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Application of phase imaging and force modulation mode for description of dispersion of carbon nanotubes in polyol matrix

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Application of the phase imaging and force modulation SPM techniques for description of the dispersion of multiwalled carbon nanotubes (MWCNTs) in polyol (polyester diol- PED) matrix is presented. The MWCNTs-PED mixture is used to prepare polyurethane (PUR) nanocomposites. Dispersion of MWCNTs in PUR depends on the dispersion of carbon nanotubes in polyol. It is very important to evaluate the degree of homogeneity of the investigated materials. The phase imaging and force modulation microscopy connected with tapping mode allow collecting not only topography images but also images of mechanical properties of a material (hardness, adhesion, friction). By using these SPM modes, it is possible to distinguish structural elements of the mixture and hence to obtain direct information about the distribution of MWCNTs in PED matrix.

Key words: *AFM; phase imaging; force modulation; composite*

1. Introduction

Dynamic scanning probe microscopy (DSPM) includes techniques such as intermittent contact (IC) and non contact (NC) atomic force microscopy (AFM) modes in which an external source causes a cantilever oscillation [1]. Intermittent contact AFM (called also tapping mode – TM) works in a similar way as NC AFM with exception that the cantilever oscillates in relatively large amplitude, 10–100 nm. This results in a short-time contact of the tip with the sample surface during each cycle of the oscillation [2]. In a tapping mode, a stiff cantilever is set to oscillate near or at its resonant

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frequency, with an amplitude A_0 (called a free oscillation amplitude) before a tip is brought in contact with the sample surface. As the tip is brought close to the sample surface, the characteristics of the cantilever vibration (amplitude, resonance frequency, phase angle of vibration) change due to tip-sample interaction [3, 4]. Important experimental parameter of TM is the set-point r, defined as

$$r = \frac{A_{sp}}{A_0}$$

where A_0 is the cantilever free oscillation amplitude, A_{sp} – set-point amplitude (cantilever oscillation amplitude during scanning) [2–5].

The oscillation amplitude during scanning, smaller than the free amplitude, is used as the feedback signal for the electronic controller [6]. The topographical contrast is generated by the vertical movement of the piezoelectric scanner which moves to maintain the set-point oscillation amplitude [6–8]. In TM SPM, a region of the surface of large amplitude damping is recorded as high in a topographic image and hence bright in a height image [4].

1.1. Phase imaging

In the tapping mode, material property variations can be additionally mapped by recording the phase lag (df) of the cantilever oscillation relative to the signal sent to the cantilever's piezoelectric driver (Fig. 1) [5, 7]. The phase image can be generated as a consequence of variations in properties of materials such as adhesion, friction, viscoelasticity [3, 5], hardness as well as a difference in electrical or magnetic properties

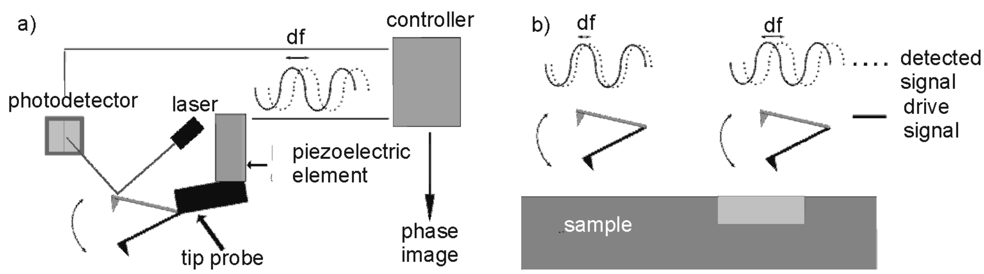


Fig. 1. Scheme of the phase imaging microscopy

[6, 8]. Under favourable conditions, the phase contrast imaging shows details of the surface roughness, which is not easily detected by topographical imaging [6]. Phase image (PI) is produced by monitoring the phase difference (df) between the oscillations of the cantilever and the standard signal, recorded by the piezoelectric element (Fig. 1) [6]. The phase contrast may not be generated if the surface is highly uniform [6]. It arises from variations in the composition of the sample surface as well as due to

variations in topography caused by changes in adhesion between the tip and specimen surface [6]. The phase contrast can be attributed to enhanced adhesion of the tip in a region of increased tip-surface contact area [6]. Due to a higher adhesion, the lateral forces on the tip increase. The effect is not only connected with the change of the chemical or mechanical material properties, as it could be related to nanoscopic topography that increases surface-tip contact area [6]. In the topographic contrast mode, small features of a rough surface are often hardly visible because the contrast of the image corresponds to variations in the topography. Image processing, e.g. highpass (edge detection filter), can normally enhance the resolution of an image which remains unsatisfactory anyway [6].

