Mechanical characterization of polymer-based composite materials at micro- and nanoscale using AFM

Eduard S. Batyrshin, Yuriy S. Zamula, Svyatoslav S. Chugunov, Ivan V. Sergeichev, Iskander S. Akhatov
batyrshine@mail.ru

Abstract

The mechanical characterization of fiber-reinforced polymer composites at micro- and nanoscale is an essential experimental approach for the development of multi-scale mechanical representation of macroscopic composite parts. The study of elastic moduli variation within fiber and matrix phases, as well as properties of the fiber-matrix interface, is of particular importance. In this paper, we present the results of studying of the mechanical properties of fiber-reinforced polymer composite materials, using atomic force microscopy (AFM) based force modulation technique. The force modulation AFM operates in a contact mode with the tested material surface. It uses low frequency excitation of the probe, exploiting the fact that the amplitude of excited probe oscillation is sensitive to the elasticity of the sample surface. As the result of composite material characterization with AFM technique, the surface elastic moduli was quantitatively mapped. We additionally studied the effect of AFM operating parameters and probe characteristics on the resulting maps.

1 Introduction

Fiber reinforced polymer composite materials are the key components in modern technological applications. Due to their low specific gravity, high mechanical strength and resistance to external impacts, they are being applied in aeronautics, automotive industry, energy applicaitons, and other industrial fields. Predicting behaviour of a part, made of composite material, under the action of a complex mechanical load is an important task. Despite the considerable progress achieved to the date in general understanding of deformation processes in composite materials, exact mechanisms affecting composite behavior at microscale have not been thoroughly studied yet. Destruction of the composite material, under the action of mechanical loads, is a complex multi-stage process [1] that involves destruction of the polymer matrix, fibers and matrix-fiber interface. Such multiphase nature of composite failure, indicates the importance of studying the mechanical properties of

composites at micro- and nanoscale, which corresponds to the typical spatial scale of fibers and the interface between the fibers and the matrix.
AFM based techniques provide solid advantage in studying mechanical properties of polymer composites at micro- and nanoscale. In particular, AFM implements a few variants of nanoindentation technique, which is direct and easy to interpret method for determining local elastic properties of the studied material. The well developed models of AFM tip contact mechanics help in estimation of effective Young modulus of the sample in the contact region of AFM tip and sample surface. For instance, sequential nanoindentation with AFM allows construction of 2D maps of elastic moduli over a selected region of interest. Despite the relative simplicity of the method, the construction of a two-dimensional map of the mechanical properties of the surface takes considerable time when traditional nanoindentation technique is utilized. AFM based force modulation methods of material characterization are more efficient than the traditional technique; additionally, they provide better spatial resolution [2, 3]. During the use of AFM force modulation mode, the scanning probe remains in permanent contact with the surface of the sample. The force that presses the tip of AFM probe to sample's surface has two components: the first component is represented with a small constant loading force which presses probe's tip into sample's surface for only a few nanometers, so that interaction between the probe and the material remains elastic; the second component is represented with harmonic osciallations (tens to hundreds of kHz) imposed on the constant loading force. As a result of the scaning procedure, the surface topography, the amplitude and the phase of the probe oscillations are recorded. These properties are correlated to mechanical properties of the studied material at the next steps of the analysis.

2 Experimental details

The samples of a glass fiber/epoxy unidirectional composite material were used in this work. The fiber glass roving contained approximately 800 elementary filaments with an average diameter of $10\mu m$ each. A bundle of roving threads was tightly packed into a polyurethane tube and impregnated with a compound, consisting of epoxy resin ED-20 and TETA hardener, taken at 10:1 mass ratio. The sample was polymerized at room temperature for 24 hours and heated in an oven for 4 hours at 60°C. The cured sample was fragmented by circular diamond saw in a direction perpendicular to the fibers. The obtained cylindrical samples, 3 mm high and 4 mm in diameter, were glued onto a 1.5cm$\times$1.5cm glass substrate with a hot melt adhesive. The samples were polished with sandpaper with a gradual decrease of grit size from 500 to 7000 grit. The grinding direction was altered by 90° after every change of grit. After the grinding, the sample surface was additionally polished with a suspension containing colloidal nano-silica particles, approximately 30 nm in size. Surface quality was controlled with an optical microscope. After polishing, the samples were cleaned in an ultrasonic bath for 5 minutes, washed with deionized water and dried at 60°C for 1 hour. Scanning of the samples was carried out on an atomic force microscope Agilent 5500AFM (Agilent, USA) using the force modulation mode (FMM). Three cantilevers with different force constants were used. The characteristics of the cantilevers are provided in Table 1. All tested AFM probe cantilevers

had diamond coated tips with radius R=100nm (according to manufacturers).

