DOI: 10.1002/masy.200850513

Development of Methods to Determine the Infrared-Optical Properties of Polymer Films

Gernot Oreski,[*1] Daniel Tscharnuter,[1] Gernot M. Wallner[2]*

Summary: In this paper, two methods for the determination of infrared optical properties of thick polymer films, based on FTIR spectroscopy, were implemented and used. Complex index of refraction data were generated for various ethylene copolymer films. Transmittance and reflectance spectra were measured in the mid infrared range using a gold-coated 100 mm-diameter integrating sphere. For the investigated films n and k values ranging from 1.3 to 1.6 and from 10^{-4} to 0.25 were determined, respectively. Regarding n, a good agreement was obtained for both methods, the transmittance/reflectance procedure (T/R method) used for transparent and semi-transparent regions, and Single Substractive Kramers-Kronig (SSKK) algorithm applied for non-transparent regions. The highest k values were determined for the CH_2 stretching vibration. The k values are dependent on comonomer content and film thickness. The combination of both methods allows for an accurate determination of n and k in the entire IR region relevant for solar application.

Keywords: complex index of refraction; ethylene copolymer films; FTIR spectroscopy; Kramers-Kronig; solar applications

Introduction

Polymeric materials are already in use for many different solar energy related components. Concerning solar thermal systems plastics play a decisive role as transparent cover and/or convection suppressing material. For such applications the infrared (IR) optical properties of plastics are of prime importance. Contrary to silica glass, which is almost completely opaque to the IR spectrum, the transparency of plastics to the IR spectrum is ranging from highly transparent to almost completely opaque depending on the molecular structure of the polymer. While for solar thermal systems with a black absorber an infrared radiation absorbing cover material is favorable, for solar thermal systems with a selective absorber a non-absorbing cover material is advantageous. For solar thermal applications, an accurate prediction of infrared optical properties as a function of film thickness and temperature is crucial.[1–3] While for low IR absorbing materials (e.g. polymers) often simple methods assuming a constant real part of the refractive index are used, for high IR absorbing materials (e.g. glass, ceramics) comprehensive methods allowing for the determination of both, the real and imaginary part of refractive index (n,k), are a prerequisite.[3,4]

To determine n and k in the infrared range, several methods are described in the literature.[3–14] Currently, mainly spectroscopic ellipsometry (SE) is used for the evaluation of n and k over a wide range of wavelengths.[5–10] By systematic combination of SE with Fourier transform spectroscopy (FT) and development of accurate calibration procedures, the range of application was extended from UV-visible to the infrared.[5] The ellipsometric data are

---

[1] Polymer Competence Center Leoben GmbH, Roseggerstraße 12, A-8700 Leoben, Austria
Fax: +43 3842 429 626;
E-mail: oreski@pccl.at

[2] Institute of Materials Science and Testing of Plastics, University of Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria

usually recorded over the whole spectral range at various angles of incidence. An optical model, which assumes geometry and microstructure, is then applied to calculate the complex index of refraction.[6] A significant drawback of the SE procedure is the necessity to investigate thin films, which are coated on a substrate (e.g. silicon wafers[7] or gold-coated glass slides[8]), or prepared as freestanding films of 12–15 μm thickness.[9] However, commercial polymer films, currently used for greenhouse or transparent insulation applications, are thicker with values ranging from 50 to several hundred microns. Roodenko et al. described the difficulties, which can occur by investigating the infrared optical properties of thick films by FTIR-SE, and the effect on ellipsometric parameters.[10]

In the past, spectroscopic methods were used for determination of the refractive index.[4,11–14] These methods, often requiring special sample preparation techniques, were limited to spectral regions with certain optical properties (transparent, semi-transparent or non-transparent) or based on assumptions such as a constant real part of refractive index. In a recent study, an advanced spectroscopic method, the transmission fringe depth method (RTFD),[11] has been developed for the determination of n and k. However, this method, which is based on the measurement of directional and hemispherical transmittance and reflectance spectra, is applicable only to thin films where interference effects can be observed.