1.2. Force modulation microscopy

Another method of determining elastic and viscoelastic properties of surfaces is the force modulation microscopy (FMM) [9, 10]; local sample elasticity is measured by oscillating a probe in such a way that its tip slightly indents into a sample. It is an imaging mode derived from the contact mode (CM) AFM that measures relative elasticity/stiffness of surface features. It is commonly used to map the distribution of elements in composite systems [6, 8].

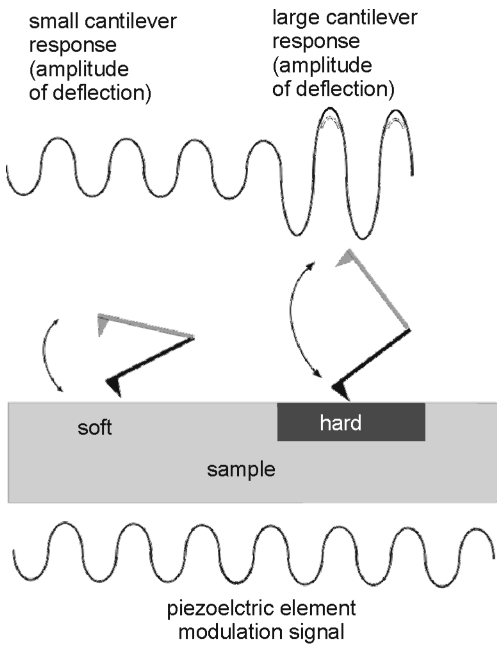


Fig. 2. Scheme of the force modulation microscopy

The measurement is performed in CM by applying an oscillation to the z-piezo and measuring the resulting cantilever amplitude (Fig. 2) [6]. Because of the periodic motion, a tip probe indents slightly into the sample during scanning across the surface.

The tip will be able to indent a soft material more easily than a harder material. The value of the cantilever deflection is inversely related to the value of indentation. In the case of an extremely soft material, the tip indents deeply into the surface, resulting in a very small deflection of the cantilever. A very hard sample allows less indentation, with the cantilever deflected by a larger value. The relative elasticity of the sample is measured by recording the amplitude of the tip deflection versus tip position over the sample [11]. When the tip encounters a hard site (dark area) surrounded by a soft medium, the hard material absorbs less energy of the cantilever, causing an increase in the cantilever response and signal amplitude. Softer sites absorb more cantilever energy, causing a reduced cantilever response and lower amplitudes, and these sites are recorded as light areas of the image [8].

2. Experimental

Materials studied were composites with PED matrix of poly(ethylene adipate) 2000 Da Alfaster T620 (Alfa Systems Poland) and multiwall carbon nanotubes (MWCNTs) obtained from Sun Nanotech Co Ltd, China. The diameter of a CNT was 10–30 nm, length 1–10 μm. Purity of the MWCNTs was over 90%. The mixture of MWCNTs and poly(ethylene adipate) was prepared by a two step process [12]. In the first stage, MWCNTs and acetone were mixed for 10 min using a mechanical stirrer. Afterwards carbon nanotubes with solvent were mixed in an ultrasonically assisted mixer VCX-750 (Sonics and Materials Inc.) at 50 °C in an ultrasonic bath under 40 kHz for 0.5 h. In the second stage, PED was added and the mixture was stirred under the same conditions as nanotubes with acetone. The MWCNT weight fraction was 0.05%. After the mixing process, acetone was evaporated.

