Determination of complex refractive index of SU-8 by Kramers–Kronig dispersion relation method at the wavelength range 2.5–22.0 µm

Ashraf Shakeel, Niskanen Ilpo, Kanyathare Boniphace, Vartiainen Erik, Mattsson Claes, Heikkilä Rauno, Thungström Göran

DOI: 10.1016/j.jqsrt.2018.11.026

Accepted Manuscript

Determination of complex refractive index of SU-8 by Kramers-Kronig dispersion relation method at the wavelength range 2.5 – 22.0 μm

Shakeel Ashraf , Ilpo Niskanen , Boniphace Kanyathare , Erik Vartiainen , Claes Mattsson , Rauno Heikkilä , Göran Thungström

PII: S0022-4073(18)30659-9
DOI: https://doi.org/10.1016/j.jqsrt.2018.11.026
Reference: JQSRT 6305

To appear in: *Journal of Quantitative Spectroscopy & Radiative Transfer*

Received date: 17 September 2018
Revised date: 19 November 2018
Accepted date: 20 November 2018

Highlights

- Determination of complex refractive index of SU-8 epoxy as a function of wavelength.
- Fourier-transform infrared (FT-IR) spectrometer is the relatively rapid and wide IR spectral range by non-contact technique
- The data analysis is based on the elegant Singly Subtractive Kramers-Kronig (SSKK) equations.
- Kramers-Kronig method is faster and more reliable in a broad spectrum range

Determination of complex refractive index of SU-8 by Kramers-Kronig dispersion relation method at the wavelength range 2.5 – 22.0 µm

Shakeel Ashraf[a], Ilpo Niskanen[a,b*], Boniphace Kanyathare[c], Erik, Vartiainen[d], Claes Mattsson[a], Rauno Heikkilä[b], Göran Thungström[a]

[a] Department of Electronics Design, Mid Sweden University, Holmgatan 10, SE-85170 Sundsvall, Sweden

[b] Faculty of Technology, Structures and Construction Technology, University of Oulu, P.O. Box 7300, FI-90014 Oulu, Finland

[c] Electronics and Telecommunications Department, Dar es salaam Institute of Technology, P.O. Box 2958 Dar es salaam, Tanzania

[d] LUT School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, FI-53851 Lappeenranta, Finland

\) Corresponding author: Ilpo.Niskanen@oulu.fi

tel: +358 44 3275850

ABASTRACT

Accurate determination of the complex refractive index of SU-8 epoxy has significant for the wide variety of applications in optical sensor technology at IR range. The complex refractive index of SU-8 is determined by recording the transmission of light spectra for the wavelength range of 2.5 – 22.0 µm. The data analysis is based on the Kramers-Kronig dispersion relation method. The method has several merits, such as ease of operation, non-contact technique, measurement accuracy, and rapid measurement. The present method is not restricted to the case of SU-8 but it is also proposed to be applicable across a broad range of applications, such as assessment of the optical properties of paints and biomedical samples.

Keywords: Complex refractive index, SU-8 epoxy, Kramers-Kronig dispersion relation method, FT-IR spectrophotometer, Infrared region.

1. Introduction

Transmission spectroscopy is one of the IR spectroscopic sampling technique to identify substances and to determine various characteristics of their structure and orientation. This technique is ideally suited for samples such as thin films and adsorbed species on liquid [1]. Transmission technique is easy to use, non-contact, non-destructive, no sample preparation requirement, and moreover this technique suitable for samples with flat, thin and smooth surfaces [2]. The light absorption of a film can be characterized with the aid of its complex refractive index. The complex refractive index is a fundamental property of gaseous, liquid and solid media. It has been widely used, for example, detection of solid purity, chemical identification of species, density and even temperature [3].

There are many well-known mathematical routes experimentally to determine the complex refractive index of a substance as a function of wavelength such as Fresnel's method [4], maximum entropy method [5], Azzam's method [6], and Kramers-Kronig dispersion relation method [7]. Kramers-Kronig dispersion relations method determines for a complex refractive index of the material by solving numerically non-linear equations. The non-linear equations consist of the phase shift and attenuation coefficient which are generated from the interaction between light and material. Part of their popularity resides in the generality of the Kramers–Kronig relations: they are derived from causality, the response must follow the excitation and not precede it, and linearity, the superposition of responses to different causes [8].

