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High-resolution setup for measuring wavelength sensitivity of photoyellowing of translucent materials

Anna Vaskuri, Petri Kärhä, Anu Heikkilä, and Erkki Ikonen

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I. INTRODUCTION

Ultraviolet (UV) radiation damages materials in various ways. In polystyrene and many other materials, photodegradation can be seen as the material turning yellow under UV exposure. This photoyellowing is a consequence of the reaction products formed in the photodegradation processes,\(^1\) which absorb radiation at the ultraviolet and short wavelength visible regions. Photoyellowing can be quantified, e.g., with Fourier transform infrared peaks at certain wavelengths, or by measuring the UV-visible transmittance spectrum and calculating the corresponding yellowness index under defined illumination conditions.\(^2\) Yellowing can be seen in spectral measurements as the suppression of reflected or transmitted radiation at blue and UV wavelengths. All photodegradation mechanisms including photoyellowing are functions of the exposure wavelength. The wavelength sensitivity can be described with an action spectrum. Knowing the action spectrum enables predicting the behavior of the material under known UV conditions. This has applications, e.g., in developing new stabilizers for plastics, wood, and in protection for organic light-emitting diode devices.\(^3\)\(^-\)\(^5\)

Testing techniques for material ageing can be divided into two categories: source-independent techniques that use monochromatic light and source-dependent techniques that use either natural or artificial polychromatic light for ageing. In the source-independent techniques, monochromatic light can be produced by band-pass filtering,\(^3\)\(^,\)\(^6\) monochromators and spectrographs,\(^7\)\(^-\)\(^9\) or lasers.\(^10\) The source-dependent techniques include, e.g., exposing samples under the solar radiation\(^11\) and using a weathering chamber\(^12\) equipped with xenon (Xe) or mercury (Hg) lamps. The outdoor weathering of materials gives estimates for the total degradation of materials under solar irradiation. However, the results depend on both the spectral distribution and the irradiance level of the sun, and thus, the results are accurate only near the location and near the season of the year, where the experiment was carried out. The results do not reveal which wavelengths are responsible for yellowing, and thus, the wavelength sensitivity cannot be determined. Similar problems arise with the weathering chambers where different light sources produce different results. The action spectrum of a material cannot be derived using source-dependent techniques only.

Kärhä et al.\(^9\) have developed and reported a spectrograph, a compact version of the Okazaki large spectrograph\(^7\) that uses spectrally dispersed radiation to expose samples in order to measure the wavelength sensitivity of the photodegradation. The spectrograph disperses the radiation of 1-kW Xe lamp spectrally from 250 nm to 500 nm and spatially onto the sample plane of 21 \(\times\) 1.5 cm\(^2\) by using a flat-field concave holographic grating. Heikkilä and Kärhä\(^13\) have further used this facility to measure the UV action spectrum of the photoyellowing of regular newsprint. One of the problems noted in the research was the relatively large measurement beam of the colorimeter used causing convolution, i.e., averaging the color over large exposure wavelength ranges. In addition, major problems arise when measuring translucent material samples, where conventional colorimeters cannot be directly applied. Most colorimeters are meant for measuring the reflectance of opaque
materials and the weak reflection of translucent samples results in low signal-to-noise ratio. This can be improved by using a back-reflector behind the sample, but the effect of back reflections needs to be corrected from the results.

To overcome the challenges in measuring color changes in translucent samples, we have developed and constructed a high-resolution measurement setup that uses 14 laser lines with wavelengths between 325 nm and 933 nm for scanning the transmittances across UV exposed material samples. This measurement setup is used together with our earlier developed spectrograph to obtain high-resolution transmittance data on regions exposed to different UV wavelengths that can be used to derive the action spectrum.

We have tested the setup by ageing and measuring atactic polystyrene, which is a commonly used and studied material. Section II describes the polystyrene samples and how they were aged with the spectrograph. Section III introduces the structure and performance of the high-resolution setup developed in this work. The feasibility of the setup is demonstrated in Section IV with the results obtained by measuring the aged polystyrene samples. Conclusions are discussed in Section V.

