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Adhesion Forces on Polymer Hybrid Materials by Distant Dependent Measurement

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ABSTRACT

Atomic force microscope is an equipment of choice for studying materials in atomic and nonometric scale. This paper illustrates the procedure of adhesion measurement for polymer samples using atomic force microscope.

Quantitative measurements of mechanical properties are based on the relations between cantilever responses and tip–sample interaction. These mechanical properties like adhesion and elastic modulus are measured implementing Atomic Force Spectroscopy. Recording the static deflection of the cantilever as a function of piezoelectric element displacement, force-distance curves are plotted. Hook's law was used for converting the distances coming from the curves to force. It was necessary to calibrate the force constant of the cantilever to perform a precise force measurement.

Force-distance curves were obtained in ten different points on the surface of polymers and distance dependent measurement was conducted 10 times per each point by 1.1s interval. Adhesion force was then calculated in every single curve and the final data was the mean of one hundred different curves.

1 INTRODUCTION

Scanning probe microscope (SPM) is one of the newest branches in the field of microscopy. Atomic Force Microscope (AFM) is one of the most important members of the SPM family. The major advantage of AFM is that it can easily be used for studying different types of materials (such as metals, semiconductors, ceramics, minerals, polymers, and biomaterials) and these experiments can be conducted in various environments (ambient air, controlled atmosphere, under liquid or under vacuum conditions) according to Stegemann et al. (2007).

The surface is scanned by a tip usually made from silicon nitride. Its diameter is around 5-30 nanometers and it is attached to a bar shaped spring mainly named as cantilever. The cantilever's length is usually in the order of 100-200 microns (Zolfaghari et al., 2004). The force between the tip and the surface is measured by sensing the cantilever deflection. A topographic image of the surface is obtained by plotting the deflection as a function of the *x-y* position (Bhushan, 2004). Employing laser beam is one of common ways of detecting the deflection of the cantilever (Figure.1). This deflection is monitored by measuring the displacement of the laser beam with a position-sensitive photodiode detector while the sample is scanned in the xy plane (Zolfaghari et al., 2004).

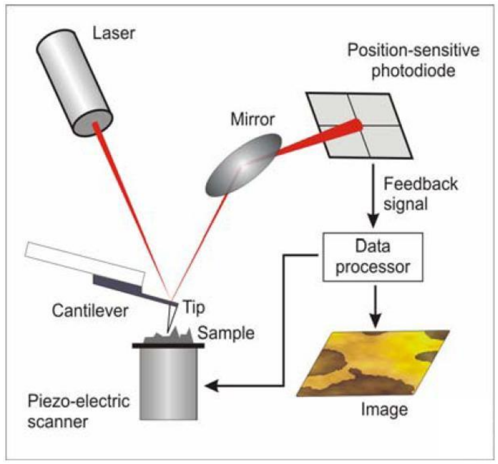

Figure 1: Principal setup of the AFM **(**Stegemann et al., 2007)

It is also possible to measure forces in nanometer range by AFM. These small forces are the result of interaction between the surface of the sample and the tip of the cantilever (Safanama et al., 2009). Measuring these small forces are based on Force-distance curves, which are the direct results of approaching and retracting of the cantilever to and from the surface of the sample, are plotted by Atomic Force Spectroscopy (AFS). AFS is one of the working modes of AFM that is typically utilized for the analysis of these interaction forces (Owen, 2004, Shadloo et al., 2009). The cantilever approaches the surface as the attractive forces overcome its spring constant. By the time the cantilever comes to contact with the surface, repulsive forces overwhelm and make the cantilever to retract from the surface (Sader, 2008). The quantity the forces, the interaction force can be measured by multiplying the force constant of the cantilever by the distance between the cantilever and the surface, horizontal axis of the force-distance curves, based on the Hook's law (Owen, 2004).

