CHARACTERIZATION OF PHASE SEPARATION IN POLYVINYL PYRROLIDONE/TRISILANOLPHENYL-POSS POLYMER BlENDS
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Abstract
Polyvinylpyrrolidone (PVP) is a polymer that has shown promise in aerospace sealant applications. Trisilanolphenyl-POSS (TPP) integration into polymers as blends has shown increased stability, structural integrity, and thermal resistance. Optical microscopy studies of 1.2 kg/mol PVP/TPP blends revealed temperature dependent morphological changes for all blend compositions that could be consistent with either dewetting or phase separation. X-ray photoelectron spectroscopy was used to further explore the morphological changes. All 1.2 kg/mol PVP/TPP films revealed elemental nitrogen and silicon on the surface before thermal annealing due to a mixture of PVP and TPP being at the surface of the sample. After annealing, all samples lacked the nitrogen peak, and the silicon peak was more intense. The lack of a nitrogen peak after annealing confirms that low molar mass PVP is not present at the surface. The increased intensity of the silicon peak reveals that TPP is adsorbing to the surface, and that the blend is undergoing phase separation rather than dewetting. TPP even completely covered the surface of blends possessing as little as 20 wt% TPP. The surface segregation of TPP during annealing may allow one to transfer a thermally and oxidatively stable TPP coating to the surface of polymer blends.

Introduction
Polyvinylpyrrolidone (PVP) is a polymer that has been used as a sealant to prevent resin ingress into water soluble tooling used for the fabrication of composite parts for aerospace applications. Polyhedral oligomeric silsesquioxane (POSS) molecules (Figure 1) are hybrid molecules with an inorganic core (SiO$_3^{2-}$) and an organic shell (R). Many multi-component polymer systems can be fabricated from POSS since a wide range of functional groups (R) can be integrated into the POSS cage structure. Incorporation of POSS into polymers as blends can dramatically affect composite properties such as the glass transition temperature ($T_g$), structural integrity, solubility, and thermal resistance. Some potential aerospace applications for POSS/polymer blends include insulation for high temperature rocket motor casings, self-healing coatings for space vehicles and satellites, and high speed jet canopies. By combining POSS with PVP, it may be possible to produce high temperature sealants and coatings for aerospace applications if phase separation occurs. In this paper, the phase separation of POSS/PVP polymer blends was studied using optical microscopy and X-ray photoelectron spectroscopy.

Experimental Procedure
Materials. Poly N-vinyl pyrrolidone (PVP) was obtained from Polymer Source, Inc. The PVP has an average molar mass of 1.2 kg/mol and a polydispersity index of $M_w/M_n = 1.2$. Trisilanolphenyl-POSS was obtained from Hybrid Plastics. Trisilanolphenyl-POSS has a molecular weight of 931.34 g/mol. The spincoating machine used was obtained from Headway Research, Inc. An optical microscope (OM) operating in the reflection mode (Axiotech Vario 100 HD, Carl Zeiss, Inc.) with a Linkam temperature controlled stage was used.

Figure 1. Closed cage POSS (top) and trisilanol-POSS (bottom) molecules used in this study. R represents organic substituents.
Silicon Substrate Cleaning Procedure. The silicon substrates were boiled in a 1:1:5 (by vol.) solution of 30% hydrogen peroxide:28% ammonium hydroxide:Millipore water, respectively, for ~1 h. The silicon wafers were then rinsed thoroughly with Millipore water, dried with nitrogen, and placed into a 3:7 (by vol.) solution of 30% hydrogen peroxide:concentrated sulfuric acid (Piranha solution) for ~3 h. After being rinsed thoroughly with Millipore water and dried with nitrogen, the silicon substrates were made hydrophobic by placing them in a 1:7 buffered etch oxide for ~5 min and then into a 40% ammonium fluoride solution for ~1 min.

Preparation of Spin-Coated Films. 3 wt% solutions of low molar mass PVP blended with TPP in different ratios were dissolved in ethanol for spincoating. 20/80, 40/60, 60/40, and 80/20 PVP/TPP blends were prepared by mass. The solutions of PVP/TPP in ethanol were then filtered using 0.5 µm Teflon filters. All of the PVP/TPP solutions were spincoated onto hydrophobic silicon wafers at 2000 rpm for 45 s to obtain films of uniform thicknesses.

