

Document downloaded from:

<http://hdl.handle.net/10251/166827>

This paper must be cited as:

Serrano, M.; Moreno, J. (2020). Spectral transmission of solar radiation by plastic and glass materials. *Journal of Photochemistry and Photobiology B Biology*. 208:1-11.
<https://doi.org/10.1016/j.jphotobiol.2020.111894>



The final publication is available at

<https://doi.org/10.1016/j.jphotobiol.2020.111894>

Copyright Elsevier

Additional Information

Spectral transmission of solar radiation by plastic and glass materials

María-Antonia Serrano*, Juan Carlos Moreno¹

*Corresponding author. Centre for Biomaterials and Tissue Engineering, Universitat Politècnica de València, Camino de Vera, s/n, 46022, Valencia, España. Tel: +34 963877000; fax: +34 96 3877529 ; mserranj@fis.upv.es

¹*Departamento de Física Aplicada, Universitat Politècnica de València, Valencia, Spain;* jcmestev@fis.upv.es

ABSTRACT

It is well known that excessive exposure to solar ultraviolet (UV) radiation can have serious adverse effects. Many everyday materials influence the UV radiation received by humans, for example, those used in construction and on the exterior of buildings such as plastics and glass can reduce the UV exposure of persons exposed to solar radiation. In this paper we analyse the spectral transmission of solar radiation of widely used materials using the transmittance parameter. The measurements were performed on clear days, at 8 h and 12 solar hours, in July 2018 (five days) and in January 2019 (three days). The spectral transmittances of these materials and the integrated transmittances in the UVB from 300 nm, UVA, visible (VIS) and near infrared ranges (NIR) were calculated. In summer in the UVB range from 300 nm methacrylate and smoked glass have the highest transmittance values (56 %) and polycarbonate present the lowest (30%). In the VIS and NIR ranges methacrylate (95%) and smoked glass (80%) have the highest transmittances and polycarbonate the lowest (45%). In general the 8 h transmittances are higher than those at 12 h and are also higher in winter than summer.

For two biological functions (erythemal and DNA-damage) and for the UVB range from 300 nm, the transmittance for most materials (except fibreglass) is in the range 6-14%. The exposure times obtained show that erythemal damage could occur after long exposure to solar radiation through the materials studied, information which should be made available to the general public.

Keywords: spectral transmittance; UVA transmittance; UVB transmittance; VIS transmittance; NIR transmittance; erythemal transmittance.

Nomenclature

Symbol	Definition
UV	Ultraviolet
UVB	Ultraviolet B (280-315 nm)
UVA	Ultraviolet A (315-400 nm)
VIS	Visible (400-700 nm)
NIR	Near infrared (700-1000nm)
UVER	Ultraviolet Erythemal
UVI	Ultraviolet Index
T	Transmittance
I_i	irradiance transmitted (mW/m ²)
I_{ni}	normal solar irradiance (mW/m ²)
MED	Minimal erythemal dose (J/m ²)
SPF	Sun protection factor applied
BE	Fractional area of skin surface exposed (per unit).
t_E	Time to induce erythema
UVD3	Vitamin D3 weighted irradiance (mW/m ²)
t_{vitD}	Time to obtain adequate dose of vitamin D3
PC	Polycarbonate
APC	Alveolar Polycarbonate

1. Introduction

The harmful effects of excessive exposure to solar UV radiation are among the most important factors in the development of skin cancer and other adverse effects such as solar erythema, skin aging, and eye damage [1-5]. As the plastic and glass materials installed in windows and decorative panels can reduce the UV exposure of persons inside, it is therefore important to measure their transmitted irradiance. However, there is still a mistaken belief among the general public that glass, for example, provides complete protection against UV radiation. Numerous authors [6-9] concluded that glass filters out the UVB band of solar radiation but transmits a large part of the UVA band. Although attention is usually focused on the damage caused by UVB radiation, recent research [10-14] suggests that UVA radiation directly contributes to the formation of DNA lesions and alters the immune microenvironment, which could contribute to melanoma development. These studies indicate that there are multiple avenues by which UVA may increase the risk of contracting melanoma.

Glass filters have received a great deal of researchers' attention [7-9, 15-18] as the glass type and thickness have a significant influence on the UV spectrum. Individuals are protected from UVB radiation by almost all types of glass used in residential, commercial and automobile applications [6-9]. In 1999, Kimlin and Parisi [7] studied UV solar radiation transmitted through normal and tinted car windows and found that the dye in the glass provided significant protection against UV radiation. Kimlin et al. 2002 [8] studied spectral UV radiation in family saloons and four-wheel drive vehicles passing horizontally through the driver's window towards the windshield with the windows both open and closed. They found that for a typical family saloon with the windows closed the total UV irradiance decreased by a factor of 3.2, while in a four-wheel drive it fell by a factor of 2.1. The authors thus recommend UV protection when driving with the windows open. In 2006, Tuchinda et al. [9] reviewed the factors affecting glass UV protective properties, such as glass type, colour, interleaves and coating. They found that clear glass allows up to 90% of VIS light and up to 72% of UV to pass through, depending on its thickness. Tinted glass reduced transmittance

to 62% and 40%, respectively. They reported values for UVA transmission by double-glazing in residential windows from 0.57 for clear and 0.2-0.33 for tinted glass.

In 2014, Parisi and Turnbull [15] described the factors that ensure quality and effectiveness in the design of shade structures. They used the protection factor parameter (ratio of UVB radiation on a horizontal plane, and horizontal UVB radiation under the shadow structure) defined in Gies et al. [16]. In 2015, Li et al. [17] studied the optical performance of glazing units in the UVA, PAR and NIR ranges and found the transmittances in the VIS region (380–760 nm) of quartz glass slab higher than 78%, and 40-80% in the UVA region, due to the absorption band. They reported a small transmittance difference in the VIS spectrum between various thicknesses of single glazing units, but a large one in the UV and NIR spectrum, with transmittance decreasing with increasing glass thickness. Liu et al. (2018) [18] compared the transmittance of a phase change material (PCM)-glazed unit with an air-filled unit and showed that the transmittance of the PCM-glazed unit with liquid (50%) was lower than with air (61%).

It is also important to measure the solar radiation reflected by different materials, since they contribute to a range of events in the biosphere. For example, the reflection of UV radiation may increase the risk of certain types of cancer [19-21]. Turner and Parisi (2018) [22] analyzed the risks of UVA radiation from exposure to reflective surfaces. They studied the UVA and VIS radiation reflected by a variety of differently oriented surfaces (metallic and non-metallic, and with and without coating). The metal surface data was used to develop a UVA reflectance/VIS reflectance correlation model.

Due to their physical and chemical composition, it is important to study plastics' response to solar radiation. Plastics are high molecular-weight polymers with chemical modifications of their monomers and respond to solar radiation according to their individual stereochemistry, which may be disordered, intertwined or amorphous. Amorphous plastics are vitreous, transparent and generally fragile. In certain sections of the chain they can also be aligned in a parallel arrangement with the rest of the chain to form close links or loops.

The transmittance (T) parameter indicates a material's behaviour with respect to solar radiation. This is defined as the ratio between the intensity of the radiation transmitted below the surface of the material and the normal incident radiation on the surface for the same wavelength. It has been observed that this capacity is a function of certain parameters such as weather conditions (degree of cloudiness), solar height, the radiometric characteristics of the type of material, its state of cleanliness, etc. The transmission of light in certain ranges of the spectrum is therefore the ability of the material to allow light to pass through in these ranges and is obtained by spectroscopy.

In this paper we analyse the spectral transmission of solar radiation of several widely used materials. Methacrylate, one of the most common plastics, is formed of polymers of methyl methacrylate and can be used as an alternative to glass in architecture, biomedicine and engineering. Methacrylate-based sheets help form shatter-resistant, clear and coloured sheets for building windows, skylights, bus shelters, signs and retail displays, among other applications. Smoked glass, also widely used, is manufactured from high quality acid-treated float glass that achieves a surface that fades in light and becomes translucent. Polycarbonate (PC) is a polymer formed of Bisphenol-A molecules bound with carbonate groups; it is highly resistant to impact, 200 times greater than that of glass, which means it can be produced in alveolar sheets. PC glazing is used in architectural window panels as well as continuous windows, domes and roofs. Alveolar Polycarbonate (APC) consists of two polycarbonate plates joined transversely and separated by air chambers. It is characterized by its high light transmission, good rigidity and low conductivity. Among its areas of application are skylights, greenhouses, window frames, roofs and advertising signs. Fibreglass consists of numerous polymer filaments based on extremely fine silicon dioxide threads (SiO_2) and is often used for acoustic and thermal insulation.

The biological effects of exposure to UV solar radiation carry a certain risk due to its negative effects on most living things and plant systems [1-5]. These effects are quantified by their action spectra, which is the measure of a biological effect as a function of the wavelength of the radiation that induces it. The weighted spectral functions of biological actions were obtained and were key in evaluating the implications of

reducing stratospheric ozone. In 1974, Setlow [23] obtained the spectral action of DNA damage, while in 1982 McLaughlin et al. [24] obtained that of vitamin D, Commission Internationale de l'Eclairage (CIE) reviewed [25] that of erythematous action spectrum in 1998, and Flint & Caldwell published two papers in 2003 [26, 27] on the spectral action of plant growth response.

