Title: Degradation of ROMP-Based Bio-Renewable Polymers by UV Radiation

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Degradation of ROMP-Based Bio-Renewable Polymers by UV Radiation

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Abstract

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1 Introduction

Aging is the primary effect limiting the lifetime of plastics. It usually leads to irreversible changes in material properties. Materials exposed to environmental influences, such as light, temperature, and humidity may lose ductility, color, or transparency. In outdoor applications of plastic materials, UV radiation is responsible for most aging damages, because the quantum energy of UV radiation is high enough to cause chain cleavage in the molecules, and this, in turn, resulting in one or more of the following chemical changes: depolymerization, crosslinking, formation of double bonds in the polymer

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chain and other low-molecular compounds [1]. These effects are usually classified as photo-degradation. Photo-degradation generally leads to an embrittlement of polymer materials and often causes a transition from ductile failure to brittle fracture. A reduction in yield stress, tensile stress, and elongation at break was observed in many photo-degraded materials [2-5]. Conductivity and dielectricity are also affected by photo-degradation [6, 7]. Because degradation will eventually cause material failure, examining and understanding the degradation effects on material properties provides key indicators when predicting the service life of a material.

The basic mechanism of photo-degradation is auto-oxidation, consisting of several steps:

\[
\begin{align*}
\text{Initiation} & : \quad RH \rightarrow R\cdot + H\cdot \\
\text{Propagation} & : \quad R\cdot + \cdot{O}_2 \rightarrow ROO\cdot \\
& \quad \text{ROO} \cdot + RH \rightarrow \text{ROOH} + R\cdot \\
\text{Termination} & : \quad \text{ROO}\cdot + R\cdot \rightarrow \text{ROOR} \\
& \quad \text{R} \cdot + \text{R} \cdot \rightarrow \text{RR}
\end{align*}
\]

The absorption of UV light provides sufficient energy to break chemical bonds in the polymer to generate free radicals, leading to the initiation of photo-degradation. Catalyst residues and impurities in the polymer are other sources for radical initiation [8]. During the propagation step, hydrocarbon free radicals react with triplet oxygen (the ground state for oxygen) to form peroxy radicals where oxygen is largely consumed. Then peroxy radicals subtract hydrogen from polymer chain, producing a hydroperoxides and other hydrocarbon radicals in reaction (3). Reactions (1), (2), and (3) form a self-accelerated auto-oxidation cycle [9]. The decomposition of hydroperoxide can lead to backbone cleavage of O-O bonds followed by β-scission mechanisms [10]. Photo-degradation is terminated when two free radicals combine, as shown in reactions (4) and (5). This typically results in cross-linking, branching, or formation of short segments of the polymer.
Henna and Larock [11] developed a bio-renewable polymer using ring-opening metathesis polymerization (ROMP) that showed promising thermal-mechanical properties, and a viable industrial processing method for these new thermosets is currently being developed. The bio-renewable polymer was prepared by copolymerizing a mixture of Dilulin and DCPD with 2nd generation Grubbs’ catalyst. The ring opening metathesis polymerization (ROMP) mechanism of two monomers is shown in Figure 1. Dilulin is synthesized from linseed oil and cyclopentadiene through a high temperature, high pressure Diels-Alder reaction. Chemical structure of Dilulin has been studied thoroughly with NMR and FTIR, indicating an average of one norbornene ring pendant group per triglyceride [11, 12]. In the polymerization of the copolymer, the unsaturated norbornene ring in Dilulin can undergo ROMP with DCPD to form a cross-linked structure. However, even after complete cure, the copolymer still contains a number of unreacted double bonds, such as unsaturated bonds in fatty acid chains in Dilulin and double bonds in cyclopentene rings in DCPD (discussed later). These unsaturated bonds are likely to be attacked by UV radiation to form free radicals during photo-degradation. Catalyst residue and other impurities in the polymer also absorb UV radiation, producing free radicals. Understanding the degradation behavior of this bio-renewable polymer is essential for exploring possible practical applications.

