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Structure-Infrared Optical Property-Correlations of C,O,H-Polymers for Transparent Insulation and Greenhouse Applications

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Summary. In this paper an understanding of the physical relationships between the material structure and the temperature dependent infrared optical properties of different transparent polymer films for solar applications is described. The infrared optical properties are relevant for the heat transport of *e.g.* greenhouse and transparent insulation structures. The properties were determined based on infrared transmittance measurements and the assumption of a constant index of refraction from the visible range. To establish structure-property-correlations molecular structure parameters such as the concentration of carbon-oxygen single bonds and carbon-hydroxyl groups were determined. For $50\,\mu$m thick films a good correlation between the concentration of the functional carbon-hydroxyl and the carbon-oxygen group and the infrared optical thickness as well as the hemispherical emittance was found. This correlation fits well for high and low infrared radiation absorbing polymeric materials consisting of carbon, hydrogen, and oxygen atoms. The carbon-hydroxyl group appears to be slightly more effective than the carbon-oxygen single bond. Interestingly, the correlation works for polymers with aromatic (*PC*, *PET*) and aliphatic (*PMMA*, *CTA*, ethylene copolymers) groups.

Keywords. Ethylene copolymer; Infrared optical properties; Transparent insulation; Polymer film; Greenhouse.

Introduction

Polymeric materials are in use for various solar energy related components. Concerning solar thermal systems plastics play a decisive role as transparent cover material. Especially for solar thermal systems 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

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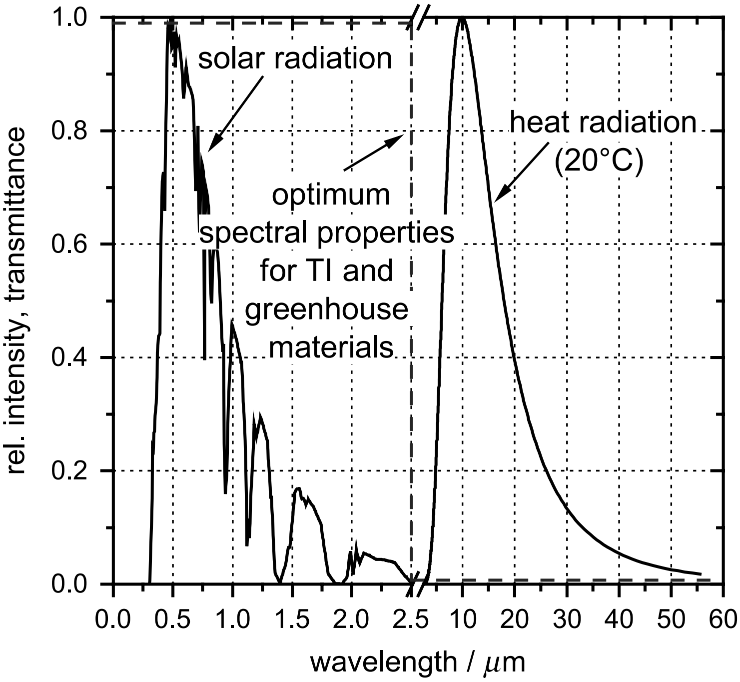

Fig. 1. Spectral selective transmittance and absorbance in the solar and heat radiation wavelength range required for greenhouse and transparent insulation (TI) materials

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 favourable, for solar thermal systems with a selective absorber a non-absorbing cover material is advantageous. Basic requirements for greenhouse and transparent insulation materials (see Fig. 1) are high transmittance of solar radiation (300–2500 nm) and high absorbance of heat radiation (2.5–60 μm).

Regarding the application of polymeric materials as transparent cover polycarbonate (*PC*) is often used. As shown in previous research work, polycarbonate is a material with average infrared transparency [1–3]. For transparent insulation (TI) systems with black absorbers polymeric materials such as poly(methyl methacrylate) (*PMMA*), poly(ethylene terephthalate) (*PET*) and in particular cellulose acetate (*CA*) with better to excellent infrared absorption have been identified [1]. Polyolefins such as polyethylene or polypropylene are well known as highly infrared transparent polymeric materials. However, despite the poor infrared absorption properties polyethylene homopolymers and copolymers are widely used as greenhouse covering materials [4]. Polyolefins are among the cheapest polymeric materials. To improve the infrared absorption of polyolefins polar copolymers of ethylene and vinyl acetate (*EVA*) have been developed. Currently further polar copolymers based on acrylates and acrylic acids, which are supposed to have a better long term stability under aging conditions, have been developed and investigated [5].