However, UV radiation can also be beneficial, since it stimulates vitamin D synthesis [28-32]. An adequate dose of vitamin D seems to be beneficial against various diseases and many types of cancers [1, 33-37]. Exposure to solar UVB is the main source of vitamin D for humans and studies suggest that very low doses of UVB can achieve significant increase in the serum vitamin D level [38-47], and although radiation filtering is important in terms of reducing the UVB band, it might not allow the body to produce vitamin D.

One of our aims was to study the protection offered by materials against solar UV radiation and the transmission of the radiation in the VIS and NIR ranges. Using materials effectively can limit UV exposure and hence its adverse health impact, especially in times of high UVI. VIS light has also been shown to induce erythema and a tanning response in dark skin, while infrared radiation produces erythema, which is probably a thermal effect [2]. Another aim was to evaluate the biologically effective action of UV solar radiation on humans, related to erythema, DNA damage and vitamin D production.

The remainder of the paper is organised as follows: Section 2.1 describes the materials analysed and the method used to obtain the transmittance of the materials is explained in Section 2.2. The spectral transmittances of these materials and the integrated transmittances in the UVB from 300 nm, UVA, VIS and NIR ranges (from 700 nm to 1000 nm) are given in Section 3, in which the biological spectral actions related to erythematous damage, DNA damage and vitamin D production are also considered and provide information on the effects on humans that can be expected when the materials are used as solar radiation barriers.

-

2. Materials and methods

2.1 Materials

The materials studied consist of flat square plates and can be seen in Figure 1. The 4 mm thick methacrylate plate was smooth, transparent, non-deformable, with low elasticity and hardness and polished, which gave it a certain surface brightness. The smoked glass plate was also smooth and 4 mm thick, but without surface gloss on one side. The APC plate was transparent, without surface gloss and 5 mm thick, consisting of two plates joined internally by cross strips of the same material. The PC plate was transparent but with transverse corrugated stretch marks 1.5 mm deep. The fibreglass was made of very fine threads interwoven perpendicularly forming a mosquito net structure.

The transmittance values were obtained from the spectral irradiance measured at 0.10 m from the surface, as indicated in Figure 2. This distance was considered adequate since the diffuse irradiance could be considered negligible due to the holding structure of the plate during measurement.

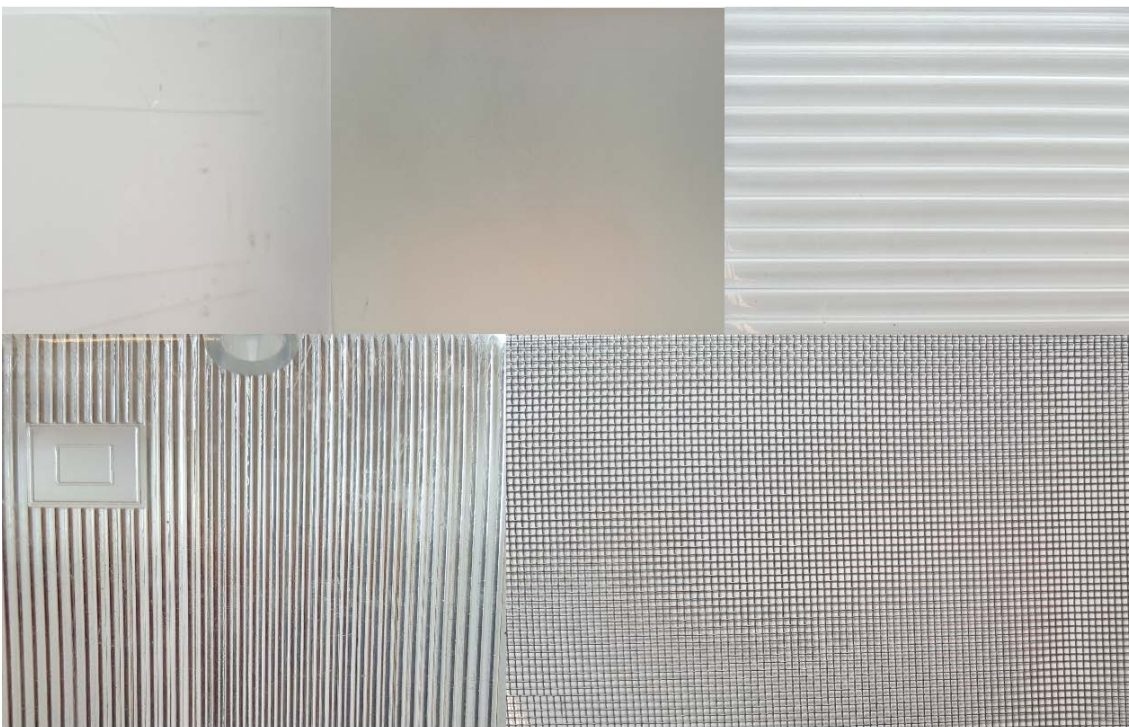


Fig. 1. Examples of the surfaces studied. Top left to right: methacrylate, smoked glass and alveolar polycarbonate. Bottom left to right: polycarbonate and fibreglass.

The sensor was first faced towards the sun to measure normal solar irradiance and immediately afterwards the material surface was placed at about 0.10 m above the sensor to measure the transmitted solar irradiance. This procedure was repeated with all the materials at 8 and 12 solar hours.

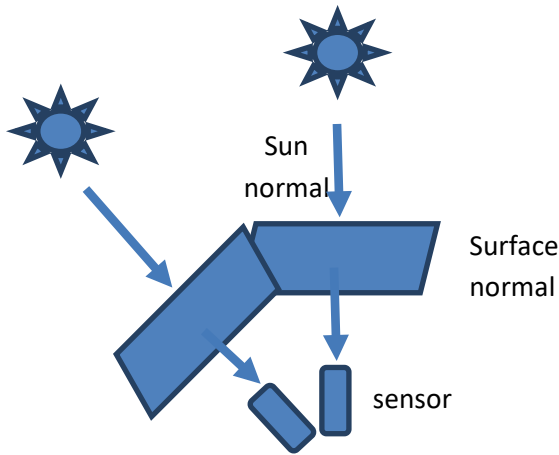


Fig. 2. Sensor orientation to measure sun direct normal measurements and position of the material perpendicular to the sensor.

2.2 Transmittance of UVB, UVA, VIS and NIR bands

When radiation reaches the surface of a semitransparent medium, a series of transformed components of the incident energy are produced, such as reflection, absorption and transmission. This can be written as a balance of irradiances, which in spectral form is as follows:

$$Irrad_{incident,\lambda} = Irrad_{reflected,\lambda} + Irrad_{absorbed,\lambda} + Irrad_{transmitted,\lambda}$$

The normal incidence of solar radiation on the surface of the material can be studied by means of Fresnel laws [48], which provide the reflection and transmission coefficients of electromagnetic radiation, according to the refractive indices. At normal radiation incidence, as in the present study, the essential components are the two measured quantities of transmitted irradiance and normal incidence. The reflected and absorption components are not evaluated, since the idea is not to calculate the energy balance, but the capacity of the material to let radiation through.

The primary aim was thus to calculate the transmittance of the UVB, UVA, VIS and NIR bands, integrating the spectral data throughout the ranges of 300-315 nm, 315-400 nm, 400-700 nm and 700-1000 nm, respectively, for each material and associated sun normal measurements, according to the following expression:

$$T = \frac{\int I_{t\lambda} d\lambda}{\int I_{n\lambda} d\lambda} \quad (1)$$

Where $I_{t\lambda}$ is the irradiance transmitted through the surface and $I_{n\lambda}$ is the normal solar irradiance.

The study took place on the campus of the *Universitat Politècnica de València* (UPV) (0° 22 ' W, 39° 28 ' N, at sea level) to the north of the city of Valencia, far from industrial areas and near open country, in the eastern Spanish region of Valencia. The measurements were performed on clear days, at 8 h and 12 solar hours, in July 2018 over a period of five days (24,26,27,30 and 31) and in January 2019 over a period of three days (25, 26 and 28). The solar zenith angle (SZA) for the different days of the study periods is shown in Table 1.

Table 1

Solar zenith angle (in degrees) for the measurements period.

	SZA (°)	
	8 h	12 h
24/07/2018	50.3	19.5
26/07/2018	50.6	19.9
27/07/2018	50.7	21.7
30/07/2018	51.1	20.8
31/07/2018	51.2	22.6
25/01/2019	78.4	59.5
25/01/2019	78.3	59.3
25/01/2019	82.8	58.8

Two spectrometers were used to measure irradiance: HR4000CG-UV-NIR (Ocean Optics) in the VIS spectrum band (400-700 nm) and the NIR spectrum (700-1000 nm) and FLAME-S-UV-VIS (Ocean Optics) in the UVB (280-315 nm) and UVA (315-400 nm) bands.

In HR4000, the size of the aperture regulates the amount of light that enters the optical bench and controls spectral resolution. The light passes through the SMA Connector, Slit, and Filter, which restricts optical radiation to a pre-determined wavelength region and then reflects off the Collimating Mirror onto the Grating. This directs the diffracted light onto the Focusing Mirror of the CCD Detector to convert the optical to a digital signal. The spectrometer then transmits the digital signal to the OOIBase32 application [49].

