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EFFECT OF FILLER PARTICLES ON ADHESIVE PROPERTIES OF POLY (m-, p-PHENYLENE ISOPHTALAMIDE) COATINGS

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The adhesive properties of composite coatings based on poly (m-, p-phenylene isophtalamide) with widely used antifriction fillers (copper phthalocyanine, molybdenum disulfide, graphite and boron nitride) were investigated. The results of measurements of adhesive characteristics are obtained by means of cross cutting test and quantitative peel test. Introduction of fillers leads to an increase in the adhesive strength of coatings, while the type of a filler virtually does not affect the adhesive properties. When the filler content is 20 wt.% and more, the cohesive fracture of the coating occurs during the peel test. Introduction of the fillers significantly reduces the value of internal stresses that is accompanied by an increase in the adhesion strength. By way of example of graphite, we showed that an increase in the particle dispersion of the filler results in an increase in the value of adhesion strength of composite coatings, but does not cause any fundamental changes in the character of the dependence of adhesion strength on the filler concentration.

Keywords: poly (m-, p-phenylene isophtalamide), aromatic polyamide, polymer coating, adhesion, composite.

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Introduction

One of the promising thermostable polymers of constructional purposes is an aromatic polyamide poly (m-, p-phenylene isophtalamide) (PMPPI) (Fig. 1) [1], also known as Phenylon-C2 (Russia) [2]. PMPPI is a copolymer based on poly (m-phenylene isophtalamide), commonly known as Nomex (USA) and Phenylon-P (Russia) [3,4].

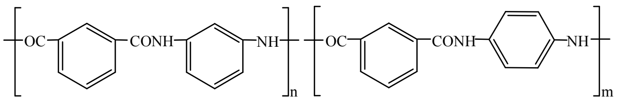


Fig. 1. The structure of poly (m-, p-phenylene isophtalamide) [1]

PMPPI has good mechanical, physical and thermal properties that led to its wide spreading as a constructional material in mechanical engineering [2]. In particular, PMPPI is used as an antifriction material in loaded friction assemblies, which operate at high temperatures. In addition, PMPPI has higher wear resistance than such traditional antifriction materials as copper, bronze, babbit, etc. [2,5].

PMPPI products can be prepared by direct compression and press molding at the temperature of 320–340°C. Fibers and films are obtained by dry forming or wet forming from the solutions using highly polar amide solvents such as N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA) [3].

One of the disadvantages of PMPPI is the inability to use it in friction assemblies, which work without lubrication, because it has a relatively high coefficient of friction (0.4–0.5). In order to overcome this shortcoming, a large number of composites were developed based on PMPPI, where layered solid lubricants such as graphite, molybdenum disulfide and boron nitride are inserted into the composition of PMPPI in order to increase antifriction properties [5,6].

One of the promising directions of improvement in tribotechnical properties of surfaces in the friction assemblies is to apply wear resistant polymer coating to them. In particular, a method of obtaining antifriction coating from PMPPI solution was developed by Sytar and Stovpnik [7]. Further studies concerning the influence of technological parameters on the process of PMPPI formation were carried out [8–10].

It should be noted that along with high levels of tribotechnical properties PMPPI like other aromatic polyamides has low adhesion to metals that makes it difficult to obtain high-quality coatings [7,11,12]. The influence of technological parameters of the process of coatings formation as well as the nature of the substrate on the strength of adhesive joint of PMPPI coatings without fillers were considered in detail in the works [1,8]. Investigation of the effect of various antifriction fillers on the adhesive properties of PMPPI coatings is quite an urgent problem, which is not covered in the literature at this point.

Internal stresses, which arise in coatings during their formation, can play an important role in the adhesive process of metal-polymer systems [11,13]. The value of the internal stress depends on many factors; one of them being a mode of the formation of the polymer coating [13,14]. The higher the rate of gelation and correspondingly the steeper concentration dependence of viscosity, the higher is the value of internal stresses. In addition, the type of solvent has a significant effect. The higher the boiling point of a solvent, the lower is the absolute value of internal stresses, since the presence of a high boiling solvent facilitates the relaxation of internal stresses. It is known [11,14] that an increase in the temperature of film formation causes an increase in the internal stresses in the formed film of a polymer.