In a previous study [1, 2] the carbon-oxygen single bond was identified as a highly effective infrared radiation absorbing group for polymers with service temperatures of up to 100°C. A good correlation between the concentration of the functional carbon-oxygen group and the infrared optical thickness as well as emittance or absorbance was found for *PC*, *PMMA*, *PET*, and *CA* films with a thickness of 50 μm. The overall objective of this paper is to establish structure-infrared optical property-correlations for polymer films, which are already in use for solar energy applications or which are currently under development. A specific objective is to extend the correlation derived for average and excellent infrared radiation absorbing polymeric materials such as *PC*, *PMMA*, *PET*, and *CA* to rather weakly infrared radiation absorbing polymeric materials such as polar ethylene copolymers.

Results and Discussion

For transparent insulation wall and greenhouse applications it is crucial to absorb the infrared radiation in order to keep the heat radiation transport low. Thus, high absorption of infrared radiation is required in the range between 200 and 1500 $\mathrm{cm^{-1}}$, in which a blackbody at 20°C emits mostly. In Figs. 2 and 3 the transmittance spectra over the medium IR range from 4000 to 370 $\mathrm{cm^{-1}}$ are shown for selected acid, acrylate, and acetate ethylene copolymers.

Significant absorptions in the investigated polar ethylene copolymers can be attributed to CH_2 groups (at about 1470 and 720 $\mathrm{cm^{-1}}$), to C–O single bonds (between 1300 and 1000 $\mathrm{cm^{-1}}$), and to hydroxyl (O–H) groups in acid copolymers

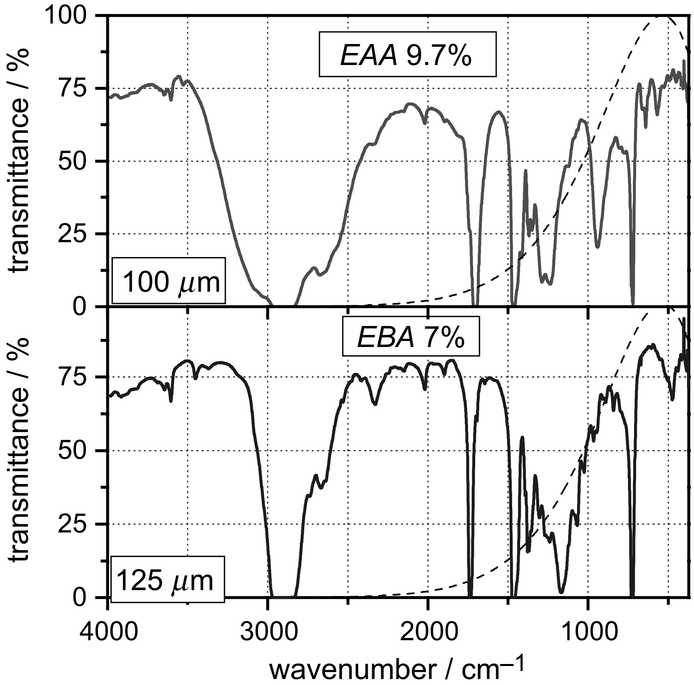

Fig. 2. IR transmittance spectra for 100 μm thick ethylene acrylic acid copolymer film with 9.7 $m\%$ (top) and for 125 μm thick ethylene butyl acrylate copolymer film with 7 $m\%$ (bottom) comonomer content and emissive power function for a blackbody at 20°C

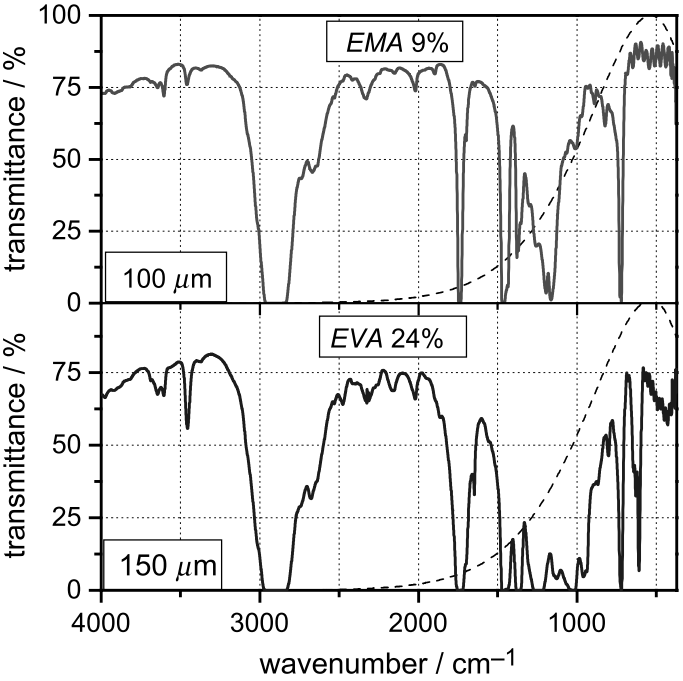

Fig. 3. IR transmittance spectra for 100 μm thick ethylene methyl acrylate copolymer film with 9 *m%* (top) and for 90 μm thick ethylene vinyl acetate copolymer film with 24 *m%* (bottom) comonomer content and emissive power function for a blackbody at 20°C

