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Characterization of interlayer adhesion on single glass fibers and planar glass using the nanoscratch test technique

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ABSTRACT

All reinforcing fibers have to be coated with a suitable interlayer (thin film) to ensure their effective functionality in fiber-reinforced polymer composites. The interlayer adhesion on the reinforcing fibers is most critical and decides the performance of the composite. In this study, we demonstrate that interlayer adhesion can be evaluated directly on single glass fibers with a diameter of 19 μm using the nanoscratch test. The feasibility of the nanoscratch test, commonly used for planar specimens, is examined for glass fibers coated by plasma polymer film with a thickness of 0.10 μm. The adhesion of thin films on glass substrate can be varied by the deposition conditions. For a given film, the nanoscratch test on fibrous samples provided reliable data resulting in consistent interlayer adhesion for both fibrous and planar glass substrates.

1. Introduction

Fiber-reinforced polymer composites are promising materials that continue to be developed for applications in the automotive industry and other industrial sectors such as construction, wind power, aerospace, and defense. An estimate of the total world market for composites is US$90 billion by 2020 (Markets and Markets, 2015), with a compound annual growth rate (CAGR) of 7% to 9% (2015–20) [1]. This market is dominated by glass reinforcement (87%) in unsaturated polyester (UP) resin (63%), together comprising approximately 60% of the total volume. The performance of the composite material is controlled by the functionality of the composite interphase, i.e., the phase between the fiber surface and the polymer matrix [2], which includes an interlayer (thin film) coated onto the reinforcing fiber. The interphase region can be observed by nanoscale imaging techniques [3]. To ensure stress transfer from the flexible matrix to the rigid fiber, the functional interlayer has to improve the compatibility between these two and form a strong but flexible link between the fiber surface and the polymer matrix. Therefore, all reinforcing fibers (glass, carbon, aramid, and natural) need to be surface treated, sized, or coated as part of the manufacturing process [4]. Recently, Karger-Kocsis et al. [5] reviewed fiber surface modifications and Mishnaevsky Jr. [6] summarized computational studies on interface/interphase damage including nanostructured interfaces.

One of the best measures of interfacial adhesion between the fiber and the polymer matrix is interfacial shear strength (IFSS), which can be determined by several techniques, including the microindentation test [7]. Using a composite cross-section, the microindentation is made by a diamond tip, pushing the end of a single fiber in longitudinal compression from the surrounding matrix [8]. In the microindentation test, shear failure of the interphase is caused by an interfacial shear failure at the interlayer/fiber or matrix/interlayer interfaces or by a shear failure of the interlayer or matrix itself. Nonlinear finite element analysis of the microindentation and experimental data indicate that interphase shear failure is controlled by the shear strength at the interlayer/fiber interface in cases where a plasma polymer film with high shear yield strength (0.6–1.5 GPa) is used as an interlayer for glass fiber/polyester composites [9]. Thus, the performance of the composite material is controlled by the interlayer adhesion on the glass fiber. Plasma polymer is a material in the form of a thin film deposited in non-thermal plasmas [10]. Plasma surface modification of glass fibers is an alternative technology to wet chemical processes employed for commercial sizing used for glass fiber-reinforced polymer composites. The IFSS for the optimized plasma polymer was 26% higher than that for the commercial sizing [9].

To investigate the influence of deposition conditions, adhesion of plasma polymer films on planar glass substrates can be characterized by the nanoscratch test [11]. The test consists of drawing a diamond tip over a film under increasing normal loads. The value of the load at which adhesion failure is detected is known as the critical load, which is used as a measure of the film adhesion. The adhesion failure (delamination) means that the locus of failure is the film/substrate interface. Finding deposition conditions that enhance interlayer adhesion can lead to an increase in composite performance. The nanoscratch test is

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ordinarily used for thin films deposited on planar substrates. The objective of this study was to explore the feasibility of the nanoscratch test for interlayers deposited on single glass fibers used as reinforcements in polymer composites.

