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# OPTICAL MEASUREMENT SYSTEM FOR QUALITY CONTROL OF PLASTICS

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**Abstract:** An optical system to measure the degree of curing of extruded plastics will be presented. The setup consists of a mercury vapour UV–lamp and filters, so that the fluorescence and the phosphorescence of the specimen can be measured. In the luminescence spectrum the information about the curing ratio is quantified. Theoretical disquisitions and preliminary measurement results will be presented in this contribution.

**Keywords:** UV, luminescence, polymer, optics

## 1. INTRODUCTION

During the polymer extrusion of thermoplastics it can happen that parts of the material partially start to cure. This happens due to increased stress inside the screw extruder and/or locally raised temperatures. This partially curing is unintended because the material is meant to cure only after a number of subsequent processes under certain conditions [1]. The aim is to accomplish a measurement system to estimate the degree of curing not only online but also inline. The difference in chemical production processes between online and inline measurements is that inline measurements are conducted directly in the production line and deliver the result more or less live, while online measurements are only performed on a part of the product in a bypass of the production line, but still live. An offline measurement is a measurement conducted on a sample in a laboratory.

Already a number of different measurement principles are on the way to become or already are state of the art in polymer melt extrusion such as dielectric measurement, ultrasonic (US), near infrared (NIR), Raman or Tera Hertz (THz) spectroscopy (see [2], [3], [4]). Most of those principles mainly focus on the amount of filler in the polymer melt [5]. Some works introduce measurement principles to monitor crosslinking processes. For example in [6] the curing of an epoxy resin is monitored by THz spectroscopy. A search for principles monitoring the curing of polymer melt delivers few result in the literature.

In this work the luminescence spectrum of a specimen illuminated and excited by a mercury vapour lamp in the UV–spectral range is acquired. It is expected that beside fluorescence also phosphorescence will be observed, both effects are compendiously called lumincescence.

This contribution is organized as follows: first the treated material and its chemical characteristics are introduced, subsequently the setup is illustrated followed by preliminary measurement results and a conclusion.

## 2. POLYMER MELT

The considered polymer is an unsaturated polyester resin (UP) with hydroxylalcylamid as curing agent. As long as the temperature of the polymer is low enough, crosslinking won't start and the polymer remains as a thermoplastic. When the temperature rises the material starts to cure and the material becomes a thermosetting polymer. The mentioned crosslinking is depicted in Fig. 1: the polyester resin has two carboxylic acids at its edges which crosslink with the hydroxylic ends of the curing agent while condensating $2H_2O$ per reacting carboxylic acid.

This chemical reaction of curing is intended to happen under certain conditions, e.g. in a furnace. But when parts of the material start to cure during the extrusion process, the properties of the polymer melt for the subsequent processing steps deteriorate. Hence this quality feature has to be detected and measured.

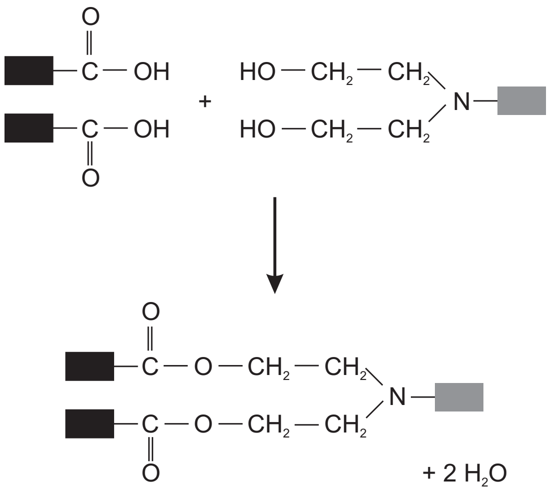

*Fig. 1:* Crosslinking of unsaturated polyester resin containing carboxylic acid with hydroxylalcylamid as curing agent (see [1], p 12).

## 3. MEASUREMENT SETUP

In the previous section the polymer melt's sought after property was introduced. As mentioned in the introduction different approaches to determine the degree of crosslinking can be used. In this contribution the luminescence spectrum of an illuminated specimen is acquired, where areas are searched for and relations are calculated which are characteristic for the crosslinking process. In Fig. 2 the schematics of the setup for the preliminary investigations is depicted. The high pressure mercury vapour lamp radiates a broad spectrum of electromagnetic waves, but only the ultraviolet part in the range of $\lambda = 340\,\text{nm}$ to $\lambda = 380\,\text{nm}$ should impinge on the specimen. This is accomplished by a filter that blocks nearly all radiation in the visible and IR range (Baader U–Filter). In Fig. 3 the emitted (dashed, blue line) and the filtered (green, continuous line) spectrum of the mercury vapour lamp is mapped using normalized data. One can see a second transmission range in the filtered spectrum with a maximum at $\lambda = 730\,\text{nm}$. That range will be dismissed in further measurements.

