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Enhanced interfacial adhesion of glass fibers by tetravinylsilane plasma modification

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ABSTRACT

Plasma-polymerized tetravinylsilane was used to surface modify glass fibers to improve interfacial adhesion of a GF/polyester composite. Plasma polymer films of controllable thickness and physicochemical properties were deposited on unsized glass fibers by RF pulsed plasma using an effective power of 0.1–5 W. The interfacial adhesion of unsized, industrially sized, oxygen plasma treated, and plasma polymer coated fibers embedded in polyester resin was determined by microindentation. The plasma modification of the glass fibers enabled a considerable increase in the interfacial shear strength compared to unsized fibers. The interfacial shear strength for the optimized plasma coating was 26% higher than that for the industrial sizing.

1. Introduction

The development of high-performance fiber-reinforced plastics (FRP) is closely connected with progress in engineered interfaces [1] through controlled interphases [2]. Theoretical and experimental studies have shown that the composite interphase can markedly influence the performance of composites with respect to their strength and toughness [3,4]. Sizing, i.e., functional coating (interlayer), is therefore tailored [5] to improve the transfer of stress from the polymer matrix to the fiber reinforcement by enhancing fiber wettability, adhesion, compatibility, etc. The key parameters affecting the performance of composite materials are the sizing thickness and modulus, the interaction at interfaces, and the reinforcement and matrix materials [4]. However, industrially produced sizing of glass fibers (GF) is not of a consistent thickness and uniformity [5]. Using the wet chemical process, the molecules of silane coupling agents have a tendency to self-condense, forming siloxane oligomers rather than complete bonding with the glass surface [6,7]. Only 10–20% of the total sizing is bonded to the fiber surface, and this amount is directly related to the composite shear strength [8].

The plasmachemical process is another way to improve composite performance via a controlled interphase. Low temperature plasma may be used as a gentle but powerful tool for surface treatment (chemical and/or physical altering of the fiber surface) or coating (plasma polymerization) of fibers, retaining their mechanical properties if appropriate plasma conditions are used. Plasma surface modification of fibers and its application in FRP has been studied since the 1980s, see the review in Ref. [9]. 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 fibers, resulting in improved wettability. Argon, air, O_2, CO_2, H_2O, and NH_3 plasmas may be used for plasma treatment of fibers to improve interfacial adhesion, but the resulting shear strength is still lower compared to industrially sized fibers. The plasma coating method, unlike the plasma treatment, seems to be one of the most effective methods of achieving both high strength and high toughness, when an appropriate material is chosen for coating [10]. Plasma-polymerized organosilicones constitute a class of materials with a rich and varied scientific background [11,12]. This class of materials possesses special characteristics, distinguishing it from other plasma polymers: the ability to vary and control its organic/inorganic character (i.e., the carbon content) and polymer cross-linking by the appropriate choice of fabrication variables [13]. This allows one to control many physicochemical properties over wide ranges, resulting in an extraordinary potential for engineered interlayers in polymer composites [14,15].

In this study, we examined chemical, mechanical, and surface properties of plasma-polymerized tetravinylsilane films controlled by RF power and their application as engineered interlayers to enhance interfacial adhesion of surface modified glass fibers in GF/polyester composites. Fiber microindentation measurements were used to evaluate the interfacial shear strength [16].

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2. Experimental

Plasma-polymerized tetravinylsilane (pp-TVS) films were prepared by plasma-enhanced chemical vapor deposition (PECVD) employing an RF helical coupling system [17], using a pulsed regime. The films were deposited on IR-transparent silicon wafers (100) ($0.8 \times 10 \times 10\ mm^3$; ON Semiconductor, Czech Republic), special microscope slides ($1.0 \times 26 \times 76\ mm^3$; Knittel Glaser, Germany), and unsized glass fiber bundles (E-glass, 1200 tex, mean diameter 19 μm; Saint-Gobain Adfors CZ, Czech Republic). Tetravinylsilane, Si—(CH=CH_2)$_4$ (TVS, purity 97%, Sigma Aldrich), was used as the monomer. The effective power (W_{eff}) of the pulsed plasma was controlled by changing the ratio of the time the plasma was switched on (t_{on}) to the time it was switched off (t_{off}), $W_{eff} = t_{on}/T \times W_{total}$, where the period was defined as $T = t_{on} + t_{off}$, $W_{total} = 50$ W, and the duty cycle, DC, as $DC = t_{on}/T \times 100\%$. The substrates were pretreated with O_2 plasma (5 sccm, 4 Pa, 25 W) for 10 min to clean the surface from contaminants and improve film adhesion. Pulsed plasma was operated at conditions given in Table 1. The deposition rate increased from 10 nm min^{-1} (0.1 W) to a sharp peak of 142 nm min^{-1} (2.5 W), followed by a descent to 82 nm min^{-1} (10 W). Film is deposited at steady-state plasma and thus has consistent thickness and uniformity. The substrate is hidden in a loadlock, separated from the deposition chamber, until steady-state plasma is reached. The low-temperature plasma was used as a gentle tool using a low power density (Table 1) and retaining mechanical properties of fibers.

Selected chemical, mechanical, and surface properties were investigated for the plasma polymer films deposited on the planar substrates. The elemental composition of the thin films was studied by conventional and resonant Rutherford Backscattering Spectrometry (RBS) and Elastic Recoil Detection Analysis (ERDA) using a Van de Graaf generator with a linear electrostatic accelerator. The RBS spectra were evaluated by computer code GISA 3 [18] and the ERDA spectra by SIMNRA code [19], both using cross-section values from SigmaBase.