The overall objective of this paper is to implement and apply spectroscopic methods to determine the infrared optical properties of thick polymer films for solar energy applications in all regions of the spectral range (transparent, semi-transparent and non-transparent regions). While for the transparent and semitransparent regions a simple method based on hemispherical transmittance and reflectance spectra was applied, for the non-transparent regions of the IR spectra a more sophisticated algorithm based on the Kramers-Kronig (KK) relation requiring was implemented and used.[3,15]

Experimental Part

Polar ethylene copolymer film types with comonomer contents between 1.7 and 30 wt-% and three different comonomer types (acids, acrylates and acetates) were investigated (Table 1). As to the acid comonomers acrylic acid (AA) and methacrylic acid (MAA) were chosen. Regarding acrylate comonomers butylacrylate (BA), ethylacrylate (EA) and methylacrylate (MA) are currently in use for ethylene (E) copolymer materials. Furthermore, widely used ethylene vinylacetate copolymers (EVA) as well as a terpolymer material with two different comonomers (acrylic acid and butylacrylate (AA/BA) were investigated. In comparison, a non-polar linear low-density polyethylene (LLDPE) was investigated.

The material resins were supplied by Arkema (EBA), Basell (EAA/BA), BP (EMAA), Dow (EAA, LLDPE), DuPont

Table 1.
Investigated ethylene (E) copolymers (material type, comonomer unit, comonomer content and film thickness).

Material type	Comonomer	Content, wt%	Film thickness
EAA	acrylic acid	9.7	125 μm
EMAA	methacrylic acid	1.7, 8.7	110 μm, 90 μm
EBA	butylacrylate	7	125 μm
EEA	ethylacrylate	12	115 μm
EMA	methylacrylate	9	100 μm
EVA	vinylacetate	9, 18	70 μm, 125 μm
EAA/BA	acrylic acid	AA 4	125 μm
	butylacrylate	BA 7	
LLDPE			42 μm, 105 μm

(EMAA, EEA, EMA, EVA). Films with various thicknesses ranging from 40 to 150 μm were cast on a Rosendahl RO400 single screw extruder (Pischelsdorf, Austria) with a chill roll unit of SML Maschinengesellschaft mbH (Lenzing, Austria).

The transmittance (T) and reflectance (R) spectra over the mid-IR range from 4000 to 580 cm^{-1} (2.5 to 17.2 μm) were recorded using a Perkin Elmer Spectrum GX (Perkin Elmer; Überlingen, Germany) with an external 100 mm diameter, gold-coated integrating sphere.

Mathematical Modelling

To calculate the complex index of refraction (n-ik), at least two input data are necessary to derive the two unknown quantities n and k. For transparent and semitransparent regions of the spectral range of the investigated sample, the infrared optical properties can be calculated by measurements of spectral transmittance (T) and reflectance (R) of a single sample.[3] Therefore this method is called T/R method. It is assumed that samples are plane-parallel and sample properties are measured normal to the sample surface. With multiple reflections taken into accounts, T and R can be expressed by surface reflectance ρ and the internal transmittance τ[16]:

$$R = \rho\left[1 + \left(\frac{(1-\rho)^2\tau^2}{1-\rho^2\tau^2}\right)\right] \tag{1}$$

$$T = \tau\frac{(1-\rho)^2}{1-\rho^2\tau^2} \tag{2}$$

First, to determine the complex refractive index, the surface reflectance ρ and the internal transmittance τ values are calculated from R and T:

$$\rho = \frac{1}{2(2-R)}\left[C - \sqrt{C^2 - 4R(2-R)}\right] \tag{3}$$

with

$$C = 1 + 2R + T^2 - R^2 \tag{4}$$

$$\tau = \left(\frac{R}{\rho} - 1\right)\frac{1}{T} \tag{5}$$

Second step is the determination of k. The absorption coefficient a can be calculated from τ and the sample thickness l, k is then derived from a and the wavelength λ:

$$a = -\frac{\ln\tau}{l} \tag{6}$$

$$k = \frac{a\lambda}{4\pi} \tag{7}$$

Finally, the real part of the complex index of refraction is given by:

$$n = \frac{1+\rho}{1-\rho} + \sqrt{\frac{4\rho}{(1-\rho)^2} - k^2} \tag{8}$$

The T/R method is sensitive to n and k as long as T is larger than zero.