The nature of interaction at the polymer-filler interface plays an important role. Thus, the work [14] reported that the particles of active fillers changing the supermolecular structure of a polymer significantly reduce the mobility of the structural elements. Deceleration of the relaxation processes in the filled polymers along with reduction of shrinkage leads to the proliferation of the internal stresses, an increase in the elastic modulus and a decrease in the tensile strength. Introduction of modified filler into the polymer coating [11,14] may also lead to the reduction of the internal stresses as a result of the strength reduction of interaction at the polymer-filler interface and the increase of coatings shrinkage.

The dependence of the internal stresses on the amount of filler is complex [11], since the introduction of the filler is accompanied by the growth of the polymer elastic modulus and reduction of thermal expansion coefficient. Therefore, an increase in the amount of the filler in one case will cause an increase of thermal stresses (the increase in the elastic modulus prevails over the reduction of the thermal expansion coefficient) and in other cases, conversely, it will cause their decrease (the reduction of thermal expansion coefficient prevails over the increase of elastic modulus). The constancy of the internal stresses after the introduction of the filler means that the increase of the elasticity modulus is compensated by the decrease of the thermal expansion coefficient. Since the thermal stresses are significantly higher than shrinkage stresses, their contribution to the overall balance of the internal stresses appears to be essential. However, the value of thermal stresses is considerable only in those cases when a polymeric coating is formed at high temperatures, and then the temperature becomes lower than the glass transition temperature of the polymer [14].

Thus, the aim of this work is to study the effect of antifriction fillers on the adhesive properties of PMPPI coatings taking into account the internal stresses arising in the coatings during their formation.

