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"Vampire Plastics": An Investigation of Poly(olefin sulfone) Depolymerization and Its Dust Mitigation Abilities

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A thesis submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of

Master of Science

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ABSTRACT

"Vampire Plastics": An Investigation of Poly(olefin sulfone) Depolymerization and Its Dust Mitigation Abilities

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Master of Science

The ubiquity of particulate contamination requires dust mitigation techniques to provide low-scatter surfaces and edges on sensitive optical devices in space. Poly(olefin sulfone)s have been shown to photodegrade with the assistance of a photobase generator when exposed to UV light (254 nm) and heat (120 °C). These polymers may be useful for minimizing dust on optical surfaces for space applications. However, their behavior in vacuum has not been fully characterized. We synthesized poly(2-methyl-1-pentene sulfone) (PMPS) and poly(1-hexene sulfone) (PHS) with and without a photobase generator. We studied the photodegradation (172 nm or 254 nm) of thin films in vacuum. Spectroscopic ellipsometry was used to quantify film thickness over time. The PMPS and PHS films both degraded when exposed to UV light in vacuum, though PHS to a lesser degree. We found that heat was not required to cause degradation, and that degradation occurred with UV irradiation even without a photobase generator. We also found that the degradation process removes dust particles as the film disappears. This investigation shows that poly(olefin sulfone)s could be used to protect optical surfaces until after their deployment in space.

Keywords: Poly(olefin sulfone), thin films, self-immolating polymers, space instrumentation, photodegradation, photobase generator

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Chapter 1

Introduction

The ability to manipulate particles is a challenge that affects many disciplines of science and technology [1]. Particulate contamination has adverse effects on space applications ranging from optical instrumentation to human space flight to the surface of extraterrestrial objects. On optical instrumentation, light-scattering particles could frustrate advances in exoplanetary discovery [2]. We investigate a dust mitigation method that involves developing a protective coating to cover a sensitive optical instrument before damaging particulates could accumulate during manufacturing and storage. This coating would self-immolate once the instrument is deployed outside of the Earth's atmosphere, leaving a clean surface.

To identify a polymer film that could protect a surface until it is outside of Earth's atmosphere, we investigate self-immolating polymers [3]. Specifically, if a polymer is sensitive to UV-C light (100-280 nm), which is only readily available naturally in space, then the polymer film would not dissociate until the object being protected is already outside of Earth's atmosphere.

1.1 Motivation

This project was motivated by the problem of dust accumulation on spacecraft prior to deployment. One specific instrument that is currently in technological development that would benefit from a protective sacrificial film is a starshade.

A starshade (Fig. 1.1) is an external occulter used in conjunction with a telescope to facilitate imaging of exoplanets. Exoplanets are small, rocky planets in the habitable zones of other solar systems. Although exoplanets have been indirectly detected for many years [4], to image one is a challenge akin to finding a strand of hair on Everest. This is because they are obscured by the light of their host stars. Exoplanets could be directly imaged for the first time using this developing technology, the starshade [4]. The starshade is useful because it suppresses the light of the host star, which is billions of times brighter than the nearby exoplanet. This works much like if an observer were to block the light of the sun with their thumb in order to better see an airplane flying by. In fact, a starshade can provide an exoplanet-seeking telescope with 10^{10} contrast [5].

1.1.1 Starshades

The National Academies of Sciences, Engineering and Medicine (NASEM) decadal survey announced that starshades will be a priority in future missions, but they are still in need of technological development [6]. It is stated that "a starshade with its highly desirable properties of very small inner working angle and overall larger area of high contrast...is rated as a medium risk with more development needed [6]." The risk in using starshades is that the petal edges and planar surfaces need to be very precise to provide sufficient contrast for imaging exoplanets. Although efforts are made to maintain a clean environment, it is estimated that the cleanrooms in which the starshade is assembled, manufactured, and stored contain between 10,000 and 100,000 particles per cubic foot [2]. A similar estimation of potential contamination is expected at launch. Furthermore, the

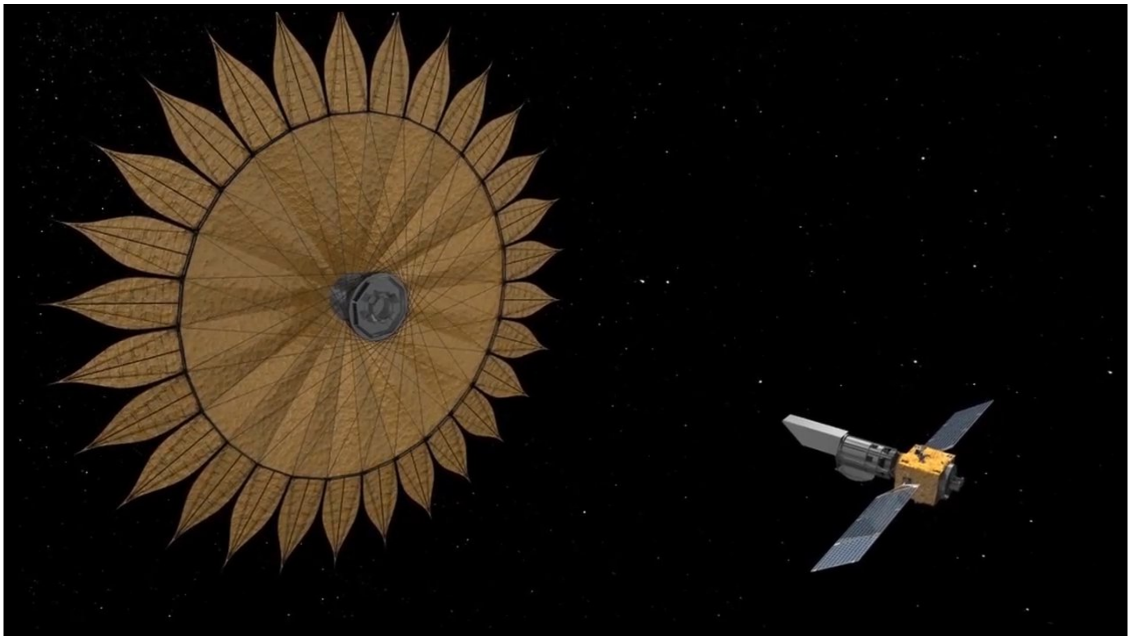


Figure 1.1 An artist's rendition of a starshade. A starshade acts as an external occultor for a telescope. [7]

starshade petals will not necessarily be co-planar. Thus, solar glint off particulates on the surfaces would cause additional scattering. Therefore, dust mitigation techniques must be implemented on both the edges and planar surfaces of the starshade to minimize the risk of compromising the images collected by the telescope. This starshade problem motivates our investigation into a dust mitigation method that involves developing a protective coating to cover a sensitive optical instrument–such as the starshade–before these particulates could accumulate during manufacturing and storage.