2. Experimental details

2.1. Materials

Argon gas (99.999%) was used to clean the plasma reactor and vacuum chambers. Tetravinylsilane, Si–$(CH = CH_2)_4$ (TVS, purity 97%, Sigma Aldrich, Czech Republic), was used as the monomer and oxygen gas (99.99%) was mixed with TVS monomer to deposit hydrogenated amorphous carbon-silicon oxide (a-CSiO:H) films.

Special glass slides without flaws ($1.0 \times 26 \times 76$ mm^3; Knittel Glaser, Germany; Young's modulus, $E = 67.7$ GPa, hardness, $H = 9.22$ GPa, Poisson's ratio, $\nu_s = 0.16$ [12]) were used as planar substrates and single fibers were separated from a bundle of bare (unsized) glass fibers (*E*-glass, 600 tex, mean diameter 19 μm; Saint-Gobain Adfors, Czech Republic; $E = 76.4$ GPa, $H = 7.8$ GPa, $\nu_s = 0.21$ [13]) and used as fibrous substrates. The root-mean-square (RMS) roughness evaluated by atomic force microscopy (AFM) for a scan area of 3×3 μm^2 from five samples was (2.1 ± 0.3) nm and (2.6 ± 0.6) nm for bare planar glass and unsized glass fiber, respectively. The RMS roughness for plasma polymer films deposited on a planar glass substrate ranged from 2.7–3.8 nm for different oxygen fractions.

2.2. Plasma polymerization

Plasma polymer films from tetravinylsilane in a mixture with oxygen gas (oxygen fraction 0–0.71), marked as pp.-TVS/O_2 films, were deposited on planar glass substrates and single glass fibers (GF) using an RF (13.56 MHz) helical coupling system [14] operated in a pulsed regime. This system uses plasma-enhanced chemical vapor deposition (PECVD) employing non-thermal plasmas. The cylindrical discharge is axially symmetrical. The planar or fibrous substrates are mounted in the axis of discharge.

First, the deposition system is evacuated to a basic pressure of $<1 \times 10^{-3}$ Pa. Then, the planar or fibrous substrates are pretreated with oxygen plasma (5 sccm, 4 Pa, 25 W) for 10 min to clean adsorbed gases from the surface and to ensure reproducible adhesion of plasma polymer films. Tetravinylsilane and oxygen molecules are activated and fragmented during the plasma process [15,16], producing free radicals, electrons, and ions; the highly reactive radicals recombine at the substrate surface to form a thin film. The pp.-TVS/O_2 film is deposited under constant deposition conditions using the selected oxygen fraction, a total flow rate (TVS + O_2) of 0.55 sccm at a process pressure of 1.4 Pa, and an effective power of 2.5 W. The oxygen fraction O_2/(TVS + O_2) in the gas mixture is varied from 0 (pure TVS monomer) to 0.71 as follows: 0, 0.10, 0.21, 0.33, 0.46, and 0.71. Finally, after film deposition, the apparatus is flushed with argon gas (10 sccm, 10 Pa) for 12 h to remove the remaining working gases. Subsequently, the chamber is flooded with air to atmospheric pressure and the specimen is used for characterization.

2.3. Thin film analyses

A phase-modulated spectroscopic ellipsometer UVISEL (HORIBA Scientific) was employed to determine the film thickness for plasma polymers deposited on planar substrates. The measurement range was 250–830 nm with a step of 2 nm; the angle of incidence was 70° and the spot size was 100×300 μm^2; the integration time was set at 200 ms. Measured data were analyzed using the DeltaPsi 2 software. The deposition rate was calculated as the ratio between the film thickness and deposition time. All deposited films used for the nanoscratch test had a thickness of (0.10 ± 0.01) μm. In the case of the fibrous substrate, a single GF is positioned along the axis of cylindrical discharge using a glass frame. Plasma density around the fiber is identical resulting in the deposition of a uniform and homogeneous coating around the fiber [9]. The thickness of the plasma polymer films deposited on a single GF is controlled by deposition time at a known deposition rate, which is constant during deposition. Using a scalpel, the plasma-coated GF was cut into small pieces 5 mm long. Each piece of fiber was positioned on a polished silicon wafer using a special tool, the Micro TouchPick Pen (S. T. Japan-Europe GmbH). No adhesive material was used to fix the fiber to the wafer.

