Variable solar control using thermotropic core/shell particles

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ABSTRACT

Subject of our recent investigations is the utilization of a reversible thermotropic material for a self-regulating sun protection glazing that controls the solar energy input in order to avoid overheating. Based on the well-established UV curing technology for laminated glass a superior thermotropic material with tunable switching characteristics and of low material costs was developed. The polymer layer contains core/shell particles homogeneously dispersed in a UV-cured resin. The particle core in turn consists of an n-alkane mixture that is responsible for the temperature-induced clear/opaque switching. To obtain particles of well-defined size and with a narrow size distribution, the miniemulsion polymerization technique was used. The visible and solar optical properties (normal–normal, normal–hemispherical, and normal–diffuse transmittance) in the off (clear) and in the on state (opaque) were determined by UV/Vis/NIR spectroscopy. Samples containing particles of high median diameter ($>800\,nm$) primarily scatter in the forward direction. However, with smaller particles ($300–600\,nm$) a higher backscattering (reflection) efficiency was achieved. The largest difference in the normal–hemispherical transmittance could be found with a particle amount of 6% and a median scattering domain diameter of $\sim380\,nm$.

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1. Introduction

A smart (or intelligent) material [1,2] is termed "thermotropic" when exhibiting a temperature-induced clear/opaque switching. So far, the most active work in creating a thermotropic sun protection glazing has been based on the concept of "phase separation" (PS) [3–6]. PS systems (hydrogels, polymer blends) consist of at least two components with different refractive indices. At temperatures below the switching point the difference in refractive index (RI) has no effect because all components are homogeneously mixed at a molecular level. In this state the material has a median refractive index and is highly transparent for solar radiation (Fig. 1, Method 1). Upon reaching a specific temperature a phase separation takes place, and domains (SD) are formed which are composed predominantly or solely of one single component. By now, the refractive index of the domains deviates from that of the matrix (M) and solar radiation is scattered at the domain/matrix interface ($n_M \neq n_{SD}$).

In a second concept a temperature-induced phase transition (PT) is responsible for the thermotropic behavior [6]. Such

systems also consist of at least two main components, namely a thermotropic additive (domain material) which is homogeneously dispersed in an appropriate matrix material. In contrast to PS systems the domains are fixed inside the matrix; thus, they exist at every temperature below as well as above the switching point (Fig. 1, Method 2). Below the switching point the refractive indices of domain and matrix are (almost) equal ($n_M = n_{SD}$) and scattering is minimized. However, in the on state the fixed domains are working as scattering centers due to a highly temperature-dependent refractive index of the domain material. A phase transition leads to a reduction of density that is in turn accompanied by a considerable decrease of the refractive index compared to that of the matrix material ($n_M > n_{SD}$). Generally, long-chain compounds with a solid–liquid phase transition in the desired temperature range (e.g. alkanes, fatty acid esters) are used as domain materials [6].

Until recently, PT systems (also referred to as "thermotropic systems with fixed domains" (TSFD) [6]) were almost exclusively the subject of patent literature [7]. The scientific literature was limited to PT materials that are not appropriate for sun protection purposes, either switching from opaque to clear with increasing temperature [e.g. 8] or with a more complex switching behavior that highly depends on the thermal history of the material [e.g. 9]. In 2008, comprehensive investigations on PT systems with adequate switching characteristics were published in a scientific journal for the first time [10]. By means of the UV curing
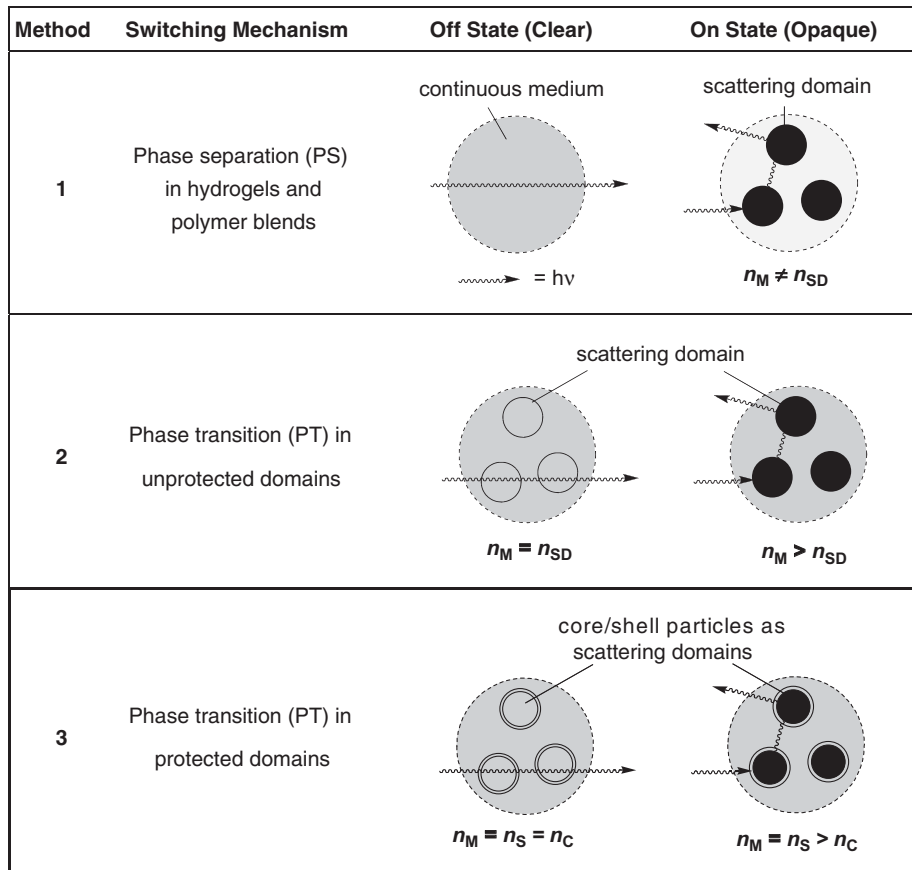
Fig. 1. Three approaches for thermotropic switching.

