Temperature-dependent surface nanomechanical properties of a thermoplastic nanocomposite

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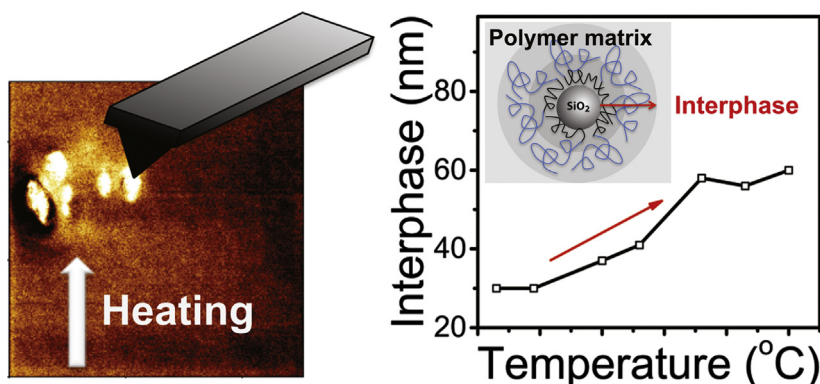
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GRAPHICAL ABSTRACT

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ABSTRACT

In polymer nanocomposites, particle-polymer interactions influence the properties of the matrix polymer next to the particle surface, providing different physicochemical properties than in the bulk matrix. This region is often referred to as the interphase, but detailed characterization of its properties remains a challenge. Here we employ two atomic force microscopy (AFM) force methods, differing by a factor of about 15 in probing rate, to directly measure the surface nanomechanical properties of the transition region between filler particle and matrix over a controlled temperature range. The nanocomposite consists of poly(ethyl methacrylate) (PEMA) and poly(isobutyl methacrylate) (PiBMA) with a high concentration of hydrophobized silica nanoparticles. Both AFM methods demonstrate that the interphase region around a 40-nm-sized particle located on the surface of the nanocomposite could extend to 55–70 nm, and the interphase exhibits a gradient distribution in surface nanomechanical properties. However, the slower probing rate provides somewhat lower numerical values for the surface stiffness. The analysis of the local glass transition temperature (T_g) of the interphase and the polymer matrix provides evidence for reduced

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stiffness of the polymer matrix at high particle concentration, a feature that we attribute to selective adsorption. These findings provide new insight into understanding the microstructure and mechanical properties of nanocomposites, which is of importance for designing nanomaterials.

1. Introduction

The properties and applications of polymeric nanocomposites are of great interest and importance [1–3]. The worldwide nanomaterials market was in 2014 valued at approximately $3.4 billion, which is one of the fastest growing markets of the global economy [4]. However, in addition to the many emerging applications, structural characterization issues with lack of extensive research and detailed description of materials at the nanoscale are key factors restraining the utilization of nanocomposites in various fields [5].

The concept that nanocomposites with low loading levels (typically less than 5% by volume) of inorganic nanoparticles in a polymer matrix can have significantly reinforced mechanical, optical and electrical properties compared with the corresponding polymer without nanoparticles or with micro-sized particles of the same composition is now generally accepted [6–8]. Numerical modeling methods combined with experimental studies have led to the conclusion that this "nano effect" is due to the dramatic increase in the volume of the interphase between the polymer matrix and the nanofillers as the size of the filler is decreased [9–11]. The interphase is a transitional volume between the fillers and the bulk matrix, with different physicochemical properties than the bulk matrix due to the interactions with the fillers. The dimension, properties and structure of the interphase are crucial in determining the global mechanical properties of the nanocomposite, and the interphase can become the dominating volume when the particles are nanometer-sized [12]. For instance, for a composite with a concentration of 1 vol% of spherical 1 nm diameter particle surrounded by an interphase that is 1 nm thick, the interphase represents 26% of the total volume of polymer. In contrast, this would only represent 0.06% of the total volume of polymer when the particles are 100 nm in diameter. This is a consequence of the large surface area of a uniform dispersion of nanoparticles.

