COPOLYIMIDE SURFACE MODIFYING AGENTS FOR PARTICLE ADHESION MITIGATION

Christopher J. Wohl[1], Samantha I. Applin[2], Leanna L. Cooper[2], and John W. Connell[1]

[1]NASA Langley Research Center
Hampton, VA 23681-2199
[2]Langley Aerospace Research Summer Scholar (LARSS)
NASA Langley Research Center
Hampton, VA 23681-2199

Introduction

Marine biofouling, insect adhesion on aircraft surfaces, microbial contamination of sterile environments, and particle contamination all present unique challenges for which researchers have adopted an array of mitigation strategies. Particulate contamination is of interest to NASA regarding exploration of the Moon, Mars, asteroids, etc.[1] Lunar dust compromised seals, clogged filters, abraded visors and space suit surfaces, and was a significant health concern during the Apollo missions.[2] Consequently, NASA has instituted a multi-faceted approach to address dust including use of sacrificial surfaces, active mitigation requiring the use of an external energy source, and passive mitigation utilizing materials with an intrinsic resistance to surface contamination. One passive mitigation strategy is modification of a material's surface energy either chemically or topographically. The focus of this paper is the synthesis and evaluation of novel copolyimide materials with surface modifying agents (SMA, oxetanes) enabling controlled variation of surface chemical composition.

Experimental

Materials. Dimethylacetamide (DMAc), *p*-nitrobenzoyl chloride, triethylamine and anhydrous toluene was purchased from Aldrich Chemical Co. and used as received. Polyoxetane (PF6320) was both donated from Ken Wynne (Virginia Commonwealth University) and purchased from Omnova Solutions Inc and 4,4'-oxydinalinie (4,4'-ODA, Wakayama Seika Kogya Co. Ltd, T_m=188 °C) was used as received. The 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) was purchased from UBE Industries Inc. and purified by refluxing in acetic acid:acetic anhydride (3:1) overnight followed by filtration and vacuum drying.

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker spectrometer operating at 300.152 MHz. XPS measurements were collected on a ThermoFisher ESCAlab 250 X-ray photoelectron spectrometer. Polymer film mechanical properties were determined on a Sintech 2W test frame with a crosshead speed of 5.08 mm/min. Data was collected and analyzed using Testworks 8.0 software. Water contact angle data was collected using a First Ten Angstroms FTA 1000B contact angle goniometer. Material surfaces were imaged using an Olympus BH-2 optical microscope.

Synthesis of Amine-terminated Oxetane Oligomers. *Nitro-termianted oxetane (*Figure 1, **II***) synthesis*: hydroxy-terminated oxetane (**I**, PF 6320, MW=3400 g mol^{-1}, 60.32 g, 17.74 mmol) was dissolved in toluene (150 mL) in a three-necked round-bottomed flask fitted with an addition funnel under nitrogen. Triethylamine (14.52 g, 0.1436 mol) was added and the solution was stirred for 10 minutes and heated to 50 °C. *p*-nitrobenzoyl chloride (10.412 g, 56.1 mmol) was dissolved in toluene (150 mL) and added dropwise to the flask for 30 minutes. The solution was stirred at reflux overnight, then cooled to room temperature, filtered, washed with an aqueous solution of $NaHCO_3$ (5 wt. %, 250 mL, twice) and distilled deionized water (250 mL) and dried over $MgSO_4$. The liquor was then rotary evaporated to yield the crude product as a viscous, honey-colored oil. Vacuum drying yielded the nitro-terminated oxetane oligomer in nearly quantitative yield. The product was characterized by ^{1}H NMR in $CDCl_3$: -CH3, 0.92 PPM, s, 53 H; last repeat unit -CH3, 1.07, s, 6 H; backbone and pendant -CH2-, 3.2-3.5 PPM, m, 122 H; -CH2CF3, 3.72-3.81, m, 41 H; last repeat unit -CH2-, 4.30 PPM, s, 4 H; aromatic -CH-, meta to nitro group, 8.19 PPM, d, 4 H; aromatic -CH-, ortho to nitro group, 8.31 PPM, d, 4 H. Calculated molecular weight: 3580 g mol^{-1}.

*Amine-terminated oxetane (**III**) synthesis*: A 100 mL reaction vessel was charged with the nitro-terminated oxetane (**II**, 8.8 g, 2.4 mmol), Pd/C catalyst (5% Pd, 0.4451 g) and ethanol (40 mL). The vessel, fitted with a rubber stopper and a gas inlet, was placed in a mechanical agitation device. The solution was degassed and subsequently backfilled with H_2 to 30 psi, and agitated overnight. Periodically, the vessel pressure was adjusted to maintain 30 psi. The next day, the remaining hydrogen gas was evacuated from the vessel and the solution was filtered through Celite followed by rotary evaporation to yield the product (8.6 g, 98%). The product was characterized by ^{1}H NMR in $CDCl_3$: -CH3, 0.92 PPM, s, 65 H; last repeat unit -CH3, 1.04, s, 6 H; backbone and pendant -CH2-, 3.17-3.5 PPM, m, 153 H; last repeat unit -CH2-, 3.57 PPM, s, 4 H; -CH2CF3, 3.72-3.81, m, 52 H; aromatic -CH-, ortho to amino group, 6.64 PPM, d, 4 H; aromatic -CH-, meta to amino group, 7.83 PPM, d, 4 H. Calculated molecular weight: 4750 g mol^{-1}.