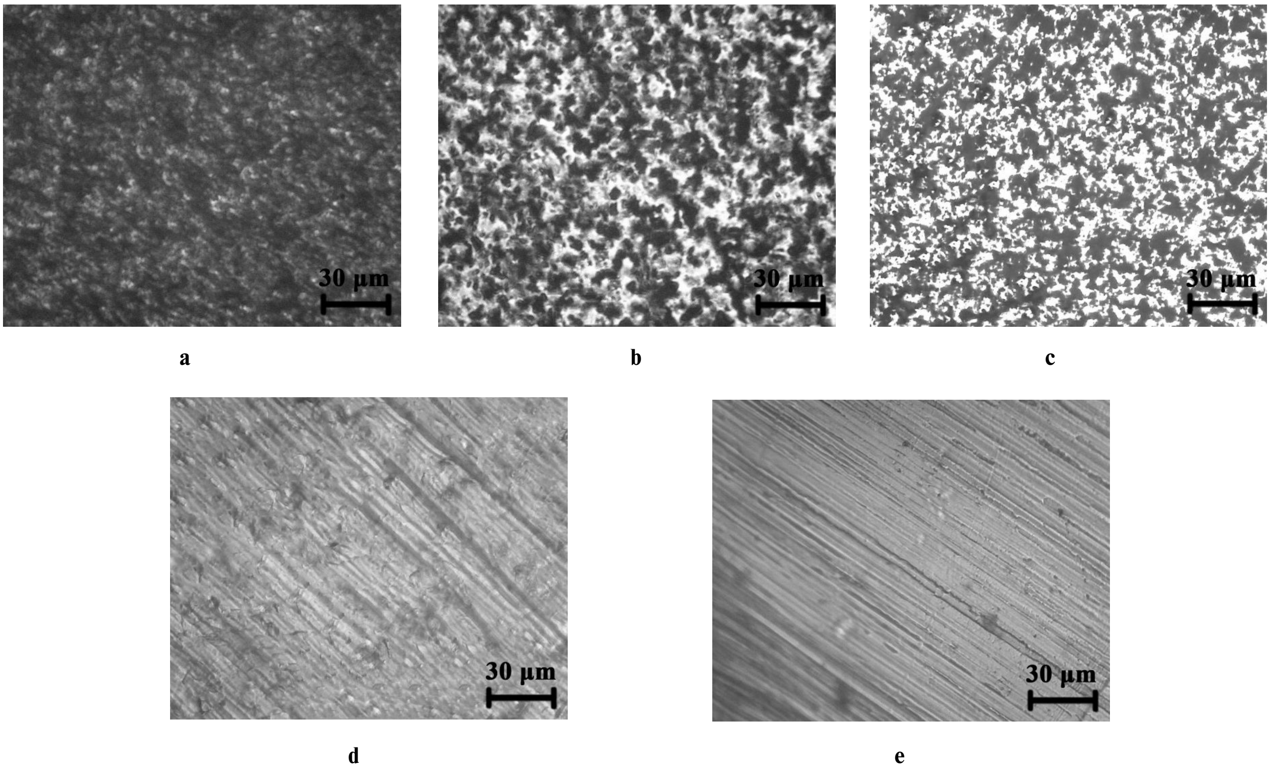
Materials and methods

The 80 mm thick composite coating was prepared by applying 17% of PMPPI solution to the surface of the metal substrate followed by evaporation of the solvent by means of drying.

Metal plates made of carbon steel (0.14–0.22% C) were chosen as the substrates. Underfeature of the substrate surface was obtained by means of abrasive grinding. Grinding wheels were used as abrasive, which provided a surface with the same roughness parameters (R_a 1.32) for all types of substrates. Before applying the coating, the surface of the substrate was cleaned and degreased.

Fine-dispersed amorphous PMPPI powder with bulk density of 0.2–0.4 g cm^{-3} was used as the feedstock material for obtaining the coatings. The following layered solid lubricants were used as fillers: copper phthalocyanine, molybdenum disulfide, graphite and boron nitride, these being widely used for creating self-lubricating materials based on polymers [2,12]. The chosen anti-friction fillers were used in a fine-dispersed form with particle size of 1–2 μm. The filler content was varied from 5 to 30 wt.%. A separate series of studies was performed using graphite of the following different dispersion: 1–2, 5–10, 10–20 and 25–35 μm. N,N-dimethyl-formamide was used as a solvent. Drying of the samples was carried out in a drying oven at the temperature of 145^{0}C during 1 h.

Before applying, the solution was stirred in a laboratory blade paddle mixer with the rotational frequency of 60 rpm during 2 min. The developed technology of coating formation based on PMPPI allows getting a good distribution of the filler in the volume of the polymer matrix (Fig. 2).



a b c

d e

Fig. 2. Microstructure of the surface of composite coatings based on PMPPI containing 20 wt.% of filler: a – copper phthalocyanine; b – molybdenum disulfide; c – graphite; d – boron nitride; e – without a filler

The primary determination of the level of the coating adhesion to the substrate was performed by means of cross cutting according to the state standard GOST 15140-78 (ISO 2409). This is the most common and fastest way to determine the quality of adhesion of various kinds of coatings and films. The wide spread of this method is due to its simplicity and universality. The method consists in perpendicular cut of a coating by a special knife. Based on the selected coating thickness and recommendations of the standard, the cuts were performed in a step of 2 mm. Further visual estimation of the coating was carried out according to four-point scale depending on the area of detachment: 1 point (the highest mark) – the coatings do not crumble and do not exfoliate after receiving the lattice and cuts' edges are smooth; 2, 3 and 4 points – the coatings exfoliate on less than 5%, 35% and more than 35% of the lattice surface, respectively.

Quantitative evaluation of the adhesive properties of coatings was carried out with the help of a peel test. The strength of adhesive joint of polymer coating with the substrate during detachment was measured on a specially designed apparatus which allow determining the force needed for detaching the film of a given width from the surface of the substrate at a constant rate of detachment (Fig. 3). The tests were carried out on the 50×30 mm metal samples with the applied 10 mm wide strip of polymer coating (Fig. 4). Each measurement was carried out on five samples.

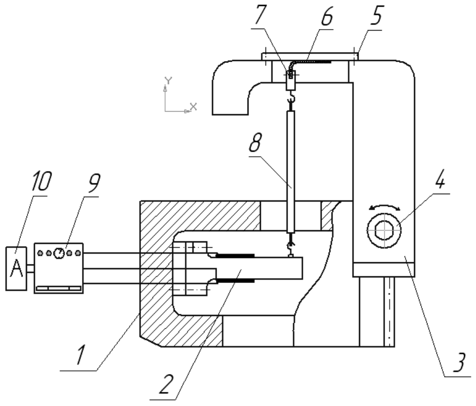


Fig. 3. The scheme of apparatus for determining the strength of adhesive joint during detachment: 1 – entablature, 2 – strain-gage beam, 3 – movable carriage, 4 – handle of a carriage actuator, 5 – coating substrate, 6 – studied coating, 7 – clip, 8 – rod, 9 – strain-gage intensifier, 10 – recording device

