Thin Solid Films 656 (2018) 37–43

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Functional interlayers with controlled adhesion developed for polymer composites

Erik Palesch, Antonin Knob, Tomas Plichta, Vladimir Cech*

Institute of Materials Chemistry, Faculty of Chemistry, Brno University of Technology, Purkynova 118, CZ-612 00 Brno, Czech Republic

ARTICLE INFO

Keywords:
Plasma polymerization
Nanoscratch test
Adhesion
Interface
Interphase
Polymer-matrix composites

ABSTRACT

The plasma coating of glass fibers is an alternative technology to the wet chemical processes employed for the commercial sizing used for glass-fiber-reinforced polymer composites. A polymer-like film prepared by plasma polymerization can be used as a compatible interlayer between the glass fiber and the polymer matrix. The shear stress distribution across the interphase in a fiber-reinforced polymer composite indicates that the interfacial adhesion at the interlayer/fiber interface is the key factor influencing the performance of the polymer composite. The plasma-polymerized tetravinylsilane deposited at an enhanced effective power was tested as an adhesion film on planar glass substrate using a nanoscratch test. The work of adhesion was used as a measure of film adhesion based on the analysis of the scratch mechanics. An enhanced effective power (0.1–10 W) resulted in a film adhesion change only in the region of 30% for plasma-polymerized tetravinylsilane. The addition of oxygen gas to the tetravinylsilane monomer enabled the depositing of films over a wide range of film adhesions. A 3.7-fold increase in film adhesion was revealed for optimized deposition conditions. For a given film, a strong correlation was found between the shear strength of the polymer composite with glass fibers coated by plasma polymer film and the corresponding film adhesion on planar glass substrate determined using the nanoscratch test.

1. Introduction

The adhesion of the thin film to the substrate is one of the most important properties in determining the thin film's application possibilities. Thin films with controlled adhesion are essential as barrier, anti-scratch, wear- and abrasion-resistant, metal, biocompatible, transparent, and antireflective coatings for surface modified materials; as semiconductor and dielectric coatings for electronic, optical, and optoelectronic devices; or as compatible interlayers in hybrid macrostructures and nanostructures. Polymer-matrix composites reinforced by (nano)fibers or (nano)particles require a compatible material in the form of a thin film (interlayer) that is built in between the reinforcing fiber or particle, and the polymer matrix to improve stress transfer from the matrix to the reinforcement [1,2]. Therefore, all reinforcements must be coated with an appropriate interlayer to ensure they function effectively in polymer-matrix composites [3–6]. Glass reinforcements in unsaturated polyester (UP) resin dominate the world market for polymer composites. Glass-fiber (GF) reinforced polyester resin is a typical polymer composite.

The microindentation test [7,8] enables the evaluation of the interfacial adhesion between the fiber and the polymer matrix using a cross-section of a unidirectional, long-fiber-reinforced composite. The microindentation measurements are carried out on the individually selected fibers using a diamond indenter and by pushing the end of a single fiber in a longitudinal compression from the surrounding matrix. The interfacial shear strength (IFSS) is determined from the debond load in microindentation test [9]. The functional interlayer enables the shear stress between the fiber and the polymer matrix to decrease significantly when the polymer composite is under mechanical or thermal loading. The interlayer's Young's modulus and interfacial adhesion are responsible for the shear strength of the composite interphase [10], which includes the interlayer and both adjacent interfaces. The nonlinear finite element method (NLFEM) was employed to simulate the interfacial stress fields in a GF/polyester composite during microindentation measurements [11]; model details are included in Ref. 9. The shear stress distribution across the interphase at the locus of maximum interfacial shear stress for different indenter displacements (loadings) is given in Fig. 1. The 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, matrix, or fiber itself. We can estimate the shear yield strength of the isophthalic polyester resin to be about 45 MPa for a shear modulus of 1.5 GPa and a