II. AGEING OF THE SAMPLES

The samples studied were atactic polystyrene sheets manufactured by the Tampere University of Technology. The samples were 19 × 3 cm² in size of which 17 × 1.5 cm² was exposed. The thickness of the samples was 0.5 mm. They were exposed to spectrally dispersed UV radiation with the spectrograph presented in Fig. 1. This spectrograph, UVEMA2, is an improved version of the spectrograph developed and reported by Kärhä et al. Its general operating principle is similar to the original version, but the optical configuration and the exposure wavelength region are slightly different.

The instrument collects the radiation of 1-kW Xe lamp and focuses it on an entrance slit. Between the condensing and focusing lenses, a water filter has been installed to remove the excessive infrared radiation of the collimated beam. The slit is imaged with a concave holographic flat field grating that at the same time disperses the light spectrally and images it by focusing the wavelengths between 273 nm and 423 nm on the sample plane. The entrance slit has a fixed height of 12 mm and its width can be adjusted horizontally from 0 mm to 5 mm. In this work, the slit width of 5 mm was used. The correspondence between the horizontal position $x$ (mm) on the sample plane and the exposure wavelength $\lambda_e$ (nm) has been measured to follow

$$\lambda_e(x) = -0.0006 \frac{\text{nm}}{\text{mm}^2} x^2 + 0.9968 \frac{\text{nm}}{\text{mm}} x + 262.76 \text{ nm},$$

where $x = 0$ mm has been set at the left edge of the sample ($19 \times 3$ cm²) corresponding to the wavelength of 262.76 nm. By taking a derivative of Eq. (1), the reciprocal linear dispersion ($\text{nm mm}^{-1}$) is obtained as

$$\frac{d\lambda_e}{dx} = -0.0012 \frac{\text{nm}}{\text{mm}^2} x + 0.9968 \frac{\text{nm}}{\text{mm}}.$$  

(2)

Scanning the sample, e.g., with a beam diameter of 1.0 mm would lead to the broadening of 0.98 nm at 273 nm. This is by a factor of 8 smaller than the bandwidth of 8 nm defined by the width of the entrance slit used (5 mm) of the spectrograph.

The measurements resulting in Eqs. (1) and (2) were carried out by placing the measurement head of an Ocean Optics USB4000 spectroradiometer in eight horizontal positions in the sample plane and by calculating the centroid wavelength of each measured spectrum. The calibration of the Ocean Optics was carried out by comparing the measurements first in the same setup with a Bentham DTMc300 spectroradiometer with D7 diffuser that has a better cosine response ($f_s = 0.93\%$) and higher wavelength accuracy (0.1 nm). We estimate the expanded uncertainty ($k = 2$) of the wavelength measurements to be within ±1 nm, which is supported by the standard deviation of 0.3 nm noted in repeated wavelength calibrations.

The uncertainty is mainly dominated by the positioning uncertainty of the spectroradiometer measurement head. The bandwidth of the Ocean Optics spectroradiometer is 1.5 nm which is significantly smaller than the 8-nm bandwidth of the spectrograph used in measurements.

With the spectrograph, it is possible to study both the spectral dependence of the photoyellowing and how the photoyellowing evolves as a function of the radiant exposure. The spectral variation of the irradiation level across the sample plane is taken into account by measuring the irradiation levels at eight points in the sample plane with the same cosine corrected and calibrated spectroradiometer that was used in the wavelength measurements. Since the spectrum of the Xe lamp changes with time, irradiance levels are measured before and after the exposure of each sample, and the average of these two measurements is used in the analysis.