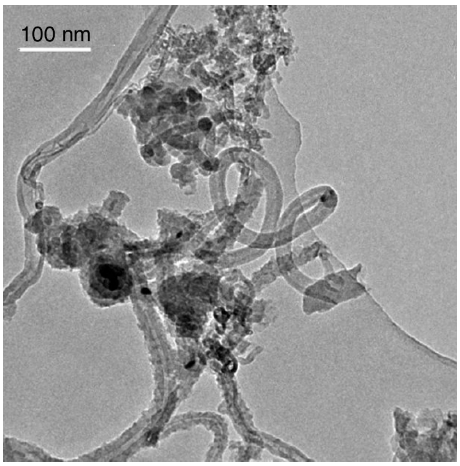


Fig. 3. TEM photograph of the carbon nanotubes

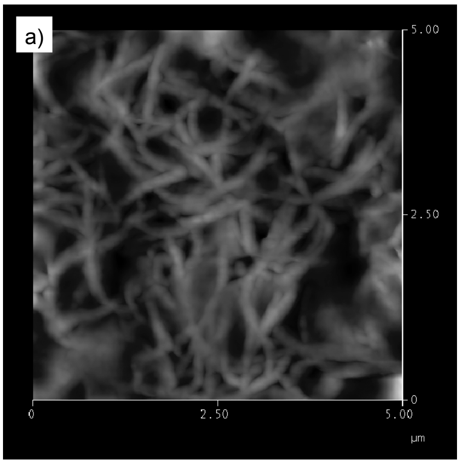
Measurements were performed using MultiMode SPM with NanoScope IIIa controller and Phase Extender Box, from Veeco Company. The microscope was equipped with a TS 150 dynamic vibration isolation system, and worked in the tapping mode with phase imaging and in the tapping mode with a force modulation mode. For the phase imaging, tip probes, model RTESP (Veeco), made of P doped (*n*) Si were used. Nominal parameters were the following: radius of curvature < 10 nm, rectangular cantilever with the length of 125 μm, width – 35 μm, resonant frequency 300 kHz, spring constant 40 N/m. In the case of the force modulation, tip probes, model LTESP (Veeco), made of (*n*) doped Si were used. Nominal parameters were the following: radius of curvature < 10 nm, rectangular cantilever with the length of 225 μm, width 38 μm, resonant frequency 190 kHz, spring constant 48 N/m. All experiments were performed under ambient conditions at room temperature.

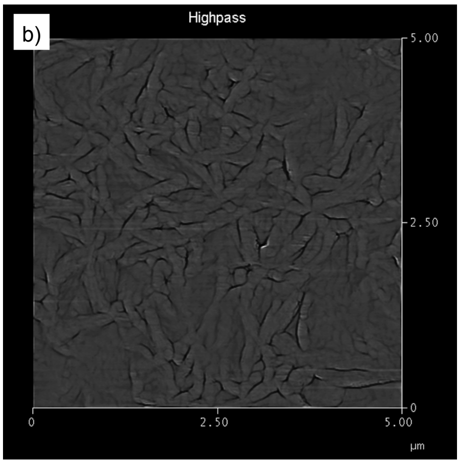
3. Results and discussion

3.1. Phase imaging

The phase imaging experiment was performed at a moderate tapping condition (set-point, $r = 0.6$) [2, 3]. This value of set-point was selected according to literature [2, 4, 5] because it was believed to provide the best phase contrast conditions, without the risk of contrast reversion [3–5] and damaging the sample surface [5]. In the case of moderate tapping, the cantilever behaviour is largely dominated by the indentation forces and hence tip-sample stiffness [3]. In the case of light tapping, the motion of the cantilever can be dominated by attractive forces and finally tip can be trapped on the sample surface [2, 3]. Hard tapping condition can make TM AFM more similar to force modulation microscopy [2, 3].

Figure 4a shows the topographic image (collected using the tapping mode) of the MWCNTs-polyol mixture after dimethylketone etching. Figure 4b is the topographic image after highpass filtering. Phase contrast image of the same area is shown in Fig. 4c. Highpass filtering replaces each data point in the image with the weighted difference between that data point and each of its eight neighbours. This filtering is useful in highlighting edges or areas with rapid changes of height in the image [13]. In the topographic image, long objects are visible with the average diameter of 180 nm covered with a droplet-like layer. The 180 nm diameter corresponds to the diameter of the bundle of nanotubes seen in the TEM photographs (Fig. 3). Slight differences may be due to the tip shape effect [8, 14] and thin polyol layer covering the nanotubes filler. Data processing (highpass filtering) allowed one to easily detect the edges of the filler and one can see that the filler was partly covered with the PED layer. The phase contrast image distinctly showed details hardly visible in topographic and processed images. From the phase image one could clearly recognize grain structure of the PED matrix and a droplet-like film of PED covered MWCNTs. This matrix grains and droplet-like structure could be an effect of chemical eching during the sample preparation. The results discussed above are clearly shown in Figs. 5a–c (magnified pictures of the right bottom corner of Figs. 4a–c, respectively). Furthermore, in Fig. 5c fibres are visible (indicated with white arrows) with diameters about 40 nm that is in very good agreement with the average diameter of single MWCNTs (shown in the TEM photograph, Fig. 3). These details are invisible in topographic, even filtered, images. For the set-point value of 0.6, the stiff (harder) region of the sample causes a positive phase shift [3, 5] because the carbon nanotubes were brighter in the phase contrast image (a tip probe is more sensitive to stiff nanotubes than to thin and relatively soft polyol layer covered nanotubes).





