

Interactions between Ps-Pmma Based Block Copolymers and Wood Derivatives

[David P. Harper](#), Forest Products Center, University of Tennessee, 2506 Jacob Dr., Knoxville, TN 37996-4570, [Seung-Hwan Lee](#), Forest Products, University of Tennessee, 2506 Jacob Dr., Knoxville, TN 37996-4570 and [Mark Dadmun](#), Chemistry, University of Tennessee, 2506 Jacob Dr., Knoxville, TN 37996-4570

Abstract

Multiblock copolymers of polystyrene (PS) and poly(methyl methacrylate) (PMMA) were investigated for use as a model coupling agent for wood-based polymer composites. The PS-PMMA copolymers with approximately 50/50 composition and 150,000 molecular weight were synthesized using atom transfer radical polymerization. The ability of the copolymers to improve the interfacial properties was evaluated in lignin/PS-PMMA and PS blend systems. The interaction of model films based on wood's main chemical components, lignin and cellulose, was investigated using calorimetric techniques and atomic force microscopy. Small addition levels of the triblock PS-PMMA-PS copolymer reveals improved phase behavior in PS-lignin blends. These results will lead to a new class of wood compatibilizers where the polymer chain architecture and functionality can be dialed in for the desired application.

Introduction

Lignin has long been of interest as a source for inexpensive and renewable adhesives and thermoplastics¹. However, the commercial utilization of lignin has not been met with success. Currently, natural polymers are gaining a great deal of attention lately with the increase in petroleum prices and the desire to seek renewable alternatives for fuels and materials. Lignin is often thought of as a waste product of the paper making process and in the conversion of celluloses to ethanol. However, it is a potential valuable source of aromatic chemicals, biodegradable polymers, and carbon fibers².

This study attempts to increase the utility of biopolymers by taking advantage of copolymers produced from atom transfer radical polymerization (ATRP). Materials produced from ATRP have very well defined molecular weights, functionality, and architectures. These attributes make these materials very efficient compatibilizers in immiscible systems³. Specifically, the amount of hydrogen bonding can be optimized by spacing the hydrogen bonding groups on the polymer chain via ATRP⁴. Thus, two polymers that are immiscible may have a copolymer engineered to deliver compatibility, stability, and thus commercial utility.

Polystyrene (PS) was used as one block because of the similarities in structure to some lignin components. PMMA is an attractive matrix material because of its amorphous structure and ability to hydrogen bond. In addition, block copolymers of PS and PMMA have been well defined and studied in other systems. Therefore, a basis has been established for controlling and understanding the hydrogen bonding ability for many of its copolymers. The objective of this preliminary investigation is to determine if a well-defined PS-PMMA copolymer can organize and stabilize lignin blends of PS and PMMA.

Methods and Materials

Preparation of copolymers

A triblock copolymer of polystyrene and poly(methyl methacrylate) was synthesized following the procedures outlined by Eastwood and Dadmun⁵. The homopolymers of PS (S) and PMMA (M) were initially polymerized. Then, following homopolymer purification, synthesis of triblock copolymers proceeds upon addition of other monomer and the addition of protecting groups. As either polymerization proceeds, copolymer samples are periodically removed for MW analysis by SEC. Multiblock copolymer structure is verified and characterized with ¹³C and ¹H NMR. The molecular weight was measured to be 153,000 with block sizes of 50,000.

Preparation of the blend

Polystyrene (PS) was purchased from Aldrich with an Mw of 230,000 and an Mn of 140,000. Atactic poly(methyl methacrylate) (PMMA) was purchased from Polysciences, Inc. with a Mw equal to 100,000 and a Mn of 62,500. Organosolv lignin (OL), purchased from Aldrich, and PS or PMMA was dissolved in THF. The total polymer concentration was prepared at 10% and the blending ratios of two polymers were 70/30, 50/50, and 30/70. The block copolymer composed of PS and PMMA (1-4 %) was added as a compatibilizer in the polymer solution. The solution was allowed to cast at room temperature for 2 days and vacuum-dried at 50°C to reach the constant weight.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) (Perkin Elmer Diamond DSC) was performed on all polymer blends and constituents. A heating rate of 50°C/min was used in heating to 170°C, held for 10 min, cooled at 50°C/min to -10°C/min, and then heated to 170°C/min a second time at 50°C/min. The glass transition was measured on the second run as the midpoint in the change of specific heat.

