

POSS INDUCED PHASE SEPARATION IN A POLYMERIC PHOTOVOLTAIC SYSTEM

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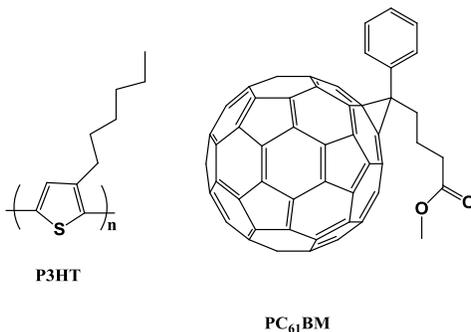
ABSTRACT

Polymeric photovoltaic cells have attracted significant attention due to their ease of processability, flexibility and tunability of structure. The photoactive thin layer of polymeric photovoltaic cells generally contains a conjugated polymer as the donor and a fullerene derivative as the acceptor. Controlling the phase separation between donor and acceptor is of great importance in determining the performance of photovoltaic cells. Strategies including using nanoparticles and changing processing conditions have been widely utilized to optimize the phase separation. However, most nanoparticles utilized in the photovoltaic systems are conductive materials that are multi-disperse in size, which increases the chance of short circuiting between the electrodes. POSS molecules are monodisperse hybrid organic-inorganic nanostructured chemicals that are generally non-conductive. In this study, POSS molecules with different functional groups were incorporated into a polymeric photovoltaic active layer film to control the phase separation. POSS functionality was varied in an attempt to control the self-assembly of the donor/acceptor phases. High resolution AFM was utilized to investigate the surface morphology and phase separation. Photoactive films were also investigated using UV-vis spectroscopy and X-ray diffraction.

1. INTRODUCTION

Development of sustainable, clean energy sources is one of the greatest challenges for scientists and engineers in the 21st century. The National Academy of Engineering has identified “making solar energy affordable” as the first of its “Grand Challenges for Engineering”.¹ Polymer-based organic photovoltaic (OPV) devices are attractive due to ease of fabrication, low-weight, flexibility and potential reduction in cost. An effective polymer-based photovoltaic cell consists of both a conjugated semiconducting polymer as the donor and a fullerene derivative as the acceptor. One of the most widely studied polymeric photovoltaic systems is a phase separated blend of poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) (Scheme 1). When a photovoltaic cell is working, a photon is absorbed by the P3HT which turns the photon into an exciton. The exciton is dissociated into free charge carriers at the donor/acceptor interface and collected as electrical energy. The formation of large domain sizes that exceed the exciton diffusion length will cause exciton recombination prior to their dissociation into free charge carriers. Weak phase separation will lead to poor charge transport between the donor and acceptor interfaces.² Therefore, it is of paramount

importance to control the domain size close to the exciton diffusion length and form continuous structures to facilitate the charge transport across the bulk heterojunction.



Scheme 1. Structures of P3HT and PCBM.

Efforts on improving the processing conditions have been made to control the phase separation of the P3HT:PCBM heterojunction system. Thermal annealing was first introduced into photovoltaic cells by Padinger et al., resulting in substantial increases in the power conversion efficiency.³ In the thermal annealing process, the OPV cells are heated above the glass transition temperature (T_g) of P3HT to allow molecular reorganization. In general, OPV cells that have not been subjected to annealing processes display little phase separation and thus demonstrate low power conversion efficiencies and fill factors.⁴ On thermal annealing, both the P3HT and PCBM molecules are reorganized into thermodynamically favored crystallized structures. Due to the lower crystallization rate of PCBM, thermal annealing results in the formation of fiber-like P3HT crystallites in a matrix consisting of PCBM clusters and amorphous P3HT.⁵ The annealing-induced P3HT crystallized domains not only adjust the degree of phase separation in accordance with the exciton diffusion length, but also decrease the space between P3HT chains to facilitate the charge transport inside P3HT domains.⁶ Also, the annealing was found to decrease the band gap difference between electrodes and the active layer, which increases the efficiency.