(at about 950 cm^{-1}). Below 1000 cm^{-1} mainly molecular vibrations of the polymer chain contribute to the absorbance. However, the molecular vibrations are rather weak for the investigated polymers. Only the narrow absorption peak of the CH_2 group at 720 cm^{-1} can be found close to the maximum of the emissive power function of a blackbody at 20°C. 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. As shown in Fig. 2, for a 100 μm thick ethylene acrylic acid copolymer film with a comonomer content of about 9 *m%* no total absorbance appears in the range below 1400 cm^{-1}. For film thicknesses above 100 μm and comonomer contents above 10 *m%* total absorbance with broad peaks can be found due to C–O functional group vibrations (Fig. 3).

In contrast to the low infrared radiation absorbing ethylene copolymers, TI materials show higher IR absorption, especially in the region of interest between 1500 and 200 cm^{-1}. Although the lower film thicknesses (50 μm for *CA*, *PET*, *PC*; 60 μm for *PMMA*), areas of total absorbance can be found between 1300 and 1000 cm^{-1}. In case of *PMMA* (see Fig. 4) the ester group absorbs between 1280 and 1120 cm^{-1} and at 990 cm^{-1}. The narrow peaks below 900 cm^{-1} can be attributed to skeletal vibrations.

Cellulose acetate (*CA*) and cellulose triacetate (*CTA*) show only little differences in their IR spectra. The total absorbance between 1300 and 1000 cm^{-1} is assigned to the ester and ether groups within the polymer structure. The peak at about

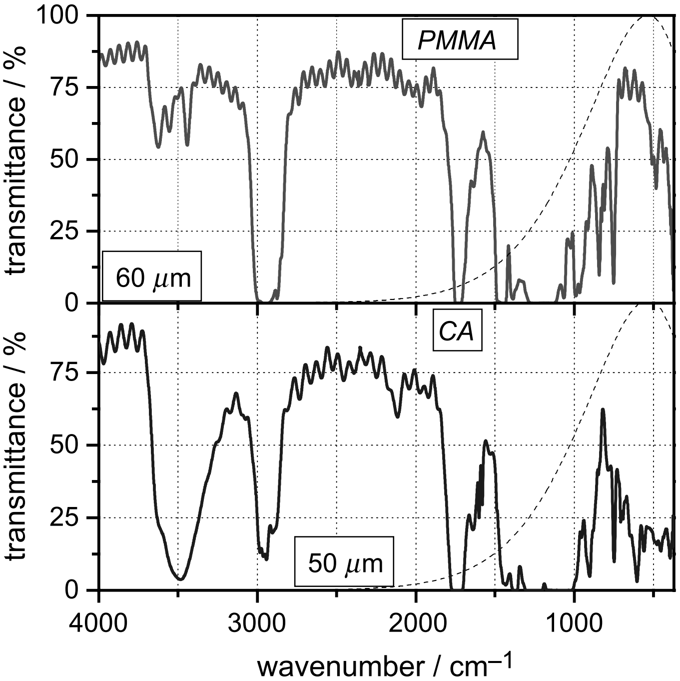

Fig. 4. IR transmittance spectra for 60 μm thick *PMMA* (top) and 50 μm thick *CA* film (bottom) and emissive power function for a blackbody at 20°C

900 cm^{-1} and the strong absorptions below 750 cm^{-1} can be attributed to hydroxyl groups and skeletal vibrations of the ring.

Due to the high thickness of the *PLA* film (230 μm) there is a broad area of total absorbance between 1500 and 1000 cm^{-1}, which can be mainly assigned to C–O, CH, and CH_3 groups. The peaks below 1000 cm^{-1} can be attributed to skeletal and carbonyl group vibrations.

PC (see Fig. 5) shows total absorption between 1300 and 1150 cm^{-1}, which can be attributed to the C–O group. The narrow peaks at 1083, 1014, 888, and 830 cm^{-1} originate from the aromatic ring. *PET* shows a broader area of total absorption between 1400 and 1050 cm^{-1}. Again, the narrow peaks below the area of total absorption can be attributed to the aromatic ring.

