

Plasma polymers used for controlled interphase in polymer composites

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The performance of fiber-reinforced composites is strongly influenced by the functionality of composite interphases. Sizing, i.e. functional coating (interlayer), is therefore tailored to improve the transfer of stress from the polymer matrix to the fiber reinforcement by enhancing fiber wettability, adhesion, compatibility, etc. The world market is dominated by glass reinforcement in unsaturated polyester. However, commercially produced sizing (wet chemical process) is heterogeneous with respect to the thickness and uniformity, and hydrolytically unstable. Companies search for new ways of solving the above problems. One of the alternative technologies is plasma polymerization. Plasma polymer films of hexamethyldisiloxane, vinyltriethoxysilane, and tetravinylsilane, pure and in a mixture with oxygen gas, were engineered as compatible interlayers for the glass fiber/polyester composite. The interlayers of controlled physico-chemical properties were tailored using the deposition conditions with regard to the elemental composition, chemical structure, and Young's modulus in order to improve adhesion bonding at the interlayer/glass and polyester/interlayer interfaces and tune the cross-linking of the plasma polymer. The optimized interlayer enabled a 6.5-fold increase of the short-beam strength compared to the untreated fibers. The short-beam strength of GF/polyester composite with the plasma polymer interlayer was 32% higher than that with commercial sizing developed for fiber-reinforced composites with a polyester matrix. The progress in plasmachemical processing of composite reinforcements enabled us to release a new conception of composites without interfaces.

Keywords: thin films, plasma polymerization, glass fiber, polymer composites, interface/interphase

1. Introduction

The development of high-performance fiber-reinforced plastics (FRP) is linked to an effort to improve the properties of reinforcing fibers and polymer matrices. The effort results in special materials such as high-modulus or high-strength fibers of stable mechanical properties and polymers of high thermal or chemical resistance. However, new materials with outstanding properties are very expensive. Another way to improve composite performance is advancement in engineered interfaces [1] or, more properly termed, composite interphases [2]. The composite interphase is a 3D region in composite material that can be found between the fiber surface and the matrix. In simple terms, the interphase comprises an interlayer (thin film), which is coated onto reinforcing fiber, and a modified matrix, which is affected by the presence of the coated fiber (Fig. 1). The concept of the interphase was schematically illustrated in Ref. 3.

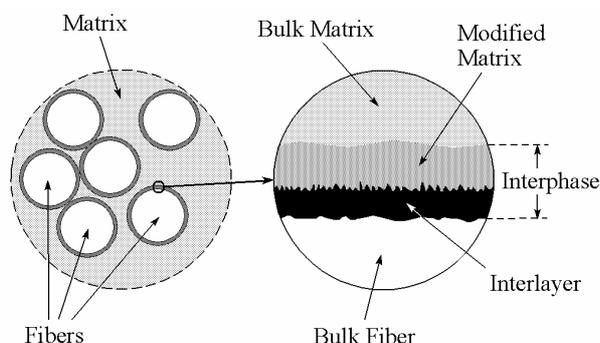


Fig. 1. A schematic illustration of a composite interphase.

The interlayer should improve compatibility and form a strong but tough link between the fiber and the

matrix, which are of distinct physical and chemical properties. Theoretical and experimental studies have shown that composite interphases can markedly influence the performance of composites with respect to their strength and toughness [4,5]. The aim of this paper was to highlight plasma polymerization [6-8] as a technology capable of preparing thin films of controlled properties [9], which could improve composite performance markedly via the controlled interphase.

2. Wet chemical process

The performance of fiber-reinforced composites is strongly influenced by the functionality of composite interphases [1]. The world market is dominated by glass reinforcement in unsaturated polyester, which comprises almost 90% of the total market. Approximately 1.8×10^6 t of E-glass fiber is manufactured annually for use in composites and 50% goes into continuous and long-fiber reinforced thermosets [10]. Sizing, i.e. functional coating, is therefore tailored to improve the transfer of stress from the matrix to the fiber reinforcement by enhancing fiber wettability, adhesion, compatibility, etc. Commercially produced sizing is heterogeneous with respect to the thickness and uniformity [11], the molecules of silane coupling agents have a tendency towards self-condensation, forming siloxane oligomers rather than complete bonding with the glass surface [12,13], and the low density of siloxane bonds with the surface decreases if water molecules diffuse to the interface since this type of bond is hydrolytically unstable [14]. Only 10–20% of the total sizing is bonded to the fiber surface and this amount is directly related to the composite interfacial strength [15]. Technological centers in glass companies search for new ways of solving the above problems. One of the alternative technologies is the low-temperature plasma technique.