According to the Hook's law, for precise measurement of the force, the force constant of the cantilever must be calibrated. There are several calibration methods like geometry of the cantilever [4], reference cantilever (Sader, 2008), added mass and thermal noise (Leite et al., 2005). Figure. 2 shows the so called force-distance curves for the PHM0 sample.

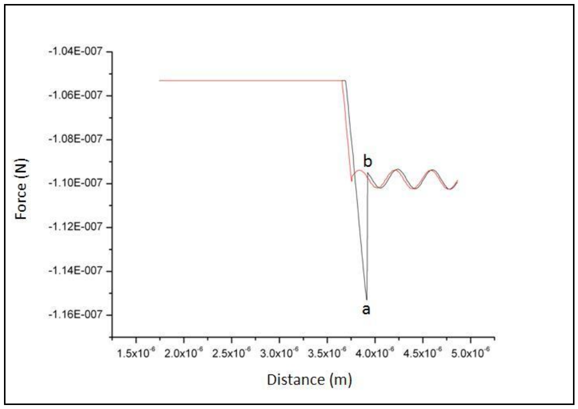

Figure 2: Force-distance curve in PHM0

According to Figure 2, the difference between these two curves is the result of the adhesion force. Finally, by overcoming the adhesion force, the cantilever is no longer in touch with the surface and will go back to its equilibrium position (Figure 2, point b).

The aim of this study is to measure the adhesion force, as one of the interaction forces. This can be performed through obtaining force-distance curves from the surface of Polymer. In order to measure this force quantitatively, the force constant of the cantilever was chosen between the range suggested by the manufacturer.

2 Experimental (Modeling)

2.1 Materials

The samples used in this study are fabricated through the polymerization process of two organic and inorganic phases (Ganjaee et al., 2008). As a result, a nanocomposite is developed which is named polymer hybrid material (PHM) by the researchers. Four samples with different percentages of the inorganic phase were investigated: PHM0, PHM25, PHM50 and PHM75. Table 1 shows the amount of inorganic phase in each sample.

Table 1 The amount of inorganic phase in each sample

Sample	**Amount of inorganic phase (in %mol)**
PHM0	0%
PHM25	25%
PHM50	50%
PHM 75	75%

It means that PHM50 has 50 mol% of organic phase while PHM0 is completely made of organic phase. The difference in the percentage of the inorganic phase makes an observable effect on the adhesion force and the decrease or the increase in the adhesion force can be discussed according to this issue.

2.2 Methods

2.2.1 Topography Imaging

The first step in the measurement of the adhesion force was to obtain the topography image of the surface of the polymer. The topography images were recorded with AFM, Dualscope/ Rasterscope C26, DME, Denmark. The non-contact working mode of AFM was used with a DC probe and a force constant between 0.07-0.4 N/m according to the manufacturer. All experiments were conducted in air atmosphere.

The scanning area of the images was 500×500 nm^2 and the resolution was 128×128 pixels. Figure 3 is the topography image of PHM0 obtained with a DC probe.

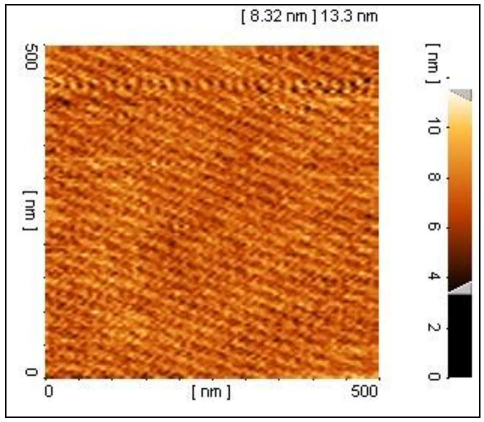

Figure 3: Topography image of the surface of PHM0

2.2.2 Distance Dependant Measurements

The second step was to obtain the force-distance curves in order to perform the quantitative measurements of adhesion forces. Calibrated force-distance curves were obtained at each point of the topography image performing distant dependant measurement (DDM). In order to get the best force-distance curve, different external loads at different points were chosen during DDM.