In Fig. 6 the infrared optical thickness data, $\kappa_{IR}{}^{*}d$, which is the product of the infrared absorption coefficient κ_{IR} and the film thickness d, are plotted for selected investigated polymer films as a function of thickness. The values for the infrared optical thickness of the investigated polymers are ranging from 0.2 to 2.0. The $\kappa_{IR}{}^{*}d$ values increase with increasing film thickness.

In contrast to highly absorbing materials the increase of the infrared optical thickness as a function of film thickness levels off only slightly for polar ethylene copolymers at higher film thicknesses. As shown in Ref. [6] for polystyrene and in Refs. [2, 7] for various polymer films including polymers with C, H, and O atoms, which are also in the primary chemical structure of the investigated polar ethylene copolymers, it is adequate to calculate the infrared optical thickness for various film thicknesses based on measured spectral data for one reference thickness. For

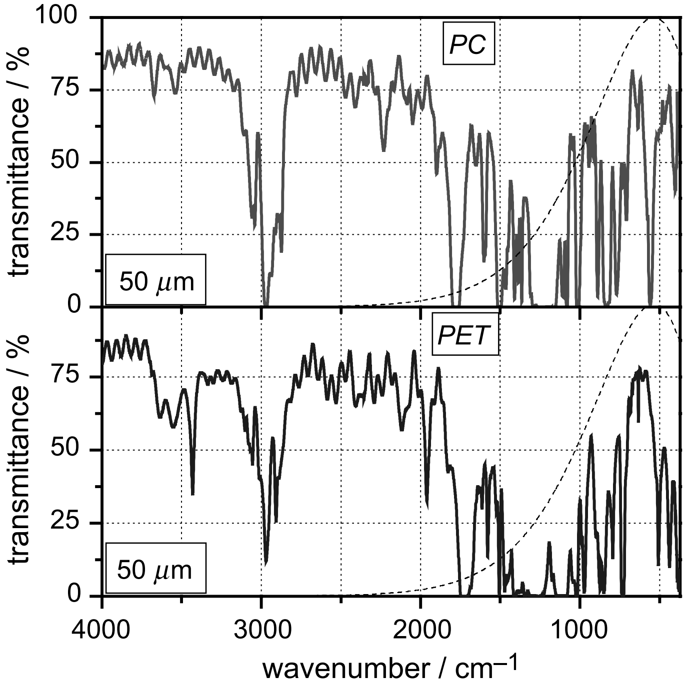

Fig. 5. IR transmittance spectra for 50 μm thick *PC* (top) and *PET* film (bottom) and emissive power function for a blackbody at 20°C

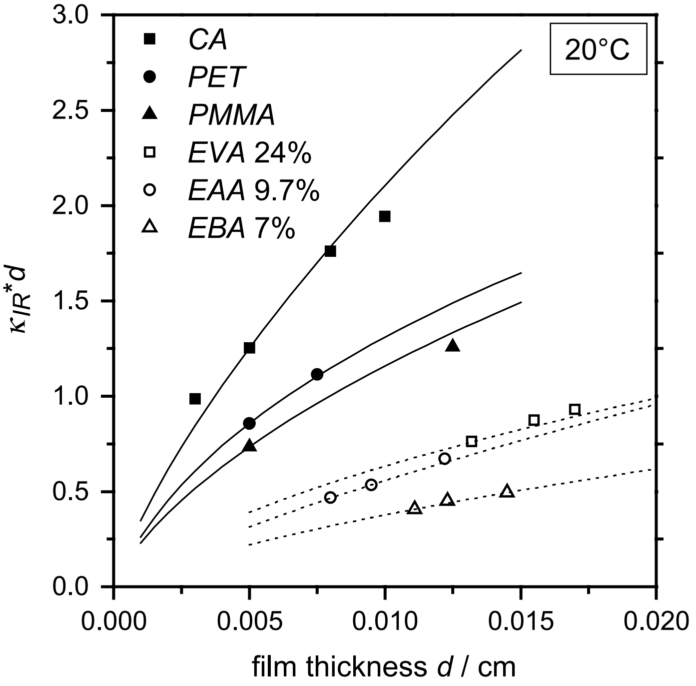

Fig. 6. Infrared optical thickness, $\kappa_{IR}{}^*d$, of selected polymer films as a function of film thickness (dots: measured values; curves are determined based on the spectral data of the thinnest film) at a blackbody temperature of 20°C

transparent insulation structures for wall applications with black absorbers in many cases polymer films with a thickness of 50 μm are appropriate. Thus, based on spectral data of films with thicknesses ranging from 50 to 230 μm, infrared optical thickness and hemispherical emittance values for 50 μm thick films were calculated. In general, a good agreement was found between experimental and theoretical curves (see Fig. 6).