Studies have been reported of incorporation of nanoparticles as additives to OPV systems with the goal of increasing efficiency, with varying results. Berson et al. reported that carbon nanotubes increased the short circuit current of P3HT:PCBM cell by a factor of two, which leads to a higher power conversion efficiency.⁷ Chul-Hyun Kim et al. embedded silver nanowires into P3HT:PCBM systems and reported the elevation of overall performance in terms of open circuit voltage, short circuit current, fill factor and power conversion efficiency.⁸ The effects of nanoparticle incorporation on OPV cell performance depend on the dispersion, size and interaction of the nanoparticles with the polymer matrix. However, it is important to control the particle size, since large conductive particles could cause short circuiting between electrodes and loss of efficiency. POSS nanostructured chemicals are hybrid organic-inorganic structures, monodisperse in size, consisting of a silicon oxide cage with a corona of organic substituents. Previous studies in our laboratories have shown that the migration and aggregation behavior of POSS molecules can be controlled in polymeric matrices to

produce desired nanostructure development with associated performance improvements,^{9,10} and POSS molecules can be tailored to serve as dispersing agents for organic and metallic nanoparticles.¹¹ POSS is also utilized to control the morphology and phase separation in polymers.¹² In previous research, it has been found that by changing the pendant functional groups on the POSS organic corona, POSS molecules act to either drive phase separation or to improve compatibility in phase separated systems.¹³ In this study, POSS molecules with different functional groups were introduced into the P3HT:PCBM system in an attempt to control the phase separation. Atomic force microscopy (AFM) was utilized to determine the morphology and nanoscale phase separation. The P3HT crystallinity was characterized by UV-vis spectroscopy and X-ray diffraction (XRD).

2. EXPERIMENTATION

2.1 Materials

Indium tin oxide (ITO) glass slides were cut into ~ 1.5 X 1.5 cm² squares. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), 1.3 wt.% dispersion in water, having resistivity in the range of 500-5000 ohm cm, was used as the hole transporter. P3HT, regioregular, electronic grade, 98 % regioregularity, average $M_n \sim 45,000$ was used as the donor. PCBM with purity >99% and molecular weight of 911 g/mol was used as the acceptor. Chlorobenzene was used as the solvent to form the actual photovoltaic donor/acceptor blend. All the materials above were purchased from Sigma Aldrich, USA. Octahydro POSS (H-POSS), tris sulfonic acid isobutyl POSS (PhSO₃H POSS) and octa(3-hydroxy-3-methylbutyldimethylsiloxy) POSS (OH-POSS) were donated by Hybrid Plastics, Inc. All materials were used as received.

2.2 Sample Preparation.

ITO (~100 nm) coated glass plates were successively cleaned ultrasonically in deionized water, acetone and isopropanol for 10 minutes each in a FS20D sonicator. They were then exposed to UV/ozone for 40 minutes and then immediately spin coated with a uniform layer of PEDOT:PSS. PEDOT:PSS was spin-coated at a speed of 5000 rpm (revolutions per minute) to form a 40 nm thick film. 25 mg/ml active layer solution having 1:1 wt. ratio of P3HT:PCBM in chlorobenzene was prepared for spin coating. The active layer was spin coated on top of the PEDOT:PSS layer at 1250 rpm for 90 sec using a WS-400B-GNDP/LITE spin coater. The thickness of the active layer was determined to be ~ 100 nm by AFM. The samples were then annealed at 150° C in argon for 30 min. to aid the crystallization process. The entire fabrication process was conducted in an air environment except for thermal annealing. The same experiments were repeated for 3 times to make sure reproducible results obtained. Representative images and curves collected from these samples are presented in this study.

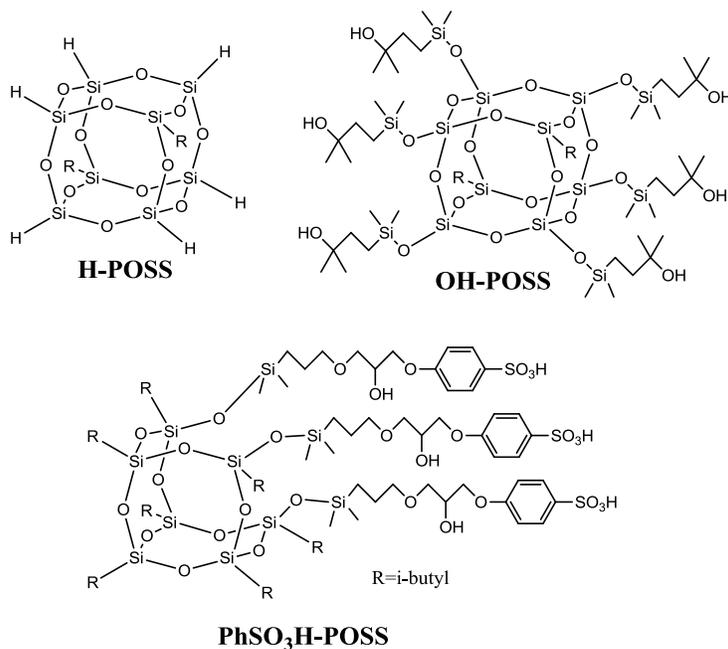
2.3 Instrumentation.