HR4000 provides a 200-1100 nm wavelength range with 0.25 nm optical resolution. It has an integration time of from 4 milliseconds to 20 seconds. The entrance aperture of the spectrometer has a 5- μm wide slit. Stray light is <0.05% at 600 nm and <0.10% at 435 nm. It has a HC-1 L and has 300 lines per nm grating. The spectra are detected with a 3648-element linear silicon CCD array, giving 0.25 nm FWHM spectral resolution [23]. The spectrometer was operated by a PC on Spectral Suite software and the acquisition parameters introduced in this program to perform the measurements were 5 scans to average every 15 ms, and an integration time of 0.5 seconds. The spectra were stored for later analysis [49].

In FLAME-S, light from a fibre enters the optical bench through the SMA 905 Connector. The light passes through the 5- μm wide slit, which acts as the entrance aperture. The collimating mirror is matched to the 0.22 numerical aperture of standard optical fibres. Light reflects off this mirror as a collimated beam towards the grating. The Focusing Mirror focuses first-order spectra on the detector plane. The Detector is a 2048- element FLAME-S (Sony ILX511B) linear CCD array. The optics split the light into its component wavelengths, which fall across the different pixels. The detector sends out an analogue signal from each pixel that is converted via the ADC into a digital signal. The driver electronics process this signal and send the spectrum via the USB connection to the software [49].

FLAME-S-UV-VIS has an effective range of 200-850 nm wavelength range with an optical resolution of 0.1 nm FWHM. Its integration time is 0.1 seconds, with a corrected linearity >99%. The acquisition parameters in the software to perform the measurements were 5 scans on average every 15 ms.

The HR4000CG-UV-NIR and FLAME-S-UV-VIS spectrometers were calibrated from 250 nm to 1000 nm and from 250 nm to 400 nm, respectively, in July 2017 by Ocean Optics. Both devices have a measurement uncertainty of approximately $\pm 10\%$ across the VIS and NIR spectrum and UV spectrum, respectively.

Since the solar spectrum show negligible measurements below 295 nm, there should not be any transmission below this wavelength, and so the measurements from the FLAME-S below 295 nm were not considered. Besides, from 295 nm to 300 nm the instrument had a lot of background noise, so we did not consider these measurements in the calculations.

To obtain the average value of the transmittance of each range of the solar spectrum studied the spectral data were integrated every 0.10 nm increments from 300 to 400 nm, and every 0.25 nm increments from 400 to 1000 nm. The transmittance was calculated at these values for each range of the solar spectrum according to Eq. (1) for each measurement time. The average of this transmittance was then calculated for each type of material and solar time.

2.3 Biological Transmittance of the UVB, UVA, VIS and NIR bands

It is of interest to analyse the effect of solar radiation on various materials that affects animal and plant life. Three of the factors that determine this biological action are: skin sensitivity, solar radiation level and the materials' intrinsic transmission. The study led to a set of spectral actions which gave us the UV spectral irradiance values that promote biological changes. Basically, these are spectral functions according to the following equation:

$$Irrad_{biological\ actions} = Irrad_{incident} \cdot f(spectral\ action)(2)$$

In our case, since it is radiation after the material surface, it becomes,

$$Irrad_{biological\ action} = Irrad_{filtered} \cdot f(spectral\ action)(3)$$

Dividing both members of the Eq. (3) by the normal incident irradiance I_{nl} results in:

$$T_{biological\ action} = T_{material} \cdot f(spectral\ action)(4)$$

$T_{biological\ action}$ and $T_{material}$ being the transmittance values with biological action and the material's transmittance, respectively.

Different biological transmittance values were obtained for the UV range using weighted spectral functions of biological actions, such as DNA damage spectrum function [23], the vitamin D action spectrum function [24] and the erythema weighting function [25], which are used to study the biologically effective action of UV radiation. To obtain the value of the biological transmittance of each range, the previously obtained spectral transmittance value for each wavelength ($T(\lambda)$) was multiplied by the biological function of each wavelength (f_{bio}) according to Eq. (4), and then integrated every 0.10 nm for the range of the solar spectrum of each biological function (300 to 314 nm the vitamin D spectrum, 300 to 400 nm the DNA damage spectrum and 300 to 400 nm the erythema action spectrum), applying the following expression:

$$T_{bio} = \frac{\int T(\lambda) f_{bio}(\lambda) d\lambda}{\Delta\lambda} \quad (5)$$

These transmittance values were obtained at summer solar noon during the measurement period, when the sun is at its highest intensity, and the average of each type of material were then calculated.

2.4. Minimal erythema dose and maximum sun exposure time

The minimal erythema dose (MED) is the minimum UV erythema (UVER) dose which causes erythema with sharply defined edges 24 hours after sun exposure, without prior exposure. The harmful effects of UV radiation depend on the dose received and the sensitivity of the individual, and therefore, on the different types of skin. In 1988, Fitzpatrick [50] classified phototypes or skin types into six categories according to

its propensity to tan and burn, as shown in Table 2, being the amount of energy required to produce a MED smaller in skin type I (lighter) than in type VI. Table 2 describes the skin types and their characteristics, as well as the approximate MED for each skin type according to this standard.

Table 2

General characteristics of skin types and minimal erythema dose (J/m^2) according to Fitzpatrick [50].

Skin type	Tan	Burn	Minimal Erythema Dose(J/m^2)
I	Never	Always	200
II	Sometimes	Easily	250
III	Gradually	Moderately	350
IV	Always	Rarely	450
V	Very easily	Very Rarely	600
VI	Deeply pigmented	Never	1000

As mentioned above, the MED for each skin type and the maximum sun exposure time are different, which can be defined as the time to which you can be exposed to the sun without protection and without burning. The exposure time through the studied materials required to cause erythema was calculated by applying Eq. (1) from Serrano et al. [51] as follows:

$$t_E(\text{min}) = \frac{MED(J/m^2) \cdot SPF}{UVER(W/m^2) \cdot 60} \quad (6)$$

Where SPF is the sun protection factor applied, and UVER is the UV erythema irradiance in W/m^2 .

The UVER irradiance measurements were obtained in the historical data section corresponding to the Valencia city station from the UV-B Radiation THE ULTRAVIOLET INDEX Network of the Department

of Agriculture, Rural Development, Climate Emergency and Ecological Transition of the Valencian Community [52].

2.5. Minimum time to produce Vitamin D3

The time to produce the adequate doses of vitamin D3 is estimated by means of Eq. (7) [51]:

$$t_{UVD}(\text{min}) = \frac{UVER(s)(mW / m^2) \cdot R(s) \cdot MED(J / m^2)}{BE \cdot UVD(mW / m^2) \cdot MED(s)} \quad (7)$$

where the subscript (s) shows standard values ($UVER(s) = 250 \text{ mW/m}^2$ for $UVI=10$, $R(s)=2$), $MED(s)=250 \text{ J/m}^2$). BE is the fractional area of skin surface exposed (per unit). In summer (July) a BE of 0.25 considering exposed face, neck, hands and arms was adopted. As young adults and skin without sunscreen were also considered, we removed these factors from the original equation.

To obtain the vitamin D3 irradiance ($UVD3$) (mW/m^2) we followed Serrano et al. [51] and McKenzie et al. [53], who showed that $UVD3$ can be estimated from $UVER$ using a model with ozone content data and the solar zenith angle. The ozone data is the ozone content of the atmosphere in Dobson Units for each day of the study and for the geographic coordinates of Valencia. The ozone data was obtained from measurements performed by Ozone Monitoring Instrument (OMI/aura satellite). In the summer at solar noon the factor by which the $UVER$ irradiance must be multiplied to obtain $UVD3$ is two (see Tables 7) according to the solar zenith angle and ozone content of the atmosphere.

3. Results

3.1. Transmittances of UVB, UVA, VIS and NIR bands

In Tables 3 and 4 it can be seen that in general the 8 h transmittances are higher than at 12 h and they are also higher in winter than summer (Section 3.2 justifies this for each material). Table 3 shows that in the UVB band from 300 nm, methacrylate and smoked glass have the highest transmittance values (range 56-68 %), and PC, APC the lowest. In the UVA range these materials allow practically no light to pass through,

whereas smoked glass has the highest transmittance value, around 70%, similar to fibreglass, which reaches high values in the UV spectrum, but as it has a grid-like structure (e.g. mosquito netting) it lets the light pass through.

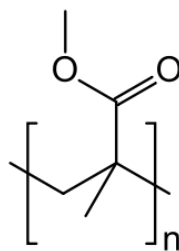
Table 3

Transmittance of UVB from 300 nm and UVA bands of the materials in summer and winter at 8 and 12 solar hours.