Furthermore, to establish structure-property-correlations the concentrations of functional groups within the macromolecular structure of the polymers were determined using the equation $c = a^* \rho / M$, where a is the number of bonds or groups per polymer repeat unit, ρ is the bulk density of the polymer, and M is the molecular weight of the polymer repeat unit [8].

Figure 7 shows the correlation between $\kappa_{IR}{}^* d$ and the concentration of carbon-hydroxyl (c_{C-O-H}) and carbon-oxygen-carbon groups (c_{C-O-C}) for the investigated polar ethylene copolymers at a blackbody temperature of 20°C.

The lowest infrared optical thickness values were obtained for the ethylene methacrylic acid copolymer (*EMAA*) with a comonomer content of 1.7 *m*%. Ethylene methyl acrylate copolymer (*EMA*) with 30 *m*% comonomer content and ethylene vinyl acetate copolymer (*EVA*) with 24 *m*% comonomer content exhibited the highest values. For the investigated ethylene copolymers with a film thickness of 50 μm the density of the C–O–H and C–O–C groups affects the infrared optical thickness significantly. A linear relationship between the concentration of the C–O–H or

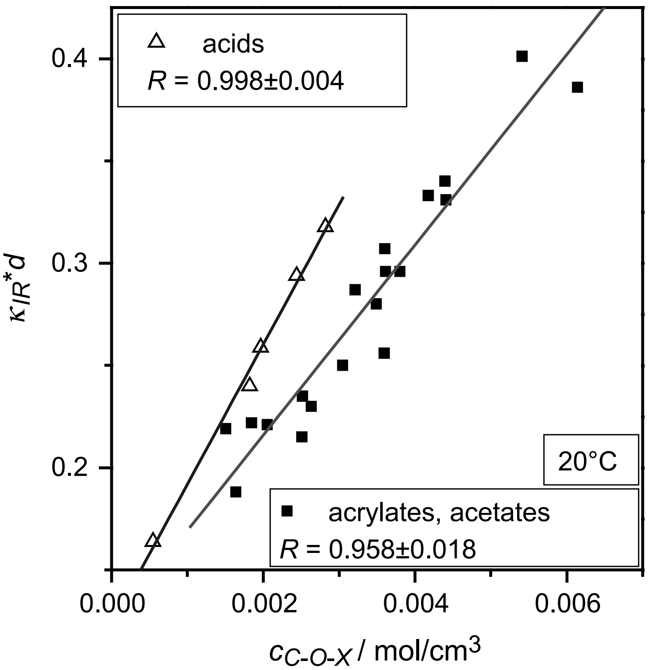

Fig. 7. Correlation between infrared optical thickness, $\kappa_{IR}{}^* d$, or hemispherical emittance, ε_h, and concentration of carbon-oxygen single bond groups (c_{C-O-X}) of ethylene acrylic acid copolymers (X = H; *EAA*, and *EMAA* with comonomer contents ranging from 1.7 to 9.7 *m*% and of ethylene acrylate or acetate copolymers (X = C, *EBA*, *EEA*, *EMA*, and *EVA* with comonomer contents ranging from 5 to 30 *m*%

C–O–C groups and the infrared optical thickness and the total hemispherical emittance was found.

A detailed, material specific analysis reveals differences in the $\kappa_{IR}{}^{*}d$ *vs.* c_{C-O-H} and $\kappa_{IR}{}^{*}d$ *vs.* c_{C-O-C} correlations. For a certain concentration of the C–O–H or C–O–C functional group, the acid copolymers *EAA* and *EMAA* exhibit better infrared absorption properties than the acrylate (*EBA*, *EMA*) and acetate (*EVA*) copolymers. Furthermore the tendency can be perceived, that acrylate comonomers with bigger side groups (methyl *vs.* butyl) exhibit slightly better infrared absorption efficiency. This can be attributed to material dependent differences in the IR spectra, especially in the region between 1300 and 900 cm^{-1}. The acidic copolymers show a peak at about 950 cm^{-1} caused by the carboxylic group of the polymer. This intense peak is close to the emittance maximum of a blackbody at 20°C. For acrylic and acetic copolymers following ranking as to infrared optical thickness was obtained: *EVA* > *EBA* > *EMA*. For *EEA* and *EMAA* no linear fit was done due to few material variations [9]. The ranking can be explained by differences in the chemical composition of the copolymers. *EVA* shows an intense peak at 1020 cm^{-1}, which is less pronounced for *EBA* and *EMA*. The maximum absorption for *EBA* (1175 cm^{-1}) and *EMA* (1160 cm^{-1}) is nearly at the same wavenumber, but *EBA* shows more medium absorption peaks between the maximum and 900 cm^{-1}.

