Rheological properties of PS-PMMA and layered silicate nanocomposites.

Mai Ha and Ramanan Krishnamoorti
Department of Chemical and Biomolecular Engineering
University of Houston, Houston, TX, 77204-4003
Tel: (713)743-4300 Email Address: ramanan@uh.edu

Abstract

The goal of this research is to study the effect of nanoparticles on immiscible polymer blends. Using layered silicate as nanoparticles and polystyrene – poly(methyl methacrylate) as immiscible blend model, the influence of nanoparticle on the phase-separated morphology, rheological and mechanical properties of the blends was examined. Theoretical models developed to predict the relationship between linear viscoelastic properties and morphology of immiscible polymer blends are used to quantify the effect of nanoparticles. Nanoparticle segregation at the interface of polymer blends was found to give better properties than one resides exclusively in one phase.

1. Introduction

More than a third of world plastic consumption is in forms of blends. When blending two or more polymers to make new material, manufacturers can achieve certain properties (performance, processability) at reasonable costs and do not have to stock different raw materials in their warehouses. In recycling industry, input materials usually are mixtures of several polymers. However, using polymer blends is hindered by the fact that most polymers are not mixed with others. High free energy of mixing causes components to retract to their own phases and reduce interfacial area. Hence, under processing conditions, blends tend to separate into large domains. The unpredictable changes in morphology lead to uncontrolled and usually lower than expected properties of the final materials. Therefore, to be able to control or predict the morphological evolution of the blend is a very important issue.

2. Objective

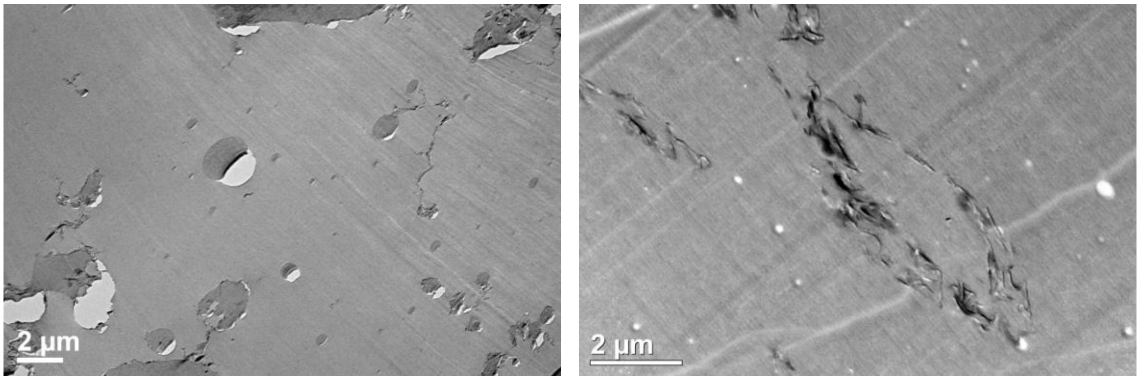
Observe and quantify the effect of nanoparticles in immiscible polymer blends by examining the morphological, rheological and mechanical properties of the blends.

3. Experimental details

Two sets of PS-PMMA blends with various silicate contents are formed by solution blending in THF: 20 vol.% PS – 80 vol.% PMMA – XX wt.% silicate (20-80-xx) and 80 vol.% PS – 20 vol.% PMMA – XX wt.% silicate (80-20-xx). Hexane was used as non-solvent to precipitate the samples. Samples were dried in air at room temperature for a day before annealed in vacuum oven at 180ºC for 24 hrs. Solid samples were then mold to disk-shape 1-1.5 mm thick and kept away from moisture until being tested in rheometer. Transmission electron microscopic samples were sliced from the disk to make ~100 nm thick slices.

4. Discussions

When the silicates are introduced into PS-rich system, they mainly located in PS phase. None of them is found in the curvy interface between PMMA and PS domains. When the interface is relatively flat at the contact between very large domains, few silicates segregate there. As seen in figure 1 right, some of them locate at the interface of the small PS domains within large PMMA droplets. On the other hand, when the particles are added into the 20-80 blends, we found them segregate at the interface as expected (figure 1 left). Also, the size of PS domains in the blend that has silicate are more uniform and range from 200-500 nm, which are about the same order of the silicate disk size.



20-80-1.0 **80-20-1.0**

Figure 1. TEM images of 80-100 nm thick film microtomed from annealed bulk samples (dark region: PS, bright: PMMA): (left) 20-80-1.0, (right) 80-20-1.0. Note that on the 20-80-1.0 sample, the PS-rich droplets covered by silicates tend to separate when microtomed.