Contemporary dust mitigation techniques, such as First Contact® Polymer, may be used [8]. However, they leave a window of time where dust can accumulate. A First Contact® Polymer coating must be peeled off by hand before launch, leaving the surface uncovered throughout the transportation process. The advantage of a self-immolating coating is that there would be no period of time between production and deployment that the starshade would be unprotected.

Although this project was specifically motivated by the starshade problem, contamination control is a concern that spans microelectronics, military technology, hydraulics, optics, and many more fields. Therefore, the results of this project should be of general importance as well as potentially informative for future research on space instrumentation.

1.2 Background

Developing a thin film coating that disappears outside of Earth's atmosphere demands that we find a material that would be sensitive to extraterrestrial solar irradiation. Certain polymers have been previously shown to depolymerize when exposed to UV-C light. The specific polymer that we investigate is poly(olefin sulfone).

1.2.1 Poly(olefin sulfone)

Poly(olefin sulfone) is a 1:1 alternating copolymer of olefin monomers and sulfur dioxide (Fig. 1a). Previous characterization has indicated that "they possess sulfonyl groups (-SO_2-) in the main chain and are easily synthesized by radical polymerization of an olefin monomer in a liquefied sulfur dioxide [3]." The sulfonyl group is electron-withdrawing, attracting the electrons from the adjacent carbon atoms. This leaves an acidic proton that can be easily abstracted by a base. When this happens, a chain depolymerization reaction then occurs that reverts the poly(olefin sulfone) back into its subunits of sulfur dioxide and olefin monomers [9].

1.2.2 Previous Work

Experiments have shown that poly(olefin sulfone) degrades when mixed with a photobase generator (PBG) upon irradiation with UV-C light and subsequent heating (Fig. 1.2a) [9, 10]. The PBG is physically altered when subject to 254-nm light, generating reactive intermediates that act as a base for the depolymerization chain reaction (Fig. 1.2b) [11]. The 254-nm wavelength is a strong mercury line [12]. One study found that using an [(O-nitro benzyl)oxy]carbonyl moiety as the PBG was the

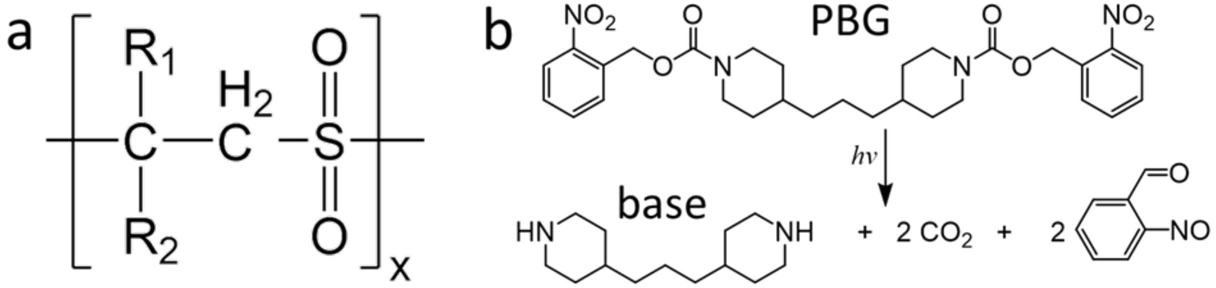


Figure 1.2 (a) Structure of poly(olefin sulfone)s where R_1 = CH_3 and R_2 = $CH_2CH_2CH_2$ for poly(2-methyl 1-pentene sulfone) (PMPS) and R_1 = H and R2 = $CH_2CH_2CH_2CH_3$ for poly(1-hexene sulfone) (PHS). (b) Photobase generator (PBG). With UV irradiation, the PBG converts to related photodegradation products, including the secondary amine, which acts as a base.

most effective for depolymerization [13]. The [(O-nitro-benzyl)oxy]carbonyl-derived carbamates in the PBG structure absorb light from approximately 400 nm to the deep UV wavelengths [14].

Sasaki et al. investigated the photoinduced depolymerization of poly(olefin sulfone) mixed with a photobase generator, comparing various olefin monomers [10]. After irradiation, poly(2-methyl 1-pentene sulfone) (PMPS) had the lowest residual ratio of all the poly(olefin sulfone)s that were tested. Residual ratio is a critical consideration in our experiment. According to Sasaki's publication, "the [degradation] extent of PMPS irradiated at 600 mJ/cm^2 followed by heating at 150°C for 15 minutes was estimated by the change in absorption spectra to be 95% [10]." According to extraterrestrial solar irradiance spectrum, we can expect up to 0.293 $W\ m^{-2}\ nm^{-1}$ at these wavelengths [15]. Therefore, we can estimate that this process would take about 45 minutes if the irradiation occurred using extraterrestrial solar irradiance.

Sasaki showed that PMPS degraded the most efficiently relative to other poly(olefin sulfone)s tested [10]. For this reason, our experiment focuses on characterizing the depolymerization conditions of PMPS in particular. We also chose to experiment with another poly(olefin sulfone), poly(1-hexene sulfone) (PHS), as it is potentially less costly.

Based on Sasaki's investigation of PMPS, we know that the polymer can degrade after irradiation and subsequent heating. Previously, poly(olefin sulfone) has been studied for use in composite photoresists to allow for dry photolithography methods [16]. Our study uniquely focuses on its use on optical equipment in space, such as starshades.

In completing the work for my senior thesis, I further concluded that that poly(olefin sulfone) can photodegrade in vacuum when exposed to a 172 nm UV lamp without the need for a heating step [17]. It does not degrade in a vacuum environment without UV exposure. Moreover, a degradation pattern was observed whether the PMPS was doped with PBG or not. These results indicated that PMPS does degrade under the conditions necessary for space applications, warranting further investigation.

1.3 Problem Addressed

The intent of this experiment is to investigate a potential solution to optical scattering from particulate contamination by characterizing a polymer film that will evaporate when exposed to ultraviolet light outside of Earth's atmosphere. This technique could be useful for a variety of applications, including telescopes, sensitive optical equipment, and other surfaces that need to be dust-free in space. To accomplish this, the experiment must consist of two parts: first, we complete characterization of the depolymerization process, and second, we quantify the coating's ability to mitigate dust particulates.

Chapter 2

Methodology

To investigate poly(olefin sulfone) for potential use in space applications, we make thin polymer films of various compositions. We characterized the degradation of PMPS and PHS thin films by placing them in vacuum and exposing them to either 254-nm or 172-nm UV light to simulate a space like environment. Their degradation rates were measured using spectroscopic ellipsometry. Later, particulate contamination on the samples was quantified using a digital microscope and subsequent analysis. The goal of the second portion of the experiment was to produce quantitative descriptions of the change in contamination levels on a polymer thin film sample after treatment.