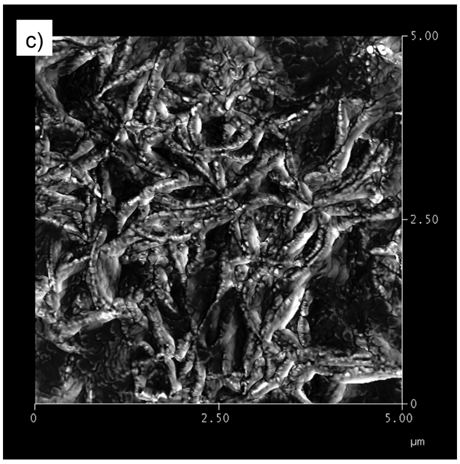
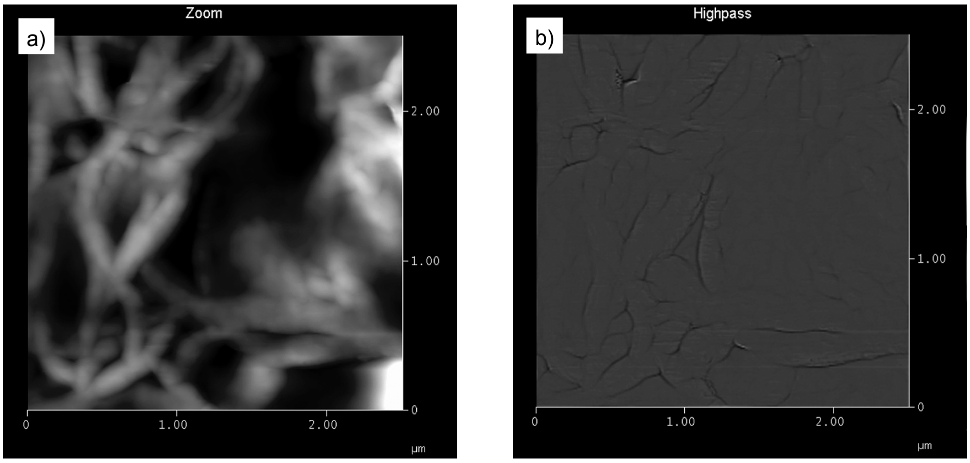


Fig. 4. Images of the MWCNTs-PED mixture: a) topographic (tapping mode) image (the vertical full grey scale is 300 nm), b) filtered (highpass) topographic image, c) phase contrast image (the vertical full grey scale is 700 nm)

Another effect visible in the phase contrast images is a difference in hydrophilicity. Hydrophilic elements of the structure cause positive phase shift (light parts of the image), and hydrophobic ones cause negative phase shift (darker parts) [4]. In this way, MWCNTs not covered with polyol droplets are visible in dark contrast (MWCNTs indicated with arrows in Fig. 5c).



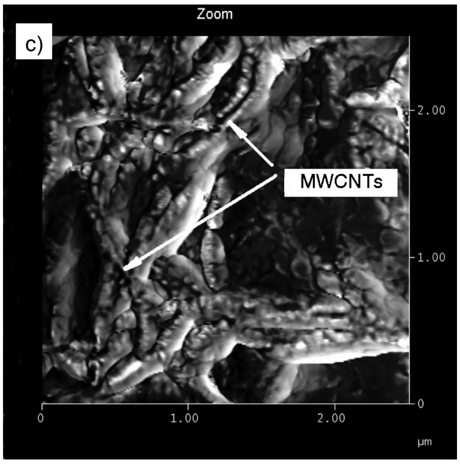


Fig. 5. Images of MWCNTs-PED mixture: a) topographic (tapping mode) image; magnification of the bottom right corner of Fig. 4a (the vertical full grey scale is 300 nm), b) filtered (highpass) topographic image; magnification of the bottom right corner of Fig. 4b, c) phase contrast image; magnification of the bottom right corner of Fig. 4b (the vertical full grey scale is 700 nm)

3.2. Force modulation microscopy

Figure 6 shows the topographic (collected in tapping mode), highpass processed topographic and force modulation images. In Figure 6a, large variations in topography can be seen. There were no clearly resolved structural elements of the MWCNTs-polyol mixture. Even image processing (highpass filtering, partly successful as discussed above) could not improve the quality of the image (Fig. 6b). Dark, long objects can be clearly distinguished (indicated with arrows) in Fig. 6c which is the force modulation image. In the case of the force modulation contrast, a dark contrast means that these objects are harder than the surrounding matrix. An average diameter of these elements was 170 nm which was in good agreement with the diameter of the bundle of nanotubes, as shown in TEM photographs. Objects of similar diameters were visible in phase images (described in Sect. 3.1). The diameter coincidence and high hardness indicate that the object shown in the force modulation image was the carbon nanotube filler. Using the force modulation microscopy, it is possible to distinguish in an easy way structural elements of the hybrid material even if there is no differences in sample topography.

