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Energy Procedia 30 (2012) 471 – 477

Energy Procedia

SHC 2012

Thermotropic glazings for overheating protection

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Abstract

In this paper, the effect of material composition on the overheating protection performance of thermotropic systems with fixed domains (TSFD) is studied. Several thermotropic layers were formulated by variation of both, matrix material and thermotropic additive. Refractometry was applied in order to obtain refractive index data as a function of temperature of all material constituents and to screen wether material combinations are promising to formulate or not. Investigations concerning optical properties, switching temperature and switching process were carried out applying UV/Vis/NIR spectrometry. Morphological analysis was conducted with a Scanning Electron Microscope (SEM). Several TSFD showed reasonable light-shielding efficiency. Nevertheless further optimization of scattering domain size and shape is necessary to improve the light shielding performance.

Keywords: thermotropic glazings; overheating protection; material formulation

1. Introduction

Thermotropic systems with fixed domains (TSFD) change their light transmittance from transparent to light diffusing upon reaching a certain threshold temperature reversibly [1, 2]. Due to their autonomous temperature-triggered mode of operation, they are superior to actively operated shading devices which may be more prone to component malfunction [3]. Thus TSFD can provide efficient overheating protection for buildings as well as for solar thermal collectors [4, 5]. Especially for the establishment of solar collectors made from cost-efficient plastics thermotropic overheating protection is a key technology [5, 6]. TSFD consist of at least two components: a thermotropic additive as the minor component, which

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Selection and peer-review under responsibility of the PSE AG
doi:10.1016/j.egypro.2012.11.056

is finely dispersed in a matrix material [1]. Both components exhibit similar refractive indices at temperatures below the threshold temperature [1]. As a result incident solar radiation is not scattered and the TSFD appears transparent [1]. A mismatch of refractive indices of both components above the threshold temperature leads to intense scattering of radiation, which causes the layer to turn opaque [1]. TSFD formulated so far exhibit a reduction of solar hemispheric transmittance of less than 16% [7]. However, a reduction of solar transmittance of at least 25% is required for efficient overheating protection in an all-polymeric flat plate collector, when maintaining a solar transmittance of 85% below the threshold temperature [6]. Thus the major objective of this work is to establish structure-property-relationships between light-shielding performance and morphology of TSFD in order to reveal further material optimization potential.

2. Experimental

2.1. Characterization of TSFD constituents

Thermal transitions of thermotropic additives were determined by Differential Scanning Calorimetry (DSC). Thermograms were recorded under static air on a DSC 822^e (Mettler Toledo GmbH, Schwerzenbach, CH). A heating rate of 10K/min was applied. The sample mass was 10±1mg. Melting temperature was evaluated as peak temperature according to ISO 11357-1 from the second heating run. The data were averaged over two measurements.

A thermo mechanical analyzer TMA/SDTA 840 (Mettler Toledo GmbH, Schwerzenbach, CH) was utilized for characterization of thermal expansion of matrix materials and thermotropic additives. A heating rate of 5K/min was applied. Measurements were carried out in penetration mode with a load of 0.005N. Cuboid samples (4x4x~1mm³) were prepared. Samples were put into an Aluminum-pan for DSC in order to avoid pollution of measurement apparatus. Thermal expansion of the samples was corrected for the thermal expansion of the respective Al-pan detected by the TMA. Coefficients of thermal expansion were calculated from expansion data [8].

Refractive indices as a function of temperature of thermotropic additives and matrix materials were determined on an Abbé-type refractometer AR4 (A. Krüss Optronic GmbH, Hamburg, DE) equipped with a water bath to maintain operation temperature. Measurements were conducted in a temperature range between ambient temperature and a maximum of 90°C using a LED illumination unit with a wavelength of 589nm (Sodium D line). The temperature of the prisms was recorded with a two-channel temperature measurement instrument T900 (Dostmann electronic GmbH, Wertheim-Reicholzheim, DE) equipped with a precision K-type thermocouple. Refractive indices of matrix materials and thermotropic additives were averaged over three measurements.

2.2. Preparation of thermotropic systems with fixed domains

Various TSFD were manufactured by dissolving a thermotropic additive in a UV-curable resin matrix. Dissolutions were poured into the intervening space between two glass panes which were sealed around the edge. Samples were irradiated with a dose of 2.1J/cm² from a Mercury-lamp of a Light Hammer 6 equipped with a LC6E Benchtop Conveyor (Fusion UV Systems Inc., Gaithersburg, MD, US). Removal of glass panes resulted in 900µm thick free standing films. For the current investigation, four different types of resin systems (A, B, C and D) were selected, each consisting of 57wt% pre-polymer, 40wt% reactive diluent and 3wt% photo-initiator. Eleven different thermotropic additives (1 to 11) were utilized. Theoretical additive content of the dissolution was 5wt%. In consideration of mismatch of refractive index between several additive and matrix types already at low temperatures in total 36 material

formulations were prepared. As to nomenclature, a system denoted A1 consists of matrix A and thermotropic additive 1.