Figure 2 shows the polystyrene sheets that were aged with the UVEMA2 spectrograph. The exposure times were selected as powers of two ranging from 2 h to 256 h. As can be seen, the samples turn yellowish at the lower wavelength end. The yellowing increases with the increasing time and radiant exposure. All samples were kept in the dark before and after the ageing. The sample sheets were aged already in 2012, and the transmittance measurements were conducted in 2014. During this waiting period, the samples have undergone all possible post-radiation changes, and thus, the results show permanent changes induced. During the ageing, the ambient air temperature in the spectrograph was 30 ± 2 °C. Controlling and monitoring the temperature are crucial during the ageing since the increasing temperature accelerates the degradation process. The average irradiance levels during the exposure of each sample are presented in Table I. The samples were...
FIG. 2. Polystyrene samples exposed to UV radiation for 0–256 h.

not aged in the order presented, i.e., starting from the shortest ageing times and ending up in the longest. High irradiance values indicate measurements with a fresh lamp. Irradiance values reduce as the lamp ages. Variation in the values gives an estimate for the lamp ageing.

Table II presents the uncertainty budget for the irradiance levels measured and presented in Table I. The Bentham spectroradiometer used to calibrate the Ocean Optics spectroradiometer was calibrated with an incandescent lamp traceable to the spectral irradiance scale of Aalto University. The transfer uncertainty includes stability issues and the cosine response of the Bentham D7 measurement head. Measurements of the Xe lamp spectra suffered stabilities that were smoothed out from the spectra. Repeated measurements throughout the life cycle of the lamp were used to derive the relative shape of the lamp spectrum which remains constant with a relative standard deviation of 1.5%. The stated uncertainties at each wavelength are standard deviations of the mean of the derived values. Measurements before and after the ageing sequence were used to derive the absolute level for the spectrum. The stated value for uncertainty, 3.1%, is the standard deviation of the corrections and denotes the order of magnitude of the stability issues. Uncertainty in the spatial alignment of the spectroradiometer has been derived as the standard deviation of repeated measurements. The wavelength resolution of the Ocean Optics spectroradiometer is 1.5 nm which propagates to the wavelength dependent uncertainties presented. The overall expanded uncertainty is \( \sim 7\% \), rather independent of the wavelength, and it is mainly dominated by the Xe lamp instabilities. The uncertainties of the radiant exposures are practically the same. The uncertainty in the exposure times was 1 min. This introduces a maximal additional uncertainty of 0.8% in the 2-h exposure time which is negligible as compared to the uncertainties in the irradiance.

III. DESIGN OF THE HIGH-RESOLUTION MEASUREMENT SETUP

The structure of the measurement setup developed is presented in Fig. 3. Four lasers; a helium cadmium (HeCd) laser, a krypton argon ion (KrAr\(^+\)) laser, a helium neon (HeNe) laser, and an infrared diode (IR diode) laser are used as light sources.

Four laser beams are directed using mirrors M\(_1\)–M\(_4\) towards a motorized optical rail (OWIS LIMES 84-270-HiDS), where one beam at a time is selected by a sliding mirror M\(_5\). A similar mirror-based selector has been previously introduced by Hoyt and Foukal. The unused beams are absorbed by beam dumps. The selected beam travels through a spatial filter for improving the beam profile. This is not absolutely necessary for the power transmittance measurements described, but the setup is also used for the power calibration of optical detectors, where the beam profile is more critical.

TABLE I. Irradiance levels \( E \) measured at eight exposure wavelengths \( \lambda_e \) in the sample plane of the spectrograph, calculated as an average of the measurements before and after each sample ageing experiment, with relative expanded uncertainties \( U \ (k = 2) \) for each wavelength.

