PLASMA SURFACE TREATMENT AND MODIFICATION OF FIBRES FOR FIBRE-REINFORCED POLYMER COMPOSITES

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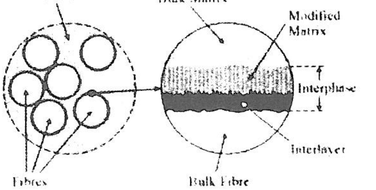
Abstract

A development of high-performance composites is tightly bound with a designing of composite interphases. The interphase is a region intermediate to the fibre and the matrix which are in a contact. In fact this region includes the fibre coating and a part of the matrix affected by the presence of the coated fibre. Theoretical and experimental studies have shown that the properties of fibre reinforced composites are given by the coating material with its thickness and modulus, by the interaction at interfaces with the fibre and the matrix, and by the reinforcement and matrix materials. Therefore, sophisticated interphases can lead to higher strength and higher toughness of the specific composite system. Low temperature plasma technology is the new technique used for surface modification of reinforcements. This technology is able to prepare controlled interphases. Actual possibilities and achievements of the plasma technology are outlined.

1. Introduction

Fibre reinforced composites combine high strength of rigid reinforcements with high toughness of flexible matrix. Synergism of the two phases produce mechanical properties of the composite material that cannot be achieved with either of the constituents acting alone, due to the presence of an interphase between the reinforcement and the matrix. The interphase is a region intermediate to the fibre and the matrix, the composition and/or structure and/or properties of which may be variable across the region and which also may differ from the composition and/or structure and/or properties of either of the two constituents [1,2]. This concept of the interphase is schematically illustrated in Fig. 1. We can distinguish two interfaces at the interphase region. One of them at the fibre surface (fibre/interphase) is relatively sharp and the other at the matrix (interphase/matrix) is a diffused one. If the surface of the fibre is modified by a coating (interlayer) there is the third inner interface between the interlayer and the modified matrix. Interphases influence and may control the mechanical properties of composites using fibres with a diameter of 5-25 ìm and the common fibre volume fraction ranging from 0.5 to 0.7 as it is evident from experimental and model data. Therefore, the interphase properties are becoming gradually accepted as design and process variables to be tailored for particular end applications [3].



The primary function of the interphase is to transmit stress from the matrix to the fibres and to protect the fibres from environmental damage. An ability of this region to transmit stress depends upon the interphase strength, as well as the mechanical properties of fibre, matrix, interphase, and the bonding forces (adhesion) at interfaces. The nature of bonding is not only dependent on the atomic arrangement, molecular conformation and chemical constitution of all the phases, but also on the morphological properties of the fibre and the diffusivity of elements in each constituent. Adhesion in general can be attributed to mechanisms including, but not restricted to, adsorption and wetting, mechanical interlocking, electrostatic attraction, molecular entanglement, and hydrogen and chemical bonding. The surface of reinforcements has to be modified to improve wetting and adhesion to the matrix for sophisticated composites. A lot of techniques for surface treatment of fibers are known and they differ depending on the fibre nature (glass, carbon, aramid, polyethylene, etc.) [2]. In recent years, plasma techniques found great applications in a development of high-tech composites. This paper outlines new progress in tailored interphases using plasma technologies.

2. Plasma surface treatment and modification

The surface modification of reinforcements is a useful way to influence the chemical and physical structures of their surface layer, tailoring fibre-matrix stress transfer, but without influencing their bulk mechanical properties. Generally, chemical reactions that involve the implantation of special elements (oxygen, nitrogen, fluorine atoms, etc.) or moieties (hydroxyl, carbonyl, carboxylate, etc.) and the grafting of special monomers are applied for modification process. The input energy supplied from the outside of the fibres to initiate the chemical reactions must not penetrate into a deeper layer of the fibre materials. From the viewpoint, plasma is used as a source of the input energy.