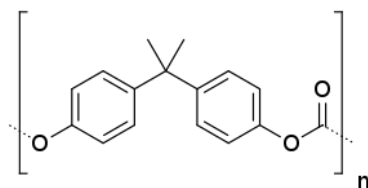
Material	T-UVB				T-UVA			
	Summer		Winter		Summer		Winter	
	8h	12h	8h	12h	8h	12h	8h	12h
Methacrylate	0.56	0.26	0.68	0.47	0.32	0.29	0.33	0.31
Smoked glass	0.56	0.29	0.68	0.49	0.72	0.78	0.72	0.70
Alveolar polycarbonate	0.38	0.16	0.60	0.30	0.08	0.05	0.09	0.06
Polycarbonate	0.30	0.11	0.60	0.28	0.04	0.02	0.10	0.04
Fibreglass	0.71	0.63	0.80	0.66	0.70	0.67	0.70	0.79

Table 4 shows that methacrylate and smoked glass have higher transmittance in the VIS and NIR ranges than PC. The path travelled by radiation inside these materials develops heat transfer mechanisms such as conduction heat and radiation heat. The thermal conductivity of the chosen materials is very similar for methacrylate and PC, around $0.17\text{-}0.22 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and $0.8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for glass, which indicates that this phenomenon does not determine or explain their transmittance. This is more than likely due to their stereochemical composition, i.e. the spatial arrangement and magnitude of the monomers.

For methacrylate $(\text{C}_5\text{O}_2\text{H}_8)_n$



And PC has the most voluminous monomer,



Taking this into account, the large monomers intercept more radiation, so that the UV and VIS transmittance of PC is lower, with a value of around 0.45. The arrangement of the layers in the APC produces an effect that allows radiation to be transmitted at values around 0.8.

Table 4

Transmittance of VIS and NIR bands of the materials in summer and winter at 8 and 12 solar hours.

Material	T-VIS				T-IR			
	Summer		Winter		Summer		Winter	
	8h	12h	8h	12h	8h	12h	8h	12h
Methacrylate	0.94	0.93	0.96	0.98	0.95	0.94	0.96	0.94
Smoked glass	0.85	0.79	0.86	0.80	0.78	0.79	0.79	0.76
Alveolar polycarbonate	0.63	0.86	0.77	0.77	0.64	0.89	0.78	0.78
Polycarbonate	0.46	0.40	0.48	0.44	0.48	0.42	0.47	0.45
Fibreglass	0.75	0.65	0.70	0.66	0.73	0.66	0.70	0.65

3.2. Spectral Transmittances of UVB, UVA, VIS and NIR bands

This section gives the spectral transmittance values of the materials studied in summer and winter at 8:00 and 12:00 solar hours. The values recorded on July 30 at 08.00 solar hours and solar noon are shown as examples in Figures 3a and 3b respectively, for UV ranges.

All materials except fibreglass showed an exponential decay of transmittance in the UVB range from 300 to 315 nm. In methacrylate, transmittance is significantly reduced in the first half of the UVA range and acquires high values in the second. In smoked glass most of the UVA band is transmitted virtually unaffected. Both polycarbonate compositions have almost no transmittance in the UVA range, while fibreglass has a high transmittance (range 65-75%) in the UV band.

In figures 3a and 3b in the far UV region it is observed that the transmittances of PC are higher in summer at 8:00 h than at solar noon. This might be due to the influence of temperature (increases from 20°C to 35°C), which produces electronic delocalization in the chemical bonds of the molecules, increasing possible harmonic resonances, and decreasing transmittances.

When materials are exposed to UV solar rays, electrons from the valence band could be excited to an upper band. In the case of polymers, such as polycarbonate, the excitation energies in the $\pi \rightarrow \pi^*$ transitions are moderately high, corresponding to the far UV region, which is close to the visible spectrum. The π orbitals originate from the association of the "p" orbitals of carbon atoms, being π^* an excited π orbital of higher energy.

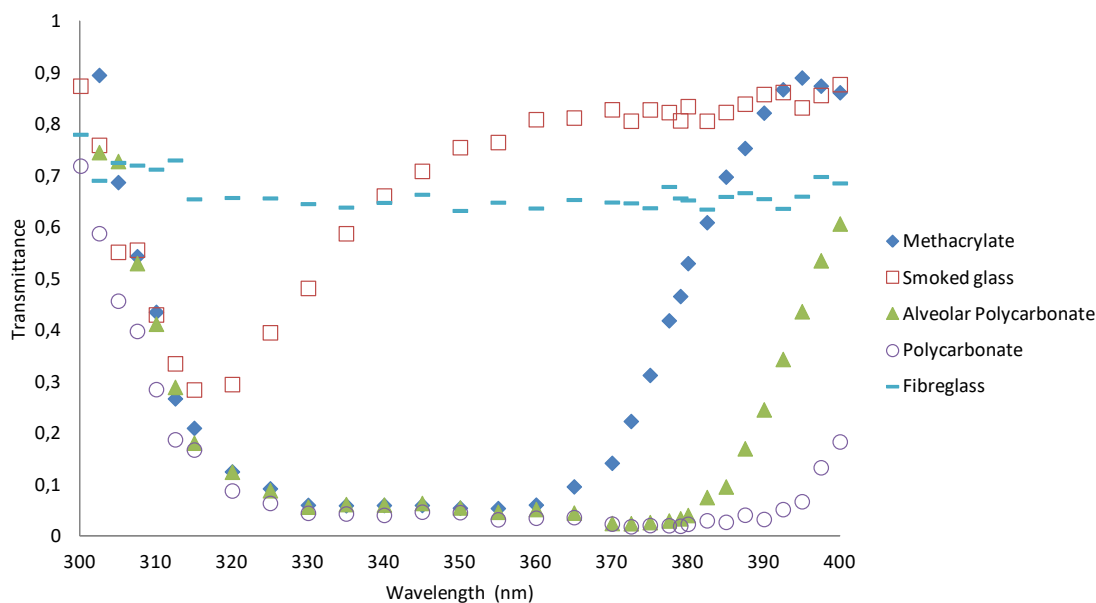


Fig 3a. Spectral transmittance of the materials in the UV band in summer at 8 solar hour on 30-July.

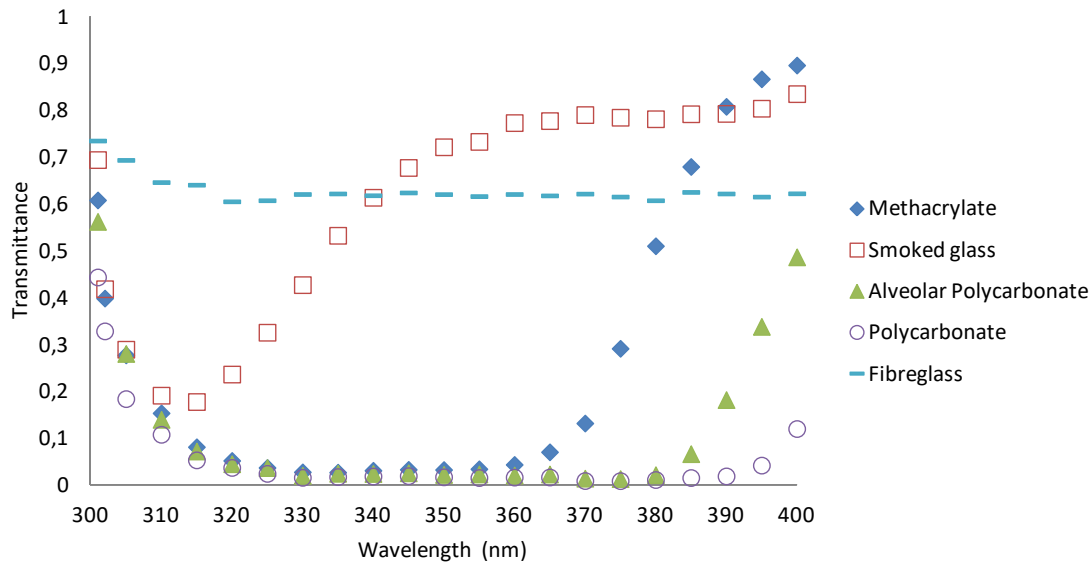


Fig 3b. Spectral transmittance of the materials in the UV band in summer at solar noon on 30-July.

The values recorded on July 30 at 08.00 solar hours and solar noon are shown as examples in Figures 4a and 4b respectively, for VIS and NIR ranges.

If the spectral results at solar noon are compared with those at solar 08.00 hours, the materials' transmittance values at noon are lower, a tendency already seen in Tables 3 and 4 with the values integrated by ranges.

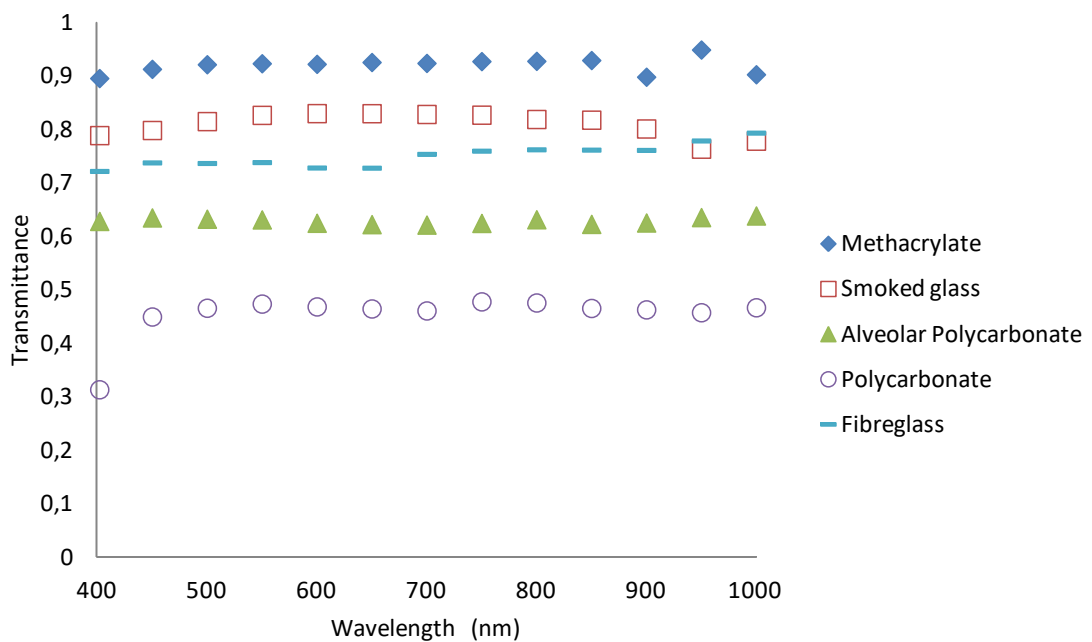


Fig. 4a. Spectral transmittance of materials in the VIS and NIR bands in summer at 8 solar hour on 30-July.

