

Absolute optical spectroscopy for determining the degree of cross-linking of plastics

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Abstract

Cross-linking is a cost-effective method to improve the thermal, chemical and mechanical material properties of thermoplastics and expand their range of application. Cross-linked polyethylene (PE-X), used for water pipes or surgical implants, is a well-known example. In addition, thermosets, which are important in the context of the energy revolution and e-mobility, cure by cross-linking.

The degree of cross-linking or curing of these materials has a major impact on various material properties and thus needs to be controlled. To date, only destructive and time-consuming laboratory tests are used to determine this crucial parameter. Accordingly, there is a great demand for fast, non-destructive testing, which can be carried out during the process or on the finished product.

Absolute optical spectroscopy, where absorption and scattering coefficients of a sample can be determined separately, offers a promising approach to solve this problem. In the research work presented here a demonstrator based on an integrating sphere was used to investigate various PE-X materials and different thermoset resins. Wet chemical analysis, differential scanning calorimetry (DSC) as well as dielectric analysis (DEA) served as references.

The results show that different PE-X materials can be well distinguished by their absorption and scattering in the visual (VIS) and near-infrared (NIR) wavelength range, respectively. Moreover, conclusions on their degree of cross-linking are possible. Similarly, the curing of the resins can be monitored based on the absorption.

The assembled integrating sphere demonstrator is suitable for non-destructive determination of the degree of cross-linking or curing and has the potential for use as an at-line device for in-process quality assurance.

1 Motivation

Cross-linking can improve the material properties of thermoplastics at low cost, enabling them to perform tasks that would otherwise be reserved for more expensive engineering or high-performance plastics [1]. Examples of applications for PE-X are water distribution pipes, heating systems and surgical implants, while cross-linked polyamide is used in the automotive sector. The network formation that takes place during cross-linking is comparable to that which occurs during the curing reaction of thermosets, which are used, e.g., in thermoset injection moulding, fibre-reinforced plastics and adhesives. They are becoming increasingly important in the context of the energy turnaround and e-mobility [2, 3].

The degree of cross-linking respectively curing of these materials has a significant influence on their mechanical, thermal, and chemical properties. Therefore, quality assurance of this parameter is crucial – especially since cross-linked materials can no longer be melted and thus recycled. Most available test methods for the degree of cross-linking are destructive laboratory methods, each with different disadvantages. For example, the classic wet chemical determination of the degree of cross-linking of PE-X is very time-consuming and not suitable for long-chain polymers such as ultra-high molecular weight PE (UHMWPE) [4, 5].

An alternative approach using dynamic mechanical analysis is faster, but still destructive and requires special sample preparation [5]. The same applies to established thermal analysis like DSC [6–8]. DEA is mainly used in the thermoset sector and requires direct sample contact and needs to start in the liquid state, so that subsequent testing of solids is not possible [9, 10]. A fast, non-destructive method would be desirable for monitoring the degree of cross-linking respectively curing during production and afterwards. Absolute optical spectroscopy offers a promising approach to solve this problem. Here, the absorption and scattering coefficients of a sample can be determined separately by considering the light propagation within the sample. Thus, properties like crystallinity and the degree of cross-linking in semi-crystalline materials such as PE-X can be investigated independently, or the influence of fillers in thermosets or adhesives can be studied.

In the joint research work presented here, a demonstrator based on an integrating sphere was set up and various PE-X materials cross-linked by electron beam radiation as well as different resin materials were investigated. Wet chemical analysis, DSC and DEA were used as reference.

