Solution processed oxygen and moisture barrier based on glass flakes for encapsulation of Organic (Opto-) Electronic Devices

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**Abstract**

The concept of transparent barriers against oxygen and water based on polymer films filled with glass flakes is presented. Barriers are prepared by casting PVB films containing glass flakes of different aspect ratios at different loadings to systematically study the effect of these parameters on barrier quality and optical transmission. It is found that the glass flakes are distributed homogeneously in the PVB film, with an almost perfect orientation of the long axes of the platelets parallel to the film surface. For glass flakes having an aspect ratio of 2000, barrier films with optical transmittance exceeding 85% and water vapor transmission rates of 0.14 g.m-2.day-1 are obtained at a glass loading of 25 vol%. The haze of the glass flake filled PVB films, which is mainly due to surface roughness of the films according to optical simulations, is reduced by coating a smoothing layer on top. The barrier properties persist even after 20,000 cycles of bending at a radius of 3 cm. The lifetime of organic solar cells (OSCs) increases to beyond 1000 h under damp heat conditions as well as under constant illumination, when the devices are encapsulated with the PVB/glass flake composite films.

1. Introduction

Organic electronics, namely organic light emitting diodes, organic solar cells (OSCs), and organic field effect transistors have opened up new fields of application, attributable to their intrinsic characteristics, e.g., light weight, mechanical flexibility and semitransparency.[1–5] This is especially true for organic solar cells, as these properties make them the perfect choice for mobile chargers and building integration.[4,6,7] Very recently, organic photovoltaics have experienced a boost of power conversion efficiencies to over 17% [8] on the cell level and of almost 13% on the module level, [9,10] which brings them into the same league as inorganic thin film technologies. Another intriguing property of organic electronics is their printability which allows large scale roll-to-roll processing, using flexible substrates.[1,11] However, in order to be viable in the market, such products should offer not only high efficiencies at low cost, but must also show adequately long lifetimes.[12–14] As the degradation of unprotected organic devices is primarily caused by oxygen and water [15–19], their lifetime can be extended significantly by encapsulation with appropriate barrier materials. Hauch *et al*. [20] have shown that for OSCs a barrier material having water vapor transmission rate (WVTR) of about 10-3 g m2 day-1 @ 25 oC/40%RH can serve well to provide lifetimes of 3-5 years. From the product’s point of view, it is important that the encapsulation does not compromise the appealing qualities of the devices. Thus, the barrier material should be flexible, optically transparent, light weight and cost efficient.[21,22] For obtaining medium quality barriers at reasonable cost, solution processed barriers are promising alternatives to those manufactured by vacuum assisted vapor deposition techniques.[23–25] An advantage of solution processed barriers is the possibility to coat them in-line on top of the device to be encapsulated. In some cases, e.g. for devices of 3-dimensional shape, coating is often the only possible way of applying barriers.

There are mainly two approaches for manufacturing transparent barrier films by solution processing,[25] namely coating polymer substrates with impermeable films, e.g., by converting precursor inks to metal oxide layers,[23] and employing the tortuosity concept, i.e., coating polymer films filled with transparent high aspect ratio platelets,[26,27] which increase the diffusion path lengths of permeant molecules. WVTR values of down to 10-3 g.m-2.day-1 have been reached using nano-clay platelets.[28] Gaume *et al.* [29] produced a barrier film of polyvinyl alcohol filled with Montmorillonite nanoclay particles and thus reduced oxygen permeation by a factor of around seven. These barrier films were employed for the encapsulation of poly(3-hexylthiophene-2,5-diyl) (P3HT): [6,6]-phenyl-C61-butyric acid methylester (PCBM) based OSCs. Under irradiation by a solar simulator, OSCs encapsulated with PVA/nanoclay films exhibited lifetimes improved by 60% as compared to cells encapsulated with PET barrier.

In this work, we use glass flakes of different aspect ratios (AR; the ratio of the diameter of the flake to its thickness) as filler particles because they offer several favorable properties with respect to their use in transparent and flexible barriers.[30] Glass flakes are available in large quantities at low cost and are easily incorporated in a wide variety of polymers. They are transparent in the visible range of the spectrum with refractive indices which are close to those of the polymer matrices in which they are incorporated. They offer large aspect ratios and are easily aligned parallel to the film surface during the coating process, due to their large lateral extension which is on the same order as the film thickness. Due to their particulate nature, the resulting barrier is expected to be resilient towards bending.