If the sample material is non-transparent and the experimental determination of two independent optical properties i.e. the reflectance and transmittance is not possible, the complex refractive index may be calculated from a single quantity such as the reflectance by a Kramers-Kronig integral. If the reflectance has been measured, the phase of the complex reflection coefficient is given by

$$\varphi(\nu) = -\frac{\nu}{\pi}P\int_0^\infty \frac{\ln(R(x))}{(x^2-\nu^2)}dx \tag{9}$$

Because in practice the measurement can only be carried out over a finite range of wave numbers, extrapolation procedures have been developed for the inaccessible wave numbers. However, the result of the integration tends to depend on the kind of extrapolation.[15] To reduce the ambiguity associated with this dependence, Ahrenkiel[15] introduced the Singly Subtractive Kramers-Kronig method (SSKK). The idea is to use the phase known at one wave number, which is obtained by reflectance and transmittance measurements, to improve the convergence of the Kramers- Kronig integral and therefore make it less dependent on the extrapolation. By using the known phase φ_0 at a wave number ν_0 in the

Kramers-Kronig integral, Ahrenkiel derived the subtractive Kramers-Kronig integral

$$\varphi(\nu) = \frac{\nu}{\nu_0}\varphi(\nu_0) + \frac{\nu(\nu_0^2 - \nu^2)}{\pi} P \int_0^\infty \frac{\ln(R(x))}{(x^2 - \nu_0^2)(x^2 - \nu^2)} dx \tag{10}$$

By using cubic splines to represent ln(R(x)) the integrand is a proper rational function on each interval defined by the spline nodes and therefore the integral can be simplified by partial fraction decomposition,

$$\frac{ax^3 + bx^2 + cx + d}{(x^2 - \nu_0^2)(x^2 - \nu^2)} = \frac{A}{x - \nu} + \frac{B}{x + \nu} + \frac{C}{x - \nu_0} + \frac{D}{x + \nu_0} \tag{11}$$

where A, B, C and D depend on ν, ν_0 and the spline parameters a, b, c and d. For each of the four terms the standard integral as well as the Cauchy Principal Value integral, which needs to be taken when either ν or ν_0 are in the interval, can be solved in terms of logarithms.

However, the SSKK method is sensitive to *n* in the entire spectral region, but insensitive to *k* in the transparent and semitransparent region.[3]

Results and Discussion

For greenhouse or transparent insulation wall applications it is crucial to absorb the infrared radiation as well as possible in order to keep the heat radiation low. Thus, high IR absorption is required in the range between 200 and 1500 cm^{-1}, in which a blackbody at 20 °C emits mostly. Figure 1 displays the transmittance and reflectance spectra over the medium IR range for selected ethylene copolymer films with film thicknesses ranging from 40 to 125 μm.

Significant absorptions in the investigated polar polyethylene copolymers can be attributed to CH_2 and CH_3 groups (between 3000 and 2800, at about 1470, 1380 and 720 cm^{-1}), to C=O double bonds (between 1750 and 1700 cm^{-1}) to C–O single bonds (between 1300 and 1000 cm^{-1}) and to hydroxyl (O–H) groups in acid copolymers (at about 950 cm^{-1}). Below 1000 cm^{-1} mainly molecular vibrations of the polymer chain contribute to the absorption. However, the molecular vibrations are rather weak for the investigated polymers. Close to the maximum of the emissive power function of a blackbody at 20 °C, the narrow absorption peak at 720 cm^{-1} of the CH_2 group can be found for all investigated polymers. CH_2 groups are rather weak dipoles with low absorbance in the relevant IR wavelength range. In contrast, C–O and O–H single bonds are stronger dipoles with a higher specific absorbance in the relevant range. However, in polar ethylene copolymers CH_2 groups are dominating.

The reflectance values of all investigated polymer films are rather constant over the mid-IR range, only little variations can be seen in the areas of high absorbance. The reflectance values are well below 10%.