2.1 Materials

The first step in this process was to make PMPS and PHS into thin film coatings. In the early stages of this experiment, the polymer was acquired from Dr. Takeo Sasaki, but later, we were able to synthesize PMPS and PHS at BYU. All reagents for the synthesis of poly(olefin sulfone) were purchased from a commercial supplier (Sigma-Aldrich) and used without further purification. PMPS and PHS were synthesized using an adaptation of the procedure described by Sasaki et al. [10]. In a round-bottom flask under nitrogen gas, 1 g of olefin, either 2-methyl-1-pentene for

PMPS or 1-hexene for PHS, was combined with 250 μL of the initiator, t-butyl hydroperoxide, at -196°C (liquid$_2$). The flask containing olefin and initiator was evacuated, warmed to -30°C, and backfilled with nitrogen gas. This freeze-pump-thaw process was repeated three times, and the flask was returned to -196°C. Next, approximately 10 g of SO_2 was added to the cold reaction flask from a lecture bottle. The mass added was determined by measuring the mass of the lecture bottle before and after adding SO_2. The cold reaction flask was warmed to -70°C by transferring into an ethanol/dry ice bath for one hour and then a saltwater ice bath (-10°C) for one hour. The reaction flask was then allowed to warm to room temperature over one hour. Following reaction, the resulting polymer was dissolved in 25 mL of acetone overnight and then precipitated in 500 mL of methanol. The precipitated polymers were removed from methanol, dried under vacuum, and characterized by ^{1}H NMR (500 MHz, $CDCl_3$).

2.1.1 Sample Preparation

The thin film samples were prepared by dissolving the PMPS or PHS in tetrahydrofuran (THF). Some samples were mixed with approximately 10% by weight of a photobase generator. Substrates were obtained by cleaving 6-inch, single-crystal (100) silicon wafers. The polymer solutions were made into thin films by applying drops to a silicon wafer using an eyedropper, then spinning it to create an evenly-coated surface. This process typically resulted in a film thickness of about 80-200 nm. These films were stored for at least 24 hours to allow for solvent to evaporate before proceeding.

2.2 Experimental Setup

The goal of our experiment is to test the poly(olefin sulfone) in a space-like environment, so we need the samples to be placed in vacuum and simultaneously exposed to ultraviolet light. We built a vacuum system that is connected to a lipless 25-mm-diameter quartz tube with one end closed. The base pressure inside the vacuum system was typically about 10^{-5} to 10^{-6} torr. Quartz is exceptionally transparent to UV light [18], so samples placed in the quartz tube could be in vacuum while irradiated by a UV light outside the tube. Micro Combustion tubes from QSI were employed. This synthetic quartz is preferred because it can transmit wavelengths below 0.2 microns. This was necessary for the studies using the 172-nm lamp.

2.2.1 UV Light Sources

For these experiments, we used a 172-nm Xe-excimer lamp (REX-4, Resonance Ltd, Barrie, ON) and a 254-nm 25-W germicidal UV-C lamp (UVC CFL 25W, G6 Wellness). The excimer lamp produces ozone, so it and the quartz tube were placed in a ventilated chemical fume hood. While in the tube, the samples were 4 cm away from the 172-nm light source or 9 cm from the 254-nm light source.

We were not able to measure photon flux from our experimental setup. However, we were able to estimate the irradiance of the 172-nm and 254-nm lamps from manufacturer specifications. The 172-nm lamp behaves as an extended source and has an average irradiance of 12 mW/cm^2. The 254-nm lamp was a compact fluorescent mercury vapor lamp. Conventional mercury vapor UV-C lamps operate at about 36% efficiency [19]. The irradiance was estimated at 9 cm from the UV lamp using Keitz formula (Eq. 2.1) [20] where E is measured irradiance, D is is distance from the lamp to the sample, L is the lamp arc length, and α is the half angle (radians) subtended by the lamp at the sensor position:

$$E = P(2\alpha + sin(2\alpha))/(2\pi^2 DL) \tag{2.1}$$

Based on this approach, the irradiance of the 254-nm lamp at 9 cm onto 1 × 1 cm sample was estimated as 11 mW/cm^2. Thus, the irradiance from both lamps was comparable within 10%.

2.3 Procedure

The two different studies, characterizing the degradation and quantifying dust mitigation, required different procedures. For the degradation study, we used spectroscopic ellipsometry to incrementally track the degradation pattern of the thin films. In the dust mitigation study, we was more interested in the effects of degradation than the mechanism. Therefore, we used a digital microscope and analysis software to quantify dust on the surface of the thin film before and after treatment.

2.3.1 Procedure for Degradation Studies

To characterize the degradation of the polymer films, a sample was irradiated by the 172-nm lamp or 254-nm lamp for about 20 minutes in the vacuum system. Next, the sample was removed, and the thickness was measured using ellipsometry. Finally, we returned to exposing the sample, and the process was repeated until a degradation pattern was observed. Samples of each type, with and without photobase, were also subjects of control experiments: vacuum-only and heat-only. By testing each of these experimental groups, we were able to draw conclusions about the need for a photobase generator, the previously reported heating step, and the ability of PMPS to degrade in a space-like environment.

The thickness of the samples at each increment was determined using ellipsometry. Ellipsometry data was acquired using a J.A. Woollam RC2 variable-angle, spectroscopic ellipsometer (J.A. Woollam Company, Lincoln, NE, USA). The analysis was performed with CompleteEASE® instrument analysis software. We used a general oscillator ellipsometry model to evaluate the thickness of the PMPS. The Cody-Lorentz dispersion equation [14] and a Gaussian best fit the thin film sample. The rest of the layers' optical constants are from the CompleteEASE® database: NTVE-JAW2 [21], INTR-JAW2 [22], and Si-JAW2 [23].

2.3.2 Procedure for Dust Mitigation Studies

We prepared samples for the dust mitigation study by applying a light coating of dust to the surface. We used a silicate dust simulant, DUST-Y (Exolith Lab) to perform the dust mitigation experiments [24]. Dust was deposited on a thin film sample using an atomizer. The sample was placed in a plastic bag, the atomizer was held approximately ten inches from the sample inside the bag, and then squeezed once to deposit an even coating of dust. After about ten seconds, the sample was removed from the bag.

To collect data on the amount of dust on the surface, we gathered images of the thin film using a Keyence VHX-7000 Microscope. Images were collected of the entire surface of each sample at the same magnification across all samples.

ImageJ's FIJI software was used to identify and count dust particles in the images that were collected by the microscope through the following procedure. First, we calibrated the particle measurements based on the actual width of the images collected. Next, we used a "color threshold" to account for thin film interference. This step ensured that most of the color in the background caused by the incident light on the thin film would not be counted as particulate. Finally, we ensured that the program would only "count" particles that were above a threshold diameter of 5 microns (approximating a circular particle). This threshold accounts for "noise" caused by the ring lighting and features that are unlikely to be dust particles [24].

This analysis procedure allowed us to collect data on the number of particles, their size, and the percent area coverage (PAC). Therefore, the results of this process include information about relative number of dust particles, as well as relative PAC, in each image collected.