In this paper, the effect of UV radiation on physical and chemical properties of thick, bio-renewable polymer samples was studied utilizing various methods. In general, photo-degradation in thick specimen is governed by diffusion of oxygen into the polymer over time [13]. The distribution of oxygen through the specimen thickness results in varying concentrations of oxidation products with changing depth [14-16]. Profile analysis of photo-degraded samples was used as an effective way to study the time dependent degradation process. Photo-acoustic FTIR (PAS-FTIR) was used to examine chemicals on the surface layer of degraded materials. Together with an MTEC microlap system, it allowed to generate depth profiles of degraded materials with good resolutions.
2 Experimental

2.1 Sample Preparation

All samples were prepared from bio-renewable polymers consisting of 30 wt.% Dilulin and 70 wt.% dicyclopentadiene (DCPD, Sigma-Aldrich). Dilulin was used as a commercially available, modified linseed oil from Cargill (MN). The mixture of Dilulin and DCPD was cured with 0.125 wt.% recrystallized 2\textsuperscript{nd} generation Grubbs’ catalyst [12] following a cure schedule of 1 h at 65 °C and subsequent 3 h at 150 °C. The resin was used to manufacture 100 mm × 60 mm × 0.8 mm sheets via a modified injection molding process. The mold consisted of a rubber gasket sandwiched between two glass plates. Resin was injected slowly from the top of the mold with a syringe. Dogbone samples for tensile tests were punched from the sheet material using an ASTM D 638 type-V punch. Six dogbone samples were produced from one piece of sheet. The remaining sheet was cut into rectangular specimens (30 mm × 40 mm) for further characterization analysis. The samples were attached to aluminum plates (75 mm × 125 mm) to fit the sample holder in the environmental chamber.

2.2 Exposure Procedure

The specimen were exposed to UV radiation according to ASTM G 154-06 (cycle 1 in ANNEX 2) in a QUV accelerated weathering chamber with a UVA-340 lamp. UV-340 lamps typically have little or no UV output below 300 nm wavelength (cut-off wavelength), which closely matches terrestrial solar radiation in the ultra-violet range. Samples were exposed on a 12 h cycle: 8 h UV at 60 °C black panel temperature followed by 4 h condensation at 50 °C black panel temperature, for total exposure times of 250 h, 500 h, 750 h, 1000 h, and 2000 h, respectively. A group of control samples was stored in a desiccator in dark cabinet to avoid exposure to light before further characterization.

2.3 Characterization

Tensile tests were carried out on an Instron 5569 universal testing machine (50 kN load cell and Bluehill software) with a constant crosshead speed of 1 mm/min. The longitudinal strain was measured by
a non-contacting video extensometer (AVE). Young’s modulus \( E \), ultimate strength \( \sigma_m \), breaking strain \( \varepsilon_b \), and tensile toughness were calculated and analyzed.

Soxhlet extraction was carried out to estimate the crosslink density. Samples weighing between 0.8 and 1.0 g were cut from unexposed and exposed polymer sheet and refluxed in 750 ml methylene chloride at a temperature of 60 °C for 24 h. After extraction, the solution was concentrated in a rotary evaporator and subsequently vacuum dried. \(^1\)H NMR spectra of the soluble portion were taken with a Virian spectrometer (Palo Alto, CA) at 300 MHz using CDCl\(_3\) as the solvent. The insoluble portion was dried in a vacuum oven overnight at 60 °C and then weighed.

The chemical changes that occurred on the sample surface after varied amounts of UV radiation were analyzed by Fourier transform infrared photo-acoustic spectroscopy (PAS-FTIR). PAS-FTIR is a non-destructive, near-surface analysis technique widely used for analysis of layered [17, 18] and degraded materials [19, 20]. During testing, samples were put in a sealed chamber filled with helium gas. The temperature fluctuation on the sample surface caused by absorbed infrared radiation initiated a pressure change in the surrounding gas, thus generating acoustic waves in the sample chamber. These acoustic signals were detected by a sensitive microphone and then underwent Fourier transformation. A Digilab FTS 7000 FTIR spectrometer equipped with an AMTEC Photoacoustic (PAC300) detector was used to acquire PAS spectra. These spectra were collected at a modulation frequency of 5 kHz and a spectral resolution of 8 cm\(^{-1}\).

