The glass fiber–polymer matrix interface/interphase characterized by nanoscale imaging techniques

V. Cech a,⇑, E. Palesch a, J. Lukes b

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

b Department of Mechanics, Biomechanics and Mechatronics, Czech Technical University, Technicka 4, CZ-166 07 Prague 6, Czech Republic

A R T I C L E   I N F O

Article history:
Received 11 December 2012
Received in revised form 5 March 2013
Accepted 11 April 2013
Available online 26 April 2013

Keywords:
A. Glass fiber
B. Polymer–matrix composites (PMCs)
C. Interface
D. Interphase
E. Atomic force microscopy (AFM)

A B S T R A C T

Atomic force microscopy (surface topography, phase imaging, lateral forces), atomic force acoustic microscopy, and dynamic mechanical analysis (modulus mapping) were used to characterize the interphase region in unsized, industrially sized, and plasma coated glass fibers (GF) in GF/polyester composite. The nanoscale imaging techniques revealed the sharp changes in mechanical properties within 0.1 µm of the interlayer/fiber and matrix/interlayer interfaces for plasma polymer coated fibers, or at the matrix/fiber interface in the case of unsized fibers. A region of modified matrix with a thickness of 0.5 µm was determined near the fiber surface in the case of industrially sized fibers.

1. Introduction

The interphase is a three-dimensional region between the bulk fiber and bulk matrix according to Drzal’s conception [1]. It includes not only the two-dimensional (2D) area of contact (interface) between the fiber and the matrix, but also a region of some finite thickness extending on both sides of the interface in both the fiber and matrix. A schematic illustration of the composite interphase is given in Fig. 1 (adapted from Ref. [1]) with a cross-section of fiber–reinforced composite (left) and a detail of the region at the fiber surface (right). The interphase comprises the functional interlayer and the part of the matrix affected by the presence of the coated fiber. The coated interlayer should improve compatibility between the fiber and the matrix by forming a strong but tough link between both phases [2]. We can distinguish three interfaces in the region, i.e., three 2D contact areas, between the composite phases. It is well known that the composite interphase control the mechanical properties of a composite [1]. Details on interface/interphase properties in polymer–matrix composites and their characterization were discussed by Kim and Mai–[2,3] Jesson and Watts in the recent review [4].

Many attempts have been made to reveal the interphase region in specific composite systems and evaluate its thickness, and determined interphase thicknesses varied depending on the technique employed for evaluation. Ikuta et al. [5] investigated the interphase region in a glass fiber (GF) reinforced vinylester composite system using microscopic FTIR spectroscopy. Scanning the region while recording spectra, which were compared with that of the bulk vinylester resin, they evaluated the interphase thickness as 80 µm. The interface region in GF/polymer composites was investigated using nanoindentation and nanoscratch techniques, which seemed to be more efficient and sensitive for such investigations [6]. The nanoindentation measurements revealed an interphase thickness of 2 µm for GF/polyester and 6 µm for GF/phenolic composite systems. The interphase thickness was evaluated as the thickness of the transition zone, where the matrix hardness increased and the friction coefficient decreased close to the fiber surface. Kim et al. [7] used nanoindentation, nanoscratch, and thermal capacity jump measurements for fine investigation of the interphase region in GF/vinylester composites. They found that the measured interphase thickness varied between 0.8 and 1.5 µm depending on the type and concentration of silane coupling. The trend of decreasing interphase thicknesses determined by increasingly precise techniques is evident. The greater resolution of current analytic techniques enables to characterize the interphase region at nanoscale. However, the resolution of nanoscale imaging techniques still has limits due to measurement artifacts as discussed by Young et al. [8].

