{p}_{L1}\cdot\gamma^{p}_{SV}}\right) \quad (2)$$

$$\left(1+\cos\theta_{L2}\right)\cdot\gamma_{L2}=2\left(\sqrt{\gamma^{d}_{L2}\cdot\gamma^{d}_{SV}}+\sqrt{\gamma^{p}_{L2}\cdot\gamma^{p}_{SV}}\right) \quad (3)$$

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

Table 2

The test liquids surface tension (γ_{LV}) and its dispersive (γ^{d}_{LV}) and polar (γ^{p}_{LV}) components

Liquid	γ^{p}_{LV}, J·m^{-2}	γ^{d}_{LV}, mJ·m^{-2}	γ_{LV}, mJ·m^{-2}
Water	50.8	21.8	72.6
Diiodine-methane	2.3	48.5	50.8
Octane	-	21.8	21.8

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

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

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 Eqs. (3–4).

1) non-polar liquid $Wdd=\gamma_S+\gamma_O-\gamma_{SO}$ (3),

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

The values γ_{SO}, $\gamma_{S(W)W}$ and $\gamma_{S(O)W}$ in Eqs. (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 and 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 h [6, 9]. Then the air bubbles and octane or water drops contact angles at the polymer surfaces were measured.

The contact angles were measured in accordance [10].

The following equations were used for calculations:

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

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

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

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 (Fig. 1b) [10];

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

where θ_V is the air bubble contact angle at the polymer surface immersed in water (Fig. 1c) [6, 9].

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

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

$$\gamma_{SO}=\gamma^{d}_{SO}+\gamma^{p}_{SO}+\gamma_O-2\sqrt{\gamma^{d}_{SO}\gamma_O} \quad (9)$$

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

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

where θ_{WO} – contact angle of the water droplet at the polymer surface immersed in octane (Fig. 1d) [6, 9].

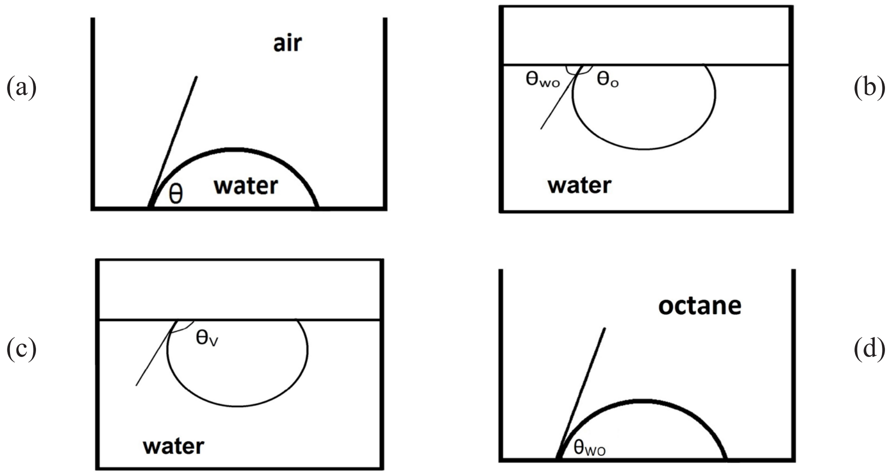


Fig. 1. The scheme of contact angle measurements: (a) – water droplet at the polymer surface in the air environment; (b) – octane droplet at the polymer surface immersed in water (θ_O); (c) – the air bubble at the polymer surface immersed in water (θ_V); (d) θ_{WO} – the water droplet at the polymer surface immersed in octane.

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 Eqs. 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.

3. Results and Discussion

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.

VKT-2 and SKTN-A + K18 are silicone polymer binders with small value of free surface energy which is typical for silicones. Each Si-atom of SKTN-A is connected with two methyl groups that makes the composition hydrophobic and the impact γ^p of on free surface energy is negligible. The modification of silicone resin by copolymer of butyl methacrylate and methacrylic acid which increases a contribution of polar component γ^p and γ for VKT-2 due to the influence of -COOH and -COOC$_4$H$_9$ groups.

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

Butyl methacrylate and methacrylic acid are also copolymers of MBM-5C which appeared to be a high energy water-soluble 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 Eq. 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.

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, $mJ \cdot m^{-2}$	*Wpp*, $mJ \cdot m^{-2}$	*Wdd*, $mJ \cdot m^{-2}$	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

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.

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.

Table 5
Free surface energy of polymers on the interface with water and octane, *-values were calculated using Eqs. 11–12 $[\gamma] = mJ \cdot m^{-2}$

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 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 SKTN-A + K18 instead of VKT-2 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, which doesn't contain hydrophilic functional groups and has the lowest value of free surface energy. This fact demonstrates that polymer binder with ≤23 mJ/m^2, is not able to provide sufficient adhesion to both surfaces of stainless steel and graphite foil.

4. Conclusions

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, which has high γ^p value because of COOH and COOR functional groups, 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 agreement RFMEFI57914X0028).

References

[1]. M.L. Kerber, V.M. Vinogradov, G.S. Golovkin, in A.A. Berlin (ed.), Polymer Composite Materials: Structure, Properties and Technology, Professiya, St. Petersburg, 2014, p. 165.
[2]. A. Adamson, A. Gast, Physical Chemistry of Surfaces, A Wiley-Interscience Publ., 1997, p. 465.
[3]. Y.G. Bogdanova, V.D. Dolzhikova, I.M. Karzov, A.Y. Alentiev, 17th Intern. Symp. Molecular Mobility and Order in Polymer Systems, St. Petersburg, 316 (1) (2012) 63.
[4]. C.J. Van Oss, R.J. Good, M.K. Chaudhury, J. Colloid Interface. Sci. 111 (1986) 378–392.
[5]. J. Vojtechovska, L. Kvitek, Acta Univ. Palacki. Olomuc. Chemica. 44 (2005) 25–48.
[6]. E. Ruckenstein, S.V. Gourisankar, J. Colloid & Int. Sci. 107 (1985) 488–502.
[7]. B.D. Summ, Yu.V. Goryunov, Physico-Chemical Fundamentals of Wetting and Spreading, Chemistry, Moscow, 1976, p. 232.
[8]. L.H. Lee, Langmuir 12 (1996) 1681-1687.
[9]. E. Ruckenstein, S.V. Gourisankar, Biomaterials 7 (1986) 403–422.
[10]. E. Ruckenstein, S.H. Lee, J. Colloid & Int. Sci. 120 (1987) 153–161.
[11]. G.F. Deyev, Surface Phenomena in Fusion Welding Processes, CRC Press, U.K., 2005. p. 222.