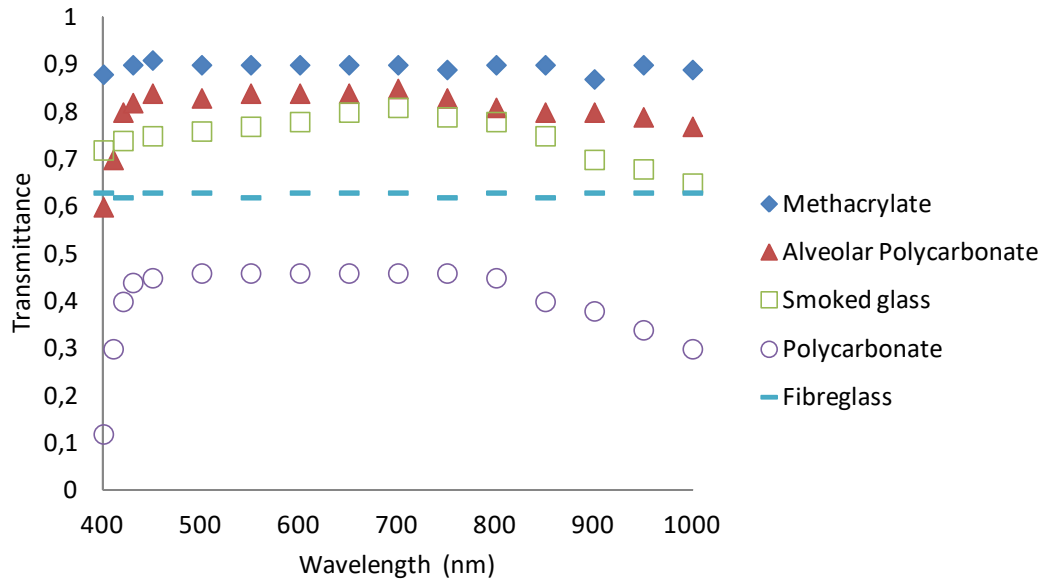


Fig. 4b. Spectral transmittance of materials in the VIS and NIR bands in summer at solar noon on 30-July.

Methacrylate and APC partially remove UVB and UVA radiation but lets a good deal of the VIS and NIR bands pass through (85-90% range).

Methacrylate transmittance does not show an appreciable variation with temperature at 8 h and solar noon. Monomers contain carboxylic groups that prevent the delocalisation of the charges and atomic vibration (by the double bond), involving inertia to the thermal effect.

The APC transmittance increases by around 25% from 8 h to solar noon. This could be due to the fact that the APC plate is formed of two thin parallel layers of PC (see Section 2) and contain air. The temperature variation in summer in Valencia represents an increase of 15°C between early morning and noon. The temperature at 8 h (around 20°C) finds air with low thermal conductivity, which increases as it reaches 35°C, favouring transmission.

Smoked glass has high transmittance in the UVA and VIS and NIR bands (range 70-80%), VIS transmittance being about 7% higher than NIR. The internal composition, a mixture of limestone and silica, has a more delocalised thermal behaviour, partially disorganizing and ultimately, altering the transmission in this area.

It can be seen in Figures 4a and 4b that the transmittance of smoked glass is lower at higher temperatures. This may be due to the reduced thermal conductivity when the temperature rises [54].

Figure 4b shows that the transmittance of smoked glass first increases and then falls, probably because silicon dioxide, the basic constituent of glass, has absorption maximums around 400 and 1000 nm [55].

In the VIS range (Figures 4) PC lets 45% of the radiation pass through, and in the NIR region it has an even lower transmittance, indicating that a structure exposed to solar radiation should contain this material to thermally insulate its interior. As can be seen from the data, an outer structure composed of this material would reduce radiation from the UVB, VIS and NIR bands.

The PC plate was 4 mm thick and had higher transmittance (13%) at 8h, which could be because the thermal diffusivity is higher at a lower temperature, favouring transmission. On the other hand, when the ambient temperature increases, its diffusivity decreases and the material behaves with greater thermal inertia [56]. Ultimately, this means lower transmittance.

PC transmittance in the 800nm-1000nm wavelength falls, as shown in Fig. 4b. The PC absorption spectrum shows greater absorption in the 800 to 1000 nm area, so that transmittance is lower [57].

Fibreglass transmittance shows a drop of about 15% from 8 h to solar noon in the summer. This cannot be assigned to the material's properties, since it forms an interlacing of very fine threads in squares of approximately 1 mm side. The wire netting (mosquito net) acts as a shield for solar radiation by dividing two zones (exterior and interior) partially interconnected by the holes in the net, creating air convection currents that contribute to transmittance.

3.3. Biological Transmittance: Erythema, vitamin-D and DNA damage

Concern is growing about the effects of solar UV radiation on humans. The most frequent issues are those related to the protection offered by obstacles to solar radiation. This section assesses whether a person can

be affected by the radiation that passes through the surface of the materials studied here, and analyses their transmittance values with erythemal biological action, vitamin D3 production and DNA damage.

3.3.1. Erythemal transmittance

In 1998 a committee of the CIE [25] proposed a review of the action spectrum for erythema induced in humans by UV radiation. Erythemal spectral transmittance is calculated according to Eq. (4), considering CIE standard [25] erythemal weighting function for all materials. The example of methacrylate is shown in Figure 5. It can be seen that the spectral evolution of the transmittance strongly decreases exponentially, so that the erythemal transmittance at 300 nm is 45% greater than that at 320 nm. In the rest of the UV range, UVER radiation is practically removed.

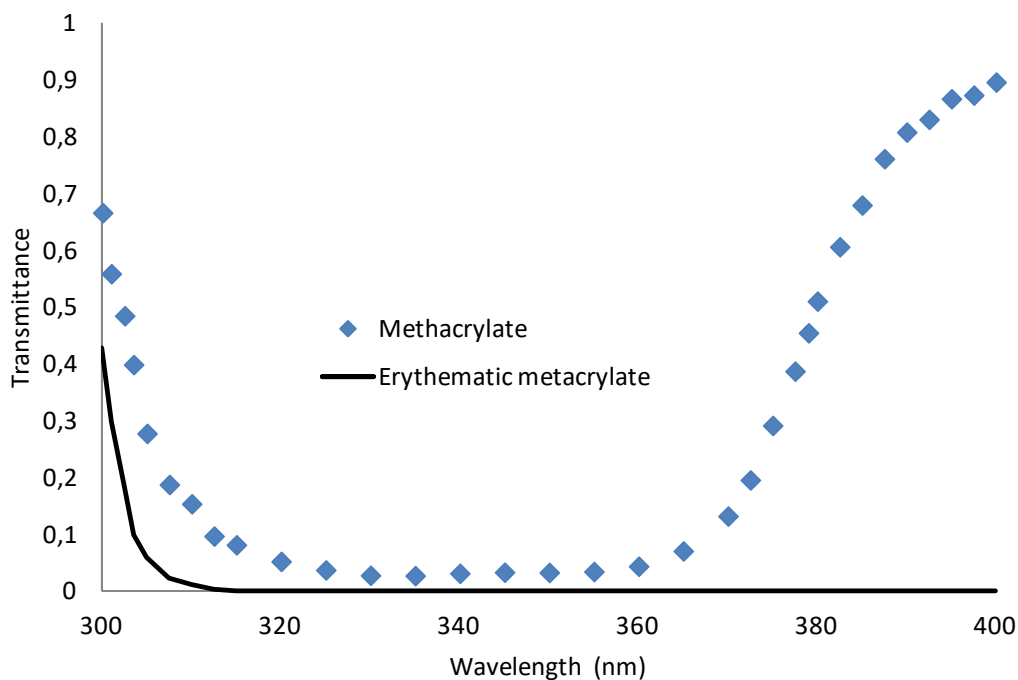


Fig.5. Spectral erythemal transmittance of methacrylate.

3.3.2. Transmittance DNA damage

DNA damage is another health consequence of UV solar radiation and certain studies have addressed this point [58]. In this section we apply Setlow's [23] spectrum of biological action in DNA damage to calculate transmittance by means of Eq. (4).