Infrared measurements in the wavenumber range of 500–4000 cm^{-1} were made using a VERTEX 80 vacuum Fourier transform infrared (FTIR) spectrometer (Bruker Optics). Transmission spectra were obtained on films deposited on infrared-transparent silicon wafers. An absorption subtraction technique was used to remove the spectral features of silicon wafer, and background correction was carried out before each measurement. The spectral resolution was 4 cm^{-1}. Approximately 256 scans were recorded to achieve a reasonable signal-to-noise ratio.

The mechanical properties (Young's modulus, hardness) and adhesion (scratch test) of the pp-TVS films were investigated using 2D TriboScope (Hysitron) attached to an NTegra Prima Scanning Probe Microscope (NT-MDT). A Berkovich tip with a radius of curvature of about 100 nm was used. The Young's modulus and hardness of films were determined from unload–displacement curves using the Oliver–Pharr method [20]. The scratch parameters were as follows: linear, 10 μm at 0.33 μm/s, load 1 μN–5 mN. The normal and lateral forces were measured simultaneously together with the normal displacement. The root-mean-square (RMS) roughness of the plasma polymer films deposited on planar substrates was computed using AFM images (scan area $5 \times 5\ \mu m^2$) measured in semicontact mode. The glass fibers coated by pp-TVS film were examined using a scanning electron microscope (SEM) (Philips XL 30/EDAX/Microspec).

The sessile drop method (tangent method) employing an OCA 10 goniometer (DataPhysics) was used to measure the equilibrium contact angles. Water and diiodomethane were used as probe liquids. The surface free energy as well as the dispersion and polar components were evaluated using the Owens–Wendt–Kaelble geometric mean method [21–23].

Industrially sized GF bundles (E-glass, 1200 tex, mean diameter 19 μm; Saint-Gobain Adfors CZ, Czech Republic) were designated for GF/polyester composites. The commercial sizing based on silane coupling agents was tailored by the glass fiber manufacturer. Unsized, oxygen plasma treated, industrially sized, and plasma polymer coated glass fibers were embedded into unsaturated polyester resin (isophthalic) Viapal HP 349 F (Sirca S. p. A., Italy) to form a GF/polyester composite. A bundle of fibers was impregnated with the resin, and extra resin was carefully wiped from the bundle. The impregnated bundle was positioned axially in a silicon rubber mold, which was filled with resin and cured at 140 °C to form a polymer disk 14 mm in diameter and 5 mm in height. Details on sample fabrication can be found in Ref. [24]. The disk was embedded in a metallographic specimen mount with the fibers normal to the specimen surface and the surface was polished using conventional metallographic techniques.

The microindentation test [16] was carried out on the individually selected glass fibers on a polished cross-section of GF/polyester composite using an Interfacial Testing System (ITS) (Dow Chemical Company) [25]. A diamond tip with a diameter of 12 μm was applied to push single fibers from their surrounding matrix. The interfacial shear strength, IFSS (MPa), was determined from the debond load, P (g), using a generalized empirical equation [25] (adapted for IFSS in (MPa))

$$IFSS = A\frac{P}{D^2}\left[B\left(\frac{G_m}{E_f}\right)^{\frac{1}{2}} - C\log\left(\frac{d}{D}\right) - E\right], \quad (1)$$

where D is the fiber diameter (μm), G_m and E_f are the matrix shear modulus and fiber axial modulus, respectively, d is the matrix thickness between the tested fiber and its nearest neighbor (μm), and $A = 1.249 \times 10^4$, $B = 0.8757$, $C = 0.01863$, $E = 0.02650$. A matrix shear modulus of 1.3 GPa and a fiber axial modulus of 73 GPa correspond to the polyester resin used and the glass fiber, respectively.

Table 1
Deposition conditions used for preparation of the pp-TVS films.

Frequency	13.56 MHz
t_{on}, t_{off}	1 ms, 4–499 ms
Period	5–500 ms
Duty cycle	0.2–20%
Effective power	0.1–10 W
Effective power density	2×10^{-3}–1×10^{-1} W cm^{-3}
Basic pressure	8×10^{-4} Pa
Process gas pressure	1.3 Pa
Monomer vapor flow rate	0.80 sccm

3. Results and discussion

Tetravinylsilane molecules are activated and fragmented during the plasma process, forming free radicals due to collisions with high-energy electrons, and the highly reactive radicals recombine at the surface of growing film. An increasing number (0–4) of vinyl groups bonded to the silicon atom are eliminated from TVS molecules at enhanced effective powers, as was monitored by mass spectroscopy. If the effective power is further increased, the eliminated vinyl is fragmented into smaller carbon species in a form of mono- and bi-radicals. Therefore, by changing the effective power one is able to control not only the plasma species but also the elemental composition and chemical structure of the deposited film. The elemental composition of pp-TVS films was determined from RBS and ERDA spectra. Atomic concentrations were 9–5 at.% (silicon), 36–42 at.% (carbon), and 55–53 at.% (hydrogen), depending on the power used. The carbon to silicon ratio, which characterizes the organic/inorganic character of plasma polymer, increased from about 4 (0.1 W) to 8 (10 W) with enhanced power, as shown in