An MTEC Microlap system coupled with PAS was used to measure IR spectra of degraded materials as a function of depth. The Microlap system contained a micro-abrasive machine and a micro-gage, allowing control of the thickness of the removed layer within several micrometers. PAS spectra were collected on each new surface after abrasive removal of about 10 µm of the top layer until the spectra did not show any additional change. Then, typical spectra were selected to show a clear surface depth profile.
of the degraded layer. In this test, PAS spectra were collected at a spectral resolution of 8 cm\(^{-1}\) and a modulation frequency of 20 kHz.

The morphology of the exposed and the transverse surfaces, cut with a razor blade, were studied using scanning electron microscopy (SEM, JSM-6060LV) operating at 20 kV in high vacuum. Polymer samples were sputtered with carbon prior to examination.

3 Results and Discussion

3.1 Appearance of the Degraded Surfaces

A discoloration from yellow and transparent to dark brown was observed with increasing UV exposure time. Discoloration is a common sign of plastic aging and usually caused by the formation of chromophores during photo-oxidation reactions. Figure 2 shows the SEM images of degraded surfaces after varied exposure times. Surface cracks formed spontaneously during UV exposure and the degree of degradation increased with increasing exposure time. It can be seen that even after only 250 h of UV exposure, many cracks formed randomly on the sample surface. Surface cracking is usually caused by the gradient stress in degraded samples. Post-crosslinking of the surface material initiated by UV radiation, which usually results in tension stress on the surface, is a major reason why gradient stress builds up in materials from the surface to the inner layers [21]. With increasing exposure time, cracks propagated and intersected with each other, forming a network structure, as can be seen in Figure 2 (b) and (c). In the accelerated weathering test, the cycling changes in moisture and temperature were additional important factors that caused the formation of surface cracks. Bulk samples expanded and contracted with cyclic temperature conditions, while sample surfaces swelled and shrank under cyclic condensation conditions as a result of absorbing and desorbing moisture. These alternating changes caused a gradient stress from the surface to the inner layers of the sample, initiating crack formation. Figure 2 (d) shows the “wrinkled” surface of a sample exposed to UV radiation for 2000 h. This surface effect is presumably a consequence
of the increasing mismatch of thermal-induced expansion and contraction between surface and interior of the sample.

### 3.2 Soxhlet Extraction Analysis

The insoluble fraction is plotted as function of exposure time in Figure 3. The insoluble fraction increased from 86.9% for unexposed specimens to 90% for specimens exposed for 750 h, which is mainly attributed to UV induced post-crosslinking. With exposure time increasing beyond 750 h, the insoluble fraction slightly decreased. It is possible that after 750 h of exposure, UV-induced chain scission became the dominant degradation process. As exposure time further increased, more bulk material was decomposed and the cross-linked structure was broken into small segments. These decomposed segments were extracted by methylene chloride in the Soxhlet extraction process, resulting in a decrease in insoluble fraction.