Low temperature plasma is used for surface modification [4] of reinforcements and is characterized by the high electron temperature (10^3–10^4 K) and the low ion temperature (10^2 K). The former affords a sputtering effect on the fibre surface and the possibility of chemical modification. The latter, being as low as room temperature in most cases, enables fibres to experience such plasma modification without loss of their mechanical properties. Plasma contains activated species able to initiate chemical and physical reactions at the fibre surface, when it contacts with the surface of reinforcements. As a result, modification reactions at the surface occur and cause alteration of surface properties and surface morphology   plasma surface treatment. Likewise, when plasma interact with organic molecules in vapor, polymers are formed (plasma polymerization [5,6]), and all surfaces of substrates in the plasma zone are coated with the polymers – plasma surface modification. This type of synthesis has an atomic character in contrast to conventional radical and condensation polymerizations. In many cases, plasma polymers show distinguished chemical composition, structure, and chemical and physical properties from those formed by conventional polymerizations using the same monomer. High-frequency glow discharge proves to be an ordinary tool for plasma surface modification. Various monomers and gases are used to improve interphases and the usual deposition parameters are given in Table 1.

Table 1. Typical process parameters for plasma surface modification of reinforcements.

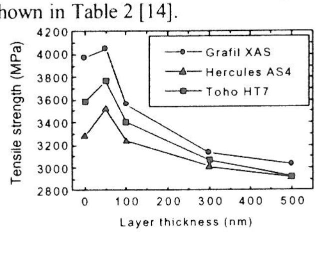
Frequency	10^3 – 10^9 Hz
Power supply	10 – 500 W
Process gas pressure	10^{-1} – 10^2 Pa
Process gas/vapor flow	1 – 100 standard cm^3 min^{-1}
Deposition/treatment time	1 – 30 min
Deposition rate	0.1 – 10 ìm h^{-1}

4. Plasma treated and modified fibres in composites

Plasma surface modification of fibres and their application in fibre reinforced composites is widely used from the 1980s. A lot of theoretical and experimental studies are devoted to plasma treatment and plasma coating (polymerization) processes [9]. An insight into interphase functionality together with bonding forced at interfaces is very difficult. Therefore, scientists try to understand relations among chemical composition, structure, surface morphology, and mechanical properties of interphases, and how can be influenced by deposition parameters of plasma technology. First, effects of plasma treatments and coated plasma polymers are analyzed using optical, electron, and atomic force microscopies, infrared, photoelectron, ion spectroscopies, contact angle measurements, and many others methods. Then, the data are envisaged with those characterizing mechanical properties of interphases in model composites (fibre fracture test, pull-out test, microdroplet test, microindentation test [10]) – interfacial shear strength (IFSS), and/or in complete laminae (short beam shear test [2]- ASTM D2344) – interlaminar shear strength (ILSS). An influence of plasma surface modification on interphase and polymer composite properties is outlined for carbon, aramid, polyethylene and glass fibres.

The tensile strength of single fibers can be decreased using intensive plasma treatment (high power and/or long treatment time) owing to the etching effect, as it was observed by Bettge and Hinrichsen [11] that treated polyethylene fibres with oxygen plasma. Since carbon fibres are easily damaged by the ablation effect, plasma polymers were coated on the fibre surface to avoid the loss of strength of the fibres. Weisweiler [12] have used a mixture of acetylene/air plasma to deposit a plasma polymer on commercial carbon fibres. The tensile strength increases till a film thickness of about 50 nm is reached (Fig. 2). It was proposed that the plasma coatings effectively heal some of the surface flaws of the fibres, and so the tensile strength increases. However, with increasing volume of the layer, the number of surface flaws is growing due to Griffith's theory, resulting in a decrease of the tensile strength above about 50 nm layer thickness.

Plasma surface treatment of carbon fibres has been studied using air, O_2, CO_2, and NH_3 plasmas, and plasma polymers have been deposited using dioxane and xylene; acrylonitrile and styrene; aniline, pyridine, and benzene monomer [9]. Organic vapors, such as polyamide; polyimide; organosilanes; styrene and maleic anhydride; propylene; and acrylonitrile and styrene were used as well [2]. Jang and Kim [13] have applied oxygen plasma treatment to modify an interphase in carbon fibre/PEEK composites. The interlaminar shear strength and the flexural strength as a function of plasma treatment time are shown in Fig. 3. It was confirmed that the mechanical properties of CF/PEEK composites are strongly influenced by the roughness of the carbon fibre surface and improved fibre wettability. A higher increase of ILSS can be found for carbon fibre/epoxy composites using organosilanes (Fig. 4) [2]. The improvement in interface bond strength was confirmed using microcomposite tests. However, all these beneficial effects of improved strength properties are inevitably accompanied by a loss in the impact fracture toughness of unidirectional laminates (Fig. 4). An effect of different surface treatment techniques on an improvement of interlaminar shear strength is shown in Table 2 [14].