2 Theory

2.1 Cross-linking and Curing

Cross-linking of thermoplastics is characterized by the formation of a three-dimensional network, which affects the material chemical, thermal and mechanical properties in a variety of ways. For example, hardness is increased and solubility is decreased. Cross-linked material can no longer be melted and thus may be used for more demanding applications. The cross-linking process from the semi-crystalline PE to PE-X is achieved via radicals, which can be generated in various ways. Either special additives (PE-Xa with peroxides or PE-Xb with silanes) or high-energy electron radiation (PE-Xc) are used for this purpose. Cross-linking only occurs in the amorphous regions of the semi-crystalline PE. The final material properties are directly related to the degree of crosslinking. For this reason, it is well suited as a quality indicator. [1, 5]

The curing reaction of thermosets (and reactive adhesives) is started by adding the curing agent or the necessary activation energy. Complete curing depends on the correct mixing ratio of the components and ambient conditions (temperature, humidity). During the curing reaction, a dense molecular network is formed. The degree of curing is also decisive for the thermomechanical properties of the thermoset and (in addition to the correct surface treatment) for the strength of bonded joints. [8, 11]

2.2 Absolute optical spectroscopy

Absolute optical spectroscopy offers a promising non-destructive and therefore time saving and economical monetary saving method to monitor the degree of cross-linking as well as the curing of resins. The diversity of absolute optical spectroscopy measurement systems enables principal in-line and at-line investigations. Spatially resolved or spatial frequency resolved setups on the one side are usable for in-line investigations using larger measurement distances and shorter time spans but also need a higher effort for the perfect match of measurement and theory. An integrating sphere on the other side is a relatively simple and robust measurement system concerning the reproducibility of measurements, which additionally enables the precise determination of the optical properties in an easier manner [12, 13]. The integrating sphere measurement consists of a minimum of two measurements, the total remission and the total transmission measurement of an illuminated sample. For integrating purposes, a highly reflective coated sphere adjacent to an illuminated sample is used to measure the total remission and transmission, which in fact, is influenced by port openings for detection. Due to the diffusion process within the sphere, the detection signal is lowered and the measurement takes principally longer for similar samples compared to spatially resolved or spatial frequency resolved measurements. The time requirement and the higher number of measurements allows in the first instance at-line investigations.

In absolute optical spectroscopy, the sample is measured and compared to a calibration standard, which is known

precisely in its optical properties. For an absolute optical measurement three conditions have to be fulfilled: the unit of the sample measurement has to be in absolute intensity or the measurement has to be compared to a calibration standard, the experimental and theoretical description of the setup have to match ideally to avoid systematic errors and, for the evaluation of the measurements, the theory of light propagation within the sample has to be valid to enable the separation and the absolute determination of optical properties like scattering and absorption. As a consequence, calibration series like for classical wet chemical analysis are not necessary.

The optical properties, within the framework of radiative transport theory, are the quantities refractive index n , absorption coefficient μ_a , reduced scattering coefficient μ_s' , scattering coefficient μ_s , and phase function [14], that are used in combination with a light propagation model to describe the light propagation in a medium. Highly scattering media can be well described by the absorption coefficient, the reduced scattering coefficient, and the averaged refractive index of a medium due to the loss of the single scattering behavior which is described by the phase function. Separating the absorption coefficients and reduced scattering coefficients enables the determination of the concentration of known constituents as well as the estimation of the scattering particle dimension. Therefore, the absolute optical spectroscopy has a major advantage compared to conventional spectroscopy, measuring the absorbance. The knowledge of the absorption of thermoplastics in the VIS and NIR wavelength range, respectively, allows to draw qualitatively conclusions about cross-linking processes as well as alterations of curing in resins.

3 Experimental

3.1 Materials

Within this work PE-Xc samples based on high density PE (HDPE) and UHMWPE were investigated. The PE samples were provided by Röchling Engineering Plastics SE & Co. KG, Haren, in form of plates and cross-linked with different absorbed doses via electron radiation by BGS Beta-Gamma-Service GmbH & Co. KG, Wiehl. The crystallinity formed during the production of the plates was not changed by the irradiation.

Additionally, the curing behaviour of selected two-component (2C) resins, two epoxy resins and an acrylate (PMMA) resin from S u. K Hock GmbH, Regen, were analysed. The components were mixed according to the recommendation given by the manufacturer and observed until they were fully cured. In order to evaluate the influence of fillers, DSC and DEA tests were also conducted by adding 5 wt.% silica powder (Silbond 126 EST) in each case. For the experiments with the integrating sphere 3 vol.% of TiO_2 were added to achieve a larger reduced scattering coefficient. The curing times specified by the manufacturer are given in Table 1. The first value (pot life) describes the time during which the resin can still be processed.