Phase morphology by Atomic Force Microscope (AFM)

For phase morphology, thin films of polymer blends with or without PS-PMMA block copolymer was prepared by placing a droplet of the 1% THF solution onto silicon wafer and spinning it at 2500 rpm at room temperature for 45 second. The

blends were annealed for 30 min at 160°C in a vacuum oven to avoid oxidation and thermal degradation. The phase morphology of thin films was visualized using true non-contact mode AFM (PSIA Inc.) Topographic and phase images were recorded simultaneously.

Results and Discussion

The synthesis of multi-block copolymers is difficult with conventional synthetic techniques. Anionically, styrene cannot be added onto living PMM. S-M-S cannot be made anionically. A methodology to use ATRP was developed to synthesize multiblock copolymers composed of styrene (S) and methyl methacrylate (M) regardless of direction of cross-propagation⁵.

The multiblock copolymer is used to tack groups on one end and then create loops at the interface of the immiscible polymer. Figure 1 and 2 display the DSC traces for 50:50 blends of Lignin with PS and PMMA with varying copolymer added. The difference in the T_g is not large for each of the constituent materials (Figure 3). Each of the blends exhibits a single T_g that is lower than the starting materials. There is a degree of interaction observable in PS-lignin and PMMA-lignin blends that interfere with chain interaction in the homopolymers. However, the solvent cast PS blends were observed to phase separate without the addition of copolymer to stabilize the blends.

AFM images display a change in domain sizes in PS-lignin blends containing as little as 1% copolymer (Figure 4). The change in domain size was observed for all copolymer addition levels investigated and did not change significantly in size or with annealing time. The same was not true for PMMA-lignin blends where the morphology a large change in the sizes of the domians with copolymer addition was not observed (Figure 5). The difference in structure with copolymer addition appears to be a narrowing and rounding of domains. The consequence of this observation is not known at this time.

The difference between the PS-lignin and the PMMA-lignin lends insight into how the copolymer is assembling in the blends. The PMMA is likely hydrogen bonding with the lignin and the styrene ends of the copolymer are interacting with the PS. The interaction between the styrene blocks and the lignin does not appear to be great enough to allow for assembly of the polymers in the lignin-PMMA blends. However, these blends did not phase separate with time as was observed with PS-lignin blends. An attempt to quantify these results is currently in progress.