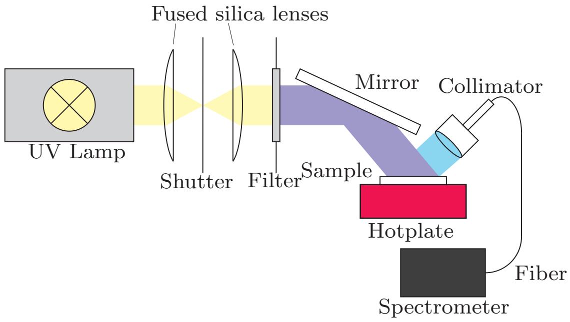

*Fig. 2:* Schematic of the measurement setup.

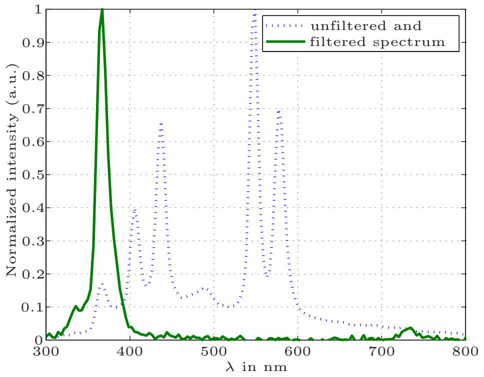

*Fig. 3:* Normalized spectrum of the high pressure mercury vapour lamp (blue, dashed line) and viewed through a UV transmitting filter (green, continuous line).

Located between the light source and the filter there are two fused silica lenses and a shutter. The shutter (Prontor Magnetic E/40) is used to block the light from the filter and the specimen when no measurements are conducted. Since the filter is made of dielectric layers it should not be overworked and the exposure time should be minimal. Additionaly, the material under test can be damaged by exposing it to a too high amount of UV flux. The shutter is placed in the focal plane of the lenses, hence the light source can be blocked in a very short time because the image of the lamp appears in the focal plane nearly as a point. This effect can be used in later investigations. The filtered light is subsequently directed via a mirror to the specimen, which is placed horizontally on a hotplate. The hotplate's function is to cure material while it is monitored. Therefore, a temperature control is implemented using a microcontroller (ATMega8) and a thermistor, whose characteristic curve was identified using a Pt1000 sensor element. A collimator lens is directed at the specimen and collimates the reflected and emitted light. Additionally, a UV/IR blocking filter is placed in front of the collimator lens to collect only wavelengths which are not part of the excitation. Spectrums are acquired with a UV/VIS Microspectrometer from Boehringer Ingelheim Microparts which is connected to the collimator lens via a fiber. The Microspectrometer is equipped with a line scan camera, delivering 256 values of intensity for wavelengths reaching from $\lambda \approx 300\,\text{nm}$ to $\lambda \approx 1180\,\text{nm}$.

## 4. EXPERIMENTS

For measurements the specimen is placed on the hotplate. For the preliminary investigational measurements, two different samples are placed consecutively on the disabled hotplate. The first sample is a solid, cooled down part of polymer melt which is not cured at all. It mainly consists of unsaturated polyester resin, some parts of curing agent and negligible parts of further components. The second sample is from the same polymer melt but cured in a furnace at 180°C for 10 minutes, again cooled down and solidified. One can assume that the second sample is – in contrast to the first sample – completely cured.

In Fig. 4 the acquired normalized spectra from the different samples are plotted in the range of $\lambda = 400\,\text{nm}$ to $\lambda = 700\,\text{nm}$. Because of the UV/IR blocking filter no reflections from the excitation are acquired. Hence, the measured radiation is assumed to originate in luminescence effects. The summed up normalized intensity shows an increase after the material was cured in a furnace.

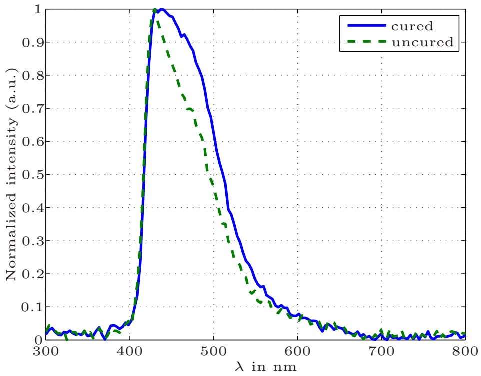

*Fig. 4:* Acquired normalized spectra with cured (blue, continuous line) and uncured (green, dashed line) samples.