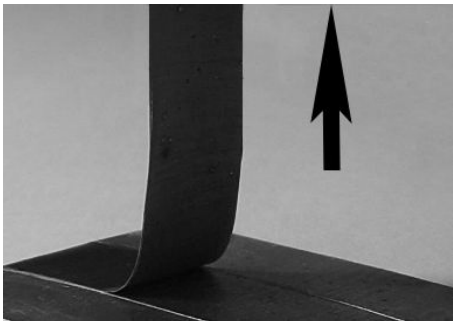


Fig. 4. Detachment of the coating during adhesive joint test

Cantilever method based on the measurement of the value of deviation (h) from the initial position of the free end of resilient metal plate cantilevered with a coating under the influence of internal stresses was used to evaluate the internal stresses arising in a polymer coating during its formation (Fig. 5).

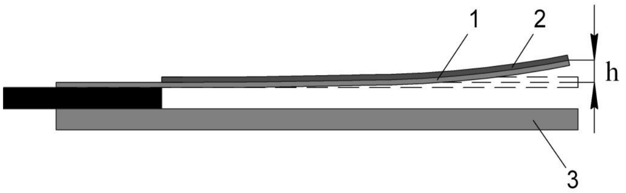


Fig. 5. A sample for measurement of internal stresses by cantilever method: 1 – substrate plate; 2 – polymer coating; 3 – base plate

A sample consists of two 80×15 mm sized stainless steel plates (0.1 mm thick substrate plate and 1 mm thick base plate) joined by spot welding through a 20×15 mm sized 1 mm thick stainless steel pad. The substrate plate is fixed in a stainless steel holder. There are four holes 10 mm in diameter in the base plate to measure the thickness of the coating. Deviation of console was measured with the help of a cathetometer KM-8 at room temperature. To eliminate statistical error each measurement was carried out on five samples. Sensitivity of the method is 0.05 MPa.

Results and discussion

Testing of the investigated coatings by means of cross cutting test (Table) showed the highest mark (1–2) for all samples with the filler content of over 15 wt.%. PMPPI coating containing 20 wt.% of copper phthalocyanine has the highest mark. Cross cutting of surfaces without the filler showed 4 points. The examined 1–2 μm fraction type of filler has practically no influence on the result of the tests that can be attributed to the lack of or small chemical interaction between the filler particles and the polymer matrix for all selected antifriction additives as well as the same type of layered structure of all fillers.

During testing by quantitative peel test, all samples with less than 20 wt.% content of a fine-dispersed filler showed an adhesive nature of fracture. In all cases, the adhesive strength increases with an increase in the amount of a filler (Fig. 6). The character of the dependence of adhesive strength on the concentration is the same for all selected fillers. Coatings filled with copper phthalocyanine had slightly higher values of adhesive strength.

When the content of the filler was 20 wt.% and more, cohesive fracture occurred, i.e. destruction in the volume of the polymer. Conglomerates of particles of the fillers can be observed on the sample

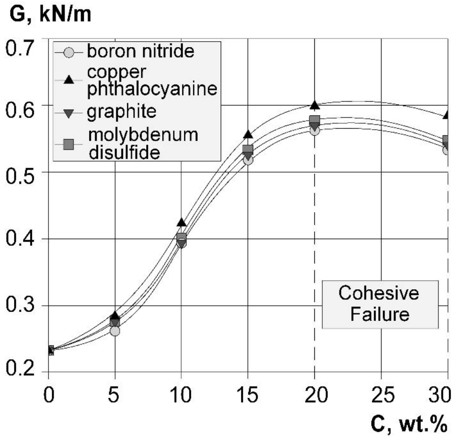
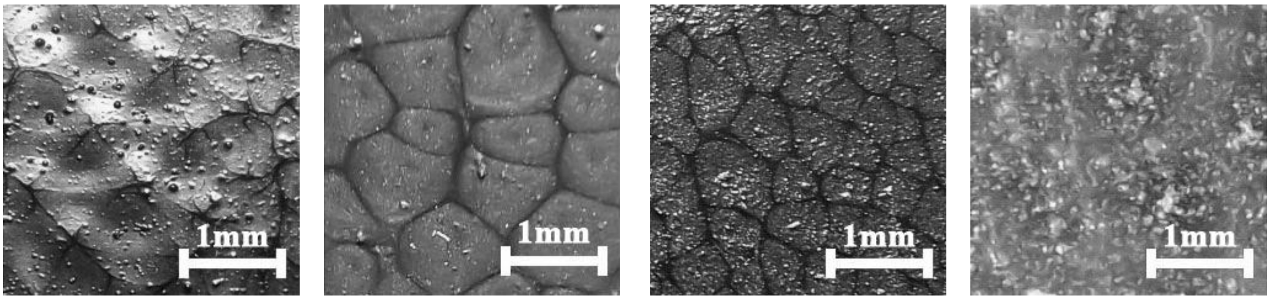