The spectral transmittance of methacrylate is given as an example in Figure 6. The spectral evolution of transmittance has a more pronounced exponential decay than that of erythemal transmittance, so that the value at 300 nm is 50% higher than that at 310 nm. Radiation is practically negligible in the rest of the UV range.

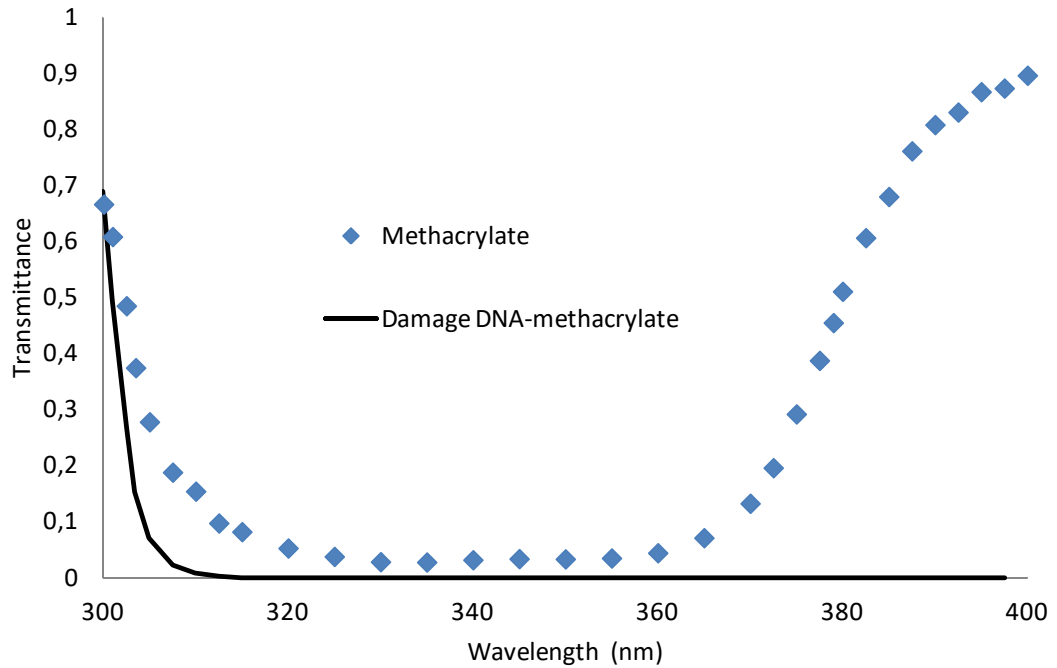


Fig. 6. Spectral transmittance of DNA action damage of methacrylate.

3.3.3. Vitamin-D transmittance

Solar UV radiation is beneficial for the production of vitamin D. This does not require prolonged exposure to the sun and it is known that between 90-95% of vitamin D is synthesized when UVB radiation is active (290 to 315 nm range) [38-47]. The CIE [60] proposed extending the spectrum for the production of vitamin D to 330 nm. Figure 7 shows the spectral transmittance of methacrylate calculated by Eq. (4) using Mclaughlin's vitamin D action spectrum function [24], since beyond 315 nm there is no transmitted UVD3 radiation.

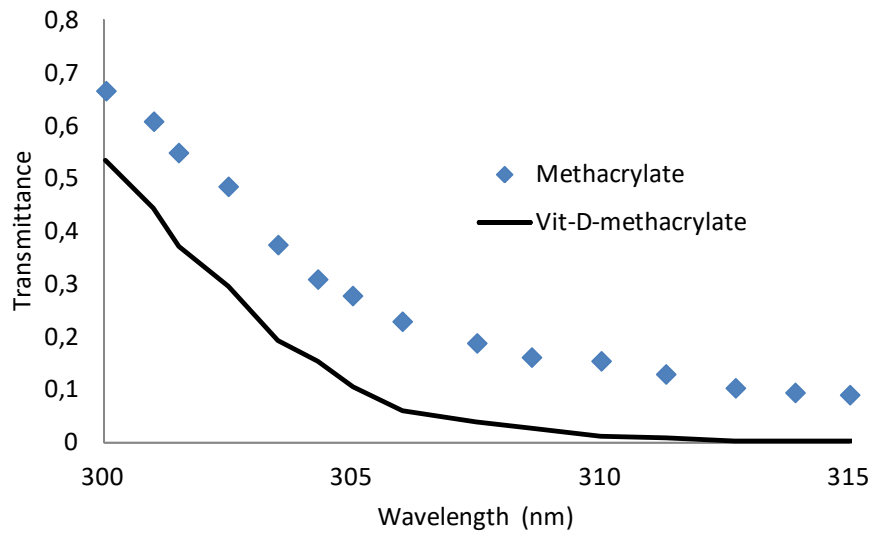


Fig.7. Methacrylate potential vitamin-D spectral transmittance.

The biological transmittance values of each spectrum range were obtained for all materials by applying Eq. (5) and are shown in Table 5. It can be seen that for the UVB range from 300 nm the transmittance for most materials and for all biological functions shown is in the range 0.08-0.15, which indicates that they allow 15% of the biological irradiance to pass through. Fibreglass, due to its structural characteristics, transmits 30% of the erythemal and vitamin D biological radiation. PC has the least biological transmittance, and best protects against harmful radiation (Erythemal and DNA) but at the same time hinders vitamin D formation.

The values obtained are negligible in the UVA range for biological functions that act in this range, so that all these materials can be considered to prevent the effective transmission of these types of biological irradiance.

Table 5

Biological transmittance of the materials.

Material	T-Vit.D3		T-DNA damage			T-Erythemat	
	300-315nm	300-315nm	315-400nm	300-315nm	315-400nm		
Methacrylate	0.12	0.11	10^{-4}	0.08	10^{-4}		
Smoked glass	0.15	0.14	$4 \cdot 10^{-3}$	0.10	$5 \cdot 10^{-4}$		
Alveolar polycarbonate	0.12	0.12	$2 \cdot 10^{-5}$	0.075	$9 \cdot 10^{-5}$		
Polycarbonate	0.082	0.087	10^{-5}	0.055	$6 \cdot 10^{-5}$		
Fibreglass	0.30	0.10	$3 \cdot 10^{-3}$	0.35	0.21		

3.4. Calculated exposure times

Since PC has the lowest UVB erythemal transmittance and fibreglass the highest, the UVER transmitted by these materials was individually calculated for both, as shown in Table 6a. The rest of the materials have a similar UVER transmittance and the UVER transmitted was calculated with the average value (0.085). The results are shown in Table 6b.

Table 6a

Time to induce erythema for several skin types around solar noon in Valencia in summer for PC and fibreglass.

	UVER (mW/m ²)	UVER transmitted (mW/m ²)		t _E (min) PC			t _E (min) Fibreglass		
		PC	Fibreglass	skin type I	skin type III	skin type V	skin type I	skin type III	skin type V
24/07/2018	214	11.8	74.9	283	496	850	45	78	134
26/07/2018	204	11.2	71.5	297	519	890	47	82	140
27/07/2018	211	11.6	73.9	287	503	862	45	79	135
30/07/2018	205	11.3	71.6	296	519	889	47	82	140
31/07/2018	202	11.1	70.8	300	524	899	47	82	141

The exposure time through these materials required to cause erythema was calculated by applying Eq. (6), differentiating between PC, fibreglass and other materials. Tables 6a and 6b show the minimum exposure time that would cause erythema at UVER noon irradiance to skin types I, III and V with no sunscreen. As can be seen, a skin-type I person should not be exposed for more than approximately 45 minutes through fibreglass and no more than 180 minutes for the rest of the materials, except for PC, which allows longer exposure times due to its lower transmittance (about 283 minutes).

Table 6b

Time to induce erythema for several skin types around solar noon in Valencia in summer for the other materials.

	UVER transmitted (mW/m ²)	t _E (min) Average others materials		
	Average of the other materials	skin type I	skin type III	skin type V
24/07/2018	18.2	183	321	550
26/07/2018	17.4	192	336	576
27/07/2018	17.9	186	325	557
30/07/2018	17.4	192	336	575
31/07/2018	17.2	194	339	581

The time to produce an adequate dose of vitamin D3 was estimated by means of Eq. (7) also differentiating between PC, fibreglass and the rest of the materials and is shown in Tables 7a and b.

The minimum exposure time at noon irradiance UVD3 (mW /m²) to obtain the recommended dose of vitamin D3 with 25% body exposure without sun protection for skin types I, III and V is shown in Tables 7a and b. As indicated, a skin type I person would have had enough with 30 minutes of sun exposure through most materials, except for PC, which needs a longer time due to its lower transmittance (around 48 minutes). Since people with darker skin need more exposure time to acquire an adequate dose, it should be borne in mind that a type V person would need to be exposed for 91 minutes through most materials to obtain it.

Table 7a

Time to obtain adequate dose of vitamin D3 for several skin types around solar noon in Valencia in summer for PC and Fibreglass.

