

NANO-THERMOMECHANICAL DETERMINATION OF THE ADHESIVE STRENGTH IN NANOCOMPOSITE MEMBRANES

René M. Overney and Jason.P. Killgore

Department of Chemical Engineering, University of Washington, Seattle, WA 98195, USA.

Introduction

Poly(trimethyl silyl propyne) (PTMSP) blended with nano-scale silica particles make up nanocomposite systems that have garnered significant attention regarding their unique properties.[1,2] Specifically, when used as a gas membrane, PTMSP exhibits reverse selectivity, thereby showing higher permeability to large soluble gases than for small permanent gases. Typically it is expected that the introduction of an impermeable filler material will result in a corresponding volumetric decrease in permeability,[3] which is further amplified by an increase in diffusing path length.[4] However, in the case of PTMSP and silica, enhanced permeability with increased filler concentration is observed. The significant permeability enhancement suggests that physical or chemical alteration of the polymer has occurred at the composite interface. In an effort to better understand the interfacial properties of PTMSP-silica composites, heated tip atomic force microscopy (HT-AFM)[5] is used here to study the adhesive strength between PTMSP and silica nanoparticles.

Experimental

Materials. PTMSP was obtained from Gelest, Inc. and dissolved into a 2 % solution in toluene. Silica particles of 190 nm diameter were prepared by mixing 200 ml anhydrous ethanol, 6 ml tetraethyl orthosilicate and 12 ml of 30 wt% ammonia in water in a glass beaker for 12 hours.

Characterization: Contact angle measurements with water were performed on neat polymer samples of PMMA and PTMSP, as well as a third sample of

Polystyrene. HT-AFM measurements were performed using a Topometrix Explorer AFM with heated probes provided by Anasys Inc. HT-AFM uses variably doped resistive cantilever materials to integrate heating directly into the cantilever probe.

Results and Discussion

Figure 1 shows a representative forward direction line trace for the lateral deflection signal. The deflection, as the cantilever impacts an embedded particle, is described by magnitude, ΔF_{max} and duration, α . ΔF_{max} and α are recorded at each temperature from the forward and reverse lateral force signals and compared to the baseline polymer-particle signal, β .

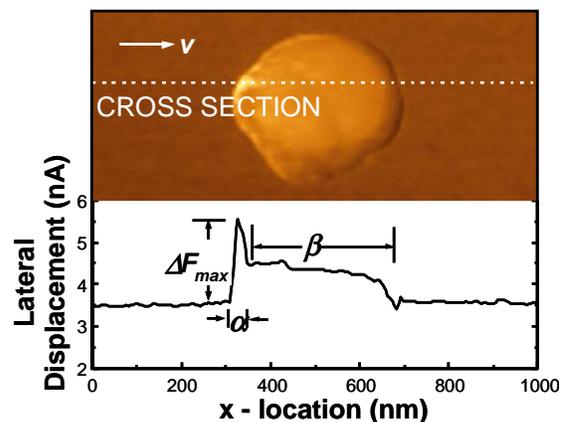


Fig. 1 Lateral force line trace of polymer embedded silica nanoparticle.

Investigation of lateral impact forces, i.e., the lateral peak forces ΔF_{max} (see Fig. 1), on silica in PMMA and PTMSP reveal dramatically different thermal responses in the vicinity of the transition temperature. As shown in Figure 2, the impacting force ΔF_{max} for PTMSP decreases slowly from 200 nN at room temperature to 50 nN at

~300 °C, before it sharply increases to ~450 nN prior to debonding at T_{DB} , 326 °C. Softening creates a feedback delay as the probe impacts the particle, and ultimately induces greater torsional deflection of the lever. The onset of the force increase is attributed to the local transition behavior of PTMSP at the particle interface. The onset, T' , occurs ~30 °C below T^* . The critical temperature T^* , above which adhesive failure is noticeable, provides insight into the mobility of the polymer phase in close vicinity to the particle. As adhesive failure under such slow sliding conditions and fast normal force feedback control can be expected to be dominated by transition properties, and as $T' < T^* < T_g$, we can conclude that the polymer matrix in the interfacial region possesses increased mobility. This confirms current models, based on global free volume measurements, that showed an increase in free volume on average over the bulk composite.[6] Thus, the experimentally observed increase in polymer matrix mobility in the interfacial region allows for the formation of larger free volume cavities which contribute to increased local sorption and diffusion. It can also be concluded, based on the direction of the interfacial transition temperature change, that a repulsive interface is present.[7] Particle debonding is visually captured in Fig. 3.

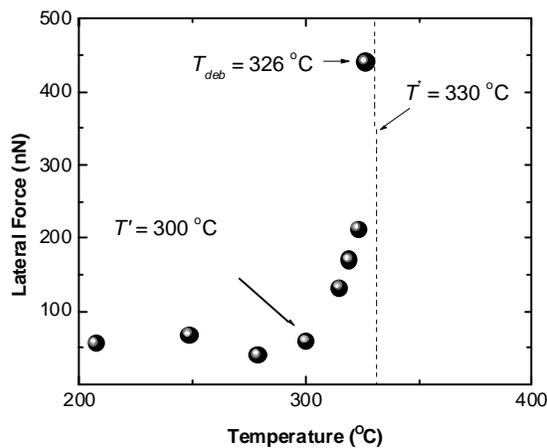


Fig. 2 Debonding force ΔF_{max} to remove silica particles embedded in PTMSP as function of the probe temperature.

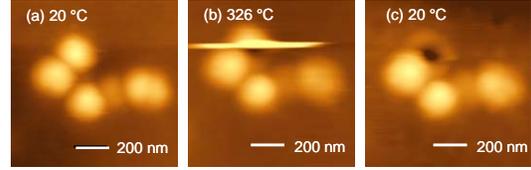


Fig. 3 Debonding of particle captured with AFM.

Conclusion

In addition to local transition property analysis, HT-AFM provides direct access to manipulation of isolated particles in nanocomposite thin films. Local thermal analysis with subsequent imaging yielded a transition of 330 °C that was found to be caused by thermal degradation. The study and manipulation of embedded nanoparticles in PTMSP revealed an impact force transition temperature ~30°C below the measured degradation transition, suggesting the presence of more mobile polymer chains at the particle interface. This is an interesting finding as the properties of the interfacial region are responsible for the enhanced mass transfer properties of the PTMSP-silica composite over virgin PTMSP. The debonding strength of single particles with the polymer matrix, which offers a simple measure of the interface, was determined to be 450 nN.

References

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