Polyvinyl butyral is selected as the polymer matrix because it is easily processed and offers high flexibility and shows excellent adhesion [24,30,31] to almost all kinds of materials. Moreover, PVB can maintain high transparency along with good dimensional stability.

The PVB/glass flake composite films will first be investigated with respect to their optical properties. The effect of the glass flakes on total and diffuse transmittance of the barrier will be investigated by experiment and simulation. While haze of encapsulation materials can be even beneficial for solar cells,[32] it is an undesired effect for other optoelectronic devices, especially for those included in display applications. Therefore, the role of glass flake induced surface roughness of the films on transmission haze will be scrutinized.

Finally, the barrier performance of the composite films will be demonstrated by encapsulating printed organic solar cells, which will then be subjected to more than 1000 hours of accelerated degradation tests, both in damp heat and under constant illumination.

1. Material and methods

## Materials

Glass flakes (thin platelets of glass, typically having thicknesses of less than a micrometer and average diameters of 100 µm to 300 µm) with nominal aspect ratios of 200, 400, and 2000 (as specified by the manufacturer) were purchased from Eckart GmbH, Germany. PVB was purchased from Sigma Aldrich Chemie GmbH, Germany. Commercial barrier foil was purchased from Mitsubishi (VIEW-BARRIER, VD-K3DA). All the coatings were produced by doctor blading (ZAA 2300, manufactured by Zehntner Testing Instruments, Switzerland). PET substrates were purchased from DuPont.

## Preparation of the barrier coatings

PVB was dissolved in benzyl alcohol with 30 wt% concentration. The solution was stirred at 80 oC on a hot plate for a few hours. As soon as the solution became homogenized, glass flakes were blended in the solution at different volume fractions (): 0 vol%, 5 vol%, 10 vol%, 15 vol%, 20 vol%, 25 vol%, 30 vol%. Once the glass flakes had been properly dispersed in the PVB matrix, the solution was exposed to vacuum for at least 15-30 mins to extract entrapped air from the solution. Barrier films were prepared by depositing the disperision onto PET films by doctor blading. Coating was performed at low coating speeds, i.e., , and the blade gap was varied between 500 – 2000 µm. After the coating, the samples were positioned in an oven at 80 oC for complete evaporation of the solvent. The layers were peeled off the subrates and characterization was carried out on free standing layers.

## Encapsulation of organic photovoltaic devices

Bulk heterojunction organic photovoltaic cells of inverted structure (glass/indium tin oxide (ITO)/ZnO/poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/Ag) were prepared and subsequently encapsulated with PVB/glass flakes based barrier using UV cured adhesive. The devices were prepared on ITO coated glass substrates having sheet resistances of 21 Ω/. All the layers were coated via doctor blading in ambient conditions except the top silver electrode which was vapor deposited. After coating, the ZnO layer was annealed for 5 min at 120 oC in air. The P3HT:PCBM blend with a ratio of 1:0.8 (wt/wt) was coated via doctor blading from o‑xylene:1-methylnaphthalene (19:1, v/v) solution. A layer of PEDOT:PSS was prepared from HTL Solar diluted with 1:1 ratio in water. After deposition of all layers, the silver (Ag) (50 nm) top electrode was deposited by thermal evaporation in ultrahigh vacuum (10-4 Pa) through a mask to define an OSC active area of 0.1 cm2. The thickness of the Ag film is kept as small as 50 nm to avoid any additional gas barrier effect. Initial current voltage characteristics and power conversion efficiencies were measured in inert atmosphere. After the initial measurement, the OSC was encapsulated by lamination with PVB/glass flakes-based barriers or a commercial barrier (Mitsubishi VD-K3DA, 70 µm film thickness, having moisture permeation of < 3\*10-3 g.m-2.day-1 at 40°C and 90% RH) by means of a 10 – 20 µm thick layer of commercial epoxy based adhesive (DELO Katiobond LP655), which was subsequently cured with UVA ~400 nm light for 2 minutes.

## Characterization

### Spectroscopic analysis

A Perkin Elmer Lambda 950 double beam spectrometer including a 150 mm integrating sphere with a photomultiplier and an InGaAs detector was used for the optical measurements of PVB films with and without fillers. For measurement, the samples were positioned in the transmission and reflection ports of the sphere with the rougher side facing illumination.

### Permeability measurements

Moisture permeability measurements were performed using an M7002 water vapor permeation analyzer (SYSTECH Illinois, UK), having lower detection limits of 0.02 g.cm.m-2.day-1 or 0.002 g.cm.m-2.day-1, depending on the size of the sample. Oxygen permeation was measured by using an oxygen permeation chamber equipped with optical oxygen sensing spot PSt9 (Manufactured by PreSens Precision Sensing GmbH) with a detection limit of 0.1 cm3.m-2.day-1.bar-1.