2.3. Characterization of formulated TSFD

Solar transmittance as a function of temperature, threshold temperature and switching process were characterized applying UV/Vis/NIR spectroscopy. A double beam UV/Vis/NIR spectrophotometer Lambda 950 (Perkin Elmer Inc., Waltham, MA, US) equipped with an Ulbricht-sphere (diameter 150mm) was utilized. A purpose built heating stage was located in front of the port hole of the Ulbricht-sphere in order to maintain sample temperature [9, 10]. Sample temperature was varied within a temperature range between ambient temperature and a maximum of 115°C with an increment of 5°C. Prior to measurement, the sample was equilibrated at the selected temperature for 5 minutes. Hemispheric and diffuse transmittance were recorded at normal incidence in the spectral region from 250 to 2500nm. The integral solar transmittance was acquired by weighting the recorded spectral data in steps of 5nm by the AM1.5 global solar irradiance source function. A single determination was carried out for each material.

Subsequently a comprehensive characterization of thermotropic layers as to relevant morphological parameters was performed. Scattering domain size and shape was determined applying microscopy techniques. An optical light microscope BX51 (Olympus Deutschland GmbH, Hamburg, DE) was utilized for characterization of morphological features. More in detail information on sample morphology was obtained by cracking the samples after immersion in liquid nitrogen and imaging the cracked surface with a Scanning Electron Microscope (SEM) DSM 962 (Carl Zeiss SMT AG, Oberkochen, DE).

3. Results

3.1. Light-shielding efficiency

In Fig. 1 the DSC trace upon heating of representative additive 4 (upper left) is shown along with refractive index as a function of temperature of matrix D and additive 4 (upper right). Furthermore solar

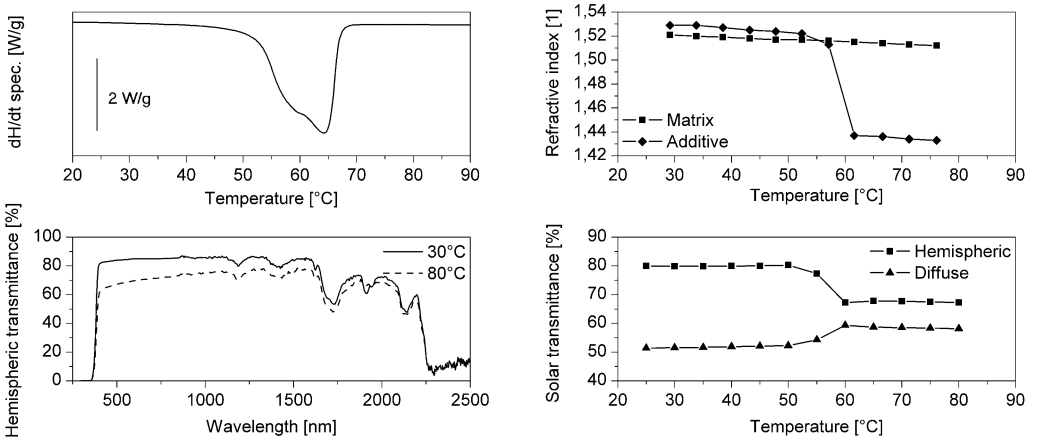

Fig. 1. DSC thermogram of additive 4 (upper left) along with refractive index as a function of temperature of matrix D and additive 4 (upper right). Hemispheric transmittance of TSFD D4 as a function of wavelength at 30°C and 80°C (lower left) and hemispheric and diffuse solar transmittance of TSFD D4 as a function of temperature (lower right).

hemispheric transmittance spectra of TSFD D4 at temperatures of 30°C and 80°C are depicted (lower left). Moreover hemispheric and diffuse solar transmittance as a function of temperature of TSFD D4 are displayed in Fig. 1 (lower right). Melting process of additive 4 corresponds to its refractive index change. Furthermore a good correlation of solar transmittance change with melting of the additive is observable. With the onset of melting of the additive, hemispheric and diffuse solar transmittance start to decrease and increase, respectively. Hemispheric and diffuse solar transmittance change from 79.9 and 51.3% at 25°C to 67.7 and 58.5% at 70°C, respectively. A rather steep switching process within a temperature frame of 10°C is observable. The switching threshold is 50°C.

