As discussed in section 2.2, the characterization of cross-linking and especially its spatial distribution is crucial for the fabrication of micro optics, MEMS, and semiconductors. Some studies have found that the measurement of the refractive index over the cross-linking process can be used as an indicator for the degree of cross-linking of a sample. According to Kudo et al., [130], the cross-linking of a polymeric material leads to a densification which can be directly related to an increase in refractive index using the Lorentz-Lorenz equation. The characterization of the refractive index is therefore a suitable measure for the degree of cross-linking, [139].

Based on the spectral interferometric approach utilized for surface profilometry in section 3.2 of this work, a characterization method was developed, tested and evaluated. It is based on the fact that the wavelength-dependent refractive index $n_{smp}(\lambda)$ of a sample in correspondence with its thickness t_{smp} determines the spectral output of a low-coherence interferometer, [278, 279]. In contrast to dispersion-encoded profilometry, in cross-linking characterization, the sample itself is the dispersive element. Hence, the dispersion characteristic of $n(\lambda)$ is the unknown quantity.

In the most basic configuration a two-beam interferometer with spectral detection is used to analyze a sample, Fig. 4.1 a). In this case, the signal at the spectrometer $I(\lambda)$ can be described as an adaptation of Eq. (3.20),

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$$I(\lambda) = I_0(\lambda) \cdot [1 + \cos\varphi(\lambda)] \quad (4.1)$$

$$\text{with } \varphi = 2\pi \frac{[n^{smp}(\lambda) - 1] t_{smp} - \delta}{\lambda}, \quad (4.2)$$

where $I_0(\lambda)$ is the spectral profile of the light source and φ the phase. In the assumed simple case, the thickness of the sample t_{smp} is a constant whereas the path difference δ can be altered with a translation stage.

4.1 Temporal Approach

A temporal approach of the aforementioned two-beam interferometer was realized in a MICHELSON configuration where the sample is a transmissive part of one interferometric arm while the reference arm mirror is translatable to achieve temporal control, Fig. 4.1 a). According to Eq. (4.1), the signal depends on the wavelength-dependent refractive index $n^{smp}(\lambda)$, the sample thickness t_{smp} and the path difference between the arms δ . As $n^{smp}(\lambda)$ and t_{smp} are material constants for a supposed bulk material, the path difference is the only variable which can be used to evaluate the refractive index. A variation of the path difference leads to a deformation of the phase and

Figure 4.1 a) Simple setup for the characterization of transmissive samples where a WLS—white-light source is splitted by a BS—beam splitter so that in one arm the light transmits through the SMP—sample with the thickness t_{smp} before and after it is reflected from SMP-M—sample mirror while in the second arm the light is reflected from REF-M—reference mirror which can be adjusted in the x -dimension; both signals are analyzed after recombination using a SPEC—spectrometer. b) Simulated, spectrally-resolved phase data from such a setup with a sample of N-BK7 with a thickness of 5 mm for a number of different delays of the reference arm noted in δ

most notably to a shift of the phase minimum according to Eq. (4.1), Fig. 4.1 b). The minimum is described by its wavelength, the equalization wavelength λ_{eq} and can be tracked as a function of the path difference $\delta(\lambda)$ or the temporal delay $\tau(\lambda)$. This information can be used to calculate the group refractive index of the material using

$$n_g^{smp}(\lambda) = \frac{\delta(\lambda)}{t_{smp}} = \frac{\tau(\lambda) \cdot c}{t_{smp}}. \quad (4.3)$$

The measurement can be performed either in a relative or absolute way. For relative measurements, the delay introduced relative to a starting position (noted with λ_{eq}^0) is used to calculate the relative group refractive index $\Delta n_g^{smp}(\lambda)$. Absolute values of $n_g^{smp}(\lambda)$ can be obtained, if the delay is referenced to the stationary phase point of the interferometer in a dispersion-free status.

Figure 4.2 a) Measured temporal delays for N-BK7 samples of 1, 3 and 5 mm nominal thickness respectively in the spectral range from (400-1000)nm and b) calculated group refractive indices for the three nominal thicknesses in relation to the values known from literature according to [280]

In an initial experiment, a reference mirror was placed onto a precision stage which was then used to introduce defined delays to the signal in form of path differences δ_n . By tuning the delay to reach a certain equalization wavelength λ_{eq}^n , repeated measurements to calculate $n_g^{smp}(\lambda)$ were possible. In order to quantify the method, measurements on a set of samples of N-BK7 glass with nominal thicknesses t_{nom} of 1, 3 and 5 mm were performed, Fig. 4.2 a). In an experiment with ten measurements per nominal thickness it was found that the mean standard deviation over all equalization wavelengths for $t_{nom} = 1$ mm was $\overline{\sigma_1(\tau)} = 1.86 \times 10^{-3}$ ps, for $t_{nom} = 3$ mm

was $\overline{\sigma_3(\tau)} = 1.99 \times 10^{-3}$ ps and for $t_{nom} = 5$ mm was $\overline{\sigma_5(\tau)} = 3.75 \times 10^{-3}$ ps. The mean values of all three delay slopes were used to calculate the group refractive index according to Eq. (4.3), Fig. 4.2 b). The errors of the measured data have been calculated for every equalization wavelength relative to the respective literature values for N-BK7, [280]. The root-mean-square error for the calculated mean group refractive index of the nominal thickness $t_{nom} = 1$ mm was $\Delta n_{g1} = 2.08 \times 10^{-4}$, $\Delta n_{g3} = 6.54 \times 10^{-5}$ for $t_{nom} = 3$ mm and $\Delta n_{g5} = 1.45 \times 10^{-4}$ for $t_{nom} = 5$ mm. The mean standard deviation over all equalization wavelengths was $\overline{\sigma_1(n_g)} = 5.72 \times 10^{-4}$, $\overline{\sigma_3(n_g)} = 1.93 \times 10^{-4}$ and $\overline{\sigma_5(n_g)} = 2.13 \times 10^{-4}$ for the three nominal sample thicknesses. As the delay was acquired as primary information, it was used in conjunction with the thickness of the sample in order to calculate the refractive index for each equalization wavelength. This calculation is not reliant on any knowledge about the underlying material model. In case of a known material composition, a model can be chosen in order to fit the measured data. For the evaluation data of N-BK7, a fit using the basic Sellmeier equation was performed using the parameters B_1, B_2, B_3, C_1, C_2 and C_3 ,

$$n^2(\lambda) = 1 + \frac{B_1 \lambda^2}{\lambda^2 - C_1} + \frac{B_2 \lambda^2}{\lambda^2 - C_2} + \frac{B_3 \lambda^2}{\lambda^2 - C_3}. \quad (4.4)$$

It was found that the root-mean-square error of the fitted data in relation to literature data for the refractive index was calculated $\Delta n_{g1}^{fit} = 2.71 \times 10^{-4}$, $\Delta n_{g3}^{fit} = 2.06 \times 10^{-4}$ and $\Delta n_{g5}^{fit} = 2.30 \times 10^{-4}$ for the three nominal sample thicknesses. These results prove the accuracy of the method to determine the refractive index of transmissive samples which in turn can be utilized to characterize cross-linking of polymers as typical cross-linking differences in the range of $\Delta n = 0.001 - 0.02$ are expected, [138]. An error propagation for the temporal approach was performed and documented in section 4.3.1.