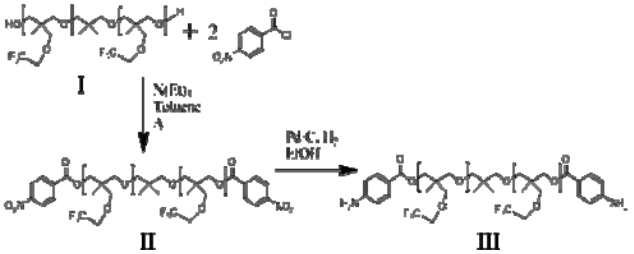

Figure 1. Synthesis of amine-terminated oxetane.

Synthesis of Copoly(imide oxetane)s. Copoly(imide oxetane)s were prepared by the condensation reaction of an aromatic dianhydride with a mixture of an aromatic diamine and the amine-terminated oxetane (**Figure 2**). Reactions were carried out under nitrogen using a 1:0.95 molar ratio of dianhydride and diamines in DMAc. The diamine was dissolved in DMAc, to which the oxetane in DMAc was added followed by the dianhydride and additional solvent to make a 20% (wt.) solids solution. The reaction mixture was stirred overnight. Homopolyimides were generated in the same fashion without the introduction of the oxetane component. Inherent viscosities (η_{inh}) were determined at 25 °C using an Ubbelohde viscometer and solution concentrations of 0.5 g/dL. Films were cast on glass plates using a doctor blade and placed in a forced air drying chamber until "tack-free." Films were then thermally imidized under nitrogen using a cure cycle with stages at 150, 175, 200, and 250 °C with at least a 40 min hold at each temperature.

Evaluation of Substrate-Particle Force of Adhesion. A custom-built particle adhesion detection device was generated to determine the force of adhesion between the copolymer films and particulate contaminants. The details of this device, data collection, and analysis have been reported.[3] Briefly, a 6 mm diameter polymer film sample was adhered to the end of a sonication device. This surface was then coated with an approximate monolayer of the particles of interest (for this work lunar dust simulant, NASA/USGS lunar highland simulant < 30 μm diameter), which was verified using optical microscopy. The particle-coated surface was subjected to a series of sonication steps of increasing magnitude. As the surface acceleration induced a detachment force greater than the force of adhesion, the particles fell from the surface and were collected in an optical particle counter. The surface acceleration at which 50% of the dislodged particles were detected was used to calculate an adhesion force of particles on the surface of interest.

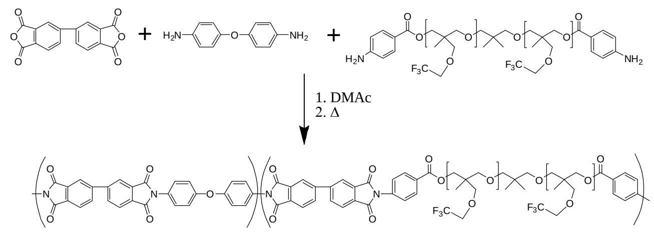

Figure 2. Synthesis of copoly(imide oxetane).

Results and Discussion

Copoly(imide oxetane)s. Surface modifying agents are thermodynamically drawn to the surface of a multicomponent system due to more favorable interactions at the material interface compared to within the bulk matrix (**Figure 3**). This phenomenon was employed to generate polyimide materials with controlled, predetermined, surface chemical compositions. In order to successfully integrate the oxetane SMAs into the polyimide chemistry, their end-groups needed to be modified to either anhydride or amine termini. Therefore, the hydroxyl-terminated oxetanes were converted to amine-terminated species by reaction with *p*-nitrobenzoyl chloride followed by the reduction of the nitro groups (**Figure 1**). These reactions were completed with nearly quantitative yield. The amine-terminated oxetane oligomers were next reacted with aromatic diamine and dianhydride monomers to generate copolyimides through condensation reactions. The oxetane composition was varied from 0.1 to 5.0 wt. % to evaluate the effect on mechanical properties, surface chemistry, and surface energy. The inherent viscosities of the polyamide acid solutions indicated that the copolymers were synthesized at a considerably high molecular weight and would be amenable to generation of free-standing films (Table 1).

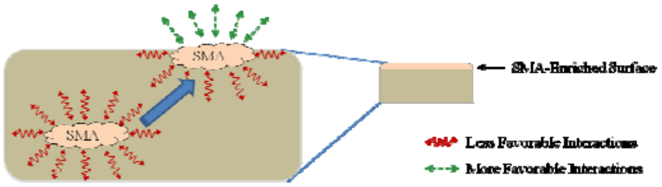

Figure 3. Surface migration arises from more favorable interactions at the sample surface compared to within the bulk matrix.