In the current study, atomic force microscopy (AFM), atomic force acoustic microscopy (AFAM), and dynamic mechanical analysis (nanoDMA) were used for mapping of the surface topography, phase shift, lateral forces, AFAM signal, and viscoelastic properties of a cross-section of fiber–reinforced composite. These techniques
were employed to characterize the interphase region and distinguish the interfaces of unsized, industrially sized, and plasma polymer coated glass fibers in GF/polyester composite. We tried to identify if the interface is sharp or diffusional as a sharp interface could be of critical importance for composite performance.

2. Experimental

Unsized and industrially sized glass fiber bundles (E-glass, 1200 tex, and mean diameter 19 μm) were supplied by Saint-Gobain Adfors CZ, Czech Republic. The unsized fibers were plasma polymer coated using tetravinylsilane, Si-(CH = CH2)4 (TVS, purity 97%, Sigma Aldrich) as the monomer. Plasma-polymerized tetravinylsilane films were prepared by plasma-enhanced chemical vapor deposition (PECVD) employing an RF helical coupling system [9], operated in a pulsed regime. The fibers were pretreated by O2 plasma (5 sccm, 4 Pa, 25 W) for 10 min to improve film adhesion. Plasma polymer film, from a few nanometers to 10 μm thick, was deposited on bundles of unsized glass fibers at an effective power of 2.5 W. Pulsed plasma was operated at a monomer flow rate of 0.80 sccm and a corresponding pressure of 1.3 Pa. The free radicals (plasma species) diffuse into the central part of the bundle, forming a thin film even on the surface of central fibers during the plasma polymer deposition. However, the deposition rate decreases radially into the fiber bundle due to a shadowing effect of the surrounding fibers; thus, the film coating on the central fibers is thinner than on the fibers at the bundle edge.

Unsized, industrially sized, and plasma polymer coated glass fibers were embedded in unsaturated polyester resin 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. 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. Using nanoscale imaging techniques, we investigated the fiber–polymer matrix interface/interphase of a polished cross-section of composite samples.

The surface characteristics of the samples were observed using an NTegra Prima Scanning Probe Microscope (SPM) (NT-MDT). Surface topography and phase imaging were measured in semicontact (tapping) mode, under ambient conditions, using silicon probes (NSG03 (Rc < 10 nm, NT-MDT) of resonant frequency 90 kHz and force constant 1.1 N m⁻¹). The polished cross-section of composite samples was also investigated in contact mode under a constant force, using lateral force (LF) and atomic force acoustic microscopy (AFAM) measurements. Silicon probes (CSC10 (Rc < 10 nm, NT-MDT) of resonant frequency 20 kHz and force constant 0.1 N m⁻¹) were used in this case.

A Hysitron TI 950 TribolIndenter nanomechanical test instrument with a nanoDMA III (Dynamic Mechanical Analysis) package was employed to assess the viscoelastic properties of the fiber–polymer matrix interface/interphase. The Modulus Mapping package combines the in situ SPM imaging capability of Hysitron’s nanomechanical testing instruments with the ability to perform nanoDMA III tests. During a test, the indenter is raster-scanned across the surface to image the topography of the sample. While scanning, the probe is oscillated sinusoidally with a specified frequency and load amplitude. The resulting signal from the transducer is then analyzed to determine the displacement amplitude and phase lag of the oscillation at each pixel in the image. The software plots these measurements in separate image files, and once the scan is completed, the images can be analyzed to determine the storage and loss modulus at each point. A Berkovich diamond indenter with a radius of curvature of about 100 nm (Rc) was used. A dynamic force amplitude of 5 μN at an oscillation frequency of 220 Hz was superimposed on the normal contact force of 15 μN to keep the dynamic displacement amplitude at 4 nm while scanning the interface surface in an in situ SPM regime.

3. Results and discussion

The polished cross-section of composite samples with unsized, industrially sized, and plasma polymer coated fibers was investigated using different AFM modes and modulus mapping to distinguish the composite phases and evaluate the interphase region on the basis of surface topography and/or the difference in mechanical properties of the phases.