* Corresponding author.
E-mail address: cech@fch.vut.cz (V. Cech).

https://doi.org/10.1016/j.tsf.2018.04.035
Received 3 October 2017; Received in revised form 9 April 2018; Accepted 23 April 2018
Available online 24 April 2018

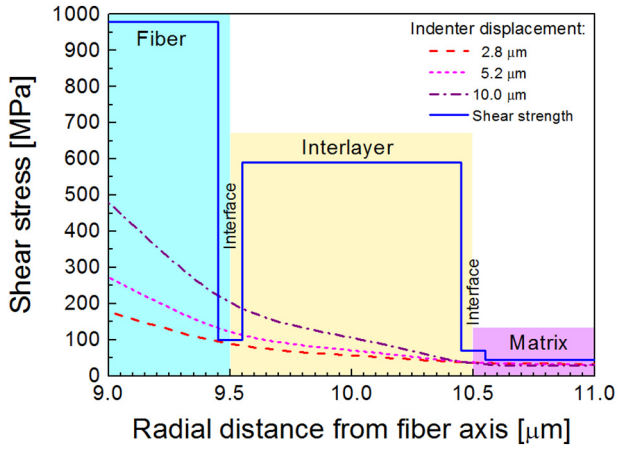

Fig. 1. The shear stress distribution across the interphase at the locus of maximum interfacial shear stress for different indenter displacements, an interlayer modulus of 10 GPa, and a 1 μm interlayer thickness, using model simulation (NLFEM) of the GF/polyester composite for microindentation test.

yield strain of 3% [12]. The shear strength of fiber-reinforced plastics (FRP) is not particularly good. This is because they (FRPs) are strongly dependent on the polymer matrix, which is weak in shear [13]. For the same reason, thermosetting or thermoplastic coatings are also unsuitable for use as functional interlayers for an FRP.

Plasma coatings fabricated by plasma-enhanced chemical vapor deposition (PECVD) are materials of viscoelastic or elastic-plastic behavior, and their Young's modulus can be varied across a wide range (10^0–10^2 GPa) by changing the deposition conditions [14]. The model simulation suggests that the interlayer should be polymer-like and not a stiff material [11]. A plasma polymer film with a Young's modulus below 25 GPa can be prepared at low powers using pulsed plasma (a form of PECVD). Such a material is a prospective interlayer due to having a relatively low modulus, but a sufficiently high shear yield strength of 590 MPa, corresponding to a shear modulus of 3.8 GPa and a yield strain of 16% [15]. The theoretical value of the shear yield strength for GF is about 980 MPa using a shear modulus of 28 GPa and a yield strain of 3.5% [2]. The shear yield strength for the GF, polyester resin, and the interlayer (plasma polymer film) with a thickness of 1 μm are schematically plotted in Fig. 1. As the shear stress distribution indicates (Fig. 1), the interfacial shear strength at the matrix/interlayer interface should be only slightly higher (e.g., 50–70 MPa) than the shear yield strength of the matrix. However, the interlayer/fiber interface has to be stronger as it corresponds to an increased shear stress at this interface and will be responsible for the shear failure of the composite interphase. If the shear strength at the interlayer/fiber interface is 100 MPa, as indicated in the example in Fig. 1, then the IFSS, determined by microindentation test, will have the same value. The model and experimental data indicates that the interfacial shear strength at the interlayer/fiber interface is the key factor influencing the mechanical response of the plasma-coated fibers in a GF/polyester composite under microindentation testing [11].

This study focuses on the development of low-modulus (< 25 GPa) plasma polymer films with controlled adhesion that will be useful as a functional interlayer in a GF/polyester composite with a controlled interphase. Plasma-polymerized tetravinylsilane (TVS), pure or in a mixture with oxygen gas, was used to deposit thin films on planar glass substrates under different effective powers. Film adhesion was characterized using a nanoscratch test [16] and correlated with the IFSS in a GF/polyester composite reinforced by GFs coated by the same plasma polymer film.

