Analysis of Carbon Fibers Treatment Technology to Obtain Composites Materials with Metal and Non-Metal Matrix

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Abstract. When designing any composite material, the compatibility between the component elements must be considered, a compatibility that can be seen from a physical and chemical point of view. Chemical compatibility refers to the existence or development to a small extent of reactions between components. Thus, at high temperatures, the diffusion processes intensify, and fragile compounds can form, which cancel the direct connection between the components, resulting in a significant decrease in the mechanical strength of the composite material. A successful process of manufacturing carbon fiber-reinforced composites requires that the fiber to be protected, usually with a coating, during their manufacture and use. The paper aims to analyze the process of Chemical Vapor Deposition (CVD) which is a successful process of manufacturing carbon fiber reinforced composites. They require that the fiber be protected with a coating during their manufacture and use.

1. Introduction

Complementary materials, used to reinforce the energy of the matrix or to induce the self-lubricating property of the composite material, differ from each other in chemical nature and configuration [1-4].

According to the configuration, the complementary materials are divided into two main categories: fibers and particles, each category including numerous other types, differentiated by size, by length / diameter ratio and by chemical composition in cross section [5-8].

Compared to fibers, particles are easier to make and incorporate into the matrix material. Instead, the fibers are irreplaceable if the aim is to obtain a composite with high toughness [9].

The fibers are used as reinforcing elements, having the role of taking over a large part of the stresses to which the matrix material is subjected. Depending on the nature of the matrix and the purpose pursued, the fibers are made of organic substances, metals, ceramics or pairs of such materials, of different shapes and sizes [10-15].

An important criterion for the classification of fibers (figure 1) is the ratio between length and diameter. Depending on the structure, the fibers can be polycrystalline, monocrystalline or amorphous.

2. Fiber production techniques

Fiber production methods have developed in parallel with the growing interest in these materials. Although there is a wide variety of manufacturing processes, current technologies can fall into the following three main distinct categories [16,17]:

- melt extraction, used to produce 50-60% of glass and alumina-silica fibers, or melt extraction, used to obtain fibers from amorphous alloys.
solid state transformation, a method used in the production of carbon fibers, silicon carbide, alumina-silica, or zirconium oxide, both for the continuous ones (multifilaments) and for the usual discontinuous ones. The process is based on the use of a precursor in the form of fibers, transformed after a heat treatment into the material to be obtained in the end.

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\text{Figure 1. Classification of fibers used in the production of composite materials [14].}
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- vapor growth, a method used to produce very short (monocrystalline) fibers or continuous monofilament fibers. Monofilament fibers are obtained by depositing a material on backing fibers (such as depositing silicon carbide or boron on tungsten or carbon backing fibers) [17].

Carbon fibers have become popular lately due to their many advantages: outstanding mechanical properties, low cost, high temperature stability, good chemical compatibility with organic matrices and the possibility of using a wide range of raw materials. The term carbon fibers mean fibers that contain more than 80% C in the form of amorphous carbon and graphite and have a density between 1.50 and 1.96 g/cm³ (the density of graphite being 2.265 g/cm³), which means the existence of a porosity of 16.5...18%. The porosity is created by microcavities elongated much in the direction of the fiber [18-20].

3. Surface treatments specific to the preparation of carbon fiber, to obtain polymeric composites.

The basic physical parameters that influence the formation of the matrix-fiber bond are the specific surface and the degree of surface roughness, both parameters characterizing the surface topometry and effectively determining the contact surface between the matrix and the fiber.

The chemical composition of the surface, in the case of carbon fiber, is different from that of the interior, so that at the surface are present oxygen atoms (in variable numbers), up to a depth of 3 μm and hydrogen atoms. Thus, in order to obtain an adhesion between fiber and resin, it is necessary to obtain a physico-chemical reactivity at the interface, simultaneously with the achievement of optimal compositions of matrix materials and their modifications, at sintering [21].

Theoretically, a tight adhesion of the fiber-matrix is achieved by advanced wetting of the fiber surface with the liquid resin.

Carbon fibers, even in the case of high-performance ones, cannot be used as such to reinforce polymeric (or metallic) matrices. For carbon fibers, the means by which good adhesion can be achieved is their surface oxidation treatment [22].
The most important methods for such treatments are [23]:

- electrochemical oxidation;
- dry oxidation;
- wet oxidation.

Anodic oxidation allows the strict maintenance of the necessary oxidation conditions, as well as a rigorous control, without difficulties, on the speed of the process.

Most experiments on the electrochemical oxidation of carbon fibers aim to produce physicochemical changes at the surface, which ensure the removal of some of the surface defects and, at the same time, to generate functional groups on the surface of the fibers [24].

Anodic oxidation of carbon fibers is performed under "mild" conditions, which do not produce essential morphological changes on their surface. The improvement in adhesion between oxidized carbon fibers and the polymeric matrix can be explained by the formation of chemical bonds, by physical adhesion or mechanical interactions. The reaction media in which the anodic oxidation is carried out are determined by the subsequent applications of the composites made with these fibers. Thus, solutions of various concentrations of sulfuric acid, sodium hydroxide or potassium sulphate may be used. Treatment time is also variable, from 1 minute to 10 minutes.

