Composites Science and Technology 150 (2017) 111–119

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

# Local surface mechanical properties of PDMS-silica nanocomposite probed with Intermodulation AFM

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ARTICLE INFO

*Article history:*
Received 30 November 2016
Received in revised form
8 May 2017
Accepted 11 July 2017
Available online 13 July 2017

*Keywords:*
Nanomechanical properties
Nanocomposites
Atomic force microscopy
Intermodulation
Interphase

ABSTRACT

The mechanical properties of polymeric nanocomposites are strongly affected by the nature of the interphase between filler and matrix, which can be controlled by means of surface chemistry. In this report, we utilize intermodulation atomic force microscopy (ImAFM) to probe local mechanical response with nanometer-scale resolution of poly(dimethylsiloxane) (PDMS) coatings with and without 20 wt% of hydrophobic silica nanoparticles. The data evaluation is carried out without inferring any contact mechanics model, and is thus model-independent. ImAFM imaging reveals a small but readily measurable inhomogeneous mechanical response of the pure PDMS surface layer. The analysis of energy dissipation measured with ImAFM showed a lowering of the viscous response due to the presence of the hydrophobic silica nanoparticles in the polymer matrix. An enhanced elastic response was also evident from the in-phase stiffness of the matrix, which was found to increase by a factor of 1.5 in presence of the nanoparticles. Analysis of dissipation energy and stiffness in the immediate vicinity of the nanoparticles provides an estimate of the interphase thickness. Because the local stiffness varies significantly near the nanoparticle, AFM height images contain artifacts that must be corrected in order to reveal the true surface topography. Without such a correction the AFM height images erroneously show that the stiff particles protrude from the surface, whereas corrected images show that they are actually embedded in the matrix and likely covered with a thin layer of polymer.



## 1. Introduction

Polymeric nanocomposites, and control of their properties, have been widely discussed since the emergence of nanomaterials, and they are presently considered as a key future nanotechnology [1–3]. Polymeric nanocomposites containing, for example, carbon nanotubes [4], graphene [5], carbon black [6] or silica nanoparticles [7,8] as fillers often display dramatically improved bulk mechanical properties in comparison with the conventional microcomposites or pure polymer matrix, even at low loading content. Experiments and numerical modeling have concluded that this "*nano effect*" at constant additive volume is due to the dramatic increase in the total interfacial area as the size of the additive decreases [9,10]. The interfacial region, also referred to as the interphase, is a transitional volume between filler and bulk matrix, which differs in its chemical and physical properties compared to the bulk matrix due to polymer-filler interactions. Understanding the properties of the interphase is crucial for the design of desired bulk properties of the nanocomposites [11–19]. The rubber process analyzer, nuclear magnetic resonance and theoretical calculations have all demonstrated the existence of the matrix-filler interphase [6,10,20]. However, it is still challenging to directly measure the mechanical response of the interphase around an individual nano-sized particle due to its small size and the inhomogeneity of the nanocomposite system. With the above-mentioned methods it is impossible to distinguish the elastic and viscous response of the interphase from that of the matrix [21].

The most direct way to assess the interphase at a free surface is

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http://dx.doi.org/10.1016/j.compscitech.2017.07.013
0266-3538/

atomic force microscopy (AFM), a powerful tool with unparalleled lateral resolution for characterizing not only morphology but also local surface mechanical properties [22]. AFM-based methods have provided useful information on the mechanical properties of nanocomposites and there are several dedicated modes available for distinguishing surface features based on mechanical response [23–25]. One of the most commonly used AFM modes is Tapping Mode™ (trademark of Bruker Corporation) that excites the cantilever at a single frequency. In addition to surface topography, this single frequency method provides a phase image showing contrast corresponding to changes in material properties [26].

More recently, dynamic AFM techniques have been extended to multiple frequencies, where the probe is excited and the response is measured at two or more frequencies, allowing for a more detailed understanding of the tip-surface interaction [27]. The Intermodulation AFM (ImAFM) technique is one such multi-frequency dynamic AFM method [28]. Instead of exciting the higher eigenmodes or higher harmonics of the cantilever, ImAFM employs two drive frequencies close to the single cantilever resonance to capture the response of several frequency mixing products, also known as intermodulation products, which arise due to the nonlinear character of the tip-surface interaction. Both the cantilever and deflection sensor are calibrated from the same thermal noise measurement, and ImAFM uses this calibration to accurately measure the tip-surface force as a function of the cantilever deflection at fixed probe height. The ability to measure how both the dissipative and conservative components of the interaction depends on the amplitude of oscillatory motion that provides a route to map the local viscous and elastic response of the nanocomposite [29,30].

