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Textile solar light collectors based on models for polar bear hair

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ABSTRACT

Concepts of technical fibers following models for the polar bear hair to be used for textile solar collectors are discussed. The approach to coat fibers with a thin layer into which fluorescent dyestuff was dispersed was studied experimentally. Modified fibers made of different polymers were characterized with respect to optical properties relevant for the bionic model. In the case of poly(methylmethacrylate) fibers, the envisaged effect could be achieved to high efficiency. The optical performance could be enhanced by ultrasonic dispersion of the dyestuff in the coating matrix. The effect is less significant in semi-crystalline fibers such as poly(ethylene terephthalate), which is attributed to diffuse scattering.

1. Introduction

Technical textiles find increasing application in industries as diverse as automotive, aerospace, medical, and are also used as components in industrial facilities and machinery. Besides building construction, an innovative field of application is modern architecture where textile products are used as design elements and/or (large area) roofs. Nowadays, textile roofs constructed from coated fabrics are found worldwide in, e.g., football or tennis arenas, airport malls, hangars to name but a few.

As highly specialized products, technical textiles are produced to high standards and, making use of modern concepts of material science and soft matter physics, provided with specific surface properties and function. Besides topics such as the creation of depot and release functions [1], biological activity [2,3], or catalytic function of fibers [4]—to name but a few—, present research concentrates on fibers acting as sensor and energy-transforming properties, the latter aiming at the use of fibers or textiles as solar energy collectors or photovoltaic transformers. One application of interest could be, e.g., life boats and jackets, the textile forming a flexible power supply for GPS or radio units. On the other hand, solar collector functions would form an innovative functionality of the textile roofs mentioned before.

A first approach to photovoltaic thin-layer structures on flexible textile fabrics has been published lately by Knittel et al. [5]. Using standard deposition methods, the authors established Cu(In,Ga)Se_2-structures on fabrics, which were coated before the deposition process in order to give a smooth surface. Thermo-stable materials, e.g. glass fibers, had to be chosen for fibers and coating material because of the temperatures involved with the deposition process. While these photovoltaic systems show a rather high efficiency, one drawback is the opaque nature of the finished textiles, which reduces their applicability for textile architecture, which largely relies on translucent-coated fabrics.

Alternative solutions have been sought after, one potential concept being the optical function of the hair of the polar bear as proposed by Grojean et al. [6,7], Tributsch et al. [8] and Nachtigall [9] to describe the solar collector function of the bear's fur. In the model of these authors—referred to as, Tributsch's model' in the following—the fur is regarded as a heat pump (inverse Carnot cycle). Here, the function of the hair within the cycle is the capture of optical (solar) energy and its transport to the bear's skin, where it is absorbed and transformed into thermal energy. In Tributsch's model, certain optical properties are attributed to the hair which form the background of the work presented here. The following considerations refer to his principal paper [8].

Basic optical functions of the hair are scattering of incident light into the hair, wavelength-shifted luminescence and wave guide properties due to total reflection. The hair has an opaque, rough-surfaced core, called the medulla, which scatters incident light. Luminescent centers in the medulla specifically absorb the UV part of incident light and emit with a wavelength shift of about 100 nm. As was experimentally found, illumination at 352 nm provokes luminescence over a broad spectral range with a maximum between 420 and 490 nm through a Stokes process [8]. In this process, conservation refers to number of photons, not the energy flux. As described in Tributsch's original work [8], the

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flow of fluorescent energy in all directions, Q_s, is given by

$$Q_s = Q_a \frac{(v_e - v_a)}{v_a}, \quad (1)$$

where Q_a is the incident optical energy, v_a the frequency of absorbed light, v_e the frequency of the emitted (fluorescent) light, and $\Delta v = v_e - v_a$ the frequency shift. Due to the smooth outer surface of the hair, a part of the fluorescent light is transported to the bear's skin as in a fiber optic wave guide. The actual solar energy conversion within the heat pump cycle involves the absorption of the fluorescent light by the black skin. According to Eq. (1), a high energy conversion can be expected from high frequency shifts. With wavelengths as stated by Tributsch et al. [8] for the polar bear hair, the frequency shift is of the order of 2×10^{14} Hz.