<table>
<thead>
<tr>
<th>( \lambda_e ) (nm)</th>
<th>2 h</th>
<th>4 h</th>
<th>8 h</th>
<th>16 h</th>
<th>32 h</th>
<th>64 h</th>
<th>128 h</th>
<th>256 h</th>
<th>( E ) (W m(^{-2}) nm(^{-1}))</th>
<th>( U ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>276</td>
<td>1.29</td>
<td>1.02</td>
<td>1.34</td>
<td>1.11</td>
<td>1.13</td>
<td>1.40</td>
<td>1.08</td>
<td>1.19</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>294</td>
<td>2.17</td>
<td>1.72</td>
<td>2.27</td>
<td>1.88</td>
<td>1.90</td>
<td>2.37</td>
<td>1.83</td>
<td>2.02</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>317</td>
<td>5.55</td>
<td>4.39</td>
<td>5.79</td>
<td>4.81</td>
<td>4.86</td>
<td>6.05</td>
<td>4.68</td>
<td>5.15</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td>341</td>
<td>9.41</td>
<td>7.44</td>
<td>9.83</td>
<td>8.16</td>
<td>8.25</td>
<td>10.26</td>
<td>7.94</td>
<td>8.74</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>364</td>
<td>8.10</td>
<td>6.40</td>
<td>8.45</td>
<td>7.02</td>
<td>7.10</td>
<td>8.82</td>
<td>6.82</td>
<td>7.52</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>386</td>
<td>6.58</td>
<td>5.20</td>
<td>6.87</td>
<td>5.71</td>
<td>5.77</td>
<td>7.17</td>
<td>5.55</td>
<td>6.11</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>407</td>
<td>5.78</td>
<td>4.57</td>
<td>6.03</td>
<td>5.01</td>
<td>5.06</td>
<td>6.30</td>
<td>4.87</td>
<td>5.36</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>421</td>
<td>5.16</td>
<td>4.08</td>
<td>5.39</td>
<td>4.48</td>
<td>4.53</td>
<td>5.63</td>
<td>4.35</td>
<td>4.80</td>
<td>6.7</td>
<td></td>
</tr>
</tbody>
</table>
To avoid chromatic aberration, the spatial filter is constructed from two off-axis parabolic mirrors OAP$_1$ and OAP$_2$ with the reflective focal lengths of 10.16 cm and 5.08 cm and a pinhole with a diameter of 150 μm. The principle of the spatial filter is similar as in the research by Minoni et al. Due to the stationary pinhole, the filtering is more effective at longer wavelengths, since its diameter was selected according to the diffraction limited spot size of the 933-nm beam of the IR diode laser, which has initially a distorted, elliptical beam profile caused by the spatial free carrier density distribution and the rectangular-shaped junction. In the ultraviolet region, the filtering is not as good as in IR but sufficient since the beam profiles are good naturally. Also the beams are not attenuated much, which provides better signal-to-noise ratios. The height of the beam is adjusted with a periscope.

A laser power controller (BEOC LPC-VIS) with the operational wavelength range of 425–780 nm is used for stabilizing the beam. By further monitoring the power fluctuation of the stabilized beam with a laser beam splitter and a monitor Si-trap detector (Hamamatsu S1337-11) and by correcting the power levels for noted drifts, the relative standard deviation of <0.007% with a peak-to-peak deviation of <0.05% in the laser power is achieved over a time period of 8 h. With higher power levels, stability is improved due to the improved signal-to-noise ratio of the laser power controller and the monitor detector. In addition, the signal-to-noise ratio has a spectral dependence as the spectral responsivity of the monitor detector increases towards longer wavelengths. Outside the operational range of the LPC, the relative standard deviation of the power corrected by the monitor detector signal is <0.02% with a peak-to-peak deviation of <0.2%. More specific information on the stability is given in Table III. A filter wheel with six holders is added to adjust the power level or to block the beam. One holder has been left empty, second holder blocks the beam, and two absorptive and two reflective neutral density filters with nominal transmittance values of ~1% and ~10% have been mounted in the remaining holders. After the LPC, the polarization of the beam can be further adjusted by a Glan-Thompson calcite crystal polarizer. The material sample is attached to a motorized XY translation stage (2 × OWIS LIMES 150-300-HiDS) with the travel of 300 × 300 mm$^2$ and bidirectional accuracy of <2 μm.