Different characterization techniques have confirmed the existence and importance of the interphase in nanomaterials, not the least the reinforcement of their mechanical properties [5,13–18]. The pioneering work by Kaufman et al. in 1971, using nuclear magnetic resonance to study carbon black filled rubber composites, proposed that there is an immobile region and a relatively free region constrained by the carbon black particles [13]. This model agrees well with the famous "bound rubber" theory [19,20]. Recently, Holt et al. show that the thickness of the interphase in poly(2-vinylpyridine)/silica nanocomposites is 4–6 nm using broadband dielectric spectroscopy and small-angle X-ray scattering [14]. Experimental and/or numerical nanoindentation tests for studying the constituents of polymeric composites are common nowadays [5,15,16]. For instance, a recent study by Cheng et al., aimed to determine the local elastic modulus of the interphase between poly(methyl methacrylate) (PMMA) and silica/alumina plates [15]. However, characterization of the interphase between individual nanoparticle and the polymer matrix using nanoindentation remains a challenge [5].

The recent developments of nanomechanical AFM methods and numerical simulations have increased the possibilities to obtain a detailed description of the interphase properties on surfaces and its effect on nanocomposites [11,21–24]. For instance, Qu et al. used a torsional harmonic AFM-based technique to visualize the nanomechanical properties of the bound rubber interphase in carbon black-elastomer nanocomposites, and found an average thickness of the bound rubber region of 19 ± 8 nm. In addition, the numerical simulations used in their study predicted that the interphase thickness should decrease with increasing temperature [21]. In another study performed by the same group, numerical simulations predicted the elastic properties of particle-interphase-polymer nanocomposites with low loading fraction of well-dispersed and spatially isolated nanoparticles [22]. Recently, some dynamic simulation studies from Wang et al. also demonstrated the temperature dependent properties of the interphase [23]. In a cooling process, polymer atoms become immobile, spreading from the nanoparticle surface outwards into the polymer matrix, whereby broadening the interphase [23].

On the basis of the above-mentioned investigations and others, three issues are considered in the present study: (1) The structure and nanomechanical properties of the interphase region on the composite surface as evaluated by AFM-based techniques. (2) Possible changes in interphase properties due to temperature variations. (3) Surface nanomechanical properties at high nanoparticle concentrations (larger than 10 vol%), which contrasts to most current studies that concerns the microstructure of polymer-interphase-particle system at low loading fraction (typically less than 1 vol%). This is of relevance due to a common experimental observation from dynamic mechanical analysis (DMA) that suggest that with increasing particles volume fraction the glass transition temperature, T_g, first shifts towards higher temperature and then towards lower temperature [25,26]. A high filler loading often results in nanoparticles agglomeration; however, the detrimental impact of agglomeration on the polymer matrix is far from being understood.

In this study the surface interphase region is defined as the surface area around a particle in the polymer matrix with different nanomechanical properties than for the polymer and particle. Since it is conceivable that particle-tip convolution effects could contribute to a change in nanomechanical properties, we define the interphase from the measured topography AFM image displaying the already convoluted particle diameter. Thus, this study focuses on surface nanomechanical characterization and not on the bulk nanocomposite and interphase properties. To this end we adopt quantitative imaging and force mapping spectroscopy AFM modes under temperature-controlled conditions. We compare the structure and mechanical response of a pure poly(ethyl methacrylate) (PEMA)–poly(isobutyl methacrylate) (PiBMA) polymer matrix with those of a nanocomposite consisting of PEMA-PiBMA and hydrophobized silica nanoparticles.

Considering the general low T_g (usually < 0 °C) and inconspicuous change with increasing temperature of thermosets, we used the thermoplastic polymer PEMA-PiBMA in our experiments. Thermoplastic, or thermo-softening plastic, polymers become pliable above a specific temperature and can thus be solidified into another shape upon cooling. This property is due to weak intramolecular forces between polymer chains that can be overcome by thermal motion at higher temperatures [27]. During the curing process, thermosets undergo irreversible chemical cross-linking and achieve a rubbery nature [28]. The PEMA-PiBMA polymer matrix was chosen to allow us to understand the temperature dependence of surface interphase properties associated with inter-