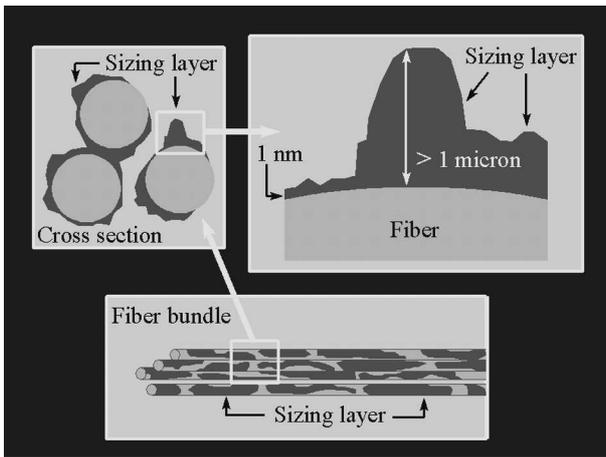


Fig. 2. Scheme of the nonuniform distribution of sizing layers that is characteristic of commercial glass fiber products (adapted from [11]).

3. Plasmachemical processes

Low temperature plasma may be used as a gentle but powerful tool for surface treatment and coating of fibers, which retain their mechanical properties. Plasma surface modification of fibers and its application in FRP has been widely used since the 1980s, see the reviews in Refs. 16 and 17. Plasma treatment (surface etching and/or functionalization) and plasma polymerization (film coating) have remained very popular up to today. Oxygen plasma is often used for surface treatment of carbon [18,19], polyamide [20], polyethylene terephthalate (PET) [21], poly(p-phenylene-2,6-benzobisoxazole (PBO, Zylon) [22], poly(p-phenylene terephthalamide) (PPTA, Kevlar) [23], and sisal [24] fibers, carbon nanotubes [24,25], polyamide [26] and carbon [27,28] nanofibers. The oxygen plasma may increase the surface roughness and introduce functional groups, such as $-OH$, $C-O$, $C=O$, and $O-C=O$, into the surface layer of material, which results in an improvement of wettability. Argon, air, CO_2 , H_2O , and NH_3 plasmas may also be used for plasma treatment [19,21,27,29].

4. Plasma polymerization

Most researches employ the plasma-treatment technique as described above to increase the wettability and the roughness of fiber surface, and consequently the fiber/matrix adhesion, which supports composite strength enhancement, but at the expense of composite toughness [17]. An effective solution how to simultaneously improve the composite strength and toughness is the coating technique (plasma polymerization) [5]. Thin polymer films prepared by the plasma-polymerization technique may be formed as homogeneous with respect to thickness, uniformity, composition and structure. Plasma polymerization, as a film-coating technique, offers a greater range of surface modifications for e.g. glass [30-32] and carbon [19,33,34] fibers or silica particles [35].

The composite interface/interphase is specific to each fiber-matrix system [3]. An RF helical coupling pulsed-plasma apparatus [25] can be used for continual or static surface modification (treatment and coating) of fibers. Plasma polymer films of hexamethyldisiloxane

(HMDSO), vinyltriethoxysilane (VTES), and tetravinylsilane (TVS), pure or in a mixture with oxygen gas, were engineered as compatible interlayers for the glass fiber/polyester composites. Thin and ultrathin films were deposited on planar glass, silicon substrates, and glass fiber (GF) bundles to characterize their physical and chemical properties.

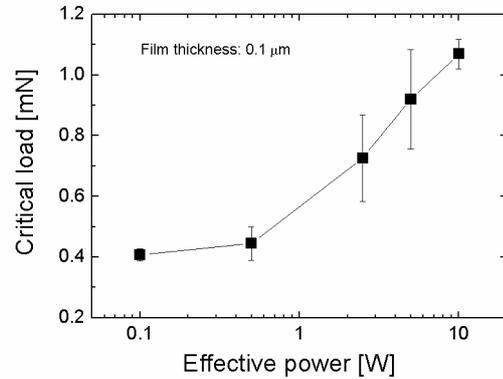


Fig. 3. Adhesion of pp-TVS film on glass substrate.