For further evaluation, two epoxy-based samples in different states of cross-linking have been investigated with the described method. Both samples were distinctively different in their appearance as one sample was made of bulk material (Araldite epoxy, $t_{sm}^A = 3.04$ mm) while the second one was a thin-layered SU-8 ($t_{sm}^{SU8} = 0.23$ mm). The properties of both samples have been studied using the setup described in Fig. 4.1 a) over a spectral range from $(0.4-1) \mu\text{m}$. The dispersion related temporal delay was recorded and referenced to the sample thickness for comparison, Fig. 4.3 a). The materials show significant differences in their refraction behavior over the spectral range. While Araldite shows a delay ranging from 1000 ps/m (@900 nm) to over 1200 ps/m (@450 nm), the SU-8 sample just causes delays of 850 ps/m to 1050 ps/m at the same spectral points. Both data sets could be

Figure 4.3 Results of the temporal approach measurements for Araldite and SU-8 samples with a) recorded delays due to dispersion and corresponding CAUCHY fitted curves as well as b) calculated dispersion D from fitted curves

well fitted with a CAUCHY model to approximate their behavior using the parameters A_1 , A_2 and A_3 , [281]

$$\tau(\lambda) = A_1 + \frac{A_2}{\lambda^2} + \frac{A_3}{\lambda^4}. \quad (4.5)$$

The difference in the relative temporal delay is an indicator of the different degrees of cross-linking. The first derivative of the temporal delay τ in relation to the wavelength λ was used to calculate the corresponding dispersion $D = D(\lambda)$, Fig. 4.3 b),

$$D(\lambda) = \frac{\partial \tau(\lambda)}{\partial \lambda \cdot t_{\text{sm}}} = -\frac{1}{t_{\text{sm}}} \left(\frac{6A_2}{\lambda^3} + \frac{20A_3}{\lambda^5} \right). \quad (4.6)$$

This representation of the measured optical properties focuses on the slope of the dispersion induced delay. The differences between both materials are still evident but much smaller than the relative delay. Especially for shorter wavelengths, the differences are significant which indicates a different absorption behavior, hence a different molecular composition. This results indicates that the two materials are similar in their composition, but show differences in cross-linking. In the spectral region below 600 nm a higher dispersion of SU-8 is visible. A reason for that might be the different mechanism of the cross-linking initiation. While the polymerization of SU-8 is initiated by UV-light radiation, the polymerization of Araldite is initiated chemically. In the wavelength range from (600 – 750) nm the dispersion of both materials is approximately the same. In the near infrared region, Araldite shows

Table 4.1 Conclusive representation of key properties measured for both polymeric samples with the CAUCHY coefficients, the micro hardness and the sample thickness

	Araldite	SU-8
CAUCHY coefficients		
$A_1[\frac{ps}{m}]$	956.9 ± 3.1	793.9 ± 2.7
$A_2[\frac{ps\mu m^2}{m}]$	9.9 ± 1.0	15.3 ± 0.7
$A_3[\frac{ps\mu m^4}{m}]$	0.7 ± 0.1	0.1 ± 0.1
hardness $[HV]$	1.40 ± 0.01	1.57 ± 0.07
thickness $t_{smp} [mm]$	3.04 ± 0.01	0.23 ± 0.02

a slightly higher dispersion. Both curves are significantly different in terms of the measured standard deviation.

In order to support the observations made in temporal low-coherence interferometry, an additional material characterization were undertaken by VICKERS micro hardness tests. The results were compared to the obtained optical properties, Tab. 4.1. Hardness measurements have been performed on a micro indenter device operating with a force of 0.245 N in 5 indentations per sample. The micro hardness tests support the measurements of the optical properties as only minor differences are to be noted. This corresponds with the fact that both materials have a similar chemical composition. The slight differences therefore have to be caused in a difference of the cross-linking. SU-8 on the one hand is harder than Araldite but on the other hand constantly shows lower refraction over the recorded spectral range. An effect similar to that has been shown in literature, where the refractive index of SU-8 was determined at different baking steps, [282]. Here, the samples which were subjected to longer baking have shown higher cross-linkage as well as lower overall refraction.

However, it should be noted that the experimental approaches for the mechanical and optical properties are fundamentally different. Since micro hardness is measured at distinct points on the samples' surfaces, it can be heavily influenced by residual stresses and local inhomogenities. In contrast to that, the dispersion measurements integrate the properties spatially over the sample's thickness as well as over the cross-section (dependent on the spot size of the light setup). Therefore, the hardness measurements are only used as a tool for the classification of the determined optical properties. With the aid of these measurements, it was possible to determine the existence of differences in cross-linkage; these should be observable in optical measurements as well.

While the presented results were gathered from samples of slightly different materials, further experiments were carried out that only examined one material with defined degrees of cross-linking. A sample set of ethylene-vinyl acetate (EVA) was used for this purpose. The samples were prepared from sheet material. The sheets were exposed to a temperature of 150 °C in an industrial laminator. The exposure time determined the state of cross-linking. Beforehand, the samples have been analyzed with state-of-the-art methods by Hirschl et al., [124].

Especially in the field of photo voltaics (PV), EVA, which are used as encapsulants there, have to maintain their properties over an operation time of 20–30 years, [283]. Mainly, these encapsulants serve as a protection to prevent damage from mechanical, electrical and humid sources. They have to provide high strain and temperature stability to compensate for the different thermal expansion coefficients. Besides, they have to compensate for stresses and prevent cracks of the substrate materials. Another important function is the optical coupling of the light in the desired wavelength region. That demands a transmission of >90% with tolerated losses of maximal 5% in 20 years, [284]. EVA is a random co-polymer of ethylene and vinyl acetate with a percentage of vinyl acetate typically in the range from 28 to 33 weight-% for PV module applications. The native EVA would not fulfill the thermo-mechanical requirements due to its melting range between 60 and 70 °C. By chemical cross-linking utilizing hydroperoxides during PV module lamination, the moldable EVA sheet is transformed into a highly transparent elastomer with the required thermo-mechanical stability up to 100 °C, [124, 284]. It shows good adhesion, high transmission in the interesting wavelength region and it is sufficiently long-term stable regarding its properties. In order to establish the desired properties of polymers like EVA, it is necessary to develop and control appropriate curing processes.

The prepared EVA samples of different cross-linking states were cut from sheets in proper pieces with a thickness of 400 μm . The temporal delay τ of each sample in relation to the white-light point was recorded in repeated measurements with 10 repetitions each. The data was then normalized to the corresponding sample thickness t_{smp} and plotted as an averaged curve in relation to the wavelength, Fig. 4.4 a). The data points were also fitted using the CAUCHY equation Eq. (4.5). From the plot it becomes obvious that the differences in the delay due to dispersion are $\leq 10 \text{ ps/m}$. It is also obvious that the differences between an un-laminated sample (NLT) and a laminated sample (LT 1 min) are rather high. That must be considered especially in relation to a longer lamination period from LT 1 min to LT 8 min. This fact leads to the assumption that the curing reaction starts fast.

In order to gather additional information, the dispersion parameter D was calculated as first derivative of the fitted data according to Eq. (4.6), Fig. 4.4 b). The

Figure 4.4 a) Results for the measured temporal delays τ due to the different lamination times normalized to the material thickness t_{smp} for three representative lamination times with NLT—no lamination, LT 1 min—1 minute and LT 8 min—8 minutes lamination and the corresponding fits using a CAUCHY model according to Eq.(4.5) and b) derivation of the temporal delay relative to the wavelength according to Eq. (4.6)

results reveal that there is no particular difference between the varying degrees of cross-linking. Although some differences in the wavelength range of $(0.4\text{--}0.6)\mu\text{m}$ can be observed, the corresponding errorbar proves that the dispersion slope in relation to the wavelength is constant for different degrees of cross-linking. This leads to the assumption that the magnitude of the temporal delay and therefore also of the group refractive index can be used as a measure for cross-linking differences. In contrast, the slope of the wavelength-dependent curves is not a suitable measure to make out cross-linking differences.

The most important information, the degree of cross-linking, can be extracted by plotting the differences in temporal delay $\Delta\tau/t_{smp}$ versus the lamination time, Fig. 4.5. The data acquisition over a broad spectral range enables the analysis at different wavelengths. For comparison, the relative delay at three probing wavelengths (0.5, 0.7 and $0.9\mu\text{m}$) was analyzed. It is visible that the data is equal within the standard deviation of the measurements especially for the spectral probing points of (0.7 and $0.9\mu\text{m}$). The data at $0.5\mu\text{m}$ shows a slight deviation. In order to compare the results to other methods, the measurements have been fitted using a pseudo-first order reaction kinetics model¹ of the form $y = a + b \cdot e^{-kt}$ where k is the characteristic

¹ In situations where the amount of cross-linker is small compared to the amount of polymer, the reaction can be described as a first order reaction. In this context, the term *pseudo-first order* is used, [124].