### Bending of the barrier layers

Bending fatigue tests were performed with an in-house developed dynamic cyclic bend testing machine, where one end of the barrier film is fixed and the other one is moved back and forth linearly thus cycling the film between its planar shape and the adjustable minimum bending radius. The sample size used in the mechanical flexibility test was 3 x 10 cm2. Three samples were employed for each test. The WVTR measurements after the bending were carried out on samples of 3 x 3 cm2, cut from the middle of the bent film.

### SEM images

Scanning electron microscopy (SEM) images were recorded using a JSM-7610F from JEOL with secondary electron image detector. For operation at 2 kV accelerating voltage, a working distance of 6 mm in low probe current mode (~65 nA) were used. An r-filter expands the capabilities by allowing selective electron detection from the specimen according to the energy range. Secondary electrons, backscattered electrons, or a mixture of both were detected to create images. SEM cross section samples were prepared by braking at low temperature (liquid nitrogen cooling) or using an IB-19500CP cross section polisher.

### Accelerated lifetime experiments

In the accelerated lifetime tests, the effect of different encapsulation foils on the lifetime of the OSC devices is determined under well controlled conditions. The devices were encapsulated with three different types of flexible and transparent barrier foils: either with a neat PVB film of a thickness of 125 µm, with a glass flakes/PVB composite film of between 80 µm and 210 µm in thickness, or with a commercial barrier (Mitsubishi barrier film of a thickness of 70 µm with a specified WVTR of 3 \* 10-3 g m-2 day-1). The encapsulation was carried out by laminating the barrier films onto the devices using a UV curable adhesive (DELO Katiobond LP655) in the glove box.

The encapsulated devices were positioned in an artificial weathering chamber (ESPEC LHL-114), with the pre-set condition of 40 oC and 85%RH. Accordingly, degradation tests were performed under the same conditions that were used to measure the barrier characteristics. To analyze degradation by light, the encapsulated devices were placed under continuous irradiation in ambient air in the chamber of a SUNTEST XXL+ sun simulator (Atlas Materials Testing Technology GmbH) with daylight filter. The light source is a Xenon lamp with an irradiation intensity set to 60 W/m² in the range of 300-400 nm, which corresponds to 1000 W/m² over the full spectral range. The chamber temperature was kept at 40 °C, while the black body temperature was 65 oC.

Current-voltage characteristics and power conversion efficiencies of the solar cells were measured during the ageing experiments by a LOT solar simulator (Class AAA) at 1000 W/m². For this purpose, the solar cells were taken out of the respective ageing chambers and put back after the measurement.

1. Results

## Barrier performance of PVB/ glass flake composite films

In the following, the barrier properties of free standing PVB/glass flake composite films as obtained by water vapor transmission rate (WVTR) as well as oxygen transmission rate (OTR) measurements will be characterized and compared to those of neat PVB films and commercial barriers.

### Water vapor permeability

Pristine PVB films of 70 µm in thickness show WVTR of 65 g.m-2.day-1 (@40 °C/85% RH). Upon addition of glass flakes, the WVTR values are reduced significantly, due to the increasing tortuous path length. The WVTR decreases with both, increasing AR and growing volume fraction of the glass flakes (**Table 1** and **Fig. S1**). The smallest WVTR value of 0.14 g.m-2.day-1, corresponding to a permeability of 3\*10-3 g.cm.m-2.day-1, is achieved for glass flakes with an AR~2000 at 25%. This corresponds to a reduction of the permeability with respect to the value of pristine PVB by a barrier improvement factor of BIF = 150.

**Figure 1** shows the development of the BIF with increasing volume fraction of the glass flakes. BIF of 30, 56 and 150 are achieved for glass flakes with aspect ratios of 200, 400 and 2000, respectively for the layers containing 25 vol% of the flakes. The plot alsoshows a comparison of theexperimental values of the BIF for different AR (200-2000) to Bharadwaj’s theoretical model (Eq. 1), which gives the BIF as a function of the volume fraction of glass flakes, of their width, *L*, of their thickness, *W*, and of the order parameter, *S*.