\(^1\)H NMR spectral analysis of soluble extracts revealed the presence of unreacted monomers and oligomers after copolymerization. The representative structure of the copolymer and \(^1\)H NMR spectra of soluble extracts from 250 h-treated sample are shown in Figure 4 (other \(^1\)H NMR spectra can be found in supporting materials). The characteristic peaks at \(\delta = 4.1\) and \(4.3\) correspond to the hydrogen atoms of the glycerol unit in the Dilulin. The presence of carbon-carbon double bonds in the fatty acid chains (labeled \(a\)) in Dilulin is confirmed by the appearance of a peak at \(\delta = 5.38\). The peak at \(\delta = 5.45\) can be attributed to the metathesized double bonds of the polymeric backbone (labeled \(b\)). The small peak at \(\delta = 5.68\) corresponds to double bonds in the cyclopentene portion of DCPD (labeled \(c\)). DCPD is a diene with a rigid bicyclic structure containing two double bonds of unequal reactivity: one norbornene double bond that undergoes rapid olefin metathesis and one less reactive cyclopentene double bond. The absence of peaks between \(\delta = 5.9\) and \(\delta = 6.1\) confirm that all C=C bonds in the norbornene rings in DCPD have reacted.
The peak areas of unsaturated bonds \((a, b,\) and \(c)\) were compared between aged samples by setting the integrated area under the peaks at 4.1 and 4.3 to 1. Due to the difficulties in integrating peaks area at 5.38 and 5.45 separately, the overall area between 5.3 and 5.5 is measured. As listed in Table 1, a decreasing trend was found for all unsaturated bonds within 750 h exposure, which is primarily due to the post-crosslinking in samples subject to UV irradiation. The decrease of the peak area indicates that the number of \(\text{C}=\text{C}\) was reduced greatly in the early stage of degradation. This is the net effect of double bond consumption and generation. In other words, the consumption rate of double bonds is higher than the rate of generation. There are several ways to convert \(\text{C}=\text{C}\) bonds in UV degradation. \(\text{C}=\text{C}\) bonds are chromophoric groups which absorb UV light and form hydrocarbon radicals quickly. If this happens at the sample surface where sufficient oxygen is available, hydrocarbon radicals will be oxidized immediately to form hydroperoxides, as shown in equation (2) and (3). If the hydrocarbon radicals were formed at the inner part of the sample, it could combine with other hydrocarbon radicals to form cross-linked structure. In our case, from the polymer property aspect, the cross-link density of the copolymer increased after a short-term UV irradiation. Then beyond 750 h exposure, peak areas start to increase instead, indicating a growth in the number of unsaturated bonds in the soluble extracts. The increased double bonds are likely from a Norrish II reaction (Figure 5) during photo-degradation. As we know, a large number of carbonyl groups are formed in polymer materials upon UV irradiation. Those carbonyl groups absorb UV light readily and decompose through two types of Norrish reactions, see Figure 5. The Norrish II reaction, which usually breaks the polymer backbone into enol and alkene, is more probable since its activation energy (0.85 kcal/mol) at room temperature is lower than that of Norrish I reaction (4.8 kcal/mol)[10]. Oligomers containing enols and alkenes from Norrish reactions could be extracted by methylene chloride, leading to the decrease of insoluble fraction and the increase of unsaturated bonds.

To sum up, in UV degradation of unsaturated polymers, the evidence suggests that UV-induced post-crosslinking and chain-scission occur simultaneously and compete with each other. The insoluble fraction
curve and NMR analysis of soluble extracts both demonstrate that post-crosslinking dominates at the early stage of exposure (≤ 750 h) and then decomposition and chain-scission dominate the later stage.

3.3 Tensile Test

The effect of UV exposure on mechanical properties was evaluated by tensile testing. Strain-stress curves for specimens after various times of UV exposure are shown in Figure 6. Tensile strength, average breaking strain, Young’s modulus, and tensile toughness are summarized in Table 2. The control specimens (no exposure to UV radiation) showed ductile behavior with a clear yielding point and a low degree of plastic deformation. As exposure time increased, a ductile–brittle transition was observed in the strain-stress curves. After UV exposure for 750 h, the specimen exhibited brittle failure. Both breaking strain and tensile toughness dropped dramatically. The average breaking strain decreased from 17.8% for the control specimens to 2.9% after 750 h and 2% after 2000 h of UV exposure. The tensile toughness dropped from 4.7 MPa for the control specimens to 0.4 MPa for specimens exposed to UV radiation for 2000 h. The significant decrease in breaking strain and tensile toughness was mainly attributed to the formation of surface cracks during photo-degradation. It is interesting to note that the Young’s modulus $E_Y$ exhibited an increase beyond the value of the control specimen after 500 h of UV exposure, which is presumably a consequence of UV-induced post cross-linking. At the same time, tensile strength for samples exposed to UV radiation for less than 750 h showed only minimal changes. A similar trend was observed by J.R. White in a study of photo-degradation in polypropylene [22], which reported a ductile band between the degraded surface and the interior in specimens that were exposed to UV radiation for a short time. During tensile testing, cracks initiated at the surface started to grow and propagated into the sample interior. The propagation was arrested by the ductile layer, so that the undamaged interior showed ductile deformation. These samples still showed slightly ductile behavior and left serrated fracture surfaces, formed at about 45° to the tensile stress direction. As the exposure time further increased, the strength of the degraded layer became too low to transfer stress at the crack tip into the interior and crack
growth terminated. At sufficiently long exposure times, the degraded layer became partially detached from the inner material layers and flaked off. Embrittlement is another factor that affects tensile properties. During polymer degradation, embrittlement is caused by oxidation reaction, chain-scission, and decomposition of materials. Embrittlement develops gradually over time, from the surface into the interior of the sample. Samples exposed to UV radiation for more than 750 h showed typical brittle fracture behavior, as shown in Figure 6. This behavior was likely the result of the combined effects of surface cracks and embrittlement.