Temperature-Ramp Optical Microscopy. TPP/PVP films were placed on a heating stage under a microscope camera. The films were then heated at a rate of 1 °C/min. The temperature ramp began at room temperature and continued to 200 °C. In addition, some films were ramped to 200°C from room temperature at a rate of 30 °C/min and held at 200 °C until no additional morphological changes occurred (temperature jump experiments). Morphological changes in the films were noted and studied, and pictures were taken of the films every minute during the heating process.

X-ray Photoelectron Spectroscopy. Films were subjected to X-ray photoelectron spectroscopy to study the surface of the films after heating. The surfaces of the films were hit with X-rays at a take-off angle of 45°. Energies of electrons bouncing off of the surface were measured to deduce binding energies. The composition of the surface of the films was quantitatively deduced using XPS software.

Results and Discussion

Morphological changes began occurring in 20 wt% 1.2 kg/mol PVP/80 wt% TPP films around 160 °C during a slow temperature ramp (Figure 2).

Figure 2. Optical micrographs of morphological changes in an 80% TPP/20% 1.2 kg/mol PVP blend film as a function of temperature, heating at a rate of 1°C/min: A) 50 °C, B) 150 °C, C) 175 °C. All images are 0.76 mm x 0.57 mm.

Fast heating rate temperature ramps of 20, 40, 60, and 80 wt% 1.2 kg/mol PVP blends with TPP also
showed morphological changes occur below 200 °C. Morphological changes in the films observed by optical microscopy were dewetting and/or phase separation. Hence, an additional characterization technique was required to differentiate between these possibilities. XPS proved to be a suitable technique.

XPS of 20, 40, 60, 80, and 90 wt% PVP of unheated blend films showed elemental nitrogen at 400 eV and silicon bound to oxygen at 102 eV (Figure 3). These features are consistent with PVP and TPP, respectively. Once films were thermally heated, all blend films showed an increase in silicon bound to oxygen at 102 eV. Furthermore, no peak for elemental silicon was observed indicating that only phase separation is occurring in all blends, except for the 20 wt% PVP (Figure 4). In addition, no elemental nitrogen was observed by XPS for blend films after annealing to 200 °C, except for the 90 wt% PVP blend with TPP. Silicon bound to oxygen being present for XPS spectra arises from the inorganic cage structure associated with TPP being present at the surface of the film. In 20 wt% PVP blend films, elemental silicon was found. This elemental silicon arises from holes in the film that allow silicon from the substrate to be measured. These holes in the film cause the data point to be skewed to higher atomic % Si for the 20 wt% PVP film. Before heating the films, XPS shows that the surfaces of the films are a combination of TPP and PVP since both silicon and nitrogen are present. After ramping the films to 200 °C, and after morphological changes have occurred, XPS shows that the surface of the films are purely TPP, since no nitrogen from PVP is seen (Figures 5 and 6).

Figure 3. XPS survey spectra of 60 wt% PVP before annealing. Nitrogen is present at the surface of the film suggesting PVP is present at the surface.

Figure 4. XPS survey spectra of 60 wt% PVP after annealing. A nitrogen peak is no longer present and the silicon peaks have increased in intensity suggesting the surface is 100% TPP.

Figure 5. Atomic % nitrogen versus weight percent TPP in the bulk blend. At 100% PVP at the surface, atomic % nitrogen should theoretically be 12.5%.

Figure 6. Atomic % silicon versus weight percent TPP in the bulk blend. For a surface with 100% TPP, atomic % silicon should theoretically be 11.48%.

Conclusions

Optical microscopy showed structural changes in TPP/PVP blends occur when the blends are heated above 160 °C. Since XPS shows no elemental nitrogen and no elemental silicon at the surfaces of annealed samples, low molar mass PVP and TPP blends are phase separating and not undergoing dewetting. The TPP combined with the low molecular weight PVP seems to phase separate so that the TPP covers the entire surface of the blend. Even blends containing as little as 20 wt% TPP form completely TPP surface coatings upon annealing. In contrast, previous studies of
TPP in high molecular weight (>10^6 g/mol) PVP blends with TPP, failed to completely cover the surface at high PVP blend compositions after thermal annealing. Aerospace applications based on toolless manufacturing seem quite feasible with TPP/PVP blends. In this process, TPP may be transferred from a TPP/PVP blend sealants to enrich the surface of the ultimate part. Such a process would enhance the thermal and oxidative stability of the final part.

**Future Work**

Slow temperature ramps of low molecular weight PVP/TPP blends must be further studied to look at the phase diagram of the blend. Also, lower concentrations of low molecular weight PVP/TPP blends must be studied to determine the lowest concentration of TPP possible to cover the entire surface of the blend.

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