AFM studies were conducted in tapping mode on a Dimension ICON scanning probe microscope from Bruker. A silicon probe from Bruker (RTESP) with nominal spring

constant of 20-80 N/m was employed. Surface topographies of film samples were studied at different scan sizes at image resolution of 512 X 512 pixels and scan rate of 1 Hz. Multiple images were obtained of macroscopically separated areas of the surface, and representative images are shown. AFM studies were performed in a temperature (22 ± 2 °C) and humidity (40-45%) controlled room. UV-vis spectra were obtained using a Perkin-Elmer Lambda 6 UV/Vis spectrophotometer. All spectra were normalized to the intensity at 700 nm, where the absorption from P3HT or PCBM is not observable. X-ray diffraction studies were obtained using a Rigaku D/MAX-Ultima-III diffractometer at room temperature using Cu K α radiation at a tube current of 44 mA and an acceleration voltage of 40 kV. Scan range was 4° - 8° at a step interval of 0.01° and a scanning rate of 0.05°/min.

3. RESULTS

In this study, three POSS structures with different functional groups were chosen for evaluation due to their expected range of interactions with the donor and acceptor phases. The structures of the POSS materials analyzed are shown in Scheme 2. H-POSS, without organic functionality, was chosen to study the effect of the silicon-oxygen cage alone. The hydroxy-terminated octa-substituted organosiloxane OH-POSS was chosen to examine the effect of potential hydrogen bonding with the PCBM ester. The PhSO₃H-POSS, with both hydroxyl and phenyl groups substituents was expected to have potential for both H-bonding and π - π interactions with the PCBM phase. POSS incorporation was limited to one weight percent to avoid interference of the insulating POSS molecules with conductivity.