### 4.1 Quantification by summed up normalized intensity

A series of measurements was conducted after an uncured sample was placed on the activated hotplate. The temperature of the hotplate is set to 180°C, so that curing of the material starts and continues to a point of nearly complete crosslinking. Spectra are acquired during the curing process every 10 s which are plotted in Fig. 5. In the 3D plot one can hardly identify the change in luminescence: the peak of the luminescence is shifting towards slightly longer wavelengths. The summed up intensity of the normalized luminescence spectrum

$$I_{sum}(t) = \sum_{\lambda} I(\lambda, t) \qquad (1)$$

at each time step, shown in Fig. 6, might be a better measure to indicate the degree of curing.

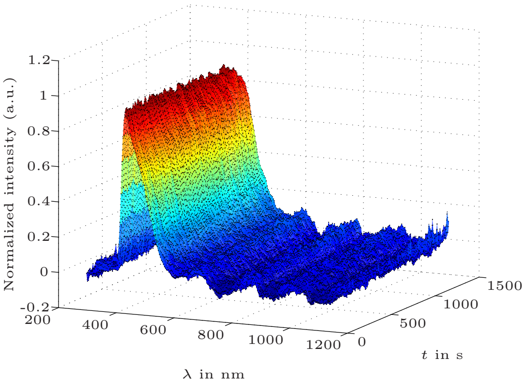

*Fig. 5:* Normalized luminescence spectra of the polymer captured during curing process.

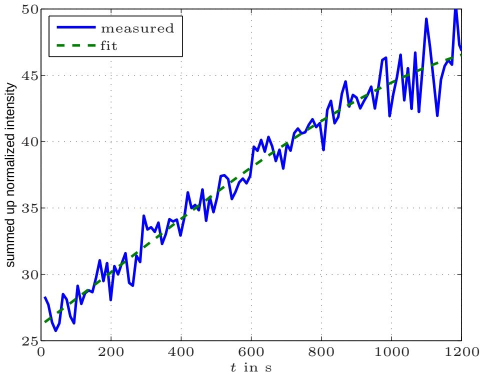

*Fig. 6:* Summed up normalized intensity at each time step during the curing process of the polymer (blue, continuous line), and the corresponding fit using a third order polynomial (green, dashed line).

The summed up intensity $I_{sum}$ shows a linear trend with some measurement noise. They assumedly trace back to the used spectrometer which shows some insufficiencies in converting the intensities to digital values. In Fig. 6 a third order polynomial fit of the summed up intensity is also plotted.

### 4.2 Quantification by ratio of intensities

More reliable than calculating the summed up normalized intensity to quantify the degree of curing is to compare the intensities at different wavelengths. Figure 7 shows such a relation

$$r_{\lambda_1,\lambda_2}(t) = \frac{I(\lambda_1,t)}{I(\lambda_2,t)} \tag{2}$$

where the chosen wavelengths are $\lambda_1 = 430\,\mathrm{nm}$ and $\lambda_2 = 479\,\mathrm{nm}$[1]. As with the first approach of summing up intensities at each time step, measurement noise occurs which traces back to the used spectrometer as mentioned above. In Fig. 7 a third order polynomial fit

$$r_{fit}(t) = p_3 \cdot t^3 + p_2 \cdot t^2 + p_1 \cdot t + p_0 \tag{3}$$

of the measurement data is also mapped. Such a fit will be used to classify samples by their degree of curing in future works when a different spectrometer will be used.

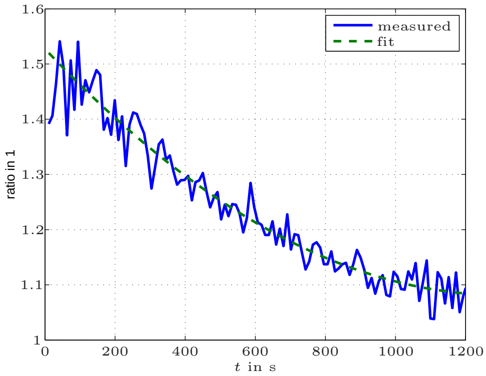

*Fig. 7:* Ratio of intensities $r_{\lambda_1,\lambda_2}(t)$ at $\lambda_1 = 430\,\mathrm{nm}$ and $\lambda_2 = 479\,\mathrm{nm}$ acquired during the curing process of the polymer.