Table 1: Characteristics of AFM probes

#No.	Probe	Manufacturer	Force constant, N/m
1	HA_HR_DCP-B	NT-MDT, Russia	17
2	HA_HR_DCP-A	NT-MDT, Russia	34
3	HA_HR_DCP-A	TipsNano, Estonia	85

3 Results and discussions

The modulation of the force on AFM probe is performed with a piezo element (Fig.1a). The oscillations are transmitted to AFM probe through the probe holder, probe substrate, cantilever beam, and other components of AFM system. A signal proportional to the deflection of the cantilever $D(t)$ is recorded (Fig.1b) during AFM scanning. The tip deforms the surface of the sample and partially penetrates into it, to a depth of $\delta(t)$. If the tip deformation is neglected, the probe position, the cantilever deflection, and the indentation depth are interrelated $z(t) = D(t) + \delta(t)$. The AFM keeps constant drive of the piezo element during the scan, so that the alternating amplitude of the $z(t)$ is also constant. As a result, for stiffer sample areas, where the deformation of the material is relatively low, the FM amplitude $D(t)$ increases, and for softer areas of the surface the FM amplitude decreases. A 2D map of the oscillation amplitude of the cantilever implicitly characterizes the stiffness of the material over the entire scaned area.

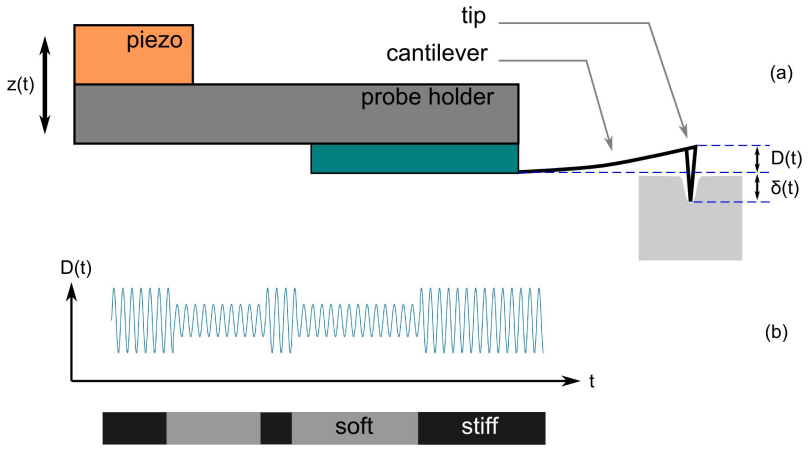
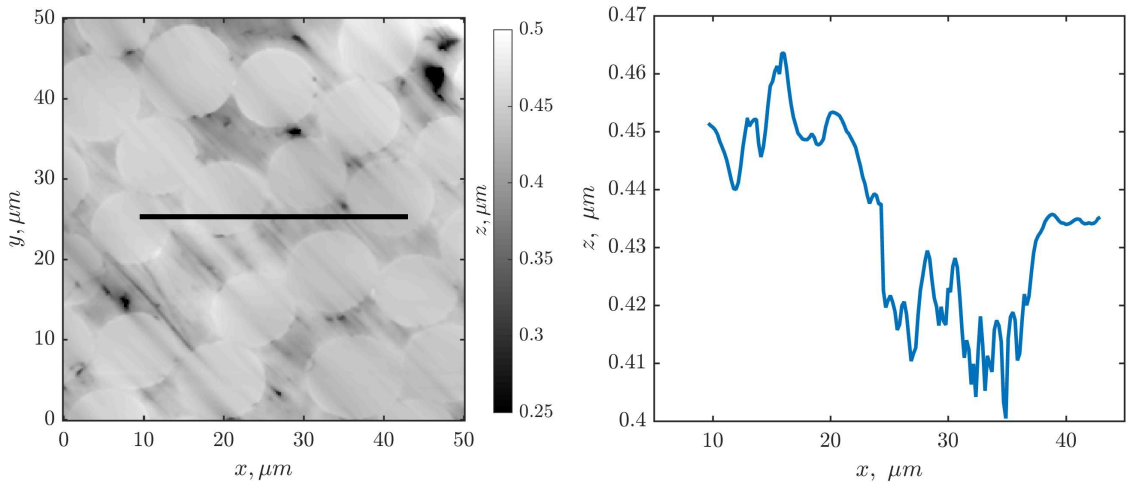