Table 1 Curing times of 2C resins at room temperature.

Material	Type	Curing times
SKresin 3075	Epoxy	30 min / 7 d
SKresin 3221	Epoxy	10 – 30 min / 6 h
SKresin 1702	Acrylate	2 – 4 h / 7 d

3.2 Reference methods

For the quantification of the degree of cross-linking of the PE-Xc samples the standardized wet chemical analysis according to DIN EN ISO 10147 [2] was carried out. For this purpose, thin sections of the materials with previously determined weight were cooked in Xylene for 8 h and dried for at least 3 h. From the remaining material the degree of cross-linking D_x was derived from equation (1):

$$D_x = m_{\text{remaining}} / m_{\text{initial}} \cdot 100 \% \quad (1)$$

In addition, DSC experiments were conducted with a NETZSCH DSC 204 F1 Phoenix (NETZSCH-Gerätebau GmbH, Selb) and standard sample pans. In the DSC, PE-X was observed in the two common heating cycles followed by cooling (temperature range: 0 – 200 °C, heating/cooling rate: 10 K/min). During radiation crosslinking, the initial crystallinity of the material was not changed. However, the non-meltable cross-linked amorphous regions hinder the reformation of the crystallinity during the defined cooling process after the first cycle. From the difference in crystallinity between the two cycles, it is possible to draw conclusions about the degree of cross-linking.

The degree of curing D_C of thermosets can be determined with one DSC heating cycle. It results from the ratio of the reaction enthalpies ΔH of the tested sample in comparison with a freshly mixed sample according to equation (2) [6]:

$$D_C = (1 - \Delta H_{\text{current}} / \Delta H_{\text{fresh}}) \cdot 100 \% \quad (2)$$

The resins were heated from -30 to 290 °C with a heating rate of 20 K/min.

Moreover, a NETZSCH DEA 288 Ionic (NETZSCH-Gerätebau GmbH) with single-use interdigitating sensors was used to monitor the curing process of the thermoset resins at room temperature. For this purpose, the ion viscosity, which is increasing with the degree of curing, was measured at different frequencies.

3.3 Integrating sphere

The integrating sphere setup, which was used as a demonstrator, is an often-used measurement method to determine the optical properties of media with known refractive index. The method has been well known for decades and is often used in the literature, but the precise evaluation, including the exact angular distribution of the calibration standard and the sample as well as the exact sphere geometry considering the port openings and the detector field of view, has to be performed, see Foschum et al. [12] and Bergmann et al. [13]. Compared to other methods of the absolute optical spectroscopy, the integrating sphere is one of the most accurate measurement systems nowadays. The integrating sphere system consists of a light source that is

imaged to a sample on the sample port and a detection system with integrating sphere itself, optical components like fibre optics and a spectrometer. The presence of port openings in the sphere and the angular distributions of the light from sample and calibration standard affect the light propagation within the sphere and therefore has to be considered in the evaluation process. Due to the large volume dimension of a few millimetres of samples which are investigated via integrating sphere, the evaluation process is based on transport theory [15, 16]. Numerical solutions of the transport equation enable the exact description of the experimental geometry which is necessary for a better match of experiment and theoretical setup. For the acceleration of the evaluation process lookup tables are expedient for inverting solutions of the light propagation model. The conducted measurements have been performed with the laboratory integrating sphere setup of the ILM, see figure 1. In cooperation with Gigahertz-Optik GmbH, Türkenfeld, Germany, a publicly available integrating sphere setup SphereSpectro 150H for a spectral range from 240 to 2150 nm was developed.