Fig. 2 summarizes hemispheric solar transmittance at ambient conditions obtained for all thermotropic layers investigated within this study. Furthermore, Fig. 2 displays the achieved change in hemispheric solar transmittance upon heating for these TSFD. For efficient overheating protection of an all-polymeric solar thermal collector, a minimum hemispheric solar transmittance of 85% is required at ambient conditions [6]. Furthermore, a reduction of hemispheric solar transmittance by at least 25% is mandatory [6]. These limits are represented by the dashed lines in Fig. 2. None of the formulated TSFD can cope with the minimum performance requirements [6]. At ambient conditions, hemispheric solar transmittance varies between 58.9 and 85.3%. Changes of hemispheric solar transmittance by -31.8 up to +23.8% are detectable upon heating. Materials A2, A3, A8, B1, B2, B3, B5, B7, B8, B11, C1, C2, C3, D1, D2 and D3 display an increase in hemispheric solar transmittance upon heating. A decrease is observable for TSFD A4, A6, A7, A9, A10, A11, B4, B6, B9, B10, C4, C11, D4, D5, D6, D7, D8, D9, D10 and D11. The hemispheric solar transmittance reduction by -31.8% obtained for TSFD B4 is irreversible. Upon heating, formation of crack-like structures inside the layer is detectable, yielding opaque appearance. Comparison of hemispheric transmittance data obtained prior to heating up and after cooling down to ambient conditions confirms a significant irreversible portion of transmittance change for this layer. Layers C4 and D4 exhibit a significant reduction in hemispheric solar transmittance by -13.7 and -12.2%, respectively.

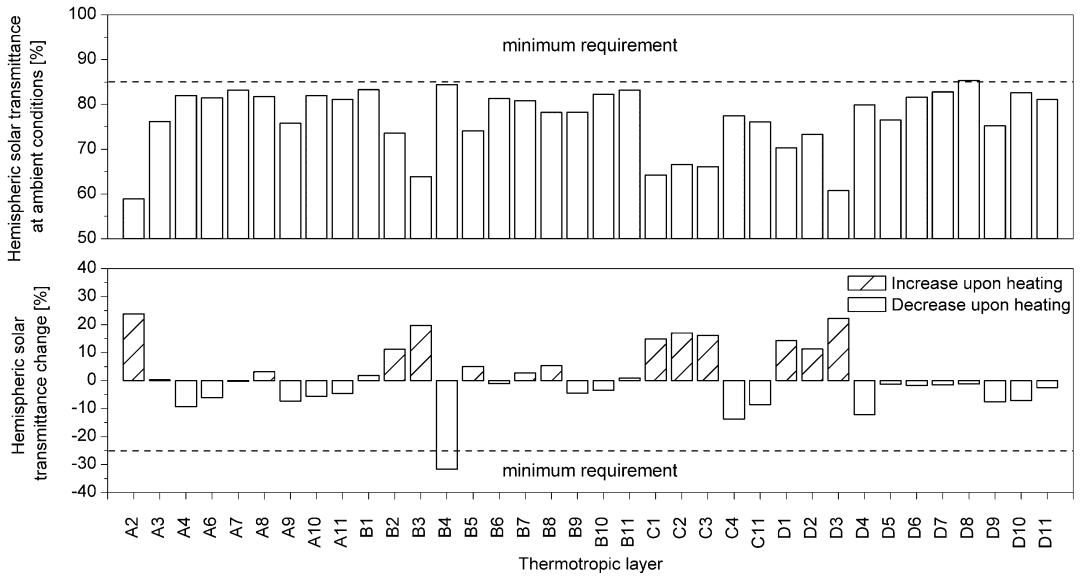

Fig.2. Hemispheric solar transmittance at ambient conditions of formulated TSFD (top) along with change of hemispheric solar transmittance upon heating (bottom).

Light-shielding efficiency of TSFD is dependent on refractive index difference between matrix and thermotropic additive and on scattering domain size and shape [11]. The difference in refractive index has to be minimized below the threshold temperature and maximized above the same in order to obtain sufficient light-shielding capability of thermotropic glazings [11, 12]. Refractive index data of the applied constituents suggest a reduction of hemispheric solar transmittance of all formulated TSFD without exception provided they exhibit a proper two-phase morphology. Thus in order to impart detailed knowledge on the detected different switching characteristics of the investigated TSFD, layer-morphology is addressed within the next sub-section.