Figure 2 shows the integrated transmittance (T), reflectance (R) and absorbance values (A), which were determined by averaging the spectral values, weighted by a blackbody emissive power function, P(ν,T) at a temperature of 20 °C, at each wave number.[11–14] The reflection values of the investigated polymer films show little difference and are ranging from 0.042 to 0.048, except for the 18% EVA film (125 μm), with a significant lower value of 0.031, and for the EAA 9.7% film (125 μm) with a significant higher value of 0.056. As expected, the absorption of the LLDPE films was lowest, with transmission values of 0.82 (42 μm film) and 0.74 (105 μm film). For EMAA 1.7% also low absorption was observed, which can be attributed to its low comonomer content. The ethylene acrylate copolymers (EBA; EMA; EEA) exhibit medium transparency in the IR region with absorption values ranging from 0.33 to 0.38, despite the different film thicknesses and

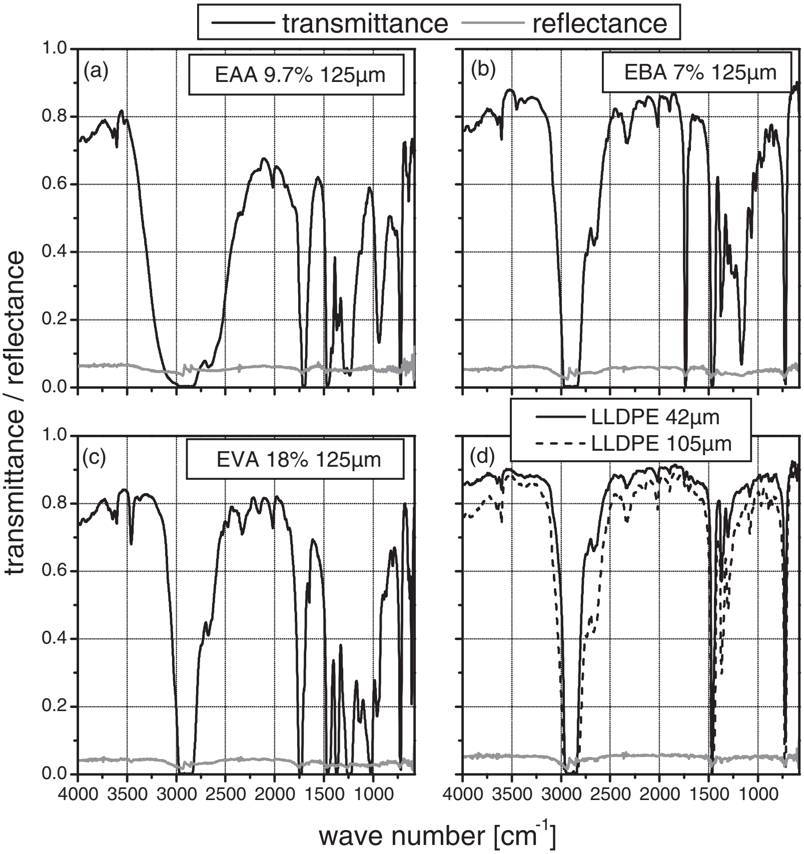

Figure 1.

Transmittance and reflectance spectra of (a) EAA 9.7% (125 µm film), (b) EBA 7% (125 µm film), (c) EVA 18% (125 µm film) and (d) LLDPE (42 and 105 µm film).

conomomer contents. In comparison, for the ethylene acid copolymers higher absorption values of about 0.41 for EMAA 8.7% (90 µm), 0.52 for EAA-BA 11% (125 µm) and EAA 9.7% (125 µm) were found. Due to the high amount of vinyl acetate groups EVA 18%, for these films the highest absorption values of about 0.6 were determined. As already reported in previous studies,[13,14] ethylene copolymers containing acid groups exhibit the highest infrared absorption values, provided that film thickness and comonomer content are identical. This can be attributed to material dependent differences in the IR spectra, especially in the region between 1300 and 900 cm^{-1}. Copolymers containing an acid group (EMAA, EAA, EAA-BA) show a medium peak at about 950 cm^{-1} (Figure 1a) caused by the carboxylic group of the polymer. This intense peak is located very next to the emittance maximum of a black body at 20 °C.[13,14]

Usually T, R and absorbance A are independent of film thickness in the transparent region of the spectral range. Banner et al.[17] defined the transparent region by an absorption coefficient $a < 10^0\ \mathrm{cm}^{-1}$. In the non-transparent region ($a > 10^3\ \mathrm{cm}^{-1}$), the internal transmittance becomes zero and reflectance and absorbance are almost surface properties. In the semitransparent region (absorption coefficient between 10^0 and $10^3\ \mathrm{cm}^{-1}$) transmittance, reflectance and absorbance are strongly thickness dependent. In case of