2. Material and methods

2.1. Materials

Microscope slides made from a special, improved, soda-lime float glass (1.0 × 26 × 76 mm^3; Knittel Glaeser, Germany; chemical composition: 72% SiO_2, 13% Na_2O, 9% CaO, 4% MgO [17]) and polished silicon wafers (100) (0.8 × 10 × 10 mm^3, ON Semiconductor, Czech Republic) covered with a 3 nm-native-SiO_2 layer were used as planar substrates. Argon gas (99.999%; Linde Gas, Czech Republic) was employed to clean the plasma reactor and vacuum chambers before and after the thin film deposition. The substrates were pretreated in a plasma reactor with oxygen plasma (oxygen gas 99.99%; Linde Gas, Czech Republic; 5 sccm, 4 Pa, 25 W, continuous wave) for 10 min to clean any adsorbed gases from the surface and to ensure the reproducible adhesion of plasma polymer films. TVS, liquid $Si(CH{=}CH_2)_4$ (purity 97%; Sigma Aldrich, Czech Republic), was the monomer used to deposit the plasma-polymerized tetravinylsilane (pp-TVS) and plasma-polymerized tetravinylsilane/oxygen gas (pp-TVS/O_2) films.

2.2. Plasma polymerization technique

The plasma polymer films were prepared by PECVD, employing an radiofrequency (RF) helical coupling system [18], using a pulsed regime. The basic pressure in the plasma system was $< 1 \times 10^{-3}$ Pa. Plasma polymerization means that the TVS and oxygen molecules in a gaseous state are activated and fragmented during the plasma process [19,20], producing free radicals, electrons, and ions; the highly reactive radicals recombine at the surface of the growing film.

The oxygen-plasma pretreated substrate was stored in an evacuated load lock to avoid its contamination before the film deposition, and the plasma reactor was cleaned for 10 min using an argon discharge (10 sccm, 10 Pa, 25 W, continuous wave) to remove the remaining oxygen gas. The residual gases in the plasma reactor were checked using a process gas analyzer (HPR-30, Hiden Analytical). Using a linear driver, the pretreated substrate was placed into the plasma reactor after the deposition conditions had been set up and the plasma had reached a steady state that was characterized by a constant process pressure. The effective powers used for the deposition of the pp-TVS films from pure TVS were 0.1, 0.5, 2.5, 5.0, and 10 W. The pp-TVS and pp-TVS/O_2 films were deposited at a total flow rate (TVS + O_2) of 0.55 sccm, and a corresponding pressure of 1.4 Pa. The oxygen fractions O_2/(TVS + O_2) in the gas mixture were 0.00 (pure TVS), 0.10, 0.21, 0.33, 0.46, and 0.71. The pp-TVS/O_2 films were deposited at effective powers of 2.5 and 5.0 W. The plasma reactor was flushed with argon gas (10 sccm, 10 Pa) for 12 h to remove the remaining working gases after the film deposition. Subsequently, the reactor was flooded with air to atmospheric pressure and the specimen was used for characterization. The mean deposition rate, given by the ratio of film thickness to deposition time, was in the range from 11 to 200 nm/min, depending on the effective power and the oxygen fraction.

2.3. Thin film characterization

The nanoscale tribological (adhesion) and mechanical (Young's modulus) properties of the plasma polymer films were investigated using a 2D TriboScope (Hysitron) attached to an NTegra Prima Scanning Probe Microscope (NT-MDT). The force and displacement accuracy were 100 nN and 0.2 nm, respectively. The measurements were carried out at 22 °C under ambient conditions.

A scratch test consists of drawing a diamond indenter over a film under increasing normal loads. The value of the load at which adhesion failure is detected, as evidenced by an abrupt decrease in the lateral force [21], is known as the critical load, which is used as a measure of film adhesion; experimental details and data of the scratch test are