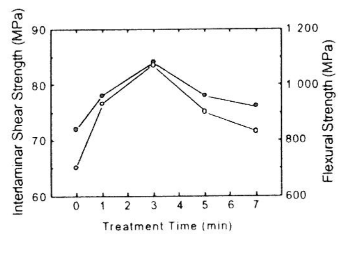
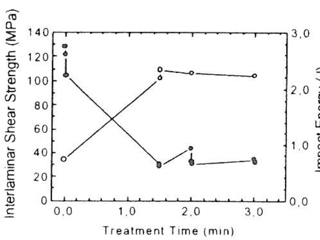


Table 2. Surface modification of carbon fibre and improvement of resulting composite interlaminar shear strength (ILSS). Adapted from Ref. 14.

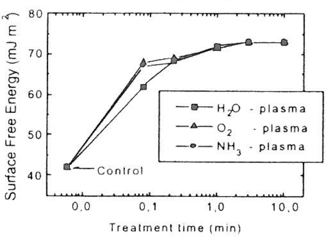
Modification	Improvement in ILSS%
Gaseous oxidation (air, ozone, plasma)	10–15
Liquid-phase oxidation (HNO_3, H_2O_2, electrolytic)	100–200
Whiskerization (Si_3, N_4, TiO_4, SiC)	200–300
Pyrolytic carbon coating (CH_4, FeC, SiC)	60–100
Polymer grafting	80–100
Plasma polymerization	0–250

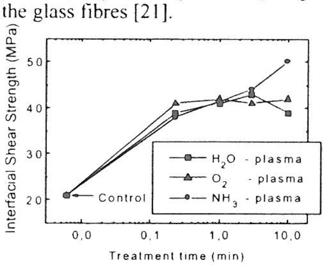
Promising results have been obtained by modifying the aramid fibre surface with air, oxygen, ammonia and water plasmas [9]. The improvement in bond strength varies between 50-400%, depending on the exposure time and gas. Plasma treatment in ammonia increases the amine concentration on fibre surfaces, which is thought to be responsible for strong covalent bonding at the interphase with epoxy resins. The treatment also increases the surface free energy of aramid fibres (Fig. 5) and the ILSS of aramid fibre/epoxy composites with the treatment time (Fig. 6) as well [15].

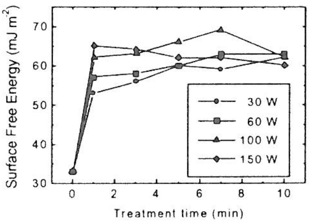


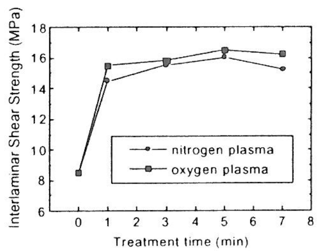
Obviously, polyethylene fibres are treated with an oxygen plasma to improve the wettability and the interface shear strength [9]. Li and Netravali [16] have reported about the interfacial shear strength of polyethylene fibres in epoxy resin. They coated a plasma polymer using allylamine monomer and the IFSS increased by a factor of 2 to 3. Surface free energy of polyethylene fibres increases rapidly with the treatment time if oxygen plasma is applied (Fig. 7) [17]. Moon and Jang [18] have improved considerably the interlaminar shear strength in polyethylene fibre/vinylester composites (Fig. 8). The fibres were treated by oxygen and nitrogen plasmas. The improved adhesion of fibre/matrix is attributed to the increased surface energy, the oxygen-containing moieties, and the surface area.