Scheme 2. Structures of POSS molecules

3.1 AFM Study

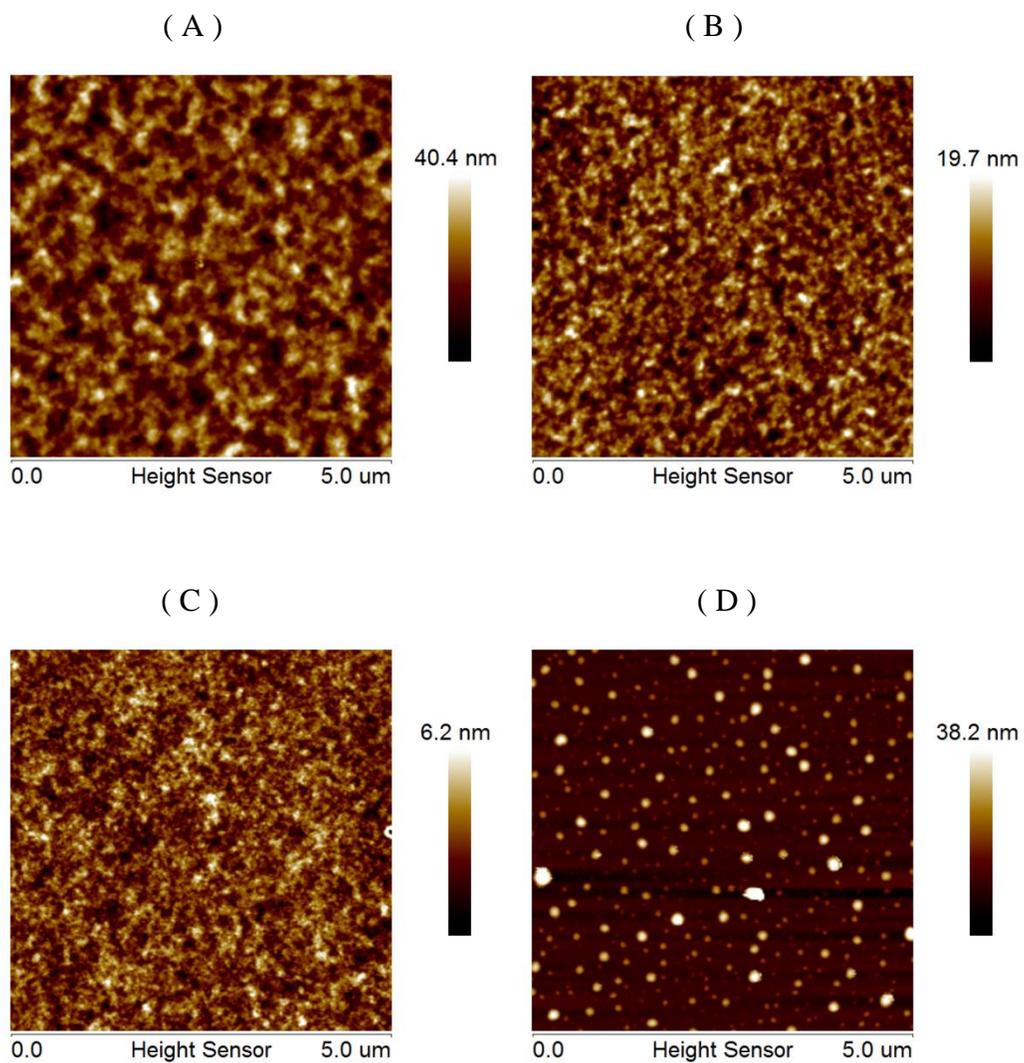


Figure 1. AFM height images of the (A) Neat P3HT:PCBM (B) H-POSS (C) OH-POSS and (D) PhSO₃H-POSS modified P3HT:PCBM films. Image size is 5μmX5μm.

