Performance Assessment of Novel Transparent Insulation Materials for Integrated Storage Collectors

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Abstract: Transparent insulation structures play a pivotal role in harnessing solar energy efficiently, akin to the greenhouse effect in the atmosphere. This study undertakes a systematic evaluation of a novel sorbitol- or bio-based polycarbonate (bio-PC) for thermal insulation (TI) structures and hot water collector systems. Employing optical and mechanical methods, the bio-PC was comprehensively characterized on the polymer film level. Subsequently, the technical and ecological performance of these structures in various hot water collectors and systems was rigorously modelled and simulated. Results indicated that the novel bio-PC exhibited superior properties compared to conventional materials like cellulose acetate or fossil-based PC, showcasing promising prospects for widespread adoption.

Drawing parallels to the greenhouse effect of CO\textsubscript{2}, the functional principle of transparent insulation structures is rooted in high solar transmittance and infrared absorbance, primarily governed by carbon-oxygen bonds. While fossil-fuel based transparent insulation materials have been prevalent, they suffer from drawbacks such as average infrared absorbance and susceptibility to yellowing. In contrast, the newly introduced bottom-up biopolymer bio-PC, derived from sorbitol derivatives, offers a compelling alternative. The study sheds light on the potentials and limitations of bio-PC for transparent insulation structures in integrated storage or flat plate collectors, aiming to mitigate environmental impacts associated with traditional materials.

Future research directions emphasize refining modelling tools and addressing input data deficiencies, particularly for life cycle analysis. Concurrently, efforts are directed towards enhancing simulation accuracy and reliability through concurrent measurements of collector systems equipped with bio-PC-based transparent insulation. This research underscores the critical role of innovative materials in advancing sustainable energy solutions, with bio-PC emerging as a promising candidate in the realm of transparent insulation technology.

Keywords: Transparent Thermal Insulation, Sorbitol-Based Bio-Polycarbonate (Bio-PC), Solar Energy, Integrated Storage Collector
1. Introduction

The main driver for climate change is the annual fossil CO₂ emissions, which amount to about 40 bill tons/a worldwide [1], [2]. Due to the asymmetric structure and the polarity of CO₂, this greenhouse gas is absorbing heat radiation while it is fully transparent for solar irradiation. The current greenhouse gas level in our atmosphere has increased from 325 ppm in 1970 to already 420 ppm in 2023 [3].

Quite similar to the greenhouse effect of CO₂ in our atmosphere, C-O bonds play also a main role in engineering transparent insulation structures [4]. Their functional principle is also based on the greenhouse effect characterized by high solar transmittance and high infrared absorbance [5], [6]. For solar heating and cooling, transparent insulation structures are well established for integrated storage collectors (e.g., Solcrafte), but also for advanced flat-plate collectors (e.g., TIGI Solar). The transparent insulation honeycomb structure is positioned in between the front glass cover and the absorber.

So far, fossil-fuel based transparent insulation materials such as polycarbonate (PC) were commercialized and used. Moreover, cellulose derived top-down materials such as cellulose acetate (CA) structures are commercially available (e.g., Wacotech). Both of them have significant disadvantages. While fossil-fuel based PC shows an average infrared absorbance and is prone to yellowing upon UV ageing, CA requires plasticizers which get lost over time resulting in significant embrittlement of the honeycomb structure. Just recently, a novel bottom-up biopolymer (bio-PC) based on sorbitol derivatives has been introduced into the market and commercialized. Similar to synthetic, fossil-fuel based plastics, the sorbitol-based bio-PC is manufactured from well-defined small molecules or monomers. The main objective of this paper was to evaluate the potentials and limitations of this new class of bottom-up bio-PC for transparent insulation structures in integrated storage or flat plate collectors.

2. Experimental & Modelling

A commercially available sorbitol-based bio-polycarbonate (Bio-PC; brand: DURABIO; manufacturer: MITSUBISHI Chemicals) was used to prepare thin films with a thickness ranging from 20 to 100 µm and to investigate the main optical properties in the solar and infrared wavelength.

In the exploration of transmission and reflection behaviors within the solar radiation spectrum, the UV/Vis/NIR spectrometer PerkinElmer Lambda 950 was employed. The diffuse and hemispherical transmission, as well as hemispherical reflection, were measured using this instrument.

Figure 1 provides a schematic representation of the employed methodologies, wherein the incident beam consistently impinges perpendicularly (normal) upon the sample. In hemispherical measurements, radiation transmitted or reflected in all spatial directions is detected. Conversely, in diffuse transmission measurements, the normally directed radiation is excluded, and only the diffuse component is detected. The measurements were conducted within a wavelength range of 250 to 2500 nm, with a spectral resolution of 5 nm. Prior to the measurements, the dual-beam apparatus was calibrated using a white standard.