As an example, we can demonstrate physical and chemical properties of plasma-polymerized tetravinylsilane (pp-TVS) films. The pp-TVS films with a thickness of $0.1 \mu m$ were deposited on planar glass substrates. The adhesion of films was evaluated by scratch test. The test consists of drawing a tip over a film under increasing normal loads. The value of the load under which adhesion failure is detected is known as the critical load. The failure events were examined by atomic force microscopy (AFM). The critical load increased significantly with enhanced power, used for film deposition, as can be seen in Fig. 3. The critical load was almost three times higher for the film deposited at 10 W than that for the film deposited at 0.1 W.

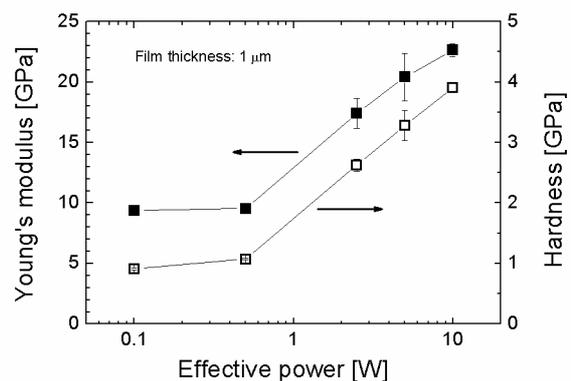


Fig. 4. Young's modulus and hardness of pp-TVS film as a function of the effective power.

Nanoindentation measurements enabled to characterize selected mechanical properties of $1 \mu m$ -thick films deposited on silicon wafers (Fig. 4). The Young's modulus (full symbol) increased from 9.4 to 23 GPa with power enhanced by two orders of magnitude (0.1 – 10 W). A similar trend was observed

for hardness and the values increased from 0.9 to 3.9 GPa with enhanced power. The mechanical parameters (Young's modulus and hardness) of pp-TVS films increased with enhanced power due to a higher cross-linking of plasma polymer network [36]. Monomer molecules are more activated and fragmented forming a higher density of free radicals, if the plasma energy (power) increases, and the reactive species result in a highly cross-linked polymer.

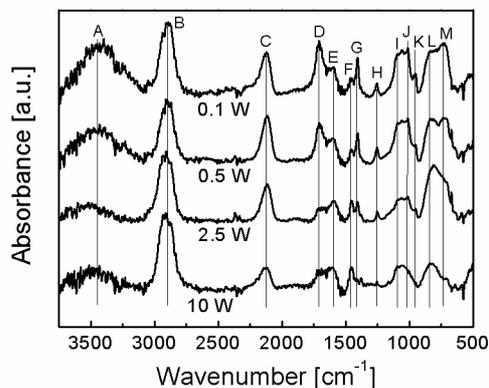


Fig. 5. FTIR spectra corresponding to pp-TVS film deposited at different effective powers.

Typical infrared spectra of pp-TVS films deposited at different powers are given in Fig. 5. The intensity and area of absorption bands A, D, and I, corresponding to species such as OH, C=O, and Si-O-C, respectively, descended with enhanced power and the trend was in good agreement with a descent of oxygen concentration in plasma polymer revealed by Rutherford Backscattering Spectrometry measurements [37]. The SiH (band C), SiC (band M), and CH_x species (band B) in the plasma polymer film were identified as responsible for post-deposition oxidation (ageing) of the deposited material [37]. A decrease of bands C, H, L, and M assigned to species containing silicon atoms was observed as well and the trend corresponded to an increase of C/Si ratio with enhanced power. An occurrence of vinyl groups in plasma polymer was evident from IR spectra corresponding to pp-TVS films deposited at lower power (≤ 2.5 W). The concentration of vinyl groups decreased with enhanced power as a descent of bands E, J, and especially G, K indicated. The vinyl groups are responsible for chemical bonding to polyester resin (matrix) at the matrix/interlayer interface.