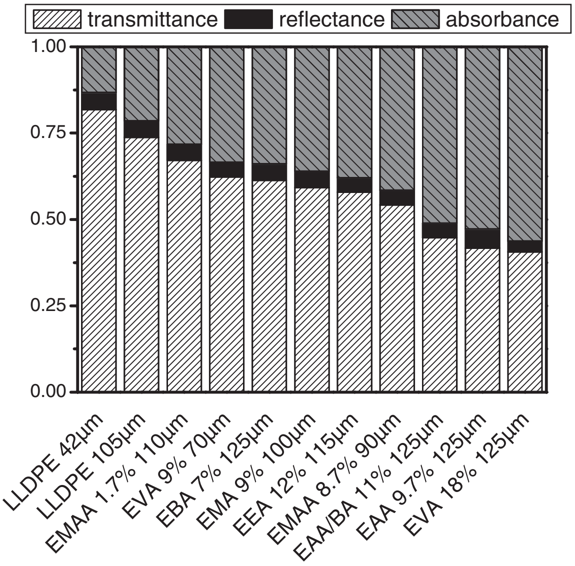

Figure 2.
Transmittance, reflectance and absorbance values, weighted with the emissive power function of a blackbody at 20 °C, for the investigated polymer films.

LLDPE (Figure 1(d)) it could be observed, that transmittance values show a higher dependence on film thickness than reflectance values, which are nearly identical.

In general, scattering in the infrared wavelength range of the material is neglected.[16] This assumption was confirmed by comparing hemispherical transmittance spectra measured with an integrating sphere to spectra measured directionally. The results for 125 μm thick EVA (18%) and EAA (9.7%) films are shown in Figure 3. Only small differences solely in areas of high transmittance can be seen.

In Figure 4 the validity regions of the T/R and the SSKK method is shown with reference to a transmittance spectrum of a 125 μm EAA 9.7% film. The threshold to distinguish the non-transparent from the semitransparent region was defined at a transmittance value of 0.01. Regarding the real part of the refractive index, the SSKK algorithm is sensitive over the whole spectral range and therefore the fastest method to determine n accurately. But, since the investigated ethylene copolymers are highly transparent in the IR range, also the T/R method is applicable nearly over the whole spectral range. Only small areas of total absorption have to be excluded. The determination of the imaginary part of the refractive index is more complicated. A combination of both methods (Figure 4)

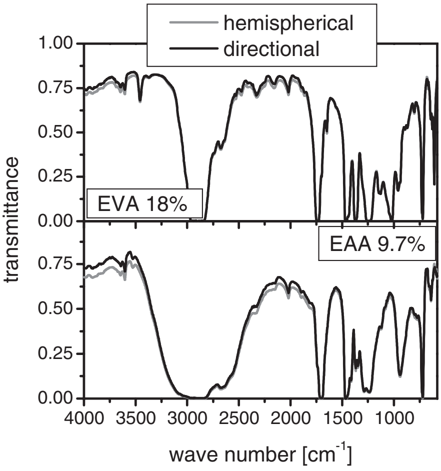

Figure 3.
Comparison of hemispherical (recorded with an integrating sphere) and directional transmittance spectra of 125 μm EVA 18% (top) and EAA 9.7% film (bottom).

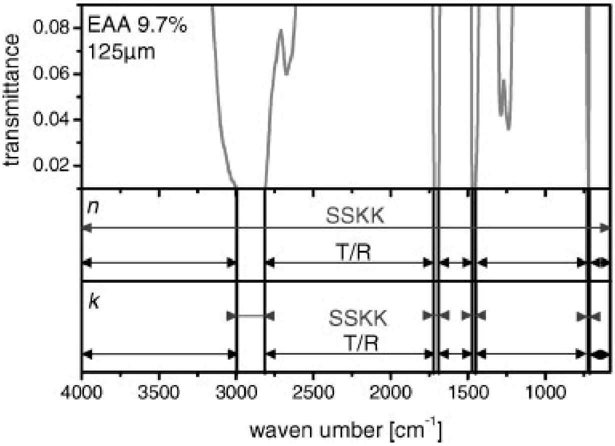

Figure 4.
Validity of the T/R and the SSKK method shown with reference to the transmittance spectra of 125 μm EAA 9.7% film.

has to be applied to calculate k over the whole spectral range.