The surface topography (Fig. 2a) and phase distribution (Fig. 2b) of the composite with plasma polymer coated fibers were measured simultaneously using semicontact mode. The interlayer (plasma polymer film) can be seen as a white annular ring surrounding the fiber (Fig. 2a). Both the interfaces between the interlayer and the fiber and between the matrix and the interlayer are evident. The surface topography clearly distinguishes the composite phases due to their different mechanical properties, influencing the shape of the polished cross-section. The Young’s modulus was 3.3 GPa and 60 GPa for polyester resin and the single glass fiber, respectively, as determined by tensile tests. The plasma polymer film deposited on planar glass substrate was characterized by static nanoindentation measurements; here the Young’s modulus was evaluated as 17 GPa. When scanning in the phase imaging mode, the tip of the oscillating probe periodically comes into contact with the sample surface. Its behavior is affected by the surface properties of the sample. This can affect both the oscillation amplitude and phase. If mechanical properties of the sample surface are inhomogeneous, some shift of the phase occurs. Thus, the phase shift distribution over the sample surface can characterize the distribution of mechanical properties, and could distinguish between stiffer (fiber) and more pliant (interlayer, matrix) phases. In the phase distribution image (Fig. 2b), a sharp interlayer/fiber interface and a less clear matrix/interlayer interface can be seen. The height (dashed line) and phase (solid line) profiles across the interphase region are given in Fig. 2c. The position of the profile is marked by a short white line in Fig. 2a and b. The height profile delimits the interlayer position, highlighted by dashed-and-dotted lines in Fig. 2c. The phase distribution at the matrix/interlayer interface is somewhat too noisy to clearly distinguish the interface, as the phase for the interlayer and matrix are similar. And at the interlayer/fiber interface there is a phase shift, likely due to a greater difference in Young’s modulus between the interlayer and the fiber. The phase shift is quite abrupt, occurring within a distance of 100 nm.

The composite phases could be distinguished on the basis of different frictional characteristics resulting from their different
mechanical properties. Therefore, lateral force microscopy, using contact mode AFM, was employed to investigate the cross-sectioned composite sample with plasma polymer coated fibers.

A feedback loop maintained a constant force on the sample by adjusting the height of the cantilever to compensate for topographical features of the surface, resulting in a surface topography image (Fig. 3a). Simultaneously, the torsion of the cantilever supporting
the probe depended on the frictional characteristics of the surface, resulting in the distribution of lateral forces given in Fig. 3b. In this case, a sharp matrix/interlayer interface and a less clear interlayer/fiber interface can be observed in the distribution of lateral forces. The height profile (dashed line) and the current profile (solid line), representing the lateral force, are plotted in Fig. 3c. The profiles across the interphase region correspond to the position marked (short white line) in Fig. 3a and b. We can see that the torsion of the cantilever changed sharply, within a distance of 80 nm, at the matrix/interlayer interface (marked by a dashed-and-dotted line) but changed only slightly at the interlayer/fiber interface (dashed-and-dotted line), which can be identified from the height profile in Fig. 3c. The frictional characteristics of the interlayer and fiber thus seem to be similar.

Atomic force acoustic microscopy is a combination of ultrasonics with atomic force microscopy, where the vibration behavior of the AFM cantilever in contact with the composite sample surface is sensitive to its local elastic properties [10]. In the AFAM arrangement, the composite sample is coupled to a piezoelectric transducer. The ultrasonic transducer emits longitudinal waves into the sample, which cause ultrasonic vibrations of the sample surface. These vibrations are transmitted via the tip into the cantilever and excite it to bending vibrations. The high-frequency vibrations are detected by a four-sectioned photodiode, as used for topogra-

Fig. 4. AFM images of cross-sectioned GF/polyester composite with unsized fibers using AFAM mode: (a) Surface topography; (b) Distribution of AFAM signal.

Fig. 5. Modulus mapping of cross-sectioned GF/polyester composite with plasma polymer coated fibers: (a) Distribution of storage modulus (the modulus scale is in GPa; the black line indicates the position of the modulus profile); (b) Height (dashed line) and storage modulus (solid line) profiles across the interphase region.