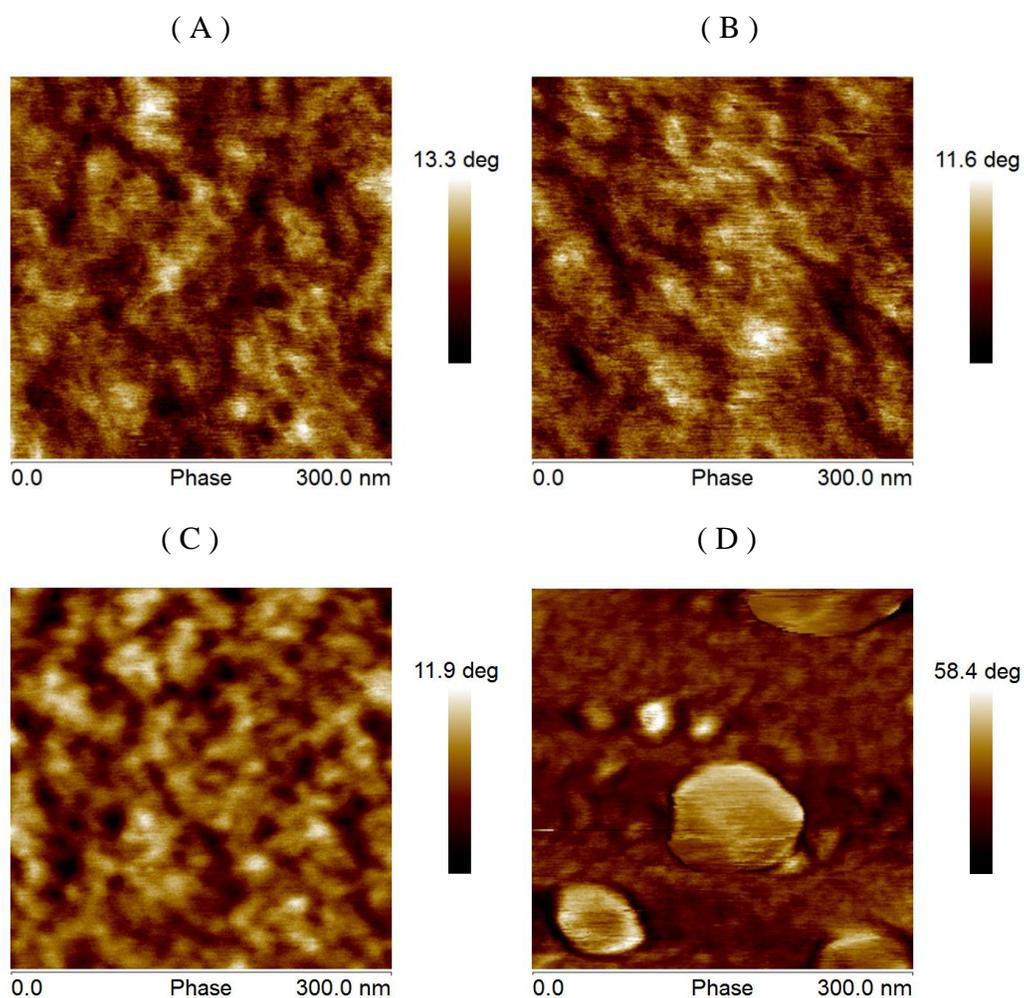


Figure 2. AFM phase images of the (A) Neat P3HT:PCBM (B) H-POSS (C) OH-POSS and (D) PhSO₃H-POSS modified P3HT:PCBM films. Image size is 300 nm X 300 nm.

Table 1. Roughness of the neat P3HT:PCBM and POSS-modified films.

	Neat	H-POSS	OH-POSS	PhSO ₃ H-POSS
RMS (nm) from 5μmX5μm	5.78	2.82	0.90	5.23
RMS (nm) from 300 nm X 300 nm	2.5	1.7	0.50	1.34

*All the RMS values are collected from the height images.

Morphology and phase separation evaluations were performed using AFM. Figure 1A displays the height image of the neat P3HT:PCBM film after 30 min thermal annealing. Fiber-like features (~150 nm diameter) are uniformly dispersed on the surface, attributed to P3HT crystallization and thermally induced phase separation. H-POSS has no organic

substituents, and thus allows analysis of the effects on morphology of addition of the silicon-oxygen cage alone. A finer phase separated morphology with closer domain packing is observed in the H-POSS containing sample in Figure 1B in comparison to that of the control, indicating the function of POSS as a dispersant. A similar phenomenon is observed in the OH-POSS modified films (Figure 1C). The domain spacing is further decreased and the domain size drops to ~100 nm diameter. This is attributed to hydrogen bonding of OH-POSS with PCBM, which alters the interactions between the P3HT and PCBM domains. A large number of uniformly dispersed aggregates (~200 nm diameter) are observed in the PhSO₃H-POSS modified film (Figure 1 D). A similar phenomenon was observed in our previous study of octa-phenyl POSS as an additive to P3HT/PCBM films, where it was found that POSS-PCBM clusters were formed in the active layer film, attributed to π - π interactions between POSS phenyl groups and fullerene substituents.¹³ In this research, the PhSO₃H-POSS molecules contain both phenyl groups and hydroxyl groups functionality, allowing both π - π interactions and hydrogen bonding, resulting in the formation of a large number of aggregates.

The root mean square roughness values collected from the AFM height images are shown in Table 1. For the 5 micron images, the RMS values were observed to decrease for all of the POSS-containing samples, except for the PhSO₃H-POSS modified film which contains large aggregates, where an increase in roughness was observed. To obtain a better understanding of the size of the phase separated domains, AFM analysis was performed on 300 nm X 300 nm sections of the films. In the PhSO₃H-POSS modified film the RMS value was collected from the 300 nm size height image excluding those large aggregates. The RMS values collected from the 300 nm size images displayed in Table 1 show reduced roughness for all of the POSS-containing samples in comparison to that of the standard. The reduction in the RMS values indicates the function of the silicon-oxygen cages as dispersants. Phase images at 300 nm scale are shown in Figure 2. Figure 2A displays the phase image of the neat P3HT:PCBM film. Small fiber like bright features (10-20 nm diameter) are observed embedded in the previously observed 150 nm domains. These smaller sized features found in the larger continuous domains are expected not only to help exciton diffusion but also to facilitate electron hopping in the bulk heterojunction system. Similar features were found in the H-POSS modified film (Figure 2B). A regular, phase separated morphology with uniformly dispersed network is exhibited in the OH-POSS modified film. Because of the presence of the large aggregates in the PhSO₃H-POSS modified film, it is difficult to discern the morphology of the underlying P3HT/PCBM blend.