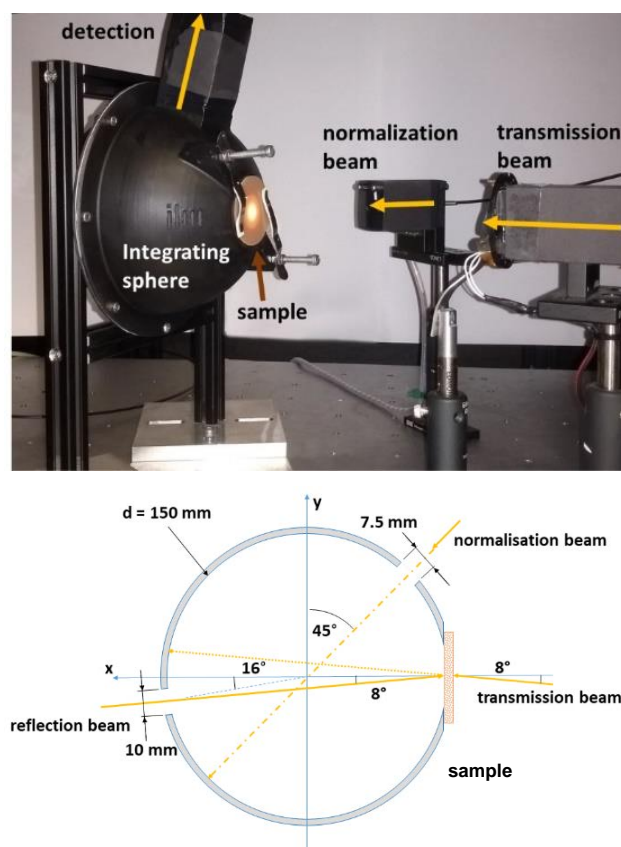


Figure 1 The laboratory integrating sphere setup consists of an integrating sphere, a detection system and the light source, not shown here, imaged onto a sample. In the upper part the side view of the setup is shown and below the sketch is depicted.

4 Results and Discussion

4.1 PE-Xc

4.1.1 Wet chemical analysis

Figure 2 shows the degrees of cross-linking of the (UHMW)PE-Xc sheets determined by wet chemical analysis as a function of the absorbed dose introduced during radiation cross-linking. For the HDPE materials, there is a clear correlation between the two parameters. The homogeneity of the radiation cross-linking of the PE-Xc samples is considered good, since the standard deviation of the degree of cross-linking for the measurements are typically less than 3 %.

The results of the UHMWPE samples confirm that the wet chemical analysis is no longer suitable for UHMWPE-Xc. Here, a high degree of cross-linking even without or low absorbed doses is suggested, although cross-linking should occur in the same way as for HDPE. The reason is the very large molecular mass of the material. The solvent cannot completely dissolve the long molecular chains and the undissolved and not cross-linked residue is incorrectly interpreted as cross-linked during evaluation. In the following, the absorbed doses are used as a reference value.

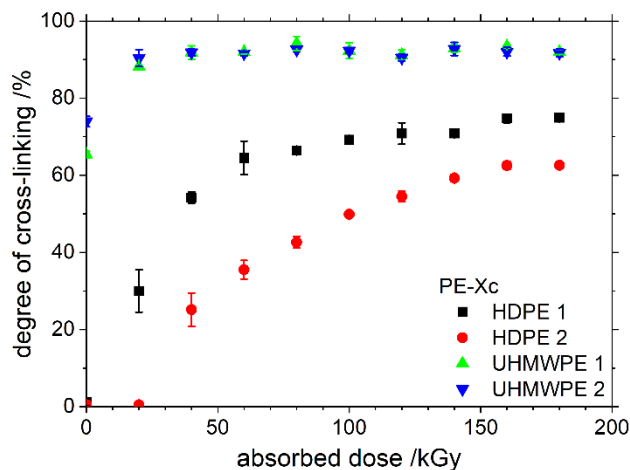


Figure 2 Degrees of cross-linking of different (UHMW)PE-Xc samples determined by wet chemical analysis. The values of the UHMWPE samples for low absorbed doses are falsely overestimated by the measurement method.

4.1.2 Dynamic scanning calorimetry

During radiation crosslinking, the crystallinity of the (UHMW)PE is not changed. Only when the sample is melted and cooled again the renewed formation of the crystallinity is hindered. For the analysis of the cross-linking of (UHMW)PE-Xc, it is necessary to consider the difference of the crystallinities of both heating cycles. This is shown in Figure 3 for the investigated (UHMW)PE-Xc samples. Due to the large error bars, it is difficult to distinguish between states with different cross-linking. However, when considering the mean values, the expected decrease of crystallinity with increasing absorbed dose (and thus

higher degree of cross-linking) is visible from the increasing amount of the difference of the crystallinities.

