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Temperature dependent loss tangent measurement of polymers with contact resonance atomic force microscopy

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ABSTRACT

The loss tangent of individual components in a blend of polypropylene (PP) and polystyrene (PS) is measured as a function of temperature with contact resonance atomic force microscopy. The loss tangent is calculated directly from the experimentally obtained contact resonance frequency, cantilever quality factor and other operating parameters. The temperature dependent variation of the loss tangent, measured at the high frequency of AFM measurements, shows peaks at different temperatures for the different polymer materials. The loss tangent peak at approximately 53 °C for PP is identified as an alpha peak signifying crystal relaxation while the loss tangent peak at approximately 75 °C for PS is identified as a glass transition.

1. Introduction

Atomic Force Microscope (AFM) [1] is a useful and popular tool for nano-scale characterization of materials. In recent times, increasingly complicated polymer blends are being developed in the polymer industry that consist of micrometer and nanometer sized domains. Due to its high spatial resolution and nondestructive nature of measurements, the AFM is extensively used in the polymer community for characterization purposes. Extracting quantitative nanomechanical properties is important to understand the expected performance of these polymers.

Dynamic AFM (or amplitude modulated AFM or intermittent contact AFM) is regularly used to image polymers due to its ease of use. Dynamic AFM provides qualitative contrast based on the mechanical properties of the sample. The phase and the amplitude of dynamic AFM have been related to the dissipation and conservative interactions [2,3] and recently to the viscoelastic properties, namely the loss tangent of the sample [4]. However, extracting information about quantitative material properties from dynamic AFM remains a challenge [5].

Contact resonance (CR) AFM has been used to successfully map quantitative visco-elastic properties such as the storage modulus and the loss modulus [6–9]. In contact resonance AFM, the cantilever is excited as the tip remains in contact with the sample. The resonance frequency of the cantilever when it is in contact with the sample (or the contact resonance frequency) is measured along with the dissipation or the damping, which is measured in terms of the quality factor. CR AFM has been used for quantitative imaging of various materials ranging from thin films to nanotubes as well as polymers [10–13]. In addition to CR AFM, other AFM based methods, such as nano-indentation and force-modulation have been used to determine the visco-elastic properties of polymers [14–16].

The loss tangent [17] is an important visco-elastic property, and it is defined as the ratio of the loss modulus to the storage modulus of the material under cyclic loading. The viscoelastic properties of materials such as the storage modulus, loss modulus, and loss tangent undergo changes with temperature and are commonly measured in rheological experiments by dynamic mechanical analysis. Loss tangent is a common empirical rheological measurement to pinpoint thermal, structural, and other transitions in polymer materials. Typically, these transitions present as peaks in a loss tangent vs. temperature curve (or equivalently, loss tangent vs. frequency curve). Transitions that are commonly measured in this way include the glass transition (T_g) and other thermal transitions [17].

In a recent development [18,19], the loss tangent of visco-elastic materials is estimated directly from the contact resonance measurement. This method does not require a reference material for measuring the visco-elastic property, which is an important development over the previous methods [8,9,20].

In the current work, the loss tangent of the individual components of a blend of PP and PS is measured as a function of temperature with

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contact resonance AFM. The measurements revealed an alpha transition of crystal relaxation in PP and a glass transition in PS. The transitions are identified from the peaks in the loss tangent vs. temperature curves obtained from the AFM experiments.

2. Experiments

2.1. Materials

The sample material used in the AFM experiments is a blend of thermoplastics isotactic polypropylene [PP] (ExxonMobil Chemical Company) and polystyrene [PS] (PolySciences). A blend of 4:1 (by mass) of PP and PS was prepared by melt processing. To prepare a flat surface for imaging, the sample was cryo-faced with a cryomicrotome (Leica) at −100 °C.

2.2. AFM setup

The polymer sample is heated with a sample heater (PolyHeater, Asylum Research) while imaging. A commercial AFM (MFP 3D, Asylum Research) is used for the experiments. The cantilever is glued to the specially damped cantilever holder to improve the signal to noise ratio [20,21].

The sample is clamped by a metal sample holder with a flat round bottom, and it is placed on the sample heater where the temperature is kept constant by a feedback loop. The sample is heated throughout the experiment. As the temperature of the heating stage is raised in steps, sufficient time (15 min) is allowed to elapse before the AFM measurements are conducted, so that the temperature of the sample surface does not change during the measurement. The sample is heated from the bottom of the sample holder, however the surface (where the AFM measurement takes place) temperature of the actual sample is of interest.