Figure 4.5 Plot of the differences in $\Delta\tau/t_{smp}$ over the lamination time selected probing wavelengths

constant of the reaction process and a , b describe the absolute position of the slope. This model is commonly used to describe cross-linking behavior determined by characterization approaches, [124]. As good fits ($R^2=0.976, 0.985$ and 0.989) could be obtained at all probed wavelengths, an averaging over a range of wavelengths can be used to determine the degree of cross-linking with higher statistical confidence. In comparison to other technologies, the presented results show reasonable errors in the range of 6.35–8.39%. Also, the trend of the data is in good analogy to reference technologies like soxhlet-extraction, Raman spectroscopy, DSC or DMA, [124]. EVA samples show fast cross-linking at the beginning of the lamination process which significantly slows down after 3–4 minutes. The calibration of the $\Delta\tau/t_{smp}$ data to a degree of cross-linking on a percentage scale can be done by choosing an appropriate reference technology.

In consequence, the temporal approach showed the ability to gather model-free refractive index data over a large spectral range, $(0.4\text{--}1)\mu\text{m}$, with deviations to literature values in the range of $2.06 \times 10^{-4} - 2.71 \times 10^{-4}$. It could be shown that cross-linking of polymers for industrial applications can be evaluated on the basis of the refractive index measurements. The results proved to be comparable, and in terms of their standard deviation, more reliable than the results of established technologies such as soxhlet-extraction or Raman spectroscopy. The additional statistical confidence through the measurement over a large spectral range as well as the ability to gather spectrally-resolved refractive index data are advantages of this approach over established methods.

4.2 Scan-free Approach

4.2.1 Wrapped-phase Derivative Evaluation (WPDE)

One significant drawback of the temporal approach to estimate the degree of cross-linking with the refractive index is the need for mechanical scanning of one interferometric arm. It possibly introduces additional errors and increases the measurement time.

From Eq. (4.2) it is known that the wavelength-dependent refractive index $n^{smp}(\lambda)$ is contained in the phase of the interferometer output in combination with the sample thickness t_{smp} and the path difference δ . Under the assumption that t_{smp} as well as δ are known, the relevant cross-linking information can be found in the refractive index.

By rewriting Eq. (4.2) the measured phase-term φ_{meas} , containing the refractive index, can be extracted

$$\varphi_{meas} = \cos^{-1} \left(\frac{I(\lambda, x)}{I_0(\lambda)} - 1 \right) = 2\pi \frac{(n^{smp}(\lambda) - 1)t_{smp} - \delta(x)}{\lambda} + \varphi_{off}. \quad (4.7)$$

Inherent to this approach is the ambiguity of the resulting values as φ is not limited to the range of $0 - \pi$. Other works have shown methods to perform the correct quadrant selection in order to resolve this ambiguity, [285]. In contrast, an alternative method to avoid quadrant selection was developed by performing a local signal analysis in the spectral range close to λ_{eq} , Fig. 4.6 a). In the first stage, this approach determines the phase minimum and defines a ROI around the minimum. For this purpose, the raw measured data is analyzed using a STFT where a FFT is performed in one small

Figure 4.6 a) Simulated data of a wrapped phase due to the $\cos^{-1}$ operation according to Eq. (4.12) with marked equalization wavelength λ_{eq} and ROI for the extraction of φ_{loc}

window of the complete data set which is then slid over the signal successively along the wavelength dimension, see subsection 3.3.2. This approach accounts for the non-uniform frequency of the signal. As a result, the minimum of the extracted frequency slope can be determined from the power spectrum. It represents the position of the phase minimum which also occurs at λ_{eq} . The ROI is defined as a local wavelength range λ_{loc} in the proximity of the detected λ_{eq} where only unambiguous phase data is included. This so-called local phase, φ_{loc} , is subject to a phase offset, φ_{off} , with regard to the absolute phase due to the $\cos^{-1}$ -operation, Eq. (4.12).

A second analytical step implements a newly developed approach called WPDE, where φ_{loc} is differentiated with respect to the wavelength, noted with $\frac{\partial}{\partial \lambda}$,

$$\frac{\partial \varphi_{loc}}{\partial \lambda} = \frac{\partial}{\partial \lambda} \left(2\pi \frac{[n(\lambda_{loc}) - 1]t_{smp} - \delta(x)}{\lambda_{loc}} + \varphi_{off} \right). \quad (4.8)$$

This eliminates the phase offset φ_{off} and enables the evaluation of the cross-linking characteristics in terms of the group refractive index $n_g^{smp}(x, \lambda)$ as well as the relative derived optical thickness (RDOT) t'_{OPT}

$$n_g^{smp}(x, \lambda) = 1 - \frac{\kappa}{t_{smp}} \quad (4.9)$$

$$\text{with } \kappa = \frac{\varphi'_{loc} \cdot \lambda^2}{2\pi} - \delta \quad (4.10)$$

$$t'_{OPT} = n_g^{smp}(x, \lambda) \cdot t_{smp} = t_{smp} - \frac{\varphi'_{loc} \cdot \lambda^2}{2\pi} - \delta \quad (4.11)$$

where φ'_{loc} is calculated from the measured data using the difference quotient with $\Delta\lambda$ as interval. This case holds true when experiments, as sketched out in Fig. 4.1 a), are performed where one simple sample is part of the interferometer as well as the primary source of dispersion. In situations where samples with low dispersion are to be measured or the simultaneous measurement of the samples surface profile should be realized, a modified setup with additional dispersion is favorable, Fig. 4.7. In this case, the phase term of Eq. (4.7) has to be expanded by an appropriate term for the dispersive element,

$$\begin{aligned} \varphi &= \cos^{-1} \left[\frac{I_{meas}(x, \lambda)}{I_0(\lambda)} - 1 \right] \\ &= 2\pi \frac{[(n^{smp}(x, \lambda) - 1)t_{smp}] + [(n^{DE}(\lambda) - 1)t_{DE}] - \delta}{\lambda}. \end{aligned} \quad (4.12)$$

According to this equation, the derivative in order to access the group refractive index can be noted as

$$\varphi'_{loc} = \frac{\partial}{\partial \lambda} \left(2\pi \frac{[(n^{smP}(x, \lambda) - 1)t_{smP}] + [(n^{DE}(\lambda) - 1)t_{DE}] - \delta}{\lambda} + \varphi_{off} \right), \quad (4.13)$$

which leads to a new description of the group refractive index and the RDOT t'_{OPT} for the approach with additional dispersion

$$n_g^{smP}(x, \lambda) = 1 - \frac{\lambda^2 \cdot \xi}{2\pi \cdot t_{smP}} \quad (4.14)$$

$$\text{with } \xi = \varphi'_{loc} - \frac{2\pi}{\lambda^2} \left[(1 - n_g^{DE})t_{DE} + \delta \right] \quad (4.15)$$

$$t'_{OPT} = n_g^{smP}(x, \lambda) \cdot t_{smP} = t_{smP} - \frac{\lambda^2 \xi}{2\pi}. \quad (4.16)$$

A detailed derivation of Eq. (4.9) and (4.11) for the sample-only approach as well as for the approach with additional dispersion resulting in Eq. (4.14) and (4.16) can be found in the appendix in the Electronic Supplementary Material (ESM).

In order to evaluate the algorithm, the group refractive index of a N-BK7 sample with a nominal thickness of 5 mm was determined. The averaged standard deviation of 10 consecutive measurements of the sample was found to be 9.97×10^{-5} . The averaged group refractive index data of these 10 measurements was fitted using a SELLMEIER equation, Fig. 4.7 b). In resemblance to the literature values, [280], a root-mean-square error of 1.65×10^{-4} and of 3.36×10^{-5} was achieved for the averaged measured and for the fitted data respectively. Compared to the measurements using the temporal approach, subsection 4.1, this demonstrates an improvement as the RMS error was $\Delta n_{g5}^{fit} = 2.30 \times 10^{-4}$. An additional advantage over the temporal approach is the ability to gather the wavelength-dependent group refractive index without the need for mechanical scanning. The result shows that the WPDE approach achieves a comparable accuracy to state-of-the-art refractive index measurement technologies. Furthermore, the refractive index resolution is sufficient to characterize cross-linking in waveguide polymers, where differences in the range of $\Delta n = 0.001 - 0.02$ are expected, taking the respective sample thickness into account, [138].