Eq. 1

The experimental data is in fairly close match with Bharadwaj’s BIF, except for the higher loadings, especially for large aspect ratio flakes. The order parameter *S* is calculated from the SEM cross section image (***Figure 1*b**), wherein the average angle of orientation of the flakes with respect to the barrier film surface is found to be *θavg* = 4o, which corresponds to an order parameter of *S* = = 0.98. The main reasons for the difference between calculated and experimental BIF values are the wide distribution of aspect ratios around the mean value of AR = 2000 on one hand and defects in the stacking of the glass flakes, such as the voids visible in ***Figure 1*b**, on the other hand. These defects act as open diffusion paths for the permeating gas and thus increase permeability.

|  |  |
| --- | --- |
| a) | b) |
| ***Figure 1a)*** *Experimental barrier improvement factor (BIF) of the PVB/glass flakes composites vs. glass flakes volume concentration. Experimental data (symbols) are compared to calculated BIF values according to Bharadwaj’s model, calculated for S = 0.98, (dotted lines) for the flakes with AR~200 (black), AR~400 (blue) and AR~2000 (dark yellow).* ***b)*** *SEM cross section image of PVB filled with 25 vol% of glass flakes of AR~2000.* | |

**Table 1** WVTR (@40 oC/85 % RH) and OTR (@25 °C) of PVB films filled with different concentrations of glass flakes with AR ~2000.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Water vapor permeability | | | | | |
| G. flakes vol% | Thickness  µm | WVTR  g.m-2. day-1 | Permeability  g.cm.m-2.day-1 | BIF | calculated |
| 0 | 70 | 65 | 0.45 | 1 | 1 |
| 5 | 78 | 2.1 | 0.017 | 26 | 34 |
| 15 | 150 | 0.24 | 0.0035 | 109 | 110 |
| 25 | 160 | 0.14 | 0.003 | 160 | 210 |
| Oxygen permeability | | | | | |
| G. flakes vol% | Thickness  µm | OTR  cm3.m-2. day-1.bar-1 | Permeability  cm3.cm. m-2. day-1.bar-1 | BIF |  |
| 0 | 90 | 110 | 0.98 | 1 | 1 |
| 5 | 80 | 4.8 | 0.04 | 25 | 34 |
| 15 | 190 | 0.45 | 0.008 | 122 | 110 |
| 25 | 210 | 0.35 | 0.007 | 140 | 210 |

### Oxygen permeability

Neat PVB films show OTR values of 110 cm3 m-2 day-1 bar-1. The incorporation of glass flakes reduces the OTR significantly (**Table 1**). The PVB film filled with 5 vol%, 15 vol% and 25 vol% of glass flakes with AR = 2000 exhibits OTR values of 4.8 cm3.m-2.day-1.bar-1, 0.45 cm3.m-2.day-1.bar-1, and 0.35 cm3.m-2.day-1.bar-1, respectively. The lowest permeability of is cm3.mm.m-2.day-1.bar-1obtained for 25 vol%, which corresponds to a BIF of 140*.* The BIF values determined from oxygen permeation show, within the accuracy limits of the experiment, the same dependence on the volume fraction of glass flakes as the BIF in the case of humidity permeation (**Fig.** **S2**). This is in accordance with the tortuous path model, which assumes that the improvement of the barrier with increasing filler content does not depend on the nature of the diffusant, as long as it does neither permeate nor interact with the filler particles. Oxygen permeability can thus also be predicted by Bharadwaj’s model.

## Flexibility

Flexibility is one of the key requirements for water and oxygen barriers for flexible OSCs. Therefore, the barriers based on glass flakes were subjected to bending tests with a bending radius of 3 cm. For this purpose, the PVB film containing 15 vol% glass flakes of AR = 2000 was selected. The WVTR value of the layer equals 0.24 g.m-2.day-1 before and after 20,000 bending cycles (**Figure 2**). Furthermore, no visible damage to the film is observable after bending. Obviously, the glass flakes always return to their initial position after bending, neither loosing adhesion to the PVB matrix nor damaging it. For PVB films with a content of 25 vol% glass flakes, an increase of ~21% in WVTR is observed after 20,000 bending cycles, which indicates interaction of adjacent flakes during their movement by bending.



**Figure 2** WVTR of a PVB film with 15 vol% glass flakes (AR = 2000) vs. number of bending cycles using a bending radius of 3 cm.

## Transparency of the layers

Neat PVB films (thickness ~70 µm) deposited by doctor blading show a total transmittance of ~93% throughout the visible range of the spectrum, while diffuse transmittance increases con­tinuously from 5% at 800 nm to 12% at 400 nm, due to scattering at crystalline domains (**Figure S3**). Total reflectance of ~7% is observed in the visible region of the spectrum. The diffuse reflectance shown by the PVB layer increases steadily from 3% at 800 nm to 7% at 250 nm.