Tributsch's model has been discussed heavily in the past mainly with regard to the hypothesis of the wave guide function of the hair (exemplary papers can be found in Refs. [10–14]). This aspect has been studied experimentally by light transmission measurements in various animal hairs, but also glass plates.

Irrespective of the merits of Tributsch's model as well as the diverging points raised by other authors, the fundamental concept has a certain potential to design optically active textile fibers and textile solar collectors manufactured from these fibers. Accordingly, the scope of the work reported here was to evaluate a technical layout of fibers to achieve an optical activity as postulated for the polar bear hair. Fiber polymers under study were poly(methylmethacrylate) (PMMA), with well-established wave-guiding properties, and poly(ethylene terephthalate) (PET), a typical fiber polymer for technical textiles. The fibers were optically modified on laboratory scale and characterized with respect to longitudinal light transmission, i.e. wave guide properties, and fluorescence, i.e. 'polar bear' function.

2. Fiber concepts mimicking the polar bear hair

In general, highly oriented textile fibers made from polymers such as PET show an optical anisotropy. Due to the manufacturing process, a 'core–shell' structure with a higher orientation of the macromolecules at the surface than in the fiber core is generated. As a consequence, the refractive index varies over the fiber diameter (see e.g. Ref. [15]). In principle this would provide a certain wave-guiding property of the fiber. In order to achieve a 'polar bear hair' effect, organic or inorganic substances could be added to the polymer master batch before the spinning process. Substances could be fluorescent dyes or inorganic, particulate matter. While basically possible, this concept is connected to large-intensity losses along the light path due to scattering as will be further discussed in Section 4. More similar to Tributsch's model of the polar bear hair are concepts, where the generation and the transport of fluorescent light are confined to separate domains. Basically, three different geometries can be thought of.

(1) Rather similar to Tributsch's model of the polar bear hair, a bi-component fiber could be manufactured with a fluorescent core, i.e. fluorescing additive containing polymer, and a wave-guiding outer (Fig. 1a). Alternatively, this can be inverted with a wave-guiding core polymer and a fluorescing outer.
(2) Similar to the latter, a hollow fiber made of a fluorescing polymer would provide a wave-guiding core through the included air (Fig. 1b).
(3) A fiber with sufficient wave-guiding properties could be finished with an optically active, i.e. fluorescing, coating (Fig. 1c).

With regard to manufacturing on a larger scale, the latter concept variants have marked advantages. Hollow fibers, of which a textile fabric is to be produced, are easily spun on an industrial scale. Even more convenient, standard fibers or even the ready-made fabric can be coated according to the concept sketched in Fig. 1c.

3. Experimental

Experimental fibers according to the scheme shown in Fig. 1c used commercial core fibers made of PMMA supplied by Goodfellow GmbH, Germany; and PET supplied by Monofil-Technik, Hennef, Germany. Both fibers had a diameter of 1000 μm.

These fibers were coated with a matrix of 5% polyvinyl acetate (PVA) in methanol, into which fluorescent dyes were dispersed. On the background of their absorption and emission properties, 4,6-dimethyl-7-ethylaminocoumarin (Coumarin 2), 7-diethylamino-4-methylcoumarin (Coumarin 47), Stilbene 3 and 2,5-diphenyloxazole (PPO), which are supplied as laser dyes by Lambda Physics, Göttingen, Germany, were chosen for these experiments. According to the suppliers' specification, methanol was chosen as the solvent. As can be taken from the data given in Table 1, the absorption and emission wavelengths and the resulting wavelength shift of the dyestuffs are comparable to the properties of the polar bear hair, which has a luminescence maximum between 420 and 490 nm if illuminated at 352 nm [8].

In order to characterize the absorption properties of the fluorescent systems, absorption spectra of dyestuff solved in methanol as well as dispersed in the PVA matrix were measured using an EPP 2000 UVN spectrometer (StellarNet Inc., USA). These measurements were performed under variation of dyestuff concentration. Additionally, PMMA film was coated in a similar manner to the fibers, and characterized with regard to its absorption properties.