In our approach, Fourier-transform infrared (FT-IR) spectrometer was used to recode the transmission spectra of the SU-8 epoxy. Beer-Lambert-Kramers-Kronig dispersion relation analysis method makes it possibly fast to get information on the complex refractive index of the SU-8 epoxy film. The reason for SU-8 epoxy popularity can be found in its unique properties such as high chemical and mechanical stability, biological compatibility, high aspect ratio capability and low cost of fabrication [9]. Furthermore, due to excellent optical transparency and proper optical parameters. The properties of SU-8 open it up to a wide range of components in all application areas of micro-technology such as electroplated micro-parts, multilevel components, photonic pressure sensors and diffractive optical elements [10-12]. The refractive index of SU-8 has been reported in the visible and NIR spectral range in the literature. Piruska et al. have determined the refractive index of SU-8 from different batches using the ellipsometer in several different spots in samples in the visible spectral range [13]. Their result indicates that the refractive index of SU-8 was 1.603±0.001 at 532 nm and 1.593±0.001 at 633nm. The refractive index of SU-8 does not change so much in different manufacturing batches. Unfortunately, the refractive index of SU-8 epoxy at the wavelength range of 2.5 – 22.0 μm has not been reported in the literature.

2. Theory

The optical properties of any material may be described by the complex refractive index,

$$N(\lambda) = n(\lambda) - ik(\lambda)\,, \tag{1}$$

where λ is the wavelength, k is the extinction coefficient, and n is the real refractive index. The refractive index is defined as the speed of light in a vacuum divided by the speed in the medium. The extinction coefficient (imaginary part) is therefore described as the reciprocal damping of the oscillation amplitude of the incident electric field in the medium [14]. In mathematical form this is

$$k(\lambda) = \frac{\lambda\alpha(\lambda)}{4\pi}\,, \tag{2}$$

where α is the absorption coefficient and it can be calculated using the Beer-Lambert law

$$\alpha(\lambda) = -\ln(I/I_0)/d\,, \tag{3}$$

where, I_o is the initial light intensity, I is the light intensity after it passes through the sample, d is the thickness of the medium [15]. The infrared spectrum of transmission generated noise too. Therefore, the extinction coefficient becomes an incorrect background, which can be fixed using the Wavelet transform analysis. The Wavelet transform analysis is effective tool for elimination of different kinds of noise to background, since the signal being processed usually contains contributions with different localizations and different locations in the time and frequency domains [16].

The definition of real part of complex refractive index *n* of SU-8 can be calculated by using Kramers-Kronig dispersion (K-K) relation method. The K-K relation connects the extinction coefficient *k* and the real refractive index *n* of the medium. The conventional K-K relation is modified to include the anchor point. The method is called Singly Subtractive Kramers-Kronig dispersion relations, SSKK. In the case of SSKK analysis the dispersion integrals are as follows:

$$n(\lambda') - n(\lambda'') = \frac{2(\lambda'^2 - \lambda''^2)}{\pi} P \int_0^\infty \frac{\lambda k(\lambda) d\lambda}{(\lambda^2 - \lambda'^2)(\lambda^2 - \lambda''^2)} \,, \tag{4}$$

where λ is the wavelength of light at which the transmission data was measured, λ' is the wavelength corresponding to the calculated/extrapolated refractive index using SSKK, λ'' is the anchor point wavelength, *n*(λ') is the wavelength-dependent refractive index, *n*(λ'') is a priori known refractive index value at an anchor point λ'' and *P* denotes the Cauchy principal value [17]. For practical purposes, the integral especially in the case of SSKK analysis can be usually truncated to correspond to the initial and final point of the measured transmittance. Here we use the method of optimal choice of the anchor point λ'' to minimize possible data inversion error. The SSKK relation gives stronger convergence of the integral than a conventional Kramers-Kronig relation, hence the accuracy of data inversion is good even for finite range spectral data [17]. The SSKK dispersion relation was based on the Lucarini's Matlab code [18].