In immiscible polymer blend, at low frequency region, an order of magnitude higher of G' compared to either PS or PMMA is observed. In case of blends between two immiscible polymers, the increasing in G' is because of the relaxation of macroscopic droplet deformation under applied stress and directly related to the interfacial tension between two phases and size of the droplets. It is not easy to observe the relaxation experimentally because it normally occurs at low frequency and/or low stress. Theoretically, the relaxation of the droplet will cause a plateau in G' curve of the blends, and at frequency lower than the relaxation time of the droplet, the matrix behavior is dominate again. In 80-20 blends, as observed through TEM images, silicates mainly locate in PS-rich phase. Hence, the PS phase gets reinforced by the nanoparticles, but the interface between two polymers is not affected. The minimal increasing in storage modulus at low frequency region solely comes from the contribution of reinforced PS phase. On the other hand, in 20-80 blends, rheological data show magnitudes increasing in G' at terminal region with adding silicates. The increasing is significantly higher than in 80-20 blends in the measured low frequency region.

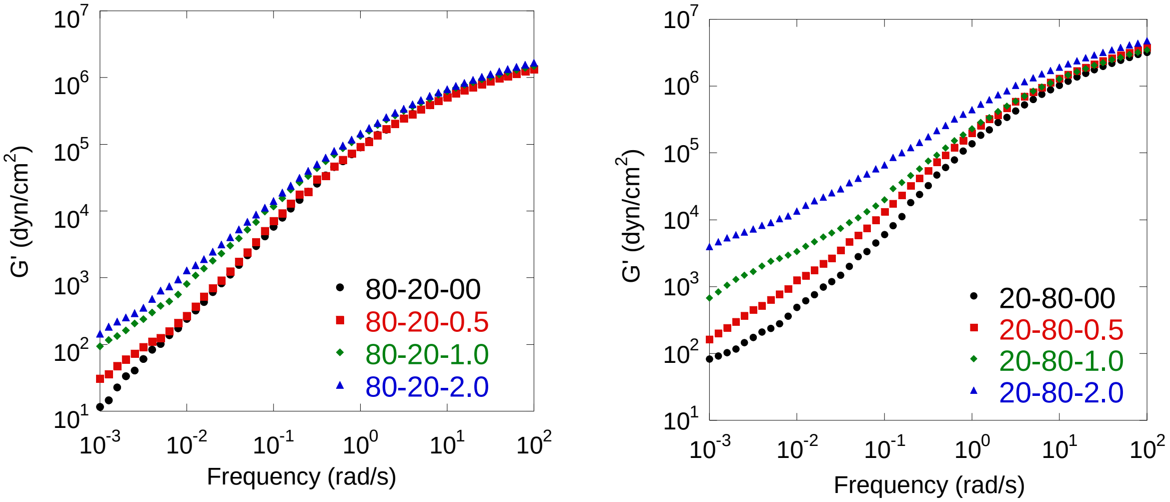


Figure 2. Frequency dependence of storage modulus at 180^{0}C for 80-20-xx blends (left) and 20-80-xx blends (right)

5. Conclusions

The anisotropic nature of LS makes them a good candidate for being surface active agent. Due to different affinity toward each polymer in PS-PMMA blends, the flat surfaces of LS prefer to contact with PS phase while the edges tend to point to PMMA phase. The segregation of LS at the interface leads to higher storage moduli of blends at low frequency.

6. Acknowledgement

- Texas Institute for Intelligent Bio-Nano Materials and Structure for Aerospace Vehicles, funded by NASA Cooperative agreement No NCC-1-02038 and the National Science Foundation (CMMI-0708096)
- Dr. Zhiping Luo and Rick Littleton at Microscopy and Imaging Center, Texas A&M University

7. References

P. J. Flory. Thermodynamics of high polymer solutions. The Journal of Chemical Physics, 10(1):51 - 61, **1942**.

M. L. Huggins. Solutions of long chain compounds. The Journal of Chemical Physics, 9(5):440 - 440, **1941**.

G. He, V.V. Ginzburg, and A.C. Balazs. Determining the phase behavior of nanoparticle-filled binary blends. Journal of Polymer Science, Part B (Polymer Physics), 44(17):2389 - 403, **2006**.

H. M. Lee and O O. Park. Rheology and dynamics of immiscible polymer blends. Journal of Rheology, 38(5):1405 -1425, **1994**.

J.F. Palierne. Linear rheology of viscoelastic emulsions with interfacial tension. Rheologica Acta, 29(3):204 -14, **1990**.

Bousmina, M., Effect of interfacial tension on linear viscoelastic behavior of immiscible polymer blends. Rheologica Acta, 38(3): 251-4, **1999**.

Lagaly, G., M. Reese, and S. Abend, Smectites as colloidal stabilizers of emulsions - I. Preparation and properties of emulsions with smectites and nonionic surfactants. Applied Clay Science, 14(1-3): 83-103, **1999**.

Yan, N.X. and J.H. Masliyah, Characterization and demulsification of stabilized oil-in-water emulsion. 1. Partitioning of clay particles and preparation of emulsions. Colloids and Surfaces a-Physicochemical and Engineering Aspects, 96(3): 229-242, **1995**.