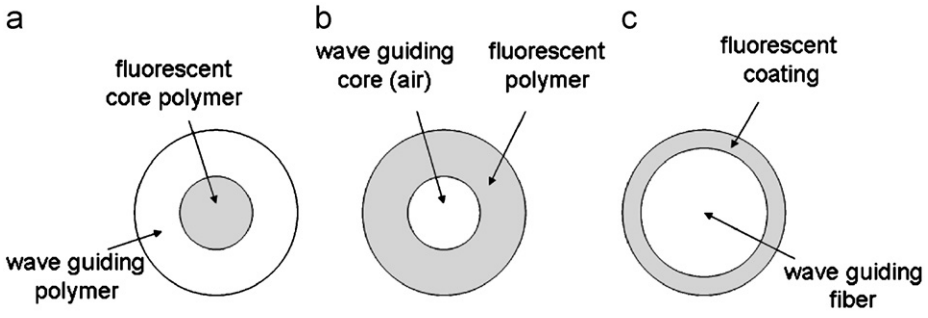
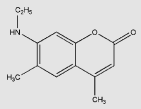
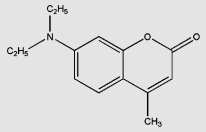
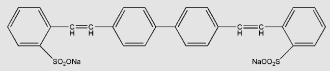
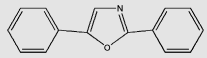


Fig. 1. Design concepts of optically active fibers: (a) bi component fiber; (b) hollow fiber; (c) coated fiber.

Table 1
Characteristic properties of laser dyes used as fluorescent media [16]

Dyestuff	Chemical formula	Molecular weight	Max. absorption at (nm)	Range of fluorescent light (nm)
Coumarin 2		217.27	366	430–490
Coumarin 47		231.29	373	440–490
Stilbene 3		568.74	350	410–460
PPO		221.26	303	360–390

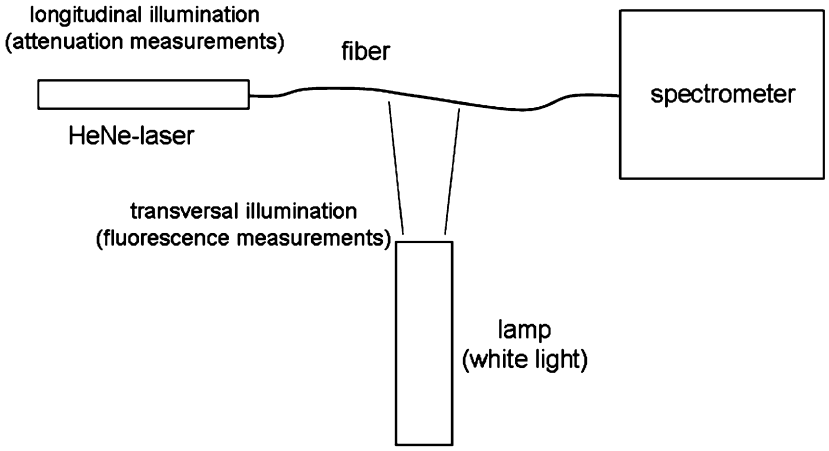


Fig. 2. Optical setup for the measurement if attenuation and fluorescence.

The optical setup for the characterization of the fiber properties is sketched in Fig. 2. For attenuation measurements, the fibers were illuminated with a 5 mW HeNe laser (623.8 nm), which was coupled into one end of the sample fiber. In order to measure fluorescent light the fibers were illuminated from the side using a 75 W Xenon short arc lamp with condensing/collimating lens assembly. The lamp was focused to illuminate the sample fiber over a length of 1 cm at a distance of 10 cm to the spectrometer input. The spectrometer was shielded to avoid stray light sampling.

In either case the transmitted or fluorescent light was collected at the fiber end and characterized using a fiber-optical spectrometer (Stellar Net EPP 2000 UV–vis). The fiber were coupled to laser and spectrometer using standard SMA-connectors into which the fiber ends were either pressed—in the case of the 1000 μm thick fibers—or glued using optical resin P501.

4. Results and discussion

A first set of measurements served to characterize the fluorescent systems as such. Absorption spectra were recorded of the dyestuffs (in methanol) as well as dyestuffs dispersed in PVA/methanol by photometry in dependence of the dyestuff concentrations. As is shown for the example of the dyestuff Coumarin 47 in Table 1, the specific extinction at 375 nm (maximum of the absorption band) is rather constant up to concentrations of 0.4 g/l. Dyestuff interaction affects the extinction at higher concentrations. Accordingly, the dyestuff concentration was 0.2 g/l in the ensuing experiments. Following dispersion in the PVA matrix, an increase in specific extinction of approximately 5% is observed.