After collecting this data, we used MATLAB to implement a 1.5 IQR (interquartile range) test to eliminate outliers. Once outliers were removed, we recorded the mean and standard deviation of the particle count and PAC for the sample based on all the corresponding images. This process allowed us to use statistical analysis to determine if significant quantities of dust were leaving the sample after the polymer degradation process compared to the controls.

Chapter 3

Results

This chapter describes the results of both phases of this experiment: first, characterizing degradation, and second, quantifying dust mitigation.

3.1 Characterizing Poly(olefin sulfone) Degradation

We characterized the degradation of poly(olefin sulfone) by making PMPS and PHS thin films so that we could quantify their thicknesses using spectroscopic ellipsometry. These films were placed in vacuum and exposed to 172-nm and 254-nm UV light to perform the experiment in a space like environment. We also performed control experiments in which the samples were placed in a vacuum environment or exposed to heat without being irradiated.

3.1.1 Control Experiments

First, control experiments – in which six PMPS thin film samples with PBG were placed in vacuum – showed that there were no statistically significant changes in thickness over 24 hours, as determined from their p-value and coefficient of determination ($p = 0.16$ and $R^2 = 0.14$). We performed a similar control experiment in which three PHS samples with PBG were placed in vacuum. These experiments also showed that there are no statistically significant changes in thickness over 72 hours ($p = 0.25$). Thus, the polymer is stable until exposed to UV light. This experiment also confirms that any decrease in film thickness is not simply due to solvent removal under reduced pressure.

Another control experiment tested the effect of heat on the stability of the polymer. We exposed two thin film PMPS with PBG samples (approximately 1000 nm and 200 nm thick) to 120°C, but without UV light or vacuum. A small decrease in thickness (less than 20%), over 1000 minutes was observed for the 1000-nm sample (for five measurements, $p = 0.17$ and $R^2 = 0.75$). A 10% decrease was observed for the 200-nm film (for nine measurements, $p = 0.08$ and $R^2 = 0.94$). Thus, there is a small but significant decrease due to heating at 120°C. PHS samples without PBG (250-290 nm) decreased in thickness by approximately 15% over 4365 minutes. We conclude that there is also a small but significant decrease due to heating of the PHS samples at 120°C ($p = 0.05$, $R^2 = 0.62$).

3.1.2 PMPS and PHS

Next, we exposed samples coated with PMPS or PHS to vacuum and UV light. The experiment on PMPS-coated samples consisted of four experimental groups: PMPS with and without PBG exposed to 172-nm light, and PMPS with and without PBG exposed to 254-nm light. The behavior of these four types of samples is plotted in Fig. 3.1. Similar experiments were conducted on PHS-coated samples: PHS with and without PBG exposed to 172-nm light, and PHS with and without PBG exposed to 254-nm light (Fig. 3.2).

While the PBG was necessary for degradation of poly(olefin sulfone)s in air [10], our results indicate that in vacuum, the degradation of both PMPS and PHS is possible at both 172 nm and 254 nm even in the absence of the photobase generator. The only sample where the PBG made an obvious difference under our vacuum conditions is in the degradation of the PHS film at 254 nm. In every other case, the film degradation without PBG is comparable to the film degradation

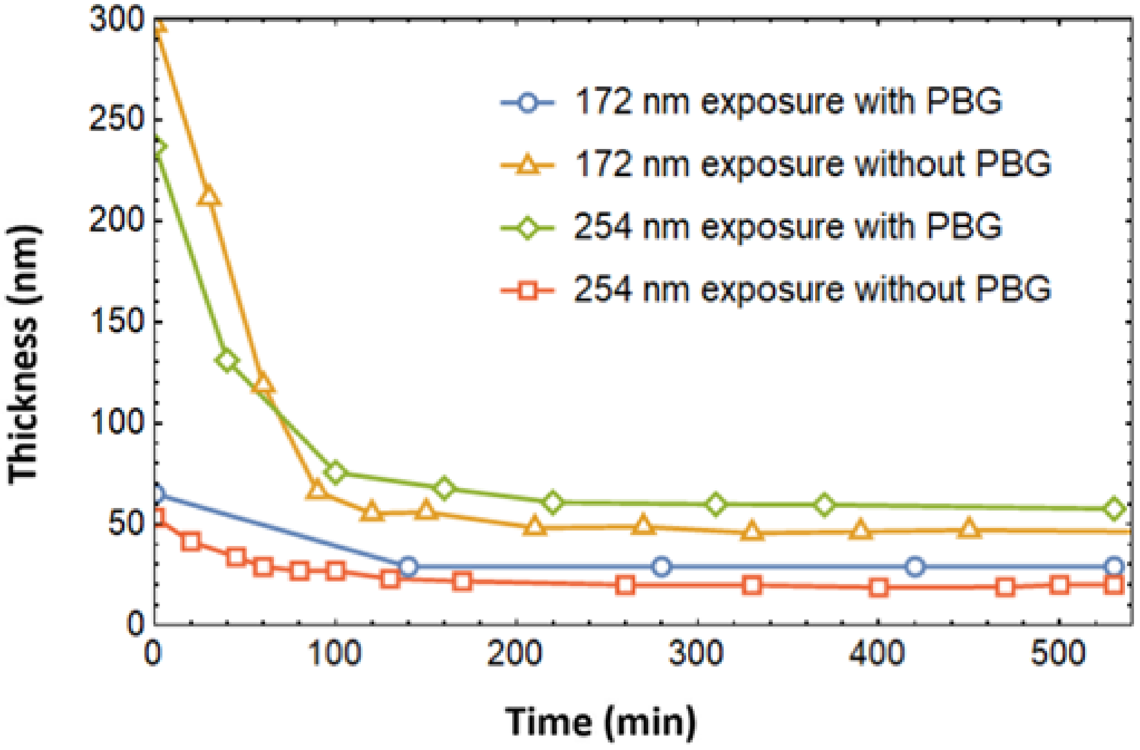


Figure 3.1 Degradation of PMPS samples from each experimental group over 530 minutes, at 172-nm or 254-nm irradiation and with and without photobase generator (PBG). The films had varying thicknesses to start because different polymer-solvent solutions produced different viscosities before the spin-coating process. The initial film thickness seems to influence the degradation rate and final thickness.

with PBG. In the case of PMPS, PBG makes no difference in degradation results under vacuum conditions with either 172- or 254-nm exposure. Furthermore, even in the case of PHS without PBG, significant degradation is still possible, albeit at a slower rate.

There was one case from which we observed more extensive degradation in four PMPS samples (with PBG) that were irradiated together simultaneously. These samples degraded from an initial thickness of approximately 200 nm a very low residual ratio. These residual thicknesses after 470 minutes of irradiation by the 172-nm lamp in vacuum were 0.68 nm, 0.51 nm, 1.06 nm, and 0.72 nm. While these results were indicative of potential for near-complete polymer degradation, they were not reproducible, and therefore, not included in our main results.

3.2 Dust Experiments

Polymer thin films that can disappear in a vacuum are remarkable, but we also investigated its ability as a potential dust mitigation technique.