3.4 Fourier Transform Infrared Photoacoustic Spectroscopy (PAS-FTIR)

In PAS experiment, the effective sample depth at which signals can be collected is determined by the thermal diffusion length ($\mu$) of the sample. The thermal diffusion length not only depends on the thermal diffusivity ($\alpha$) of the sample, but also on the modulation frequency ($f$) of the incident radiation. Here, $f = 2\nu v$, where $v$ is the velocity of the mirror (cm/s) and $\nu$ is the excitation frequency (wavenumber, cm$^{-1}$).

$$\mu = \left[ \frac{\alpha}{\pi f} \right]^{1/2} = \left[ \frac{\alpha}{\pi \nu v} \right]^{1/2}$$

As a result, signals penetrate deeper at low excitation frequencies and shallower at high excitation frequencies. For the materials studied here, spectra at a frequency of 4000 cm$^{-1}$ originated from a depth of 5.6 µm and spectra at a frequency of 400 cm$^{-1}$ originated from a depth of 17.7 µm. The thermal diffusivity value used here was $1.25 \times 10^{-7}$ m$^2$/s, which is a mid-value for common polymers.

The PAS spectra of degraded bio-polymer specimens after different UV exposure times are shown in Figure 7. The wide absorption peak at 3400 cm$^{-1}$ was assigned to the hydroxyl group associated with oxidation products, such as hydroperoxide, carboxylic acid, and alcohols. The absorption between 2850
and 2950 cm\(^{-1}\) was attributed to stretched C-H bonds. The peak at 1740 cm\(^{-1}\) was associated with stretch vibration of the carbonyl group in ketones, acids, esters, and aldehydes. In the fingerprint region, multi-peaks at 1000–1300 cm\(^{-1}\) were generally associated with C-O stretch vibrations that are largely formed during photo-degradation. The decreases in intensity of C-H bond absorption after UV exposure indicated that a large number of C-H bonds were consumed during the photooxidation reaction. UV radiation either converted them into free radicals by removing the hydrogen atom during the initiation step; or they reacted with a peroxo radical to form hydroperoxide and another free radical during the propagation step. Simultaneously, the intensities of the hydroxyl and the carbonyl peak increased, because both hydroperoxides and carbonyls are the main products of photo-degradation. It is interesting to note that as the exposure time increases, IR peaks tended to broaden and overlap with each other, while detailed features for absorption peaks were lost in the spectrum. This effect was probably caused by oxidation products that contain a very large number of individual molecules, so that the examined bond, e.g., the hydroxyl group, showed IR absorption at slightly different frequencies for each of these bonds. Thus, as a result, the IR peak is the average of all these slightly different absorptions and appears broadened. The PAS spectra in Figure 8, recorded at a modulation frequency of 20 kHz, represent chemical changes with various surface depth of specimen aged for 1000 h. Spectrum collected on the surface after a removal of 43 µm is labeled 43 µm.