The dry oxidation of carbon fibers is performed in air or oxygen, at temperatures between 500 ÷ 800° C. The dry oxidative treatment time varies in a wide range of values (from 30 seconds to 2 hours), depending on the nature of the fibers and their subsequent applications.

The third process, that of wet oxidation, is the most used, because it does not require the existence of complex treatment facilities. The solutions used in this process are generally inorganic acids having oxygen atoms in their molecular structure. Thus, we currently work with nitric acid of various concentrations. The duration of wet oxidative treatments is in the range of 10 minutes ÷ 150 hours.

The improvement of the mechanical properties of oxidized carbon fiber composites is due to the chemical activation of the fiber surface.

The mechanical properties decrease in size due to damage to the carbon fiber during thermal oxidation. The maximum mechanical strength of the composite is obtained after short oxidations, while for long oxidation times, the effect of fiber damage is predominant, leading to the impossibility of embedding in the matrix.

The analyzes performed on the treated carbon fibers, in order to determine the structural changes occurred, showed that, in the case of wet oxidation, acid and non-acid groups are formed on the surface of the component filaments of the polyfilament carbon cable. On dry oxidation the formation of non-acidic groups was confirmed.

In the case of anodic oxidation, it is found that appropriate results are obtained, if working under the conditions of the transition range between non-corrosive and corrosive treatment.

All the surface treatments applied to the carbon fibers presented above, lead to the formation of reactive oxide groups on the surface of the fibers. The improvement of the fiber-matrix adhesion can be directly correlated with the increase of their concentration at the surface of the fibers.

4. CVD coatings applied to carbon fibers intended for metallic composite materials.

Among the new composite materials, metal matrix composites reinforced with carbon fibers have experienced a special development, given the possibilities of use they have in various fields. A successful process of manufacturing carbon fiber-reinforced composites requires that the fiber be protected, usually with a coating, during their manufacture and use.

Chemical Vapor Deposition (CVD) is a modern technology for fiber coating. The experience gained so far shows that there can be large differences between the theoretical and real values that have the properties of a composite material. The results of the experiments show that the mechanical strength is much lower than expected.

The reason for such a difference is, in part, the result of the fiber-matrix interaction. At high working temperatures, the fiber can react with the matrix, losing some of its properties. Residual stresses as well as thermal instability of fibers can also contribute to this phenomenon.
In order to keep the fibers intact during processing and to produce the desired surface properties, the process by which the composite material is manufactured almost always comprises a process by which the fiber is coated. The coating protects the fiber during the operation in which the fiber is combined with the matrix. Simultaneously, the wetting and binding of the fiber with the matrix is favored; In some cases, the coating is a sacrificial layer, which is destroyed during processing. In general, the structure, composition and morphology of the coating affect the strength of the composite after manufacture.

Chemical vapor deposition (CVD) and its variants are used for fiber coating. A typical coating has a thickness of about 2 μm. Figure 2 shows a hot-walled vertical reactor for fiber coating. The installation contains the reactive gas supply system and the deposition cell, into which the carbon fiber coating substrate is introduced.

![Diagram of a chemical vapor deposition plant](image)

Figure 2. Scheme of the chemical vapor deposition plant [4].

An obvious problem is the oxidation of carbon fibers during and after processing; the phenomenon can be ameliorated by coating the fibers with carbides or metal oxides. The most successful carbon fiber reinforced composites were produced from pyrocarbon coated fibers, SiC or BN, by a CVD process.

The CVD process can be defined as the transport of solid particles by vapors, the chemical reactions being inherent in this process.

An example of a fiber coating CVD reactor is the cylindrical reactor through which the fiber is moved as gaseous reactants circulate around it. The gases and the surface of the fiber are heated to the reaction temperature. A hot-walled reactor can be used, as in figure 2, or the fiber can be electrically heated. The reactions occur in the gas phase and several chemical species can form. Thermodynamic equilibrium may or may not be reached in CVD reactions. If homogeneous nucleation occurs in the gas phase, solid nuclei will result. Such nucleation products (sometimes called "snow") are usually unwanted in the deposit on the layer.
The reaction products diffuse to the surface, producing surface reactions, which lead to the formation of a deposit on the surface of the fiber. The limiting factor in the deposition process may be the reaction kinetics or the diffusion of vapor species to the surface. At higher temperatures (above 1300°C for xylans), the process tends to be controlled by diffusion. Low temperature deposition rates are limited by reaction kinetics. Some reactors may operate in a transient mode, in which the deposition rate is also determined by the reaction kinetics and vapor diffusion.

5. Conclusions

Due to the current demand for advanced materials, the use of materials with a monolithic structure and, implicitly, of metal matrix composites has been widely used, especially for those applications that require a high specific resistance to high temperatures or chemical attack.

The Chemical Vapor Deposition process is the preferred method for coating fibers, due to its advantages like low deposition temperatures and high purity coatings. Various microstructures can occur, deposits can be made on felt or bundles thus the induced thermal stresses are low.

Among the critical parameters of the coating process we mention: temperature distribution in the reactor, reactant concentration and pressure, gas velocity distribution, system geometry.

In addition to these critical parameters, they can also be mentioned: fiber feed speed, reaction kinetics in gases and at the fiber surface, thermodynamics of gas phase reactants and solid products and gas transport coefficient such as diffusivity and viscosity.

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