Copoly(imide oxetane) free-standing films were generated by solution casting the polyamide acid solution followed by thermal imidization in a nitrogen oven. The films were then characterized for mechanical properties and surface chemical properties. According to the tensile tests conducted, incorporation of greater amounts of oxetane resulted in a decrease in the modulus of the film samples (Table 1). This is expected as the modulus of the oxetane component is significantly lower than that of the homopolyimide.

Table 1. Copoly(imide oxetane) characterization values.

oxetane wt. %	η, dL g^{-1}	Modulus, MPa	Contact Angle, °
0	1.4	3590	80.8
0.1	1.2	3560	95.1
0.2	1.2	3510	94.7
0.4	1.3	3450	94.2
0.5	1.1	3350	93.5
0.8	1.0	3460	93.7
1	1.3	3440	97.6
2	1.2	3380	94.3
5	1.3	3140	95.4

Contact angle goniometry was conducted using water as the test fluid. Approximately 8 mL water droplets were placed on the film surface, either air or glass side, and the contact angle of the sessile drop was determined using drop shape analysis (Table 1). Surprisingly, the contact angle on the air-side of the copoly(imide oxetane) films quickly increases from 81 to 95 for the homopolyimide and the copoly(imide oxetane) with 0.1 wt. % oxetane, respectively. At higher oxetane loading levels, the increase in water contact angle is marginal. This result suggested that the surface concentration of the oxetane fluorinated functionalities has already become saturated at only 0.1 wt. % oxetane. To further investigate this, XPS analysis was performed.

XPS measurements conducted on a series of the copoly(imide oxetane)s indicated that saturation of the surface by fluorine functionalities occurred at significantly greater oxetane loading levels, 0.5 wt. % compared to one order of magnitude lower from contact angle results (**Figure 4**). One plausible explanation for this would be that the interrogation depths of contact angle goniometry and XPS are different, 10 Å and 50 Å, respectively. The surface fluorine concentration does not reach that of a pure oxetane layer, likely due to steric hindrance resulting from the covalent attachment to the aromatic imide components. However, the oxetane functionalities clearly migrated to the film surface as indicated by the significant different in surface fluorine concentration as determined by XPS compared to that calculated from the bulk chemical composition.

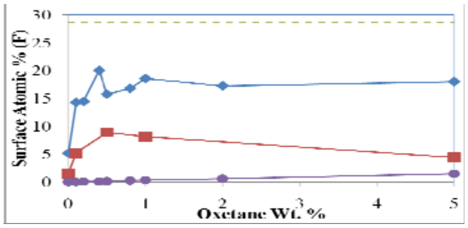

Figure 4. XPS surface fluorine composition data collected on copoly(imide oxetane) film air-side (diamonds), glass-side (squares), and calculated from the bulk chemical composition (circles). The dashed line represents the surface fluorine composition of a pure oxetane layer.

Based on these results, it was intriguing to consider the oxetane loading level required to generate a surface comprised only of oxetane functionalities. With the assumptions that 1) a film was generated from the polyamide acid solution approximately 25.4 cm by 45.7 cm, 2) that the oxetane oligomers are oriented with the polymer backbone parallel to the film surface, 3) the fluorionated functionalities extended above the sample plane and 4) that there was no steric consideration preventing oxetane layer formation, the amount of oxetane required to cover this surface was calculated. Using Hyperchem Lite (Hypercube, Inc.), the area of an oxetane oligomer in a thermodynamically stable geometry with 23.9 repeat units was calculated to be 538 $Å^2$. This would require 3.58×10^{-8} moles of oxetane. Using a partition coefficient of 50 between the surface and bulk and considering the surface to be the first 10 Å, the oxetane concentrations were calculated to be 0.309 M and 6.17 mM for the surface and bulk, respectively. This correlated to a starting oxetane loading of approximately 1.5 wt. %, which was significantly larger than that determined by both contact angle goniometry and XPS.

Particle Adhesion Testing of Copoly(imide oxetane)s. Determination of the force of adhesion between a lunar simulant particle and the copoly(imide siloxane) surfaces was determined using a custom-built particle adhesion testing device. Preliminary results indicate that the copoly(imide oxetane)s exhibit improved surface clearance and potentially lower adhesion force values compared to the homopolyimide. It is anticipated that the adhesion force should have a dependence on the amount of oxetane in the copolymer and that is currently being evaluated.

Conclusions

Copoly(imide oxetane)s were generated with controllable surface chemistries and reduced surface energies as indicated by contact angle goniometry and XPS. Initial particle adhesion studies indicate that these materials could potentially be of utility for the purposes of environmental contamination mitigation. Pairing these materials with an active mitigation strategy is likely to be more effective and methodologies to do so are currently being investigated.

Acknowledgements. The authors would like to thank Dr. Kenneth Wynne from Virginia Commonwealth University for supplying hydroxyl terminated oxetane oligomers and for helpful technical discussions, Drs. Everett Carpenter and Dmitri Pestov for XPS analysis at the VCU Nanomaterials Characterization Facility, and the NASA Langley Creative and Innovative program for financial support of this research.

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