In Fig. 8 the correlated data for the investigated low infrared absorbing ethylene acrylate and acetate copolymers are plotted together with the data of the better infrared absorbing TI wall materials investigated in Refs. [1, 2, 7].

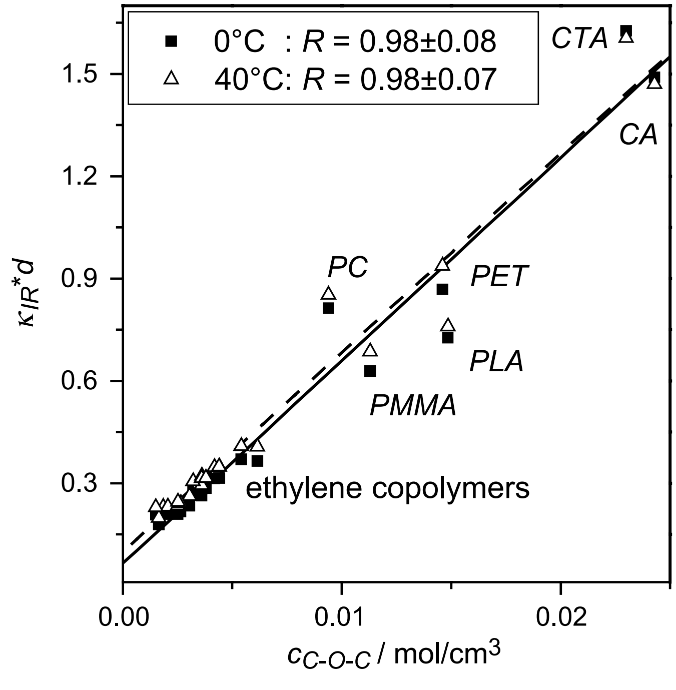

Fig. 8. Correlation between infrared optical thickness, $\kappa_{IR}{}^{*}d$, and concentration of carbon-oxygen single bonds within the macromolecular structure of various polymers for a film thickness of 50 μm at a blackbody temperature of 0°C and 40°C

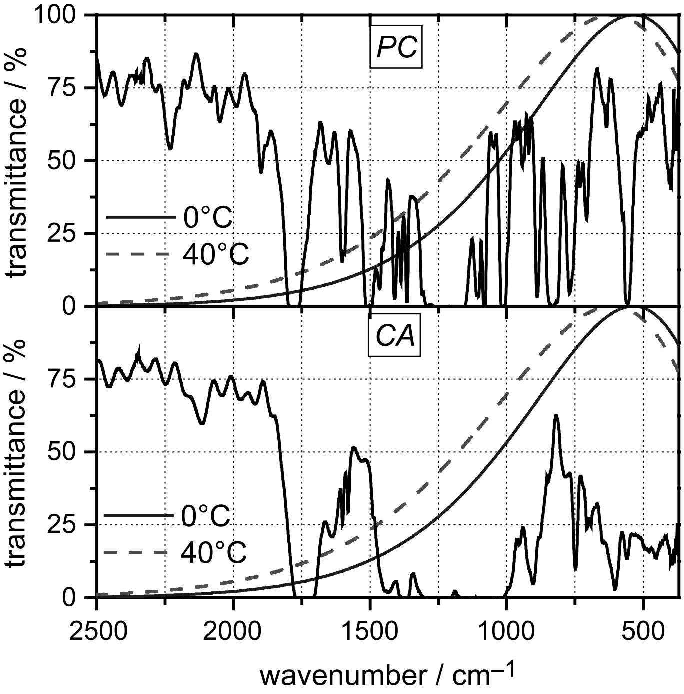

Fig. 9. IR transmittance spectra for 50 μm thick *PC* (top) and *CA* film (bottom) and emissive power function for a blackbody at 0°C and at 40°C

The correlated data is depicted at blackbody temperatures of 0 and 40°C. A linear correlation between the infrared optical thickness and the concentration of C–O–C groups was found for polymeric films with a thickness of 50 μm for both, excellent infrared absorbing polymers such as cellulose triacetate (*CTA*) and weakly infrared absorbing polymers such as ethylene copolymers with low polar comonomer content.

The infrared absorption coefficient, the infrared optical thickness values, and the emissive power function of a blackbody are in general temperature dependent. With increasing temperature the maximum of the blackbody radiation shifts to higher wavenumbers, from 536 cm^{-1} at 0°C to 614 cm^{-1} at 40°C (see Fig. 9).

The temperature induced shift in the emission spectrum of a blackbody results in increasing $\kappa_{IR}{}^{*}d$ values for all polymer films except for *CA* and *CTA* (see Fig. 10).