Table 2
Specific extinction of the fluorescent dyestuff Coumarin 47 solved in methanol and dispersed in the PVA matrix ('coating matrix') at 375 nm

Dyestuff concentration (g/l)	Specific extinction of dyestuff solution ($mm^{-1}\,g^{-1}\,l$)	Specific extinction of coating matrix ($mm^{-1}\,g^{-1}\,l$)
0.1	98.8	95.6
0.2	98.6	102.2
0.4	97.7	101.4
0.6	90.0	Not measured

In order to estimate the thickness of the fluorescent layers, coatings were applied to PMMA film and characterized with regard to their absorption properties at 375 nm. Absorption spectra were recorded from coated film (dyestuff concentration 0.2 g/l) and from uncoated, i.e. 'as-received', film and the differential spectra calculated. Assuming an extinction of 102.2/$mm^{-1}\,g^{-1}\,l$ (cf. Table 2), a coating thickness of the order of 3.5 μm

can be estimated from the experimental data. This is in agreement with additional SEM analyses of coated fibers.

A second set of experiments was focused on the wave-guiding properties of the uncoated 'as-received' fibers, i.e. attenuation of transmitted light, and the scattering of incident light by the fiber polymer, if illuminated sidewise. Both aspects form essential factors in the 'Tributsch-model'.

As a typical material for wave guide fibers, PMMA exhibits a very low attenuation of transmitted light. Standard literature states attenuation coefficients of the order of 125–150 dB/km at 650 nm [17]. In the case of the 'textile' PET fibers, attenuation measurements were made in the framework of this work. The monochromatic light of a HeNe laser was coupled into the ends of PET fibers of varying length and the transmitted light analyzed using the fiber-optical spectrometer as sketched in Fig. 2. The use of the spectrometer allowed to identify the actual laser signal at 632.8 nm and to quantitatively determine the intensity of this signal, only. The experimental data are shown graphically in Fig. 3 in the form of intensity as a function of fiber length, $I(x)$. From the experimental data, a mean attenuation coefficient of 172 ± 10 dB/m (at 632.8 nm) can be calculated, which is approx. 3 orders of magnitude higher than the attenuation coefficient of PMMA.

In order to analyze the wave-guiding behavior of the PET fiber over greater lengths qualitatively, a logarithmic fit was made to the data taken from fibers of 15 to 18 cm length, only. The fit is also plotted in Fig. 3. It can be seen, that the measured values divert from the ideal fit at larger fiber lengths and are smaller than would be expected from Beer's law. Although the deviation from the Beer-behavior is small, the effect is experimentally verified by multiple measurements. This is attributed to the light-scattering effects due to the characteristic polymer structure of PET fibers as shall be discussed below.

In an ideal wave guide, one would assume a damping behavior according to Beer's law, i.e. $I(x)$ following an exponential function. In the case of PET, however, it has to be stated that the polymer basically does not absorb in the visible spectrum. Accordingly, (amorphous) PET films are in general totally clear.

In contrast to film, however, commercial PET fibers have a degree of crystallinity of the order of 80% [18]. In the production process, the fiber, i.e. the macromolecules, are highly drawn, a typical draw ratio being of the order of 6. The high orientation of the macromolecules is frozen-in during the cooling process. As a consequence, the fiber is composed as a side-by-side arrangement of fibrils—a regular sequence of triclinic crystal domains and domains of low order as can be shown by small-angle X-ray scattering (SAXS) [18]. The structure is well defined with regard to the fibrillar orientation (approx. 6° to the fiber axis) and the distance of crystal centers (12 nm). Given this, the attenuation of light traveling along the fiber is governed by scattering losses.

The strong light scattering by the 'textile' PET fiber is also seen in the spectra recorded at the end of fibers, which were illuminated sidewise using a white light lamp (Fig. 4). In the spectral range between 500 and 1000 nm, the intensity of light recorded at the PET fiber end is approximately 10 times as large as is in the case of the PMMA fiber, in spite of the markedly higher transmission losses. The shorter wavelengths of the lamp spectrum—i.e. smaller than 500 nm—are not recorded at the end of the PET fiber. The PMMA fiber is more homogeneous and doesn't show similar effects. Accordingly, the recorded intensity is low at all wavelengths despite the good light transmission in the PMMA fiber.