	UVER (mW/m ²)	UVD3 (mW/m ²)	UVD3 transmitted (mW/m ²)		t _{vitD3} (min) PC			t _{vitD3} (min) Fibreglass		
			PC	Fibreglass	skin type I	skin type III	skin type V	skin type I	skin type III	skin type V
24/07/2018	214	428	35	128	46	80	137	12	22	37
26/07/2018	204	409	34	123	46	81	139	13	23	39
27/07/2018	211	422	35	127	46	81	139	13	22	38
30/07/2018	205	409	34	123	48	83	143	13	23	39
31/07/2018	202	405	33	121	48	84	145	13	23	40

Table 7b

Time to obtain adequate dose of vitamin D3 for several skin types around solar noon in Valencia in summer for the others materials.

	UVD3 transmitted (mW/m ²)	t _{vitD3} (min) Average of other materials		
		Average other materials	skin type I	skin type III
24/07/2018	55.6	29	50	86
26/07/2018	53.1	30	53	90
27/07/2018	54.9	29	51	87
30/07/2018	53.2	30	53	90
31/07/2018	52.6	30	53	91

If we consider a 15% exposed body area (face, neck, hands and half the arms) then the above calculation times should be multiplied by $0.25/0.15=1.67$ to obtain the minimum exposure time to obtain the adequate

vitamin D3 dose. A skin type I person would then need 50 minutes exposure through most materials and a skin type V 151 minutes.

4. Discussion

The study of the transmission of the UVB from 300 nm, UVA, VIS and NIR bands through methacrylate, smoked glass, APC, PC and fibreglass surfaces indicates that methacrylate and smoked glass have the highest transmittance from 300 to 315 nm (around 60%). In the UVA range smoked glass and fibreglass, transmit similar values of around 70%. Fibreglass reaches high values in all the studied spectrum, but it should be borne in mind that its grid structure allows light to pass through and thus it cannot be compared with other materials.

Methacrylate and APC partially remove UV radiation but transmit a considerable level of the VIS and NIR bands (methacrylate has the higher transmittance, around 95%), so that these would be suitable materials for installation on terrace roofs, bus shelters, windows and household areas that require good lighting.

PC gives the most protection against UV radiation since it only transmits 30% of UVB from 300 nm and about 5% of UVA. It can therefore be recommended as an alternative to glass in windows, since glass has higher transmittance. Recent studies indicate transmittance values of 57% [9] and 40-80% [17] for clear glass in the UVA region. We obtained a transmittance of 75% for smoked glass in the UVA band, in the same order of magnitude found by other authors [9, 17].

In the VIS range, PC shows a 60% drop in incident radiation, and transmits even less in the NIR region, indicating that a structure exposed to solar radiation should contain this material as thermal insulation. As can be seen from the data, an outer structure containing this material would reduce radiation from the UVB, VIS and NIR bands.

We found that winter transmittances were higher than those in summer and were higher at 8 h solar than at noon, possibly due to the higher summer thermal level causing the network elastomers to rotate and vibrate,

intercepting most of the solar radiation incident photons. Another reason could be related to the mechanical properties of the materials, since thermal diffusivity is higher at a lower temperatures and this raises transmittance. At solar noon the temperature is higher, so that diffusivity is reduced [56] and transmittance is higher.

The study of biological transmittance of the materials showed that erythema damage could also occur after long exposure to solar radiation in people who work near windows, especially if they are made of clear glass. We found that a skin-type I person should not be exposed for more than 45 minutes through fibreglass or 180 minutes through the others (except PC) to prevent erythema. This information should be available to the general public and especially for those with skin type I. It should also be taken into account that the times indicated above to produce a MED, will probably be shorter since the irradiance from 295 nm to 300 nm has not been considered due to the background noise.

If around 15% of the body surface is exposed to solar radiation through the materials studied, except PC and fibreglass, a skin-type I could easily obtain the recommended dose of vitamin D3 with daily exposures of less than 1 h. However, skin-type V would need about two and a half hours exposure.

In future work we will combine the transmission properties of different materials. The initial idea is that the simplest combinations would be in series, as two different material surfaces would lead to an overall transmittance equal to the product of their transmittances ($T_1 \times T_2$). If I_i is the irradiance incident on material 1, then the outgoing irradiance from material 1, I_1 will be, $I_1 = T_1 \cdot I_i$. If the radiation then passes through material 2, this means $I_2 = T_2 I_1$; or, $I_2 = T_2 T_1 I_i$. It would be a question of studying the appropriate combinations of materials to provide the recommended transmittance for the use in question (buildings, greenhouses, canopies, roofs, etc.).

We will also analyze the effects of certain plastics in greenhouse awnings on solar radiation on plants. Doses higher than those considered normal cause serious damage to the plant systems due to the alteration of their chlorophyll functions, such as diminishing crops and marine phytoplankton.

Future studies also will analyse the transmittance of materials with radiation at a certain angle of incidence to the surface, also the reflection of radiation by different materials, both in broadband and spectral, and the possible associated biological effects.

This study project did not receive any specific grant from funding agencies in the public, commercial or not-for-profit sectors.

Acknowledgments

The authors wish to thank the Generalitat Valenciana for providing us with access to weather data.

References

- [1] A.Juzeniene, P. Brekke, A. Dahlback, S.Andersson-Engels, J. Reichrath, K.Moan, M.F.Holick, W.B. Grant, J.Moan, Solar radiation and human health, Rep. Prog. Phys. 74: 066701 (2011) (56pp).
- [2] L.R.Sklar, F. Almutawa, H.W.Lim, I. Hamzavi, Effects of ultraviolet radiation, visible light, and infrared radiation on erythema and pigmentation: a review. Photochem. Photobiol. Sci.12 (2013) 54–64.
- [3] R. Greinert, E.de Vries, F.Erdmann, C.Espina, A.Auvinen, A.Kesminiene, J.Schuz, European code cancer fourth edition: Ultraviolet radiation and cancer. Cancer Epidemiol. 39: S75-83, (2015).
- [4] Bais A, Topaloglou C, Kazadtzis S, et al. Report of the LAP/COST/WMO Intercomparison of Erythemal Radiometers, Thessaloniki, Greece, 13-23 September 1999, 2001 WMO-GAW report No. 141 (WHO TD No. 1051) Geneva.
- [5] R. M. Lucas, S. Yazar, A. R. Young, M. Norval, F. R. de Gruijl, Y. Takizawa, L. E. Rhodes, C. A. Sinclair and R. E. Neale, Human health in relation to exposure to solar ultraviolet radiation under changing stratospheric ozone and climate, Photochem. Photobiol. Sci., 2019, 18, DOI:10.1039/C8PP90060D.
- [6] A.Parisi, Quantitative evaluation of the personal erythemal ultraviolet exposure in a car Photodermatol.Photoimmunol. Photomed. 14 (1998),12–16.

- [7] M.G.Kimlin, A.Parisi, Ultraviolet radiation penetrating vehicle glass: A field based comparative study. *Physics in Medicine & Biology*, 44(4), (1999) 917.
- [8] M.G.Kimlin, A.Parisi, B.Carter, D.Turnbull, Comparison of the solar spectral ultraviolet irradiance in motor vehicles with windows in an open and closed position. *International journal of biometeorology*, 46(3), (2002), 150-156.
- [9] C.Tuchinda, S.Srivannaboon, H.W.Lim, Photoprotection by window glass, automobile glass, and sunglasses. *Journal of the American Academy of Dermatology*, 54(5), (2006) 845-854.
- [10] J.Cadet, A.Grand, T.Douki, Solar UV radiation-induced DNA Bipyrimidine photoproducts: Formation and mechanistic insights. *Top Curr. Chem.* 356: (2015) 249–275.
- [11] S.Mouret, A.Forestier, T.Douki, The specificity of UVA-induced DNA damage in human melanocytes. *Photochem. Photobiol. Sci.* 11 (2012) 155–162.
- [12] E.Sage, P.M.Girard, S.Francesconi, Unravelling UVA-induced mutagenesis, *Photochem. Photobiol. Sci.* 11 (2012) 74–80.
- [13] C.Battie, S.Jitsukawa, F.Bernerd, S.del Bino, C.Marionnet, M.Verschoore, New insights in photoaging, UVA induced damage and skin types. *Exp. Dermatol.* 23 (2014) 7–12.
- [14] A.Q. Khan, J.B. Travers, M.G. Kemp, Roles of UVA radiation and DNA damage responses in melanoma pathogenesis, *Environ. Mol. Mutagen*, 21 (2018) 21
- [15] A.Parisi, D.J.Turnbull, Shade provision for UV minimization: A Review, *Photochemistry and Photobiology*, 90 (2014) 479-490.
- [16] P.Gies, J.Makin, Dobbinson S, Javorniczky J, Henderson S, Guilfoyle R, Lock J. Shade provision for toddlers at swimming pools in Melbourne. *Photobiol. Photochem.* 89 (2013) 968-973.