Corresponding transmittance and reflectance measurements were carried out for the PVB/glass flake composite layers (**Figure 3**). PVB layers filled with glass flakes having aspect ratios of 200 and 400 show total transmittance values of around 90%, even at the highest glass loading, whereas for AR = 2000, the total transmittance decreases from 89% to 85% with increasing volume fraction of glass flakes. The total reflectance is between 8% and 9% for all samples, while the absorption by the glass flakes is significant only below 350 nm. We postulate that the drop in transmittance can be attributed to measurement artefacts induced by pronounced light scattering at the rough surface of samples with AR = 2000. In a previous work we demonstrated that such scattering can lead to underestimation of total transmittance when measuring it using an integrating sphere, as some amount of the scattered light can be lost at the sides of the sample [33]. These observations confirm the results of Scharfe et al.,[30] who found that the glass flakes are ideally suited as filler particles for PVB films, as the total transmittance of the film remains around 90% even at high glass loading and thus is hardly reduced with respect to pristine PVB. This is mainly due to the almost perfect refractive index matching of soda lime glass (*n* @550 nm = 1.52) and PVB (*n* @550 nm = 1.48).

In contrast to total transmittance, diffuse transmittance varies significantly with the concentration of glass flakes. For glass flakes of aspect ratios of AR = 200 and 400, diffuse transmittance remains around 5% and 10% for concentrations of 5 vol% and 15 vol%, respectively, but for 25 vol% the diffuse transmittance inreases to around 30% at 550 nm (**Figure 3**). For glass flakes of AR = 2000, all of the glass flake loadings show a high diffuse transmittance of around 33%. Diffuse reflectance in all cases remains around 6% (**Fig. S4**).

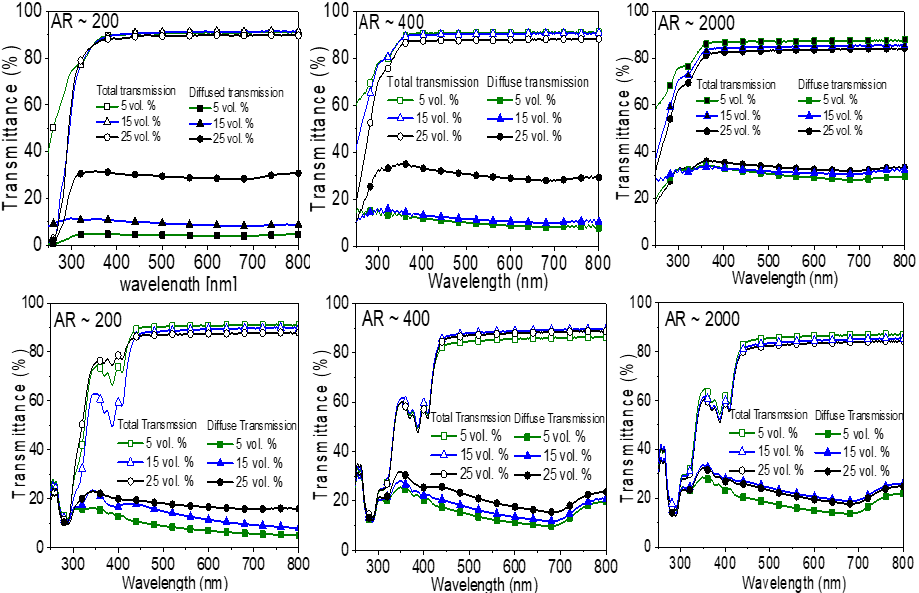


Figure 3 Total and diffuse transmittance spectra of PVB films filled with 5-25 vol% of glass flakes of different AR, without and with epoxy smoothing layers (top and bottom row, respectively).

The high degree of haziness of PVB/glass flake composite films, especially at high glass loadings, has already been recognized by Scharfe et al. [30] and ascribed to the enhanced surface roughness of the glass flakes containing films. This interpretation is coroborated by the confocal micrographs in **Figure 4** and **Fig. S5**, whichexhibit considerable surface roughness on the order of 100 µm. This surface roughness is attributed to the large lateral extension of the glass flakes (200-300 µm), together with their high volume fraction. As soon as the solvent starts to evaporate, the PVB matrix contracts around the flakes and as a result leaves behind substantial surface roughness.