3.2.1 Dust Mitigation Results

We chose to focus our efforts in this study on PMPS because it degrades more efficiently than PHS. We also chose to mainly use a 254-nm light, which is more widely used in experiments.

Dust was deposited on PMPS films that were not doped with PBG and degraded using the same process as discussed in section 2.3.1. As a control, another group of the same kind of sample were stored in the vacuum system for the same period of time, but without exposure to the UV light. Another group was stored in the lab environment and received no treatment. Furthermore, we performed the irradiation treatment and the vacuum control with the samples upside-down to probe the effects of gravity on this experiment. The results can be found in Fig. 3.3.

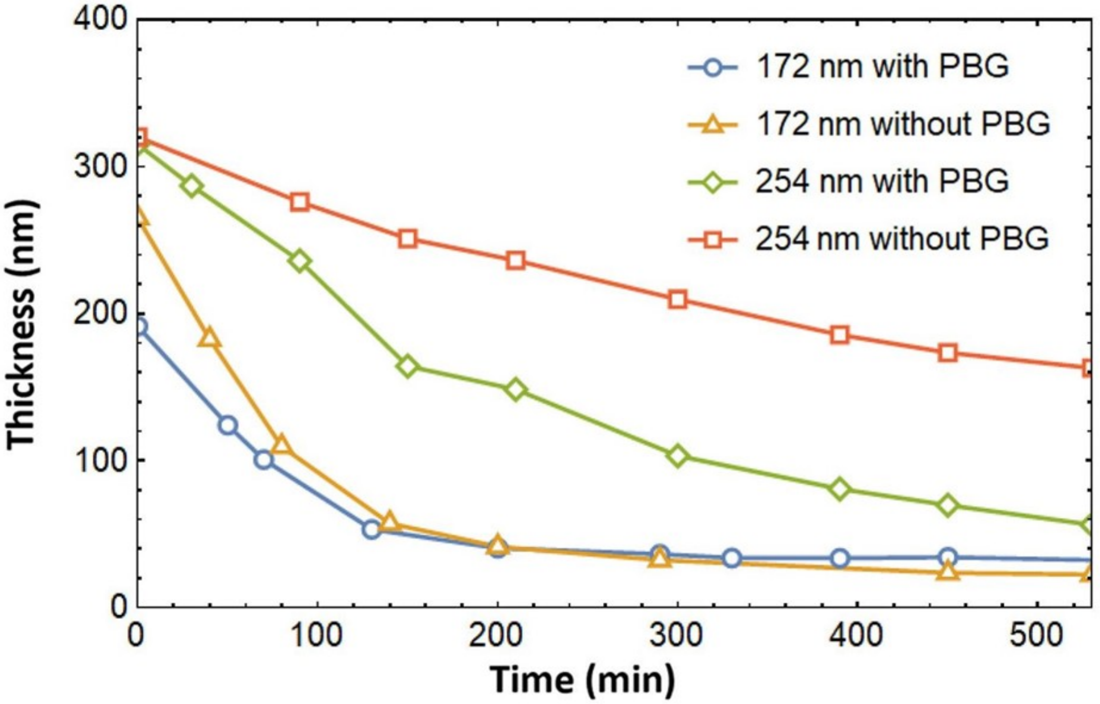


Figure 3.2 Degradation of PHS samples from each experimental group over 530 minutes, at 172-nm or 254-nm irradiation and with and without photobase generator (PBG). Similarly to Fig. 3.1, these films had varying thicknesses to start because different polymer-solvent solutions produced different viscosities before the spin-coating process. The initial film thickness seems to influence the degradation rate and final thickness in the case of these experimental groups, as well.

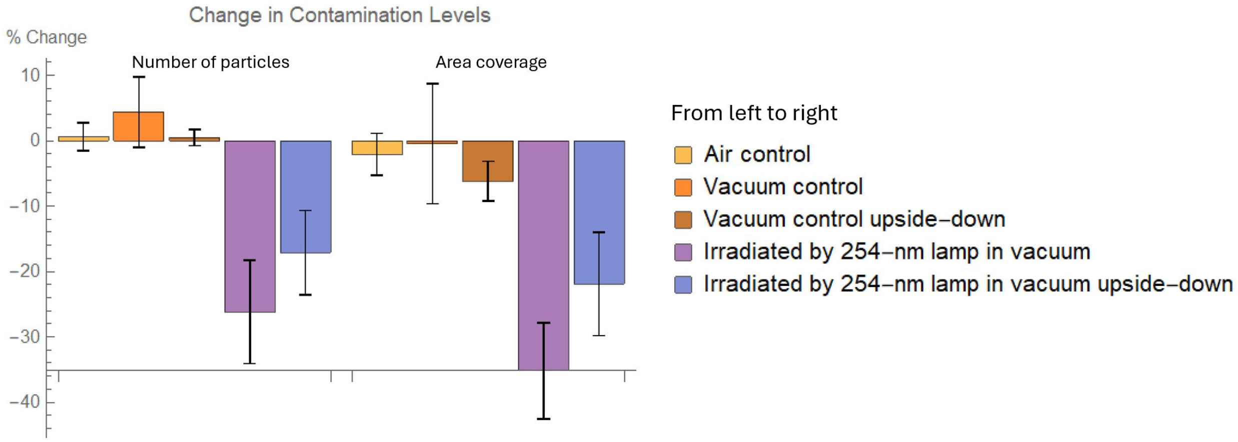
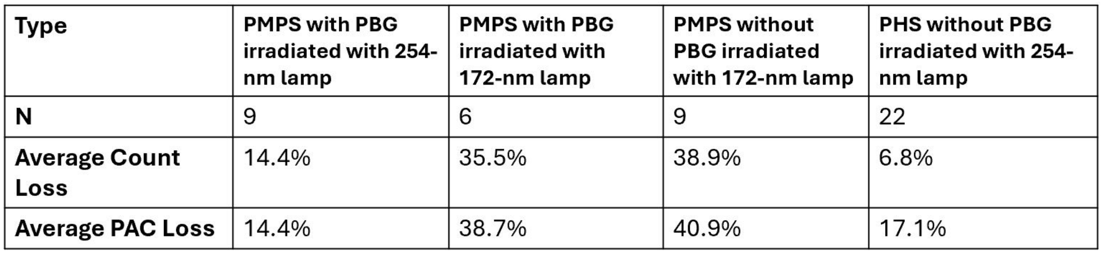


Figure 3.3 Relative change in contamination levels on PMPS thin film samples. Each color represents a different experimental group. Each bar represents the average of all the samples in an experimental group, and the error bars represents the corresponding standard error. The data in the left is calculated based on the change in particle count. The data on the right represents change in percent area coverage (PAC).

We see that the results are similar whether we consider the number of dust particles or the PAC. In both cases, the samples that are exposed the UV light experience a significant loss of particles on their surfaces compared to the controls. On average, the samples decreased in particle count and PAC by 26.2% and 35.2%, respectively.