This result is calculated only within the ROI and is dependent on the amount of dispersion, represented by $n_g^{smP}(\lambda)$. Therefore, it is valid only within a small spectral range. Different approaches have been considered to gather information over the

Figure 4.7 Setup for the imaging approach to cross-linking characterization with WPDE incorporating a WLS—white light source which is split into a reference arm with a REF-M reference mirror and a sample arm which consists of a SMP—sample of t_{smp} on a SMP-M—sample mirror and an optional DE—dispersive element of t_{DE} . The beams of both arms are recombined by the BS—beamsplitter and imaged by a LE—lens onto the IMSPEC—imaging spectrometer. LE can be translatable in the y-dimension to gather areal cross-linking information and b) Plot of the averaged measured group refractive index of N-BK7 ($t = 5$ mm, 10 measurements) which was calculated using the WPDE approach and its corresponding SELLMEIER fit in comparison to the literature values according to [280]

complete spectral range of the data set. On the one hand, the WPDE analysis algorithm can be applied to other ROIs within the data. The advantage is that the group refractive index can be calculated without an a priori knowledge of the underlying material model. On the other hand, one can calculate the group refractive index over the complete spectral range, if the material model of the sample is known.

4.2.2 Spatially-resolved Approaches

All approaches described so far have been based on point-wise measurements of spectra and relied on scanning either one arm of the interferometer to gather wavelength-dependent information (temporal approach) or on scanning the sample in order to gather information from different locations of the sample (WPDE).

Scan-free temporal approach

The evaluation of the refractive index of a sample and therefore of the degree of cross-linking relied on mechanical scanning of one interferometer arm in order to scan the spectral domain for certain equalization wavelengths λ_{eq} . The underlying principle

Figure 4.8 a) Proposed setup for the scan-free temporal evaluation of samples with a WLS—white-light source split by a BS—beam splitter into one arm that focuses light into a SMP—sample which then gets back reflected by a mirror and a second arm, known as REF—reference arm where light is focused in the same way before it gets back reflected on a mirror which introduces controlled temporal delays in the x -domain δ_n and a IMSPEC—imaging spectrometer in order to analyze the signal in a spatially-resolved manner and b) a simulated signal of the imaging spectrometer with different temporal delays δ_n and corresponding equalization wavelengths λ_{eqn}

is the introduction of different temporal delays to the setup. A possible method to introduce the delays all at once, relies on the spatially encoding of them and the appropriate detection, Fig. 4.8. For this purpose, the standard one-dimensional spectrometer is replaced by an imaging spectrometer with appropriate optics. The imaging setup enables the detection of spectral information in one spatial domain. In the proposed setup, the probing beam is focused in the sample volume and re-collimated onto a mirror. Consequently, the beam of the reference arm is also focused and re-collimated without a sample being present. The mirror of the reference arm is designed to introduce temporal delays to the beam with a spatial distribution. After recombination of both beams and their spectral detection, this distribution of delays can be recorded as spectra with different adequate equalization wavelengths. Analogous to section 4.1, these wavelengths can be used to calculate the refractive index of the sample at these discrete points. Depending on the number and size of the delays as well as the construction of the spectrometer, a large spectral range can be covered. Model-based fits can be calculated accordingly. The introduction of delays can be done by means of a stepped mirror, a deformable micro-mirror array or a transmissive element with a refractive index gradient.

Imaging WPDE

In a second approach, the aforementioned implementation of an imaging spectrometer was also used to perform WPDE with spatial resolution using the setup described in Fig. 4.7 a). Within the setup, a sample with the thickness t_{smp} is placed on a reflecting substrate and is used as a mirror for one interferometer arm. Correspondingly, the reference arm only comprises a mirror and no additional dispersive element. Depending on the thickness and amount of dispersion of the sample, an element with additional dispersion with the thickness t_{DE} might be necessary in the sample arm in order to enhance the measurability. A detailed explanation on the usage of an additional dispersive element is given in subsection 4.3. The setup is also equipped with a translation stage for the imaging lens LE. This lens enables the recording of areal cross-linking information. As the imaging spectrometer allows capturing refractive index data along a line, the translation of the imaging lens in the y -dimension enables the stacking of these line profiles in order to receive information on the whole two-dimensional plane, refer also to Fig. 3.36 a). Using this method neither the sample nor the reference arm have to be moved during measurements which prevents obstructions of the interferometric measurement due to movement. The data analysis was performed analogously to the WPDE approach described in section 4.2.1. As already pointed out, in case of the usage of an additional dispersive element, a modified set of equations, Eq. (4.14), has to be applied.

This approach was used to characterize lithographically generated structures in a photo-resist, Fig. 4.9. The resist was spin-coated on a Si-wafer with a thickness of $t_{smp} = 750 \mu\text{m}$. Afterwards, it was exposed to visible light, (400–420) nm, for primary cross-linking and to UV-radiation, (300–360) nm, in a secondary cross-linking process. The secondary cross-linking was performed through a mask to generate structures of rectangular refractive index patterns which also lead to the shrinkage of the cross-linked areas. The goal of the investigations was to determine the surface height profile that is altered due to shrinkage as well as the refractive index profile which is due to different degrees of cross-linking.

The surface height profile of the sample was characterized with the described setup using the front-surface reflex and the profilometry approach described in chapter 3, Fig. 4.9 b). It is obvious that apart from a slight overall waviness, the sample shows a regular height pattern with the expected pitch of $50 \mu\text{m}$. The depth of the shrunken areas is about 120 nm, which lies in the expected range. In consequence, these calculated height profiles enable the separation of shrinkage from the refractive index information for every sample individually and simultaneously.

With the knowledge of the surface height profile of the sample due to shrinkage, the correct thickness along the spatial domain, $t_{smp} = t_{smp}(x) \sim z(x)$, can be calculated. Therefore, the surface height profile was measured in relation to the

Figure 4.9 a) Detail of the photo-resist sample under test with a lithographically generated, spatially-dependent refractive index pattern and a resulting surface height profile due to shrinkage. After transmission through a DE—dispersive element with t_{DE} a FSR—front-side reflex from the sample can be used to interfere with light from the REF-arm—reference arm in order to calculate the surface height profile $z(x) \sim t_{smp}(x)$ while a BSR—back-side reflex can be used in conjunction with $t_{smp}(x)$ to calculate the refractive index profile $n(x)$ as a measure for the degree of cross-linking across the sample b) plot of the measured surface profile $z(x)$ from a polymer sample under investigation utilizing a wavelength-calibrated imaging spectrometer

substrate. By the application of either Eq. (4.14) or (4.16), the group refractive index or the relative derived optical thickness can be calculated corresponding to its position on the sample, Fig. 4.10 a). For the results pictured above, the RDOT profile of the sample was calculated for a single wavelength of 557 nm. The spatial profile allows a resolution of cross-linking differences of $4 \mu\text{m}$ in the lateral domain. Although the results are affected by noise and batwing-effects, [263], a dynamic range of $\pm 1.5 \mu\text{m}$ in the RDOT for the given sample was revealed over a lateral range of nearly $550 \mu\text{m}$, while a section of $250 \mu\text{m}$ is displayed here. Furthermore, it also has to be noted that the plateaus do not show completely flat RDOT profiles. This behavior was attributed to a mixture of effects ranging from diffraction during exposure of the structures to deformation during shrinkage and diffraction during measurements. As the profile was taken at a specific wavelength, it represents only a fraction of the captured information, which was originally analyzed over a spectral range of 20 nm.

In order to estimate the effect of cross-linking, the RDOT differences have been measured over the complete spectral range as a mean value of two different exposed

Figure 4.10 Results of the measured RDOT a) spatially resolved along one sample dimension of a lithographically structured photo-resist layer with structures having a nominal pitch of 50 μm on a Si-substrate at a wavelength of 557 nm and b) mean values and fitted data for two marked areas with different degrees of cross-linking over a spectral range

areas, Fig. 4.10 b). An RDOT difference of about 3 μm between the differently cross-linked areas could be resolved while the RDOT slope for every area was determined over 10 nm. The results are affected by noise in the original data which is amplified by the process of taking the derivative. Some smoothing with a Gaussian filter was applied to the data.