After obtaining the best curve, experiments were performed at 10 random points on the surface of the polymers. 10 force-distance curves were obtained with a time interval of 1.1 second at each point. Adhesion force was measured in all 100 curves for each polymer and reported as the mean of these curves.

2.2.3 Adhesion Force Measurement

Adhesion force is the result of the difference between the approaching and retracting force-distance curves. While the cantilever is trying to snap-out from the surface, adhesion force between the surface sample and the tip makes the cantilever stay in contact with the surface. The adhesion force can be measured by subtracting the two curves (Figure 4).

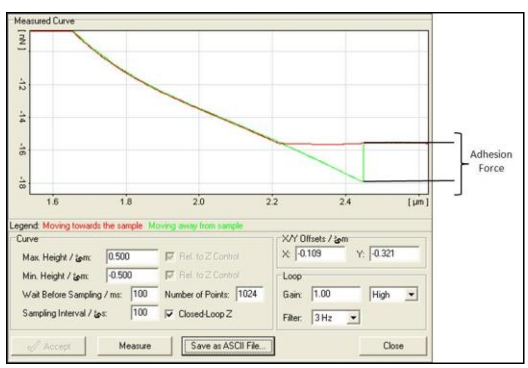

Figure 4: Adhesion force in force-distance curve from PHM50

3 Results and Discussion

The mean adhesion force measured based on 100 force-distance curves obtained for each sample is given in Table 2.

Table 2. Measured adhesion force from 100 force curves obtained for polymer samples

Sample	Adhesion Force (mean)	Standard deviation
PHM0	5.18 nN	±0.77
PHM25	4.33	±0.33
PHM50	2.42 nN	±0.076
PHM75	1.18	±0.13

Figure 5 is the typical example of the 100 different force curves obtained from all four polymer samples.