3.2.2 Other Experimental Groups

Although the focus of this experiment was on samples irradiated by the 254-nm lamp that contained no PBG, we did test some other experimental groups to probe their potential. Fig. 3.4 gives the results of these preliminary experiments.



Type	PMPS with PBG irradiated with 254-nm lamp	PMPS with PBG irradiated with 172-nm lamp	PMPS without PBG irradiated with 172-nm lamp	PHS without PBG irradiated with 254-nm lamp
N	9	6	9	22
Average Count Loss	14.4%	35.5%	38.9%	6.8%
Average PAC Loss	14.4%	38.7%	40.9%	17.1%

Figure 3.4 Results of tests probing the potential of alternative experimental groups. N = number of samples.

Chapter 4

Discussion and Conclusions

In this section, I discuss the differences between PMPS and PHS that explain some of our results. I also mention sources of potential error in our experiment and a defense of my methodology. Finally, I illuminate areas for further research and enumerate the conclusions from my study.

4.1 Discussion

4.1.1 Differences Between PMPS and PHS

One obvious conclusion to our degradation studies is that PMPS depolymerizes more efficiently than PHS in vacuum when exposed to 254-nm or 172-nm UV light. This result agrees with Sasaki's experiment in air with heat [10]. This is due to the differences in depolymerization reactions between PMPS and PHS that exist irrespective of those experiment variables [25].

The depolymerization reactions in PMPS and PHS are distinct because each has a different number of hydrogen types in their main chains. PMPS has one type of hydrogen, methylene hydrogen, in the main-chain. Meanwhile, PHS has two, methylene and methine (Fig. 4.1a). The base removes protons from the main chains of the polymer. In PMPS, only one type of proton

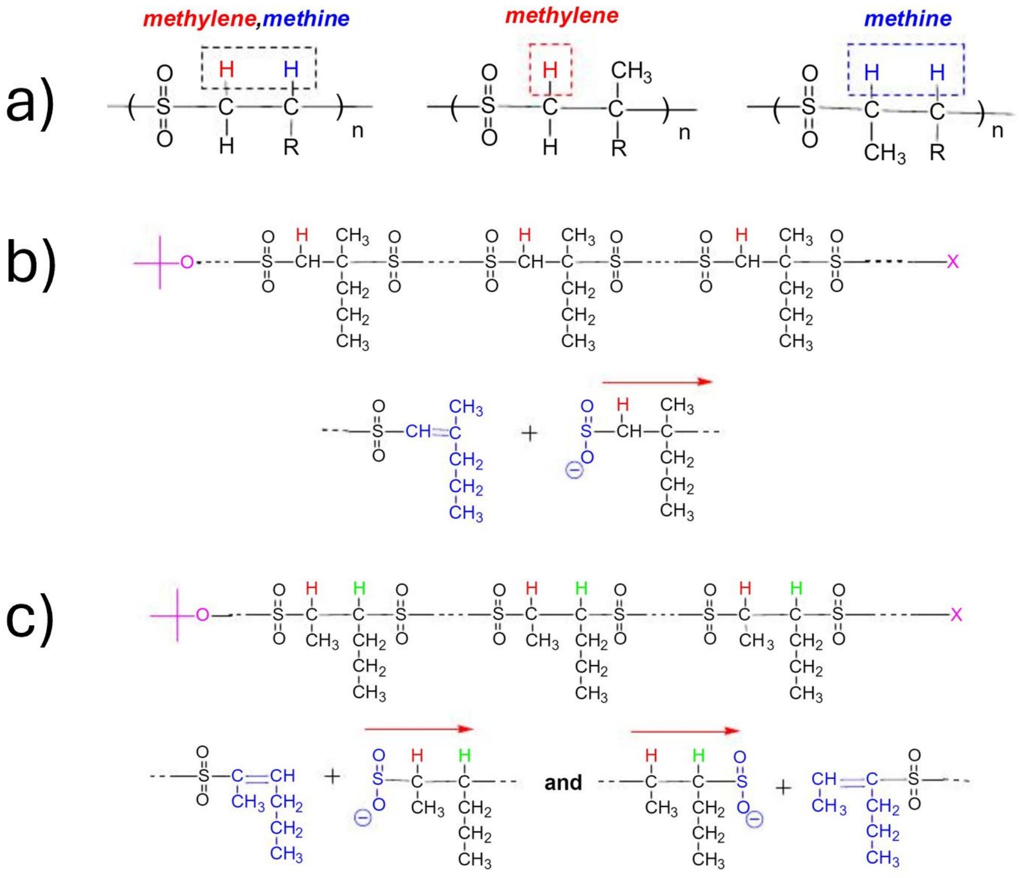


Figure 4.1 a) PMPS has only one type of hydrogen (methylene hydrogen) in the main-chain, while PHS has two types (methylene and methine). b) In PMPS, only one type of proton gets removed during depolymerization, which makes the reaction simple and smooth. c) In PHS, there are two types of protons that can be removed by a base, making the depolymerization reaction complex and prone to termination [25].

gets removed during depolymerization, which makes the reaction smooth (Fig. 4.1b). However, in PHS, there are two types of protons that can be removed by a base, making the depolymerization reaction more complex (Fig, 4.1c). The existence of two types of hydrogen makes PHS more prone to termination.

4.1.2 Sources of Error

It is important to note that our methodology necessitates a statistical analysis of our data. There are many potential sources of error that make exactly counting dust particles impossible. These sources of error during data collection include variation in the boundaries of the images collected, removing or shifting particles due to handling, and light-oversaturated particles appearing bigger than they are. Sources of error in the data analysis may include limitations in the program's ability to distinguish particles from features of the thin film. Some of these features can be seen in Fig. 4.2.

Moreover, in the nature of partially transparent thin films such as the ones used in this experiment, we observe the effects of thin film interference. In some samples, this interference would cause the "background" to be colorful or grainy. To analyze these samples, we neutralized the problematic background by manipulating the color threshold. This would involve excluding pixels of a certain color, saturation, or brightness from the particle count. While this was effective, it also excluded any part of a "real" particle that was in the spectral band defined by the color threshold.

To mitigate the influence of these potential sources of error, we sought to collect enough data for thorough statistical analysis. Each experimental group contained at least thirty samples to comply with the central limit theorem [26]. Each sample consisted of about 200-300 images of the thin film surface. In total, the team collected over 100,000 images, allowing for robust statistical analysis.