The results of the Owens-Wendt-Kaelble geometric mean method are given in Fig. 6, where the total surface free energy and its polar and dispersion components are plotted as a function of the effective power. The total surface free energy (full symbol) increased from 40 mJ m⁻² up to a saturated value of 49 mJ m⁻² reached at a power of 5 W. The values of the dispersion component (empty symbol) were responsible for the increase of the surface free energy due to decreased concentration of vinyl groups in plasma polymer with enhanced power. The polar component (half symbol) of value about 4 mJ m⁻² was approximately independent of the power.

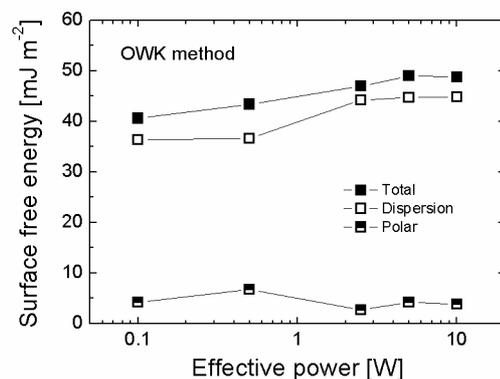


Fig. 6. Surface free energy of pp-TVS film depending on the effective power.

The plasma polymer films were deposited on bundles of unsized glass fibers. Free radicals diffuse into the central part of the bundle and form a thin film even on surface of central fibers during the plasmachemical deposition. However, the deposition rate decreases in radial direction into the fiber bundle due to the shadowing effect of surrounding fibers and thus the film thickness of coating on central fibers is lower with respect to that on surface fibers. Unsized, industrially sized (wet chemical process), and plasma polymer coated glass fibers were embedded into unsaturated polyester resin and cured to form GF/polyester composite.

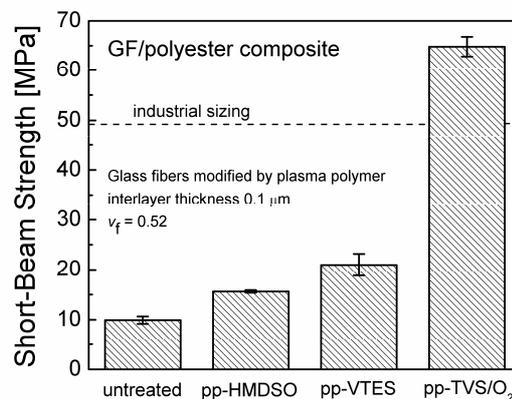


Fig. 7. Short-beam strength of GF/polyester composite for different surface modifications of glass fibers. The volume fraction of fibers was 0.52.

Short-beam composites were evaluated in a three-point bending test according to ASTM D 2344/D 2344M - 00 [38] to compare their performance (Fig. 7). The interlayers of controlled physicochemical properties were tailored using the deposition conditions with regard to the elemental composition, chemical structure, and Young's modulus in order to improve adhesion bonding at the interlayer/glass and polyester/interlayer interfaces and tune the cross-linking of the plasma polymer. The optimized interlayer, using pp-TVS/O₂ film, enabled a 6.5-fold increase of the short-beam strength compared to the untreated fibers. The short-beam strength of GF/polyester composite with the plasma polymer interlayer was 32% higher than that with industrial sizing developed for fiber-reinforced composites with a polyester matrix [39].

The progress in plasmachemical processing of composite reinforcements enabled us to release a new conception of composites without interfaces [9].

5. Composites without interfaces

A region of the modified matrix (spontaneous interphase) could be formed around the fiber if untreated (unsized) fiber is embedded into the polymer matrix and a composite is formed. A simple schema of the elastic modulus profile across such an interphase is shown in Fig. 8(a). The Young's modulus, E , of the fiber often differs from that of the matrix by one order or more, e.g. $E_{GF} = 73$ GPa for glass fiber and $E_{PES} = 4$ GPa for polyester matrix. Adhesion bonding between the fiber surface and the modified matrix has to be strong to ensure stress transfer from the matrix to the fiber. We can then expect the modulus of the modified matrix affected by the fiber surface to be higher than that of the bulk matrix. Regardless of this, the fiber/matrix interface is very sharp and the modulus change very high, resulting in high stress concentration under both mechanical and thermal loading. Formation of a strong bond at the interface is possible using a gentle plasma treatment of the fiber surface. Thus the enhanced surface roughness and wettability together with new functional groups result in high interfacial shear strength, while the mechanical properties of the fiber are retained. However, an increase in the shear strength is inevitably accompanied by a loss in the impact fracture toughness, with the result that the composite material is too brittle to be applicable. It is very difficult to control interfacial bonding with respect to bond strength and/or bond density by technology.