Since the transmitted beam can be diffuse, a photodiode with an integrating sphere is used to collect and measure the transmitted beam. Transmittance (%) is obtained by comparing the transmitted beam with respect to the incident beam, and thus, the results do not need any corrections related to the characteristics of the integrating sphere photodiode. The setup is automated and controlled with LabVIEW. Automated transmittance scanning allows measuring with high resolution. In addition, the measurement time of one point is shortened to a couple of seconds, thus preventing the sample from further degrading in the measurement process. The setup could also be extended to measure reflectance, and thus opaque materials. In addition, the measurement setup can be used to characterize optical detectors, as the facilities at the Physikalisch-Technische Bundesanstalt in Germany and the National Institute of Standards and Technology in the United States. Detectors can be, e.g., interchanged to characterize their absolute power responsivities, or they can be scanned to obtain spatial uniformities. Due to the wide operational spectral range of the components in the developed setup, also tunable laser sources could be used in the setup to continuously cover the visible spectrum.

Characteristics of the laser beams on the sample plane of the setup are listed in Table III. Depending on the laser line, its power level can be adjusted between 0 and 29.4 mW. Beam diameters were determined from the beam profiles measured with a dual scanning slit beam profiler (Thorlabs...
TABLE III. Characteristics of the laser beams used as radiation sources in the high-resolution transmittance measurement setup. Maximum power $P_{\text{max}}$ and diameter $d$ of each beam have been measured on the sample plane. Stabilities $\sigma$ and $\sigma_{\text{pp}}$ depict the relative standard deviation and a peak-to-peak deviation in the beam power $P$ after correcting the detected power with the monitor detector signal.

<table>
<thead>
<tr>
<th>Laser</th>
<th>Manufacturer and model</th>
<th>$\lambda$ (nm)</th>
<th>$P_{\text{max}}$ (mW)</th>
<th>$\sigma^a$ (%)</th>
<th>$P$ (µW)</th>
<th>$\sigma_{\text{pp}}$ (%)</th>
<th>$d$ (1/e$^2$) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HeCd</td>
<td>Kimmon Koha IK5551R-F</td>
<td>325</td>
<td>3.6$^b$</td>
<td>&lt;0.02</td>
<td>350</td>
<td>&lt;0.2</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>442</td>
<td>29.4</td>
<td>&lt;0.002</td>
<td>550</td>
<td>&lt;0.02</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>476</td>
<td>5.1</td>
<td></td>
<td></td>
<td></td>
<td>1.32</td>
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<tr>
<td></td>
<td></td>
<td>483</td>
<td>6.1</td>
<td></td>
<td></td>
<td></td>
<td>1.34</td>
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<tr>
<td></td>
<td></td>
<td>488</td>
<td>9.6</td>
<td></td>
<td></td>
<td></td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>496</td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
<td>1.36</td>
</tr>
<tr>
<td>KrAr$^+$</td>
<td>Melles Griot 35-KAP-431</td>
<td>514</td>
<td>6.0</td>
<td>&lt;0.007 at 488 nm</td>
<td>300</td>
<td>&lt;0.05</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>521</td>
<td>11.3</td>
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<td>1.40</td>
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<td></td>
<td>531</td>
<td>14.5</td>
<td></td>
<td></td>
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<td>1.39</td>
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<tr>
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<td></td>
<td>568</td>
<td>5.3</td>
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<td></td>
<td></td>
<td>1.44</td>
</tr>
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<td></td>
<td></td>
<td>647</td>
<td>6.7</td>
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<td>1.56</td>
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<td></td>
<td></td>
<td>676</td>
<td>1.4</td>
<td></td>
<td></td>
<td></td>
<td>1.57</td>
</tr>
<tr>
<td>HeNe</td>
<td>Thorlabs HRP005S</td>
<td>633</td>
<td>0.3</td>
<td>&lt;0.002</td>
<td>160</td>
<td>&lt;0.02</td>
<td>1.80</td>
</tr>
<tr>
<td>IR diode</td>
<td>Power Technology, Inc.,</td>
<td>933</td>
<td>6.6</td>
<td>&lt;0.02</td>
<td>460</td>
<td>&lt;0.1</td>
<td>1.06</td>
</tr>
</tbody>
</table>

$^a$Relative standard deviation $\sigma$ and peak-to-peak deviation $\sigma_{\text{pp}}$ of the power $P$ of over a period of 8 h.