3. Material and methods

The SU-8 epoxy molecule consists of eight epoxy groups, manufactured by Microchem (USA). In order to make the sample, the SU-8 epoxy was deposited on a silicon substrate by spin coating technique followed by soft baking at 95 °C. Square pattern openings of measuring 10 x 10 mm were formed on silicon substrate through a UV-photolithography and a silicon wet etching process. Prior to etching process the sample was hard backed at 150 °C for five minutes through a hotplate. The thickness of the SU-8 film was estimated using atomic force microscopy and the result was given as 3.870 μm.

Spectroscopic data from the SU-8 epoxy was acquired by the Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific). The recorded spectra were in the form of means of 32 spectra, performed in the range of 2.5 – 22.0 µm wavelength with a 0.005 µm resolution on at room temperature (22°C). The background of transmission was recorded with dry air.

4. Results and discussion

Initially, the transmission spectrum (2.5 – 22.0 µm) was measured at 0.005 µm intervals from SU-8-films (thickness, 3.87 µm) using a Nicolet 6700 FT-IR spectrophotometer. The transmission spectrum of the SU-8 is shown in Fig. 1. It can be observed from Fig 1., that OH vibrations, and aliphatic CH stretching wavelength bands at 2.83 - 2.91 µm (3440 – 3540 cm−1) and 3.35 – 3.5 µm (2850 - 2900 cm−1), respectively. In addition, we can see from spectrum CC aromatic ring stretch at 6.22 µm (1606 cm−1) and 6.64 µm (1507 cm−1), the stretch modes of CO groups at 8.00 µm (1247 cm−1), and of CC groups at 9.67 µm (1034 cm−1). The phenyl bending modes can be detected at 8.46 – 8.89 µm (1124 – 1182 cm−1) the phenyl ring modes finds at 12.6 µm (829 cm−1). These results are in accordance with Airoudj et al. research [19].

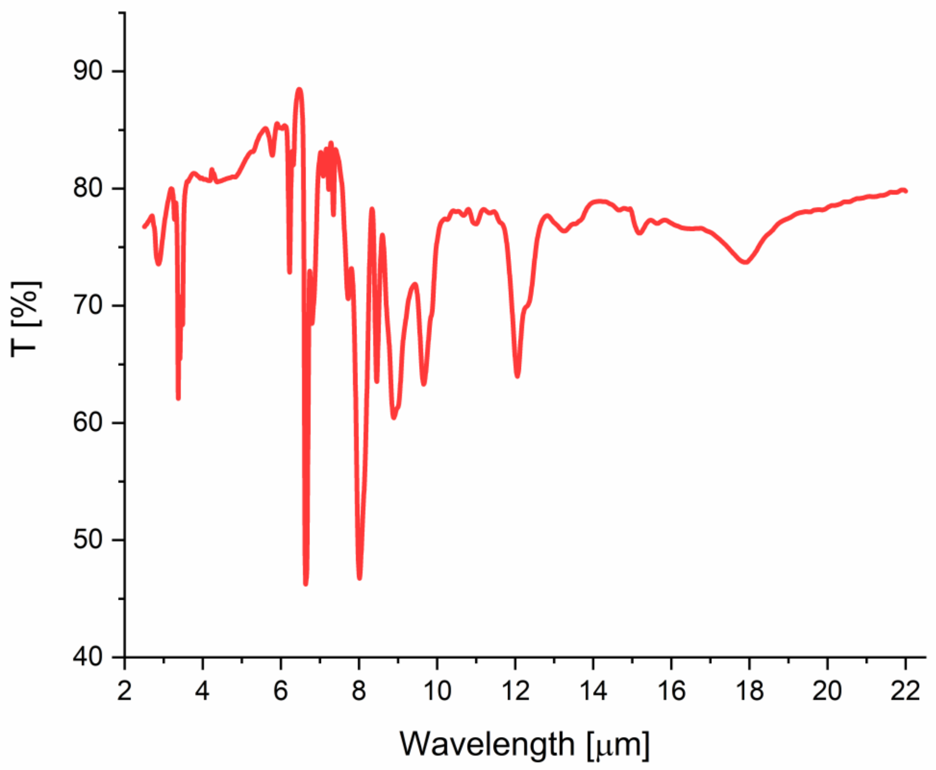

Fig. 1. Transmission results for SU-8 as a function of wavelength.