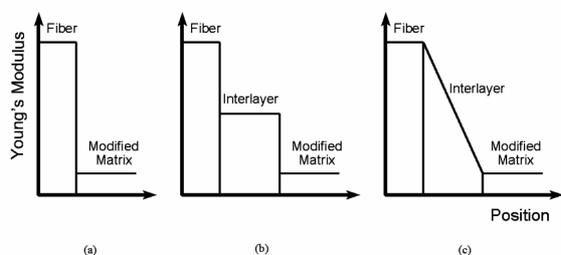


Fig. 8. Schematic illustration of the elastic modulus profile across the interphase: (a) without interlayer, (b) homogeneous interlayer, (c) gradual interlayer.

The fiber-coating method for toughening composites seems to be one of the most effective methods for achieving simultaneous high strength and high toughness when an appropriate interlayer material is chosen [1,3]. Thus, an interlayer is inserted between the fiber and the matrix (Fig. 8(b)), and the film must be strongly bonded at both interfaces to form a strong but tough link between the fiber and the matrix. It is evident that the specific composite system with an interlayer material of a modulus comparable to that of the fiber or matrix results in similar disadvantages to the composite system without an interlayer. Therefore, we can expect that the interlayer modulus should be lower than that of the fiber. Some theoretical and experimental studies have shown that the coated material should be ductile or

flexible [5]. Even though we do not know fully in advance which coating material is most suitable for a specific composite system; the variables that affect the properties of FRP have been identified as follows: interlayer modulus, interlayer thickness, matrix modulus, coating material (composition) and interaction at the interfaces [5].

In general, utilization of an interlayer with the modulus about that of the matrix or even lower results in problems with a strong mismatch at the fiber/interlayer interface. A simple gradual interlayer could suit better, see Fig. 8(c). In that case, there is no mismatch at either interface and the interlayer material is not so stiff. A more sophisticated modulus profile can be suggested to ensure a strong but tough composite using a functionally gradual nanostructured interlayer, see Fig. 9 (solid line). Preparation of an interlayer with chemical and physical properties continuously varying from those of the fiber to those of the matrix without any interface could be an ambitious aim. Such an interlayer could eliminate problems with a modified matrix, whose properties are controlled only with difficulty.

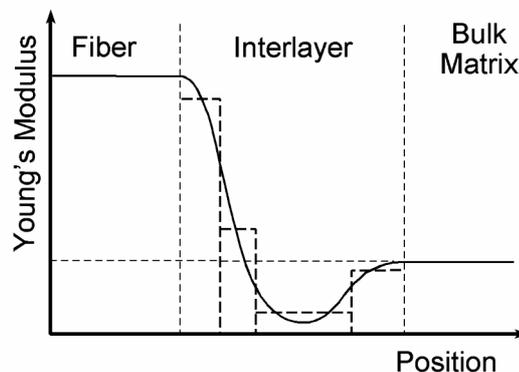


Fig. 9. Schematic illustration of the elastic modulus profile across the interphase with a functionally gradual nanostructured interlayer prepared layer by layer (dashed line) or in one deposition (solid line).

Structured films (multilayers) can be prepared using the "bottom-up" method. Thus a nanostructured interlayer can be prepared layer by layer (Fig. 9, dashed line), where the film thickness of an individual layer could be only a few tens of nanometers, and the individual layers must be bonded to each other using strong chemical bonds. We could construct a functionally gradual nanostructured interlayer without interfaces if a coating technology were available that could prepare film of continuously varying properties in one deposition. Such a nanotechnology could be valuable for the formation of the controlled interphase. Plasma polymerization has technological potential to fabricate nanostructured thin films of controlled properties in one deposition.

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