Silane coupling agents are applied to glass fibre surface to promote the adhesion with the polymer matrix. Nevertheless, the formed siloxane bonds are hydrolytically unstable, which results in worsening of mechanical properties of the composite in the presence of water and, eventually, in failure of the material. This problem may be resolved with plasma surface modification. Various organosilane monomers have been used to form plasma polymers [19,20], but an application for reinforcements is at the beginning. Plasma polymer layers prepared from a mixture of dichloro(methylphenylsilane) vapor and gaseous hydrogen have an excellent and hydrolytically stable adhesion to the glass fibres [21].







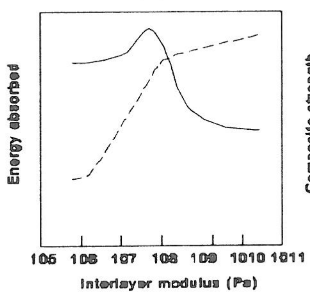


4. Composite strength and toughness – controlled interphase

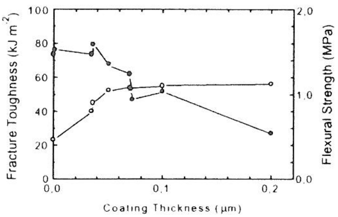
The above outlined attempts aim to a surface modification of fibres, which should results in strong bonding of fibres in matrix. However, an improvement of the bonding often results in an increase in the shear strength at an expense of the impact strength (Fig. 4). Due to good bonding, debonding is more difficult and therefore the advancing crack propagates through the fibres, resulting in low impact strength. Hence a strong interface favors a brittle fracture with low energy absorption, whereas a weak interface favors multiple delaminations with high energy absorption. Furthermore, good adhesion exacerbates the physical mismatches which exist between the fibres and the matrix, increasing the stress concentration caused by imposed loads and/or thermal cycles. The fibre coating method for toughening composites seems to be one of the most effective methods for achieving simultaneously high strength and high toughness when an appropriate polymer is chosen [22]. Theoretical and experimental studies have shown that the coated material should be ductile or flexible with an interlayer modulus lower than that of the matrix [23] (Fig. 9) and that the layer thickness is very critical [24] (Fig. 10). The introduction of the flexible interlayer reduces or eliminates interfacial stresses, both under mechanical loading and temperature cycles and relieves the stress concentration into the matrix, resulting in improved mechanical performance, crack resistance and impact strength of the structural composite. Even thought it is not yet completely known which coating materials are most suitable for a specific composite system, the variables which affect the properties of a fibre reinforced composites have been identified as follows: interlayer modulus, interlayer thickness, matrix modulus, coating material (composition), interaction at the interfaces [25].

5. Conclusions

Plasma surface modification is an effective technique to influence physical and chemical properties of interphases in fibre reinforced polymer composites. The tensile strength of single fibres is sensitive to both the plasma treatment and plasma polymerization. The plasma treatment changes surface morphology of fibres increasing the roughness of surfaces and thus increasing the surface area which may result in an improving of the adhesion between reinforcing fibres and matrices. Strong adhesion is promoted by increasing the surface energy of fibres, as a result of plasma modification, decreasing its contact angle so that the wettability of fibres with the polymer matrix is improved. The chemical composition of the fibre surfaces can be changed by



the plasma technology as well. The strength of composites is enhanced introducing excited and/or polar groups. An introduction of moieties available for a specific composite system is favorable to form strong chemical bonds between the fibre and the matrix. An improvement of the bonding often results in an increase in the shear strength at the expense of the impact strength.



The aim is to produce a composite with the optimal strength and toughness with respect to industrial application of the material. This may be achieved forming a controlled interphase for a specific composite system (fibre-matrix). Therefore, the surface treatment in itself is an insufficient technique, and only a coating technique capable prepare defined interlayers with a high accuracy has a chance. The interphase should be a multilayer with a strong bonding to the fibre and matrix, wherein the chemical, physical, and mechanical properties vary continuously into properties of the bulk matrix. Properties of the interphase at outer interfaces may be conformable, in chemical and physical sense, to those of the bulk fibre and bulk matrix. The bulk interphase may be a flexible material able to absorb energy and eliminate stress concentration. We believe the plasma surface modification is the true technique for attempts with controlled interphases, although we are still at the beginning.

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