3.2 UV-vis Spectroscopy Study

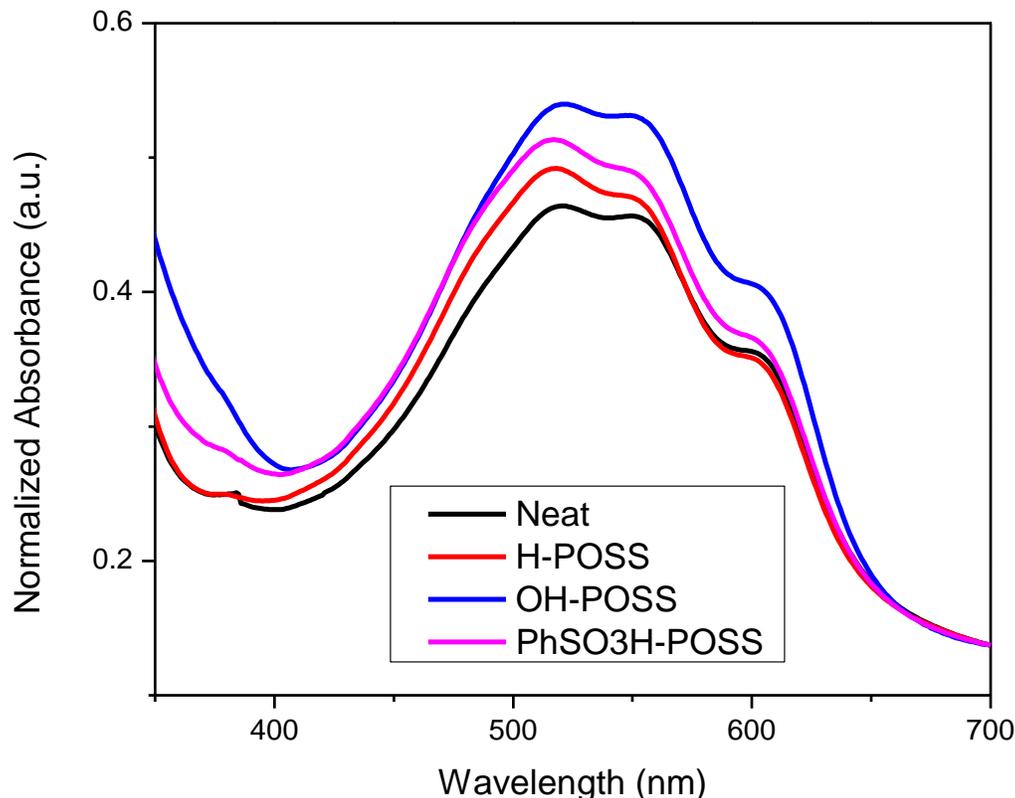


Figure 3. UV-vis spectra of the neat P3HT:PCBM films and POSS modified films.

In Figure 3 the UV-Vis spectra of thermally annealed neat and POSS-modified samples are shown. All POSS-modified samples display higher intensity peaks between 400 nm and 700 nm than those observed in the neat sample, which suggests a greater degree of crystallinity in the P3HT phase and enhanced phase separation in the heterojunction system.¹⁴ The improved light absorption also suggests higher energy available during the light to electricity transition, affording the possibility of higher power conversion efficiency. The higher degree of crystallinity is attributed to the rigid POSS structures, which serve as nucleating agents for P3HT crystallization. This periodic seeding effect results in more ordered P3HT phase-separated domains, as shown in the height images of the H-POSS and OH-POSS modified films in comparison to the standard. The OH-POSS modified film displayed the most regular morphology with most highly dispersed phases in both 5 μm and 300 nm AFM images, and also exhibits the highest absorption, suggesting the highest crystallinity and closest π - π stacking for these films. The light absorption decreases in the order of OH-POSS > PhSO₃H-POSS > H-POSS > neat film. It should be mentioned that even though a large number of aggregates are observed in the

PhSO₃H-POSS sample, those aggregates are expected to act as light scattering vectors within the film, which serves to increase the light absorption.¹³