Scharfe et al. reduced the surface roughness by a combined vacuum and heat treatment between polished steel plates and subsequent lamination of the film between glass plates for optical measurements. In order to comply with the requirements of an industrial roll-to-roll process, we chose a different approach, which consists in the deposition of an additional UV curable epoxy layer on both sides of the glass flakes filled PVB layers. The epoxy layer reduces the roughness of the sample surface from 20 µ RMS to < 1 µm RMS (**Figure 4**). The epoxy polymer was selected because of its easy processing and solvent free nature, which avoids re-dissolution of the PVB layer. Additionally, the refractive index of the epoxy is *n* @550 nm = 1.51, which ideally matches the glass flakes (*n* @550 nm = 1.52).

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| --- | --- |
|  |  |
| **Figure 4** Confocal images of a PVB film containing 15vol% of glass flakes of AR =2000 without (left) and with (right) epoxy smoothing layer. | |

The optical behaviour of the epoxy coated composite films is summarized in the bottom row of **Figure 3**, which shows the dependence of diffuse transmittance at 550 nm on glass loading, before and after coating epoxy onto both sides of the PVB/glass composite films. The additional epoxy layers slightly reduce total transmittance, due to absorption of UV light and enhanced reflectance at the surfaces of the epoxy layers. However, the most striking effect of the smoothing layer is the significant reduction of haze in all those cases where diffuse transmittance in the uncoated composite films exceeds values of 30%. This is the case for the highest loading of 25 vol% with the flakes of AR = 200 and AR = 400 as well as for all loadings with the flakes of AR = 2000. The epoxy layer has no significant effect on haze for all PVB/glass flake composites for which diffuse transmittance is only around 10%. These observations suggest that there is a certain extent of light scattering by the bulk film, but that a substantial part of diffuse transmittance is caused by the surface roughness introduced by the glass flakes.

In order to quantify the contributions of glass particles inside the PVB matrix and at its surface to diffuse transmission, light scattering by the PVB/glass flake composite was modeled by optical simulations. For this purpose, an optical model of light scattering and propagation in polymer filled with particles, developed at the University of Ljubljana,[34] was integrated in the optical simulator CROWM (Combined Ray Optics / Wave Optics Model),[34,35] which is based on the combination of three-dimensional ray tracing and transfer matrix methods to analyze light propagation in thick and thin layers, respectively.

In the first step, the optical transmittance at 550 nm of a single glass flake of refractive index *n* = 1.525, [31] fully surrounded by a PVB matrix of *n* = 1.49,[36] is simulated for different angles θ of light incidence, corresponding to different tilting angles θ of the surface normal of the glass flake against the surface normal of the PVB film. In these simulations, the glass flake was taken as an infinite slab with a thickness of 1 μm. The results presented in ***Figure 5a*** reveal that up to tilt angles of θ=70°, 99 % of light is transmitted through the flake, retaining the specular direction of propagation. Reflectance is virtually negligible at these angles, due to the very small refractive index contrast between the glass flake and the surrounding PVB. Only above tilt angles of 70°, reflectance becomes large enough so that the reflected (scattered) component becomes „visible“ as a loss in the transmitted light. In realistic samples, however, it is not expected that flakes would be tilted by more than 10° (as seen from ***Figure 1*b**), which already suggests that bulk scattering should not have a dominant effect on the overall light scattering properties of the layers.

To study this further, the entire 200 μm thick PVB layer embedded with glass flakes was simulated in the second step. In these simulations, the volume concentration of the flakes was varied from 5 to 30 %, while each individual flake was assumed to be randomly oriented in any direction. The only control of flake orientation was imposed by the maximum tilt angle θ; for some specified θ, each flake was assumed to be randomly rotated around the Z axis and also randomly tilted up to the maximal tilt angle θ. To simplify simulations, however, the individual flakes were still treated as 1 μm slabs with plane-parallel surfaces, while for the purpose of modelling they were treated as point objects (i.e., no crossing of the flakes, and no AR dependency). While these simulations are therefore not expected to provide exact results in terms of absolute values, they should provide valid trends from which the scattering behaviour of the studied layers can be discerned.



a)

b)

***Figure 5 a)*** *Simulated direct/total transmittance of a single glass flake filled in PVB matrix at a wavelength of 550 nm for different polarizations of the incident light.* ***b)*** *Simulated transmittance (total and diffuse) (@550 nm) of PVB films filled with glass flakes at different particle volume concentrations having random tilt and random rotation around the vertical axis.*

The results of these simulations are presented in ***Figure 5b***. It can be seen that the effect of flake tilting is negligible for maximum tilt angles below 70°, which is in line with the previous results of isolated flakes. Only above maximum tilt angles of 70°, the total transmittance of the layer experiences a slight drop while the diffuse transmittance begins to increase to more substantial values. As already mentioned, however, such extreme tilting is not expected in realistic layers where glass flakes are mostly well aligned.