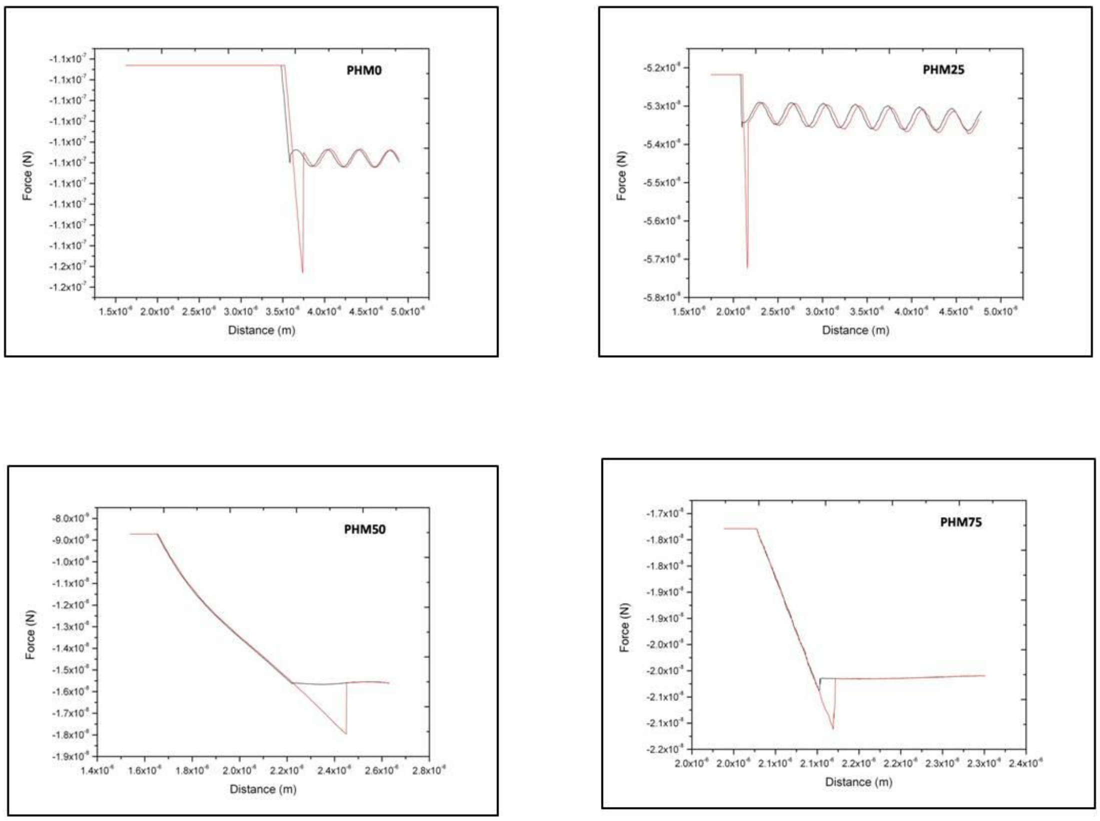

Figure 5: An example of 100 force curves in 10 random points on all polymer samples

It can be observed that the adhesion force decreases from about 5.18 nN for PHM0 to 1.17 nN for PHM75. Accordingly, it can be concluded that the adhesion force is declined by the rise in the amount of inorganic phase. Figure 6 is a comparison between the polymeric samples.

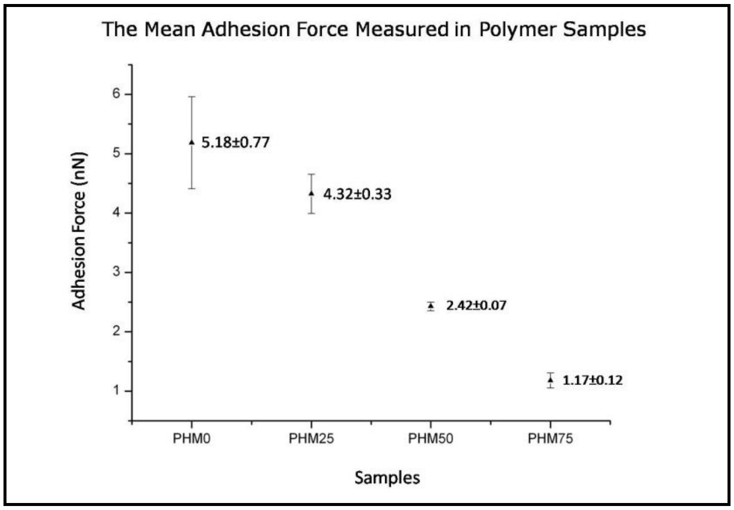

Figure 6: Investigation of the effect of inorganic phase on the adhesion force

4 Conclusion

It was demonstrated that Atomic Force Spectroscopy is a suitable force measurement technique for probing surface interactions on all engineering sample surfaces. These measurements can be performed on different kinds of samples with the least need of sample preparation.

Adhesion forces were measured through 100 force curves in 10 random points for each sample. By 25% increment of inorganic phase from one sample to another, the adhesion force decreases from 5.18 nN for PHM0 to 1.17 nN for PHM75. It can be said that by the addition of the inorganic phase, the sample becomes harder.

The decrease in the amount of adhesion force by the addition of the inorganic phase, can also be observed through the gradient of the standard deviation. In the first two samples which exhibited the greatest amount of adhesion, the standard deviation is much bigger than the next two samples samples and also the adhesion force is changing in a much bigger range in comparison to the last two samples.

The other major thing that is observable is that the force-curve in the first two samples (PHM0 and PHM25) is wavy and the lines are not straight. It can be said that because of the greater amount of adhesion force in these two samples, the cantilever does not retract completely from the surface of the sample and makes the curve looks like a wavy curve.

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