One of the main advantages of the described approach is the lack of necessity for a model in order to calculate the spectrally-resolved refractive index. As some compromise towards the size of the spectral measurement range was made by the choice of the dispersive element, subsection 4.2.1, the application of a refractive index model might become interesting in post-processing. In the context of (photo-)polymers, a variant of CAUCHY's equation was selected, [281, 286]. Using this model, the group refractive index $n_g^{smg}(\lambda)$ can be calculated according to Delbarre et al. [246] with

$$n_g^{smg}(\lambda) = n(\lambda) - \frac{dn(\lambda)}{d\lambda} \cdot \lambda = A_1 + \frac{3A_2}{\lambda^2} + \frac{5A_3}{\lambda^4}. \quad (4.17)$$

By appropriate fitting, the CAUCHY coefficients A_1 , A_2 and A_3 were determined which enable the calculation of the refractive index and the group refractive index over any given spectral range where the CAUCHY model is valid.

4.3 Influences and Limitations

The measurement range as well as the accuracy of the cross-linking determination is dependent on the accuracy of the determination of the equalization wavelength λ_{eq} , the sample thickness t_{smp} and the path difference of the interferometer δ amongst other parameters, Eq. (4.1) and Eq. (4.7). While the position of the equalization wavelength depends on the path difference between both interferometer arms, the width of the fringe around λ_{eq} is determined by the amount of optical dispersion. Hence, thicker materials show tighter fringe spacing than thinner samples of the same refractive index, Fig. 4.11. The different measurement approaches discussed in this chapter demand different signal types for analysis. While the detection of just the equalization wavelength with the temporal approach works with very little dispersion, hence a very wide fringe spacing, the WPDE method requires a tighter fringe spacing in order to resolve the phase minimum in the power spectrum, Fig. 4.12. The estimation of the phase minimum is performed as tracking for the minimal frequency of the component carrying the most power in the spectrogram. An analysis of the frequency content for three distinct wavelengths, $\lambda_{eq} = 0.6 \mu\text{m}$ as well as 0.5 and $0.8 \mu\text{m}$, visualizes the problem of low dispersion, Fig. 4.12 b).

Figure 4.11 Simulated signal in order to demonstrate the influence of dispersion on the relative signal intensity and phase slope at an equalization wavelength of $\lambda_{eq} = 0.6 \mu\text{m}$ and sample of N-BK7 with a) $t_{smp} = 1 \text{ mm}$, b) $t_{smp} = 3 \text{ mm}$ and c) $t_{smp} = 5 \text{ mm}$

Figure 4.12 a) STFT analysis of the simulated signals in order to demonstrate the influence of dispersion at an equalization wavelength of $\lambda_{eq} = 0.6 \mu\text{m}$ and a sample of N-BK7 with (I) $t_{smp} = 1$ mm, (II) $t_{smp} = 3$ mm and (III) $t_{smp} = 5$ mm with colored markings to indicate the data used for b) visualization of the limitation to determine λ_{eq} for setups with dispersive elements < 1 mm where the frequency resolution of the STFT is not sufficient to resolve the peak for the phase minimum (here at $0.6 \mu\text{m}$) from the rest of the phase signal

The lower the dispersion in the setups, the closer the not infinitely sharp peaks of the power spectrum move towards the lower frequencies. For samples of N-BK7 with thicknesses below 1 mm, a distinct separation is not possible anymore. Potential solutions to this problem can be the application of an adaptive windows size during the STFT which would decrease the peak width for frequency peaks as well as the introduction of additional dispersive elements. The exact thickness which necessitates additional dispersion is dependent on the sample's refractive index. Also, it has to be noted that the increase in dispersion reduces the spectral range as only the data within one phase jump around λ_{eq} is used in the algorithm. In order to compensate for the loss in resolution due to the additional dispersion, the before mentioned precision fit of the spectral data around the equalization wavelength can be utilized.

A detailed description of significant influences and error sources is given in the following section.

Influence of shrinkage

The curing and cross-linking of polymeric materials results in a change of the refractive index as well as in dimensional changes like shrinkage. As pointed out in Eq. (4.1), both properties influence the measurable signal in low-coherence interfer-

Table 4.2 List of key properties of an exemplary positive photo-resist before and after processing in a UV-harden cross-linking step which were used during the simulation, [H. Aßmann\ Th. Albrecht, personal communication, 12.07. & 30.08.2018]

property	value
resist type	positive photo-resist
t_{smp} before processing	1878.32 nm
t_{smp} after processing	1755.49 nm
$\Delta t_{smp} / t_{smp}$	6.5%
n^{smp} before processing (@675 nm)	1.6168
n^{smp} after processing (@675 nm)	1.6702
$\Delta n^{smp} / n^{smp}$	3.2%

ometry. In order to provide a meaningful metrology tool, the influence of both properties on the measured data was to be studied. For this purpose, simulations using an industrial photo-resist material system were performed. The material properties after different processing, e.g. softbake/hardbake and UV-hardening, were determined with the reference techniques tactile profilometry and spectral ellipsometry, [H. Aßmann\ Th. Albrecht, personal communication, 12.07. & 30.08.2018], Tab. 4.2. It can be seen, that significant changes in thickness as well as in refractive index occur in a counteracting fashion. In order to calculate the influence of these two properties on the measurement data, two simple simulation cases have been studied.

- (A) transmissive sample:** A transmissive sample with a given thickness t_{smp} and a reflective index n^{smp} is placed in one arm of the interferometer. By changing one of the parameters during simulation while leaving the second fixed, the individual influences can be estimated, Fig. 4.13 a).
- (B) reflective sample:** A defined layer of photo resist is spin-coated on a reflective surface (e.g. Si or glass). In this configuration, the expected measurement signal can be composed of the different components such as the front side reflex of a shrinked and non-shrinked sample as well as of the back side reflex from a sample with different states of cross-linking, Fig. 4.13 b).

When analyzing case (A), a thickness change due to shrinkage of 6.5% was used to calculate the influence on the phase signal and equalization wavelength by also using a fixed refractive index of $n^{smp}(\lambda)$ for the sample., Fig. 4.14 a). The resulting phase signal showed a relative change of about 0.13% in its amplitude for the

Figure 4.13 a) Setup for the simulation of the influence of a thickness or refractive index change on the signal in transmission mode of case (A) with LS—light source path, SMP—sample with refractive index $n^{smp}(\lambda)$ and thickness t_{smp} , SMP-M—sample mirror and REF—reference beam path; b) setup for the simulation of shrinkage and cross-linking of a polymer on a reflective sample of case (B) with DE—dispersive element having a refractive index $n^{DE}(\lambda)$ and a thickness t_{DE} , non-cross-linked sample with thickness t_{ncl} and cross-linked sample with thickness t_{cl} as well as the respective FSR—front side reflexes which influence the path difference δ_{ncl} and δ_{cl} and the BSR—back side reflex which is influenced by $n^{smp}(\lambda)$ or $n^{smp}_{cl}(\lambda)$

equalization wavelength, whereas the equalization wavelength showed a change of about -0.038% . It can be noted, that the changes are small relative to the thickness change. Furthermore, the equalization wavelength change is an order of magnitude smaller than the change of the phase signal. In order to evaluate the influence of a change in refractive index Δn , the thickness of the simulated material was kept constant, while the refractive index was changed by 3.2% , Fig. 4.14 a). In this case, the phase change was found to be -0.18% , while the change in equalization wavelength was 0.074% . These results make clear that the influence of the refractive index change alone is stronger than a thickness-induced change. Furthermore, as both effects are counteracting, a separation of the changes during a measurement might be obscured. Although shrinkage-induced changes of thickness and refractive index are expected to be in the single percentage regime, [138], this effect has to be taken into account. This result also reveals the necessity of a more profound data analysis as shown in chapter 3. Especially the fit of the measured data in the region of the equalization wavelength, enables high precision in the measurement of both thickness and refractive index of a (polymeric) sample.