The real part of the refractive index, determined by the SSKK algorithm, is shown in Figure 5 as a function of wave number for selected ethylene copolymer films. Whereas the highest values for *n* ranging from 1.5 and 1.6, were found for EAA 9.7%, EVA 18% exhibited the lowest values for *n* ranging from 1.3 and 1.4. The *n* values of the other ethylene copolymer films are lying between 1.4 and 1.5. The order of the n values is in agreement with the measured reflectance values.

For LLDPE it is observable, that slight differences in reflectance cause significant differences in *n* (Figure 6). On average, the 42 μm thick film showed a value of about 0.02 lower than the 105 μm thick film.

Figure 7 shows the real part of refractive index, calculated by the T/R and the SSKK

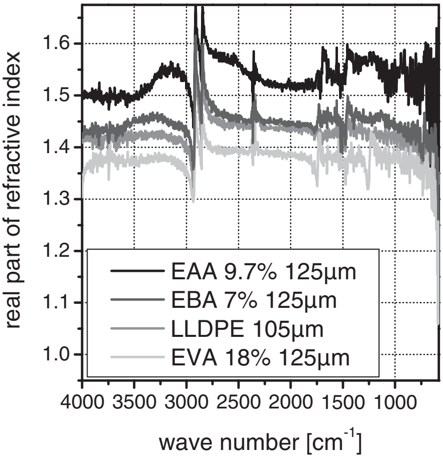

Figure 5.
Real part of refractive index calculated by the SSKK algorithm for selected ethylene copolymer films, as a function of wave number.

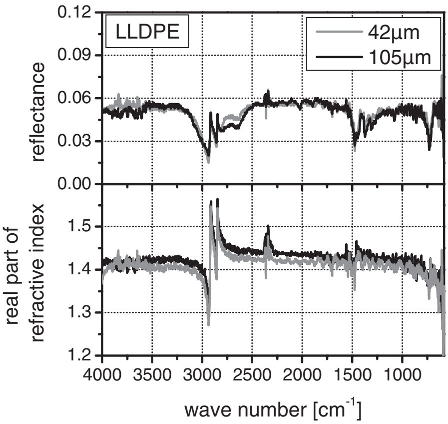

Figure 6.
Reflectance spectra and real part of refractive index, calculated by the SSKK algorithm for 42 and 105 μm thick LLDPE films as a function of wave number.

