

The analysis of adhesion effect on properties of the modified polymeric nano composites

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Summary. The analysis of the adhesion effect on the structure and properties of nano-modified composites is given in the article. Existing theories of adhesion were considered. The analysis results showed that the introduction of nano modifiers into the epoxy matrix leads to improvement of the physical and mechanical properties of polymer composites [6].
Key words: epoxy matrix, nano modifiers, physical and mechanical properties, polymeric composite materials.

INTRODUCTION

Replacement of metal structural components in the aerospace technology of polymeric materials produces a significant gain in the weight of an aircraft. Consequently, it also gives the technical and economic advantages.

However, polymeric composite materials (PCM) must have strictly regulated physical and mechanical characteristics. These include: high impact strength, low water permeability, electrical conductivity etc [18].

Obtaining the PCM with specified characteristics is a priority technology of the XXI century. According to the forecasts of the European Union, the amount of funding in development in the field of nano technology in the world will reach 1 trillion euros by 2015 [1].

The study of information of international conferences NANO-2008 (Minsk), NANO-2010 (Kiev), NANO-2011 (Moscow), the annual conferences "Composite Materials in Industry" at Yalta and Moscow International Conference "Theory and Practice of manufacturing technology of products made from composite materials and new metal alloys, "2006-2011, was conducted.

Sources points to the wide interest to the nano modified PCM with carbon-modifiers.

However, there is an insignificant number of the papers about creation, study of the effect on adhesion properties of PCM and the use of thin films as the structural materials and the coatings for special purposes.

Proceeding from above, the study of the adhesion effect on the properties of polymer composite materials is an important task.

The purpose of article is the analysis of the adhesion effect on the structure and properties of nano-modified composites.

OBJECTS AND PROBLEMS

At present time there are a number of theories of adhesion.

Adsorption theory of adhesion assumes that the adhesion is caused by the secondary valent bond force [12] between the molecules of the padding (substrate) and adhesive on the minimum range of 5 Å. Van der Waals forces, dipole-induced and dipole molecular interaction and hydrogen bonding may be involved here. To obtain stable adhesion the polar surfaces should be agreed [16].

Diffusion theory assumes that the adhesion of polymers is the result of diffusion of the substrate of molecules or their entities. Interdiffusion but with different mobility occurs when both layers are polymers. For example, glass (glass fiber) is recommended to be covered with

the silane, which is capable for mutual diffusion of the resin.

The theory of surface energy states that good adhesion can be obtained by any polymer and the surface of any material. This is possible if the surface tension of the substrate material is higher. In this case, the polymer which is in a liquid state will have a minimal contact angle with the surface and spread out well on it.

Reactionary theory of adhesion is applicable in cases where the covalent bond can occur between the binder and the substrate. Adhesive compound becomes like a part of the massive block of the copolymer.

There is a semi-empirical theory of adhesion of macromolecular compounds (MMC) [2]. Most of polymeric adhesives are solutions MMC. Adhesion processes involving polymeric adhesives play a key role in the creation of various types of adhesives and composite materials.

Existing theories consider the specific mechanisms of adhesion at the interphase boundary "adhesive - substrate" in dilute solutions mainly. Therefore it is important to solve the problem of interfacial solid connection at the "polymer - adhesive - substrate" boundary. Semi-empirical model does not analyze the intermolecular forces at the interphase boundary.

Theory prerequisites are the following ones: non-ideality of adhesives solutions is expected; various forces in the interaction of the polymer adhesive with the substrate are considered - van der Waals, chemical, electrostatic (however, details of every interaction is not conducted); set of polymer globules forms a cluster; adhesive forces are determined by the interaction of clusters with the substrate; expansion of the polymer particles and clusters into the structural defects and pores of the substrate occurs under the influence of the field of molecular interaction; concentration dependence of the adhesion forces obeys the law of non-ideal solutions. Each type of clusters is making its contribution to the "expansion".

In contrast to the perfectly smooth surface of the substrate which is assumed in [2], the adhesive forces have not superficial but the volume nature. Hence the dimension of force is evaluated in N/m^2 , and the work of the adhesion forces - in J/m^3 .

The work of these forces according to the first law of thermodynamics is determined by the formula:

$$\delta Q = dU + \delta A + \pi dV, \quad (1)$$

where: δQ - amount of heat released (absorbed) by the system; A - work which was

being done over the system; U - internal system energy; dV - volume change of the considered system [19].

As it is shown by the theory of adhesion (classical and semi-empirical) and the results of their practical confirmation, glass fiber plastics strength increases with adhesion strength increasing [17-18].

Therefore, to increase the strength of fiberglass products the different ways of modifying the surface of the filler and the binder is required to be used. It will lead to increasing of adhesion strength [20].