technology several thermotropic films were prepared by embedding a thermotropic additive in a suitable UV curable resin. However, only moderate switching ranges of the normal–hemispherical solar transmittance ($\Delta T_{nh} \leqslant 9\%$) have been observed [10].

The subject of this paper is an improved PT system (Fig. 1, Method 3) which is based on the UV curing technology for laminated glass, as well. In contrast to method 2 this new approach incorporates a preliminary step, namely the encapsulation of the thermotropic additive. In this way, an easy to handle, powder-like material is obtained that contains the thermotropic component as well-defined core/shell particles. The following steps are similar to the known PT procedure [10]. Compared to method 2 in which the phase transition occurs in "unprotected" domains this new strategy has several advantages: first, special encapsulation techniques allow the adjustment of the particle size. With these techniques in hand, it is now possible to investigate the effect of different scattering domain sizes in order to optimize the switching characteristics. Second, the switching range, namely the difference in transmittance between off and on state, can be varied easily by adding different amounts of thermotropic particles to the matrix material. Third, the particle shell works as a "protective shield" that impedes diffusion processes between thermotropic core and matrix. As a result, the long-term stability is essentially enhanced [11].

Regarding the refractive indices of the involved components in a corresponding thermotropic layer, here applies: at all temperatures below the switching point the refractive indices of matrix (n_M), particle shell (n_S), and particle core (n_C) should have the best possible matching especially in the visible wavelength region ($n_M = n_S = n_C$) to obtain a high transparency in the off state (Fig. 1, Method 3). During the switching process, only the RI of the

thermotropic core changes significantly ($n_M = n_S > n_C$). Thus, particle shell and matrix should have the same refractive index over the whole relevant temperature range ($n_M = n_S$) and can be regarded as one uniform matrix medium. In other words, scattering occurs predominantly at the core/shell interface which in turn implies that the scattering domain size is given by the core diameter of the particles.

2. Experimental methods

2.1. Preparation of thermotropic core/shell particles

The thermotropic core/shell particles were prepared by radical o/w miniemulsion polymerizations [12]. A mixture of different n-alkanes with a melting point between approx. 30 and 40 °C (n-octadecane/n-eicosane/n-docosane/n-tetracosane = 1:1:1:1 mass ratio) was chosen as the thermotropic mixture (TM). n-Docosanol (5 wt%) was added as a nucleating agent to prevent supercooling of the n-alkanes [13]. The vinyl monomers methyl methacrylate (MMA, 90 wt%) and ethylene glycol dimethacrylate (EGDMA, 10 wt%, cross-linking agent) were used to create a cross-linked polymer shell with a similar refractive index to that of the cured acrylate-based resin matrix ($n_{M,589\,nm} \approx 1.49$). A stable o/w emulsion was formed by using an ultrasonic processor (HIELSCHER, UP200S, Sonotrode S3, 200 W, 24 kHz). Induced by the high shear of the ultrasonication TM/monomer droplets with a relatively narrow size distribution can be generated compared to conventional homogenization methods [12]. The TM/monomer droplets were stabilized in water by means of poly(vinyl alcohol) (PVA, degree of hydrolysis = 87–89%) as a nonionic polymeric surfactant. In order to create core/shell particles