Figure 1: Schematics of force modulation mode (FMM) of AFM (a) and a typical profile of the signal obtained during FMM scanning (b)

It should be noted that, in addition to the contact of AFM probe and sample surface, AFM system contains a number of other mechanical contacts (AFM probe to probe holder, etc.) that affect the response of the system. To minimize this effect, the scanning frequency is selected far from the resonant peaks of the system; in this study, it was set at 60kHz, 85kHz and 20kHz for cantilevers #1, #2 and #3,

respectively. The amplitude of the piezo element oscillation is determined by the amplitude of the voltage U_{piezo}., applied to the piezo element. With each cantilever, the sample surface was scanned at $U_{piezo} = 1$, 2 and 4 V_{pp}.
Typical results of material characterization with AFM are shown in Fig.2. On the image of topography (Fig.2a) there can be clearly seen some scratches, which result from mechanical polishing of sample surface, and defects of epoxy matrix (dark areas), which, apparently, are the voids formed during fabrication of the sample. The fiber surface, although not everywhere, is located somewhat higher than the surface of the polymer matrix - by tens of nanometers (Fig.2b) - which is also a result of mechanical polishing of sample surface. During polishing operations, softer materials, such as epoxy, are removed in excess to harder materials, such as glass fibers. The height difference between the highest and the lowest point at the studied sample surface, not accounting for voids, is less than 100 nm.

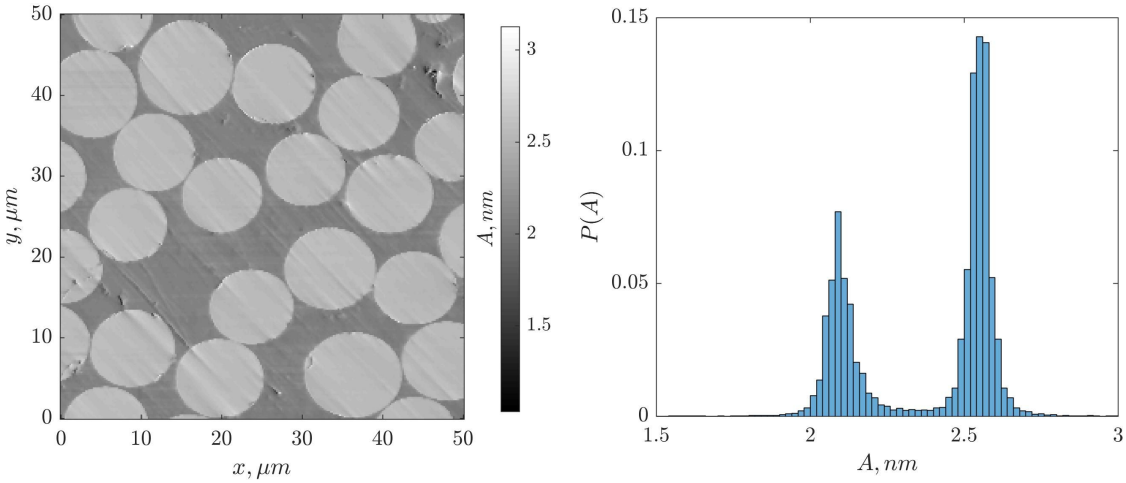


(a) (b)

Figure 2: AFM image of the surface topography (a) and a surface profile along a dark line (b) (probe #2, $U_{piezo} = 2$ V_{pp})