From these simulations, it is to be concluded that light scattering due to the inclusion of glass flakes into the PVB film does not lead to a significant reduction of total transmission, which is in perfect accordance with the experimental data. However, the simulations also demonstrate that the pronounced haze of the sample without epoxy layers cannot be attributed to bulk scattering alone. Therefore, other causes for significant haze values are investigated in the following.

To investigate the influence of surface roughness on the haze theoretically, we have performed further simulations where the surface was modeled according to confocal microscope measurements of the surface relief of the respective films with and without the additional epoxy smoothing layer (see ***Figure 4***). For the first set of simulations, the bulk of the film was assumed as homogeneous, i.e. not containing any glass flakes, while for the surface morphology we applied the measured surfaces of the two samples with AR = 2000 and ΦS= 5% without and with the smoothing layer. Therefore, only surface scattering was considered in these simulations, and no volumetric scattering at the glass flakes. We obtain transmission haze values of 76% and 2% for the films without and with the smoothing layer, respectively. Similarly, when applying the surface scans of samples with AR = 2000 and ΦS = 15%, the simulated transmission haze values are 75% and 0.5%, respectively (see Tab. S3 for all the results). Then, in the second set of simulations, we also considered volumetric scattering by including the glass flakes in the model. Since we wanted to test the most extreme case of volumetric scattering, we assumed that the flakes can be randomly oriented in any direction (maximum tilt angle of θ=90°). For the samples with AR = 2000 and ΦS = 5%, we obtained transmission haze values of 78% and 10% for the films without and with the smoothing layer, respectively, and for AR = 2000 and ΦS=15%, we obtained values of 78% and 9%. From these results it can be concluded that the light scattering behavior of these films is by far dominated by surface scattering at the uneven surface of the fabricated layers, so that consequently the addition of a smoothing layer results in a clear reduction of the haze.

We have to note that the calculated haze values are significantly higher than the measured ones for the films without smoothing layer. This discrepancy may be explained by artifacts, i.e. high frequency noise, in the measurements of the surface relief. With respect to the films with the smoothing layer, the measured haze values are slightly higher than the calculated ones, which could be explained by residual air bubbles and glass flakes debris with tilting angles exceeding θ=70°. Both these effects are hard to quantify and were therefore not included in the modeling.

## Lifetime of OSC

For accelerated lifetime testing of photovoltaic devices, organic solar cells based on the active layer system P3HT:PCBM, whose degradation behavior is well characterized, [19] were prepared on standard glass/ITO substrates. Each glass substrate contained six solar cells of 0.1 cm² active area. For each lifetime test, a total of nine substrates were examined, of which three substrates each were laminated with the same barrier foil, namely (1) a commercial high-quality barrier foil, (2) PVB/ glass flakes composite barrier films, and (3) pristine PVB films.

### Damp heat

For the damp heat degradation tests, the encapsulated solar cells were placed in a climate chamber with controlled test conditions of 40 oC and 85% RH. These conditions were chosen to be compatible with those at which the WVTR were measured. **Figure 6** provides the degradation data of the samples within 1040 hours of exposure to damp heat conditions. (Note: the corresponding current-voltage (J-V) curves can be found in **Fig. S6**).



**Figure 6** Damp heat degradation test (40 °C/85% RH) of P3HT:PCBM-based devices encapsulated with commercial high-quality barrier foil (70 µm thick) Mitsubishi (black), PVB films (160 µm thick) filled with 25 vol% glass flakes (AR = 2000) (red), and pristine PVB (90 µm thick) films (blue). a) Power conversion efficiency (PCE), b) short-circuit current (JSC), c) fill factor (FF), and d) open-circuit voltage (VOC). Error bars represent the standard deviations for 18 cells.

A constant loss of PCE is observed for the devices encapsulated with pristine PVB films (blue data points). The device parameter affected most is the short-circuit current, which primarily causes the PCE of the device to drop below 80% of its initial value after ~500 h (“t80”). In contrast, the devices encapsulated with either the commercial barrier foil (black data points) or the PVB/glass flakes composite film (red data points) do not show such degradation behavior and do not reach their t80 lifetime within 1040 h in damp heat. Since water ingress through the barrier foil into the photovoltaic device is known to be the limiting factor under these conditions, [21] the PVB/glass flakes composite film is obviously capable of preventing this process to happen (as good as the commercial barrier foil) within the duration of this experiment.