- [17] D.Li, Z.Li, Y.Zheng, C.Liu, L.Lu, Optical performance of single and double glazing units in the wavelength 337–900 nm, *Solar Energy* 122 (2015) 1091–1099.
- [18] C.Liu, Y.Wu, Y.Zhu, D.Li, L.Ma, Experimental investigation of optical and thermal performance of a PCM-glazed unit for building applications, *Energy and Build.* 158, (2018) 794-800.
- [19] A.Milon, P.E.Sottas, J.L.Bulliard, D.Vernez, Effective exposure to solar UV in building workers: influence of local and individual factors, *J. Expo. Sci. Environ. Epidemiol.* 17, (2007) 58-68.
- [20] P.Gies, J.Wright, Measured solar ultraviolet radiation exposures of outdoor workers in Queensland in the building and construction industry, *Photochem. Photobiol.* 78 4 (2003) 342-348.
- [21] N.Hakansson, B.Floderus, P.Gustavsson, M.Feyching, N.Hallin, Occupational sunlight exposure and cancer incidence among Swedish construction workers, *Epidemiology* 12 5 (2001) 552-557.
- [22] J.Turner, A.Parisi, Investigation of correlation of broadband UVA reflection to broadband visible reflection for variety of surfaces in the built environment. *Building and Environment*, 138 (2018) 259-268.
- [23] R.B. Setlow, The wavelengths in sunlight effective in producing cancer: a theoretical analysis. *Proceedings of the National Academy of Sciences USA*, 71 (1974) 3363-3366.
- [24] J.A.MacLaughlin, R.R. Anderson, M.F. Holick, Spectral character of sunlight modulates photosynthesis of previtamin D₃ and its photoisomers in human skin. *Science*, 216 (1982) 1001-1003.
- [25] Commission Internationale de l'Eclairage (1998) Erythema Reference Action Spectrum and Standard Erythema Dose. CIE S007E-1998. CIE Central Bureau, Vienna, Austria.
- [26] S.D.Flint, M.M.Caldwell, A biological spectral weighting function for ozone depletion research with higher plants. *Physiologia Plantarum* 117 (2003) 137-144.
- [27] S.D. Flint, M.M. Caldwell Field testing of UV biological weighting functions for higher plants. *Physiologia Plantarum* 117 (2003) 145-153.

- [28] M.F.Holick, Vitamin D: Importance in the prevention of cancers, type 1 diabetes, heart disease and osteoporosis. *Am. J. Clin. Nutr.* 79 (2004) 362-371.
- [29] M.F. Holick, The vitamin D epidemic and its health consequences. *J. Nutr.*: 135: (2005) 2739–2748.
- [30] M. F. Holick, Vitamin D deficiency, *N. Engl. J. Med.* 357 (2007) 266–281.
- [31] M.F.Holick, T.C.Chen, Z.Lu, E.Sauter, Vitamin D and Skin Physiology: A D-Lightful Story. *Journal of Bone and Mineral Research*, 22 (2) (2007) 28-33.
- [32] O. Engelsen, The relationship between ultraviolet radiation exposure and vitamin D status, *Nutrients*. May; 2(5) (2010) 482-95.
- [33] A.Hosseini-Nezhad, M.F.Holick, Vitamin D for health: A global perspective. *Mayo Clin. Proc.* July: 88(7) (2013) 720-55.
- [34] P.Pludowski, M.F. Holick, S. Pilz, C.L.Wagner, B.W. Hollis, W.B. Grant, Y.Shoenfeld, E. Lerchbaum, D.J.Llewellyn, K.Kienreich, M.Soni, Vitamin D effects on musculoskeletal health, immunity, autoimmunity, cardiovascular disease, cancer, fertility, pregnancy, dementia and mortality- a review of recent evidence, *Autoimmun Rev.* Aug. 12(10) (2013) 976-89.
- [35] C.F.Garland, J.J.Kim, S.B.Mohr, E.D. Gorham, W.B.Grant, E.L. Giovannucci, L. Baggerly, H. Hofflich, J.Ramsdell, K.Zeng, R.P.Heaney, Meta-analysis of all-cause mortality according to serum 25-hydroxyvitamin D. *Am. J. Pub. Health.* Aug,104(8) (2014) 43-50.
- [36] W.B.Grant, 25-Hydroxyvitamin D and breast cancer, colorectal cancer, and colorectal adenomas: case-control versus nested case-control studies, *Anticancer Res.* 35(2) (2015) 1153-60.
- [37] S.L.McDonnell, C.Baggerly, C.B.French, L.L.Baggerly, C.F.Garland, E.D.Gorham, J.M.Lappe, R.P. Heaney, Serum 25-Hydroxyvitamin D Concentrations ≥ 40 ng/ml Are Associated with $>65\%$ Lower Cancer

Risk: Pooled Analysis of Randomized Trial and Prospective Cohort Study. PLoS One. 2016 Apr 6; 11(4): e0152441.

[38] M.K.Bogh , A.V.Schmedes , P.A.Philipsen , E.Thieden, H.C.Wulf, Vitamin D production depends on ultraviolet-B dose but not on dose rate: a randomized controlled trial. *Exp. Dermatol.* 20(1) (2011) 14–18.

[39] M.K. Bogh, A.V. Schmedes, P.A. Philipsen, E. Thieden, H.C. Wulf, A small suberythemal ultraviolet B dose every second week is sufficient to maintain summer vitamin D levels: a randomized controlled trial, *Br. J. Dermatol.* 166 (2012) 430–433.

[40] K.Va'ha'vihu, L.Ylianttila, H. Kautianen, Narrowband ultravioletB course improves vitamin D balance in women in winter, *Br. J. Der-matol.* 162 (2010) 848–53.

[41] A.R.Webb, R.Kift, J.L.Berry, L.E.Rhodes, The vitamin D debate: Translating controlled experiments into reality for human sun exposure times, *Photochem. Photobiol.* 87 (2011) 741–745.

[42] Z. Lagunova, A.C. Porojnicu, L. Aksnes, M.F. Holick, V. Iani, O.S. Bruland, J. Moan, Effect of vitamin D supplementation and ultraviolet B exposure on serum 25- hydroxyvitamin D concentrations in healthy volunteers: a randomized, crossover clinical trial, *Br. J. Dermatol.* 169 (2013) 434–440.

[43] E. Sallander, U. Wester, E. Bengtsson, D. Wiegleb Edstrom, Vitamin D levels after UVB radiation: effects by UVA additions in a randomized controlled trial, *Photodermatol. Photoimmunol. Photomed.* 29 (2013) 323–329.

[44] M. Grigalavicius, J. Moan, A. Dahlback, Vitamin D and ultraviolet phototherapy in Caucasians *J Photochem Photobiol B*, 147 (2015) 69-74.

[45] M.Rivas, E.Rojas, M.C.Araya, G.M.Calaf, Ultraviolet light exposure, skin cancer risk and vitamin D production, *Oncol. Lett.* 10 (2015) 2259-2264.

- [46] T.Karppinen, M.Ala-Houhala, L.Ylianttila, Narrowband Ultraviolet B Exposures Maintain Vitamin D Levels During Winter: A Randomized Controlled Trial, *Acta Derm. Venereol.* May, 96(4) (2016) 490-493.
- [47] F. O’Sullivan, E. Laird, D. Kelly, J. van Geffen, M. van Weele, H. McNulty, L. Hoey, M. Healy, K. McCarroll, C. Cunningham, M. Casey, M. Ward, J.J. Strain, A.M. Molloy, L. Zgaga, Ambient UVB dose and sun enjoyment are important predictors of vitamin d status in an older population, *J. Nutr.* 147 (2017) 858–868.
- [48] Landsberg, G.S. Óptica. Editorial Mir. Moscú 1983.
- [49] Ocean Optics (<https://www.oceaninsight.com/products/spectrometers/>) Accessed on 25 of February 2020.
- [50] T.B.Fitzpatrick The validity and practicality of Sun reactive skin types I through VI. *Arch. Dermatol.*124 (1988) 869–871.
- [51] M.A. Serrano, J.Cañada, J.C. Moreno, G. Gurrea. Solar, Ultraviolet Doses and Vitamin D in a northern mid-latitude, *Science of the Total Environment*, 574 (2017) 744–750.
- [52] UV-B Radiation THE ULTRAVIOLET INDEX Network. Accessed on 12 of February 2020. (<http://www.agroambient.gva.es/es/web/calidad-ambiental/datos-historicos-uv>).
- [53] R.L.McKenzie, J.B.Liley, L.O. Björn, UV Radiation: Balancing Risks and Benefits. *Photochemistry and Photobiology*, 85 (2009) 88-98.
- [54] F.Fernández-Rojas, C.Frenández-Rojas, K.J. Salas, V.J.García, E.Marinero, Conductividad térmica en metales, semiconductores, dieléctricos y materiales amorfos. *Rev. Fac. Ing. UCV Caracas* 23 (2008) 5-15.
- [55] A.Morales, F.Pérez, Caracterización por espectroscopía en el infrarrojo de óxidos de silicio depositados en ambiente de N₂O, *Superficies y Vacío* 16(2) junio (2003) 16-18.

[56] V.Serini, Polycarbonates. In Ullmann's Encyclopedia of Industrial Chemistry (Ed.) 2000. Doi.org/10.1002/14356007.a21_207.

[57] J.R.Velanda, Identificación de polímeros por espectroscopía infrarroja. Revista Ontare 5, (2017) 115-140.

[58] R.B.Setlow, E.Grist, K.Thompson, A.V.Woodhead, Wavelengths in the induction of malignant melanoma, Proc. Nat. Acad.Sci. 90 (1994) 6666-6670.

[59] R. Bouillon, J. Eisman, M. Garabedian, M. Holick, J. Kleinschmidt, T. Suda, I. Terenetskaya, A. Webb, Action Spectrum for the Production of Previtamin D3 in Human Skin, UDC 612.014.481-06 CIE Vienna, 2006.