The two-dimensional map of the amplitude of the cantilever oscillations (Fig.3a) shows correlation between stiffness of the surface and FM amplitude level - on glass fibers, that are stiffer than the epoxy matrix, FM amplitude increases. The histogram of the FM amplitude values (Fig.3b), collected over the scanned area, clearly demonstrates two narrow peaks corresponding to the fibers and the matrix. The analysis of FM amplitude and FM phase maps results in quantitative estimates of viscoelastic parameters of the sample [4, 5].
The elasticity map is constructed from FM amplitude values, using a technique based on results of [6, 7]. The main assumption is based on the fact that the typical values of YoungвЂ™s modulus for epoxy resins (several GPa) are significantly smaller than those for glass fibers (70 GPa). Hence, the deformation of the glass fibers during contact with the AFM tip can be neglected. In this case, an analytical expression that relates the stiffness of the tip-matrix contact to the values of FM amplitude of glass fibers and epoxy matrix can be obtained:

$$k_m = \frac{k_c}{< A_f > /A_m - 1}, \tag{1}$$



(a) (b)

Figure 3: A 2D map of the FM Amplitude (a) and a histogram of FM Amplitude values collected from map (b) (probe #2, $U_{piezo} = 2\ V_{pp}$)

here $< A_f >$ is the average FM amplitude over the fibers surface, A_m is the FM amplitude over the polymer matrix. Alternatively, the contact stiffness can be calculated in the framework of the Hertz contact mechanics [6, 8], with the correction for adhesion force, that provides the following relation:

$$k_m = 6^{1/3} E^{*2/3} R^{1/3} (F_0 + F_{ad})^{1/3}, \tag{2}$$

where R is the tip radius, F_0 is the constant component of the indentation force (set point), F_ad is the adhesion force, E^* is the reduced Young's modulus of the epoxy matrix, which can be expressed as $E^* = E_m/(1-\nu_m^2)$ if the tip deformation is negligible. E_m and ν_m are the Young's modulus and the Poisson's ratio of the matrix. The constant force F_0 is a predefined scanning parameter, and F_{ad} was determined from the standard AFM force-distance curves. The values of the tip radius used for calculations is R=100nm. The relations (1) and (2) are employed to calculate the elasticity modulus of the epoxy matrix of the samples.
Elasticity map is obtained using AFM probes characterized with different force constants; there are three different driving voltages used for piezo element $U_{piezo} = 1V_{pp}$, $2V_{pp}$ and $4V_{pp}$. Figure 4a shows the map of the effective modulus of elasticity of the epoxy matrix. Due to the assumption of abscence of fiber deformation, the fiber part remain uncomputed in the map. The histogram of the modulus of elasticity (Fig.4b) shows the average value of $E^* \approx 5$GPa which is typical for epoxy resins [9]. Considering influence of piezo element driving voltage and cantilever stiffness on the estimation of elastic modulus (Fig.5), the estimates obtained for probes #1 and #2 provide quite high values. There may be several reasons for this, including variations of the true radius of AFM tip, degradation of the tip during the scan, irregularity of amplitude-frequency response of the measuring mechanical system (Fig.1), which contains a lot of peaks of resonant frequencies. Under such circumstances, selecting a scanning frequency far from the resonant peaks of the system does not guarantee a constant amplitude of the probe during the scan. Thus, quantitative estimates of the elastic moduli should be done with care. The estimates of elastic moduli,