While *CA* and *CTA* absorb significantly at the maximum of the emissive power function, ethylene copolymers or *PMMA* show some narrow peaks in this range. Due to the shift of the emission maximum to higher wavenumbers the absorption between 1300 and 1000 cm^{-1} is weighted stronger for higher temperatures. This results in a slight decrease of the infrared absorption coefficient in case of *CA* and *CTA*. In contrast, for all other investigated polymer films a slight increase of the infrared absorption coefficient was found.

It should be emphasized that the linear correlation works for polymers with aliphatic (all included polymers) and aromatic (*PC* and *PET*) groups within the molecular structure. The influence of aromatic groups is weak in comparison to the influence of ester and ether groups. Although the absorption peaks are closer to

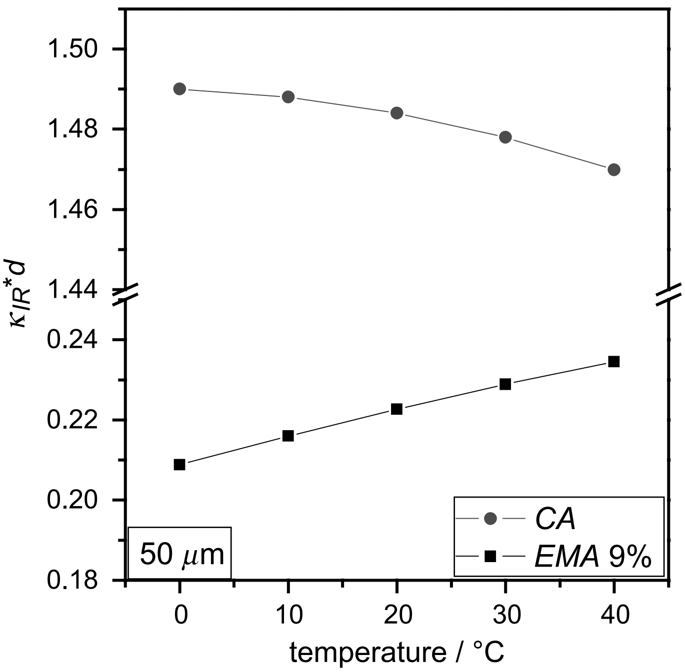

Fig. 10. Infrared optical thickness, $\kappa_{IR}{}^*d$, as a function of temperature for cellulose acetate (*CA*) and ethylene methyl acrylate copolymer with 9 *m*% comonomer content

the maximum of a blackbody emissive power function at temperatures between 0 and 40°C, the narrow peaks contribute less significant to the non-spectral infrared absorption coefficient.

Experimental

Polymer Film Types

In this study the infrared optical properties of transparent polymer film types consisting of carbon, hydrogen, and oxygen (C,H,O) were determined. In addition to the homopolymers poly(methyl methacrylate) (*PMMA*), polycarbonate (*PC*), and poly(ethylene terephthalate) (*PET*), cellulose acetate (*CA*), cellulose triacetate (*CTA*), polylactic acid (*PLA*), polar ethylene copolymers (Table 1) with comonomer contents between 1.7 and 30 *m*%, and three different comonomer types (acids, acrylates, and acetates), were investigated.

As to the acid comonomers acrylic acid (*AA*) and methacrylic acid (*MAA*) were chosen. Regarding acrylate comonomers butyl acrylate (*BA*), ethyl acrylate (*EA*), and methyl acrylate (*MA*) are currently in use for ethylene (*E*) copolymer materials. Furthermore, widely used ethylene vinyl acetate copolymers (*EVA*) as well as a terpolymer material with two different comonomers (acrylic acid and butyl acrylate (*AA*/*BA*) were investigated.

The ethylene copolymer resins were supplied by Arkema (Paris, F: *EBA*, *EVA*), Basell (Brussels, Belgium: *EAA*/*BA*), BP (Cologne, D: *EMAA*), Dow (Horgen, CH: *EAA*, *EEA*), DuPont (Wilmington, USA: *EMAA*, *EBA*, *EEA*, *EMA*, *EVA*), Exxon (Machelen, B: *EAA*, *EVA*), Leuna (Leune, D: *EVA*), Polimeri Europa (San Donato Milanese, I: *EVA*), and Repsol YPF (Madrid, E: *EVA*). Except the Polimeri Europa materials, which were supplied as films, films with various thicknesses ranging from 90 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).