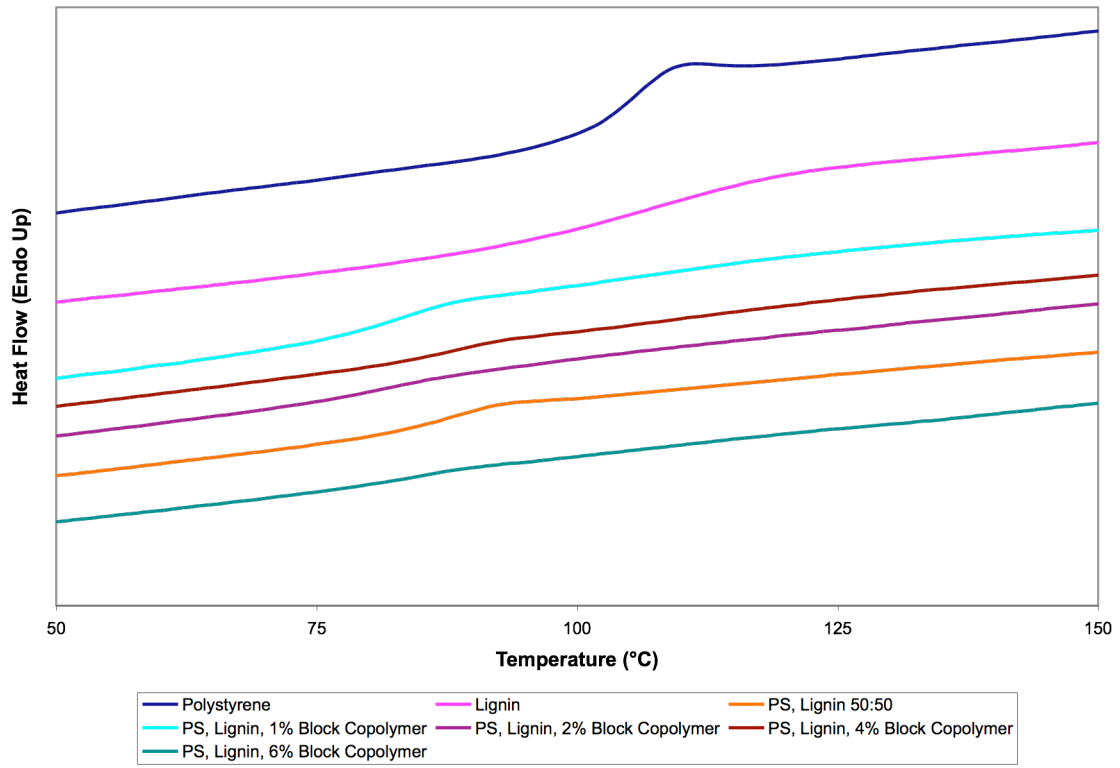


Figure 1: DSC traces for PS:lignin blends with varying addition of S-M-S copolymer.

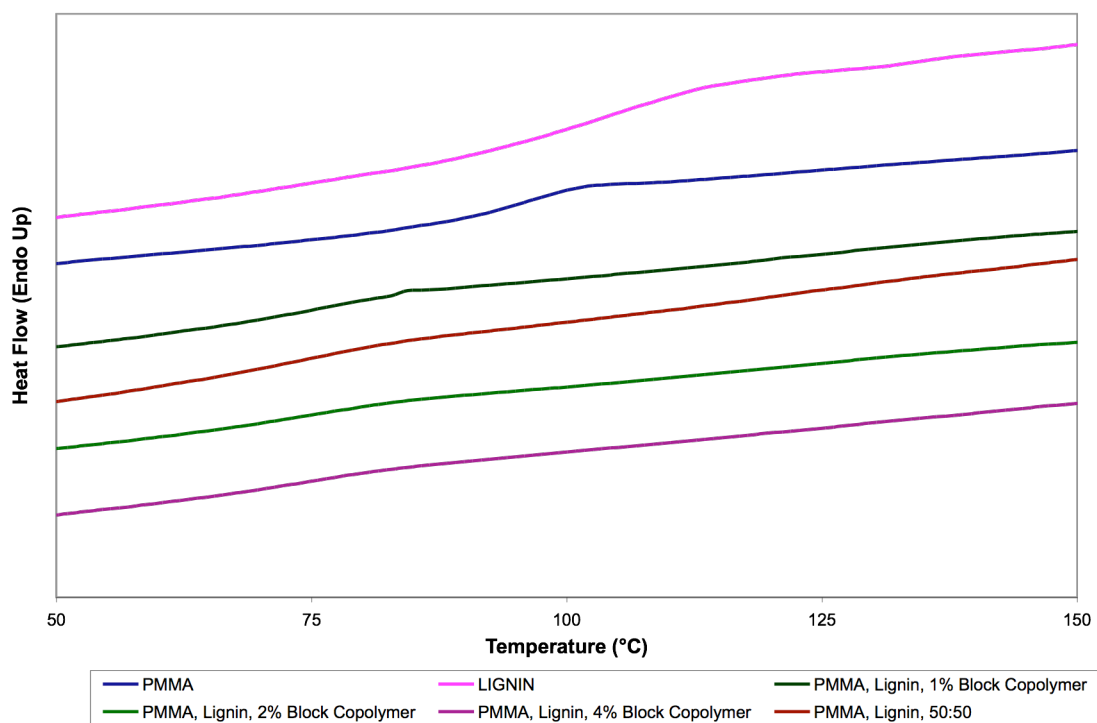


Figure 2: DSC traces for PS:lignin blends with varying addition of S-M-S copolymer.