The distinctive molecular compounds of the material were analyzed utilizing a PerkinElmer Spectrum 100 Fourier Transform Infrared (FT-IR) spectrometer. The instrument was configured to operate within a wavenumber range of 4000 to 650 cm⁻¹, with a data interval of 2 cm⁻¹. Normal-directed transmission was measured through 16 scans, while normal-hemispherical transmission employed 128 scans. A gold-coated Ulbricht sphere, equipped with a mercury-cadmium-telluride (MCT) detector, was utilized for hemispherical measurements. The spectral data were processed, and the infrared-optical thickness was derived. Moreover,
standardized specimens were injection moulded and characterized by Dynamic Mechanical Analysis as to the long-term creep behaviour.

![Image](image.png)

**Figure 1.** Schematic representation of the optical measurement methods for UV/Vis/NIR spectroscopy: (a) hemispherical transmission; (b) diffuse transmission; (c) hemispherical reflection

Dynamic Mechanical Analysis (DMA) investigations on elastic and viscous properties, as well as glass transition temperature, were conducted using an Anton Paar Physica MCR 501 rheometer. Measurements were executed under torsion with low torque, and rectangular cross-section sample rods were securely clamped. Linear viscoelastic range determination involved an amplitude test at room temperature. Temperature-dependent storage and loss moduli were measured between -50 and 150°C at frequencies of 1, 3, 10, and 30 Hz. The displacement amplitude was set at 0.05%, and the heating rate at 2 K/min. The glass transition temperature was derived from the temperature sweeps based on the maximum loss factor, and the activation energy was determined using the Arrhenius approach.

Creep tests were also conducted with the Anton Paar Physica MCR 501 rheometer equipped with a solid-state clamping device. Determination of the linear viscoelastic range involved short-term creep tests with a 10-minute duration at constant stresses of 1, 2, 4, 7, and 8 MPa. For assessing creep behavior, creep curves were generated over 30 minutes under a constant stress of 2 MPa. The temperature range for measurements spanned from 20 to 100 °C, increasing in 10 K increments. A rheologically simple behavior (i.e., horizontal shift) was assumed for time-temperature shift, and displacement factors were derived using the Arrhenius approach, as schematically depicted in Figure 2.

![Image](image.png)

**Figure 2.** Generation of the master curve via the time-temperature shift and shift factors, derived from the Arrhenius approach

To assess the performance on collector level, numerical simulations were carried out for integrated storage and flat plate collectors with transparent insulation structures based on
fossil-PC, CA and the novel bio-PC grade. Moreover, a life cycle assessment was carried out evaluating the effect of these transparent insulation materials on the energy-pay-back time and the environmental impacts of the investigated solar heating systems for hot water preparation [7], [8], [9], [10]. Within IEA SHC Task 69, these collector systems should be compared comprehensively to well-established flat-plate or vacuum tube or photovoltaic module solar hot water systems.

3. Results & Discussion

The optical assessment of the novel Bio-PC material revealed a notable hemispherical transparency within the solar radiation spectrum and a relatively limited scattering effect. As illustrated in Figure 3, the polymer films exhibited a maximum solar-hemispherical transmission of 92%, prominently maintained across the entire wavelength spectrum, particularly evident in the 11 µm thick film. Conversely, the robust transmission behavior observed in samples with thicknesses of 22, 29, 43, and 91 µm was confined to the range of approximately 400 to 1650 nm. An increase in film thickness led to a more pronounced decrease in transmission in the UV range (300-400 nm) and NIR range (1650-2500 nm). The absorption observed around 340 nm in Figure 3 is presumably caused by UV absorbers or absorption within the primary structure of Bio-PC. C-H bonds account for NIR absorption within the ranges of approximately 1650 to 1800 nm and 2200 to 2500 nm, while carbonyl groups (C=O) absorb within the range of 2085 to 2180 nm. The peak around 1910 nm is attributed to water molecules within the material [5], [6]. The increasing absorption with thicker films adheres to Lambert-Beer’s law, where a thicker sample leads to a higher concentration of absorbing groups along the radiation path [11].

The transmittance of Bio-PC is comparable to that of PMMA or CA, yielding a refractive index of 1.49, as supported by [12], consistent with the provided datasheet [13]. The solar reflectance stood at approximately 8%, confirming negligible solar absorption. Absorptions were noted in the UV and NIR ranges, possibly indicating modification of Bio-PC with UV absorbers. NIR absorption is attributed to resonances of overtones from C-H, C=O, and O-H groups.

Figure 3. Hemispherical solar transmission spectra of the Bio-PC of different film thicknesses
The macromolecular structure of this sorbitol-based material comprises aliphatic ether groups and ring structures, closely resembling those of cellulose acetate. A key distinction from CA lies in the connection of aliphatic ether rings to an ester group (refer to Figure 4).