Figure 4.14 Simulated phase signals of the influence of changes in sample thickness and refractive index for a) study of case (A) where a sample is transmitted and both changes are analyzed separately and b) study of case (B) where front side (FSR) and back side reflections (BSR) from a non-hardened and hardened sample have been investigated

A more realistic assessment of the signals has been performed by the study of case (B), Fig. 4.13 b). This case describes four relevant signal components in the analysis of a single layer of polymer, where in one part the sample is assumed to be non-cross-linked (*initial*) and in the other fully cross-linked (*hardened*). As described before, all signals passed through a known dispersive element. In case (B).1 the front side reflex (FSR) of the non-cross-linked material interface interferes with the reference signal while in case (B).2 the front side reflex of the cross-linked material is analyzed. In this case, as pure shrinkage was studied, a change in the equalization wavelength of 0.19% and a change in the phase signal of -0.52% could be observed. In the cases (B).3 and (B).4 the effect of the refractive index is studied for both samples while the shrinkage effect is included in the signal of the cross-linked material. By analyzing the back reflected signal from both, the cross-linked and the non-cross-linked sample, it is possible to investigate not only the effect of shrinkage but also the effect of refractive index variation due to cross-linking. The results show clearly the counteracting nature of shrinkage and refractive index alternations during cross-linking with a change in the equalization wavelength being 0.037% and a change in the phase signal being -0.036% . This highlights that a refractive index induced change can be nearly obscured by the influence of the shrinkage of a material. For this reason, all experiments within this work performed an evaluation of the FSR as well as of the BSR signal. This approach enables separating signal changes due thickness variations from those that are caused by refractive index variations and

can deliver information on the surface profile of the sample. During the evaluation of thin materials ($t < 100 \mu\text{m}$), the signals of front and back side reflection mix. In order to perform the correct interpretation of the measured data from cross-linked and non-cross-linked samples, both signal parts have been separated. This can be done by filtration or temporal separation.

4.3.1 Error Parameters of the Temporal Approach

The determination of a sample's group refractive index, based on the temporal approach, relies on the translation of the reference mirror in order to capture the path length difference for a number of equalization wavelengths, see subsection 4.1. The final calculation relies on the path length difference δ_λ and the thickness of the sample t_{smp}

$$n_g(\lambda) = \frac{\delta(\lambda)}{t_{smp}}. \quad (4.18)$$

In order to estimate the error for this measurement, an error propagation was performed with respect to both relevant features

$$\Delta n_g = \sqrt{\left(\frac{\partial n_g}{\partial \delta(\lambda)} \cdot \Delta \delta(\lambda)\right)^2 + \left(\frac{\partial n_g}{\partial t_{smp}} \cdot \Delta t_{smp}\right)^2}. \quad (4.19)$$

The calculation of the derivative of the respective terms leads therefore to

$$\Delta n_g = \sqrt{\left(\frac{1}{t_{smp}} \cdot \Delta \delta(\lambda)\right)^2 + \left(-\frac{\delta(\lambda)}{t_{smp}^2} \cdot \Delta t_{smp}\right)^2}. \quad (4.20)$$

Based on the parameters used for the experiments, the error limits were calculated for the dispersive elements of $t_{smp} = (1, 3 \text{ and } 5) \text{ mm}$ while the measurement accuracy on these thicknesses was $\Delta t_{smp} = 20 \text{ nm}$ when measured with a tactile profilometer, [275]. The covered path length differences were $\delta(\lambda) = (49.8, 185.5 \text{ and } 345) \mu\text{m}$ respectively while the resolution of the translation stage was $\Delta \delta(\lambda) = 1 \text{ nm}$, [287]. This resulted in values of $\Delta n_g^1 = 1.41 \times 10^{-6}$, $\Delta n_g^3 = 5.30 \times 10^{-7}$, $\Delta n_g^5 = 3.41 \times 10^{-7}$ for the different measured samples in section 4.1.

4.3.2 Error Propagation in WPDE

Independently of the kind of WPDE, sample-only or with an additional dispersive element, the accuracy of the refractive index calculation is dependent on the deviation of the measured input parameters such as the sample thickness t_{smp} , the wavelength λ or the thickness of the dispersive element t_{DE} . Therefore, a propagation of deviations of these parameters was performed to estimate their relative influences following the scheme

$$\Delta n_g = \sqrt{\left(\frac{\partial n_g}{\partial t_{smp}} \cdot \Delta t_{smp}\right)^2 + \left(\frac{\partial n_g}{\partial t_{DE}} \cdot \Delta t_{DE}\right)^2 + \left(\frac{\partial n_g}{\partial \lambda} \cdot \Delta \lambda\right)^2}. \quad (4.21)$$

For all investigations on this topic, samples are supposed to have thicknesses varying from (0.1–5) mm which were measured with a deviation ranging from (0.16–20) nm, [275]. The dispersive element was made of N-BK7 glass with the given thicknesses. Wavelength dependencies were investigated in a spectral range of (400–1000) nm which was determined with a deviation of 0.1 nm, [288].

Sample-only WPDE

When using the WPDE method for simple transmissive measurements of bulk materials, see section 4.2.1, the refractive index depends only on the deviation of the sample thickness Δt_{smp} and the wavelength $\Delta \lambda$

$$\Delta n_g^{sngl} = \sqrt{\left(\frac{\partial n_g^{sngl}}{\partial t_{smp}} \cdot \Delta t_{smp}\right)^2 + \left(\frac{\partial n_g^{sngl}}{\partial \lambda} \cdot \Delta \lambda\right)^2}. \quad (4.22)$$

According to this notation the partial derivative of the group refractive index relative to the sample thickness

$$\frac{\partial n_g^{sngl}}{\partial t_{smp}} \cdot \Delta t_{smp} = \frac{\partial}{\partial t_{smp}} \left(1 - \frac{\varphi'_{loc} \lambda^2}{2\pi t_{smp}} - \delta\right) \cdot \Delta t_{smp} = \frac{(1 - n_g^{smp}) t_{smp}^{eff}}{t_{smp}^2} \cdot \Delta t_{smp} \quad (4.23)$$

reveals a simple quadratic dependency which is countered by the effective thickness t_{smp}^{eff} and the relative path difference δ that contribute to the measured phase signal φ'_{loc} . In the given range of sample thicknesses the deviation of $\Delta n_g(t_{smp})$ could be estimated at the sodium D1 line ($\lambda = 589.592$ nm), Fig. 4.15 a). The quadratic dependence becomes visible. The data here was plotted on a semi-logarithmic scale;

it has to be noted that the error is smaller than 1×10^{-5} for samples thicker than $500 \mu\text{m}$. In a measurement situation this might be considered as a limiting factor for the characterization of thin samples or layers.

Figure 4.15 Error contribution of the sample thickness to the group refractive index $\Delta n_g(t_{smp})$ for the sample-only WPDE approach with a) over a given thickness range at the sodium D1 line ($\lambda = 589.592 \text{ nm}$) and b) over a spectral range with $t_{smp} = 5 \text{ mm}$ and the measurement error for $\Delta t_{smp} = 20 \text{ nm}$

Furthermore, the contribution to the error for a sample of N-BK7 having the thickness $t_{smp} = 5 \text{ mm}$ was analyzed over a spectral range from $(0.4\text{--}1) \mu\text{m}$, Fig. 4.15 b). The calculated error for this sample at the sodium D1 line is 2.16×10^{-6} . It changes less than 0.3×10^{-6} over the given wavelength range. In consequence, for high precision measurements the analysis wavelength should be as low as possible in order to achieve results with minor error although the gain in accuracy is small. Accordingly, the error contribution resulting from the wavelength measurement uncertainty

$$\frac{\partial n_g^{sngl}}{\partial \lambda} \cdot \Delta \lambda = \frac{\partial}{\partial \lambda} \left(1 - \frac{\phi'_{loc} \lambda^2}{2\pi t_{smp}} - \delta \right) \cdot \Delta \lambda = - \frac{2\lambda \left[(1 - n_g^{smp}) t_{smp}^{eff} + \delta \right]}{\lambda_{eff}^2 \cdot t_{smp}} \cdot \Delta \lambda \quad (4.24)$$

was estimated for a N-BK7 sample having the thickness $t_{smp} = 5 \text{ mm}$ over the spectral range of 0.4 to $1 \mu\text{m}$, Fig. 4.16 a). Interestingly, the error contribution is quite high with $\pm 5 \times 10^{-5}$ but becomes zero at a wavelength of 494.9 nm . This results from the ratio of the group refractive index to the wavelength squared which in case of N-BK7 results in a zero error within the wavelength range of interest. In this

Figure 4.16 Spectral dependency in a range from 0.4–1 μm with a) error contribution of the wavelength to the group refractive index $\Delta n_g^{\text{singl}}(\lambda)$ for the sample-only WPDE approach with $t_{\text{smp}} = 5 \text{ mm}$ and the measurement error for $\Delta \lambda = 0.1 \text{ nm}$ and b) total error on the calculated group refractive index of the sample with all discussed error contributions according to Eq. (4.22)

case, experiments should be designed to measure the group refractive index with the WPDE method in a wavelength range close to this minimum. The error varies from 5.17×10^{-5} at 0.4 μm to 4.93×10^{-5} at 1 μm. In case of different materials, simulations have to be performed to find an optimized probing wavelength.