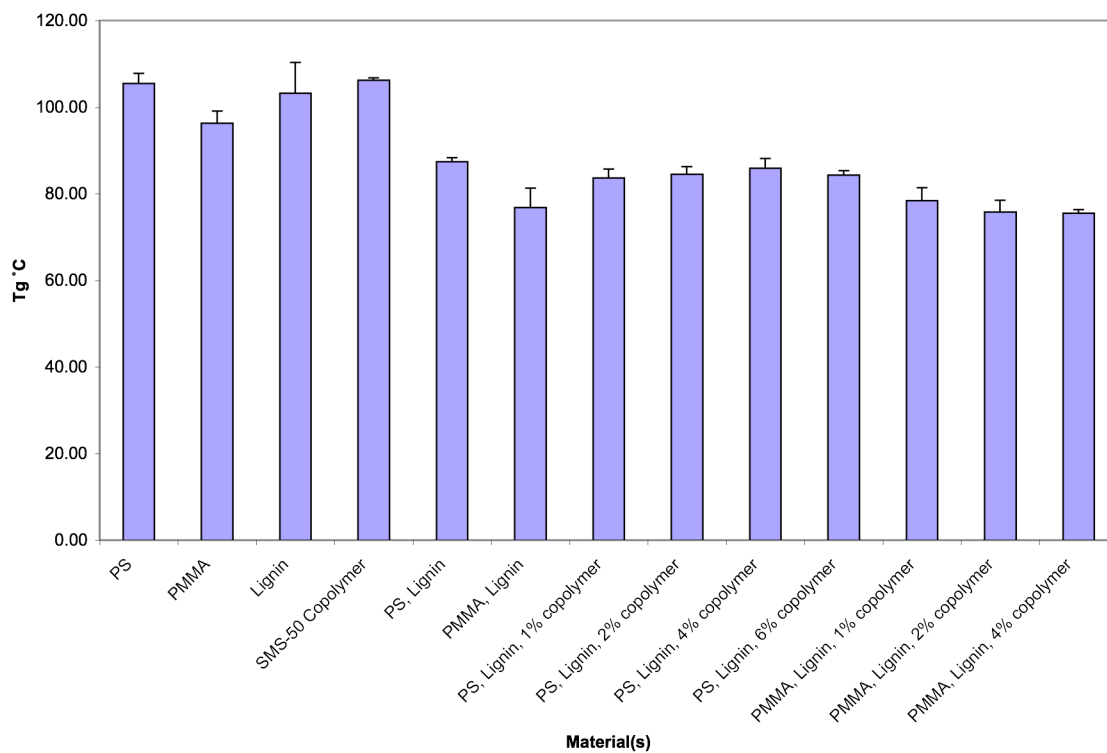


Figure 3: Measured glass transition temperatures with range (error bars) for each of the polymer blends.

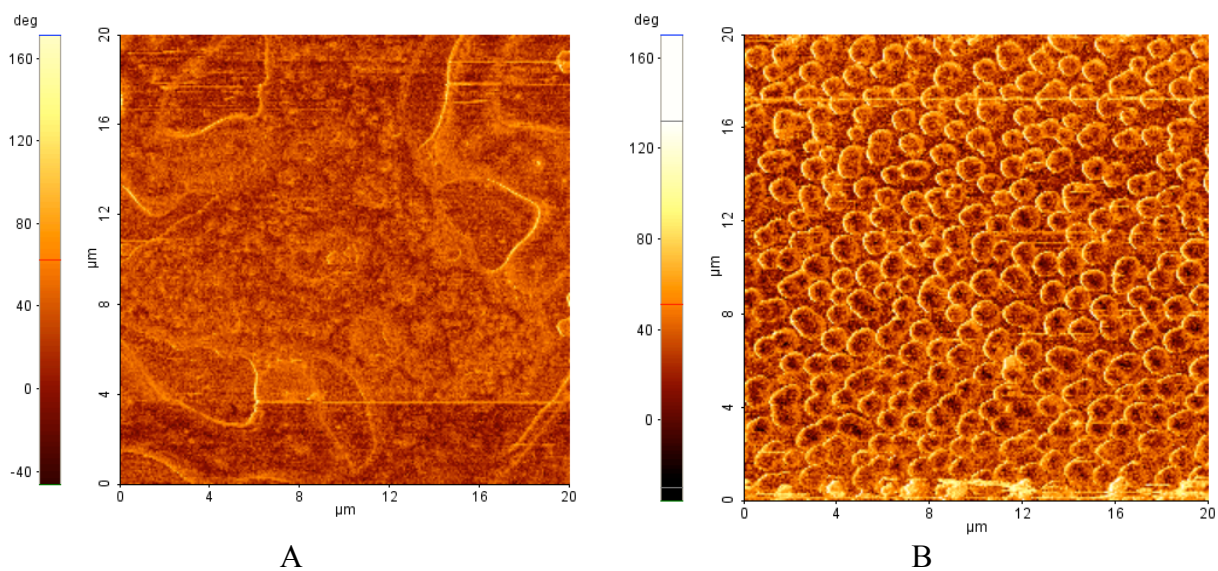


Figure 4: AFM images of (A) 50:50 blend of PS:lignin and (B) 50:50 blend of PS:lignin with a 1% addition of S-M-S copolymer.