This emphasizes that, in addition to the high effort of sample preparation, DSC also entails a large inaccuracy in the estimation of the degree of cross-linking.

The DSC results confirm the problem of wet chemical analysis for UHMWPE, since here the expected trend of increasing degree of cross-linking with increasing absorbed dose is seen.

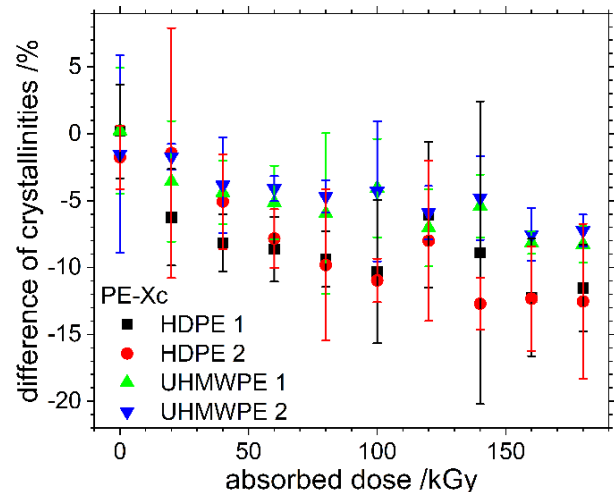


Figure 3 Differences of the crystallinities of the PE-Xc samples determined in two DSC cycles.

4.1.3 Integrating sphere

The investigation of PE-X samples, cross-linked by electron beam radiation, with the integrating sphere shows a systematic alteration in the absorption coefficient μ_a in the VIS spectral range below 900 nm, see figure 4.

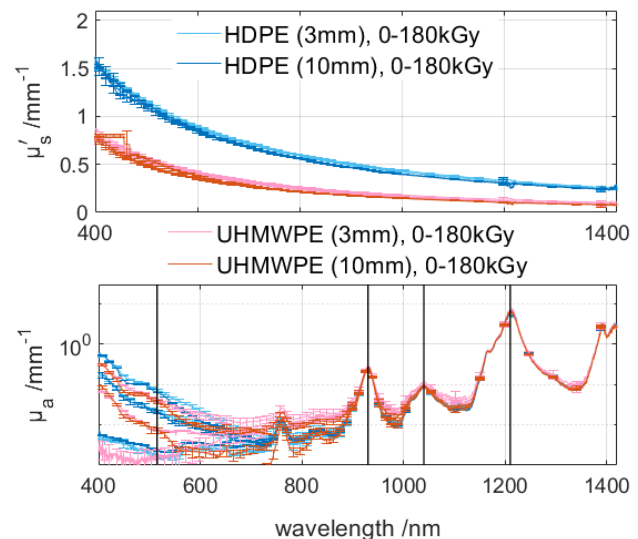


Figure 4 The optical properties, reduced coefficient μ'_s (upper subfigure) and absorptions coefficient μ_a (lower subfigure) of HDPE and UHMWPE samples having different thicknesses and absorbed doses. There is no colour differentiation in the graphics between the shown absorbed doses of 0, 60 and 180 kGy, but for the different sample thicknesses (3 mm and 10 mm).

Higher electron beam radiation results in a higher absorption coefficient. The relative alteration at around 500 nm is depicted in figure 5. For the HDPE and long-chain polymers such as UHMWPE samples, a dependence of the absorbed dose and relative absorption coefficient alteration can be found. For HDPE the dependence is linear. The absorption coefficient in the NIR as well as the reduced scattering coefficient remains unchanged for a variation in the absorbed dose. The determination of the degree of cross-linking is only indirectly possible for well characterized materials, for which the dependence of the alteration in μ_a over the degree of cross-linking is known [17], see figure 6.