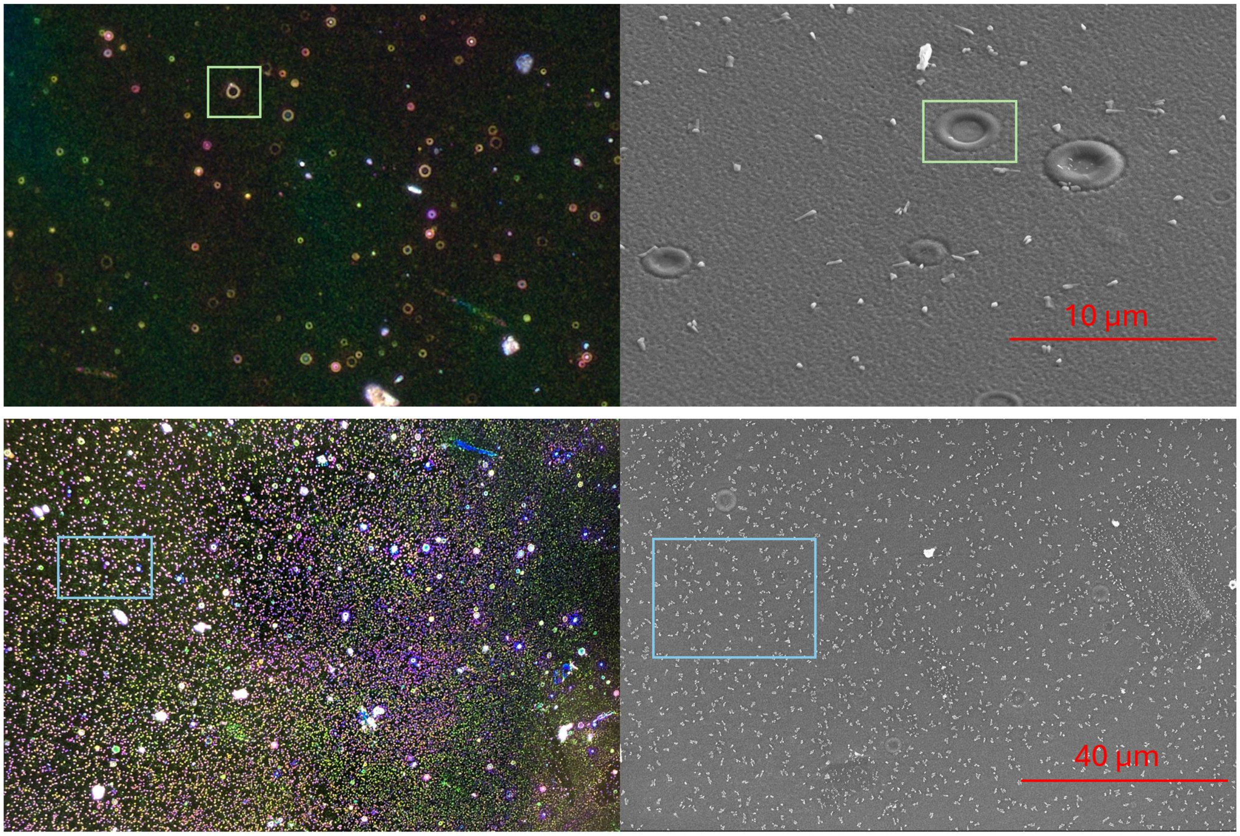


Figure 4.2 Features observed under the Keyence microscope during data collection (left) and an investigation of those features using scanning election microscopy (SEM) (right). Each of these images show a small portion of a sample that has been irradiated. These selected portions are good representations of the features we wanted to investigate, but are not necessarily representative of the whole sample's surface. a) These rings are common in the images collected by the light microscope. Using SEM, we were able to observe that these circles were donut-shaped features in the film. b) Small dots that light up like glitter under the ring light are also common. These dots are significantly smaller and appear more colorful than dust particles. They could also be observed using SEM.

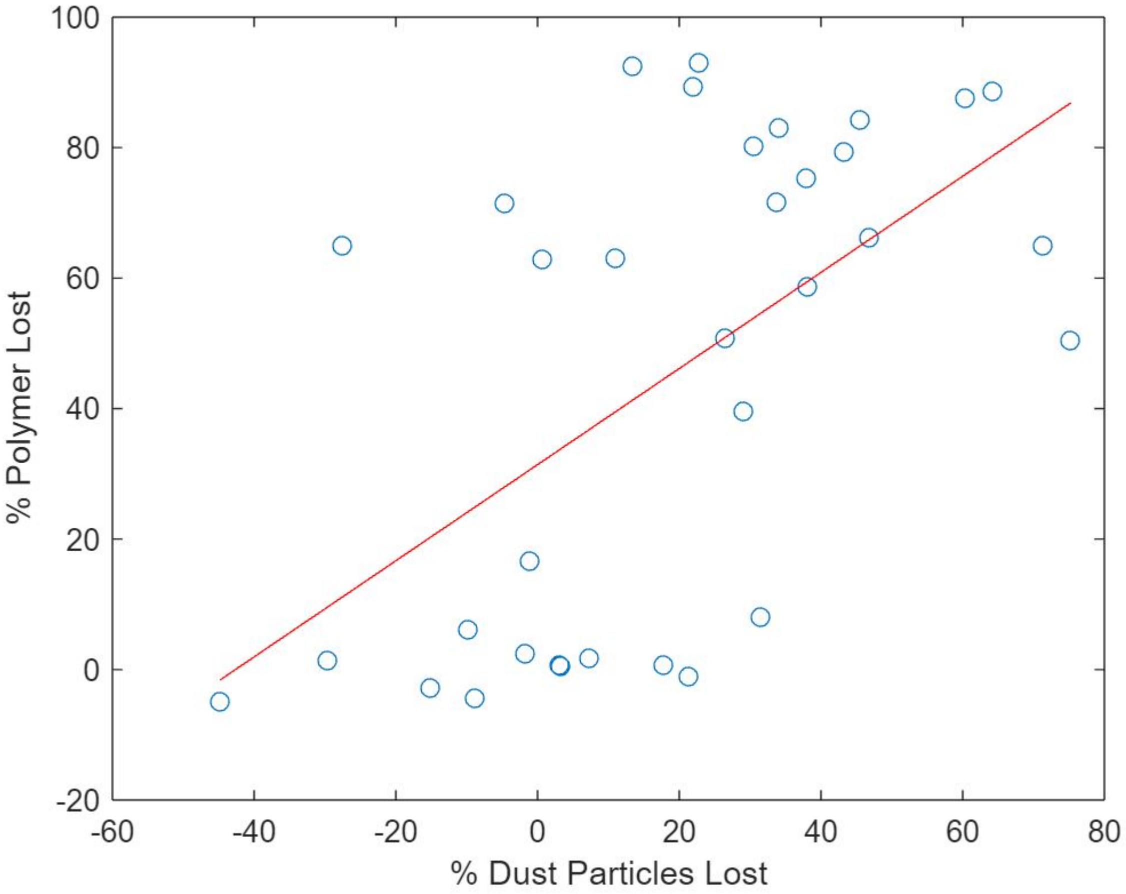


Figure 4.3 34 samples plotted based on their percent polymer lost and percent dust lost. The red line represents the result of a linear regression model applied to this data set: y=31.41*0.73664x. The R-squared value of this model is 0.33.