$^b$Measured without the LPC and the polarizer.

BP209-VIS/M). Two examples of the beam profiles are presented in Fig. 4. Smaller spot sizes could be achieved by focusing the beams onto the sample with a lens. However, when measuring samples aged with the spectrograph as in this work, the dominant factor limiting the spectral resolution is the 3–8-nm tunable bandwidth of the spectrograph.

IV. RESULTS AND DISCUSSION

Transmittances of the UV-exposed polystyrene samples shown in Fig. 2 were scanned horizontally at 1-mm intervals using the high-resolution measurement setup. The horizontal locations on the samples were converted to their corresponding exposure wavelengths using the dispersion of the spectrograph in Eq. (1). A vertical position of 18 mm from the upper edge of each sample was chosen for all measurements for consistency. Accuracy of the manual sample alignment was estimated to be ±0.25 mm. The corresponding uncertainty in the wavelength scale due to the dispersion is within ±0.22 nm.

Figure 5 presents transmittances as a function of the exposure wavelength, measured for the sample aged for 256 h, at various laser wavelengths. Ageing can be seen as decreased transmittance over the exposure wavelength range of 270–370 nm. Results show that the laser lines with the lowest measurement wavelengths produce the highest absorption, as can be expected with yellowing. With the developed measurement setup, the best resolution is thus achieved at the wavelength of 325 nm.

The transmittances measured have three major sources of uncertainty: the wavelength uncertainty, the power fluctuations of the measurement beam, and the spatial properties of the samples. The wavelength uncertainty introduces highest uncertainty in transmittance in the regions, where the transmittance changes fast, i.e., at the wavelengths around 340 nm. The highest standard uncertainty due to the wavelength, 0.8%, appears with the 325 nm measurement laser. The uncertainty due to power fluctuations listed in Table III is smaller than 0.02% with any of the lasers. The highest contribution to the uncertainty originates from the spatial properties of the samples. As can be seen in Fig. 5, the transmittances of the sample aged for 256 h are rather inhomogeneous due to the properties of the manufacturing process. This ripple

FIG. 4. Beam profile of (a) the 442-nm laser line provided by a HeCd laser and (b) the 676-nm laser line by a KrAr$^+$ laser, measured on the sample plane of the high-resolution setup with a dual scanning slit beam profiler. Pseudo-2D images have been reconstructed from the horizontal and vertical cross sections.
is most pronounced with the 442-nm beam with the relative standard deviation of 1.2% due to the short wavelength and the narrow beam diameter of 0.94 mm. The uncertainty in the transmittance depends on the wavelength and laser used but remains below 4.2% ($k = 2$) under all circumstances.

Transmittances presented in Fig. 6(a) were measured for all samples aged for 2–256 h, with the uncertainty ($k = 2$) of 2.0%, using the 325-nm measurement beam giving the highest sensitivity. Photodegradation over the exposure wavelength range of 270–300 nm can already be detected after 2 h of ageing. Due to the fact that absorbance is directly proportional to the concentration of the absorbing substance,\textsuperscript{25} we converted the measured transmittances $T$ to absorbances $A$ as

$$A = -\log_{10}(T). \quad (3)$$

The absorbances are presented in Fig. 6(b). The uncertainties of the transmittance measurements can be converted to uncertainties in the absorbances as

$$\frac{\Delta A}{A} = \frac{\log_{10}(1 + \Delta T/T)}{\log_{10}(T)}. \quad (4)$$

The baseline of the unexposed sample is $A = 0.086$ and has the highest uncertainty ($k = 2$) of 10.0%. The early symptoms of ageing (2–32 h) can be seen as reduced transmittance at 270–280 nm wavelengths. Between 32 h and 128 h, the maximum effect gradually shifts from 270 nm to 290 nm wavelengths. With increasing exposure time further to 256 h, we can see a new absorption process being introduced, causing a new absorption peak at the wavelength of 325 nm.