Adhesion strength depends on many factors related not only to the nature of the contacting materials but also particularly technological interface preparation; these include the surface area and roughness, the polarity of the molecules, the interphase tension etc [15].

There is a relation between the surface and material bulk properties. Consideration of the processes which are occurring at the interface from a molecular point of view helps to explain the relations of physical and mechanical properties of the structure of the PCM [3-5].

The difference in the coefficients of thermal expansion in composite materials may create the additional effect at the rigid inclusion point [17]. Thus, in the "epoxy resin-fiberglass" there is an additional pressure on the surface of the glass up to 7 MPa in the polymerization process. Factors that affect the adhesion strength are shown in fig. [1].

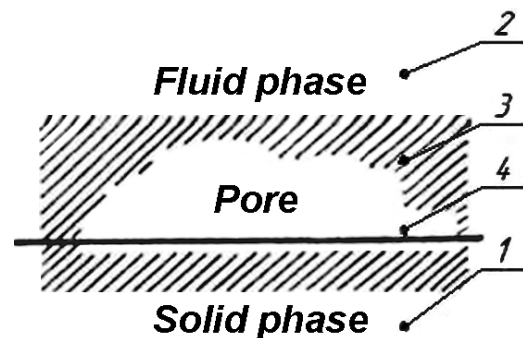


Fig. Factors that affect the adhesion strength: 1-solid body; 2-fluid phase; 3- pores; 4- surface separation

Analysis of the literature on the acquisition polymeric composite materials with regulated characteristics showed that nanotechnology is an interdisciplinary science. To solve any technical problem the whole complex of the physicochemical investigations is required [11].

Particularly for obtaining composite materials with specific characteristics it is

necessary to consider the following processes: to justify the choice of nanomodifiers, to establish mechanism of interaction of nanomodifiers with the matrix; to determine the optimum ratio "nanomodifiers - matrix" [6].

One of the problems in modern aviation and space technology is to reduce the weight of the aerial vehicles through the use of structural elements made of polymer composite materials. Applied to this polymer composites must combine high strength, resistance to dynamic loads and exploitation in various climatic conditions.

The basic material as a binder in obtaining the adhesives, glues, protective coatings are the thermosetting epoxy resins [13].

The progress in science and technology causes the creation of new materials with a set of required properties. Important factors in the ensuring of operational reliability are: the adhesive strength, strength characteristics resistance for use in a variety of environments [14].

Influence of processing of thin composite coatings on steel was studied by the authors. It showed that the injection of the filler of various nature into the epoxy matrix increased the strength of the "coating-base" [7].

The mechanism of interfacial interaction in the epoxy resin filled with dispersed particles was explained by the methods of structural and spectral analysis. It was found that the molecular mobility of the epoxy oligomer near the surface of the filler decreases independently on the chemical activity of the filler.

The change in the infrared spectra (IR), that is the shift of the band of the hydroxyl group (3760 cm⁻¹) at 20 cm⁻¹ and a decrease in the intensity of the absorption band of the C = O demonstrates the chemical interaction at the phase boundary [7-9].

Layer structure was studied on a microscope with an increase in 104 times. The processed results allowed us to calculate the value of the area of the layers around the particles. They showed that not only the first but the second layer is affected by the active filler particles. Physical relations are being formed during the interaction.

Particle size of fillers (zinc oxide, carbon black, technical graphite, electrocorundum) was about 40-60 microns. Although the nanodimensional (50-500 nm) particles are used in our experiments, the study of adhesive strength of the modified epoxy resin represents statistical interest (table).

Table. Adhesive strength of the protective coatings

Properties	Modifier material			
	Cuprous oxide	Carbon black	Electrocorundum	Technical graphite
Adhesive strength σ_{max} , MPa	56,95	52,6	67	69

CONCLUSIONS

The conducted analysis of the influence of adhesion on the properties of polymer nano-modified composite materials leads to the following conclusions:

1. Tensile stress is considerably increased (in 2,5-3 times).
2. Optical properties of thin films of polymer composites vary.
3. The extent of water absorption decreases with the introduction of nanomodifiers of 30%. This allows to use them as a sealing layer.
4. Adhesive strength of nano-modified composites increases.

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АНАЛИЗ ВЛИЯНИЯ АДГЕЗИИ НА СВОЙСТВА ПОЛИМЕРНЫХ НАНОМОДИФИЦИРОВАННЫХ КОМПОЗИТОВ

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Кашкаров, Игорь Непран*

Аннотация. В статье дан анализ влияния адгезии на структуру и свойства полимерных наномодифицированных композитов. Рассмотрены существующие теории адгезии. Результаты анализа показали, что введение наномодификаторов в эпоксидную матрицу приводит к улучшению физико-механических характеристик полимерных композитных материалов. Ключевые слова: эпоксидная матрица, наномодификаторы, физико-механические свойства, полимерные композиционные материалы.