

POLYMER-SURFACE INTERACTIONS IN NANOFILLED POLYMERS

Alamgir Karim, Jack Douglas

Polymers Division, National Institute of Standards and Technology
Gaithersburg, MD 20899

There are many practical reasons for studying perturbing effects by complex geometrical constraints such as inorganic fillers in polymer blends. Polymer materials are hardly ever used in their pure form in applications. They are often filled with additives that improve their processibility (lubricants and stabilizers) and filler particles that modify modulus and strength (carbon black, silica, glass beads and fibers, chalk, clay, mica), appearance (pigments and surfactants), conductivity (metal flakes, carbon black, carbon nanotubes), and flammability (flame retardants)¹. Moreover, a large number of applications necessitate the use of polymer blend materials (impact modified blends, barrier polymers for packaging, filled elastomers) so that the situation where the filler particles interact with the phase separation process is widely encountered. An understanding of polymer-filler interactions and the ramifications for the properties of filled polymer blends is clearly a matter of practical interest that requires further investigation.

An understanding of the influence of polymer-surface interactions on the interfacial properties of nanoparticle fillers in polymer matrices is critical for applications of nanoparticle filled polymer materials. The influence of nanoparticle-surface interactions is additionally important in understanding and controlling the morphology of coated polymer films containing filler particles. We summarize some of our recent investigations of filler effects on the properties of bulk and polymer film materials.

First, we consider simple turbidity measurements to gauge the influence of a model filler (fumed silica) on the phase diagram of a blend of polystyrene (PS) and polybutadiene (PB). Our measurements show that the filler can shift the phase boundary much like solvent additives².

Next, we utilized atomic force microscopy to study the influence of a low concentration of filler ($\approx 100\text{nm}$ silica beads made using the StÖber process) particles on the phase separation morphology of ultrathin ($\approx 100\text{nm}$) filled blend (PS/PB) films³. The experimental studies are accompanied by simulation studies of phase separation in idealized two-dimensional blend films with filler particle inclusions^{3,4}. Our measurements and simulations both show that the phase separation morphology of near critical composition blends becomes perturbed by the presence of the filler particles in the intermediate and late stages of phase separation.

Measurements were also performed on fumed silica filled polymer blends. The blend morphology was found to depend greatly on particle dispersal as determined by the mixing time of the blend with filler in a mini twin screw extruder prior to phase separation. We also considered solvent cast films of a polymer blend with a fumed silica particle filler to study the extreme limit of low particle dispersal where the fumed silica form large aggregates. The segregation of the polymer to the fractal-like aggregate structure of the fumed silica formed by solvent casting seemed to dominate the phase separation process even after long times so that the filler makes a large impact on the late-stage phase separation morphology⁵.

Finally, we consider the influence of model nanofiller particles (buckyballs) on the dewetting of single component polymer coated films⁶⁻⁹. A combination of optical and atomic force microscopy and neutron reflection measurements indicates that these nanofiller particles can effectively suppress dewetting by pinning the moving contact line of the growing holes of dewetting films. This finding has important potential ramifications for improving the wetting of sizing agents on relatively large ($> 1\mu\text{m}$) filler particles. A suppression of dewetting in this context should lead to better filler-matrix adhesion and improvements of the property modifications in many filled polymer materials.

Certain commercial materials and instruments are identified to adequately specify the experimental procedure. This does not imply recommendation or endorsement by NIST nor does it imply that materials or equipment identified are necessarily the best available for the purpose.

ACKNOWLEDGEMENTS We thank Jon De-Groot of Dow Corning for providing the fumed silica samples.

REFERENCES

- (1) H.E.H. Meijer, P.J. Lemstra, P.H.M. Elemans, *Makromol. Chem., Makromol.Symp.* 16, 113 (1988).
- (2) A. Karim, D.W. Liu, J.F. Douglas, A.I. Nakatani, E.J. Amis, "Modification of the Phase Stability of Polymer Blends by Fillers", (Submitted).
- (3) A. Karim, J.F. Douglas, G. Nisato, D.W. Liu, E.J. Amis, "Transient Target Patterns in Phase Separating Filled Polymer Blends", *Macromolecules*, In Press.
- (4) B.P. Lee, J.F. Douglas, S.C. Glotzer, "Filler-Induced Composition Waves in Phase Separating Polymer Blends", (Submitted).
- (5) A. Karim, D.W. Liu, J.F. Douglas, E.J. Amis, "Particle Dispersion Effects on Phase Separated Filled Blends", In Preparation.
- (6) K.A. Barnes, A. Karim, J.F. Douglas, A.I. Nakatani, H. Gruell, E.J. Amis, "Suppression of Dewetting in Nanoparticle Filled Polymer Films", (Submitted).
- (7) J. Dudowicz, K.F. Freed, J.F. Douglas, *Macromolecules*, 28, 2276 (1995).
- (8) Reiter, G., *Phys. Rev. Lett.*, 68, 75 (1992).
- (9) R. Xie, A. Karim, J.F. Douglas, C.C. Han, R.A. Weiss, *Phys. Rev. Lett.*, 81, 1251 (1998).

DISCLAIMER