Since the spectral irradiance is not constant over the sample plane of the spectograph as was presented in Table I, different areas of the samples are exposed to different radiant exposures. The radiant exposure (J m$^{-2}$) is defined as

$$H = \int \int E(\lambda_e) \, d\lambda_e \, dt, \quad (5)$$

where $E(\lambda_e)$ is the irradiance (W m$^{-2}$ nm$^{-1}$), $t$ is the exposure time (s), and $\lambda_e$ is the exposure wavelength (nm).

Figure 7 shows the absorbances of the exposed samples as a function of the radiant exposure at five exposure wavelengths. Since the ageing time was accurately controlled ($\sim$1 min), the uncertainties ($\sim$7%) for irradiance levels listed in Table I describe also the uncertainties for the radiant exposure values. With linear processes, the absorbances could directly be divided by the irradiances to obtain the action spectrum.$^\text{26}$
However, the results show that for polystyrene, the development of absorbance is highly nonlinear, and the induction times increase for longer exposure wavelengths. Based on these test measurements, the developed measurement setup is a powerful tool for measuring the wavelength sensitivity of the photodegradation as a function of the radiant exposure, needed for developing a complex action spectrum as in Refs. 9 and 13.

V. CONCLUSIONS

A new high-resolution transmittance measurement setup has been developed for measuring the photodegradation of translucent materials aged with spectrally dispersed UV radiation. The measurement setup directs a stable, collimated laser beam with a narrow beam diameter to a sample holder unit mounted on a high-resolution XY translation stage. Fourteen laser lines with the peak wavelengths of 325–933 nm are available in the setup. The relative standard deviation of the intensity measured over a time period of 8 h was <0.007% with a peak-to-peak deviation of <0.05% for the wavelengths between 425 nm and 780 nm. Outside this range, the intensity varied <0.02% with a peak-to-peak deviation of <0.2%. The laser used can be selected automatically with a moving mirror, which allows measuring with up to four laser lines with one measurement sequence.

The setup was tested by measuring atactic polystyrene sheets exposed to spectrally dispersed UV radiation for different time periods. Measurements were carried out by scanning transmittances horizontally at 1-mm intervals. The best resolution was achieved using the laser line with the shortest wavelength, i.e., 325 nm of the HeCd laser, since the photobleaching increases the absorption of material mostly in the UV-blue region. Using the 325-nm laser line, photodegradation was detected after 2 h of ageing only. The resolution might still increase by shortening the measurement wavelength. The setup could be further improved by introducing a wavelength tunable laser, which would allow measurements at any wavelength.

Scanning the transmittances across the polystyrene sample sheets with the developed measurement setup demonstrated the usability and high resolution of the setup. The spectral dependence of the photodegradation and its temporal development could be measured. The absorbance spectrum developed nonlinearly as a function of the exposure. The very first changes of the absorbance could be seen at the exposure wavelength of 270 nm. The maximum wavelength of this absorption gradually shifted to 290 nm with increasing exposure. After 256 h of exposure, we could see another absorption process evolving at the wavelength of 325 nm. These test measurements showed that the developed measurement setup is a powerful tool for measuring the wavelength sensitivity of the photodegradation as a function of the radiant exposure needed for constructing a complex action spectrum. With minor modifications, the measurement setup could also be extended to measure reflectance, and thus opaque materials. In addition, the setup can be used to characterize optical detectors, e.g., for absolute power responsivities, or they can be scanned to obtain spatial uniformities. Smaller spot size could be achieved by focusing the beam onto the sample with a lens.

In conclusion, the combination of the earlier developed UV spectograph and the new high-resolution laser-based transmittance measurement setup enables a novel method for studying the UV-induced ageing of translucent materials with a spectral resolution of 3–8 nm, limited by the adjustable spectral bandwidth range of the spectograph, which is a significant improvement over earlier methods.

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