### Constant irradiation

For the sun degradation test, OSCs encapsulated with PVB / glass flakes composite films and, for reference purposes, with pristine PVB films as well as with commercial Mitsubishi films were subjected to constant irradiation by a solar simulator (“Suntest”) providing 1000 W m-² @ 65 °C black body temperature. **Figure 7**shows the photovoltaic key parameters (PCE: power conversion efficiency, Jsc: short-circuit current, FF: fill factor, Voc: open-circuit voltage) of the encapsulated devices during the course of this accelerated lifetime experiment. Devices comprising the commercial barrier (black data points) show a slight decrease in JSC and FF, which, however, only accounts for ~15% PCE loss at the end of the experiment. Consequently, as for the damp heat degradation, the devices exhibit a t80 lifetime of more than 1040 h also under constant irradiation.

The devices encapsulated with pristine PVB films (blue data points) degrade rapidly, again especially in JSC, but in this case also in FF and VOC, reaching 80% of their initial PCE value already after 50 h of irradiation. This infers that PVB is not a good barrier against oxygen, since oxygen is known to be the main culprit for degradation under these conditions, due to photo-oxidation of the photoactive materials of the solar cell.[15,19] This is in line with the changes observed in the J-V curves of the devices (see **Fig. S6**), namely a pronounced loss in JSC and FF together with an increased series resistance.

Remarkably, the devices encapsulated with the PVB/glass flakes composite films (red data points) show the same degradation curve as the commercial reference, including a t80 lifetime that lies beyond the time span of the experiment (>1040 h). This is the same behavior as previously observed in the damp heat experiment, which means that the glass flakes do not only effectively prevent water ingress into the device, but they also successfully hamper oxygen transmission through the PVB-based encapsulation foil and, by this, prevent degradation of the photovoltaic device.



***Figure 7*** *Sun degradation test (1000 W/m² constant irradiation) of P3HT:PCBM-based devices encapsulated with commercial high-quality barrier foil (70 µm thick) from Mitsubishi (black), PVB films having thickness of 210 µm filled with 25% v/v glass flakes (AR = 2000) (red), and pristine PVB films (90 µm thick) (blue). a) Power conversion efficiency (PCE), b) short-circuit current (Jsc), c) fill factor (FF), and d) open-circuit voltage (Voc). Error bars represent the standard deviations for 18 cells.*

# Conclusion

For the first time, transparent and flexible barriers for organic electronic devices have been prepared on the basis of glass flakes embedded in a polymer matrix. WVTR values of as little as 0.14 g.m-2.day-1 have been achieved, by maximizing the aspect ratio and by aligning the glass flakes with the film surface, thus maximizing the order parameter of the Bharadwaj equation. BIF values of around 140 have been achieved against both moisture and oxygen with ~2000 aspect ratio glass flakes. At the same time, the layers maintain a total optical transmittance of around 90%, along with an increase in the diffuse part of transmission, caused by the glass flakes induced surface roughness of the barrier films. As predicted by optical modeling, epoxy based smoothing layers reduce the transmission haze.

Bending tests show that the barrier quality remains unchanged even after 20,000 bending cycles, which proves the good adhesion of the PVB matrix to the glass flakes.

Application of the PVB/glass flakes composite films as barriers for the encapsulation of organic solar cells affords a significant increase of the lifetime of the devices in damp heat as well as under constant illumination. In the case of the sun irradiation test, the t80 lifetime of OSCs is extended from 50 h to beyond 1040 h.

In summary, PVB/glass flake composite films show excellent properties with respect to barrier quality, optical transmission, and flexibility. Considering that these films can be easily produced in roll-to-roll coating processes from low-cost raw materials, they have a high potential as cost-effective and environmentally friendly encapsulation films for printed electronics.

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Solution processed oxygen and moisture barrier based on glass flakes for encapsulation of Organic (Opto-) Electronic Devices

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**ToC text:**

Poly(vinylbutyral)/glass flake composite films processed from solution are flexible as well as highly transparent and show barrier improvement factors of up to 150 against oxygen and moisture. Upon encapsulation with these films, the lifetime of organic solar cells is enhanced from few hours to beyond 1000 hours under accelerated ageing conditions.

**ToC figure:**