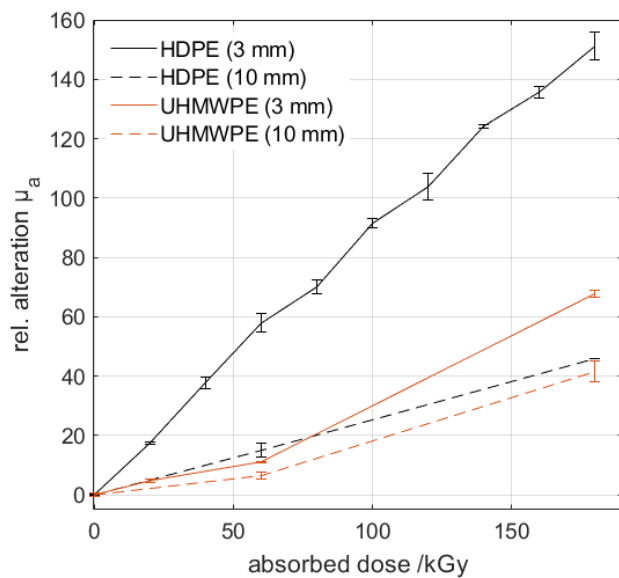


Figure 5 Relative alteration of the absorption coefficient at around 515 nm over absorbed dose of HDPE and UHMWPE samples with different thicknesses. A linearity for HDPE was found.

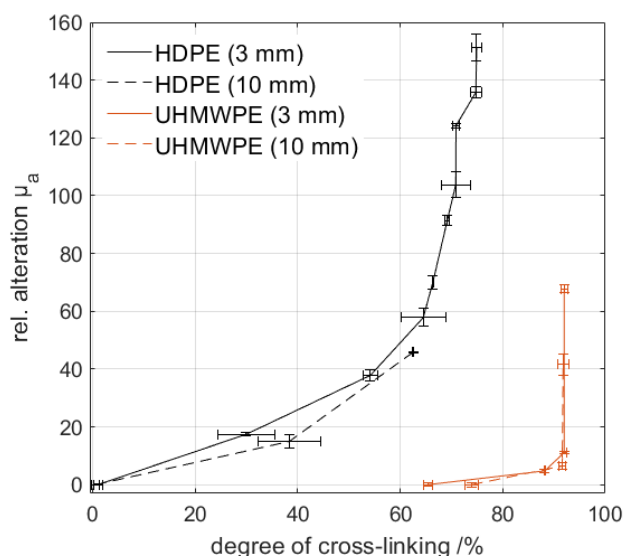


Figure 6 Relative alteration of the absorption coefficient at around 515 nm over the degree of cross-linking. The knowledge of the behaviour of μ_a over the degree of cross-linking of an examined material enables the determination of the degree of cross-linking.

4.2 Thermoset Resins

4.2.1 Dynamic scanning calorimetry

The curing of the thermosets can be determined directly from the DSC signals at different curing times. Figure 7 shows the degree of curing of the epoxy resins SKresin 3075 and 3221 calculated from the measured areas of the exothermic reaction enthalpy according to equation (2). The use of the filler shows no or only minor differences compared to the unfilled resin sample, i.e. the curing is not hindered by this filler. The different kinetics of the two resins are well visible in DSC measurements.

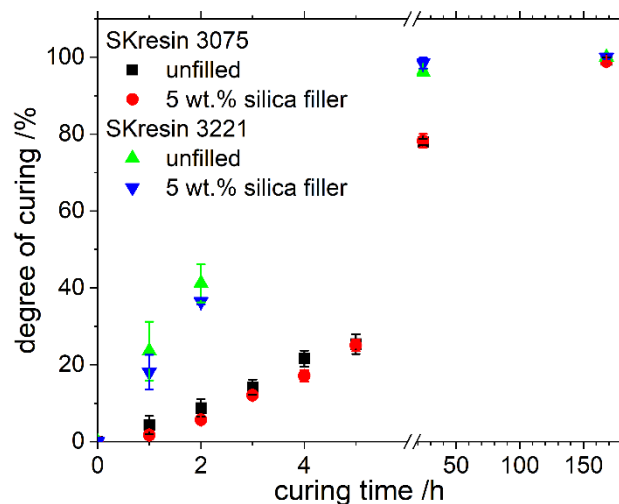


Figure 7 Curing calculated from the DSC peak areas of the epoxy resins investigated with and without filler.