Here we focus on understanding how hydrophobic silica nanoparticles affect the local mechanical properties of poly(-dimethylsiloxane) (PDMS) nanocomposites as compared to that of a pure PDMS sample. We used the ImAFM technique to characterize local surface mechanical properties and provide an estimate of the interphase thickness. Because we do not apply any model from contact mechanics or make any specific assumptions about the exact nature of the interaction, our approach has the advantage of not introducing errors or misconceptions by fitting to an inappropriate tip-surface interaction model. The disadvantage is that the measured properties do not directly correspond to well-known bulk mechanical properties such as the Young's modulus. The PDMS matrix was chosen since it is a widely used polymer known for its viscoelasticity and its hydrophobicity [31–33]. Further, the PDMS-hydrophobic silica nanocomposite coating used in our investigation has also recently been shown to offer favorable corrosion protection properties to carbon steel [34], and it is thus relevant to further understanding the interactions between the matrix and the nanoparticles in such coatings.

## 2. Materials and methods

### 2.1. Materials

A model PDMS-based polymer coating, containing as few components as possible, was prepared using hydroxyl terminated PDMS [Rhodosil Huile 48 V from Bluestar Silicones with a weight-average molecular weight, $M_w$, of circa 80000 g/mol and a dynamic viscosity of 20 kg/(m s) at 25 °C] as the prepolymer. Curing was achieved using the curing agent (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane (from Fluorochem Ltd.) together with the catalyst dibutyltin diacetate (technical grade, from Sigma-Aldrich). Hydrophobic fumed silica particles (reacted with dimethyldichlorosilane, Aerosil R 972 from Evonik) with a primary particle diameter of 16 nm were used as fillers in the nanocomposites. Anhydrous methanol (99.8%, Sigma-Aldrich) and xylene mixture of isomers (95%, Sigma-Aldrich) were employed as solvents. All chemicals were used as received.

### 2.2. Sample preparation

Two types of samples were prepared, i.e. PDMS coating without silica particles and PDMS coating with 20 wt% hydrophobic silica nanoparticles. The PDMS coating with 20 wt% of such particles was prepared as follows: First, the hydrophobic silica nanoparticles (0.6 g) were suspended in xylene (6 mL) and ultrasonically mixed (VWR ultrasonic bath, $f = 45$ kHz, power efficiency = 60 W) in a glass beaker for 1 h. Next, 3 g PDMS prepolymer was added to the particle sol, and the mixture was left to stir for 15 h using an impeller set to 85 rpm. In the next step, the curing agent was dissolved in 1 mL methanol and then added to the mixture, which was allowed to stir for 1 h. After that, the catalyst dissolved in 1 mL xylene was added. The uncured composite was quickly spin-coated at 2000 rpm for 60 s onto silicon wafer substrates, which had previously been cut to size and cleaned with Piranha solution ($H_2SO_4$: $H_2O_2$, 7: 3) at 80 °C and Milli-Q water successively. The coated silicon wafer was cured at 80% relative humidity (20 °C) for one week. Due to the slow diffusion of water inside the coating, this long curing time was used to ensure complete curing. The pure PDMS coating without silica particles was prepared using the same steps except that xylene without silica particles was added to the PDMS base. The thickness of the PDMS coating is influenced by the spin coating speed and the viscosity of the PDMS prepolymer [35], and the resulting thickness in our experiments is typically 50–70 μm.

A schematic illustration of the cross-linking reaction (curing reaction) is illustrated in the Supporting Information (Scheme 1). The polymerization proceeds via two steps; hydrolysis of the alkoxide groups on the curing agent followed by the water-producing condensation reaction with the hydroxyl-terminated PDMS [36]. The cured sample can be regarded as a three-dimensional network structure.

### 2.3. Methods

A Dimension Icon AFM (Bruker, Santa Barbara, USA) acquired the Tapping Mode™ images and data analysis was performed in the NanoScope Analysis software (Version 1.50, Bruker). A second order polynomial-flattening algorithm was employed to remove surface tilt from the height images. All other images were unaltered. ImAFM measurements were performed on the Bruker Dimension Icon AFM connected to a multi-frequency lock-in amplifier (Intermodulation Products AB, Sweden), which generates the drive signals and records the intermodulation spectra. The IMP software suite (Version 1.1, Intermodulation Products AB) was used to analyze the data. All experiments were performed in ambient air.

Rectangular cantilevers with approximate dimensions of 125 μm length and 40 μm width (BudgetSensors Tap300Al-G, spring constant ≈ 40 N/m, tip radius < 10 nm as specified by the manufacturer) were used to perform both Tapping Mode™ and ImAFM experiments. The spring constant of each cantilever was determined with the non-invasive thermal noise method as implemented in the ImAFM Software Suite (Intermodulation Products AB, Sweden) [37,38].

#### 2.3.1. Tapping mode AFM

Tapping Mode™ AFM, also known as amplitude modulation atomic force microscopy (AM-AFM) is the most widely used dynamic AFM technique and it has been thoroughly explained in the literature [26]. In addition to giving topography it provides some