### 4.3 Estimation of curing time

When trying to quantify the measurements from Fig. 4 using the relation introduced in Eq. (2), the ratios amount to

$$r_{uncured} = 1.426$$

for the uncured material and

$$r_{cured} = 1.181$$

for the cured material. At this point of the project, it is not possible to derive a quantified degree of curing. This is ascribed to the measurement noise originated by the used spectrometer, as mentioned above. If one still tries to calculate an equivalent time of curing $t_{eq}$ by solving the polynomial fit Eq. (3) leads to

$$\begin{aligned} t_{eq,uncured} &\approx 160\,\mathrm{s} \\ t_{eq,cured} &\approx 700\,\mathrm{s}. \end{aligned} \tag{4}$$

Although this is a weak estimation, the tendency is obvious although the calculation of the equivalent time $t_{eq}$ is imperfect.

For comparison, one can try to estimate the equivalent time of curing using the summed up intensity from Eq. (1) and the polynomial plotted in Fig. 6. The summed up normalized intensities of the cured and uncured samples from Fig. 4 amount to

$$\begin{aligned} I_{sum,uncured} &= 26.33 \\ I_{sum,cured} &= 31.28. \end{aligned}$$

Using those two values to estimate an equivalent time of curing results in

$$\begin{aligned} t_{eq,uncured} &\approx 7\,\mathrm{s} \\ t_{eq,cured} &\approx 250\,\mathrm{s}. \end{aligned} \tag{5}$$

The comparison of the results in Eqn. (4) and (5) shows, that both approaches show the same trend. The quantification is at this moment of the project not feasible (see above), therefore the values are not reliable and should not be used for further calculations.

## 5. CONCLUSION AND OUTLOOK

The preliminary measurements of luminescence spectra from cured and uncured polymer melt illuminated and excited by a mercury vapour lamp show a sensitivity in the intensity for the degree of crosslinking. Hence, two different approaches to quantify this measure are introduced: First, the summed up normalized intensity $I_{sum}$, and second, the relation of intensities at different wavelengths $r_{\lambda_1,\lambda_2}$. Both show the tendency for the degree of curing, but the used spectrometer delivers noisy measurements so that the quantification is hard to estimate. Finally the degree of curing is estimated for two samples which are uncured and completely cured using the polynomial fit of the ratio, the result mirrors the tendency.

For future works an enhanced spectrometer with higher spectral resolution and better conversion to digital values will be used. Furthermore the long term aim is to build a setup for conducting inline measurements.

## 6. ACKNOWLEDGEMENT

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[1] Due to the fact that the spectrometer quantizes the wavelength as well, the mentioned wavelengths should be taken as center wavelengths.

## 7. REFERENCES

[1] J. Pietschmann, ”Industrielle Pulverbeschichtung”, 3. Auflage, Vieweg+Teubner, 2010.

[2] I. Alig, D. Fischer, D. Lellinger, B. Steinhoff, ”Combination of NIR, Raman, ultrasonic and dielectric spectroscopy for in-line monitoring of the extrusion process”, 16th European Symposium on Polymer Spectroscopy (ESOPS 16), pp 51-8, 2005.

[3] Author(s): P.D. Coates, S.E. Barnes, M.G. Sibley, E.C. Brown, H.G.M. Edwards, I.J. Scowen, ”In-process vibrational spectroscopy and ultrasound measurements in polymer melt extrusion”, POLYMER Volume 44 Issue 19, pp 5937-5949, 2003.

[4] M. Skrifvars, P. Niemela, R. Koskinen, O. Hormi, ”Process cure monitoring of unsaturated polyester resins, vinyl ester resins, and gel coats by Raman spectroscopy”, JOURNAL OF APPLIED POLYMER SCIENCE Volume 93 Issue 3, pp 1285-1292, 2004.

[5] N. Krumbholz, T. Hochrein, N. Vieweg, T. Hasek, K. Kretschmer, M. Bastian, M. Mikulics, M. Koch, ”Monitoring polymeric compounding processes inline with THz time-domain spectroscopy”, POLYMER TESTING Volume 28 Issue 1, pp 30-35, 2009.

[6] M. Naftaly, D. Dimitrakopoulos, R.E. Miles, S. Brown, S. Perrier, ”Polymerisation-related changes in THz transmission in SU8 and polystyrene”, Joint 31st International Conference on Infrared Millimeter Waves and 14th International Conference on Teraherz Electronics. IRMMW-THz 2006, p 56, 2006.