![Figure 4. Chemical structure of the novel sorbitol- and bio-based polycarbonate (Bio-PC)](image)

In the realm of thermal radiation, the novel Bio-PC exhibits remarkable infrared absorption characteristics, surpassing even the best-known cellulose acetate materials in certain scenarios. Figure 5 illustrates the infrared spectra in the wavenumber range of 4000 cm\(^{-1}\) to 700 cm\(^{-1}\) obtained from directed transmission measurements of Bio-PC films of varying thicknesses. Directed transmission, due to its absence of diffuse components, slightly falls below hemispherical transmission. The absorption bands observed between approximately 730 to 816 cm\(^{-1}\), 1428 to 1510 cm\(^{-1}\), and 2794 to 3062 cm\(^{-1}\) are attributable to C-H bonds. Specifically, the peaks around 2858 cm\(^{-1}\) and 2930 cm\(^{-1}\) correspond to the methylene (CH\(_2\)) band, while those at 2982 cm\(^{-1}\) and 2878 cm\(^{-1}\) denote the methyl (CH\(_3\)) band [14]. The C-O band peaks are located at approximately 1098 cm\(^{-1}\) (ether) and 1248 cm\(^{-1}\) (ester), with the C=O band in an ester group at around 1750 cm\(^{-1}\) [15]. Additionally, a weak O-H band from 3700 to 3430 cm\(^{-1}\) is discernible, confirming the presence of characteristic molecular groups within the bio-based polycarbonate. The detected O-H and CH\(_3\) groups may be present in the unknown co-monomer. Furthermore, the absence of aromatic compounds is indicated by the lack of bands around 3060 cm\(^{-1}\) and 1600 cm\(^{-1}\) [14].

![Figure 5. Directional IR transmission spectra of the Bio-PC of different film thicknesses](image)

Figure 6 depicts the linear correlation with values of PC, PMMA, PET, and CA. For 50 µm thickness, the bio-based polycarbonate exhibits an infrared optical thickness of approx-
imately 1.51. This surpasses CA by 20% [6] and demonstrates over double the efficacy compared to fossil fuel-based PC. The exceptional infrared absorption is attributed to the high concentration of C-O groups. Interestingly, the C-O concentration in Bio-PC surpasses that of the cellulose derivative CA. Although cellulose acetate contains more C-O groups per repeating unit, Bio-PC, constructed from low-molecular-weight monomers, outperforms the natural derivative CA. While cellulose acetate has a higher molecular weight and slightly lower density [16].

![Figure 6. Correlation between infrared optical thickness and C-O-C concentration for different transparent insulation materials (PC, PMMA, CA, bio-PC) at a thickness of 50 µm](image)

Through dynamic mechanical analysis (DMA), a glass transition with a peak in the loss or damping factor at 130°C was derived for the examined Bio-PC variant, as depicted in Figure 7. This value is approximately 20°C lower than conventional fossil-based PC but approximately 30°C higher than that of CA. The frequency dependency of the glass transition temperature was confirmed through DMA experiments. Using an Arrhenius approach, an activation energy for cooperative main chain rotations of 629 kJ/mol was obtained. Linear regression exhibited high goodness of fit with a coefficient of determination of 0.9974.

To characterize the long-term behavior of Bio-PC, 30-minute creep tests were conducted. As illustrated in Figure 8, the creep modulus displayed significant temperature dependence. The relaxation spectrum shifted towards shorter relaxation times with increasing temperature. Factors for horizontal curve shifting were derived based on the activation energy of the glass transition. In addition to horizontal shifting, vertical curve shifting was necessary when constructing master curves. Consequently, the bio-based polycarbonate exhibited a non-thermomechanically simple behavior.

The creep curves generated by DMA and modeled according to the principle of time-temperature shift (TTS) (see Figure 9) indicated non-critical material deformation for Bio-PC at an average operating temperature of 30°C and an assumed lifespan of 30 years.
In relation to collector-level performance, simulations are yet to be completed. Given the superior overall greenhouse properties observed at the film level, a significantly enhanced collector efficiency is anticipated. Although specific data regarding the ecological impacts of Bio-PC were not found for the life cycle assessment, Zhou et al. [17] allude to the decoupling of bio-based PC from fossil resources as a crucial aspect of optimizing green PC production. The authors of this study envision a potential avenue to utilize input data for the raw material sorbitol and extrapolate considering published data on the polycondensation of polyesters into Bio-PC. Additionally, it should be noted that high-quality input data are still lacking for thermo-siphon and photovoltaic solar water heating collector systems.
A concurrent measurement of a collector system equipped with a transparent thermal insulation based on the new Bio-PC is aimed to enhance and validate the accuracy, reliability, and efficiency of simulation studies. Hence, research efforts in the coming months will focus on the latter themes.

![Creep modulus Master Curve](image)

**Figure 9.** Master Curve for the creep modulus of Bio-PC for a reference temperature of 30 °C

**Data availability statement**

The data supporting the findings of this study are available upon request. Further work is ongoing, and upon completion, the data will be deposited in an appropriate repository for public access.

**Author contributions**

Harald Kicker: Conceptualization, Writing - Reviewing and Editing, Methodology, Investigation, Data curation, Resources, Validation, Project administration, Software, Investigation, Writing – original draft, Jonas Segsulka: Formal Analysis, Visualization, Investigation, Writing – original draft, Gernot M. Wallner: Supervision, Conceptualization, Investigation, Project administration, Funding acquisition, Writing - Reviewing and Editing, Methodology, Data curation, Resources, Software, Validation

**Competing interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