For further experiments, fibers were prepared according to the concept sketched in Fig. 1c, i.e. finished with an optically active coating, thus mimicking the polar bear hair. PMMA fibers were chosen in these experiments to minimize effects originating from the described light scattering by the fiber polymer itself. The coatings—a matrix of 5% PVA in methanol—were filled with the five different laser dyes specified in Table 1. The control sample was a fiber coated with the blank PVA matrix. Again, the fibers were illuminated from the side, and light recorded at the fiber ends. The respective spectra are shown in Fig. 5. The data show a significant increase of the fluorescent light intensity compared with the control sample. The signal is amplified by factors of 100 (Coumarin 2, PPO) to 300 (Stilbene 3) in the spectral range of emission between 400 and 500 nm. From the significant intensities recorded in the spectral range from 500 to 800 nm, however, it can be concluded that non-fluorescent scattering of incident light by the fiber polymer contributes significantly to the overall signal.

One potential reason for the small contribution of fluorescence may be seen in insufficient dispersion of the dyestuffs in the PVA matrix with a significant occurrence of agglomerates, which might affect the optical properties of the matrix.

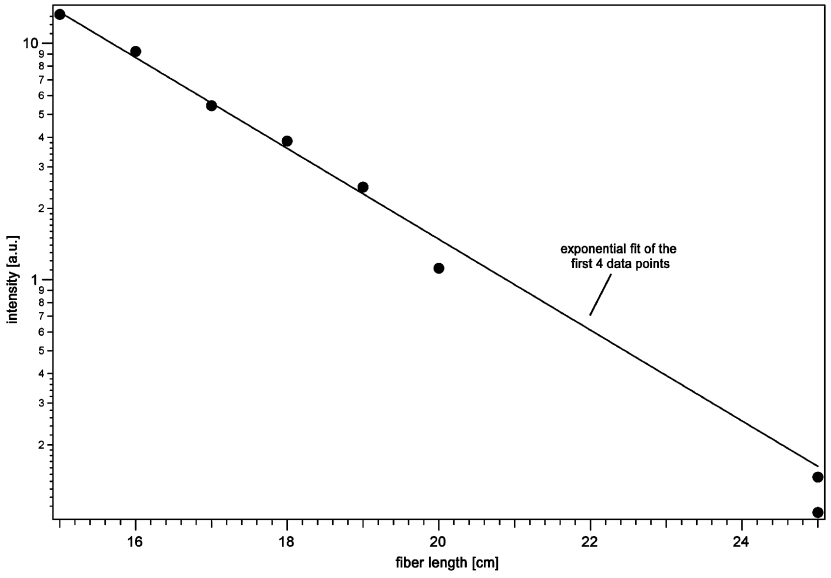


Fig. 3. Light attenuation of the PET fiber. A HeNe laser was coupled into the end of fibers of varying length and the transmitted light measured at the opposite end using the fiber-optical spectrometer. The data points show the transmitted intensity at 632 nm. *Note*: the exponential function (solid line) was fitted to the data taken from fibers of 15–18 cm length, only.