Figure 8 shows that while going from 0 to 104 µm, an increase of the band intensity of C-H absorption was observed, indicating that the consumption of C-H bonds decreased with penetration depth. At the top surface of the sample a large number of C-H bonds are consumed by UV-induced cleavage and free radical reactions. As the penetration depth increases, both reactions decreased as a result of insufficient oxygen and UV radiations availability. Finally, when the undamaged region was reached, the spectra did not change any further and the intensity of C-H absorption was the highest. It is also important to note that all peaks related to oxidation products (hydroxyl, carbonyl, and C-O) decreased rapidly with increasing penetration depth. This is caused by two photo-degradation reactions: the formation and the
decomposition of hydroperoxide. The process of conversion of the formed hydrocarbon radicals to peroxy radicals is the main oxygen-consuming reaction. This reaction occurs readily just after hydrocarbon radicals are formed, and the reaction rate depends on the concentration of oxygen “inside” the polymer [23]. Next the peroxy radical abstracts one hydrogen atom from the polymer chain to form a hydroperoxide and another hydrocarbon radical. At sample surface, there is sufficient oxygen available to produce abundant hydroperoxides. As going further away from the surface, less hydroperoxide is formed because the oxygen concentration decreases dramatically in polymer. The formation of most oxidation products (alcohols, ketones, aldehydes) is related to the radiation-induced decomposition of hydroperoxide. UV radiation is sufficient to causes cleavage of O-O, R-O, and O-H bonds in hydroperoxide whose dissociation energy values are 42, 70 and 90 kcal/mol respectively; O-O cleavage is predominant in polymer photo-oxidation due to its low bond dissociation energy[10]. After cleavage, the alkoxy radical undergoes a variety of reactions to form different oxidation products, as shown in Figure 9: abstracting hydrogen from other hydrocarbons to form alcohols, reacting with hydroxyl to form ketones, undergoing chain scission and atom rearrangement to form aldehydes. The carbonyl group formed during photooxidation also plays an important role, because it absorbs UV light readily after formation and then decomposes through a Norrish reaction. Acids, esters, enols and alkenes are general products of Norrish reaction, as shown in Figure 5.

Figure 8 also showed that carbonyl absorption shifted to higher frequencies at greater depths. In shallower material layers, carbonyl groups mainly originated from oxidation products, such as ketones (1705–1725 cm⁻¹), acids (1700–1725 cm⁻¹) and aldehydes (1720–1740 cm⁻¹). At greater depth, the oxidized material decreased and undamaged material increased. Carbonyl groups in undamaged materials mainly originated from ester groups that exhibit an excitation frequency of 1730–1750 cm⁻¹, slightly higher than other oxidation products. The shifting of the carbonyl peak is evidence of the fact that the amount of oxidation products decreased with penetration depth.
The formation of oxidation products depends strongly on oxygen content and decreases exponentially with increasing distance from the surface. In our case, PAS spectra vary a lot with depth shallower than 104 \(\mu m\) and stay unchanged beyond 104 \(\mu m\), indicating that oxidation mainly occurs in the top layer (~104 \(\mu m\)) of the material.

3.5 \textit{SEM of Transverse Surface}

To obtain a measure of the depth of surface cracks, transverse sections of aged samples were examined using scanning electron microscopy, as shown in Figure 10. The transverse sections were prepared by cutting samples with a razor blade. All images were collected on the exposed edge.

Figure 10 (a) shows the cross-section of a sample exposed to UV radiation for 250 h. The cracks penetrated into the sample to depths varying from \(~15 \mu m\) to \(~40 \mu m\). The material between cracks looked undamaged, similar to interior layers. Figure 10 (b) shows that for samples exposed to UV radiation for 500 h the crack penetration depth did not increase. However, numerous voids were generated in the material around the cracks. The created cracks also increased the area exposed to UV radiation and oxygen. Thus, oxygen diffused into the material not only from the exposed surface but also from the crack surfaces. As the exposure time further increased, cracks became wider and also penetrated deeper into the material, shown in V-shaped profiles in Figure 10 (c). The tensile stress on the sample surface initiated cracks that grew inwards from the surface. After UV exposure times of 1000 h, the crack depth reached 50 \(\mu m\). In Figure 10 (d), a severely degraded layer is shown at the edge. The degraded layer (shown in lighter color in the image) is about 60 \(\mu m\) thick. This value is much smaller than the degraded depth from PAS depth profile test, indicating that invisible degradation had occurred below the visible damaged layer.
4 Conclusions