Consequently, the overall error according to Eq. (4.22) shows a minimum at this wavelength, Fig. 4.16 b). It can be seen that for a sample thickness of $t_{\text{smp}} = 5 \text{ mm}$ the contribution of the wavelength is quite significant and introduces the main error. Furthermore, it is known from the simulations that the sample material as well as its thickness can have an even more significant influence on the error of the calculated group refractive index. This behavior should be considered when designing experiments for arbitrary materials.

WPDE with additional DE

As discussed within this chapter, WPDE can be applied in some cases with an additional dispersive element in the setup, Fig. 4.7. In this case, the propagation of deviations is based on a different equation for the determination of the group refractive index n_g^{+DE} , Eq. (4.12)

$$n_g^{+DE}(x, \lambda) = 1 - \frac{\lambda^2 \cdot \xi}{2\pi \cdot t_{smp}} \quad (4.25)$$

$$\text{with } \xi = \varphi'_{loc} - \frac{2\pi}{\lambda^2} \left[(1 - n_g^{DE}) t_{DE} + \delta \right]. \quad (4.26)$$

Furthermore, it additionally depends on the measurement uncertainty of the thickness of the dispersive element Δt_{DE}

$$\Delta n_g^{+DE} = \sqrt{\left(\frac{\partial n_g^{+DE}}{\partial t_{smp}} \cdot \Delta t_{smp} \right)^2 + \left(\frac{\partial n_g^{+DE}}{\partial t_{DE}} \cdot \Delta t_{DE} \right)^2 + \left(\frac{\partial n_g^{+DE}}{\partial \lambda} \cdot \Delta \lambda \right)^2}. \quad (4.27)$$

Similar to the case in subsection 4.3.2, the deviation relative to the error of the sample thickness is quadratically dependent on the sample thickness itself

$$\begin{aligned} \frac{\partial n_g^{+DE}}{\partial t_{smp}} \cdot \Delta t_{smp} &= \frac{\partial}{\partial t_{smp}} \left(\frac{\lambda^2 \cdot \xi}{2\pi \cdot t_{smp}^2} \right) \cdot \Delta t_{smp} \\ &= \frac{1}{t_{smp}^2} \left(\frac{\lambda^2 \cdot \varphi'_{loc}}{2\pi} - \left[(1 - n_g^{DE}) t_{DE} + \delta \right] \right) \cdot \Delta t_{smp} \end{aligned} \quad (4.28)$$

with

$$\varphi'_{loc} = \frac{2\pi}{\lambda^2} \left[(1 - n_g^{smp}) \cdot t_{smp}^{eff} + (1 - n_g^{DE}) \cdot t_{DE}^{eff} + \delta \right] \quad (4.29)$$

$$\frac{\partial n_g^{+DE}}{\partial t_{smp}} \cdot \Delta t_{smp} = \frac{1}{t_{smp}^2} \left[(1 - n_g^{smp}) \cdot t_{smp}^{eff} + (1 - n_g^{DE}) (t_{DE}^{eff} - t_{DE}) \right] \cdot \Delta t_{smp}. \quad (4.30)$$

It has to be noted that the calculation of φ'_{loc} using the effective thicknesses t_{smp}^{eff} and t_{DE}^{eff} is performed only in context of the error propagation in order to simulate the signal which is usually measured. Using the same range of sample thicknesses, with a dispersive element of $t_{DE} = 5$ mm N-BK7, a thickness-dependent error can be calculated for the sodium D1 line ($\lambda = 589.592$ nm), Fig. 4.17 a). It is clear from the equation and the plot that the contribution of the dispersive element to this particular error is minimal. The measured thickness t_{DE} as well as the effective thickness t_{DE}^{eff} , which contributes to the composition of the phase signal φ'_{loc} , only affect the error with their difference to each other. Therefore, analogous to the approach with a single sample material, the error contribution with respect to the sample thickness dominates. It is smaller than 1×10^{-5} for sample thicknesses above $420 \mu\text{m}$ for measurements at the sodium D1 line. With regard to the spectral

range of the measurement, the $1/t_{smp}^2$ behavior is smaller than 3×10^{-5} and thus neglectable in comparison to the influence of the sample thickness, Fig. 4.17 b). An error variation of 1×10^{-6} can be observed over a spectral range of $0.6 \mu\text{m}$. In consequence, the measurement wavelength range should be as low as possible in order to optimize the error contribution of the sample thickness.

Figure 4.17 Error contribution of the sample to the group refractive index $\Delta n_g(t_{smp})$ for the WPDE approach with additional dispersion a) over a given sample thickness range at the sodium D1 line ($\lambda = 589.592 \text{ nm}$) and b) over a spectral range with $t_{DE} = 5 \text{ mm}$, $t_{smp} = 750 \mu\text{m}$ and the measurement error for $\Delta t_{smp} = 4 \text{ nm}$

When partially deriving Eq. (4.25) with respect to the thickness of the dispersive element,

$$\frac{\partial n_g^{DE}}{\partial t_{DE}} \cdot \Delta t_{DE} = - \frac{(1 - n_g^{DE})}{t_{smp}} \cdot \Delta t_{DE} \quad (4.31)$$

it becomes obvious that the error contribution of the dispersive element is determined by its refractive index and not by the thickness itself. However, the thickness of the sample shows a $1/t_{smp}$ influence on this error contribution, Fig. 4.18 a). The error contribution becomes significant for samples thinner than $200 \mu\text{m}$ for the sodium D1 line where it is larger than 5.41×10^{-5} . The differences in the error contribution for different wavelengths are in the range of $\pm 0.9 \times 10^{-5}$ over the spectral range of $0.4\text{--}1 \mu\text{m}$ while its maximum value is 1.56×10^{-5} for a wavelength of $0.4 \mu\text{m}$, Fig. 4.18 b). This leads to the same consequence as for the error contribution of the sample thickness alone. In order to minimize the error in the calculation of the group refractive index, the spectral range for measurements should be as low as possible. This can be achieved by the choice of the light source, the spectrometer and by

tuning the path length difference of both arms as to shift the ROI appropriately, see Fig. 4.7.

Figure 4.18 Error contribution of the dispersive element to the group refractive index $\Delta n_g(t_{DE})$ for the WPDE approach with additional dispersion a) over a given sample thickness range at the sodium D1 line ($\lambda = 589.592$ nm) and b) over a spectral range with $t_{DE} = 5$ mm, $t_{smp} = 750 \mu m$ and the measurement error for $\Delta t_{DE} = 20$ nm