The temperature on the top of the sample is calibrated as a function of the sample heater temperature so that an accurate reading of the sample temperature can be obtained. The calibration procedure is as follows: The temperature of the top surface of the sample is measured with a thermocouple and compared with the known temperature of the sample heater prior to the AFM measurements to generate a calibration curve. The AFM measurements are conducted at those heater temperatures for which the temperatures of the top surface are previously recorded. This procedure will provide an accurate estimate of the temperature of the top of the sample for a known heater temperature during the AFM experiments.

2.3. Contact resonance measurement

The contact resonance (CR) AFM measurements are conducted with the band excitation (BE) [22] method. Although there are several ways of conducting contact resonance measurements, a point by point full spectrum acquisition via, for example, the band excitation method, has been shown to give a more accurate measure of viscoelastic properties than other methods [5,8,9]. The quality factor (Q) and the contact resonance frequency (f) are estimated by fitting the response to a damped simple harmonic oscillator model. The loss tangent ($\tan\delta$) is measured from the observables in the contact resonance measurements through a recently derived [18,19] equation:

$$\tan\delta = \frac{\gamma^2 f \beta (\lambda L)^2}{\alpha f_0} \tag{1}$$

where γ is the ratio of the length of cantilever tip from its base to the entire length of the cantilever, f is the contact resonance frequency, f_0 is the resonance frequency of the cantilever when it is excited away from the surface (free resonance frequency), λL is the root of the characteristic equation of the free vibration of the cantilever mode selected in the experiments (λL = 1.875, 4.694, 7.854 for the first three modes), α and β are the normalized stiffness and damping. A Kelvin–Voigt model is assumed to describe the viscoelastic properties of the sample where it is modeled as a linear spring and a viscous dashpot in parallel [6]. The experimentally obtained f and Q are related to the normalized stiffness and damping (α and β) of the sample by the characteristic equation of the vibrating cantilever in dynamic contact with the sample. A rectangular Euler–Bernoulli beam model is assumed for the cantilever in this analysis. The details of calculating α and β can be found in previous work [6,9].

The first contact resonance mode is used for the measurements. The cantilever (Olympus) selected has a f_0 = 76.05 kHz and the contact resonance frequency is $f = 282 \pm 3$ kHz when the sample is at ambient temperature. It is noted here that the contact resonance frequency can vary with the applied load. However the applied load is kept constant as the temperature is increased. Since the contact resonance frequency varies with the change in the sample properties with rising temperature, the cantilever is tuned separately at each temperature before making the measurements. The experiments are conducted with a loading force of around 40 nN which results in a stress field around 30 nm below the sample surface. This ensures that the near-surface effects can be neglected in the AFM measurements. The ratio of the stiffnesses of the sample and the cantilever is such that the sensitivity of the first mode is high [21].

2.4. Results

Fig. 1(a)–(c) show respectively the contact resonance frequency (f), quality factor (Q), and the loss tangent ($\tan\delta$) images for a 1.5 μm × 1.5 μm area of the polymer blend sample measured by BE-CR measurements at room temperature. The contact resonance frequency image does not show much difference between the PS and PP regions as observed in Fig. 1(a), since there is little difference in the storage moduli of PP and PS as has been previously observed [8,9]. The quality factor (Q) in CR measurements is inversely related to the loss modulus, and Fig. 1(b) shows a difference between the Q in the PP and the PS regions since the loss modulus of PP is about 4 times the loss modulus of PS in this frequency range at room temperature. The loss tangent is calculated from Eq. (1) and plotted in Fig. 1(c). The loss tangent calculated from the contact resonance measurements compares well with the loss tangent measures by the DMA analysis. At room temperature, the loss tangent measured by DMA for PP and PS respectively is 0.05 ± 0.005 and 0.011 ± 0.001 (these values are calculated for the high frequency of the AFM measurement (300 kHz) via time temperature superposition from DMA data for an appropriate comparison to the AFM contact resonance measurements). The loss tangent measured from contact resonance AFM for PP and PS are 0.0529 ± 0.007 and 0.021 ± 0.001, respectively.

The loss tangent of the PP/PS sample is measured as the temperature of the sample surface is varied from 25 °C to 82 °C. The variations of the loss tangent with temperature, measured by contact resonance AFM for PP and PS regions, are plotted in Fig. 2. The loss tangent of PP initially increases and then decreases with temperature, revealing a peak at around 53 °C. The loss tangent variation of PS shows a similar asymptotic behavior and a peak is observed around 75 °C. In Fig. 3, the loss tangent images are shown for (a) room temperature and (b) 53 °C, which reveals an overall increase in the loss tangent of the PP and the PS regimes (note that the color-scales (in web version) of loss tangent in Fig. 3(a) and (b) are identical to facilitate direct comparison). The imaging regions in