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

Material type	Comonomer	Content, *m*%
acids		
EAA	acrylic acid	6, 6.5, 9.7
EMAA	methacrylic acid	1.7, 8.7
acrylates		
EBA	butyl acrylate	6, 7, 8, 17
EEA	ethyl acrylate	12, 15
EMA	methyl acrylate	9, 9.5, 30
acetates		
EVA	vinyl acetate	5, 7, 9, 12, 14, 15, 17, 18, 24
acid/acrylate		
EAA/BA	acrylic acid butyl acrylate	*AA* 4 *BA* 7

As to the transparent insulation materials, 50 μm thick cellulose acetate (*CA*) and cellulose triacetate (*CTA*) films were supplied by LOFO (Lőrrach, D), 60 μm thick poly(methyl methacrylate) (*PMMA*) and 50 μm thick polycarbonate (*PC*) film by Röhm (Darmstadt, D) and 50 μm thick poly(ethylene terephthalate) (*PET*) film by ICI (London, UK) [7]. The poly(lactic acid) film (*PLA*) with a thickness of 230 μm was taken from an injection moulded cup supplied by Cargill-Dow (Minnetonka, USA).

Determination of Non-Spectral Infrared Optical Film Properties

Over the medium IR range from 4000 to 370 cm^{-1} (2.5 to 27 μm) the direct-beam transmittance spectra at normal incidence were obtained with a Perkin Elmer Spectrum One spectrometer (Perkin Elmer; Überlingen, Germany). Thus, the *Planck* radiation of a blackbody ranging from 0 to 40°C was covered approximately from 85.5 to 89.3%. According to *Rubin* [10] scattering of the material was neglected, because observed surface or bulk defects were much smaller than infrared wavelengths. To model the heat transport of transparent insulation structures or greenhouse covers input parameters such as the non-spectral hemispherical absorbance or equivalently emittance, α_h or ε_h, which is a function of the non-spectral infrared absorption coefficient, κ_{IR}, are required [11, 12]. The procedure for determining the integral emittance coefficient starting from the spectral, *i.e.*, wavenumber, ν dependent transmittance data is described in detail in Refs. [1, 2].

The directional spectral emittance, $\varepsilon_\phi(\nu)$, was calculated for both transverse electric and transverse magnetic polarization using the spectral normal-normal transmittance, the film thickness, and the constant index of refraction from the visible as input parameters according to *Rubin* [10]. The validity of this assumption was checked by comparison of hemispherical emittance spectra, which were calculated from both the experimental normal-normal transmittance spectra and complex refractive index data over the infrared spectral region, which are published for some polymer materials in a previous work [2]. For polar ethylene copolymers refractive indexes ranging from 1.47 to 1.52 are given in the literature (http://www.texloc.com/closet/cl_refractiveindex.html). For the calculations an average refractive index of 1.50 was assumed. For *PMMA*, *CA*, and *CTA* a refractive index of 1.49, for *PLA* 1.51, for *PC* 1.59 and for PET 1.67 was used. The hemispherical spectral emittance, $\varepsilon_h(\nu)$, for unpolarized radiation was found by ideal directional averaging with 5° steps and averaging over both polarization directions. Finally, the total hemispherical temperature dependent emittance, $\varepsilon_h(T)$, was determined by averaging the spectral values, weighted by a blackbody emissive power, $P(\nu, T)$, at each wavenumber. The effective temperature dependent absorption coefficient, κ_{IR} (T), was found by an inverse fit. Since the infrared absorption coefficient κ_{IR} is in general temperature dependent, the absorption coefficients for temperatures ranging from 0 to 40°C relevant for greenhouse or transparent insulation applications were determined.

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References

[1] Wallner GM, Lang RW, Platzer W, Teichert C (2002) Macromol Symp **181**: 399
[2] Wallner GM, Platzer W, Lang RW (2005) Solar Energy **79**: 593
[3] Tsilingiris PT (2003) Energ Convers Manage **44**: 2839
[4] Papadakis G, Briassoulis D, Scarascia Mugnozza G, Vox G, Feuilloley P, Stoffers JA (2000) J Agr Eng Res **77**: 7
[5] Jäger KM, Dammert RC, Sultan BÅ (2001) J Appl Polym Sci **84**: 1465
[6] Platzer WJ (1988) PhD thesis, Albert Ludwigs Universität, Freiburg, Germany
[7] Wallner GM (2000) PhD thesis, Montanuniversität Leoben, Leoben, Austria
[8] Sergides CA, Chughtai AR, Smith DM (1987) Appl Spectrosc **41**: 154
[9] Oreski G, Wallner GM (2006) Solar Energy Materials and Solar Cells **90**: 1208
[10] Rubin M (1982) Sol Energ Mater **6**: 375
[11] Platzer WJ (1992) Sol Energy **48**: 381
[12] Hum JEY, Hollands KGT, Wright JL (2004) Sol Energ **76**: 85