Fig. 6. Change of strength of the adhesive joint during peeling depending on the filler content

The results of cross cutting test of the coatings with fillers

Filler content, wt.%	Test results, point			
	Copper phthalocyanine	Molybdenum disulfide	Graphite	Boron nitride
5	4	4	4	4
10	3	3	3	3
15	2	2	2	2
20	1	1-2	1–2	1–2
30	2	2	2	2



a **b** **c** **d**

Fig. 7. Macrostructure of the surface of composite coatings based on PMPPI which contain 30 wt.% of a filler: a – copper phthalocyanine; b – molybdenum disulfide; c – graphite; d – boron nitride

surface. There is also the formation of the cellular structure on the surface known as Benard cells (Fig. 7). The formation of such structure is explained by the fact that the solvent evaporates and grabs a surface material rising from the depth of the coverage. At that, material enriched with solvent rises in some areas, in other areas material depleted with solvent rises forming cells, and the increase of viscosity prevents leveling of coating, i.e. local difference in the concentrations of coating components appears [13].

Because of the discovered cohesive character of fracture, the reduction of registered force during detachment for samples with 30 wt.% filler content should be linked not to the reduction of adhesive strength but to the reduction of the strength characteristics of the material of composite coating.

The conducted measurements of internal stresses arising in coatings during their formation showed their significant dependence on the concentration of the filler (Fig. 8). It was found that PMPPI coatings are characterized by compressive stresses. Introduction of all the investigated fillers makes the amount of stresses several times less. Obviously, filler particles disrupting integrity of matrix contribute to the fact that the internal stresses are balanced in smaller volumes (probably within Benard cells for coatings with a high concentration of filler), but not in the volume of the whole product or its substantial part, which consequently leads to the decrease of total value of internal stresses.

The nature of dependences shown in Figs. 6 and 8 indicates the correlation between the values of internal stresses and adhesive strength. Indeed, the joint analysis of these characteristics showed their strong correlation. Reduction of internal stresses in coatings (with increasing the concentration of filler particles) can be explicitly associated with the observed increase in adhesion strength (Fig. 9).

The influence of internal stresses on the adhesive properties can be explained in the following way. Compressive stresses, which are present in the PMPPI coating, tend to separate the coating from the substrate. Introduction of the filler particles abruptly reduces compressive stresses, thereby improving adhesive strength.

Since the antifriction properties of the selected fillers are largely dependent on the size of their particles, also the influence of dispersion of the filler

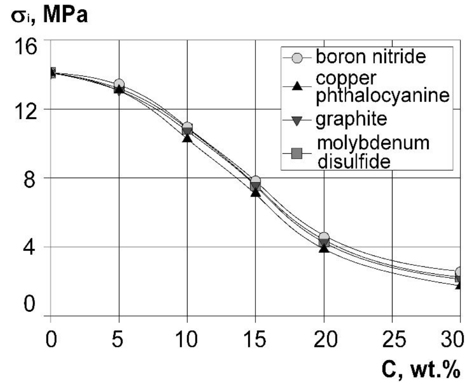


Fig. 8. Dependence of internal stresses in the composite coating on the filler content