3.3 X-ray Diffraction Study

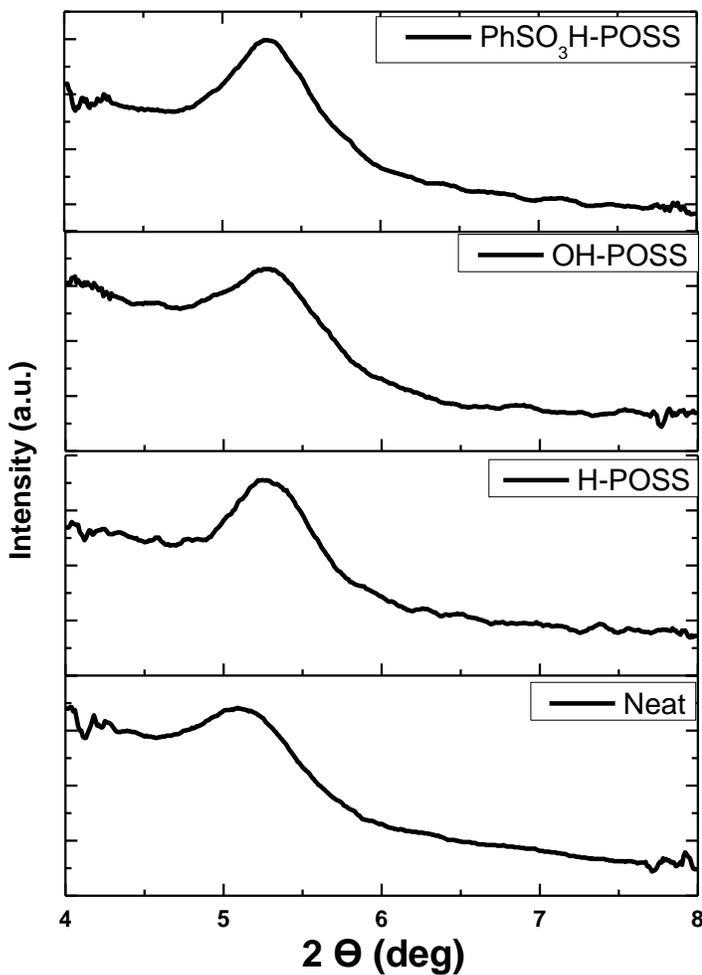


Figure 4. XRD curves of the neat P3HT:PCBM films and POSS modified films.

Table 1. d-spacing of the neat P3HT:PCBM films and POSS modified films

	Neat	H-POSS	OH-POSS	PhSO ₃ H-POSS
2θ (deg)	5.1	5.25	5.30	5.28
d-spacing (nm)	1.73	1.68	1.66	1.67

XRD was used to measure the spacing between P3HT crystals. The d-spacing is calculated using Bragg's equation:

$$d = \frac{n\lambda}{2\sin\theta}$$

the results of which is shown in Table 2, with corresponding XRD curves shown in Figure 4. In all of the film samples (100) plane diffraction peaks are observed corresponding to an ordered lamellar structure with interlayer spacing. This interlayer spacing is generated by the alkyl side chains on the backbone of P3HT which separate the parallel stacks.¹⁵ The peak maxima were used to determine the 2θ angle of all the solar cell samples. The peak position shifted to the right, suggesting decrement in the interlayer spacing and closer packing of the P3HT chains. This is attributed to POSS nucleation, which results in a greater degree of crystallization and tighter crystallite packing for the P3HT phase. For instance, when compared with the neat sample, which displays the peak maximum at a 2θ value of 5.1 deg, the sample modified with OH-POSS displays the peak maximum at 5.30 deg. Using Bragg's equation the spacing between P3HT stacking is found to decrease from 1.73 nm for the neat sample to 1.66 nm for the OH-POSS sample. Closer spacing has been found to facilitate hole mobility, allowing hopping between the P3HT chains with reduced loss of conductivity.^{6,16} The d-spacing increases in the order of OH-POSS < PhSO₃H-POSS < H-POSS < neat film, parallel to the order of decrease in the measured UV-vis absorption, confirming the conclusion that POSS enhances crystallinity and crystallite packing of the P3HT phase.

4. CONCLUSIONS

In summary, the morphology and phase separation in the heterojunction P3HT:PCBM system can be altered by the addition of POSS molecules, and the degree to which morphology is altered depends on the POSS organic functional groups. The H-POSS has been found to act as a dispersant and to lower the surface roughness. Fine phase separation was observed in the OH-POSS sample, and uniformly dispersed aggregates were formed on the addition of the PhSO₃H-POSS. Increased light absorption and decreased d-spacing between crystallites were observed for all POSS modified samples, suggesting a closer P3HT π - π stacking and higher crystallinity caused by the silicon-oxygen cages. The type of functional groups on the POSS molecule determined the extent to which crystalline packing changed. UV-vis and XRD studies indicated the π - π stacking degree decreased in the order of OH-POSS > PhSO₃H-POSS > H-POSS > neat P3HT:PCBM. In future work, solar cells will be prepared with these materials and the device performance characteristics will be measured. Studies will be designed to gain a greater understanding of the relationships between POSS structure, active layer morphology, and solar cell performance, with the goal of identifying avenues for improvement of power conversion efficiency in OPV devices. In future work, the performance of these devices will be measured and the relationship between the performance and morphology change will be evaluated to fully understand the influence from POSS functionalities.