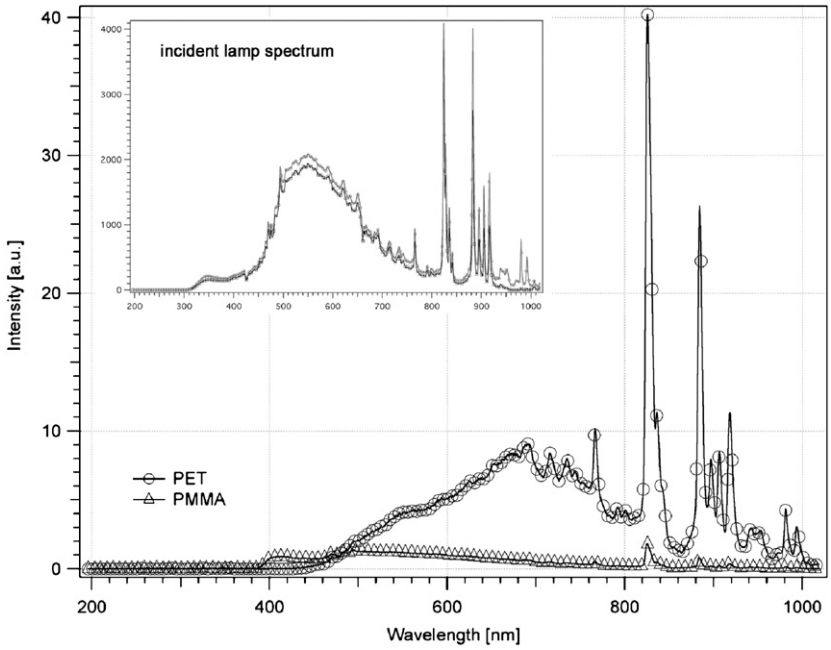


Fig. 4. Spectra as recorded at the end of uncoated fibers following illumination with the white light lamp. The spectra are normalized to show the actual relation of intensities. Inset shows the emission spectrum of the lamp.

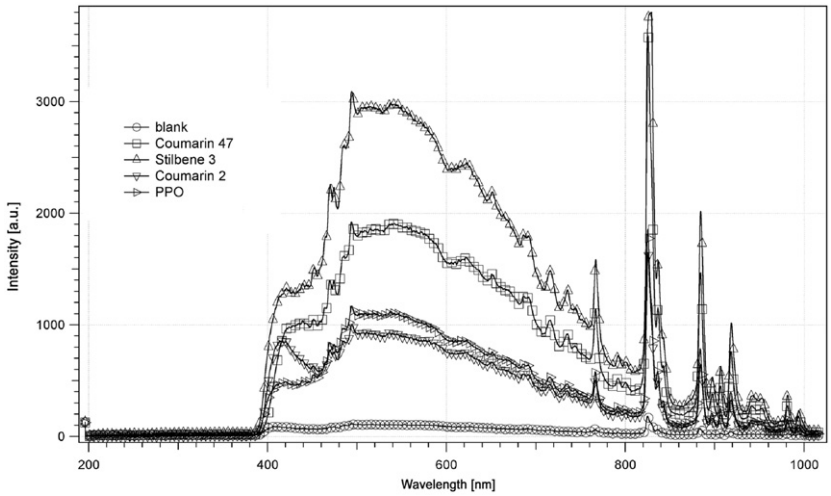


Fig. 5. Fluorescence spectra as recorded at the end of coated PMMA fibers following illumination with the white light lamp. Spectra are shown for the fiber coated with the blank PVA matrix—i.e. no dyestuff—and coated with dyestuff containing matrix. The spectra are normalized to show the actual relation of intensities.

In order to optimize dispersion, experiments were made dispersing the dyestuff into the PVA matrix over a couple of minutes in an ultrasonic bath, and coating the fiber in the ultrasonic bath, also. This was done in order to homogenize dispersion and to reduce the thickness of the optically active layer. According to the underlying concept, the ideal would be a closely packed monolayer on the fiber surface. The spectra presented in Fig. 6 have been recorded from (a) a fiber coated with the blank PVA matrix (control), (b) a fiber coated following the procedure of the earlier experiments, and (c) a fiber coated in the ultrasonic bath. The fluorescent dye was Coumarin 2 in both samples (b) and (c). As can be taken from the spectra, the preparation of the fiber in the ultrasonic bath has a remarkable effect. The signal in the main fluorescent range of the dyestuff (cf. Table 1) is amplified approximately by a factor of 10. It is notable, that the 'background' of direct light scattering by the fiber, i.e. scattering of incident light, is reduced as compared with sample (b). The shape of the spectrum is fully determined by the fluorescence spectrum of the dyestuff.

In order to investigate the effect of the ultrasonic dispersion on the optical properties of the PVA/dyestuff systems, PMMA film was coated with and without the application of ultrasound and the absorption properties measured. From these recorded spectra the absorption spectra of the actual coatings—i.e. the dyestuff containing PVA matrices—were calculated by subtraction of the absorption spectrum of the uncoated film. Exemplary spectra of Coumarin 47 containing coatings, which were applied with and without ultrasonic dispersion are shown in Fig. 7. It can be seen that the spectrum of the matrix dispersed with the aid of ultrasound mirrors the rather narrow absorption band of the