4.1.3 Potential Correlation Between Degradation and Dust Loss

I hypothesized that the relative particle loss could be determined by the relative polymer loss. To probe this hypothesis, I selected 34 samples from a variety of experimental groups and plotted their relative loss of particles against the relative polymer loss as determined by ellipsometry. The results are shown in Fig. B.1.

These results suggest that the relative amount of polymer loss only accounts for about 33% of the variance in the relative dust loss. Considering our results in Fig. 3.3, this means that an irradiated sample will lose dust significantly compared to the control, but we do not yet know how to predict what amount of dust will be removed. However, optimization of the dust mitigation process is outside of the scope of my project, so I will leave further investigation of this topic to future research.

4.2 Conclusions

Based on our research, PMPS and PHS are capable of evaporative degradation in vacuum without heating. However, the polymer remains stable in a low-pressure environment until exposed to UV-C light. Once in UV light (either 254 or 172 nm), the samples photodegrade significantly.

Importantly, we have shown that the heating step that has been used in previous experiments is not necessary for degradation in vacuum, as poly(olefin sulfone) can apparently degrade in vacuum when subjected to UV light, even without heat. Furthermore, we have observed degradation under the same conditions whether the polymer is mixed with PBG or not. PBG may help achieve quicker degradation of the film, as in the case of PHS. Although the polymers degrade at a faster rate when using the 172-nm lamp than the 254-nm lamp, differences in the distances between the lamp and the samples may affect these results. We conclude that PHS degrades slower than PMPS, but otherwise follows similar degradation patterns. While degradation was observed in each experimental group, some polymer remains on the surface. This may be consequential depending on the desired application. Future investigation may seek to minimize the residual polymer on the surface by optimizing the initial polymer thickness or composition when considering those applications. Characterizing poly(olefin sulfone) degradation was the first step in showing that these coatings could be used to protect space instrumentation such as starshades.

I have observed that the dissociative degradation of the polymer causes dust particles to be removed from a surface. However, this aspect of the project will benefit from further investigation.

Other experimental groups discussed in section 3.2.2 have shown potential to mitigate dust as well or better than the group represented in Fig. 3.3. Therefore, further experimentation will allow us to optimize the dust mitigation abilities of this polymer.

In summary, these experiments demonstrate that poly(olefin sulfone) can photodegrade in vacuum without the need for a heating step. This alone is a notable characteristic since there are many potential space applications of protective coatings which self-immolate in the light from the sun outside of earth's atmosphere. Our results indicate that poly(olefin sulfone) does degrade under the conditions necessary for space applications. Furthermore, PMPS degradation has dust mitigation abilities. Although this study was motivated by the starshade problem, these results could be relevant to optical instruments or any device that requires dust mitigation. This could allow for removal of contamination on instruments in space without any human intervention.

Appendix A

Publications

The following publications resulted from this project:

Published:

Alexandra K. Stapley, Sydney A. McFarland, Joshua J. Vawdrey, Osemudiamhen D. Amienghemhen, Kendall J. Mitchell, Takeo Sasaki, David D. Allred, Walter F. Paxton, Photodegradation of self-immolating polymers as a potential solution to particulate contamination, Solar Energy Materials and Solar Cells, Volume 272, 2024, 112902, ISSN 0927-0248, https://doi.org/10.1016/j.solmat.2024.112902. (https://www.sciencedirect.com/science/article/pii/S0927024824002149)

In progress:

Alexandra K. Stapley, Matthew Clarkson, Kira Brooks, Marian Stradling, Morgan Peterson Joshua J. Vawdrey, Osemudiamhen D. Amienghemhen, Takeo Sasaki, David D. Allred, Walter F. Paxton, Investigating the dust mitigation abilities of dissociative degradation. (Target journal: Surface and Coatings Technology)

Appendix B

Additional Material

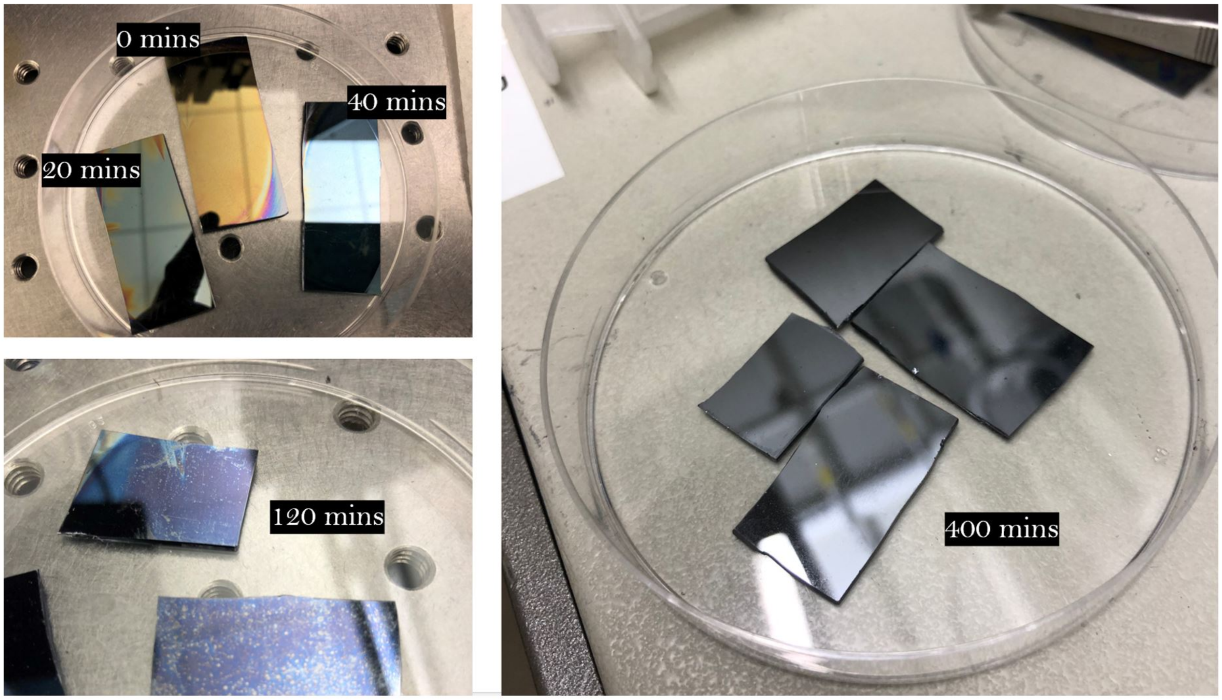


Figure B.1 Optical images of PMPS with PBG thin film samples over 400 minutes of irradiation in vacuum. The thin film presents as a color such as yellow due to thin film interference. The color changes as the film gets thinner (20-40 minutes). More material is removed and the color changes further, with visible discontinuities in the film (120 minutes). As the polymerdegrades more, the silicon substrate becomes visible. Finally after approximately 400 minutes, some residue is left on the surface, without apparent visible light interference.

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