Furthermore, the group refractive index was also partially derived with respect to the wavelength λ in order to estimate its influence on the error. For this operation, the equation was rewritten and broken down into its main wavelength dependent components X and Y

$$\frac{\partial n_g^{+DE}}{\partial \lambda} \cdot \Delta \lambda = \frac{\partial}{\partial \lambda} \left(1 - \frac{\phi'_{loc} \cdot \lambda^2}{2\pi \cdot t_{smp}} - \frac{[1 - n_g^{DE}(\lambda)]t_{DE}}{t_{smp}} - \frac{\delta}{t_{smp}} \right) \cdot \Delta \lambda \quad (4.32)$$

$$\text{where } \frac{\phi'_{loc} \cdot \lambda^2}{2\pi \cdot t_{smp}} = X \quad (4.33)$$

$$\text{and } \frac{[1 - n_g^{DE}(\lambda)]t_{DE}}{t_{smp}} = Y. \quad (4.34)$$

In this notation the derivative of X with respect to λ can be written as $\frac{\partial X}{\partial \lambda}$

$$\frac{\partial X}{\partial \lambda} = \frac{\phi'_{loc} \cdot \lambda}{\pi \cdot t_{smp}}, \quad (4.35)$$

while the derivative of Y with respect to λ can be written as $\frac{\partial Y}{\partial \lambda}$

$$\frac{\partial Y}{\partial \lambda} = \frac{\partial}{\partial \lambda} \left(\frac{[1 - n_g^{DE}(\lambda)]t_{DE}}{t_{smp}} \right) = -\frac{t_{DE}}{t_{smp}} \frac{\partial n_g^{DE}}{\partial \lambda}. \quad (4.36)$$

In the case examined here, the dispersive element is made of N-BK7 glass which leads to the use of the Sellmeier equation for the refractive index, [280],

$$n^{DE} = \sqrt{\frac{A_1 \lambda^2}{\lambda^2 - B_1} + \frac{A_2 \lambda^2}{\lambda^2 - B_2} + \frac{A_3 \lambda^2}{\lambda^2 - B_3} + 1}. \quad (4.37)$$

This equation is the basis for the calculation of $\frac{\partial n_g^{DE}}{\partial \lambda}$ under the assumption that the group refractive index is computed using, [246],

$$n_g = n - \frac{dn}{d\lambda} \cdot \lambda. \quad (4.38)$$

By calculating the derivative of the refractive index for glass with respect to the wavelength $\frac{dn}{d\lambda}$, the group refractive index for N-BK7 can be formulated as

$$n_g^{DE} = n^{DE} - \frac{G}{2 \cdot n^{DE}} \cdot \lambda \quad (4.39)$$

$$\text{with } G = \sum_{i=1}^3 \frac{-2A_i B_i \lambda}{(\lambda^2 - B_i)^2}. \quad (4.40)$$

In consequence the partial derivative of the group refractive index can be formulated as

$$\frac{\partial n_g^{DE}}{\partial \lambda} = \left(\frac{G}{2n^{DE}} - \frac{\left(\frac{\partial G}{\partial \lambda} \lambda + G \right) n^{DE} - \frac{G^2}{2n^{DE}} \cdot \lambda}{2(n^{DE})^2} \right) \quad (4.41)$$

$$\text{with } \frac{\partial G}{\partial \lambda} = \sum_{i=1}^3 \frac{2A_i B_i (3\lambda^2 + B_i)}{(\lambda^2 - B_i)^3}. \quad (4.42)$$

Eq. (4.41) is used to eventually determine the error contribution of the wavelength dependency to the calculation of the sample's group refractive index with Eq. (4.32), the solution of $\frac{\partial X}{\partial \lambda}$ from Eq. (4.35) and $\frac{\partial Y}{\partial \lambda}$ from Eq. (4.36) in conjunction with $\frac{\partial n_g^{DE}}{\partial \lambda}$ from Eq. (4.41)

$$\frac{\partial n_g^{+DE}}{\partial \lambda} \cdot \Delta \lambda = \left(-\frac{\varphi'_{loc} \cdot \lambda}{\pi \cdot t_{smp}} - \frac{t_{DE}}{t_{smp}} \frac{\partial n_g^{DE}}{\partial \lambda} \right) \cdot \Delta \lambda \quad (4.43)$$

$$\text{with } \varphi'_{loc} = \frac{2\pi}{\lambda^2} \left[(1 - n_g^{smp}) \cdot t_{smp}^{eff} + (1 - n_g^{DE}) \cdot t_{DE}^{eff} + \delta \right] \quad (4.44)$$

$$\begin{aligned} \frac{\partial n_g^{+DE}}{\partial \lambda} \cdot \Delta \lambda = & - \left(\frac{\pi}{\lambda \cdot t_{smp}} \left[(1 - n_g^{smp}) \cdot t_{smp}^{eff} \right. \right. \\ & \left. \left. + (1 - n_g^{DE}) \cdot t_{DE}^{eff} + \delta \right] - \frac{t_{DE}}{t_{smp}} \frac{\partial n_g^{DE}}{\partial \lambda} \right) \cdot \Delta \lambda. \end{aligned} \quad (4.45)$$

It has to be noted that the calculation of φ'_{loc} is only performed in context of the error propagation with the effective thicknesses t_{smp}^{eff} and t_{DE}^{eff} . In an experiment this would be the signal to measure. The wavelength contribution to the error was studied in a spectral range of (400–1000) nm for a dispersive element of $t_{DE}=5$ mm and a sample of N-BK7 with $t_{smp}=750$ μ m, Fig. 4.19 a). It is obvious that the error contribution of the wavelength to the group refractive index $\Delta n_g^{+DE}(\lambda)$ is one order of magnitude larger than the influences of the sample and the DE thickness. Furthermore, it shows a significant minimum at a wavelength of $\lambda=683.75$ nm. This behavior is similar to the sample-only approach of WPDE and is due to the spectral dependence of the refractive index of N-BK7 as sample and DE material.

Figure 4.19 Spectral dependency in a range from 0.4–1 μ m with a) error contribution of the wavelength to the group refractive index $\Delta n_g^{+DE}(\lambda)$ for the WPDE approach with additional dispersion with $t_{DE}=5$ mm, $t_{smp}=750$ μ m and the measurement error for $\Delta \lambda=0.1$ nm and b) total error on the calculated group refractive index of the sample with all discussed error contributions according to Eq. (4.27)

Finally, the total error of the group refractive index calculation for a $750\text{ }\mu\text{m}$ thick sample of N-BK7 and a 5 mm thick dispersive element of the same material has been determined as an absolute combination of all error contributions according to Eq.(4.27), Fig. 4.19. Due to the large influence of the error contribution of the refractive index measurement, the total error is dominated by it. Therefore, it shows the same characteristic minimum at $\lambda = 683.75\text{ nm}$ with a value of 1.46×10^{-5} . It is important to note that the error increases exponentially for probing wavelengths smaller than the minimum with values larger than 3×10^{-4} , while the error slowly tends towards a boundary value for probing wavelengths above the minimum. The boundary value is significantly smaller than 5×10^{-5} . As this behavior is dominated by the refractive index of the materials present in the setup, an error estimation should be performed for every experiment.

The newly developed approach for the characterization of cross-linking in polymers differs from state-of-the-art technologies in the accuracy of measurement as well as in the variety and quality of possible measurements. In comparison to classical approaches such as Soxhlet extraction, DSC and DMA, the interferometric approach determines cross-linking in an indirect manner, but works non-destructive. This results in the ability to measure samples in in-line situations as well as during the lifetime of a product. It was shown that the typical measurement error was about 0.1% in the scan-free approach. These errors are significantly lower than an error of 2–4% that classical approaches possess. Compared to other recently researched approaches, such as Raman or luminescence spectroscopy, the developed approach shows significant advantages relating its measurement speed where single profiles can be gathered in about 50 ms compared to multiple minutes. In summary, the developed approach combines high accuracy in the determination of cross-linking with high acquisition speeds and the ability to work in a scan-free fashion over lateral measurement ranges of multiple millimeters. Additionally, it allows non-destructive evaluations and combines material characterization with surface profilometry. In comparison with the identified state-of-the-art technologies for the determination of the degree of cross-linking, the DE-LCI approach shows significant advantages regarding accuracy, measurement time, inline capabilities and others, Tab. 4.3.

Table 4.3 Comparison of state-of-the-art technologies with the developed DE-LCI approach for the degree of cross-linking characterization in polymers

approach	meas. time	error	spatial resolution	inline	non-destructive	comments
Soxhlet extraction [122, 124]	42 h	2–4%	no	no	no	gold standard
DSC [145]	90 min.	10%	no	no	no	usable with many polymer types
DMA [143, 145, 149]	2–6 h	10%	no	no	no	direct determination of degree of cross-linking
spectroscopic [155, 156]	50–100 s	4–6%	yes	yes	yes	single point measurement, time consuming
DE-LCI	50 ms	0.01%	yes	yes	yes	indirect but very fast and precise

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