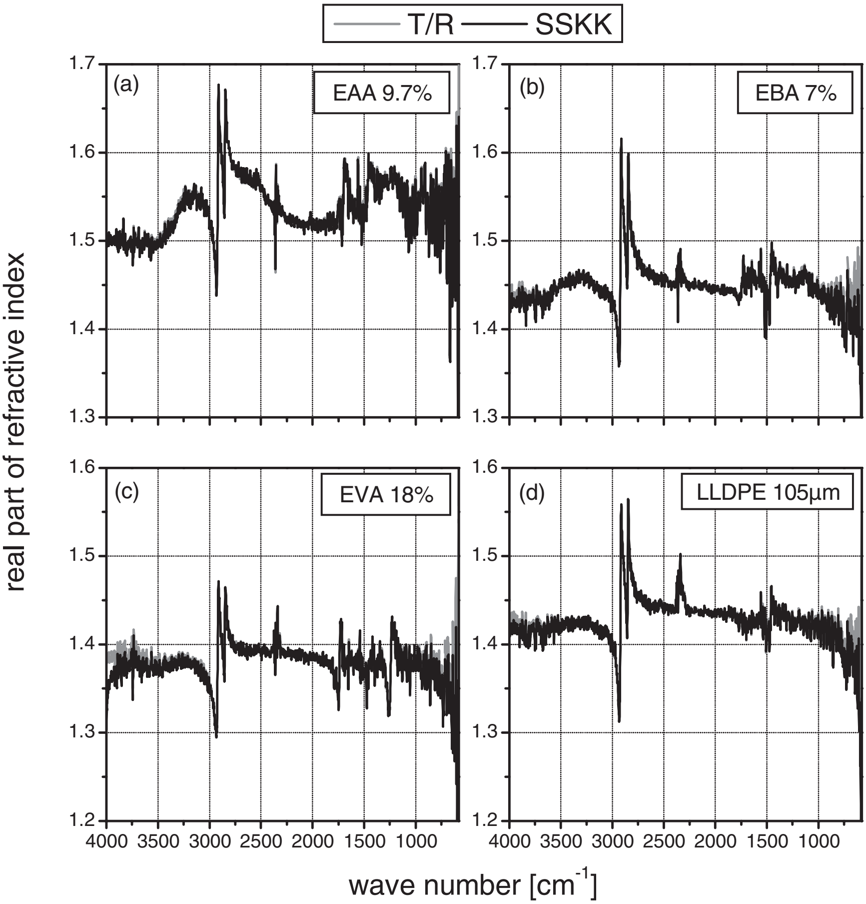

Figure 7.
Comparison of the T/R and the SSKK method for calculation of the real part of refractive index, shown for (a) EAA 9.7% (125 μm film), (b) EBA 7% (125 μm film), (c) EVA 18% (125 μm film) and (d) LLDPE (105 μm film).

method, as a function of wave number. In case of the T/R method, the non-valid values in non-transparent regions were excluded. In general, both methods are in good agreement regarding *n*. Slight differences can be seen only between 4000 and 3700 cm^{-1} and at wave numbers below 800 cm^{-1}.

Comparing both methods, the SSKK algorithm is more appropriate to calculate the real part of the refractive index, as it yields values for *n* without any limitations over the whole range of interest.

For the calculation of the imaginary part of the refractive index both methods have to be applied to obtain results over the whole spectral range. In Figure 8 the k values from 4000 to 580 cm^{-1} are shown for selected films. In the transparent region, the k is about 10^{-4}, increasing to 10^{-2} in the semitransparent region. In areas of total absorption, *k* values reach about 0.25 for the strongest absorption peak, (i.e. CH_2 stretching vibration between 3000 and 2800 cm^{-1}). Medium absorption bands (e.g. $\nu C{=}O$, $\nu C–O$, δCH_2, ρCH_2) exhibit *k* values up to 0.1. The area of change-over between the *k* values calculated by the T/R method and the values determined by the SSKK algorithm is not fully covered, especially at the absorption peaks below 1800 cm^{-1}. In some cases (e.g. ρCH_2 at