Fig. 6. Height (dashed line) and storage modulus (solid line) profiles across the interphase region using modulus mapping for cross-sectioned GF/polyester composite with unsized fibers.
Fig. 5. Adhesion of fiber to matrix can be characterized by surface topography and phase imaging mode. The composite phases can be distinguished by surface topography mode due to the specific shape of the polished cross-sectioned composite samples. The phase imaging mode was more suitable for characterization of the fiber/interlayer interface than the matrix/interlayer interface, likely due to a greater difference in the Young's modulus between the fiber and the interlayer. However, the lateral force mode was more suitable for characterizing the matrix/interlayer interface than the fiber/interlayer interface, probably due to a greater difference in the friction coefficient between the matrix and the interlayer. We can summarize all the nanoscale measurements and report that all the composite interfaces (interlayer/fiber and matrix/fiber in the case of unsized fibers) were relatively sharp with respect to a steep change in mechanical properties within a distance of 0.1 μm. Modulus mapping revealed a region of modified matrix with a thickness of 0.5 μm in the case of industrially sized fibers. Therefore, the interphase thickness in GF/polyester composites was determined by the interlayer thickness for plasma polymer coated fibers and by the thickness of the modified matrix for industrially sized fibers, with an accuracy of 0.1 μm. The sharp interfaces in multi-phase materials like composites and nanocomposites strongly influence their performance, and a more gradual interphase could increase their performance [11]. The plasmachemical technology (PECVD) is a perspective technique for construction of gradient interlayers required for novel conception of composites without interfaces [12]. Future nanoscale imaging techniques with increased resolution will give more detailed insight into composite interface/interphases.

4. Conclusion

The fiber–polymer matrix interface/interphase in GF/polyester composites with unsized, industrially sized, and plasma polymer coated fibers was characterized by surface topography, phase imaging, distribution of lateral forces, acoustic imaging (AFAM), and distribution of storage modulus using AFM and nanoindentation (modulus mapping) measurements. The composite phases could be distinguished by surface topography mode due to the special shape of the polished cross-sectioned composite samples. The phase imaging mode was more suitable for characterization of the fiber/interlayer interface than the matrix/interlayer interface, likely due to a greater difference in the Young's modulus between the fiber and the interlayer. However, the lateral force mode was more suitable for characterizing the matrix/interlayer interface than the fiber/interlayer interface, probably due to a greater difference in the friction coefficient between the matrix and the interlayer. We can summarize all the nanoscale measurements and report that all the composite interfaces (interlayer/fiber and matrix/fiber in the case of unsized fibers) were relatively sharp with respect to a steep change in mechanical properties within a distance of 0.1 μm. Modulus mapping revealed a region of modified matrix with a thickness of 0.5 μm in the case of industrially sized fibers. Therefore, the interphase thickness in GF/polyester composites was determined by the interlayer thickness for plasma polymer coated fibers and by the thickness of the modified matrix for industrially sized fibers, with an accuracy of 0.1 μm. The sharp interfaces in multi-phase materials like composites and nanocomposites strongly influence their performance, and a more gradual interphase could increase their performance [11]. The plasmachemical technology (PECVD) is a perspective technique for construction of gradient interlayers required for novel conception of composites without interfaces [12]. Future nanoscale imaging techniques with increased resolution will give more detailed insight into composite interface/interphases.

Acknowledgements

This work was supported in part by the Czech Science Foundation, Grant Nos. P106/11/0738 and P205/12/J058, and the Technology Agency of the Czech Republic, Grant No. TA01010796. The authors would like to thank Brian Rook (Composite Materials and Structures Center, Michigan State University, MI) for his kind help with sample polishing and Dr. Miroslav Sirovy and Saint-Gobain Adfors CZ s.r.o. for providing glass fibers.

References