Next, the absorbance and extinction coefficient of the SU-8 film was calculated from measured transmission data using Eqs. 2 and 1, respectively. In the literature, the real refractive index values of SU-8 can be found at wavelength range 0.4 – 2.5 µm. The determination of refractive indices were based ellipsometer technique [20]. The anchor point of refractive index is used (value was obtained by eye from the curve) value of 1.572 at the wavelength of 2.5 µm [19]. Finally, we can extrapolate the values of refractive indices over a wide wavelength range by using SSKK's formula which is given in Eqs. 4. The results are shown in Fig. 2. From Fig. 2, it is observed that the refractive index and extinction coefficient vary between 1.495 – 1.621 and 0.000 – 0.0951 at the 2.5 – 22.0 µm, respectively. The Lorentzian permittivity of equation have been used to evaluate the accuracy of the result based on the change of extinction coefficient (*k*) is equal to the change of refractive index (*n*), $\Delta k = \Delta n$ [21]. We calculated for example the *n* and *k* for minimum and the maximum values from the peaks that is located at the 12 µm. Result obtained that Δk is $0.93\Delta n$. That conclusion is consistent with the model of Lorentzian.

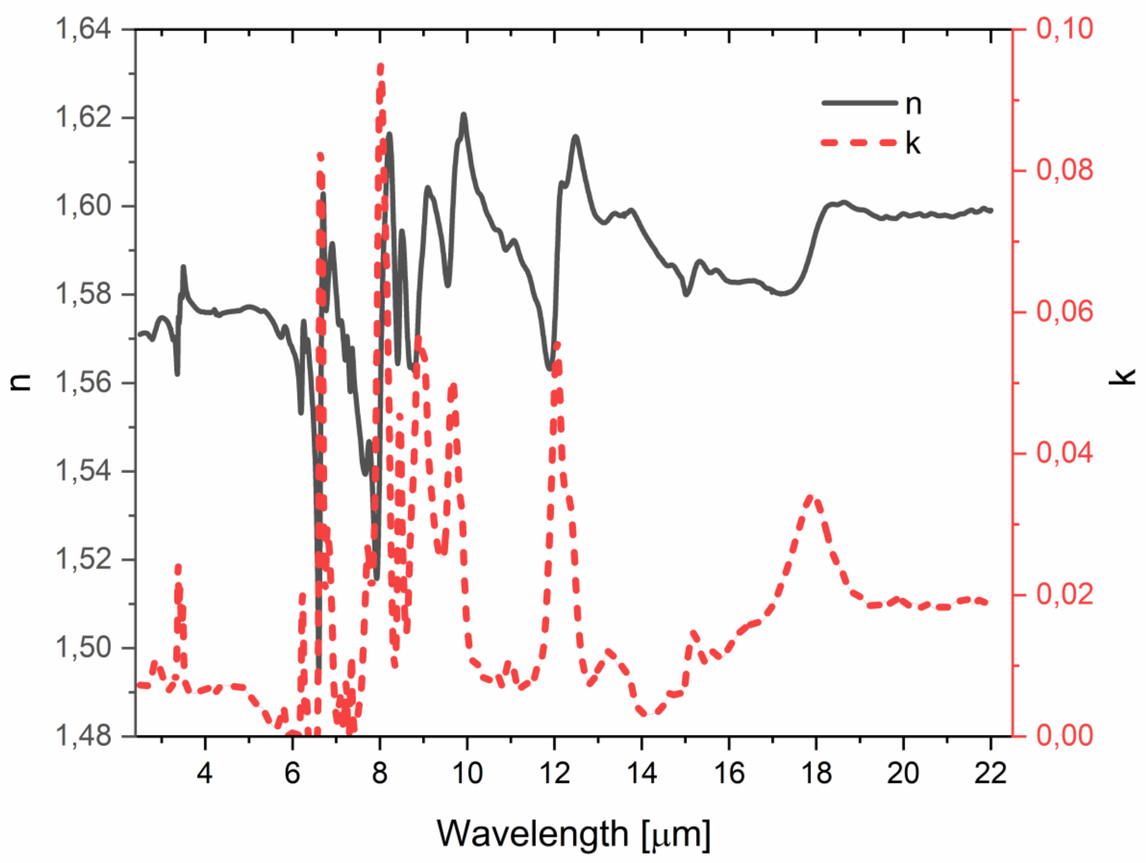

Fig. 2. Complex refractive index of nanocrystals SU-8 as a function of wavelength.

In addition, it is obvious from the data of Fig. 2 that, big variations around the resonant wavelengths both for the real part and the imaginary part curves of the refractive index. Near the resonance, the imaginary refractive index increases sharply to a maximum then falls as the frequency exceeds the resonance frequency. The real refractive index increases quickly in near resonance point, then fall below unity, and eventually makes its way back up towards unity. This behavior near resonance is called anomalous dispersion [22]. The anomalous dispersion is the phenomenon when an electromagnetic wave encounters a collection of atoms, an oscillating electromagnetic field is superimposed on the field of forces that is responsible for the coherency of the material [22]. In other words, the anomalous dispersion range determined by their material fingerprints. We propose that the FTIR and the method of this study have more general