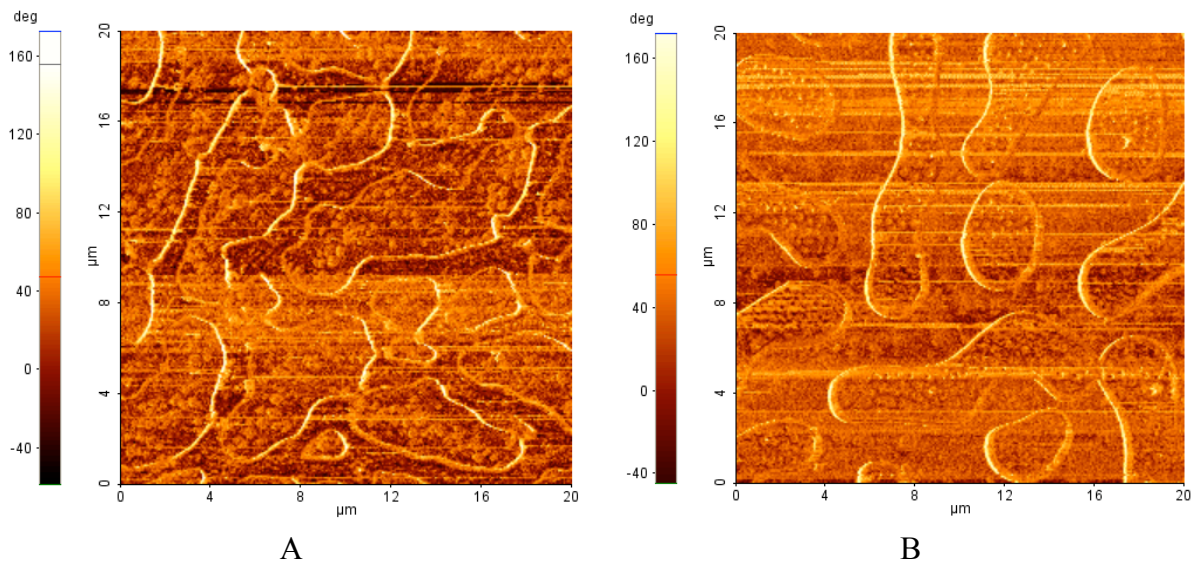


Figure 5: AFM images of (A) 50:50 blend of PMMA:lignin and (B) 50:50 blend of PMMA:lignin with a 1% addition of S-M-S copolymer.

Conclusions and Recommendations

The addition of small amounts of a copolymer has promise as being an effective method for stabilizing and making compatible polymers blends containing lignin. The use of ATRP can be used to control the hydrogen bonding and thus the assembly of these blends. This was evident in blends of lignin and PS where the addition of only 1% copolymer changed the morphology of the blend. The domain size did not change with the addition of more copolymer up to 6%.

The PMMA appears to interact more closely with the lignin than styrene. M-S-M copolymers will be investigated in the future to assess the blend morphology. In addition to triblock copolymers, pentablock and random copolymers are also currently being assessed. The impact on the mechanical performance, phase morphology, and phase transitions are also currently being addressed.

Acknowledgements

The authors would like to thank Mr. Timothy Stortz of the Tennessee Forest Products Department, Mr. Nathan Henry in the University of Tennessee Chemistry Department, and Dr. Dwight Patterson of Middle Tennessee State. Funding for this project was provided under a special grant from the United State Department of Agriculture.

References

1. Y.-R. Chen and S. Sarkenen, *Cellulose Chemistry and Technology*, **40**, 149-163 (2006).
2. W. L. G. A. L. Compere, C. F. Leitten, Jr., J. T. Shaffer. 33rd International SAMPE Technical Conference, Seattle, WA, 2001.
3. M. D. Dadmun, E. A. Eastwood, C. P. O'Brien and J. K. Rice, *Abstracts of Papers of the American Chemical Society*, **226**, U469-U469 (2003).
4. E. Eastwood, S. Viswanathan, C. P. O'Brien, D. Kumar and M. D. Dadmun, *Polymer*, **46**, 3957-3970 (2005).
5. E. A. Eastwood and M. D. Dadmun, *Macromolecules*, **34**, 740-747 (2001).