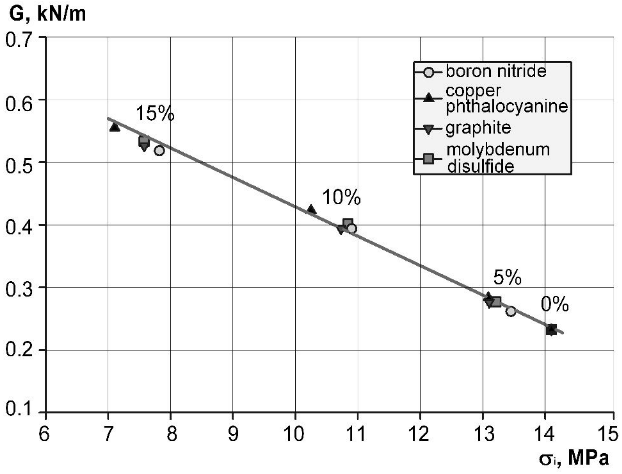
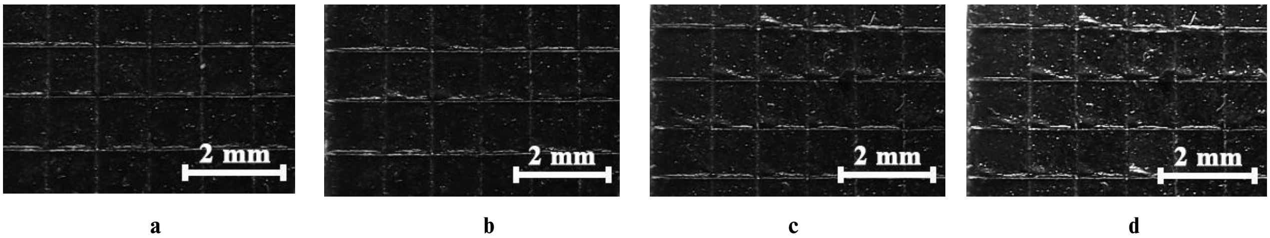


Fig. 9. Correlation between internal stresses and strength of adhesive joints of coatings at different contents of filler



a b c d

Fig. 10. Cross cuts of PMPPI based composite coatings containing 20 wt.% graphite with different dispersion: a – 1–2 μm; b – 5–10 μm; c – 10–20 μm; d – 25–35 μm

on the adhesive properties of composite coatings was of a great interest.

A second series of tests was carried out on samples containing graphite of various degree of dispersion. For coatings with graphite particle size of 1–2, 5–10, 10–20 and 25–35 μm, the cross cutting test showed 1–2, 2, 2 and 2–3 points, respectively (Fig. 10).

Quantitative peel test results showed that the change of dispersion of the particles does not cause fundamental changes in the nature of dependence of strength on the concentration (Fig. 11). However, the adhesive strength of the obtained composite coatings significantly increases with increasing dispersion of graphite filler (Fig. 11), which can be explained in the following way. At the same mass concentration of graphite, the increase of its dispersion (i.e. the reduction of the average diameter of the particles) causes the increase in the number of particles per unit of the volume. Taking into account the results given above, it can be assumed that a larger number of particles divide more effectively the polymer matrix into microvolumes, causing overall reduction of the internal stresses.

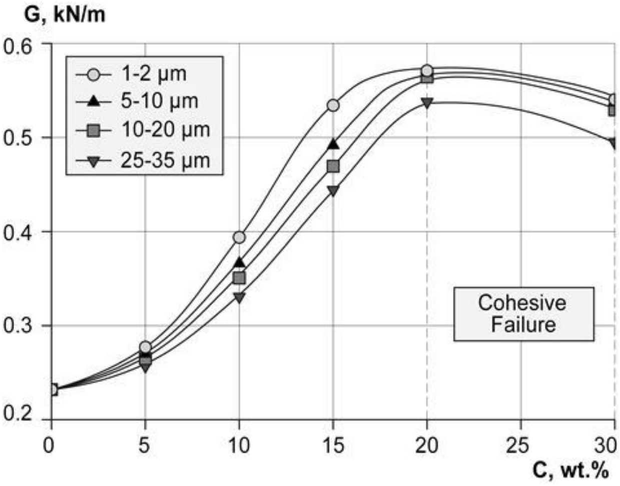


Fig. 11. Change of strength of the adhesive joint during peeling depending on the content of the graphite particles of different dispersion

Summary and conclusions

Introduction of such fillers as copper phthalocyanine, molybdenum disulfide, graphite, and boron nitride into a PMPPI antifriction coating causes an increase in the adhesive strength, as evidenced by the cross cutting test and quantitative peel test. The type of filler has virtually no effect on the adhesive properties due to the absence of chemical interaction between the filler particles and the polymer matrix.