applications, provided that the scattering is negligible and absorption bands is not very strong in the frame of using the Kramers–Kronig method. The infrared spectrum of strong absorption bands, the Kramers-Kronig method will produce erratic results that do not physically make sense, e.g., refractive index can be less than 1 [18]. Kramers-Kronig method is more practical than the Fresnel method for the extraction of the complex refractive index of a material because Kramers-Kronig method is faster and more reliable in a broad spectrum range. Ellipsometry is in itself a good experimental method, but much more difficult to implement in a broad spectrum and requires more expensive equipment than transmission measurement.

5. Conclusion

The aim of this study was to show the Beer-Lambert-Kramers-Kronig dispersion relation method for the determination of optical properties of SU-8 epoxy. To our knowledge, the wavelength-dependent complex refractive index of SU-8 has not been reported at 2.5 – 22.0 μm in the literature until now. This study has shown that, the refractive index and extinction coefficient vary between 1.495 – 1.621 and 0.000 – 0.0951 at the 2.5 – 22.0 μm, respectively. An advantage of our method is that it provides information on various optical properties of a thin film in the relatively rapid and wide IR spectral range by non-contact technique. The anomalous dispersion region of SU-8 may provide an exciting route to utilize optical properties of the material in the tailor applications. In the future plan, we continue to study how the refractive index of epoxy changes to exposed by temperature change and ultraviolet radiation as a function of time.

Acknowledgement

We gratefully acknowledge funding from the Knowledge Foundation of Sweden (2150361).

Supplementary material

Supplementary material associated with this article can be found, in the online version,

References

[1] Theophile T. Infrared Spectroscopy - Materials Science, Engineering and Technology: Z. M. Khoshhesab ZM,editors. Reflectance IR Spectroscopy, New Delhi; InTech; 2012, Chapter 12, p. 1-13.

[2] Stuart BH. Infrared Spectroscopy: Fundamentals and Applications. Chichester: Wiley & Sons, Ltd; 2004.

[3] Willard HH, Merritt LL, Dean JA, Settle FA. Instrumental Methods of Analysis. New York: Van Nostrand; 1981.