Nanoscale mechanical (Young's modulus) and tribological (adhesion) properties of the pp.-TVS/O_2 films were investigated using a 2D TriboScope (Hysitron) attached to an NTegra Prima Scanning Probe Microscope (NT-MDT). The force and displacement accuracy was 100 nN and 0.2 nm, respectively. Measurements were carried out at 22 °C under ambient conditions. The pp-TVS/O_2 films of thickness (1.0 ± 0.1) μm deposited on polished silicon wafers were used for nanoindentation measurements. The Young's modulus was determined from unload-displacement curves (Berkovich indenter, radius 50 nm) using the Oliver-Pharr method [17].

A conical, 90°, diamond indenter (Hysitron) with a tip radius of 1 μm was used to make scratches on plasma polymer films with a thickness of (0.10 ± 0.01) μm deposited on planar and fibrous substrates under normal loading, which linearly increased with time from 1 μN to 3 mN. The scratch length was 10 μm and was reached in 30 s. Ten tracks were made on each planar sample with a displacement of 10 μm between each track; five tracks were made on each of two fibrous samples along the fiber axis successively at the top of the curved surface. The normal and lateral forces were measured simultaneously together with the normal and lateral displacements. The surface topography of the scratches (scratch pattern) was characterized by AFM in semicontact (tapping) mode under ambient conditions, using silicon probes NSG03 (radius < 10 nm, NT-MDT) with a resonant frequency of 90 kHz and a force constant of 1.1 N m^{-1}.

3. Results and discussion

Six samples of thin films were deposited on planar glass substrates, varying the oxygen fraction from 0 to 0.71 in the TVS/O_2 mixture at an effective power of 2.5 W. In our previous studies, we found that if pure TVS monomer is used, the deposited material consists primarily of a carbon network with incorporated *Si*—C bonding species and side vinyl groups [15]. However, if the oxygen fraction increases, the oxygen atoms are incorporated partly into the plasma polymer network, forming Si-O-C, Si-O-Si, and C-O-C bonding species and partly forming side hydroxyl and carbonyl groups. The oxygen concentration in the plasma polymer films increased from 0 to 18 at.% as a result of the oxygen fraction enhancement from 0 to 0.71 [16]. The critical load corresponding to the first delamination of the film, which is based on an abrupt decrease in the lateral force, was used to measure the film adhesion using the nanoscratch test. The mean value and its standard deviation were calculated from ten scratches on one sample. Changing the lateral position of the scratch area within a planar sample, the mean value of the critical load was found to be position independent, evidencing uniform adhesion of the deposited film. Deposition of a sample prepared from pure TVS was repeated to demonstrate good reproducibility of the technique, as the mean critical loads from both samples, (1.62 ± 0.07) mN for a film thickness of 93 nm and (1.61 ± 0.14) mN for a film thickness of 102 nm, were within the standard deviations. The critical load as a function of oxygen concentration in pp.-TVS/O_2 films is given in Fig. 1(a). A slight increase in oxygen to 5 at.% does not change the critical load. However, a further increase in oxygen concentration resulted in improved adhesion with a maximum at 10–13 at.%. Based on detailed chemical analysis [16], we can assume that the increase to the maximum is due to an increased concentration of *Si*-O-C/Si-O-Si bonding species at the film/glass interface as a result of the chemical reactions of the plasma species with hydroxyl groups on the glass surface. The