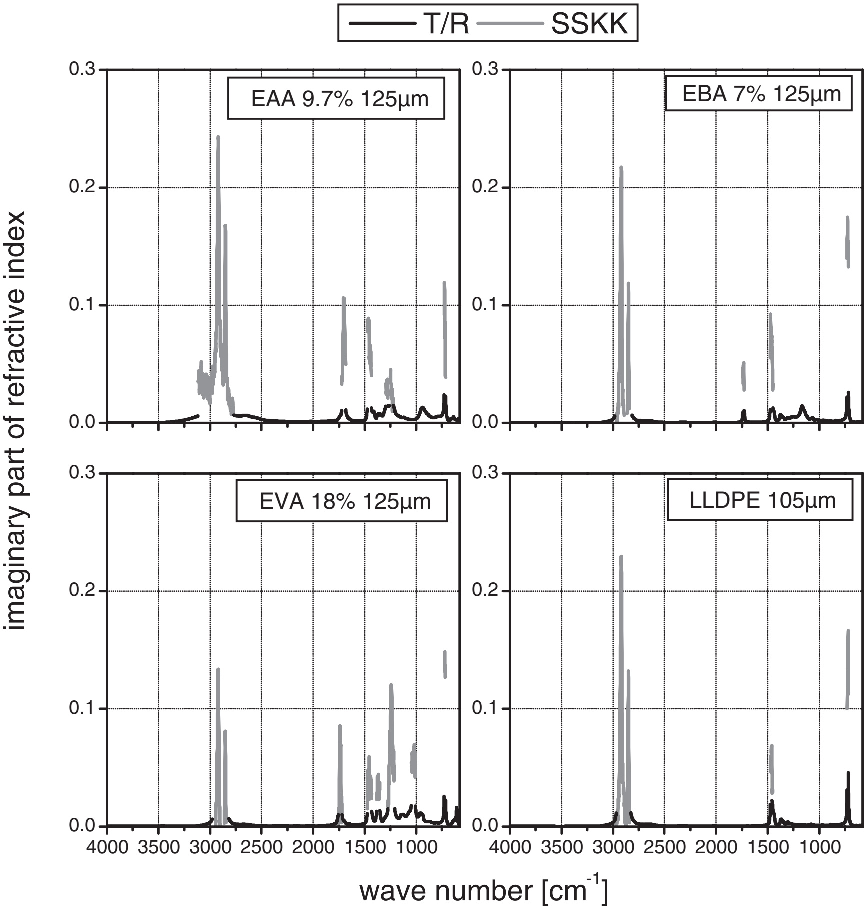

Figure 8.
Imaginary part of refractive index as a function of wave number, shown for (a) EAA 9.7% (125 µm film), (b) EBA 7% (125 µm film), (c) EVA 18% (125 µm film) and (d) LLDPE (105 µm film).

about 720 cm^{-1}) the values of k switch over one order of magnitude in one step. For a better definition of the change-over between both methods, higher resolution spectra should be measured.

Acknowledgements: This research work was performed at the Polymer Competence Center Leoben (PCCL) within the research project II-S.5 in cooperation with the Institute of Materials Science and Testing of Plastics at the University of Leoben. The PCCL is founded by the Austrian Government and the State Governments of Styria and Upper Austria within the K$_{plus}$ program of the Austrian Ministry of Traffic, Innovation and Technology. The authors wish to express their gratitude to Arkema, Basell, DOW and DuPont for providing the materials.

[1] P. T. Tsilingiris, *Energy Conversion and Management* **2003**, *44*, 2839.
[2] G. Papadakis, D. Briassoulis, G. Scarascia Mugnozza, G. Vox, P. Feuilloley, J. A. Stoffers, *J. agri. Engng Res.* **2000**, *77*, 7.
[3] H. Mehling, *"Determination of infrared optical properties and phononic thermal conductivity of non-scattering inorganic and nonmetallic materials"*, PhD thesis, Universität Würzburg 1998.
[4] G. M. Wallner, W. Platzer, R. W. Lang, *Solar Energy* **2005**, *79*, 593.
[5] B. Drévillon, *Thin Solid Films* **1998**, *313–314*, 625.

[6] J. A. Wollam, C. Bungay, J. Hilfiker, T. Tiwald, *Nucl. Instrum. Methods Phys. Res., Sect. B* **2003**, *208*, 35.

[7] D. Tsankow, K. Hinrichs,, A. Röseler,, E. H. Korte, *phys. stat. Sol. (a)* **2001**, *188*, 1319.

[8] K. Hinrichs, M. Gensch, N. Nikonenko, J. Pionteck, K. J. Eichhorn, *Macromol. Symp.* **2005**, *230*, 26.

[9] M. Gioti, A. Laskarakis, S. Logothetidis, *Thin Solid Films* **2004**, *455–456*, 283.

[10] K. Roodenko, M. Gensch, H. M. Heise, U. Schade, N. Esser, K. Hinrichs, *Infrared Physics & Technology* **2006**, *49*, 39.

[11] Y. P. Zhang, X. S. Ge, *Solar Energy Materials and Solar Cells* **1995**, *37*, 379.

[12] G. Wallner, ''*Kunststoffe für die transparente Wärmedämmung – Polymerphysikalische Einflüsse und Modellierung*'', PhD thesis, Montanuniversität Leoben 2000.

[13] G. Oreski, G. M. Wallner, *Solar Energy Materials & Solar Cells* **2006**, *90*, 1208.

[14] G. Oreski, G. M. Wallner, *Chemical Monthly* **2006**, *137*, 899.

[15] R. K. Ahrenkiel, *J. Opt. Soc. Am.* **1971**, *61*, 1651.

[16] R. Siegel, J. R. Howell, ''*Thermal Radiation Heat Transfer*'', Hemisphere, Washington 1980.

[17] D. Banner, S. Klarsfeld, C. Langlais, *HighTemp – High Press* **1989**, *21*, 347.