[4] Chiu MH, Lee JY, Su DC. Complex refractive-index measurement based on Fresnel's equations and the use of heterodyne interferometry. Applied Optics 1999;38(19):4047-4052. https://doi.org/10.1364/AO.38.004047

[5] Vartiainen EM, Peiponen KE, Asakura T. Maximum entropy model in reflection spectra analysis, Optics Communications 1992;89:37-40. https://doi.org/10.1016/0030-4018(92)90244-L

[6] Niskanen I, Räty J, Peiponen KE, Koivula H, Toivakka M. Assessment of complex refractive index of optically very dense solid layer: Case study offset magenta ink. Chemistry Physics Letters 2007;442:515-517. https://doi.org/10.1016/j.cplett.2007.06.036

[7] Yamamoto K, Ishida H. Kramers-Kronig analysis applied to reflection-absorption spectroscopy, Vibrational Spectroscopy 1997;15:27-36. https://doi.org/10.1016/S0924-2031(97)00017-9

[8] Bechhoefera J. Kramers–Kronig, Bode, and the meaning of zero. Am J Phys 2011; 79 (10):1053- 1059. https://doi.org/10.1119/1.3614039

[9] Figura D, Bartel J. Fabrication of high aspect ratio SU-8 structure using UV lithography and megasonic-enhanced development. ECS Transactions 2010;25(31):29-35. https://doi.org/10.1149/1.3327201

[10] Bertsch A, Renaud P. Special Issue: 15 Years of SU8 as MEMS Material, Micromachines 2016;6:790-792. https://doi.org/10.3390/mi6060790

[11] Nordstrom M, Zauner DA, Boisen A, Hubner J. Single-Mode Waveguides With SU-8 Polymer Core and Cladding for MOEMS Applications. The Journal of Lightwave Technology 2007;25(5):1284–1289. https://doi.org/10.1109/JLT.2007.893902

[12] Xie SQ, Wan J, Lu BR, Sun Y, Chen Y, Qu XP, Liu R. A nanoimprint lithography for fabricating SU-8 gratings for near-infrared to deep-UV application, Microelectron Eng 2008; 85: 914–917. https://doi.org/10.1016/j.mee.2008.01.072

[13] Piruska A, Bhagat AAS, Zhou K, Peterson ETK, Papautsky I, Seliskar CJ. Characterization of SU-8 optical multimode waveguides for integrated optics and sensing on microchip devices. Microfluidics, BioMEMS, and Medical Microsystems IV, 2006; 6112:edited by Ian Papautsky, Wanjun WangProc. of SPIE Vol. 6112 (611207):1-9. http://doi.org/10.1117/12.655667

[14] Jackson JD. Classical Electrodynamics, 3th ed. New York: Wiley, 1998.

[15] Peiponen KE, Vartiainen EM, Asakura T. Dispersion, Complex Analysis and Optical Spectroscopy. Berlin: Springer, 1999.

[16] Tan HW, Brown SD. Wavelet analysis applied to removing non-constant, varying spectroscopic background in multivariate calibration. Journal of Chemometrics 2002;16: 228–240. https://doi.org/10.1002/cem.717

[17] Kanyathare B, Peiponen KE. Wavelength-dependent excess permittivity asindicator of kerosene in diesel oil, Applied Optics 2018;57(12):2997-3001. https://doi.org/10.1364/AO.57.002997

[18] Lucarini V, Saarinen JJ, Peiponen KE, Vartiainen EM. Kramers–Kronig Relations in Optical Materials Research. Berlin: Springer, 2005.

[19] Airoudj A, Debarnot D, Bêche B, Poncin-Epaillard F. Development of an optical ammonia sensor based on polyaniline/epoxy resin (SU-8) composite. Talanta 2009;77(5): 1590-1596. https://doi.org/10.1016/j.talanta.2008.09.054

[20] Herzog T, Gut K, Opilski Z, Kałużyński P. SU-8 polymer based waveguides on different substrates, Proceedings 2016; 10034, 11th Conference on Integrated Optics: Sensors, Sensing Structures, and Methods; 100340M https://doi.org/10.1117/12.2244595

[21] Räty J, Pääkkönen P, Peiponen KE. Assessment of wavelength dependent complex refractive index of strongly light absorbing liquids. Opt Express 2012;20(3):2835-43. https://doi.org/10.1364/OE.20.002835

[22] Weidlich A, Wilkie A. Anomalous dispersion in predictive rendering, Computer Graphics Forum 2009;28(4):1065-1072. https://doi.org/10.1111/j.1467-8659.2009.01483.x

Graphical Abstract