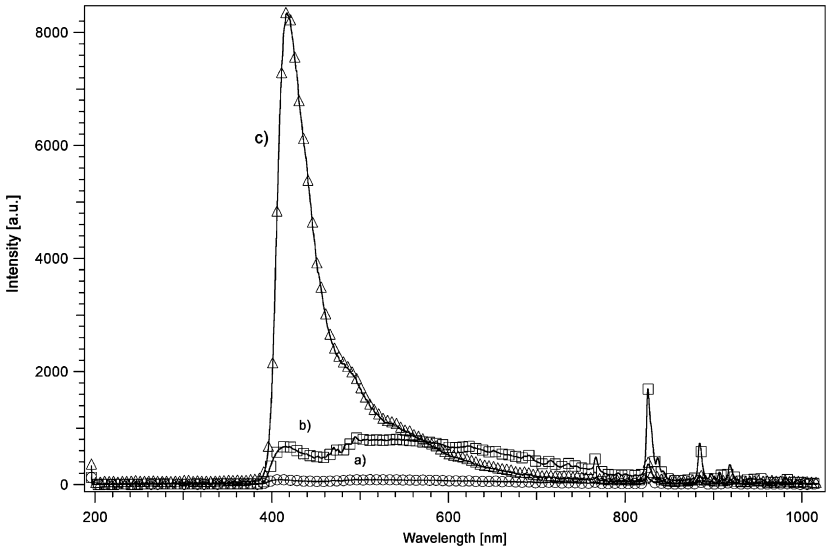


Fig. 6. Fluorescence spectra of coated PMMA fibers as recorded at the fiber end following illumination with the white light lamp. Spectra are shown for the fiber coated with the blank PVA matrix (a), a fiber coated with PVA matrix containing the fluorescent dye Coumarin 2 (b) and a fiber coated with dyestuff containing matrix in an ultrasonic bath (c). The spectra are normalized to show the actual relation of intensities.

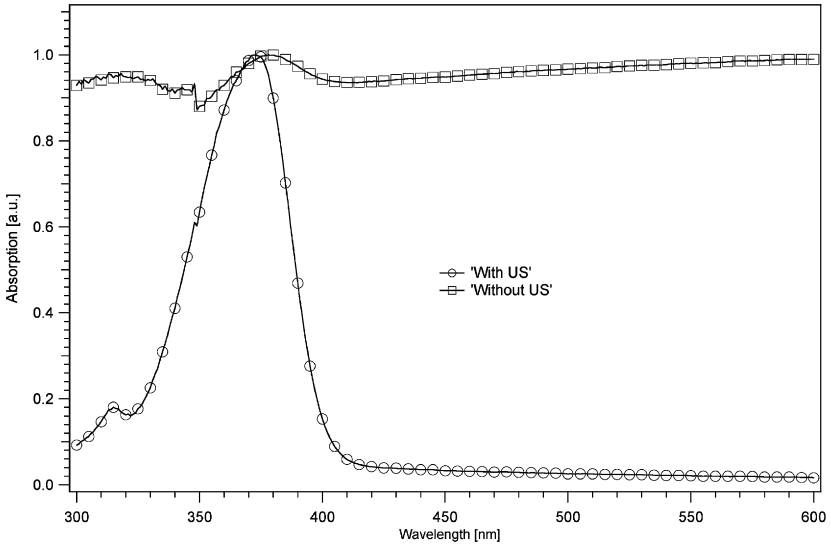


Fig. 7. Absorption spectrum of the fluorescent dyestuff Coumarin 47 dispersed in the PVA matrix. Shown are spectra from systems, which were prepared with and without the aid of ultrasonic dispersion. Note that the spectra are normalized to the absorption maximum at 375 nm.

basic fluorescent dyestuff. In contrast, the systems dispersed without the aid of ultrasound has a higher absorption at all wavelengths and absorbs especially in the range of 440–490, which is the fluorescent spectrum of Coumarin 47 (cf. Table 1). It may be concluded that the pronounced amplification of the fluorescent signal as exemplified by the spectra in Fig. 6 is due to effective dispersion of the dyestuff and minimized self-absorption in the optically active coating.