During testing of the composite coatings containing 20 wt.% of filler and more, the cohesive fracture occurs. Conglomerates of filler particles and Benard cells are found on the coating surfaces at such concentrations.

PMPPI coatings are characterized by compressive stresses. Introduction of fillers significantly reduces the value of internal stresses. Apparently, the particles of a filler breaking the continuity of the matrix promote the balancing of the internal stresses in smaller volumes, which results in a reduction of the internal stresses.

A clear correlation between the values of internal stresses and adhesive strength of coatings was revealed. Reduction of internal stresses with an increase in the filler concentration is accompanied by an increase in the adhesive strength. Introduction of the filler particles increases the adhesive strength obviously due to a sharp decrease in the compressive stresses, which tend to separate the coating from the substrate.

By way of example of graphite, it was shown that the change of dispersion of the particles does not cause fundamental changes in the nature of dependence of adhesive strength on the filler concentration. However, with increasing dispersion the adhesive strength of composite coatings significantly increases that is obviously explained by a more efficient division of the polymer matrix into the microvolumes, which causes an overall reduction of internal stresses.

REFERENCES

1. *Klymenko A., Sytar V., Kolesnyk I.* Adhesion of poly (m-, p-phenylene isophtalamide) coatings to metal substrates // Prog. Org. Coat. – 2014. – Vol.77. – P.1597-1602.

2. *Polymer* composite materials in tribotechnics / Mashkov Y.K., Ovcharov Z.N., Baybaratskaya M.J., Mamaev O.A. – M.: Nedra, 2004. – 262 p.

3. *Gallini J.* Polyamides, aromatic // Encyclopedia of polymer science and technology. – New York: John Wiley & Sons, 2005. – Vol.3. – P.558-584.

4. *High-performance* aromatic polyamides / Garcia J.M., Garcia F.C., Serna F., de la Pena J.L. // Prog. Polym. Sci. – 2010. – Vol.35. – P.623-686.

5. *Sytar V.I.* Constructional tribotechnical materials based on heat-resistant aromatic polyamides // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2000. – No. 1. – P.325-327.

6. *Effect* of layered solid lubricants on the tribological properties of composites based on aromatic polyamide / Burya A.I., Prikhodiko O.G., Kholodilov O.V., Burya A.A. // Trenie i Iznos. – 1996. – Vol.17. – No. 1. – P.105-112.

7. *Sytar V.I., Stovpnik A.V.* Development of a technique to obtain and research the properties of coverings based on phenylon // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2008. – No. 4. – P.84-89.

8. *Sytar V.I., Klymenko A.V., Kolesnyk I.V.* Influence of substrate surface condition on the adhesive properties of phenylon coatings // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2013. – No. 4. – P.35-39.

9. *Sytar V.I., Klymenko A.V., Kolesnyk I.V.* Research and selection of the optimal technological parameters of phenylone coatings formation // Bull. Chernihiv State Technol. Univ. Techn. Sci. – 2013. – No. 67. – P.78-85.

10. *Developing* heat-resistant antifriction phenilone-based coatings with enhanced adhesion characteristics / Sytar V.I., Klymenko A.V., Burmistr M.V., Dudka A.N. // J. Frict. Wear. – 2014. – Vol.35. – No. 3. – P.210-214.

11. *Berlin A.A., Basin V.E.* Fundamentals of polymer adhesion. – M.: Khimiya, 1974. – 392 p.

12. *Belyi V.A.* Metal-polymer materials and articles. – M.: Khimiya, 1979. – 312 p.

13. *Yakovlev A.D.* Chemistry and technology of paintwork coatings. – St. Petersburg: Khimizdat, 2008. – 448 p.

14. *Zubov P.I., Suhareva L.A.* Structure and properties of polymer coatings. – M.: Khimiya, 1982. – 256 p.