5. ACKNOWLEDGMENTS

Funding from the Ray C. Anderson Foundation and from The U.S. Department of Energy under grant number DE-EE0003173 is gratefully acknowledged. The authors would like to thank Hybrid Plastics, Inc. for donation of the POSS materials and for useful discussions.

6. REFERENCES

- (1) <http://www.engineeringchallenges.org/cms/challenges.aspx>, 2011.
- (2) Zheng, Y., Xue, J. "Organic Photovoltaic Cells Based on Molecular Donor-Acceptor Heterojunctions." *Polym. Rev.* 50 (2010): 420-453.
- (3) Padinger, F., Rittberger, R.S., Sariciftci, N.S. "Effects of postproduction treatment on plastic solar cells." *Adv. Funct. Mater.* 13 (2003): 85-88.
- (4) Yang, X., Loos, J., Veenstra, S.C., Verhees, W.J.H., Wienk, M.M., Kroon, J.M., Michels, M.A.J., Janssen, R.A.J. "Nanoscale Morphology of High-Performance Polymer Solar Cells." *Nano Lett.* 5 (2005): 579-583.
- (5) Salamandra, L. "Organic Photo-Voltaic Cells and Photo-Detectors based on Polymer Bulk-Heterojunctions." 2009.
- (6) Chang, Y.-M., Wang, L. "Efficient Poly(3-hexylthiophene)-Based Bulk Heterojunction Solar Cells Fabricated by an Annealing-Free Approach." *J. Phys. Chem. C* 112 (2008): 17716-17720.
- (7) Berson, S., de, B.R., Bailly, S., Guillerez, S., Joussetme, B. "Elaboration of P3HT/CNT/PCBM composites for organic photovoltaic cells." *Adv. Funct. Mater.* 17 (2007): 3363-3370.
- (8) Kim, C.-H., Cha, S.-H., Kim, S.C., Song, M., Lee, J., Shin, W.S., Moon, S.-J., Bahng, J.H., Kotov, N.A., Jin, S.-H. "Silver nanowire embedded in P3HT:PCBM for high-efficiency hybrid photovoltaic device applications." *ACS Nano* 5 (2011): 3319-3325.
- (9) Misra, R., Fu, B.X., Plagge, A., Morgan, S.E. "POSS-nylon 6 nanocomposites: Influence of POSS structure on surface and bulk properties." *J. Polym. Sci., Part B: Polym. Phys.* 47 (2009): 1088-1102.
- (10) Misra, R., Fu, B.X., Morgan, S.E. "Surface energetics, dispersion, and nanotribomechanical behavior of POSS/PP hybrid nanocomposites." *J. Polym. Sci., Part B: Polym. Phys.* 45 (2007): 2441-2455.

- (11) Wheeler, P.A., Misra, R., Cook, R.D., Morgan, S.E. "Polyhedral oligomeric silsesquioxane trisilanols as dispersants for titanium oxide nanopowder." *J. Appl. Polym. Sci.* 108 (2008): 2503-2508.
- (12) Zhang, Q., He, H., Xi, K., Huang, X., Yu, X., Jia, X. "Synthesis of N-Phenylaminomethyl POSS and Its Utilization in Polyurethane." *Macromolecules* (Washington, DC, U. S.) 44 (2011): 550-557.
- (13) Wu, Q., Bhattacharya, M., Morgan, S.E. "POSS-Enhanced Phase Separation in Air-Processed P3HT:PCBM Bulk Heterojunction Photovoltaic Systems." *ACS Applied Materials & Interfaces* (2013).
- (14) Kim, Y., Cook, S., Tuladhar, S.M., Choulis, S.A., Nelson, J., Durrant, J.R., Bradley, D.D.C., Giles, M., McCulloch, I., Ha, C.-S., Ree, M. "A strong regioregularity effect in self-organizing conjugated polymer films and high-efficiency polythiophene:fullerene solar cells." *Nat. Mater.* 5 (2006): 197-203.
- (15) Li, G., Shrotriya, V., Yao, Y., Huang, J., Yang, Y. "Manipulating regioregular poly(3-hexylthiophene) : [6,6]-phenyl-C61-butyric acid methyl ester blends-route towards high efficiency polymer solar cells." *J. Mater. Chem.* 17 (2007): 3126-3140.
- (16) Handbook of advanced electronic and photonic materials and devices; Nalwa, H.S., Ed., 2000.