However, the DSC signals of the acrylic resin SKresin 1702 could not be evaluated. In the DSC curves (not shown here), sharp (endothermic) peaks were obtained in all measurements, where a broad exothermic peak was expected. The reason for this was probably gas formation during the reaction and the resulting (partial) detachment of the sample from the crucible bottom. This massively affected the measurement.

DSC is very well suited as an accompanying test during material development and for damage analysis in order to detect incompletely cured thermosets. However, the high cost of conducting numerous destructive tests explains why the method is not used in industrial environments to accompany production.

4.2.2 Dielectric analysis

The ion viscosities recorded during the curing of the 2C thermosets with DEA, unfilled and filled in each case, are shown in figure 8. The different reaction kinetics of the respective resins can be clearly seen. Except for SKresin 3221, the use of silica fillers shows clear differences in the curing process. This was expected since the DEA is based on the conductivity of the material. Incorporated, non-conductive materials can have an interfering effect depending on their dispersion.

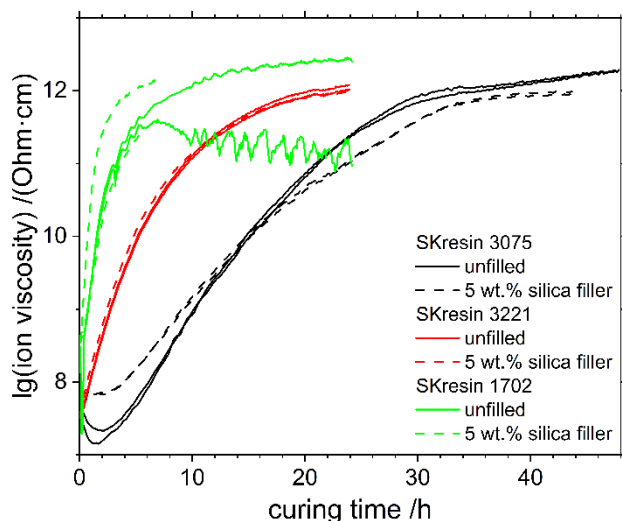


Figure 8 Ion viscosities measured with DEA during curing of the unfilled or 5 wt.% silica filled 2C resins.

The formation of bubbles during the curing reaction of the SKresin 1702, which prevented an evaluation of the DSC measurements, was clearly visible here and led in some cases to very strong fluctuations in the measurement. The reason for these measurement deviations was the fact that not the entire surface of the sensor was covered with material over the complete measurement time.

Apart from this, the DEA provides well reproducible results. The ion viscosity curves strongly resemble those of the rheological viscosity. However, DEA can still resolve differences in the areas of high curing, which are no longer measurable in rheometers due to mechanical limitations. The results show why the method has become established in the field of thermosets for process monitoring. Suitable multi-way sensors are available for certain use-cases. However, temperature and pressure-intensive applications such as thermoset injection moulding remain a challenge.

4.2.3 Integrating sphere

The resin samples have been studied during their curing process using the integrating sphere. It was possible to investigate the epoxy resins samples. The investigation is described and pictured exemplarily for SKresin 3075 without and with TiO_2 fillers. We measured the refractive index for the cured samples using the SENresearch 4.0 from SENTECH Instruments GmbH, Berlin, Germany. For the integrating sphere measurements, the sample was filled in a cuvette with known glass slides. We took the change of the volume during the curing process into account and therefore modified the sample spacer with a funnel-shaped opening on the upper side. Transparent samples have been evaluated using Fresnel's equation. The change in μ_a is well noticeable and can be seen in figure 9.