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ВПЛИВ ЧАСТИНОК НАПОВНЮВАЧА НА АДГЕЗІЙНІ ВЛАСТИВОСТІ ПОКРИТТІВ З ПОЛІ (м-, п-ФЕНІЛЕНІЗОФТАЛАМІДУ)

А.В. Клименко, В.І. Ситар, Є.В. Колесник, В.В. Анісімов

Експериментально досліджено адгезійні властивості композиційних покриттів на основі полі (м-, п-феніленізофталаміду) із широко використовуваними антифрикційними наповнювачами – фталоціаніном міді, дісульфідом молібдену, графітом, нітридом бору. Введення наповнювачів приводить до збільшення адгезійної міцності покриттів, а тип наповнювача практично не впливає на адгезійні властивості. При вмісті наповнювача 20 мас.% та більше під час випробування на відшаровування відбувається когезійне руйнування покриття. Введення наповнювачів значно зменшує величину внутрішніх напружень, що супроводжується збільшенням міцності зчеплення. На прикладі графіту показано, що зростання дисперсності частинок наповнювача збільшує величину міцності зчеплення композиційних покриттів але не викликає принципових змін характеру залежності сили зчеплення від концентрації наповнювача.

Ключові слова: полі (м-, п-феніленізофталамід), ароматичній поліамід, полімерне покриття, адгезія, композит.

EFFECT OF FILLER PARTICLES ON ADHESIVE PROPERTIES OF POLY (m-, p-PHENYLENE ISOPHTALAMIDE) COATINGS

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Keywords: poly (m-, p-phenylene isophtalamide); aromatic polyamide; polymer coating; adhesion; composite.

REFERENCES

1. Klymenko A, Sytar V, Kolesnyk I. Adhesion of poly (m-, p-phenylene isophtalamide) coatings to metal substrates. *Prog Org Coat.* 2014; 77: 1597-1602. doi: 10.1016/j.porgcoat.2014.04.028.

2. Mashkov YK, Ovcharov ZN, Baybaratskaya MJ, Mamaev OA. *Polymer composite materials in tribotechnics.* Moscow: Nedra; 2004. 262 p. (*in Russian*).

3. Gallini J. Polyamides, aromatic. In: *Encyclopedia of polymer science and technology. Vol. 3.* New York: John Wiley & Sons; 2005. p. 558-584.

4. Garcia JM, Garcia FC, Serna F, de la Pena JL. High-performance aromatic polyamides. *Prog Polym Sci.* 2010; 35: 623-686. doi: 10.1016/j.progpolymsci.2009.09.002.

5. Sytar VI. Constructional tribotechnical materials based on heat-resistant aromatic polyamides. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2000; (1): 325-327. (*in Russian*).

6. Burya AI, Prikhodiko OG, Kholodilov OV, Burya AA. Effect of layered solid lubricants on the tribological properties of composites based on aromatic polyamide. *Trenie i Iznos.* 1996; 17(1): 105-112. (*in Russian*).

7. Sytar VI, Stovpnik AV. Development of a technique to obtain and research the properties of coverings based on phenylon. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2008; (4): 84-89. (*in Ukrainian*).

8. Sytar VI, Klymenko AV, Kolesnyk IV. Influence of substrate surface condition on the adhesive properties of phenylon coatings. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2013; (4): 35-39. (*in Ukrainian*).

9. Sytar VI, Klymenko AV, Kolesnyk IV. Research and selection of the optimal technological parameters of phenylone coatings formation. *Bull. Chernihiv State Technol Univ. Techn Sci.* 2013; (67): 78-85. (*in Ukrainian*).

10. Sytar VI, Klymenko AV, Burmistr MV, Dudka AN. Developing heat-resistant antifriction phenilone-based coatings with enhanced adhesion characteristics. *J Frict Wear.* 2014; 35: 210-214. doi: 10.3103/S1068366614030155.

11. Berlin AA, Basin VE. *Fundamentals of polymer adhesion.* Moscow: Khimiya; 1974. 392 p. (*in Russian*).

12. Belyi VA (editor). *Metal-polymer materials and articles.* Moscow: Khimiya; 1979. 312 p. (*in Russian*).

13. Yakovlev AD. *Chemistry and technology of paintwork coatings.* St. Petersburg: Khimizdat; 2008. 448 p. (*in Russian*).

14. Zubov PI, Suhareva LA. *Structure and properties of polymer coatings.* Moscow: Khimiya; 1982. 256 p. (*in Russian*).