3.2. Morphology

Maximum back-scattering is achieved with spherical scattering domains exhibiting diameters in the range between 200 and 400nm [11, 13]. Recent publications dealing with morphological aspects of TSFD revealed that scattering domains were anisotropic and/or exhibited sizes which are inappropriate for high back-scattering efficiency [9, 10, 14, 15].

In Fig. 3 representative SEM images are depicted for representative layers D4 and B3. Micrographs of TSFD D4 (Fig. 3, left) reveal disk-like scattering domains with diameters in the range between 19 and 85µm. Scattering domains are 0.7 to 6.9µm thick. Thus, moderate reduction of hemispheric solar transmittance by -12.2% can be attributed to inappropriate shape and size of scattering domains. Inappropriate shape and/or size of scattering domains for maximum back-scattering efficiency have been detected for all other TSFD displaying a reduction of hemispheric solar transmittance upon heating also (TSFD A4, A6, A7, A9, A10, A11, B4, B6, B9, B10, C4, C11, D5, D6, D7, D8, D9, D10 and D11). In the micrographs of TSFD B3 (Fig. 3, right) spherical scattering domains are distinguishable. Diameters range between 1.5 and 55µm. At the circumference of the scattering domain depicted in Fig. 3 a hole is evident. This hole is a vacuole.

Optical micrographs of layers A2, A3, B1, B2, B3, C1, C2, C3, D1, D2 and D3 displayed evidence for existence of vacuoles. These vacuoles are formed in the manufacturing process, due to different coefficients of thermal expansion of additive and matrix. Vacuoles in a thermotropic layer along with different coefficients of thermal expansion of additive and matrix were found to yield an increase in solar hemispheric transmittance above the switching threshold.

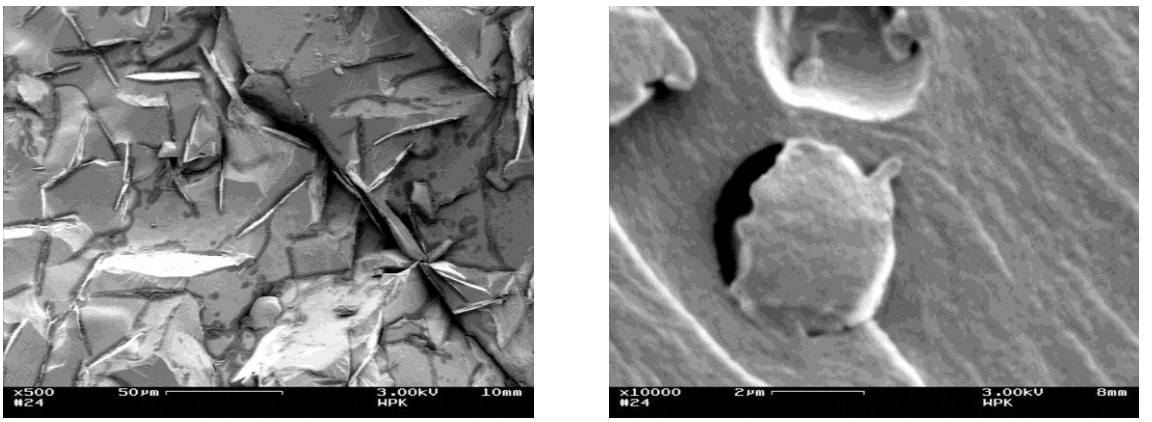

Fig. 3. Micrographs from SEM of TSFD D4 (left) and TSFD B3 (right).

4. Conclusion and outlook

In this study various thermotropic systems with fixed domains (TSFD) were formulated and characterized with regard to light-shielding efficiency and morphology. The investigated thermotropic layers exhibit a moderate overheating protection performance. Scattering domains exhibited anisotropic shapes and/or sizes which are inappropriate for high back-scattering efficiency. Further optimization of light-shielding efficiency of TSFD requires the adjustment of scattering domain size and shape. Furthermore, a mismatch of thermal expansion behavior of matrix material and thermotropic additive has to be avoided in order to suppress vacuole formation and thus detrimental effects on switching characteristic of TSFD. An optimization of layer performance comprising manufacturing process and material composition is currently under way.

Acknowledgements

This research project is funded by the State Government of Styria, Department Zukunftsfonds (Project number 5019). The authors wish to acknowledge the efforts of Andrea Schmid, who conducted the SEM measurements, and the contributions of Cytec Surface Specialities (Drogenbos, BE), Baerlocher GmbH (Unterschleissheim, DE), Chemson Polymer Additive AG (Arnoldstein, AT) and Brenntag CEE GmbH (Traun, AT).

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