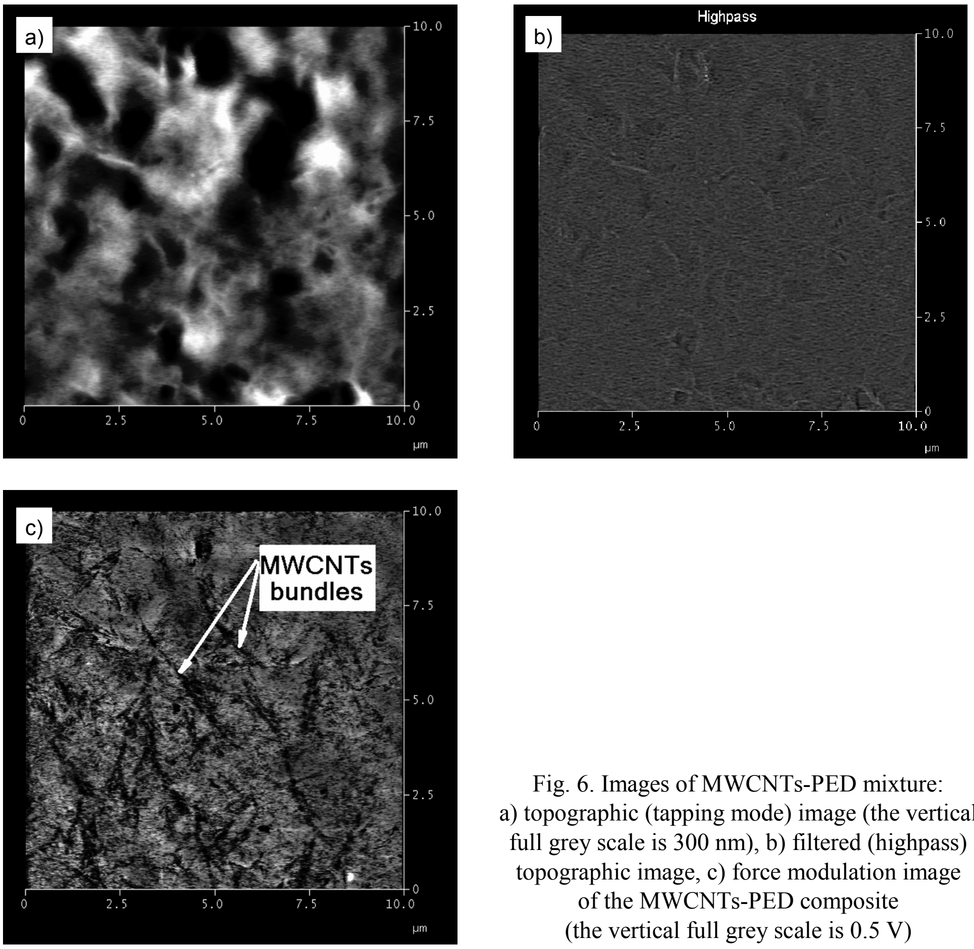


Fig. 6. Images of MWCNTs-PED mixture:
a) topographic (tapping mode) image (the vertical full grey scale is 300 nm), b) filtered (highpass) topographic image, c) force modulation image of the MWCNTs-PED composite (the vertical full grey scale is 0.5 V)

4. Concluding remarks

Phase imaging and force modulation microscopy in connection with the tapping mode allow simultaneous acquisition of both topographic and material properties of images. A phase contrast image is generated as a consequence of variations in properties of materials such as adhesion, friction viscoelasticity, hardness as well as local differences in electrical or magnetic properties. The force modulation microscopy can serve as a convenient method of investigation of elastic and viscoelastic properties of the material surface.

These SPM methods may be especially useful for imaging hybrid nanomaterials where it is possible to obtain not only a topographic contrast, but also the contrast between regions of different properties. This usefulness was proved by the case of the multiwalled carbon nanotubes (MWCNTs) in polyol (polyester diol) matrix. The above mentioned techniques allow one to distinguish structural elements of a composite material even if differences in sample topography are small or none. Moreover, using phase imaging it is possible to analyse very fine details of sample morphology. Thus a combined study of the topography and material properties leads to a better understanding of the material in question.

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