With regard to the envisaged application to technical textiles, it was of importance to perform similar experiments with a typical fiber polymer. As before, PET fibers were chosen as samples. On the background of the pronounced light scattering by the fiber polymer, as was discussed before (cf. Fig. 5), these experiments were only performed with fibers prepared in the ultrasonic bath. The concentration of the dyestuff—Coumarin 2 in all cases—and the duration of the pre-treatment of the dyestuff containing matrix were varied. The according fluorescent spectra are presented in Fig. 8. In general, the spectra indicate that the intensity of the light recorded at the fiber end can be increased by increasing dyestuff concentration, but also by increasing the duration of the pre-treatment—presumably optimizing the dyestuff dispersion. In the best example, the amplification factor is only about 3–4, which is in agreement with the integral attenuation coefficient of PET (see above). In contrast to the PMMA-based system, the recorded spectra do not mirror the spectral properties of the dyestuff with a maximum fluorescence between 430 and 490 nm, however, which indicates that in case of PET the signal is governed by scattering of incident light and not fluorescence. This assumption is supported by the comparison of the emission spectrum of the illuminating lamp and the recorded spectra with and without dyestuff in the PVA matrix (cf. Figs. 4 and 8, respectively). One may take from the spectra shown in Fig. 4 that the spectral range below 500 nm—which covers the fluorescence of the dyestuffs studied here—is not transported by the PET fiber.

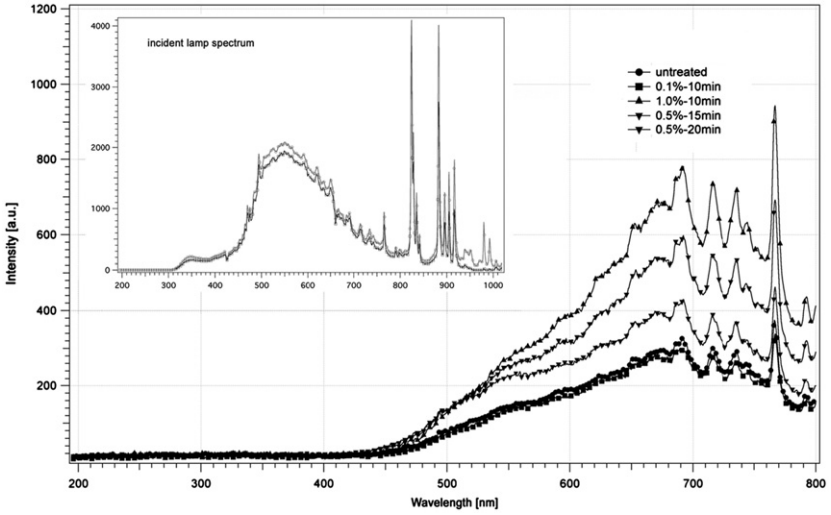


Fig. 8. Fluorescence spectra as recorded at the end of coated PET fibers following illumination with the white light lamp (emission spectrum is given in the inset). Spectra are shown for the fiber coated with the blank PVA matrix—i.e. no dyestuff—and coated with a matrix containing the fluorescent dye Coumarin 2 at varying concentrations. The matrix and the fibers were prepared in an ultrasonic bath, the duration of the pre-treatment varying from 10 to 20 min.

5. Summary and outloook

Making use of modern concepts of material science and soft matter physics, technical textiles are increasingly provided with specific surface properties and function. Present research concentrates on textiles with energy-transforming properties, aiming at the use of fibers or textiles as solar energy collectors or photovoltaic transformers. While being controversially discussed, the optical effect of the polar bear hair as postulated by Tributsch and others offers opportunities to design textile fibers for translucent textile collectors, which could be applied, e.g., for the construction of energy-converting textile roofs.

Concepts of technical fibers mimicking the polar bear hair were discussed and experimentally studied for one example. In this approach, the commercial fiber is coated with an optically active thin layer in the form of fluorescent dyestuff dispersed into a coating matrix. The envisaged optical effect could be achieved for the example of fibers made of poly(methylmethacrylate) (PMMA), which is a proven material for wave guide fibers. The effect is significantly reduced when using typical fiber polymers of technical textiles such as poly(ethylenterephthalate) (PET). The reduction is due to pronounced scattering and attenuation in the semi-crystalline fiber. The experiments indicated the need for optimized dispersion of the dyestuff in the coating matrix.

The fiber concept studied within the framework of this paper has the marked advantage of being applicable to fibers, but also to ready-made fabrics in the form of a coating process. On the background of the optical performance of the conventional fibers—as exemplified by the PET fiber in these experiments—future work could concentrate on the use hollow fibers, the air core providing the light transport.

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