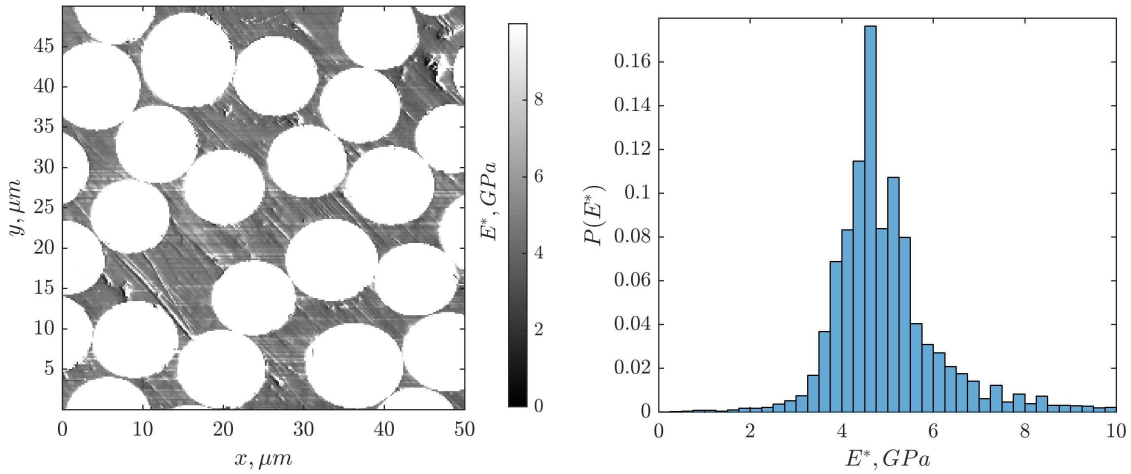


Figure 4: Map of the effective modulus of elasticity of the epoxy matrix (a) and the histogram of these data(b) (probe #2, $U_{piezo} = 2\ V_{pp}$)

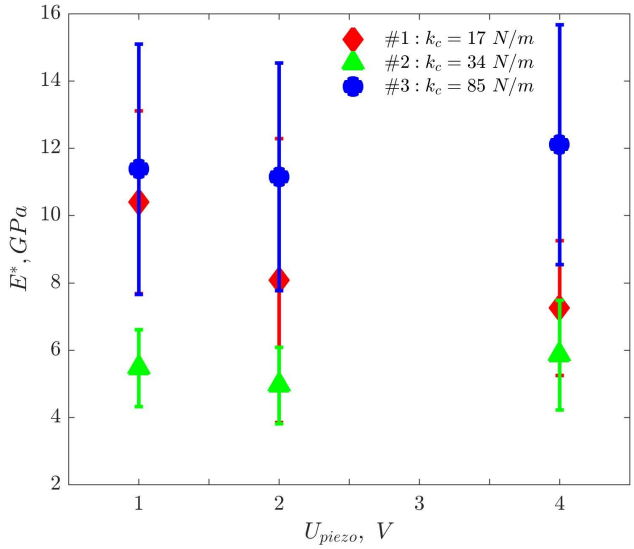


Figure 5: Effective Young's modulus of the epoxy matrix estimations obtained using various AFM probes and piezo driving voltage

obtained with stiffer probes #2 and #3, remain unchanged when the driving voltage of piezo element, U_{piezo}, changes. In the case of softer probe #1, the estimation of E^* decreases with increase of modulation amplitude. The use of stiffer cantilevers increases stability of the obtained results.

Despite the described difficulties, the AFM force modulation technique can be very efficient in the study of relative changes in surface elasticity, in characterizing the degree of polymer matrix spatial homogeneity, in detecting the change of elasticity under the action of external forces, and in studies of the properties of the fiber-matrix interface.

4 Conclusions

The application of AFM in the force modulation mode for characterizing mechanical properties of materials at micro and nano scales is demonstrated. The AFM offers several scanning modes for evaluating elastic moduli of a material. The force modulation approach seems to be better suitable for studying elastic moduli of the material, than traditional nanoindentation approaches. The use of AFM probes with a stiffer cantilever beam increases stability of the obtained signal and eads to overally better results. The applied method of AFM-based nanoindentation allows 2D mapping of surface elasticity, even in the case of multicomponent materials, where mechanical properties of components differ by orders of magnitude. This method, owing to the high accuracy (up to nanometers) of AFM probe positioning and to the high contrast of the resulting image, is an excellent tool for investigating mechanical characteristics of thin elements of the material, including sample matrix and reinforcing fibers.

Acknowledgements

This work was supported by Skoltech Partnership Program

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Eduard S. Batyrshin, Bashkir State University, Zaki Validi Street 32, 450076 Ufa, Russia
Yuriy S. Zamula, Bashkir State University, Zaki Validi Street 32, 450076 Ufa, Russia
Svyatoslav S. Chugunov, Skolkovo Institute of Science and Technology, Nobel Street 3, 143026 Moscow, Russia
Ivan V. Sergeichev, Skolkovo Institute of Science and Technology, Nobel Street 3, 143026 Moscow, Russia
Iskander S. Akhatov, Skolkovo Institute of Science and Technology, Nobel Street 3, 143026 Moscow, Russia