Photo-degradation by UV radiation of thick, bio-renewable polymer sheets was studied and SEM and photoacoustic FTIR showed that photo-degradation increased with increasing exposure time. The formation of surface cracks was attributed to the gradient stress in degraded material layers caused by UV-induced post-crosslinking and cycled weathering conditions. Soxhlet extraction test indicated that UV-induced post-crosslinking dominated during the beginning stage (less than 750 h of exposure) of photo-degradation, before chain scission and decomposition determined the effects of long time UV exposure. Mechanical properties were significantly reduced after UV exposure. Surface cracks and embrittlement were the major contributors to the failure mechanisms encountered in tensile testing. The sudden reduction in breaking strain was attributed to surface cracks. However, tensile strength and Young’s modulus were not sensitive to surface cracks after short time exposure. Depth profiles and SEM results both indicated that degradation occurred only in a thin surface layer because of limited oxygen diffusion into the interior layers. Hydroperoxides and various carbonyl groups were formed as the main degradation products, as observed in PAS-FTIR. In a next step, the effects of adding anti-oxidants and photo-stabilizers will be studied to enhance the photo-stability of biopolymers created by ROMP.

5 Acknowledgements

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References


### Table 1 Soxhlet extraction data

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<tr>
<th></th>
<th>Insoluble %</th>
<th>Soluble %</th>
<th>Area under peak c</th>
<th>Area under peak a and b</th>
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<tr>
<td>Untreated</td>
<td>86.9</td>
<td>13.1</td>
<td>1.73</td>
<td>4.78</td>
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<tr>
<td>250h</td>
<td>89.2</td>
<td>10.8</td>
<td>1.54</td>
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<tr>
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<td>10.2</td>
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<td>89.6</td>
<td>10.4</td>
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### Table 2 Tensile test data

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<th>$\sigma_{\text{max}}$ (MPa)</th>
<th>$\epsilon_b$ (%)</th>
<th>$E_Y$ (GPa)</th>
<th>Toughness (MPa)</th>
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<td>Untreated</td>
<td>38.6 ± 1.4</td>
<td>17.8 ± 3</td>
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<td>250h</td>
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<tr>
<td>500h</td>
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<td>11 ± 2</td>
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<td>750h</td>
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<td>1.86 ± 0.23</td>
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<tr>
<td>1000h</td>
<td>33.3 ± 4.7</td>
<td>2.5 ± 0.4</td>
<td>1.8 ± 0.21</td>
<td>0.49 ± 0.16</td>
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<td>2000h</td>
<td>31.6 ± 2.9</td>
<td>2 ± 0.08</td>
<td>1.6 ± 0.04</td>
<td>0.38 ± 0.05</td>
</tr>
</tbody>
</table>
Figure 1

0.125 wt% 2nd Generation Grubbs Catalyst

1h at 65°C
3h at 150°C
Figure 3

Click here to download high resolution image
Figure 9

\[ R_3H \xrightarrow{\cdot OH} R_1\text{C}R_2 + R_3\cdot \]
\[ \text{O} \cdot \]
\[ R_1\text{C}R_2 \xrightarrow{\cdot OH} R_1\text{C}R_2 + H_2O \]
\[ \beta\text{-scission at } b \]
\[ \beta\text{-scission at } a \]
\[ R_1\text{CH} + R_2\cdot \]
\[ \text{HC}R_2 + R_1\cdot \]
Figure 1 ROMP of Dilulin and DCPD

Figure 2 SEM images of degraded surfaces after varied UV exposure times. (a) 250 h; (b) 500 h; (c) 1000 h; (d) 2000 h

Figure 3 Insoluble fraction of degraded samples with varied UV exposure times

Figure 4 Structure representative of copolymer and 1H NMR spectra of soluble extracts from sample aged for 250 h

Figure 5 Norrish reactions of carbonyl groups

Figure 6 Stress-strain curves for samples after varied UV exposure times

Figure 7 PAS-FTIR spectra of degraded samples after varied UV exposure times

Figure 8 Depth-profiling using PAS-FTIR for sample after 1000 h exposure time

Figure 9 Second oxidation reactions for alkoxy radical

Figure 10 SEM images of cross-sections of UV-degraded samples after exposure times of (a) 250 h; (b) 500 h; (c) 1000 h; (d) 2000 h
Figure S1. $^1$H NMR spectra of Dilulin
Figure S2. $^1$H NMR spectra of soluble extracts from samples with varied exposure time