Therefore, the integrating sphere setup is suitable to monitor alterations of curing in epoxy resin. Depending on the spectral band in the NIR range, μ_a will increase or decrease, see figure 10 until the curing at around 30 hours was completed. The analysis was performed with transparent as well as highly scattering resin samples, adding 3 vol.% of

TiO_2 instead of silica powder. The TiO_2 was added to enable a higher reduced scattering coefficient, which is necessary for an accurate separation of absorption and scattering using an integrating sphere. For this, we could not find an influence of the added filler in the curing process.

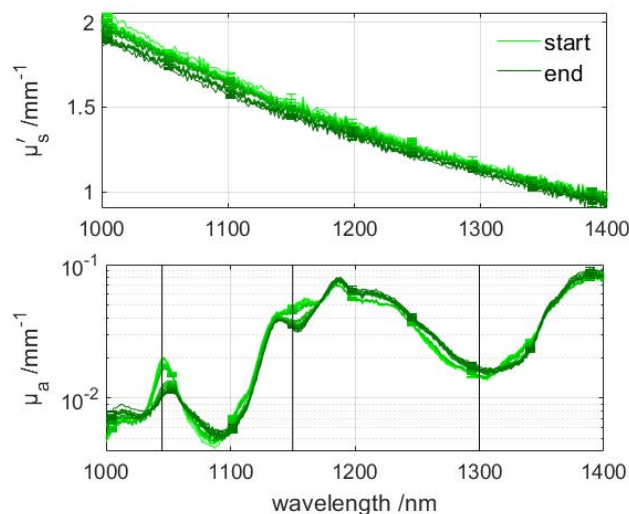


Figure 9 The spectrally resolved optical properties reduced coefficient μ'_s (upper subfigure) and absorptions coefficient μ_a (lower subfigure) of epoxy resin samples with additional 3 vol.% of TiO_2 for a time span of more than 80 hours.

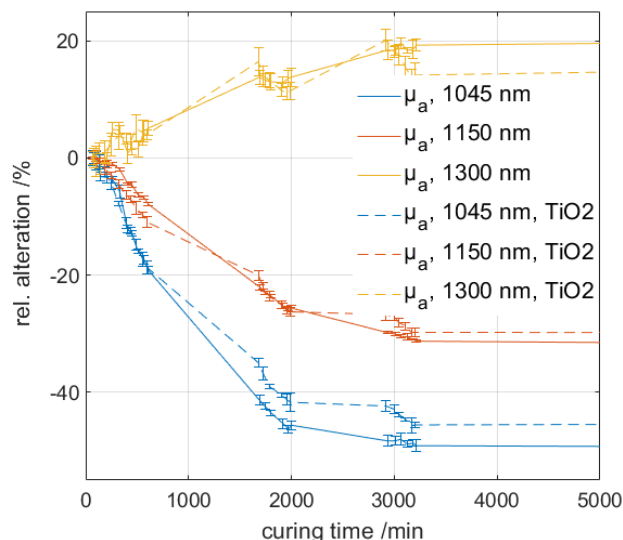


Figure 10 Relative alteration of the absorption coefficient over time. The alteration is more significant within the first 30 hours after mixing, than for the time after 30 hours until the curing was completed. Similar behaviour was found for transparent as well as highly scattering resin samples showing an independency of TiO_2 fillers below 3 vol.%.

5 Summary and Outlook

In this work, the determination of the degree of cross-linking was investigated using absolute optical measurements with an integrating sphere. PE-Xc and various thermosets were examined. Laboratory methods such as wet chemical analysis, DSC and DEA were used for comparison.

The results of the investigations on PE-X show that the various materials can be well distinguished on the basis of their absorption and scattering in the VIS and NIR wavelength range, respectively, and also allow conclusions to be drawn on the degree of cross-linking. Similarly, the curing of the resins can be monitored based on the absorption. At the same time, the limitations of the laboratory methods used to date, especially for UHMWPE and outgassing resins, were demonstrated.

The assembled integrating sphere demonstrator is suitable for non-destructive determination of the degree of cross-linking respectively curing and has the potential for use as an at-line device for in-process quality assurance.

In future studies, the method of absolute optical measurements will be extended to other spectral ranges (mid-infrared) and measurement techniques (Raman) in order to benefit from the advantages of a separate detection of absorption and scattering.

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